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# Agrochemicals in Soil and Environment

## Impacts and Remediation

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# Foreword

'Man is the only animal that fouls its own nest'. This quote sits true when we think about the rising use or rather abuse of agrochemicals in modern-day agriculture. In the quest for better profitability, agrochemicals came into existence but eventually they have become a major source of environmental pollution. Harmful impacts of agrochemicals are embedded in soil, water, air and even in human health. The rising trend of abuse of agrochemicals, which were introduced in the market in order to improve crop quality, is alarming. Thus, it requires mass spread of awareness as well as implementation of proper guidelines with sustainable and strategic planning for lowering their impact on the environment and ultimately humans.

M. Naeem and team did a commanding job to compile a comprehensive volume on the very important and challenging area '**Agrochemicals in Soil and Environment: Impacts and Remediation**'. The editors have nicely teamed up with the global subject experts to cover up a variety of chapters on agrochemicals and their impact on crop productivity. This book comprises five parts: Part I constitutes of an overview of agrochemicals in soil and environment with an in-depth discussion on what imbibes agrochemical pollution and highlighting studies where they are found in the soil and environment. Following the introduction, this part discusses detection, treatment and remediation measures detailing occurrence, source and type of agrochemicals with their environmental impacts and describes their strategic abatement. It also details the effect of agrochemicals on the texture, productivity, native microflora and nutritional balance of the soil microbiome. Various management strategies including the 4-point plan have been described in this part with a step-by-step approach to the management of agriculture pollution. Further advantages and challenges for developing an intergenerational community-based approach against agrochemical pollution have been highlighted. Part II discusses integrated pest management strategies on providing proper guidance to farmers for handling of pesticides and a detailed demonstration of how pesticides end up in every part of our ecosystem especially air, water, food wildlife, etc. Further, this part explains the magnitude of this problem with examples of deltamethrin (insecticide) and glyphosate (herbicide) by discussing their harmful effects on environment, wildlife and humans. Later in this part, abuse and impact of insecticides on the environment with proper management strategies have been suggested.

In Part III, the chapters include an in-depth mobility assessment of trace elements in the soil and ecosystem. This is followed by a detailed discussion on the serpentine soil–plant relations in order to analyse the effects of nutrient enrichment on low nutritional ecosystems. In addition, how soil erosion and sedimentation can deeply impact agriculture as contaminants have been elaborated in one of the chapters in this part. Lastly, plastics and their detrimental environmental impacts have been reviewed. Further, Part IV goes on to discuss heavy metals such as lead and cadmium and their impacts on plants and human health in addition to exploring the link between crude oil and heavy metal contamination in the farmlands. Lastly, this part strategizes to alleviate arsenic stress from cultivated plants along with guide lining implementable management tips to ward off trace elemental effects from the soil.

Lastly, Part V consists of various remediation strategies for agrochemicals present in the soil and environment along with toxicity alleviation of heavy metals from agricultural crops through the use of metal-resistant bacteria. In addition, bioremediation strategies are employed to mitigate the impact of atrazine from the environment as well as aspergillus-mediated bioremediation of agrochemicals have been expanded in detail in its chapters. The implications of using phytohormones as agrochemicals under dynamic environmental conditions have also been explored in this part. Finally, the role of genetically modified bacteria for alleviating of agrochemical impact on the environment as well as use of omics as molecular blueprint for agrochemical remediation has been discussed in detail. In conclusion, although marketing agrochemicals as fancy pesticides, insecticides, fungicides, rodenticides, etc. is no doubt profitable and intriguing, it is also undeniable that it is also leading us towards a future with polluted soil and environment. Thus, this book was written in order to instil awareness and explore proper management strategies so as to promote a judicious and conscious approach towards the production, marketing and abuse of agrochemicals.

The challenges of agrochemicals in soil and environment are visible and I heartily appreciate the editors and contributing author's dedication to discuss the impact of agrochemicals and remediation strategies that can address the problem significantly.

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# Preface

Various anthropogenic activities pose a serious threat to the agriculturally suitable land due to the release of hazardous waste substances therein. The extensive use of agrochemicals (pesticides, fungicides and insecticides), mining, unplanned disposal of municipal waste and other agrochemicals are the major causes of agricultural land contamination, thus degradation. Due to the rapid increase in urban global population, urbanization, industrialization and uncontrolled anthropogenic activities are resulting in the accumulation of large amounts of toxic substances into the environment. These effluents enter into the food chain through the soil and ultimately affect plant and human health. Various metals, metalloids, radioactive substances and other hazardous, toxic organic and inorganic substances are the most prevalent forms of environmental contaminants; their complete remediation in soils and sediments is rather a difficult task. Concerns of their toxicities led to the emphasis on the development of effective techniques to assess the presence and mobility of contaminants in soil, drinking water, irrigation water, and wastewaters. These toxic substances seriously hamper the developmental processes of agriculturally important crops. Furthermore, an increase in global population and advancement in modern agriculture technology has amplified the demand for agricultural/exotic crops and livestock.

Effective management strategies and skills for the agricultural contaminants pave the way to combat the challenges to improve the production of agricultural crops. Judicious application of targeted, and balanced quantities of agrochemicals are necessary for optimal crop production without much environment and yield penalty. At the same time, every effort should be made to improve the availability and use of secondary- and micro-nutrients, organic fertilizers and soil-conservation practices to develop overall crop production in an efficient and environmentally sustainable manner, without sacrificing soil health and/or crop yield. We hope that this book can help in the development of significant applications that feature the integration of modern technologies to remediate contaminated soil environment.

Therefore, it is a need of the hour to undertake these challenging issues rising day by day in the field of agriculture and environmental sciences. We intend to bring forth a comprehensive volume '**Agrochemicals in Soil and Environment: Impacts and Remediation'** highlighting the various prospects that are being involved in the current scenario. This book consists of 25 chapters that are categorized into different parts, written by global field experts. We are hopeful that this comprehensive volume would furnish the need of all researchers who are working or have great interest in this particular field. We are highly thankful to Springer Nature Singapore Pte Ltd. for compiling this scientific task. Heartfelt thanks are expressed to the team members (Eric Stannard, Akanksha Tyagi, Lenold Esithor and others) for their dedication, sincerity and friendly cooperation in producing out this volume.

With great pleasure, we extend our sincere thanks to all the contributors for their timely response, their outstanding and up-to-date research contribution and their support and consistent patience.

Lastly, thanks are also due to well-wishers, friends and family members for their moral support, blessings and inspiration in the compilation of this book.

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San Luis Potosí, Mexico Juan Francisco Jimenez Bremont
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# About the Editors

**M. Naeem** is an Assistant Professor in the Department of Botany at Aligarh Muslim University, India. His research focuses on escalating the production of commercially important medicinal and aromatic plants and their active principles using a novel and safe technique involving depolymerized polysaccharides as well as the application of potent PGRs. His research also focuses on abiotic stress tolerance in medicinal plants. He has published around 100 research papers in reputable international journals. Also, he has authored ten books and co-authored several book chapters published by international publishers. Based on his research contributions, he has received multiple awards and recognitions.

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**Sarvajeet Singh Gill** is presently working as Assistant Professor at Centre for Biotechnology, Maharshi Dayanand University. He has approx. 50 book chapters, published over 100 peer-reviewed publications in the journals of international repute and edited 30 books on the subject published by international publishers. He has carried out four R&D projects funded by prominent national funding agencies. He has 17,307 Google Scholar citations, h-index 45 and i10 index 92, whereas, on Scopus, he has 10779 citations, h-index 35. He was awarded NESA Junior Scientist of the Year Award 2008; DST-SERB Fast Track Young Scientist award in 2012; prestigious Web of Science ‘India Research Excellence and Citation Award-2017’, appeared in 2% global scientists list (2020 and 2021); and Teaching and Committed Research Award 2021.

# Part I

# Overview of Agrochemicals in Soil & Environment

# 1 Agrochemicals in Soil and Environment: An Overview

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## Abstract

Frequently changing environmental conditions pose serious threat to the global agriculture by putting extra burden in the form of environmental insults (biotic and abiotic factors) and challenge to food security, and thus, the global population. To ensure the food security, optimal production of agriculture is essential. Judicious and safe use of agrochemicals (like chemical fertilizers, pesticides, and plant growth regulators) has enormous potential to boost the agriculture

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productivity for meeting the food demand of rapidly growing population, but excessive use causes serious damage to the environment and contaminate the soil, water, and whole ecosystem, thus threatening the soil micro biota and soil health sustenance. The continuous use of agrochemicals often results in accumulation of metals/polychlorinated biphenyls, etc. in soil and water, and thus the food chain, and damages the human/animal health. Therefore, research on soil health and adoption of alternative measures in the form of compost and vermicompost, yard and green manures, biopesticide, beneficial fungi, and plant growth-promoting rhizobacteria are essentially required. Remediation or restoration of degraded soil can be achieved through microbe consortium/nano and biochar-assisted breakdown chemicals/pesticides.

**Keywords**

Agrochemicals · Environmental contamination · Fertilizers · Pesticides · Remediation approaches

## 1.1 Introduction

In the era of frequently changing environmental conditions/global climate change, feeding the ever-increasing population is a serious challenge, and to ensure the food security, the use of various agrochemicals increased the crop productivity, food yield, fiber content, and also helped in preventing the vector-borne diseases, but extensive research on the impact of agrochemicals revealed that their use has harmed the human and environmental health significantly (Speight 2016). It has also been reported that the presence of various agrochemicals in plant and soil system happens to be the main reason of their presence in the food chain and drinking water contamination (Sarkar et al. 2020).

Large agrochemicals represent a group of chemical substances (pesticides and chemical fertilizers) that ensure high crop productivity and safety against plant pathogens like different pesticide compounds, insecticides, herbicides, fungicides, nematicides, etc., but luxurious use of agrochemicals has contaminated environmental components such as agricultural soil, canals, rivers, etc. and the high presence of nitrate causes toxicity in plants and animals and thus poses serious health hazard (Ravichandra 2018). Among all the continents, Asia has topped the chart with 52.8% of pesticide consumption, followed by America, Europe, Africa, and other countries. In Asia, China is the primary consumer of pesticides, and globally, Saint Lucia has occupied the first position (FAO 2019). Different types of chemical fertilizers like urea, di ammonium phosphate, super phosphate, ammonium sulfate, calcium ammonium nitrate, calcium nitrate, etc. are being extensively applied to increase the produce of the crops, but their leftover presence in the soil and environments causes toxicity in plants, animals, humans, and in friendly microorganisms and earthworms. Comparatively, pesticides show their long presence in the soil may be because of their slow decomposition in the inactive soil system. The physical factors such as rainfall, heat, soil or water pH, moisture, and ultraviolet rays also decide the fate of pesticides' persistence in the environment. It has also been observed that the chemical composition of the pesticide and its water solubility/volatility and method of pesticide application also define their persistence in soil. Researchers have also demonstrated that certain bioaccumulative pesticides such as aldrin, chlordane, dichlorodiphenyltrichloroethane, dieldrin, and toxaphene showed toxicity and long stay in the biological system. The application of higher doses of pesticides and regular application induce severe toxicity in the environments (Wang et al. 2008; Sumalan et al. 2010).

Therefore, it is imperative to remediate the contaminated agricultural soil and water by adopting sustainable measures like plant-microbe partnership for bioremediation of ACs, earthworm-assisted bioremediation of ACs, and soil-biochar formulations for improved absorption and reabsorption of ACs, nanoparticles, and nanoformulations.

## 1.2 Agrochemicals

An agrochemical is a contraction of agricultural chemical used in agricultural practices. Agrochemicals are basically used to kill or prevent the wild grasses/weeds or the microorganisms (bacteria, fungi, virus, etc.), pests which can pose yield penalty (Pandya 2018). Agrochemicals refer to pesticides such as insecticides, herbicides, fungicides, nematicides, synthetic fertilizers, hormones, and other chemical growth agents (Fig. 1.1).

The Food and Agriculture Organization of United Nations (FAO 2021a) describes that pesticides are any substance or mixture of substances of chemical or biological ingredients intended for repelling, destroying or controlling any pest, or for regulating plant growth. The term pesticide applies to insecticides, herbicides, fungicides, rodenticides, molluscicides, wood preservatives, and various other substances used to control pests. Pesticides also include plant growth regulators, defoliants, and desiccants (https://www.fao.org/news/story/en/item/1398779/icode/).

Pesticides' use increased in the 2010s by more than 50% compared to the 1990s, with pesticides' use per area of cropland increasing from 1.8 to 2.7 kg/ha. Global pesticides' use in agriculture remained stable in 2019 at 4.2 million tons, equivalent to 0.6 kg/person. Pesticides' use in agriculture in Europe increased by just 3% between the 1990s and the 2010s. Total pesticides' trade reached approximately 5.6 million tons of formulated products in 2019, with a value of USD 35.5 billion.

FAO (2021a) reported the regional total pesticide uses for the same period, in particular the recent stabilization in Asia. Pesticides' exports from Asia decreased in the most recent years from 2.6 Mt in 2017 to 2.5 Mt in 2019. The region is responsible for about 60% of global insecticides use in the 2010s. Pesticides' use in agriculture in Europe increased by just 3% between the 1990s and the 2010s, most likely due to the stringent European Common Agricultural Policy put in place, which monitors and controls the use of pesticides (Fig. 1.2).

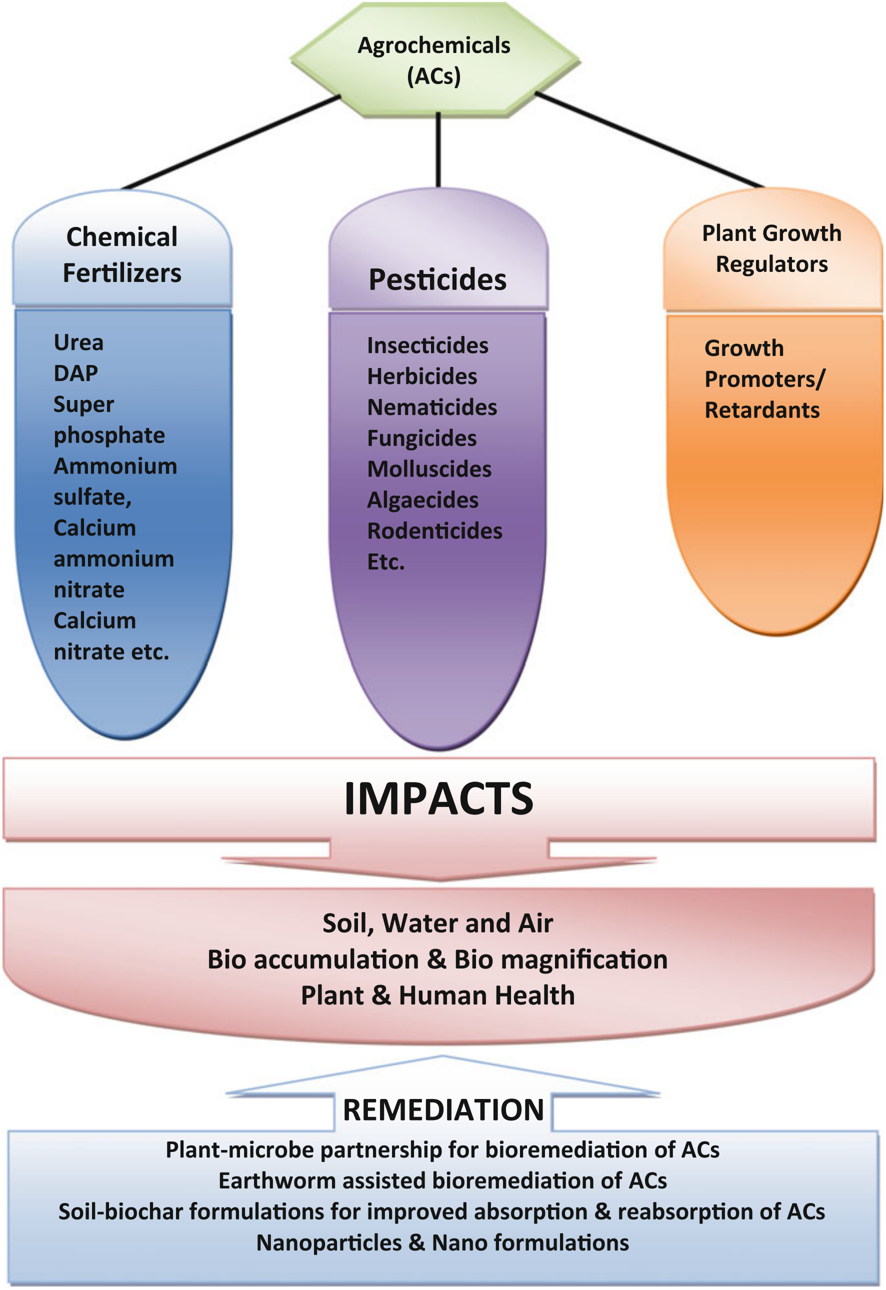

**Fig. 1.1** Agrochemicals' impact and remediation

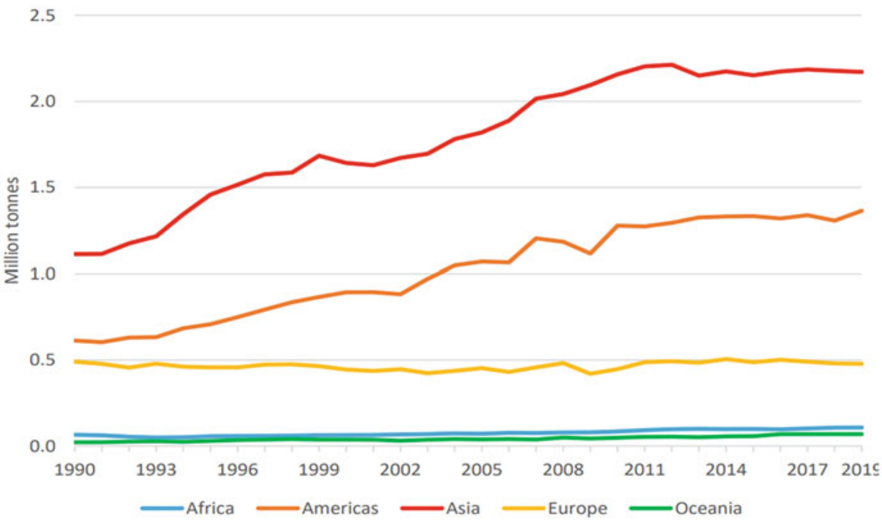

**Fig. 1.2** Total pesticide usage by region (FAO 2021a, https://www.fao.org/3/cb6034en/cb6034en.pdf)

The Americas had a high growth rate of 80% in pesticides' use from the 1990s to the 2010s. The region applies high levels of pesticides, contributing nearly one third to the global total in 2019. The Americas applied approximately 3.6 kg of pesticides per hectare of cropland each year in the 2010s, up from a mean application rate of 1.9 kg/ha in the 1990s. The region augmented herbicides' use from 353 to 840 kt, fungicides' use from 90 to 178 kt, and insecticides' use from 157 to 183 kt per year in the 2010s compared to the 1990s. It was the third largest exporter of total pesticides (averaging approximately 830 kt in the 2010s, or 17% of the global total) and second in terms of imports (averaging approximately 1.3 Mt per year in the 2010s, or 27% of the global total) (Fig. 1.3).

Although Oceania had the highest growth rate of all regions between the 1990s and the 2010s, with a doubling of 1990 values, the region applies the lowest levels, averaging approximately 60 kt of pesticides per year in the 2010s, and represents less than 2% of the global use in 2019. Oceania applied 1.8 kg/ha of pesticides in the 2010s compared to 1.4 kg/ha in the 1990s. The region increased herbicides' use from 20 to 41 kt, fungicides' use from 3 to 5 kt, and insecticides' use from 7 to 13 kt per year over the same period. Africa increased total pesticides' use in agriculture by 70% over the period analyzed and maintained low pesticides' use per area of cropland, averaging just 0.3 kg/ha in the 1990s and 0.4 kg/ha in the 2010s (FAO 2021b, Fig. 1.4).

It has been shown that China is by far the largest user of pesticides in 2019, with 1774 kt of pesticides' applications for agricultural use. Next in the top 10 are the United States of America (408 kt), Brazil (377 kt), Argentina (205 kt), Canada (88 kt), France (85 kt), the Russian Federation (77 kt), Colombia (70 kt), Australia (63 kt), and India (62 kt) (FAO 2021a, Fig. 1.5).

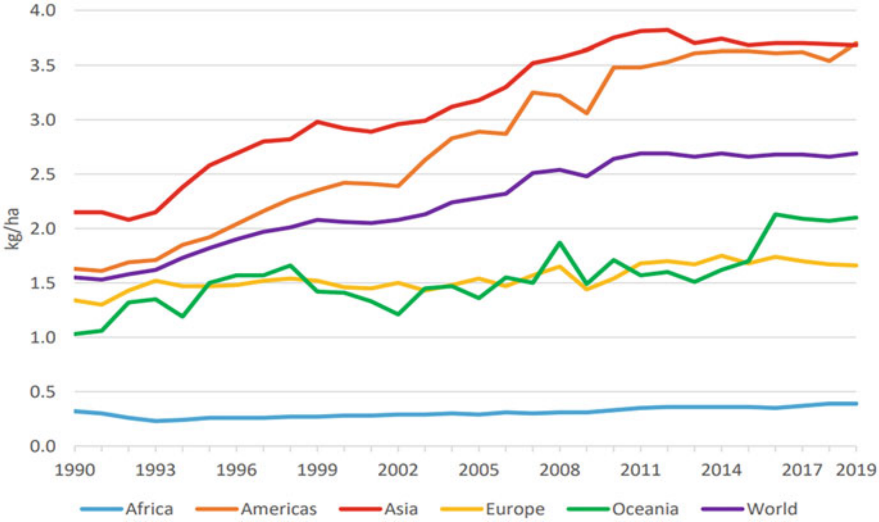

**Fig. 1.3** Pesticide use per area of crop land by region (FAO 2021b, https://www.fao.org/3/cb6034en/cb6034en.pdf)

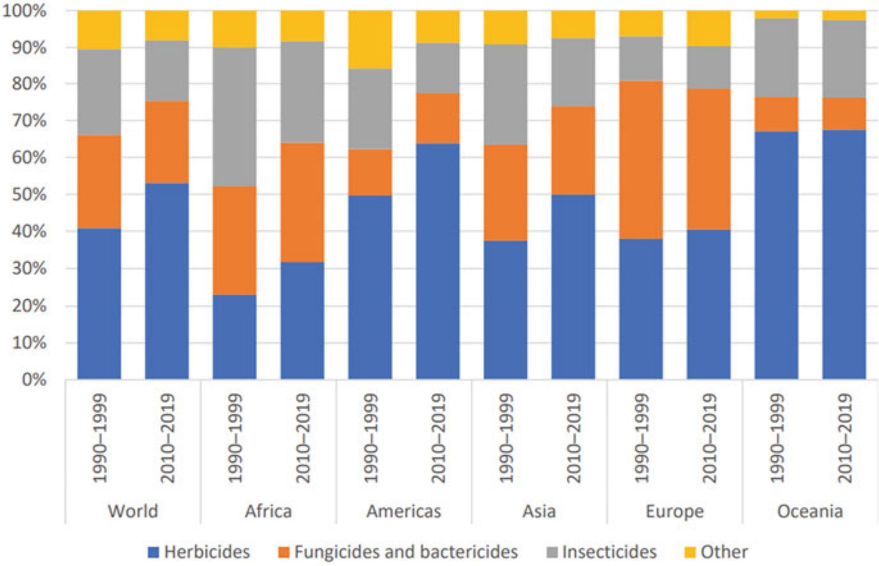

**Fig. 1.4** Regional pesticide use region and category 1990–1999 and 2010–2019 (FAO 2021a, https://www.fao.org/3/cb6034en/cb6034en.pdf)

FAO (2021a) reported the top 10 countries for pesticides' use per area of cropland for 2019, which are Trinidad and Tobago (25 kg/ha), Saint Lucia (20 kg/ha), Ecuador (14 kg/ha), China (13 kg/ha), Israel (13 kg/ha), the Seychelles (12 kg/ha),

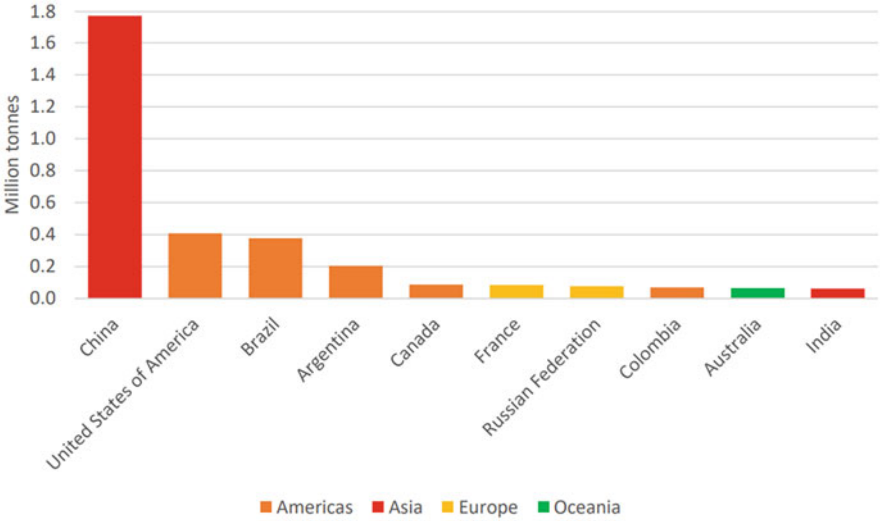

**Fig. 1.5** Top ten countries for pesticide use, 2019 (FAO 2021a, https://www.fao.org/3/cb6034en/cb6034en.pdf)

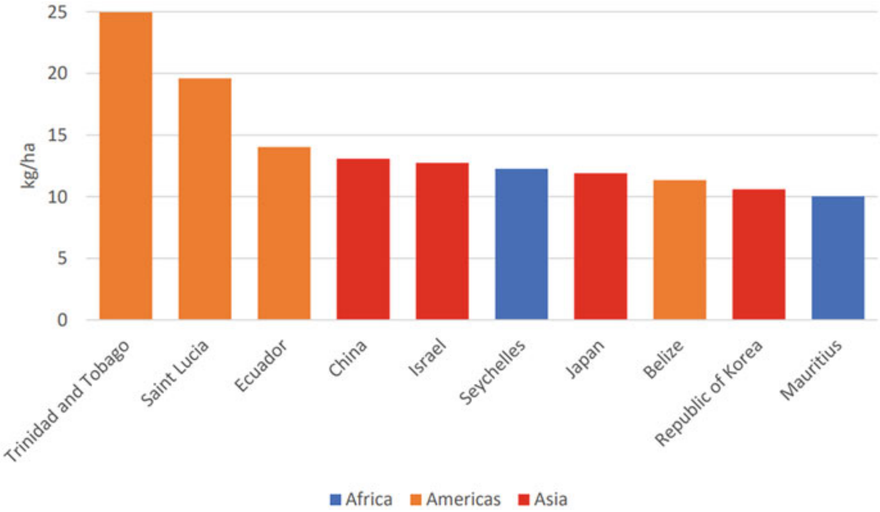

**Fig. 1.6** Top ten countries for pesticide use per crop land area, 2019 (FAO 2021b, https://www.fao.org/3/cb6034en/cb6034en.pdf)

Japan (12 kg/ha), Belize (11 kg/ha), the Republic of Korea (11 kg/ha), and Mauritius (10 kg/ha). Five of these countries are Small Island Developing States; China is also notable for being the largest pesticides' user in absolute quantities and is among the largest users per hectare of cropland (Fig. 1.6).

## 1.3 Insecticides

Insecticides are agrochemicals used in agriculture and public health programs to protect the crop plants and humans from various diseases (Nicolopoulou-Stamati et al. 2016).

### 1.3.1 Organophosphate Pesticides (OPPs)

OPPs are a class of organophosphorus compounds and used to kill the insects.

***Parathion* (*O,O-Diethyl O-*(*4-nitrophenyl*) *phosphorothioate*):** It is an organophosphate insecticide and acaricide and extensively used to control pests in cotton, rice, and fruit trees.

**Chemical Safety:** Acute toxic, irritant, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/parathion).

***Malathion* (*Diethyl 2-[*(*dimethoxyphosphorothioyl*)*sulfanyl]butanedioate*):** It is an organophosphate insecticide extensively used in agriculture, public recreation areas, and health pest control programs (mosquito eradication).

**Chemical Safety:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/malathion).

***Chlorpyrifos* (*O,O-Diethyl O-*(*3,5,6-trichloropyridin-2-yl*) *phosphorothioate*):** It is an organophosphate pesticide extensively used in agriculture and residential area to control pests, insects, and worms.

**Chemical Safety:** Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/chlorpyrifos).

***Diazinon* (*O,O-Diethyl O-[4-methyl-6-*(*propan-2-yl*)*pyrimidin-2-yl] phosphorothioate*):** It is an organophosphorus pesticide used to control pest insects in soil, on ornamental plants, and on fruit and vegetable field crops.

**Chemical Safety:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/diazinon).

***Dichlorvos* (*2,2-dichlorovinyl dimethyl phosphate*):** It is used for insect control in food storage areas, green houses, control of insects on livestock, and not generally used on outdoor crops.

**Chemical Safety:** Acute toxic, irritant, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/dichlorvos).

***Fenitrothion* (*O,O-dimethyl O-*(*3-methyl-4-nitrophenyl*) *phosphorothioate*):** It is a synthetic organophosphate acetylcholinesterase inhibitor and used as a selective acaricide and a contact and stomach insecticide against chewing and sucking insects.

**Chemical Safety:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/fenitrothion).

***Tetrachlorvinphos*** ((Z)-***2-Chloro-1-*(*2,4,5-trichlorophenyl*)*ethen-1-yl dimethyl phosphate***): It is an organophosphate insecticide widely used to control fleas and ticks.

**Chemical Safety:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Tetrachlorvinphos).

***Azamethiphos*** (***S-[(6-Chloro-2-oxo[1,3]oxazolo[4,5-b]pyridin-3(2H)-yl)methyl] O,O-dimethyl phosphorothioate***): It is an organothiophosphate insecticide widely used as a veterinary drug to control parasites in fish farming.

**Chemical Safety:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Azamethiphos).

***Azinphos-methyl*** (***O,O-Dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate***): It is a broad-spectrum organophosphate insecticide used to control insects and pests.

**Chemical Safety:** Acute toxic, irritant, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Azinphos-methyl).

***Terbufos*** (***S-[(tert-Butylsulfanyl)methyl] O,O-diethyl phosphorodithioate***): It is a chemical compound widely used in the insecticides and nematicides to control the insects and nematodes in agriculture settings.

**Chemical safety**: Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Terbufos).

### 1.3.2 Carbamates

Carbamate compounds are esters of carbamic acid which are commonly used as insecticides (Gupta 2014). The organophosphate pesticides also inhibit this enzyme, although irreversibly, and cause a more severe form of cholinergic poisoning.

***Methyl carbamate***: It is a simplest ester of carbamic acid and widely used as an insecticide.

**Chemical safety**: Irritant and health hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Methyl%20carbamate).

***Ethyl carbamate***: It is an ester of carbamic acid and widely used as an insecticide (https://pubchem.ncbi.nlm.nih.gov/compound/Ethyl%20carbamate).

### 1.3.3 Pyrethroids

Pyrethroids are organic compounds and used as commercial and household insecticides to control dragonflies, mayflies, gadflies, and some other invertebrates. Some of the examples are as follows:

***Allethrin*** (***2-methyl-4-oxo-3-prop-2-enylcyclopent-2-en-1-yl) 2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropane-1-carboxylate***): Allethrin is a cyclopropanecarboxylate ester. It has a role as a pyrethroid ester insecticide and used to kill garden insects, flies, mosquitoes, garden insects, etc.

**Chemical safety**: Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Allethrin).

***Bifenthrin*** ***rel-(2-Methyl[1,1′-biphenyl]-3-yl)methyl (1R,3R)-3-[(1Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl]-2,2-dimethylcyclopropane-1-carboxylate***): It is a pyrethroid insecticide widely used against ant infestations, e.g., red fire ant.

**Chemical safety**: Acute toxic, irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Bifenthrin).

***Cyfluthrin*** ***(R)-Cyano(4-fluoro-3-phenoxyphenyl)methyl (1R,3R)-3-(2,2-dichloroethen-1-yl)-2,2-dimethylcyclopropane-1-carboxylate***): It is a pyrethroid insecticide and a common pesticide in household activities.

**Chemical safety**: Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Cyfluthrin).

***Deltamethrin*** ***(S)-Cyano(3-phenoxyphenyl)methyl (1R,3R)-3-(2,2-dibromoethen-1-yl)-2,2-dimethylcyclopropane-1-carboxylate***): It is a pyrethroid ester insecticide used to control vectors like *Anopheles gambiae*.

**Chemical safety**: Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Deltamethrin).

***Etofenprox*** ***1-{[2-(4-Ethoxyphenyl)-2-methylpropoxy]methyl}-3-phenoxybenzene***): Etofenprox is extensively used in agriculture, horticulture, viticulture, forestry to kill insect pests, e.g., Lepidoptera, Hemiptera, Coleoptera, Diptera, Thysanoptera, and Hymenoptera.

**Chemical safety**: Environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Etofenprox).

***Permethrin*** (±)***-3-Phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate***): Permethrin is a medication and an insecticide used to treat scabies and lice.

**Chemical safety**: Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Permethrin).

***Transfluthrin*** ***(2,3,5,6-Tetrafluorophenyl)methyl (1R,3S)-3-(2,2-dichloroethen-1-yl)-2,2-dimethylcyclopropane-1-carboxylate***): Transfluthrin is a fast-acting pyrethroid insecticide used to kill flies, mosquitoes, moths, and cockroaches.

**Chemical safety**: Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Transfluthrin).

### 1.3.4 Organochlorines

Organochlorine pesticides are synthetic chlorinated hydrocarbons including dicofol, eldrin, dieldrin, chlorobenziate, lindane, BHC, methoxychloro aldrin, chlordane, heptaclor, endosufan, isodrin, isobenzan, toxaphene, and chloro propylate and extensively used in agriculture and vector control (Jayaraj et al. 2016).

**Chemical safety**: High toxicity, slow degradation, and bioaccumulation (Jayaraj et al. 2016).

***Dicofol*** ***(2,2,2-Trichloro-1,1-bis(4-chlorophenyl)ethan-1-ol***): It is an organochlorine pesticide that is used as miticide to control spider mite.

**Chemical safety**: Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/dicofol).

***Eldrin* (*1R,4S,4aS,5S,8R,8aR*)-*1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,***
***8-dimethanonaphthalene***): It is an organochlorine insecticide and a persistent organic pollutant.

**Chemical safety**: Irritant (https://pubchem.ncbi.nlm.nih.gov/compound/eldrin).

**Dieldrin** (***1aR,2R,2aS,3S,6R,6aR,7S,7aS*)-*3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphtho[2,3-b]oxirene***): It is an organochlorine insecticide and a persistent organic pollutant.

**Chemical safety**: Acute toxic, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Dieldrin).

***Lindane* (*1,2,3,4,5,6-Hexachlorocyclohexane alpha-HCH*)**: It is an organochlorine chemical and an isomer of hexachlorocyclohexane that is extensively used as agricultural insecticide and in the treatment for lice and scabies.

**Chemical safety**: Acute toxic, irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/lindane).

***Chlordane* (*1,2,4,5,6,7,8,8-Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane*)**: It is an organochlorine pesticide extensively used in agriculture.

**Chemical safety**: Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/chlordane).

**Isodrin** (***1R,4S,5R,8S*)-*1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene***): It is an organochlorine insecticide and isomer of aldrin used in agriculture.

**Chemical safety**: Acute toxic, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/isodrin).

***Isobenzan* (*1,3,4,5,6,7,8,8-Octachloro-1,3,3a,4,7,7a-hexahydro-4,7-methano isobenzofuran*)**: It is a highly toxic organochloride insecticide and extremely hazardous substance as a persistent organic pollutant.

**Chemical safety**: Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/isobenzan).

***Toxaphene* (*1,4,5,6,7,7-hexachloro-2,2-bis*(*chloromethyl*)-*3-methylidenebicyclo [2.2.1] heptane*): ** It is a very persistent insecticide used in agriculture.

**Chemical safety**: Acute toxic, irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/toxaphene).

## 1.4 Herbicides

Herbicides are used in agriculture to kill the wild grasses and weeds of nuisance value that may compromise the growth and developments of crop plants and pose yield penalty. Their use can promote the growth of desirable crop species (Holt 2013). Commonly used herbicides in agriculture are as follows:

***Glyphosate*** (***N-*****(*****Phosphomethyl*****)*****glycine***): It is a broad-spectrum systemic herbicide and crop desiccant.

**Chemical Safety:** Corrosive and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/glyphosate).

***Pendimethalin N-*****(*****1-Ethylpropyl*****)*****-3,4-dimethyl-2,6-dinitrobenzenamine***: It is a member of substituted anilines, which appears as orange-yellow crystals and is used as an herbicide.

**Chemical Safety:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Pendimethalin).

***Dicamba*** (***3,6-dichloro-2-methoxybenzoic acid***): It is a chlorinated derivative of o-anisic acid (selective translocated herbicides) and used to control broad leaf weeds.

**Chemical Safety:** Corrosive and irritant (https://pubchem.ncbi.nlm.nih.gov/compound/Dicamba).

***Simazine/Atrazine*** (***2, Chloro-4,6–bi*****(*****Ethylamino*****)*****s-triazine***): Both are selective translocated herbicides and used to control broad leaf weeds and grasses.

**Chemical Safety:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Atrazine).

***Paraquat*** (***1,1–diethyl-4-bipyridinium ion and Diquat*** (***6,7–dihydrodipyrido*** (***1,2:2, I-C***) ***Pyrazinediiumaion***): Both are contact, nonselective herbicides with zero persistence in the soil.

**Chemical Safety:** Corrosive, acute toxic, irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Paraquat; https://pubchem.ncbi.nlm.nih.gov/compound/Diquat).

***Thiobencarb*** (***S-*****(*****4-Chlorobenzyl*****)** ***N,N–Diethyl–Thicarbamate***)**:** It is used as herbicide to control the Echinochloa spp. in rice.

**Chemical Safety:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Benthiocarb).

***Alachlor*** (***92-Chloro–2,6-Diethyl-N-*****(*****Methoxymethyl*****)*****acetanilide***)**:** It is used to control the annual grasses and broadleaf weeds.

**Chemical Safety:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Alachlor).

***Butachlor*** (***Butoxymethy 2,6–diethylacetanilide***)**:** It is a selective herbicide generally used in seedbed and to control other annual weeds.

**Chemical Safety:** Acute toxic, irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Butachlor).

***Fluchloralin N-*****(*****2-Chloroethyl*****)*****-2,6-dinitro-N-prophyl*****)*****–4*** (***trifluromethyl***) ***amine***)**:** It is selective volatile preemergence herbicide and used to control number of annual weeds.

**Chemical Safety:** Environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Fluchloralin).

***2,4-D*** (***2,4-Dichlorophenoxyacetic acid***): It is selective translocated herbicide and most widely used to control dicot weeds.

**Chemical Safety:** Corrosive and irritant (https://pubchem.ncbi.nlm.nih.gov/compound/2,4-D).

***2,4,5-T* (*2,4,5-Trichlorophenoxyacetic acid*)**: It is same as 2,4-D in properties and used to control bushes and woody weeds.

**Chemical Safety:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/2,4,5-T).

***2,4,5-TP* (*2-*(*2,4,5-Trichlorophenoxy*)*propionic acid*)**: It is same as 2,4-D in properties and used to control bushes and woody weeds.

**Chemical Safety**: Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/2,4,5-TP).

## 1.4.1 Larvicides

Larvicides are insecticides specifically used to interrupt the larval life stage of the insects.

***Methoprene* (*Propan-2-yl* (*2E,4E*)*-11-methoxy-3,7,11-trimethyldodeca-2,4-dienoate*)**: It is used as an insecticide to interrupt the biological life cycle of the insect.

**Chemical safety**: Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Methoprene).

***Temephos* (*O-[4-*(*{4-[*(*Dimethoxyphosphorothioyl*)*oxy]phenyl}sulfanyl*)*phenyl] O,O-dimethyl phosphorothioate*)**: It is an organophosphate larvicide extensively used to control and interrupt the biological life cycle of disease-carrying insects like mosquitoes, midges, and black fly.

**Chemical safety**: Acute toxic, irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Temephos).

## 1.4.2 Fungicides

Fungicides are biocidal chemical compounds frequently used to prevent diseases in animals, agriculture, horticulture, floriculture, and forestry and also used to prevent many postharvest diseases caused by pathogenic fungi to protect tubers, fruits, and vegetables during storage and to avoid extensive breakdown of high-moisture commodities which can pose serious penalties (Gupta 2011; Brauer et al. 2019). Some of the frequently used fungicides are discussed here.

***Mancozeb* (*Manganese zinc ethylenebis*(*dithiocarbamate*)**: It is a dithiocarbamate nonsystemic agricultural fungicide with multisite, protective action and extensively used to protect field crops, fruits, nuts, vegetables, and ornamentals from fungal diseases.

**Chemical toxicity:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Mancozeb).

***Tricyclazole* (*[1,2,4]triazolo[3,4-b][1,3]benzothiazole*):** It is an antifungal agrochemical frequently used to prevent rice blast disease in rice.

**Chemical toxicity:** Irritant (https://pubchem.ncbi.nlm.nih.gov/compound/Tricyclazole).

***Carbendazim*** (***Methyl*** (***1H-1,3-benzimidazol-2-yl***)***carbamate***): It is systemic, broad-spectrum benzimidazole fungicide and frequently used to control ascomycetes, fungi imperfecti, and basidiomycete on a wide variety of crops, including bananas, cereals, cotton, fruits, grapes, mushrooms, ornamentals, peanuts, sugar beet, soybeans, tobacco, and vegetables.

**Chemical toxicity:** Health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Tricyclazole).

***Benomyl*** (***1-***(***Butylcarbamoyl***)***-1H-1,3-benzimidazol-2-yl methylcarbamate***): It is a systemic benzimidazole foliar fungicide used to control a wide range of Ascomycetes and fungi imperfecti in different crops and selectively toxic to microorganisms and invertebrates.

**Chemical toxicity:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Benomyl).

***Difenconazole*** (***1-***((***2-***(***2-Chloro-4-***(***4-chlorophenoxy***)***phenyl***)***-4-methyl-1,3-dioxolan-2-yl***)***methyl***)***-1H-1,2,4-triazole***): It is a broad-spectrum antifungal agrochemical used as a spray and for seed treatment.

**Chemical toxicity:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Difenconazole).

***Propiconazole*** (***1-[[2-***(***2,4-dichlorophenyl***)***-4-propyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole***): It is a triazole fungicide agrochemical frequently used in agriculture as a systemic fungicide. It is used commercially as a diastereoisomeric mixture on soft fruit like apricots, peaches, nectarines, plums, and prunes, nuts including peanuts, pecans, and almonds, mushrooms, and grasses grown for seeds.

**Chemical toxicity:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Propiconazole).

***Tebuconazole*** (***1-***(***4-chlorophenyl***)***-4,4-dimethyl-3-***(***1H-1,2,4-triazol-1-ylmethyl***) ***pentan-3-ol***): It is monochlorobenzenes fungicide used to control fungal diseases.

**Chemical toxicity:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Tebuconazole).

***Tridemorph*** (***2,6-dimethyl-4-tridecylmorpholine***): It is an antifungal agrochemical frequently used to control *Erysiphe graminis*.

**Chemical toxicity:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Tridemorph).

***Propineb*** (***zinc;N-[1-***(***sulfidocarbothioylamino***)***propan-2-yl]carbamodithioate***): It is used as agricultural fungicide.

**Chemical toxicity:** Irritant and health hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Propineb).

***Mancozeb*** (***Manganese Zinc ethylenebis***(***dithiocarbamate***): It is a dithiocarbamate nonsystemic fungicide with multisite action and frequently used in agriculture to control fungal diseases in field crops, fruits, nuts, vegetables, and ornamentals.

**Chemical toxicity:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Mancozeb).

***Myclobutanil*** **(*2-((1H-1,2,4-Triazol-1-yl)methyl)-2-(4-chlorophenyl)hexanenitrile*)**: It is a fungicide agrochemical used to control the fungal diseases by inhibiting the ergosterol biosynthesis which is a critical component of fungal cell membranes.

**Chemical toxicity:** Irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Myclobutanil).

### 1.4.3 Nematicides

Nematicides are chemicals frequently used in agriculture to prevent the negative impact of roundworms and threadworms on the growth and development of crop plants (Becker 2014).

***Metam*** **(*Sodium methylcarbamodithioate*)**: It is a member of the chemical class dithiocarbamate and frequently used as a broad-spectrum soil fumigant for the control of weeds, nematodes, soil-borne insects, and fungi.

**Chemical toxicity:** Corrosive, irritant, and health hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Metam).

***Vapam*** **(*Sodium N-methyldithiocarbamate*)**: It is an organosulfur insecticide and soil-applied nematicide. It works as pronematicide, proherbicide, proinsecticide, and a profungicide.

**Chemical toxicity:** Corrosive, irritant, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Vapam).

***Counter*** **(*Terbufos*)**: It is organophosphate and frequently used in agricultural practices as an agrochemical with nematicidal activity.

**Chemical toxicity:** Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Dithiocarbamate).

***Nemacur*** **(*Fenamiphos*)**: It is an organophosphate insecticide and an organophosphate nematicide frequently used to kill nematodes.

**Chemical toxicity:** Acute toxic, irritant, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Nemacur).

***Nemathorin*** **(*Fosthiazate*)**: It is an organic phosphonate and an organothiophosphate insecticide frequently used as nematicide.

**Chemical toxicity:** Acute toxic, irritant, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Nemathorin).

***Temik*** **(*Aldicarb*)**: It is a member of the class of oxime carbamate insecticides and frequently used as a nematicide and an acaricide.

**Chemical toxicity:** Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Temik).

***Vydate*** **(*N,N-Dimethyl-alpha-methylcarbamoyloxyimino-alpha-(methylthio)acetamide*)**: It is used as an nematicide, insecticide, and acaricide on various field crops, vegetables, fruits, and ornamentals.

**Chemical toxicity:** Acute toxic, irritant, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Vydate).

***Paladin* (*Dimethyl disulfide*)**: It is an organosulfur organic chemical compound used as nematicide.

**Chemical toxicity:** Flammable, acute toxic, irritant, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Paladin).

***Telone & Telone EC* (*1,3-Dichloropropene*)**: These are halogenated hydrocarbons and frequently used as a component in formulations for soil fumigants.

**Chemical toxicity:** Flammable, acute toxic, irritant, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Telone).

***Carbofuran* (*Furadan*) (*2,2-Dimethyl-2,3-dihydro-1-benzofuran-7-yl methylcarbamate*):** It is a carbamate ester chemical frequently used in agriculture as acaricide, an avicide, and a nematicide.

**Chemical toxicity:** Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Furadan).

### 1.4.4 Rodenticides

Rodenticides are toxic chemicals generally used for the prevention of rats, mice, squirrels, woodchucks, chipmunks, porcupines, nutria, and beavers to protect the agricultural crops. Some of the frequently used rodenticides are discussed below.

***Brodifacoum* (*3-[3-[4-(4-Bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-2-hydroxychromen-4-one*)**: It is a highly lethal 4-hydroxycoumarin vitamin K antagonist anticoagulant poison and frequently used rodenticides.

**Chemical toxicity:** Acute toxic, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Brodifacoum).

***Bromadiolone* (*3-[3-[4-(4-Bromophenyl)phenyl]-3-hydroxy-1-phenylpropyl]-2-hydroxychromen-4-one*)**: It is second-generation potent anticoagulant rodenticides widely used in commercial, residential, and agricultural settings.

**Chemical toxicity:** Acute toxic, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Bromadiolone).

***Bromethalin* (*N-Methyl-2,4-dinitro-N-(2,4,6-tribromophenyl)-6-(trifluoromethyl) aniline*)**: It is a neurotoxic rodenticide which damages the central nervous system and widely used to control the rodents.

**Chemical toxicity:** Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Bromethalin).

***Difethialone* (*3-[3-(4′-Bromo[1,1′-biphenyl]-4-yl)naphthalen-1-yl]-4-hydroxy-2H-1-benzothiopyran-2-one*)**: It is an anticoagulant and widely used as a rodenticide.

**Chemical toxicity:** Acute toxic, health and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Difethialone).

***Diphacinone* (*2-(Diphenylacetyl)-1H-indene-1,3(2H)-dione*)**: It is anticoagulant rodenticide and frequently used against rats, mice, voles, ground squirrels, and other rodents.

**Chemical toxicity:** Acute toxic and health hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Diphacinone).

***Strychnine*** (***Strychnidin-10-one***): It is highly toxic crystalline alkaloid used as a pesticide, specifically destroying rodents and predatory animals and for trapping fur-bearing animals.

**Chemical toxicity:** Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Strychnine).

***Zinc phosphide*** (***trizinc diphosphide***): It is an inorganic chemical compound and a flammable poison gas used as a rat poison.

**Chemical toxicity:** Flammable**,** acute toxic, and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Zinc%20phosphide).

### 1.4.5 Algaecides

Algaecides are used to prevent and/or kill the phytoplankton and to reduce the large blooms. Algaecide can control the slime mold, algae, fish pathogens in ponds, canals, and water bodies.

***Copper sulfate*** (***Copper***(***II***) ***sulfate***, $CuSO_4$)**:** It is commonly used as fungicide and algaecides.

**Chemical toxicity:** Irritant and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Copper%20sulfate).

### 1.4.6 Molluscicides

These are pesticides commonly termed as snail baits, snail pellets, or slug pellets and used to prevent growth of molluscs. We discuss few of the pesticides employed as a molluscicide:

***Ferric phosphate (iron(III) phosphate)***: It is the inorganic compound and commonly used as a molluscicide.

**Chemical toxicity:** Irritant (https://pubchem.ncbi.nlm.nih.gov/compound/Copper%20sulfate).

***Ferric sodium EDTA***: It is a broad-spectrum molluscicide frequently used to kill snails and slugs to protect agricultural crops and garden plants.

**Chemical toxicity:** Irritant (https://pubchem.ncbi.nlm.nih.gov/compound/Ferric%20sodium%20EDTA).

***Metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetroxocane)***: It is an organic compound frequently used as a potent molluscicide used against slugs, snails, and other gastropods.

**Chemical toxicity:** Flammable and irritant (https://pubchem.ncbi.nlm.nih.gov/compound/Metaldehyde).

***Methiocarb (3,5-Dimethyl-4-(methylsulfanyl)phenyl methylcarbamate)***: It is a carbamate pesticide frequently used as a molluscicide and acaricide.

**Chemical toxicity:** Acute toxic and environmental hazard (https://pubchem.ncbi.nlm.nih.gov/compound/Methiocarb).

### 1.4.7 Chemical Fertilizers

Chemical fertilizers are extensively used in agriculture and referred as agrochemicals and used to meet the nutrient requirement and to promote the growth and development of crop plants to achieve full genetic potential of crop plants. FAOSTAT ANALYTICAL BRIEF 27 on Inorganic fertilizers from 1961–2019 reported that global agricultural use of inorganic fertilizers has risen significantly between 1961 and 2019, from about ten million to close to 110 million tons for nitrogen, from about ten million to close to 45 million tons for phosphorus (as $P_2O_5$), and from less than ten million to over 35 million tons for potassium (as $K_2O$) (Figs. 1.7 and 1.8). A few countries with a high share of the total dominate the global use. In the last decade, China represented almost 30% of the global agricultural use. The four largest consumers (Brazil, China, India, and the United States of America) represented together almost 60% of the world total for nitrogen and close to 65% for phosphorus and potassium. The expansion of inorganic fertilizers' use since the 1960s has been stronger in Asia. In 1961–1964, it represented less than 20% of the world total, compared to over 50% of the total, for all three nutrients, in 2015–2019. In the last 5 years, however, Asia showed no growth overall in inorganic fertilizers' use. In Africa, use of inorganic fertilizers is much lower than in Asia, the Americas, or Europe, although it has expanded over time. In 2015–2019, Africa represented over 3.5% of global agricultural use for nitrogen and phosphorus and over 2% for potassium (FAO 2021a) (https://www.fao.org/3/cb5738en/cb5738en.pdf).

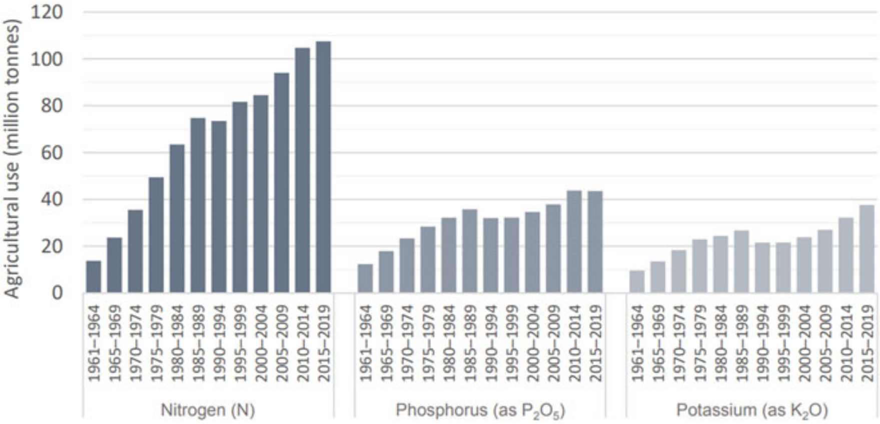

**Fig. 1.7** World agriculture use of inorganic fertilizers (by nutrient as N, $P_2O_5$, and $K_2O$) [Source: FAO 2021a (https://www.fao.org/3/cb5738en/cb5738en.pdf)]. Annual growth rates calculated as geometric averages: $[(X_n/X_0)^{(1/n)} - 1] * 100$ (ESCAP 2015)

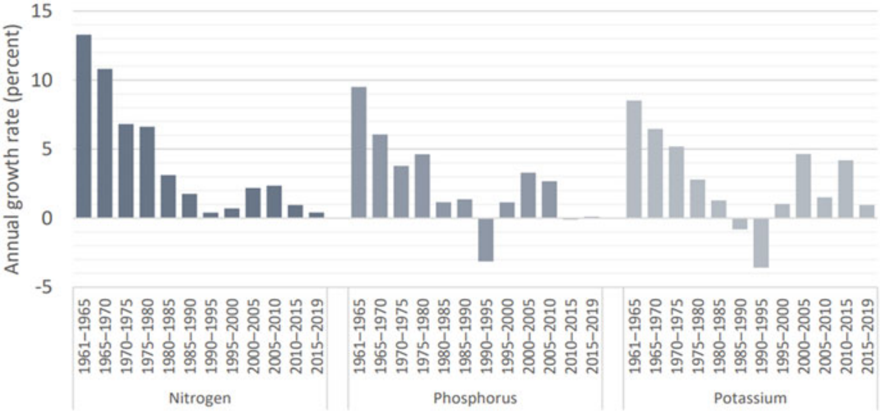

**Fig. 1.8** Annual growth rate of agriculture use of inorganic fertilizers (by nutrient) [Source: FAO 2021a (https://www.fao.org/3/cb5738en/cb5738en.pdf)]. Annual growth rates calculated as geometric averages: $[(X_n/X_0)^{(1/n)} - 1] * 100$ (ESCAP 2015)

**Table 1.1** World demand for fertilizer nutrient use, 2015–2020 (thousand tons) (https://www.fao.org/3/i6895e/i6895e.pdf)

| Year | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 |
|---|---|---|---|---|---|---|
| Nitrogen (N) | 110,027 | 111,575 | 113,607 | 115,376 | 117,116 | 118,763 |
| Phosphate ($P_2O_5$) | 41,151 | 41,945 | 43,195 | 44,120 | 45,013 | 45,858 |
| Potash ($K_2O$) | 32,838 | 33,149 | 34,048 | 34,894 | 35,978 | 37,042 |
| Total (N + $P_2O_5$ + $K_2O$) | 184,017 | 186,668 | 190,850 | 194,390 | 198,107 | 201,663 |

The Food and Agriculture Organization of the United Nations (FAO) in association with other collaborative members of the 'Fertilizer Outlook Expert Group' (Fertilizer Association of India—FAI, International Fertilizer Association—IFA, International Fertilizer Development Center—IFDC, K + S KALI GmbH—K + S, The Fertilizer Institute—TFI, Fertilizers Europe) dealing with fertilizer production, consumption, and trade of world and regional nitrogen (N), phosphorus (P) expressed as phosphate ($P_2O_5$), and potassium (K) expressed as potash ($K_2O$) fertilizer supply, demand, and potential balance and FAO (2020) summarized that global consumption of the three main fertilizer nutrients, nitrogen (N), phosphorus expressed as phosphate ($P_2O_5$), and potassium expressed as potash ($K_2O$), is estimated to reach 186.67 million tons (N, $P_2O_5$ and $K_2O$) in 2016, up by 1.4% over 2015 consumption levels. The demand for N, $P_2O_5$, and $K_2O$ is forecast to grow annually on average by 1.5, 2.2, and 2.4%, respectively, from 2015 to 2020 (FAO 2021c, d). Over the next 5 years, the global capacity of the production of fertilizers, intermediates, and raw materials is also expected to increase (Table 1.1, Figs. 1.9, 1.10, 1.11 and 1.12).

Indiscriminate use of chemical fertilizers in agricultural practices poses serious threat to the environment by toxicating the agricultural soil, water, and food which is a serious threat to the human health.

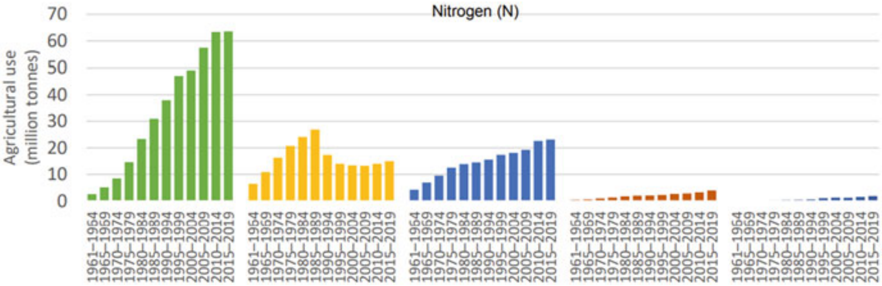

**Fig. 1.9** Fertilizer use (N) by region [Source: FAO 2021a, b (https://www.fao.org/3/cb5738en/cb5738en.pdf)]. Annual growth rates calculated as geometric averages: $[(X_n/X_0)^{(1/n)} - 1] * 100$ (ESCAP 2015)

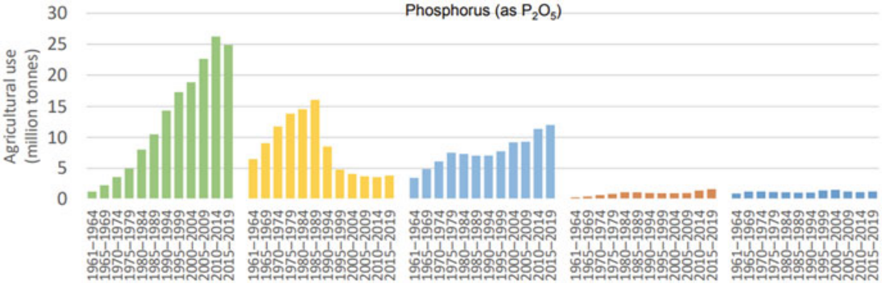

**Fig. 1.10** Fertilizer use ($P_2O_5$) by region [Source: FAO 2021a, b (https://www.fao.org/3/cb5738en/cb5738en.pdf)]. Annual growth rates calculated as geometric averages: $[(X_n/X_0)^{(1/n)} - 1] * 100$ (ESCAP 2015)

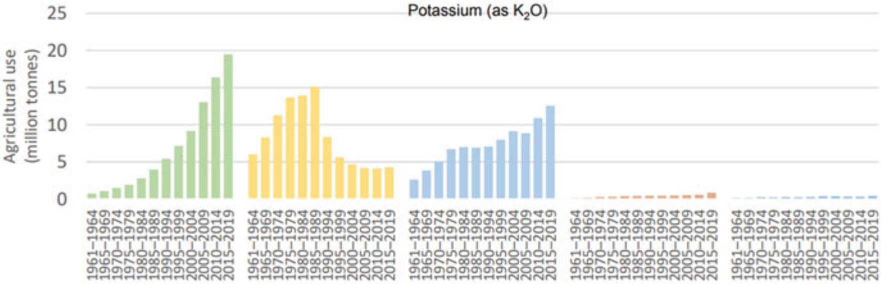

**Fig. 1.11** Fertilizer use ($K_2O$) by region [Source: FAO 2021a, b (https://www.fao.org/3/cb5738en/cb5738en.pdf)]. Annual growth rates calculated as geometric averages: $[(X_n/X_0)^{(1/n)} - 1] * 100$ (ESCAP 2015)

### 1.4.8 Plant Growth Regulators (PGRs)

PGRs are synthetic chemical substances and similarity with natural plant hormones and the usage of PGRs in agriculture regulate the growth and development of plants

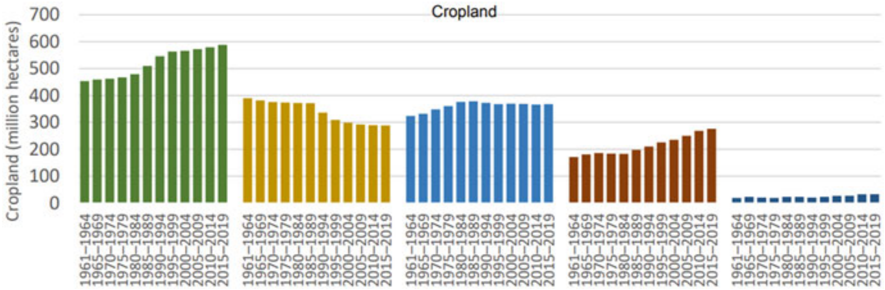

**Fig. 1.12** Crop land area, by region [Source: FAO 2021a, b (https://www.fao.org/3/cb5738en/cb5738en.pdf)]. Annual growth rates calculated as geometric averages: $[(X_n/X_0)^{(1/n)} - 1] * 100$ (ESCAP 2015)

and are regarded as boosters of agricultural yield (Vedamurthy et al. 2021). Several commercially available PGRs are used in agriculture, horticulture, floriculture, and forestry for growth regulation, yield enhancement, and disease management (Hameed and Farooq 2021).

FAO (2021a) in the explanatory noted defined the composition of pesticides and included plant growth regulators in the pesticides use domain. Excessive usage of plant growth regulators such as Alar, Alpha Naphthyl Acetic Acid 4.5% SL (Na salt), Chlormequat Chloride 50% SL, Chlorpropham 50% HN, Ethephon 10% Paste, Forchlorfenuron 0.1% L (w/v), Gibberellic Acid Technical (90% w/w), Hydrogen Cynamide 50% SL, Mepiquat chloride 5% AS, 1-Methylcyclopropene 3.3% VP, Paclobutrazol 23% SC (W/W) / (25% W/V), Paclobutrazol 23% SC (W/W) / (25% W/V), Paclobutrazol 23% SC (W/W) / (25% W/V), Prohexadione-Ca 10% WG, Sodium Para –Nitrophenolate 0.3% SL, Triacontanol 0.05% EC, and Cyclanilide 2.10% w/w + Mepiquat Chloride 8.40% w/w SC pose serious threat to environment.

**Acknowledgments** Authors sincerely acknowledge the usage of data from the reports of Food and Agriculture Organization of United Nations (FAO) in this chapter for better understanding of the chapter to the readers. SSG and RG sincerely acknowledge the support received from DBT-BUILDER-Maharshi Dayanand University Interdisciplinary Life Science Programme for Advance Research and Education vide Letter No. BT/INF/22/SP43043/2021; vide SAN No. 102/IFD/SAN/1796/2021-2022.

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# Agrochemicals: Provenance, Environmental Fate, and Remediation Measures

# 2

Poonam Bhanse, Anuja Maitreya, Ayurshi Patil, Prerna Yesankar, Lal Singh, and Asifa Qureshi

## Abstract

Across the globe, farmers have been facing numerous issues, for instance, climate change, attack of insects, weeds, rotifers, rodents, pests, etc., on crops. Agrochemicals have produced economic benefits by improving production and preventing vector-borne diseases, but their widespread use has resulted in human and environmental damage. The progress of high-tech manufacturing of agrochemicals and the fast evolution of farming have led to the release of many contaminants, viz., heavy metals, polychlorinated biphenyls, and pesticides in the environment. However, the quest for new agrochemicals to combat weeds and pest resistance problems continues. Qualitative and demand-driven research in soil science is currently needed, particularly in developing countries, to facilitate sustenance of healthy ecosystem. Certainly, feasible alternatives, viz., biochar, plant growth-promoting rhizobacteria, and fungi, become necessary. The current study highlights the prevalence of agrochemicals which have impacted ecosystem components and their fate with respect to adopted mitigation process.

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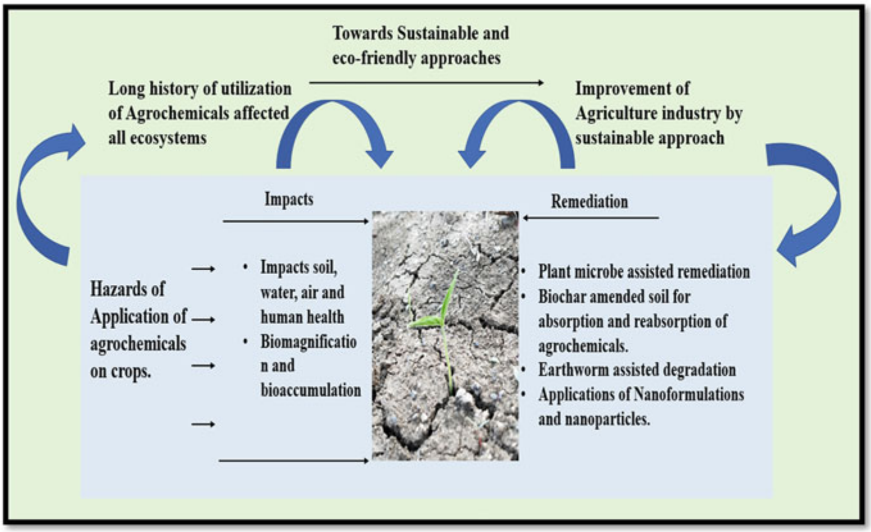
https://doi.org/10.1007/978-981-16-9310-6_2

**Graphical Abstract**



**Keywords**

Agrochemicals · Contaminants · Environmental damage · Pesticides · Remediation

## 2.1 Introduction

Crop defense chemistry has progressed from its "alchemical" origins in the late 1800s to a high-tech technology that promotes the efficient processing of fruit, feed, and fiber for an ever-increasing population (Lamberth et al. 2013). The global demand for food will continue to rise for at least another 40 years if population and consumption growth continue. Growing competition for soil, water, and electricity and overfishing would impact our ability to generate food, as will the immediate need to reduce the food system's environmental impact (Godfray et al. 2010). According to the Economic and Social Affairs (2019), significant rises in food production since the 1960s Green Revolution have allowed the world population to rise at a slower rate, exceeding 9.7 billion by 2050 and 10.9 billion by 2100.

Even though agrochemicals have provided substantial economic benefits by increasing the productivity and yield of food and fibers and preventing vector-borne diseases, research indicates that their use has harmed human and environmental health (Speight 2016; Yadav et al. 2015). In soil and plant systems, many of these agrochemicals remain in extended life creating migration risk through the supply of drinking water and the food chain (Sarkar et al. 2020). The development of novel agrochemicals continues uninterrupted and leads to a drop in resistance of conventional goods, a demand for more attractive products, a shifting pest spectrum, and an expanding agricultural requirement and practice (Sparks and Lorsbach 2017).

Agrochemicals encompass various pesticide compounds, insecticides, herbicides, fungicides, and nematicides (kills roundworms). Synthetic fertilizers, chemical growth factors, hormones, and concentrated stocks of raw animal manure are all instances of the term (Speight 2016). Excessive chemical utilization has contaminated soil and polluted rivers with nitrate, a chemical substance that is toxic to living organisms in high concentrations. Furthermore, nutrient drainage (or leaching from the ground) into waterways, lakes, and other surface waters (the aqua sphere) can promote algae proliferation, which can disrupt the life-cycle of fish and other aquatic animals (Speight 2016).

Chemicals used to kill or control insect or plant pests are referred to as "pesticides" or any material or combination of substances used to deter, kill, repel, or mitigate pests according to US Environmental Protection Agency (Ravichandra 2018). When one considers the sheer quantity of active chemicals, formulations, and environmental mixes that have not been thoroughly investigated or assessed, the magnitude of the pesticide hazard becomes clear. Furthermore, the widespread usage, persistence, transit, and bioaccumulation of these chemicals in wildlife, as well as food chain biomagnification, make the potential impact even more concerning (Hayes et al. 2017).

Farmers' use of foreign substances on crops is thought to date back to prehistoric times. Insect depravities, plant diseases, and specific simple agricultural rules, such as the periodic barring of land in the fallow condition, are mentioned in the Bible "Pest-averting sulfur," Homer states (Kohn and Baker 1992). Although research trends in agrochemicals were published in 1965, more research is being focused on agrochemicals in the last decade (Fig. 2.1).

Following World War II, agricultural techniques altered drastically. Nitrogen production methods used in explosives have been modified for use as fertilizer in agriculture. Furthermore, during World War II, pesticides used to combat disease-carrying insects were modified for the management of agricultural insect pests. Herbicides that had previously been employed as defoliants to damage food sources and help in battling troops who utilized forests as cover were eventually adapted to manage weeds in agriculture. Pesticides are widely used in agriculture, resulting in global exposure to toxic substances. Pesticides can be discovered in drinking water reservoirs, the atmosphere, on mountain summits, and even in distant parts of the Arctic where they are not utilized, since they travel through water, air, and migrating animals (Hayes et al. 2017). Furthermore, many of the issues linked with pesticide overuse, such as endocrine-disrupting effects at low doses (which are deemed nontoxic by traditional toxicological standards), have been recognized in the last two decades (Hayes et al. 2017; Vandenberg et al. 2012).

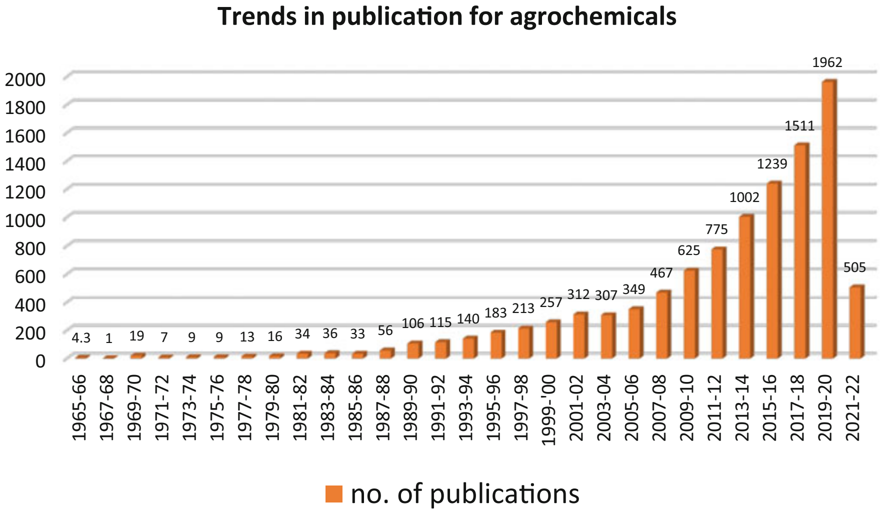


**Fig. 2.1** Graph depicting the trend of publications (Mendeley search engine) in the field of agrochemicals (https://www.mendeley.com/search/agrochemicals. Accessed 11 Aug 2021)

## 2.2 Types of Agrochemicals

Agrochemicals used primarily for crop production are roughly divided into four groups: Plant-protection chemicals/pesticides, fertilizers, plant growth regulators, and other substances (for e.g., soil conditioners and animal husbandry products) as depicted in Fig. 2.2 (Mandal et al. 2020). Different types of agrochemicals applied in agricultural sector are enlisted in Table 2.1.

### 2.2.1 Plant-Protection Chemicals/Pesticides

Plant-protecting chemicals/pesticides are chemicals that are used to kill or prevent specific plants varieties or microorganisms recognized as pests (Pandya 2018). They are further subdivided into the following:

1. **Herbicides:** Utilized to inhibit or kill herbs and weeds, e.g., glyphosate and gramoxone.
2. **Insecticides**: Utilized to destroy the insects. Insecticides such as organophosphates, carbamates, pyrethroids, and organochlorines are ovicides, which destroy eggs, and larvicides, which kill larvae.
3. **Fungicides**: Mostly utilized to prevent growth of fungi and oomycetes, e.g., mankocide.

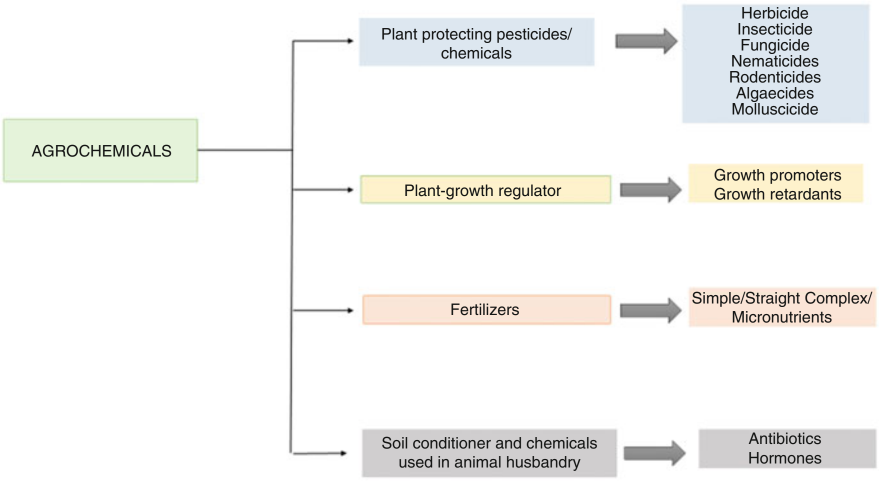


**Fig. 2.2** Schematic classification of agrochemicals

4. **Nematicides**: Specifically utilized for the prevention or killing of nematodes, e.g., furadan.
5. **Rodenticides**: Generally utilized for the prevention of rodents like mice, rat, etc., e.g., klerat.
6. **Algaecides**: Generally utilized to control algae, commonly known as algicides.
7. **Molluscicides**: Used to prevent growth of molluscs like slugs and snails, e.g., slugit.

In Asia, India leads in the production of pesticides and ranks 12th globally for the consumption of pesticides (Yadav et al. 2015). The pattern of pesticides' usage in Indian agriculture during 2015–2020 illustrate in Fig. 2.3 (Nayak and Solanki 2021; Choudhury et al. 2016; Subash et al. 2018; Koli and Bhardwaj 2018) (http://ficci.in/events/25397/ISP/Presentation_PwC_Agrochem.pdf). Agrochemicals contribute a major part in increasing the country's food output soon after the green revolution.

Organophosphates, pyrethroids, botanical and biological products, carbamates, and chlorinated hydrocarbons are the most often used insecticides. Similarly, bipiridils, triazines, phenoxy hormone products, urea derivatives, triazines, dinitroanilines, sulfonylurea, carbamates, and uracil are the most often used herbicides. Inorganic bactericides and fungicides are widely utilized, followed by dithiocarbamates, other fungicides, benzimidazoles, diazoles, morpholines, disinfectants, seed-treating fungicides, and other fungicides. Anticoagulants are the most often used rodenticides, followed by narcotics (Huang et al. 2018).

**Table 2.1** Types of agrochemicals used in agriculture

<table>
<tr><th colspan="2">Types of agrochemicals</th><th>Examples</th><th>References</th></tr>
<tr><td rowspan="6">Insecticides</td><td>Phosphorus containing insecticides</td><td>Dimethoate<br>Glyphosate<br>Malathion</td><td>Ye et al. (2018), Chowdhury et al. (2013), Upadhyay and Dutt (2017), Awumbila and Bokuma (1994), Bhandari (2017), Maloney (2001) and Meftaul et al. (2021)</td></tr>
<tr><td>Nitrogen containing insecticides</td><td>Chlordimeform<br>Benzoylphenyl urea</td><td>Beeman and Matsumura (1973) and Junquera et al. (2019)</td></tr>
<tr><td>Chlorine containing insecticides</td><td>DDT, Lindane<br>Toxaphene<br>Dieldrin<br>Aldrin</td><td>Maloney (2001), Saleh (1991), Snedeker (2001) and Bhandari (2017)</td></tr>
<tr><td>Carbamate containing insecticides</td><td>Carbofuran<br>Carbosulfan<br>Ethienocarb<br>Oxamyl</td><td>Felsot et al. (1981), Vargas-Bernal et al. (2012), Chopra et al. (2011) and Bromilow et al. (1980)</td></tr>
<tr><td>Pyrethroid containing insecticides</td><td>Cypermethrin<br>Resmethrin<br>Tetramethrin<br>Cyphenothrin</td><td>Chowdhury et al. (2013), Soderlund (2015), Tatebayashi and Narahashi (1994) and Huang et al. (2020)</td></tr>
<tr><td>Insect growth regulator</td><td>Tebufenozide<br>Methoxyfenozide<br>Halofenozide<br>Chromafenozide</td><td>Mohamed et al. (1987), Carlson et al. (2001) and Ditya et al. (2012)</td></tr>
<tr><td>Herbicides</td><td colspan="2">Glyphosate (touchdown and round-up), acetanilide, Butachlor, Chlorbromuron, flufenacet, hexythiazox, Prosulfocarb, Pyriproxyfen</td><td>Burchfield et al. (2019), Zhang et al. (2019) and Mohammed et al. (2020)</td></tr>
<tr><td>Bactericides</td><td colspan="2">Ridomil, Benzimidazoles, copper, Dithiocarbamate (Thiram), copper hydroxide, Acibenzolar-S-methyl (ASM)</td><td>Xu et al. (2021), Sun et al. (2021), Liao et al. (2021), Liu et al. (2019) and Rekanović et al. (2019)</td></tr>
<tr><td>Acaricides</td><td colspan="2">Diazinon, permethrin, Formamidines, Fenpyroximate, Dimethoate</td><td>Boncristiani et al. (2012), Singh (2008), Ye et al. (2018) and Kolbe et al. (1991)</td></tr>
<tr><td>Plant growth regulator</td><td colspan="2">Trinexapac ethyl (TE), Paclobutrazol (PAC), and abscisic acid (ABA)</td><td>Mohammadi et al. (2017) and Schiavon et al. (2019)</td></tr>
<tr><td>Fertilizer</td><td colspan="2">Nitrogen fertilizers, phosphorus fertilizers, potassium fertilizers, calcium, magnesium and Sulphur fertilizers, micronutrient fertilizers</td><td>Fixen and West (2002) and Savci (2012)</td></tr>
<tr><td>Soil conditioner and chemicals used in animal husbandry</td><td colspan="2">Alginates silicates of potassium and sodium<br>Hydrolyzed polyacrylonitrile (HPAN), vinyl acetate and the partial methyl ester of maleic acid (VAMA), isobutylene and the half ammonium salt-half amide of maleic acid (IBMA)</td><td>Martin et al. (1956)</td></tr>
</table>

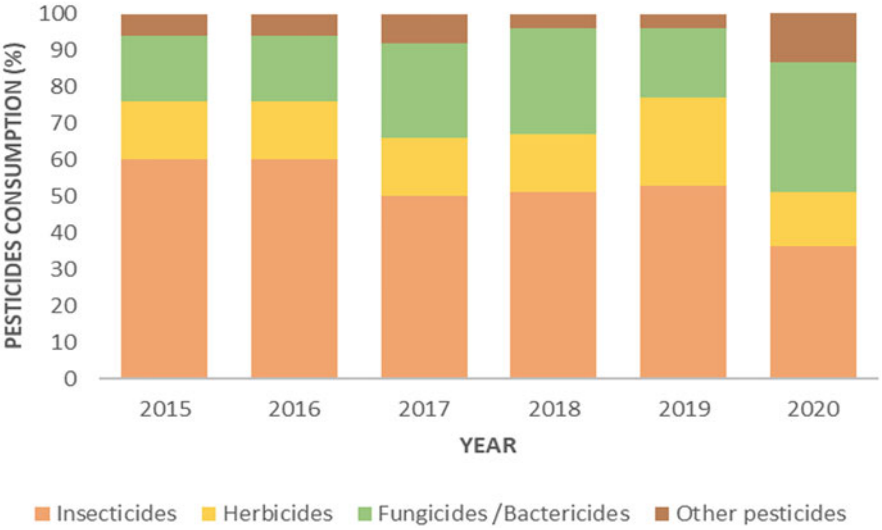


**Fig. 2.3** Pesticides' consumption scenario during 2015–2020 in Indian agriculture

### 2.2.2 Plant Growth Regulators

Plant exogenous hormones, also known as plant growth regulators, are synthetic chemicals that are comparable to natural plant hormones. They are used to control the development of plants. If used in conjunction with proper agricultural practises, plant growth regulators will not be hazardous to human health. Excessive crop growth, caused by the abuse of plant growth regulators, results in the surface of fruits ripening while the center remains raw, lowering the quality of the fruits, e.g., Trinexapac (Used for the prevention of lodging in cereals, turl, and sugarcane) (Meena et al. 2020).

### 2.2.3 Fertilizers

The chemical compounds mostly used to promote the growth of plant are fertilizers. They are capable to mitigate deficiency of nutrient in the soil. Fertilizers are further grouped into two categories: Inorganic and Organic fertilizers. The inorganic fertilizers are commonly known as synthetic fertilizers synthesized artificially by means of chemical procedures exploiting natural deposits that are altered chemically, e.g., concentrated triple superphosphate. Organic fertilizers are the substances which exist naturally and synthesized by natural ways. The maximum utilization of fertilizers is in the Asia region. In fertilizer production, China ranks first in the world, while United States ranks second and India ranks third in the world. According to FAO estimation, from 2015 to 2030, the consumption of fertilizer is predicted to rise from 138 million ton in 1997/98 to million tons in 2030 with an

0.1% annual growth rate in the world (Alexandratos and Bruinsma 2012). Wheat, maize, and rice are most leading fertilizer-consuming crops. Fertilizers are precisely used to enhance and improve the nutrient deficiencies in the land and hence their use confirms the elevation in crop rate. The most usually used fertilizers are phosphorous, potassium, and nitrogen (Schmitz et al. 2013).

### 2.2.4 Soil Conditioner and Chemicals Used in Animal Husbandry

#### 2.2.4.1 Soil Conditioner Used in Animal Husbandry

The soil conditioners keep the soils in good shape and maintain the integrity of the soil. Soil conditioner comprises of compost, manure, peat moss, and leaves. The soil conditioner is mostly placed on top of the soil (around 2–3 in. deep) and mixed with soil. Then, soil conditioner is added to improve soil condition by enhancing the water holding capacity and aeration. Livestock manure, crop residues, and peat are the commonly used materials for the production of soil conditioner (Singh et al. 2020).

#### 2.2.4.2 Chemicals Used in Animal Husbandry (Antibiotics and Hormones)

Antibiotics and hormones adversely affect the ecosystem and human health; hence, regarded as evolving environmental micro-contaminants. The use of agrochemicals results in the increase and enrichment of agriculture products. However, on the other side, agrochemicals may also cause a threat to the ecological and environmental system (Singh et al. 2020).

## 2.3 Impacts of Agrochemicals on Elements of Environment

To satisfy the food demands of ever-growing population, there was abundant use of agrochemicals in agriculture to equilibrate the difference between food production and food consumption. However, the routine excess use of agrochemicals may result in degradation of environment and generates several challenges on soil health and ecosystem (Aktar et al. 2009; Jayaraj et al. 2016). The application of agrochemicals in agriculture continuously leads to accumulation of heavy metals that contaminate the environment and food chain too, which subsequently results in human health problems and disorder as represented in Fig. 2.4 (Nasreddine and Parent-Massin 2002).

### 2.3.1 Water

The agrochemicals negatively affect the terrestrial and aquatic lives, i.e., microorganisms (Turnbull et al. 2001), plants (Frankart et al. 2003), fish (Grande et al. 1994), and invertebrates (Castillo-Martínez et al. 2006). The core recipient in

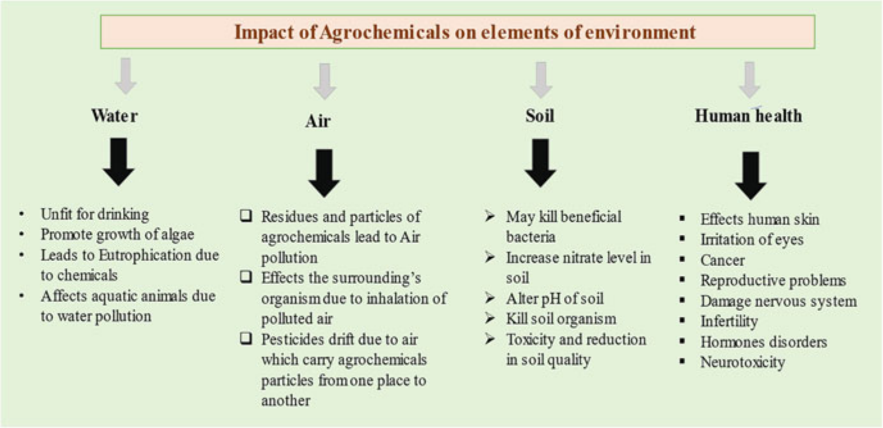


**Fig. 2.4** Diagrammatic illustration of impact of agrochemicals on elements of environment

agricultural field is the soil, whereas the water bodies situated around the agricultural field are the final collector of agrochemicals residue (Biswas et al. 2014). The main entry pathway of pesticides into watercourse is the agrochemicals' spray on soil. Extreme use of agrochemical contaminates the groundwater with nitrate, which makes the water unfit for human and livestock. The heavy load of nitrate in water can poison animals through immobilization of haemoglobin in blood and reduce the ability of oxygen transport (Brindha et al. 2017). Additionally, the agriculture runoff into lakes, streams, and sources of surface waters results in increased efficiency of those aquatic ecosystems, a well-known problem as eutrophication. Eutrophication results in extensive fish mortality and that of other aquatic animals, along with extreme nuisance growth of algae and off-taste of drinking water. A powerful insecticide like DDT (dichlorodiphenyltrichloroethane) remains persistent in environment for a long time span and contaminates well water, food, and wildlife species along with humans that come in contact. The additional components that stimulate agrochemicals for contaminating the water body are weather, water solubility, nature of soil, distance of water body from application site, variety of growing crop, etc. (Senesil et al. 1999).

#### 2.3.1.1 Case Study

The agrochemicals which are regularly sprayed in agricultural fields such as cyper methrin and chlorpyrifos contaminate the water bodies (Maltby and Hills 2008). According to the study of Kellogg et al. (2002), residues of agrochemicals were also found to be present in rainwater and groundwater. In China, the water bodies are found to be contaminated with the hexachlorocyclohexane(HCH) traces, dieldrin endrin, DDT, etc. (Zhang et al. 2011). In Lucknow, the pesticide effluent industry from Chinhat industrial zone was reported to contaminate the waterbodies with monocrotophos, α-endosulfan, chlorpyrifos, malathion, β-endoulfan, and dimethoate (Dhananjayan et al. 2020).

## 2.3.2 Air

The agrochemicals also prompt air pollution. After spraying, the agrochemicals remain suspended in air for long time and pollute the surrounding air by drifting to the other areas which is dangerous to wild animals (Ansari et al. 2014). During the application, the climatic condition is responsible for the spread of agrochemicals. Hence, the amount of inhalable agrochemicals in the environment varies from time to time (Damalas and Eleftherohorinos 2011). Additional parameters like soil texture, agrochemicals' solubility in soil, and concentration of agrochemicals play a crucial role in spread of agrochemicals in the air.

### 2.3.2.1 Case Study

At ground level, the spray of agrochemicals has very less possibility of drifting in the air compared to the aerial spraying. The residues of lindane, DDT, and aldrin were identified at high altitude cold region, on the equator in India, and also in the Greenland ice sheet due to the flow of oceans and atmospheric current resulting in enhancement of biological pesticides (Zhang et al. 2011). The organothiophosphate, insecticide, was found in the air and seawater in Artic region. Animals from Greenland show the presence of endosulfan (Vorkamp and Rigét 2014). Farmers should be well educated about the dangerous effects of agrochemicals and must try to make a buffer zone around the agriculture fields that comprise empty land or non-crop plants.

## 2.3.3 Soil

Application of agrochemicals in farming may adversely affect soil quality, population, and proliferation of beneficial soil microorganisms directly or indirectly, which majorly participate in nutrient cycling progressions, such as fixation of nitrogen, phosphorus solubilization, and biotransformation of another essential nutrient. Various biological activities of the soil are disrupted by the overuse of agrochemicals. Few studies revealed the impact of various pesticide on inhibiting the activity of soil enzymes which influence the nutrient status of soil including hydrolyzes, urease, nitrate reductase, oxidoreductases, dehydrogenase, and nitrogenase activities (Meena et al. 2020; Malik et al. 2017). The activities of soil microbial enzymes act as indicators to define the biological health, fertility, and chemical status of soil. Assimilation of agrochemicals in the soil eliminates useful microbes of soil which participate in essential enzymatic components like chain of reactions which play central role to *contemporize* key chemical processes in soil (Malik et al. 2017)**.** Soil microbes are capable to degrade agrochemicals present in soil. Sometimes, microbial incorporation of the metabolites produced during degradation may increase number of microbes in the soil and lower persistence of pesticide residues (Huang et al. 2018; Mandal et al. 2020). Due of this, the application of several agrochemicals has been banned in agriculture practices.

#### 2.3.3.1 Case Study

Historically, a huge quantity of agrochemicals is annually used as fertilizers and pesticides at agricultural soils. Applications of such chemicals may lead to increase in the proportion of heavy metals, specifically Cadmium (Cd), lead (Pb), and Arsenic (As) in the soil. Pesticide contamination including glyphosate, Propoxur, Acephate, Deet, Diazinon, Metaldehyde, Boric Acid, Dursban, DDT, Malathion, etc. is an alarm for present scenario of pollution of agriculture soil (Sparks and Lorsbach 2017). A study was conducted by Newman et al. (2016) to evaluate the effects using Glyphosate for long term on bacterial communities associated with soil rhizosphere. It was concluded that application of glyphosate for long period of time may influence the nutrient status of rhizosphere and comparative abundance of Acidobacteria decreased when expose to glyphosate. Another study on glyphosate applied in association with atrazine was analyzed by Bernardes et al. (2015) in Brazil. It was observed that the presence of atrazine temporarily decreased soil microbial biomass. General application of insecticide in agriculture and industry has led to extensive contamination of DDT (dichlorodiphenyltrichloroethane) in the environment (Thuy 2015). According to the study of Fang et al. (2017) in southwestern of China, the spreading of organochlorine pesticides (OCPs) in deep soils (−200 cm) of contaminated site had DDTs in high amount.

### 2.3.4 Human Health Impact

The people from rural sector come in contact with agrochemicals regularly either directly or indirectly. Continuous exposure of these agrochemicals results in neuropsychiatric disorder like depression, anxiety, and mood disorders. Most of agrochemicals cause change in autonomic, central nervous system, and peripheral nervous system (Bernardes et al. 2015). In Asia and America, the chance of death is extreme due to the continuous use of agrochemicals (World Health Organization 2014). In humans, the common signs of acute agrochemicals poisoning are headaches, skin discomfort, weakness, exhaustion, fatigue, circulatory problems, vomiting, excessive sweating, cramps, impaired vision, nausea, tremors, dizziness, dizziness, etc., and in extreme cases, death and coma (Bödeker and Dümmler 1993). In most cases, agrochemicals result in chronic diseases if they are incorporated for long time. Several agrochemicals, specifically pesticides which are regularly used in agriculture, are probably considered carcinogenic for humans. There is extreme risk of contracting non-Hodgkin lymphomas and leukemia in the people who are working in the fields with risky exposure to agrochemicals (Alavanja et al. 2004). The use of pesticides is directly proportional to the chronic disease such as cancer of the breasts, pancreas, prostate, testicles, ovaries, intestines, kidneys, multiple myelomas, and sarcomas along with brain tumors (Bödeker and Dümmler 1993). Agrochemicals, especially carbamates, organophosphate, and pyrethroids at low exposure level, also cause neurotoxicity (Ishigami et al. 2008). Other health effects due to use of pesticides related with cancer, disturbance of hormones, serious problem in reproduction with complication in foetal development, and agrochemicals' exposure result in allergies, hypersensitivity, and asthma (Gilbert 2012).

#### 2.3.4.1 Case Study

The first case of agrochemical poisoning in India was reported in 1958 at Kerala (Karunakaran 1958). According to the inspection report of Dasgupta et al. (2005), among people who are in continuous exposure of agrochemicals, 16% experience irritation in eyes, 6% have dizziness, 7% experience vomiting on exposure to agrochemicals, and 21% have severe headaches. As per survey report (Islam et al. 2012), among the people who are exposed to the agrochemicals in Dhaka (Bangladesh), 26% people died. A study by Orton on the effect of 37 pesticides on hormone level revealed that 23 pesticides out of 37 were antiandrogenic, while rest were androgenic. Once the foetus is exposed to the agrochemicals, it suffers with developmental disorder and malformation of sexual organs (Orton et al. 2011).

## 2.4 Environmental Fate of Agrochemicals

For ecological destiny, the evaluations required are (1) rate and course of debasement in soils, (2) versatility in soils (both draining and runoff potential), (3) destiny in amphibian frameworks, and (4) fate in air. Of these, degradation in soils is generally surely known and our comprehension of versatility in soils under regular field conditions has improved significantly as the aftereffect of multi-disciplinary approaches including pesticide science, soil science, and hydrogeology. The destiny of agrochemicals in normal amphibian frameworks has gotten significant consideration of late, principally as an immediate aftereffect of administrative necessities (Roberts 1996) as depicted in Fig. 2.5. Synthetic agrochemicals used at high concentrations in the environment for pest control inevitably spread and harm nontarget species. They will dilute spontaneously, as predicted by the second law of thermodynamics, and will be transported into accessible sinks in the environment by all available transport modes. These dispersing chemicals are found in a wide range of produced goods that are believed to be necessary for contemporary economic civilization, which is primarily reliant on the use of fossil fuels. Despite the necessity of environmental protection, pesticide-like agrochemicals will undoubtedly continue to spread into ecosystems due to the increased global food security demands that are projected to worsen (Kennedy et al. 2000).

Agrochemicals may pollute the environment in a number of ways. Nonpoint source pollution, also known as diffuse contamination and dispersion, is one of the most common ways for pesticides to get contaminated. Leaching, volatilization, wash and runoff, spray drift, and lateral drainage are all examples of pesticide transformation and mobility, whereas pesticide degradation includes photolysis as well as biotic and abiotic breakdowns. Dust from the seed treatment process can potentially pollute the environment with pesticides. Furthermore, pesticide residues can be carried by plant components and released into the soil through the decomposition of plant litter (Sarkar et al. 2020).

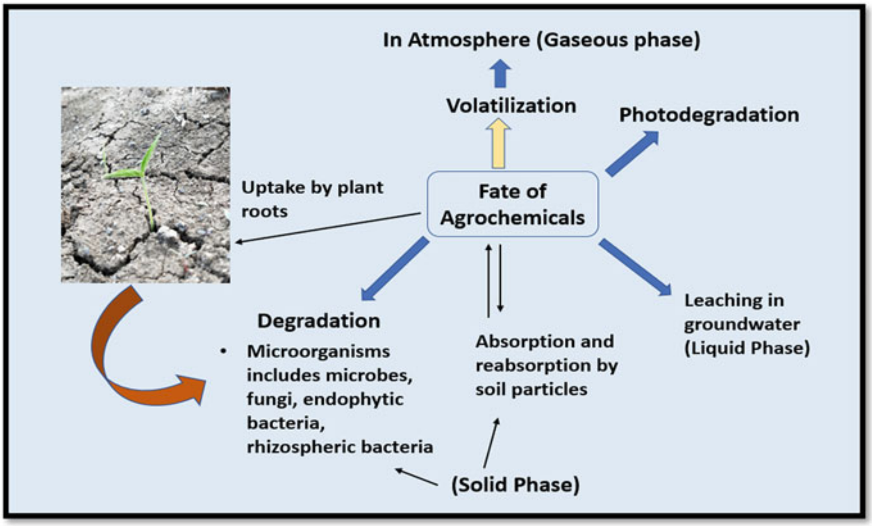


**Fig. 2.5** Fate of Agrochemicals

### 2.4.1 Bioaccumulation and Biomagnification of Agrochemicals

Bioaccumulation is the process where chemical compounds get accumulated in the tissues of organism throughout its life. When the concentration of chemical increased between the organism in the food chain from one tropic level to other tropic level, it is well-defined as biomagnification. The organism at higher tropic level has higher concentration of chemical. When the residues of chemicals in the environment of the habitat cross the limit, there is coincidence of bioaccumulation and biomagnification process. This ultimately results in accumulating deposits within the organism which are transferred to the upcoming trophic level and get biomagnified at very least toxic level as illustrated in Fig. 2.6 (Gobas et al. 2009).

Particularly persistent, longer half-life of chemicals and toxic nature of the environment are responsible for the bioaccumulation and biomagnification process. Organochlorine compounds in pesticides (DDT) and heavy metals (As, Cd, Cr, and Pd) are the examples of persistent toxic chemicals. Regarding agrochemicals, pesticides are specifically recognized due to their persistence in the environment whose half-life in air, water, and soil varies from hours to several years. The hazardous agrochemicals may come in contact with organism at different trophic levels, contaminate the agroecosystem, and negatively impact the biological diversity (Bhadouria et al. 2020). Due to heavy application of agrochemicals, there is substantial changes in natural characteristics of terrestrial and aquatic ecosystem.

In risk assessment and biomonitoring study, bioaccumulation and biomagnification played vital roles. Based on the Stockholm Convention, several countries have taken initiative on persistent organic pollutants, for regulation of the utilization of agrochemicals, to manage its distribution, and to evaluate its health and

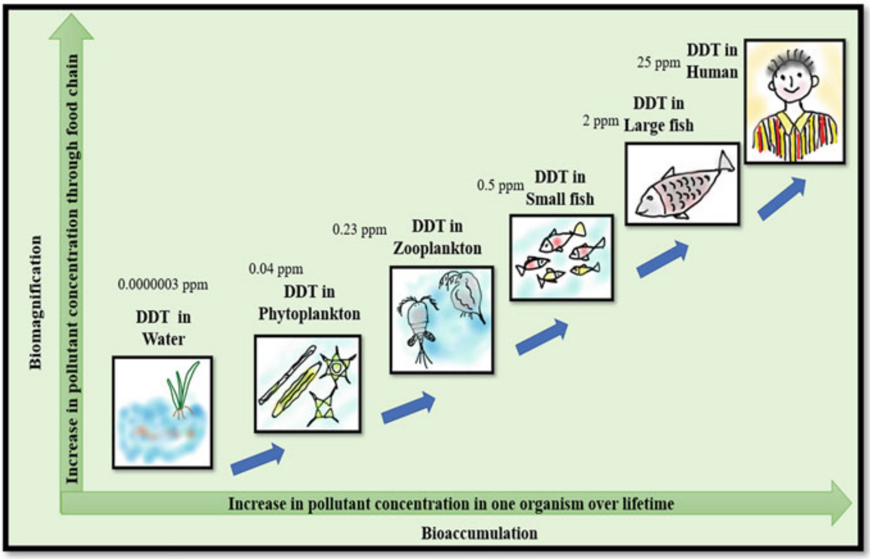


**Fig. 2.6** The process of biomagnification and bioaccumulation in natural ecosystem

environmental effects. Particularly, Canadian Environmental Protection Act in Canada (CEPA 1999), Toxic Substances Control Act in USA (USEPA 1976), and the Registration, Evaluation, Authorization, and Restriction of Chemicals program (REACH) were the most renowned acts regulating the use of persistent chemicals. But unfortunately, specifically in developing countries and underdeveloped countries, these rules were not followed as they were devoid of knowledge about bioaccumulation and biomagnification (Yadav et al. 2015).

The extreme and ancient use of agrochemicals has always been anxious condition for researchers. The random use of agrochemicals has contributed in the accumulation of toxic heavy metals in soil (Kour et al. 2021). Simultaneously, the leachate from agricultural field passes into the water body and water bodies are accumulated with heavy metals. The biomagnification process takes place through the food chain accumulating the residues of heavy metals. Hence, it is compulsory to perceive knowledge about the factors influencing the biomagnification and bioaccumulation process (Szynkowska et al. 2018).

#### 2.4.1.1 Case Study

1. Lenka et al. (2016) revealed metal residues were accumulated, and their biomagnification cycle was responsible for severe health issue in human due to heavy application of phosphatic fertilizers for long time.
2. Research on residues of heavy metals exposed their increase up to few folds beyond the standard limits due to the enhanced utilization of fertilizers for agricultural work (Zhou et al. 2015).

3. The study of Adhikari (2012) showed that various parameters such as ambient temperature, physical and chemical characteristics of compounds, chemical composition of compounds, cooperative qualities of compounds with soil, air, and water, and efficiency of absorption in crops can all impact the persistence of hazardous chemicals in soils. This altogether is accountable for biomagnification and bioaccumulation of agrochemicals.

## 2.5 Remediation Processes

### 2.5.1 Plant-Microbe Assisted in Toxification of Agrochemicals

The environmental concerns created by the widespread use of chemical pesticides are becoming increasingly significant, and microbial breakdown of chemical pesticides in the ecological environment has garnered a lot of attention (Li et al. 2020). For the treatment of polluted soils, physical remediation, chemical remediation, and bioaugmentation (biodegradative microorganisms to contaminated soils) are widely utilized. Because these remediation procedures are expensive and introduced microorganisms frequently do not survive in the environment, phytoremediation has emerged as a viable option. Plants and their associated microbes assist in the removal, transformation, or assimilation of hazardous compounds found in sediments, soils, surface water, groundwater, and also the atmosphere (Reichenauer and Germida 2008; Boudh and Singh 2019; Rani et al. 2019).

Biological decontamination approaches have proven to be more successful than traditional and costly physicochemical procedures. Individual bacteria or consortia of soil microorganisms, both native and genetically engineered, perform microbial remediation via a number of metabolic processes. These biochemical pathways are often linked to their innate growth and development of metabolic processes (Nayak et al. 2018). Some beneficial plant-microbe relationships exist in nature, specifically between plant growth-promoting rhizobacteria and plants, mycorrhizal fungi, and plant endophytic bacteria, which aid naturally in bioremediation process in polluted soil, where microorganisms enhance the availability of pollutants and can assist plants for the removal and extraction of organic and inorganic contaminants (Hare et al. 2017).

The enzymes, which operate extracellularly (breakdown of polymeric structure) or intracellularly (degradation of protein structure), are the most important instruments in the degradation process (mineralization). Microbes and enzymes from the genera *Pseudomonas*, *Micrococcus*, *Acetobacter*, and *Bacillus* are the most often utilized. Exploring and using the microbiological and genetic resources may help to minimize the hazard of xenobiotic pollutants not degrading (Nayak et al. 2018).

#### 2.5.1.1 Case Study (Table 2.2)

In the experimental dosages, the symbiotic nature between *C. ensiformis* and *Bradyrhizobium* sp. resulted in a substantial lowering in sulfentrazone residual concentration in the soil. Microbiological indications pointed to rhizosphere stability, with the 400 g/ha dosage producing the best outcomes (Mielke et al. 2020). Bacterial consortium comprising species of *Pseudomonas strains S1 and S2* was able to degrade *p*-nitrophenol (PNP). The strains were isolated from agricultural contaminated with organophosphorus pesticides (Qureshi and Purohit 2002). Góngora-Echeverría et al. (2020) suggested pure strains and microbial consortiums might be utilized as inoculum in systems as a bioaugmentation approach to improve pesticide treatment effectiveness. After 21 days, the novel bacterial isolates *B. aryabhattai* 114 and *B. vallismortis* 111 were able to utilize more than 90% of 4.40-DDE in a liquid medium (Nurzhanova et al. 2020).

Qureshi et al. (2012) observed that *Arthrobacter* HPC1223 was capable of degrading 2,4,6 trinitrophenol (TNP) (widely used in pharmaceuticals, pesticides, dyes, and explosives) as a source of nitrogen. Strain was isolated from activated biomass of effluent treatment plant. Nathiya et al. (2020) observed that two isolates, namely, *Bacillus* sp. 1 and *Lysinibacillus* sp., exhibited resistance to the pesticides, also secreted indole-3-acetic acid in the range of 56–97 μg/mL showing in vitro plant growth promotion activities *Trigonella foenum-graecum* (fenugreek leaves). A new bacterium *Pseudomonas rhizophila* S21, isolated from pesticide-contaminated artichoke field of Tunisia, showed both plant growth-promoting activities and pesticide-solubilizing activity by identifying essential genes involved in the synthesis of biosurfactants and biodegradation of xenobiotics (Hassen et al. 2018).

Among the five species of Azotobacter, *Azotobacter salinestris* was reported to fix the maximum amount of N2, produce GA and IAA, and show a P-solubilization role. It also demonstrated resistance to greater pesticide loads, the ability to catabolize harmful chemicals into nontoxic forms, and the ability to live for extended periods (Chennappa et al. 2018). Three potent phorate utilizing *Pseudomonas* sp. (*Pseudomonas* sp. strain Imbl 4.3, *Pseudomonas* sp. strain Imbl 5.1, and *Pseudomonas* sp. strain Imbl 5.2) were isolated from field soils. *Pseudomonas* sp. strain Imbl 5.1 metabolized phorate in 7 days as compared to the other two sp. in 13 days, displaying great potential for active bioremediation of phorate in agricultural soils and liquid cultures (Jariyal et al. 2015).

Bacterial consortium containing ten organisms was as follows: *Enterobacter ludwigii* JAS17, *Pseudomonas morviensis* JAS18, and Serratia marcescens JAS16 were isolated from monocrotophos-contaminated site and *Alcaligenes* sp. JAS1, *Sphingobacterium* sp. JAS3, and *Ochrobactrum* sp. JAS2 were isolated from chlorpyrifos-polluted soil; while *Halophillic bacteria* JAS4, *Enterobacter asburiae* strain JAS5, *Enterobacter cloacae* JAS7, and *Klebsiella pneumoniae* JAS8 isolated from endosulfan-contaminated soil degraded the mixture of pesticides, it produced two metabolites, (1) trans-2, 4-dimethylthiane, S,S,-dioxide and (2) cyclohexanone, 2-cyclohexylidene, making them as ideal candidates for bioremediation (Abraham et al. 2014).

**Table 2.2** Microbes capable of degrading agrochemicals and showing plant growth-promoting activity

| Microbe | Isolation of microbes | Degradation of pesticides. | Plant growth-promoting activity | Reference |
|---|---|---|---|---|
| *Bradyrhizobium* sp. | – | Sulfentrazone residue | Present | Mielke et al. (2020) |
| *Pseudomonas* strains S1 and S2 | Soil contaminated with organophophorus pesticides | *p*-nitrophenol (PNP) | – | Qureshi and Purohit (2002) |
| *B. aryabhattai 114 and B. vallismortis 111* | – | DDE | – | Nurzhanova et al. (2020) |
| *Arthrobacter* HPC1223 | Activated biomass of effluent treatment plant | 2,4,6 trinitrophenol (TNP) | – | Qureshi et al. (2012) |
| *Bacillus* sp. 1 and *Lysinibacillus* sp. | Pesticide-contaminated soil |  | Present | Nathiya et al. (2020) |
| *Azotobacter salinestris* | – | Pesticides (not specified) | Present | Chennappa et al. (2018) |
| *Pseudomonas* sp. strain Imbl 5.1 | Agricultural site | Phorate | – | Jariyal et al. (2015) |
| *Alcaligenes* sp. JAS1, *Sphingobacterium* sp. JAS3 and *Ochrobactrum* sp. JAS2 | Chlorpyrifos-polluted soil | Degraded the mixture of pesticides | – | Abraham et al. (2014) |
| *Halophillic bacteria* JAS4, *Enterobacter asburiae* strain JAS5 and *Enterobacter cloacae* JAS7 and *Klebsiella pneumoniae* JAS8 | Endosulfan-contaminated soil |  | – |  |
| *Enterobacter ludwigii* JAS17, *Pseudomonas morviensis* JAS18, *Serratia marcescens* JAS16 | Monocrotophos-polluted soil |  | – |  |
| *Escherichia fergusonii* |  | Diuron | – | Moretto et al. (2019) |
| *Stenotrophomonas maltophilia* | Contaminated refinery site | 4-nitroaniline, 4-chlorobenzonitrile, 4-chloro-2-nitrophenol | – | Qureshi et al. (2007) |
| *Pseudomonas rhizophila* S21 | Pesticide-contaminated artichoke field of Tunisia | Pesticide-solubilizing activity | Present | Hassen et al. (2018) |

Moretto et al. (2019) demonstrated that *Escherichia fergusonii* biodegrades diuron by two pathways, *adk and gyrB* and recA removed the chlorine from the herbicide molecule not being described yet. A bacterial strain *Stenotrophomonas maltophilia* isolated from a contaminated refinery site was able to grow on 4-nitroaniline, 4-chlorobenzonitrile, and 4-chloro-2-nitrophenol as a source of carbon and energy which is reported to be utilized in the production of agrochemicals. The potential of isolated strains was found to be diverse in nature for compounds such as nitro-substituted (Qureshi et al. 2007). Bacterial biofilms along with the plants can help to degrade toxic aromatic contaminants, along with the mechanisms such as HGT events, production of EPS, and chemotaxis. Quorum sensing genes and their regulators were illustrated in the biodegradation for the synthesis of EPS and several aromatic compounds (Ghosh et al. 2019).

### 2.5.2 Amendment of Biochar

Increased sorption and reduced pesticide leaching to groundwater can be achieved using biochar-amended soil. Biochar amendments of 1% and 2.5% reduced atrazine leaching in soil, according to environmental fate modelling. A biochar performance trade-off is: changes in soil hydrology may result in more leaching. Biochar implementation must take into consideration recognized trade-offs to ensure that mitigation works in each situation (Aldana et al. 2020). In a pesticide-polluted environment, biochar addition has the following benefits: (a) it increases soil water holding capacity, (b) it improves aeration conditions in the soil, and (c) it provides habitat for the growth of microorganisms, facilitating microbial community for metabolic activities and pesticide degradation (Varjani et al. 2019).

Biochars are found to be seen up to 2000 times more effective than soil at absorbing pesticides because of their unique characteristics, particularly their highly fragrant and carbonaceous nature and particular surface area. The addition of a tiny amount of fresh biochars to soil (0.05% by weight) has also been demonstrated for prevention of the microbial breakdown of chemicals which are organic in nature such as pesticides and limit their plant availability and efficacy (Kookana 2010). Using Biochar and plastic chars, heavy metals were removed successfully from 10.95% to 99.93% utilizing waste biomass (Singh et al. 2020).

*Alcaligenes faecalis* WZ-2 was immobilized on wheat straw-derived biochar and used to treat soils polluted with tebuconazole (a frequently used fungicide). Strain WZ-2 efficiently removed tebuconazole and improved soil microbial enzyme activities (Sun et al. 2020). As compared to biochar (pyrolysis of rice husk), nitrogen fertilizer ($NH_4NO_3$) was employed for remediation of Organophosphorus pesticides (OPPs)-contaminated soil and led to the largest degradation of pesticides concentration (11.07%) for the soil. Furthermore, when biochar and $NH_4NO_3$ were added, after thermal treatment, the emission rate of GHGs was significantly increased (Zhen et al. 2018).

### 2.5.3 Utilization of Earthworms for Remediation of Agrochemicals

Bioremediation is a new method that uses live organisms to remediate pesticide-polluted landscapes (Chawla et al. 2013). Some of the techniques employed in bioremediation of contaminants include using soil microorganisms, phytoremediation with plants, and verm-remediation with earthworms. One of the most compelling arguments for using bioremediation to eliminate organic pollutants is that it is a cost-effective and environmentally friendly technique that allows organic toxins to be destroyed or turned harmless by natural biological activity. Bioremediation is widely accepted by the public, and it may frequently be done on-site. While any method for removing or eliminating pollutants is expensive, biological techniques are generally the most cost-effective (Morillo and Villaverde 2017).

Earthworms are the most numerous animal biomass in soil and are dubbed "ecosystem engineers" sometimes. According to this evaluation, earthworms contribute to ecosystem services via pedogenesis, soil structure development, water management, nutrient cycling, primary production, climate regulation, pollution remediation, and cultural services (Blouin et al. 2013).

#### 2.5.3.1 Case Study

An inoculation of *L. terrestris* to a clay rich in SW, Finland, provides a nice illustration of how earthworm introduction may manage soil function and ecosystem processes through time, requiring not only inoculation but also land management. The purpose of the introduction was to promote water soil permeability, which is boosted under the current conditions by *L. terrestris* burrows, specifically which are in contact with subdrains (Shipitalo et al. 2004).

The drilosphere system is the sphere of effect that an earthworm has inside the soil environment (Brown et al. 2000). The physico-chemical and biological interactions between the soil-associated microorganisms and earthworm's body surface, gut, and external structures result in the formation of casts, burrows, and middens altering the C/N ratio and pH of surrounding soil overall improving the soil health. Earthworms generate potential advantages in the soil, which may possibly help to improve the above-mentioned factors and, as a result, aid in the bioremediation of organic pollutants (Hickman and Reid 2008).

## 2.6 Alternatives for Agrochemical in Agricultural Practices

### 2.6.1 Microbial Metabolites for Development of Eco-Friendly Agro-Based Products

The use of chemically synthesized agrochemicals indeed played an important role in enhancing the crop yields and reducing the crop damage and losses caused due to pests like weeds, insects' nematodes, and plant pathogens. The dependency of agriculture sector on synthetic agrochemicals has led to severe health and environmental hazards. These include severe health issues such as allergies, immunological disorders, cancers, and even reproductive ability.

Microbes are the ubiquitous entities of life forms displaying myriad of interactions with other living beings. Numerous microbes have been isolated and tested for their metabolites such as *Streptomyces griseus* for streptomycin, *Penicillium chrysogenum* for penicillin, and *Bacillus subtilis* for bacitracin. Secondary metabolites from actinomycetes, particularly Streptomyces group, have enormously contributed in expansion of unique and eco-friendly agrochemicals (Hahn et al. 2009). Cyanobacteria are also now explored as novel source of antibacterial and antifungal agents with pesticidal activity (Chotsaeng et al. 2011; Höckelmann et al. 2009; Becher et al. 2007; Jüttner and Wessel 2003). Many secondary metabolites from bacteria, actinomycetes, and cyanobacteria have been identified and tested for use as agrochemicals (Tables 2.3, 2.4, and 2.5).

Fungi are well-known to interact with all life forms, interacting both through positive and negative ways. Fungi produce host-specific phytotoxins that exhibit toxicity on few cultivars (Worapong 2001). They can convert organochlorine chemicals into nontoxic intermediates or labile derivatives, depending on the enzymes engaged in the process and the kind of fungus (Bokade et al. 2021). Bacteria can use these intermediates, completing the fungal breakdown process in natural circumstances. Examples like the host selective AM, AK, AF, ACT, and ACR-toxin are produced by Alternaria species (Masunaka et al. 2005; Ueno 1990). Host-specific phytotoxins have limited host range, where they bring phytotoxic

**Table 2.3** Bacterial secondary metabolites used as agroproducts

| Secondary metabolite | Microorganisms | Classification on the basis of Target | Target organism |
|---|---|---|---|
| Bt-Toxins | *Bacillus thurengiensis* | Insecticide | Butterflies and moths (Lepidoptera), Flies and mosquitoes (Diptera), and Beetles (Coleoptera). |
| Diabroticin A | *Bacillus cereus and Bacillus subtilis* | Insecticide | Southern corn rootworm (Diabrotica undecimpunctata) |
| Tabtoxin (II) | *Pseudomonas syringae var. tabaci* | Herbicides | – |
| Phaseolotoxin | *Pseudomonas syringae pv. Phaseolicola* | Herbicides | – |
| Coronatine | Pseudomonas coronafacience | Herbicides | – |
| Macrolactin A (IV) and iturin A | *Bacillus* sp. *Sunhua* | Fungicides | *Fusarium oxysporum* |
| Syringomycin E | *Pseudomonas syringae* | Fungicides | *Penicillium digitatum* |

**Table 2.4** Actinomycetes' use as agro-based products

| Secondary metabolites | Secondary metabolite producing Actinomycetes | Utilization | Target organism | Mode of action | Reference |
|---|---|---|---|---|---|
| Bialaphos | Meiji Seika | Herbicides | – | Inhibits glutamine synthetase activity | Seto et al. (1982) |
| Methoxyphenone | Developed from anisomycin isolated from *Streptomyces griseolus* | Herbicides | Barnyardgrass and crabgrass (Digitaria sp.) | | Ito et al. (1974) |
| Herbimycin *(VI)* | *Streptomyces hygroscopicus* AM3672 | Herbicides | Monocot and dicot weeds | | Hahn et al. (2009) |
| Pyrizadocidin *(VII)* | *Streptomyces* #620061 | Herbicides | – | Reversible oxidation/reduction-linked photosynthetic electron transport | Gerwick et al. (1997) |
| Albucidin | *Streptomyces albus* subsp. *chlorinus* NRRL B-24108 | Herbicides | – | Inhibits the adenylosuccinate synthetase | Hahn et al. (2009) |
| Blasticidin-S (VIII | *Streptomyces griseochromogenes I* | Fungicides | *Pyricularia oryzae* | – | Fukunaga et al. (1955) |
| Kusagamycin (IX) | *Streptomyces kasugaensis* | Fungicides | *Pyricularia oryzae, Cercospora* spp. *Venturia* spp. | – | Umezawa et al. (1965) |
| Abamectin | *Streptomyces avermitilis* | Insecticide | Motile forms of wide range of mites, leafminers, suckers, beetles, and other insects | Binding and release of GABA receptor | Jansson and Dybas (1998) |
| Spinosad (X) | *Saccharopolyspora spinosa* | Insecticide | Caterpillars, leaf miners thrips, and foliage feeding beetles | – | Thompson and Hutchins (1999) |
| Milbemycin (XI) | *S. hygroscopicus* subsp. *Aureolacrimosus* | Insecticide | Citrus red mites, kanzawa spider mites, and leaf miners | More release ofGABA, hyperpolarization | Thompson and Hutchins (1999) |

(continued)

**Table 2.4** (continued)

| Secondary metabolites | Secondary metabolite producing Actinomycetes | Utilization | Target organism | Mode of action | Reference |
|---|---|---|---|---|---|
| Tartrolone C | Streptomyces sp. *CP1130* | Insecticide | | – | Lewer et al. (2003) |
| Oxytetracycline | *Streptomyces rimosus* | | *Erwinia amylovora, Pseudomonas,* and *Xanthomonas* species | – | Finlay et al. (1950) |
| Streptomycin | *Streptomyces griseus* | | *Xanthomonas oryzae*, *X. citri,* and *Pseudomonas tabaci* | – | Finlay et al. (1950) |

**Table 2.5** Use of Cyanobacteria as agroproducts

| Cyanobacterial metabolite | Cyanobacterial sp. | Target organism | Mechanism of action | Reference |
|---|---|---|---|---|
| Cyanobacterin (diaryl-substituted-lactone) (XII) | *Scytonema hofmanni* | Broad range | Inhibition of Hill reaction as it binds to the QB protein of the photosystem II | Gleason (1986) |
| Dihydroactiniodiolide | *Phormidium angustissium* | *Amaranthus tricolor* L (Chinese amaranth) and *Echinocloa crus-galli* (barnyardgrass) | – | Chotsaeng et al. (2011) |
| 5(R)-bis-(hydroxymethyl)-3(R), 4 (R) -dihydroxy pyrrolidine (DMDP) | *Cylindrospermum licheniforme* | Aquatic insects and crustacean grazers | Inhibition ofdigestive glucosidases | Jüttner and Wessel (2003) |
| 12-epi-Hapalindole J isonitrile, 12-epi-hapalindole C isonitrile and Hapalindole L | Fischerella *ATCC43239* | Dipteran *Chironomus riparius* | – | Becher et al. (2007) |
| Eremophilane (XIV) | *Calothrix* sp. PCC7507 | *Chironomous riparius* and *Thamocephalus platyurus* | – | Höckelmann et al. (2009) |

changes and their development is commercially expensive than that of nonhost (Particularly) phytotoxins (Strange 2007). Fungal biomolecules can be used as prospective materials for adsorption of refractory pollutants, metals, and dyes, as well as futuristic green chemistry instruments for environmental contamination remediation ex-situ and in situ applications for effective biodegradation methods might involve immobilization of fungal cells or enzymes to biodegradable polymers or reactor membranes (Bokade et al. 2021).

Phytotoxins which are nonhost (particularly) exhibit broader spectrum of phytotoxicity on distinct weeds, making them suitable as commercial herbicide (Worapong 2001). Examples include Cornexistin (XIX) (acting as herbicide against monocot and dicot weeds) through inhibition of aminotransferases (Cutler et al. 2004). These fungal metabolites may also induce bleaching and chlorotic symptoms in broad-leaved weeds via travelling through phloem of plants inducing phytotoxic effects (World Health Organization 2014).

### 2.6.2 Biofertilizers as Substitute to Commercial Agroproducts

The bioaccumulation at trophic level leads to biomagnification and therefore requires the use of substitutes for agrochemicals. Recently, attempts are been made regarding the development of cost-effective and eco-friendly alternatives for agrochemicals for sustainable development in agricultural practices. One of the alternatives in use is plant growth-promoting rhizobacteria (PGPR) that mediates nutrient acquisition and also phytohormone modulation resulting in plant growth promotion. Some PGPR are known to indirectly influence the plant growth by subduing different inhibitory elements including biotic and abiotic factors.

#### 2.6.2.1 PGPRs Direct Mechanism

Nutrient acquisition is a direct interaction of PGPRs that overcomes their bioavailability in soils and prevents them from leaking away (Choudhary et al. 2011). Plant uptakes nitrogen from soil in the form of nitrate and ammonium ions. The bioconversion of the atmospheric $N_2$ to available forms is possible through nitrogen fixing bacteria via nitrogenase complex, encoded by nif genes (Tairo and Ndakidemi 2013). Symbiotic nitrogen fixers include Rhizobium species strains and nonsymbiotic bacteria consist of free-living endophytic microorganisms like Azotobacter. The non-bioavailability of soil phosphorous is also relieved by the rhizosperic microorganisms converting solubilization phosphate into monobasic or dibasic phosphate ions (Jha and Saraf 2015). Several organic acids are reported that drive phosphate solubilization through reduction in soil pH via secretion of acids as glyoxalic acid, tartaric acid, gluconic acid, malonic acid, α-ketobutyric acid, malic acid, fumaric acid, and other citrate metabolism metabolites (Alori et al. 2017). Many bacteria, including *Agrobacterium, Pseudomonas, Enterobacter,* and *Bacillus,* uses the above strategy for phosphate solubilization. Similar mechanisms are known for other nutrients such as potassium and iron, releasing bioavailable nutrients from crude mineral form. The iron complex is internalized by a chelator, reducing the bound iron within the cell of a plant. Some rhizospheric bacteria are reported for synthesis of siderophores (Organic molecules with a low molecular weight) to attract iron ions towards rhizosphere leading to its absorption (Raymond and Dertz 2004).

Phytohormone secretion by microorganisms is directly involved in influencing plant growth. These are unrelated, structurally small molecules regulating plant development and growth (Maheshwari et al. 2015). Auxin, cytokinin, gibberellin, ethylene, and abscisic acid (ABA) are the majorly studied phytohormones. Others include semisynthetic and synthetic counterparts like salicylate, nitric oxide, and jasmonic acid. These secretary molecules regulate the expression of genes encoding proteins of cellular processes like stressresponse, reproductive development, pattern formation, etc. (Mahanty et al. 2017).

#### 2.6.2.2 Indirect Mechanism of PGPRs

Indirect mechanism of PGPRs includes providing disease resistance through synthesis of antibiotics. *Pseudomonas sp*. and *Bacillus* sp. are enormously studied for synthesis of antibiotics and few biocontrol agents. *Pseudomonas species* produce antifungal antibiotics (phenazines), antitumor antibiotics (rhamnolipids), bacterial antibiotics, antiviral antibiotics (Karalicine), anti-oomycetes antibiotics (zwittermicin A), and azomycin (Gouda et al. 2018). Numerous antibacterial and antifungal antibiotics are also studied in Bacillus genera (subtilin, tas A, surfactin, and iturins) (Wang et al. 2018).

PGPRs protect plant from invasive fungal species by secreting extracellular enzymes such as chitinase, cellulase, glucanase, and protease that can hydrolyse fungal cellular components made up of cellulose, chitin, and hemicellulose (Pal and Gardener 2006). Another mechanism includes synthesis of toxic compound such as hydrogen cyanide and ammonia that acts as weedicides, colonizing the plant roots and suppressing its growth.

Hydrogen cyanide (HCN) acts on cytochrome oxidase and blocks the electron transport chain, inhibiting the energy flow in weeds (Zeller et al. 2007). Production of ammonia by PGPRs acts as a nutritional supplement, also creating an alkaline environment suppressing the fungal growth (Vylkova 2017). PGPR also produces an enzyme, 1-Aminocyclopropane-1-carboxylate deaminase (ACC deaminase), which regulates the production of ethylene by converting ACC into ammonia and alphaketobutyrate. Under abiotic stress, plants produce ACC acted upon by bacterial ACC deaminase, minimizing the stress response. Several bacterial genera, including *Burkholderia, Enterobacter Acinetobacter Azospirillum, and Agrobacterium,* are ACC deaminase producers (Mahanty et al. 2017).

Exopolysaccharides (EPSs), which play a major role in microbial aggregation and biofilm formation, may be synthesized by a variety of PGPR (Mallick et al. 2018). The adhesion of soil bacteria to plant roots is aided by EPS produced by several PGPRs in the plant-microbe interaction. Reports suggest that a number of rhizospheric bacteria (*Azotobacter vinelandii, Xanthomonas* sp.) confer protection from desiccation to plant cells by forming EPS.

### 2.6.3 Nano-Agrochemicals: The Next Generation Agro-Based Products

Nano-agrochemicals are a combination of nanotechnology with agrochemicals that have resulted in nano-fertilizers, nano-herbicides, nano-pesticides, nano-fungicides, and nano-insecticides being developed. Recently, nano-agrochemicals' use is gaining interest as they are more effective, eco-friendly, and economically viable.

**Nano-fertilizers** play a crucial role in agricultural field due to their greater surface area and penetration capacity subsequently improving the nutrient efficiency (Meena et al. 2020). Encapsulated fertilizers in nanoparticles form are designed for slow release and efficient nutrient availability dosages to the crop plants reducing wastage by leaching (Tarafdar et al. 2012).

**Nano-herbicides** are an excellent alternative to traditional herbicides since they are excellent at eradicating weeds by blocking their gene expression in the soil (Berekaa 2015). Nano-herbicides are eco-friendly, brilliant minute-sized chemicals that act on weeds that have become resistant to conventional herbicides. Herbicide nanocomposites, such as paraquat, are made from exopolysaccharide materials such as alginate and chitosan (Ghaly 2009).

Plant diseases are caused mainly due to bacteria, fungi, protozoa, viruses, and plant parasites, of which the fungi contribute nearly 85%. The traditional chemical fungicides used develop resistance among the pests and microorganisms, declining the crop productivity either slowly or instantly. Nanoparticle-based fungicides offer a wide range of uses in agriculture, including disease control. However, Sharma et al. (2017) reported their cytotoxicity in plants, requiring intense knowledge of these composites before use.

Nanotechnology has aided in developing effective pesticides and preventing their harmful spread in the environment by encapsulating these pesticides in nanoscale capsules that can precisely control the rate of pesticide release from the capsule according to crop requirements (Alfadul et al. 2017). Pesticide formulations using nano-encapsulated pesticides can minimize pesticide dose and human exposure, making them more eco-friendly for crop protection (Nuruzzaman et al. 2016).

Traditional insecticides are poisonous by nature and are used to kill insects that cause a variety of plant illnesses. A report by Vinutha et al. (2013) mentioned the management of polyphagous pest (*Helicoverpa armigera)* by synthesized nanoparticles. *Tribolium castaneum* Herbs were shown to be resistant to nanoparticles containing garlic oil (Yang et al. 2009). Mosquito larvicidal and anti-lice activity of synthesized silver nanoparticles have been observed (Jayaseelan et al. 2011).

## 2.7 Conclusion

Finding alternatives to existing agrochemicals including pesticides, herbicides, and insecticides with known site and mode of action is extremely essential for sustainable development in agriculture. Microbial secondary metabolites often possess novel chemical templates which may be developed into biorational eco-friendly counterparts of the conventional agrochemicals. Microbial natural products can be produced via fermentation processes and put to use on large scale. As they are biodegradable, it leaves no traces of secondary pollutants in the environment. Nanotechnology promises bright future in agricultural sector as it is compact, efficient, and eco-friendly. However, the extent of knowledge of these nano-agrochemicals is still under infancy and is facing ethical issues. New agro-formulations with marketing proficiency will enhance their use in near future.

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# Impact of Agrochemicals on Soil Microbiota

# 3

Shiv Kumar Giri, Neha Verma, Gulab Singh, Ritu Gill, and Anil Kumar

## Abstract

As the global population is growing exponentially, it has become necessary to meet the food requirements of the growing population. Over the last few decades, agrochemicals have become an important component of modern agricultural practices. Agrochemicals ensure enhanced crop yield by controlling the harmful and undesirable pathogens, pests, and weeds. However, concern has been raised regarding the uncontrolled and long-term use of these chemicals in agricultural settings. The unbalanced usage of agrochemicals is hampering soil health and has caused the large-scale degradation of the ecosystem. Furthermore, these chemicals have influenced the microflora composition of the soil and thus have made an adverse impact on various microbial activities such as nutrient biotransformation, phosphorus solubilization, and most importantly, the nitrogen fixation. In this chapter, we have highlighted the impacts of agrochemicals on soil microbiota and related microbial processes.

## Keywords

Agrochemicals · Microbiota · Soil health · Pesticides · Fertilizers

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## 3.1 Introduction

From the last few decades, concern has been raised to meet the food requirements of the swiftly growing worldwide population. Therefore, the global usage of agrochemicals has substantially increased, and currently, it offers a more reliable solution. To ensure food security and enhanced crop productivity, current agricultural practices have become over-dependent on agrochemicals. Later represents the substances used to control, repel, or kill plant pathogens. Pesticides such as herbicides, fungicides, insecticides, and fertilizers are the major types of agrochemicals. Over the years, the demand for pesticides has increased substantially, especially in Asian countries. The application of agrochemicals in agricultural settings has significantly contributed towards high crop yield and economical crop production. However, uncontrolled usage of these chemicals has made an adverse impact on beneficial soil microbiota and thereby has affected soil health (Jie et al. 2002). The soil microorganisms (bacteria, fungi, algae, protozoans) play an essential role in improving crop productivity, as they form an indispensable component of the agro-ecosystem and actively participate in various fundamental soil processes (Jacoby et al. 2017). They also participate in the biodegradation of several harmful chemicals released by anthropogenic activities. Further, the soil microflora diversity and activity act as indicators of soil health as they can control various fundamental soil processes (Nielsen et al. 2002). In recent years, the uncontrolled usage of agrochemicals has substantially affected soil functions and processes. Further, they also affected the various physicochemical properties such as soil carbon content, soil moisture, and pH and also shifted the dynamics of microbial community. The unplanned practice of these chemicals also has reduced soil fertility by disturbing the activities of the beneficial microorganisms involved in fundamental processes such as recycling and retention of soil nutrients (Chowdhury et al. 2008). Various studies have indicated that long-term and uncontrolled usage of agrochemicals should be avoided as they could reduce the performance of beneficial microorganisms in the agricultural soil and also may create an imbalance of important soil nutrients.

## 3.2 Agrochemicals

Agrochemicals represent a group of chemical substances that ensure high crop productivity and safety against plant pathogens. These are mainly represented by pesticides and fertilizers. In the last few decades, pesticides' consumption has increased at an alarming rate. Among all the continents, Asia has topped the chart with 52.8% of pesticide consumption, followed by America, Europe, Africa, and other countries. In Asia, China is the primary consumer of pesticides, and globally, Saint Lucia has occupied the first position (FAO 2019). The pesticides are mainly classified according to their target and chemical composition. The primarily used pesticides such as herbicides act to destroy the weeds, insecticides protect against harmful insects and other pathogens, whereas fungicides affect the growth of fungi

**Table 3.1** Classification of agriculturally important pesticides

| Pesticide | Target | Mode of action | Example |
|---|---|---|---|
| Herbicides | Weeds and herbs | Plant growth regulator<br>Seed growth inhibitors<br>Photosynthesis inhibitors<br>Blocks electron transport chain<br>Inhibit biosynthesis of amino acids | Gramoxone; glyphosate; Aldirab; methyl and ethylene bromide; and chloropicrin |
| Insecticides | Insects | Inhibit acetyl choline esterase<br>Blocks electron transport chain | Organochlorines, organophosphates; carbamates, and Pyrethroids |
| Fungicides | Fungi and Actinomycetes | Protein inhibitors<br>Inhibit the germination and germ tube growth<br>Prevent ATP formation | Bordeaux mixture; Sulphur; mercuric chloride ($HgCl_2$); dithane S-21,vM-22, Z-78, and vitavax |
| Algaecides | Algae | Growth inhibitor | Cupricsulfate, bluestone, and dichlorophen |
| Rodenticide | Rodents (rat and mice) | Affects nervous system<br>Difficulty in breathing<br>Heart and kidney damage<br>Bleeding | Bromethalin; Cholecalciferoll; zinc phosphide; strychnine |

and actinomycetes. According to their chemical composition, they have been designated as organophosphates, organochlorine, pyrethroids, and carbamates. Generally, the impact of pesticides depends on dosage, soil property, and various environmental elements. The pesticides affect their target by acting as inhibitors of plant growth, protein synthesis, adenosine triphosphate (ATP) generation, and acetylcholine esterase (ACh) activity (Table 3.1). On the other hand, fertilizers are organic and inorganic substances that aid in soil fertility. These serve as an important source of vital nutrients to the plant and function as a growth promoter. The classification of fertilizers is mainly based on the type of essential nutrients they contain. Several types of chemical fertilizers such as ammonium sulfate, calcium ammonium nitrate, calcium cyanamide, and calcium nitrate are being used to make the soil more fertile and productive. Although the agrochemicals ensure improved crop productivity and protection against plant pathogens, the concern has been raised regarding agrochemicals' toxicity and their impact on non-targeted organisms, especially the beneficial soil microbiota. However, the adverse effects of these chemicals depend on their persistence in the soil.

### 3.2.1 Persistence and Toxicity of Agrochemicals

Among agrochemicals, pesticides have shown a longer persistence tendency in soil than in animals and plants because of their slow decomposition in the inactive soil system. The pesticides' residue persistence is determined by several factors, including the soil property, environmental determinants, and pesticides themselves. The soil properties like soil types, percentage of organic content and clay in the soil, soil permeability, concentrations of hydrogen ions, and diversity of soil microflora affect their persistence. The environmental factors like precipitation, temperature and, pH, moisture and, ultraviolet (UV) rays also decide the fate of pesticides' persistence. Further, the chemical composition, water solubility, volatility, and method of pesticide application also may affect their persistence in soil (Fig. 3.1, Edwards 1975). Depending on their half-life, their persistence in the soil can be either low (<30 days) or high (>100 days). Among pesticides, organochlorines are designated as most persistent because of their slow degradation, as they contain extra chlorine atoms. Depending on the soil persistence, several pesticides such as dichlorodiphenyltrichloroethane (DDT), aldrin, p,p-mirex, chlordane, dieldrin, and toxaphene have been identified as toxic and bioaccumulative chemicals.

The toxicity of pesticides is not only decided by their chemical composition, but also depends upon soil-related abiotic and biotic factors. However, it has been determined that pesticide toxicity is mainly influenced by the application dosage.

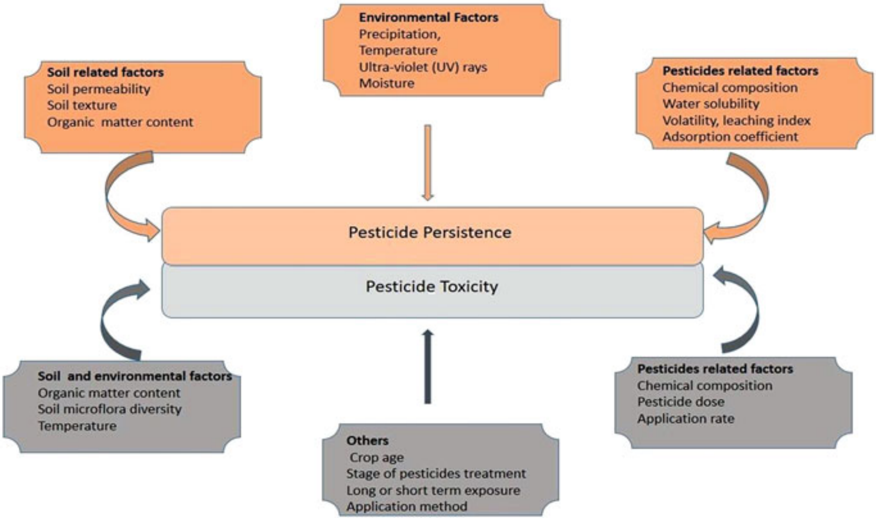

**Fig. 3.1** Factors affecting agrochemicals' persistence and toxicity

The pesticides when applied at recommended dosage are either non-toxic or may have non-determinate effects on soil-related factors and non-targeted organisms. However, long-term and higher application dosage may induce severe toxicity (Wang et al. 2008; Sumalan et al. 2010). Change in soil properties directly influences microbial diversity and associated functions; other factors like stages (pre-seed or on crop) of pesticide treatment, application rates, crop age, and modifications in soil organic content also may influence the pesticide toxicity (Rahman et al. 2005; Lupwayi et al. 2009). It has been indicated that long-term and repetitive application of pesticides produce more adverse impact on the soil microenvironment when compared to short-term and single application usage.

### 3.2.2 Agrochemical and Soil Health

The soil represents a lively and complex ecosystem that nurtures a variety of microflora. The organic matter and minerals in soil support the variety of life forms to maintain the balance between biotic and abiotic factors (Doran and Safley 1997). Soil not only fulfils the food requirement, but also plays an indispensable role in maintaining environmental health. In recent years, modern agricultural practices have become over-reliant on agrochemicals, especially on pesticides to meet global food requirements. Such action by mankind is continuously challenging soil health by interfering with a variety of physical, chemical, and biological factors (Fig. 3.2), which aid in the maintenance of soil ecology and dynamics of soil microbiota. Later not only control fundamental soil processes, but also aid in soil fertility and crop productivity. Due to the inactive and static nature of the soil, the agrochemicals, especially the pesticide residues, persist in soil for a longer duration of time and affect the soil health by disturbing the microbial diversity. Therefore, management of

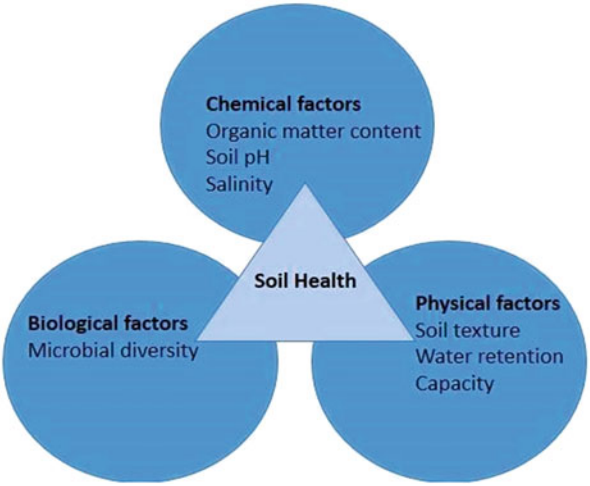

**Fig. 3.2** Factors affecting Soil health

soil health needs to be prioritized to ensure sustainable food production and enhance microbial diversity.

## 3.3 Microflora of Agricultural Soil

Agricultural soil harbours a variety of microorganisms (bacteria, actinomycete, algae, fungi, and protozoans) that constitute an essential component of the soil ecology. It has been observed that microorganisms actively participate in more than 80% of soil functions. The most abundant microbe in soil is bacteria, followed by actinomycete, fungi, algae, and other species (Sylvia et al. 1998). It has been revealed that one to ten million bacteria are present in 1 g of healthy soil (Coleman 1994). The majority of microbial biomass comes from bacteria and fungi that form approximately 1–4% of total organic matter in the soil (Brookes 2001). However, various environmental factors, management practices, and nutrients composition of soil affect the ratio of bacterial/fungal biomass in soil. The microflora of agricultural soil is very complex and is affected by changes in soil parameters like temperature, pH, $CO_2$ level, moisture, and organic matter content (Strickland and Rousk 2010). The parameters like tillage system and fertilizer usage affect the fungal/bacterial biomass ratio as well the microbial diversity in cultivated soil. It has been observed that the tillage system increases the bacterial biomass, whereas under no-tillage fungi dominate the soil (deVries et al. 2006; Strickland and Rousk 2010). Similarly, treatment with organic fertilizer enhances the microbial biomass, while contrasting results have been observed with inorganic fertilizers.

## 3.4 Impact of Agrochemicals on Soil Microbiota

A variety of prokaryotic microorganisms harbour the soil and assist in the various fundamental processes of soil. In recent years, globally, an exponential increase has been noticed in agrochemicals' (pesticides and fertilizers) consumption, and it is causing a serious threat to soil health and the ecosystem. Various studies have revealed that agrochemicals indirectly or directly impact microbial diversity, microbial biomass, and other fundamental microbes-assisted soil processes (Fig. 3.3).

### 3.4.1 Impact of Pesticides

The pesticides' application causes adverse effects on soil microbial diversity. Most of the studies have indicated that the negative impact of pesticides is dependent on the concentration and exposure duration.

#### 3.4.1.1 Herbicides

Sawicka and Selwet (1998) reported that imazethapyr and linuron can affect the activity of root-nodule bacteria; however, the inhibitory effect was dependent on its

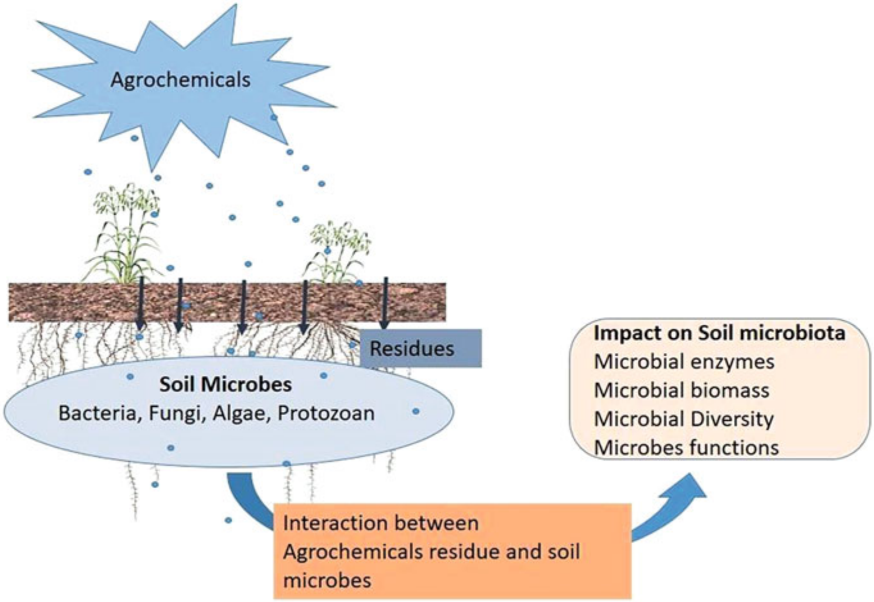

**Fig. 3.3** Impact of agrochemicals on soil microbiota

concentration and duration of application (Sawicka and Selwet 1998). Herbicides such as 2, 4-D, metolachlora tranex, dimethenamid, and agroxone affect the activity and growth of nitrogen-fixing bacteria (*Azotobacter vinelandii* and *Rhizobium phaseoli*) in a concentration-dependent manner (Govedarica et al. 2001). Cinosulfuron negatively affected the growth of nitrifying group of bacteria when the soil was treated at a field rate of 42 and 4200 mg/kg (Allievi and Gigliotti 2001). The paddy soil treated with various concentrations (0.33, 0.67, 1.00, 1.33, and 2.00 μg) of quinclorac could change the count of total soil microflora. At normal concentration (0.67 μg), no significant difference in the microbial diversity was observed between quinclorac-treated and non-treated soil. Further, it was suggested that quinclorac effects depend on its concentration (Lü et al. 2004). Under a greenhouse experiment, the effects of herbicides (flumioxazin, sulfentrazone, and azafenidin) on the community of soil microbes were assessed. Under in vitro conditions, all herbicides inhibited the mycelial growth of *Pythium* spp. *(P. ultimum, P. arrhenomanes,* and *P. aphanidermatum)* (Daugrois et al. 2005). The effects of metsulfuron-methyl on the wheat soil were evaluated by culturing the microbes. The inhibitory effect was observed on heterotrophic aerobic bacteria, while nitrifying bacteria (*Azatobactor*) and fungi showed a decrease after 30–50 days of metsulfuron-methyl application (He et al. 2006). The herbicides, viz., atrazine and alachlor, showed an adverse effect on the growth of bacteria, when applied at a higher field rate (10 mg/L) than the recommended one (Demanou et al. 2006.). Herbicides such as 2, 4-D and its metabolites negatively affect the growth of a group of gram-negative bacteria such as *Burkholderia cepacia* when applied at higher concentration (Smith and Beadle 2008). Under greenhouse conditions, glyphosate negatively impacted arbuscular mycorrhiza fungi (AMF) mycelial's growth and reduced the root mycorrhization by 40%, (Savin et al. 2009). The various herbicides (pyrazosulfuron, butachlor, 2, 4-DEE, and pretilachlor) on different field rates were evaluated for their impact on microbial communities. The results revealed that butachlor strongly affects the bacterial count on increasing concentration, whereas the microbial count was recovered after 30 days of pyrazosulfuron treatment (Latha and Gopal 2010). The factors like host type, mineral composition of the soil, and nature of symbiotic interactions could determine the overall effect of herbicides on the arbuscularmycorrhiza fungi (Kiers et al. 2011). The effect of herbicides, viz, paraquat, atrazine, primeextra, and glyphosate, was determined for 6 weeks on the diversity of soil microbes. All herbicides negatively affected the microbial population count; however, an increase in the concentration favoured the adaptation of soil microbes (Sebiomo et al. 2011). The bromoxynil herbicide-treated and non-treated soil samples were evaluated for their effects on soil microbes. The reduced bacterial population was observed in bromoxynil-exposed soil (0.67 to 1.84 × 10(8)) when compared to the non-exposed (0.87 to 2.37 × 10(8)) CFU/g soil (Abbas et al. 2014). The commonly used herbicides, viz., propaquizafop, pendimethalin, and oxyfluorfen, significantly inhibited the activity of soil microbes in chili; however, the impact of inhibition varied with herbicide type and application rate (Adhikary et al. 2014). The long-term impact of herbicides (butachlor and anilophos) on the activity of soil microbes was evaluated in commonly used crops (rice, wheat, and soybean). The result hasn't shown any adverse effect on the microbial population (Sarathambal et al. 2015). The significant impact of paraquat, glyphosate, and 2,4-D was observed on the bacterial population in field soil; however, the effects were dependent on application rate and the concentrations (Adomako 2016). The in vitro impact of herbicides (nicosulfuron, metribuzin, and glyphosate) was determined on the growth and count of actinomycetesin soil. The result indicated the transient impact of applied herbicides on actinomycetes; however, it was suggested that the overall impact is dependent on the application rate and type of herbicide applied (Šantrić et al. 2016). The effect of Wing P herbicide was determined on soil microbes and non-inhibitory effects were observed on the microbial population except *Azotobacter* sp. and actinomycetes. The result indicated the microbes' adaptation to variable concentrations of applied herbicide (Hamidović et al. 2017). The application of paraquat and round-up herbicides significantly reduced the count of fungal and heterotrophic aerobic bacteria population (Usman et al. 2017). The effects of flazasulfuron, glyphosate, and glufosinateon soil microbes were evaluated in the vineyard. The flazasulfuron showed a significantly higher CFU level as compared to other herbicide treatments (Mandl et al. 2018). The effect of various herbicides on the microbial population count was examined at different application rates and concentrations. The result indicated that application of 2, 4-D, ethyl ester 38% EC, atrazine 50% WP, and acetochlor 90% EC does not cause long-term adverse effects on the count of beneficial microbes (Tyagi et al. 2018). The effect of paraquatherbicide application was determined on the diversity of nitrogen-fixing bacteria. The study revealed that paraquat decreases the microbial count in a concentration-dependent manner (Maldani et al. 2018). The soil samples were tested for the toxic effects of 2,4-D amine and glyphosate herbicide at different application rates ranges from 0.1% to 5%. The 2, 4-D showed more inhibitory effect on soil microbes as compared to the glyphosate; however, the inhibitory effect was concentration-dependent (Ngozi et al. 2020). Long-term application of glyphosate negatively impacts the growth of cultivable fungi and also induces changes in the molecular structure of soil fungal communities (Vázquez et al. 2021).

#### 3.4.1.2 Insecticides

Insecticides such as malathion negatively impacted the growth of *Azotobacter chrococcum* when applied at higher concentrations (800 ppm) and gradually inhibited the nitrogen fixation (Nadia 1996). The application of endosulfan and butachlor inhibited the activity of methanogenic bacteria; however, the overall impact was dependent on the application rate (Kumaraswamy et al. 1998). The organochlorine pesticides such as dieldrin and lindane affected the population of nitrifying bacteria (*Thiobacillus, Nitrsomonas,* and *Nitrobacter*) (Odokuma and Osuagwu 2004). Insecticides such as cypermethrin, monocrotophos, and quinalphos when applied at the concentrations of 0, 5, 10, and 25/μg/soil have not impacted the soil microflora. Even at higher concentrations, no negative effect was observed; instead, a proliferation was observed in microbial population count (Gundi et al. 2005). Under the in vitro condition, the variable concentrations of k-cyhalothrin were tested for microbial response in loamy soil and results indicated the adverse impact on nitrogen-fixing bacteria even at day 1 (Cycoń et al. 2006). The field soil was treated with thiodan® (at 4000 and 8000 ppm) and karate® (at 6000 and 12,000 ppm); for up to 49 Daysand, the impact of both insecticides was investigated on the microbial count. No significant changes were noticed after the insecticide treatment (Adebayo et al. 2007). Various insecticides (triazophos, monocrotophos, cypermethrin, dimethoate, endosulfan, and deltamethrin) were applied at recommended dosage to the cotton field and tested for their effect on non-target soil microbes. No adverse effect was observed on the microbial diversity after the long-term application of insecticides (Vig et al. 2008). The impact of cypermethrin was investigated on the microbial population count in loamy sand soil. It was reported that cypermethrin concentration and incubation time (7 to 21 days) significantly affect the population density of fungi, *Azoyobacter,* and other beneficial microbes (Rasul et al. 2010). The antagonistic synergetic interactions were observed between *Azospirillum sp.* and ammonification, when the soil was treated with pesticides in combination (mancozeb and carbendazim) and individually (monocrotophos and chlorpyrifos) during groundnut cultivation (Srinivasulu et al. 2012). The repeated application of carbendazim under field conditions reduced microbial diversity composition, primarily due to the presence of the γ-proteobacterium (Wang et al. 2012). Under in vitro conditions, at variable concentrations (50, 100, and 250 ppm), insecticides such as dimethoate, malathion, and diazinon were incubated for up to 72 h (Haleem et al. 2013). In a study, the effects of triazophos at variable concentrations were examined for 7 days on soil bacterial and fungal population density. The results revealed a significant decrease in the microbial population (Kalyani et al. 2015). The endosulfan and profenofos were applied to the black soil collected from groundnut fields and a proliferative effect was observed, especially on the count of actinomycetes population (Nasreen et al. 2015).

The study was carried out to examine the effects of insecticide in soil treated with 100 and 200 lg/g of chlorpyrifos (CP) for 14 days. The result revealed that the application of CP favours actinomycete's growth (Supreeth et al. 2016). The soil sample treated with 5 and 10 mL concentrations of DDFORCE, THIONEX, and BEST showed a modulatory effect on bacterial population count; however, when treated at a higher concentration (20 mL), insecticidal toxicity was noticed (Wesley et al. 2017). A study by Ghosal et al. (2018) reported the inhibitory effect of carbofuran, phorate, and rynaxypyr on fungal growth. A similar effect of chlorpyrifos was recorded for the nitrifying bacteria and rhizobium population (Ghosal et al. 2018). The effect of various concentrations (10–1000 ppm) of malathion and chlorpyrifos was investigated on soil microflora and enzymatic activity of soil microbes. The higher concentration of both insecticides reduced the microbial activity as well affected the growth of the surrounding microbial community; however, at lower concentrations, beneficial effects were observed. Furthermore, it was suggested that malathion causes more adverse impact than chlorpyrifos (Walia et al. 2018). The impact of endosulfan and cypermethrin formulations on the microbial population was studied. The results revealed a significant adverse impact on both fungal and bacterial population count. However, the inhibitory effect was concentration-dependent (Aborisade and Atuanya 2020). The cypermethrin at the variable concentrations ((1–3%) could impact the growth of *Bacillus* spp. and *E. coli.* It was suggested that the effect of cypermethrin on the bacterial population depends on its concentration (Eneyi et al. 2021). The effect of organochlorine was studied on treated soil, and it was reported that endosulfan may contribute towards more ecological risk in the bacterial and fungal population (Egbe et al. 2021). Under in vitro conditions, increasing concentrations of the organochlorine pesticides (OCPs) from 50 to 200 μM inhibited the microbial (*E. cloacae*) growth and was found to interfere with microbial population count and other characteristics (Shahid et al. 2021).

#### 3.4.1.3 Fungicides

The study was carried out by Martınez-Toledo et al. (1998) to examine the effects of captan on microbial functions applied at the rates of 2.0, 3.5, 5.0, and 10.0 kg/ha in agricultural soils. The significant dose-dependent negative effects were recorded on the total culturable fungal population, aerobic nitrogen-fixing, and nitrifying bacteria (Martınez-Toledo et al. 1998). The effects of the fungicides such as mancozeb, benomyl, kitazin, and tridemorph were assessed in agricultural soil. It was revealed that all fungicides reduced the overall fungal population; however, benomyl and tridemorph promoted the bacterial population growth (Shukla 2000). The response of the fungal and bacterial populations was recorded at different application rates towards the four fungicides (captan, phenylmercuric acetate, benomyl, and pentachloro-dinitrobenzene). The more susceptible effects were observed in fungi and protozoans when compared to the effect on actinomycetes and bacteria (Ojo et al. 2007). The effect of fungicides such as triadimefon and propiconazole was assessed on soil microbial population. The results revealed that propiconazole treatment at a higher concentration could inhibit microbial growth, whereas triadimefon enhances the microbial population (Yen et al. 2009). A pot experiment was conducted on the tomato plants to examine the effect of various pesticides (carbendazim, metribuzin, and 2–4-D) on beneficial microbes of the rhizosphere. The study revealed a significant negative impact of pesticide treatment on the total microbial count of bacteria, fungi, and actinomycetes (Mohiuddin and Mohammed 2013). The alluvial soil samples from apple orchards were treated with different concentrations (0–2000 ppm) of mancozeb and examined for its effect on microbiological processes and soil microflora. Low and higher doses of mancozeb showed significantly negative effects on the fungal and bacterial populations, respectively. Furthermore, it has also affected the ammonification and nitrification process (Walia et al. 2014). Under laboratory conditions, the effect of azoxystrobin at variable doses (0.075–22.50 mg/kg soil) was assessed for its effect on biological activity in the soil. The result indicated the inhibitory effect of azoxystrobin on the growth of actinomycetes, fungi, and organotrophic bacteria (Baćmaga et al. 2015). The study conducted by Kumar et al. (2016) examined the effect of various fungicides on microbial populations. Their finding revealed a reduction in fungal colonies in copper oxychloride, mancozeb, and carbendazim-treated soil (Kumar et al. 2016). Falcon 460 EC fungicide could modify the microbial activity of soil when applied at doses 30–300-fold higher than the recommended dose (Baćmaga et al. 2016). The fungicides (mancozeb, copper oxychloride, and carbendazim) were applied to soil at application rate ranging from 0.0 to 1.0 L and examined for their effect on soil fungal populations. The results indicated a drastic reduction in the fungal population as compared to control (Ratna Kumar et al. 2017). The chlorothalonil can impact the biochemical and microbiological properties of soil. The study revealed that chlorothalonil could bring significant changes in the bacterial count and can inhibit the growth of fungi when applied at higher doses (Baćmaga et al. 2018). The combination of tebuconazole, spiroxamine, and triadimenol could affect the microbial activity and growth when applied at a higher dose (27.60 mg/kg DM of soil). A significant impact was observed on the proliferation of fungi and adverse impacts on the count of organotrophic bacteria (Baćmaga et al. 2019). In vitro experiment was carried out to reveal the effect of 25 fungicides on *leguminosarum* strain when applied at the variable concentrations (0.0–100 mg/L). The finding of the study indicated that the application of fungicides could cause toxicity to the *rhizobium* strain (Hamuda 2020). The effect of mancozeb at different concentrations was examined on rhizosphere bacterial diversity. The results revealed that the soil chemical properties, diversity, and richness of bacterial rhizosphere did not differ significantly across the mancozeb-treated soil (Huang et al. 2021).

### 3.4.2 Impact of Fertilizers

In a study, Sun et al. (2004a) revealed that a combination of chemical fertilizer with organic manure could improve the soil fertility as well as the count of soil microbes (Sun et al. 2004b). The long-term effects of chemical fertilizers' application and compost amendments were studied for the changes in the microflora structure of the rice and wheat. The changes were monitored with the FAME profile, and it was revealed that usage of chemical fertilizer significantly reduces the population growth of *pseudomonas,* whereas the bacterial population remains unaffected in untreated soil (Islam et al. 2009). The effect of organic and inorganic fertilizers was examined on microbial biomass and population density. The result revealed increased microbial population count in pots treated with organic fertilizers as compared to inorganic and control. Furthermore, the fungal population showed significant variability in fertilizer-treated pots and control (Nakhro and Dkhar 2010). Long-term repeated application of N mineral fertilizer has been reported to affect microbial composition and microbial biomass. However, the effect was dependent on crop management and environment-related factors (Geisseler and Scow 2014). The effect of KCl fertilizer was monitored for mineralization, ammonification, and soil microbial activity. Higher doses ($>400$ mg/dm$^3$) of KCl significantly reduced the microbial activity and N mineralization in soil (Pereira et al. 2019). The long-term effect of the organic and chemical fertilizer was examined in tea orchards. It was revealed that the use of organic fertilizer at recommended concentration shapes up the composition of the microbial community and simultaneously recruits the beneficial bacteria in the tea orchard's rhizosphere (Lin et al. 2019). The effect of inorganic fertilizer and compost manure was studied on the rhizobial community. It was reported that the enrichment of various microbial species (*Bacteroidetes Firmicutes, Proteobacteria, and Actinobacteria*) depends on the doses applied to soil (Enebe and Babalola 2020). The effects of inorganic, chemical (urea), and organic (cattle slurry) fertilizers were examined on the soil microbiota in ryegrass. The abundance of *Bacteriodetes* was found in organic fertilizer treatment, whereas *Acidobacteria* were more prominent in the inorganic fertilizer and urea treatments (Ikoyi et al. 2020). The effect of the application of the chemical fertilizer was investigated on the culturable growth-promoting rhizobial community. It was suggested that chemical fertilizer could reduce the rhizobacteria in wheat root soil (Reid et al. 2021).

## 3.5 Conclusion

For the last few decades, agrochemicals are intentionally being used to safeguard crops from plant pathogens so that globally increasing demands of food could be fulfilled. However, due to constantly changing environmental conditions and the uncontrolled usage of agrochemicals, especially pesticides has raised serious concerns about the health of living and non-living organisms. Due to the static nature of the soil, it is more vulnerable to adverse effects of agrochemicals than plants and animals. Pesticides affect soil health by disturbing the activity and diversity of soil microbes. To maintain the good health of the soil and to improve soil fertility, long-term and above-recommended usage of these chemicals should be avoided. This goal could be achieved by adopting good agricultural practices and creating awareness among farmers and consumers about associated risks.

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# Agriculture Pollution in Kerala, India, with Special Reference to Endosulphan

## 4

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**Abstract**

Agriculture is intricately connected with the environment. Agricultural pollutants are numerous; and they originate from different sources. This chapter discusses the different studies conducted by Centre for Water Resources Development and Management (CWRDM), Kozhikode, Kerala, related to environmental pollution. Water and soil quality of different selected areas of Kerala was monitored. Pesticide residue analysis of samples collected from various parts of Kerala, with special reference to toxic pesticide endosulphan, is reported in the study. Pesticides may additionally leave a serious negative impact on nature, though are of advantage for the crops. This chapter concludes with the different measures that can be adopted to protect, manage, and restore environment.

**Keywords**

Pesticide · Pollution · Endosulphan residues · Toxicity · Environmental management

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## 4.1 Introduction

Agriculture is inextricably connected with the environment. Agricultural production and food supplies are vital for daily human survival. Agriculture is a source of livelihood and economic development, but the pollution caused by it can lead to environmental and health hazards. Demand for food and other agricultural products is projected to extend by 50% between 2012 and 2050. Agricultural pollution is defined as the phenomena of damage, contamination and degradation of environment and ecosystem, and health hazards due to the by-products of farming practices (Abbasi et al. 2014; FAO 2017). Agricultural pollutants are numerous, and they originate from many different and often diffuse sources. Field runoff from farms, drugs and pathogens, organic matter, particulate matter, toxic compounds, and greenhouse gases are a few examples. Many of those pollutants are undetectable to the senses. Agriculture is both a victim and a source of pollution, all of which imply that solutions are complex and need to be multifaceted (Cassou 2018). The technologically based agriculture is essential to sustain the world population. This intensified agriculture has resulted in the clearance of forests, mechanization, the introduction of novel varieties of crop, dependence on artificial irrigational, and chemical aids to soil fertility and crop protection. The intensification of the farming system has always resulted in a simultaneous increase of pollution risks (Winteringham 1984). In many of the countries, agricultural water quality is of great environmental concern. The agricultural sector is responsible for pollution of water from crop and livestock activities. The pressure of agriculture from nutrients and pesticides on quality of water in different water bodies has decreased since the early 1990s in most of the developed countries. But in many cases, the absolute levels of agricultural nutrient pollution remain significant (Parris 2011). Policies, driving forces, and the state of the environment always remain relevant to water quality management as indicated in Fig. 4.1.

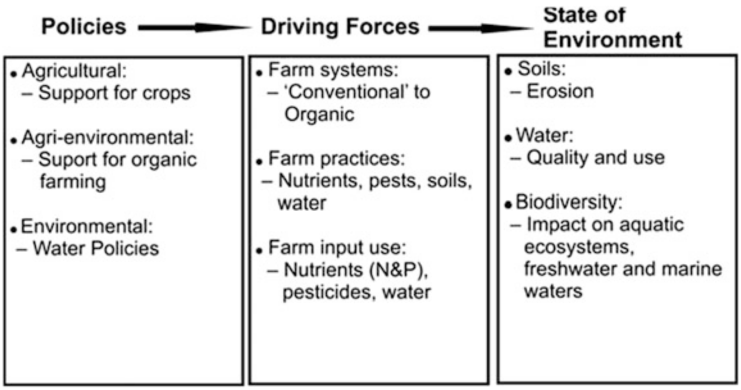
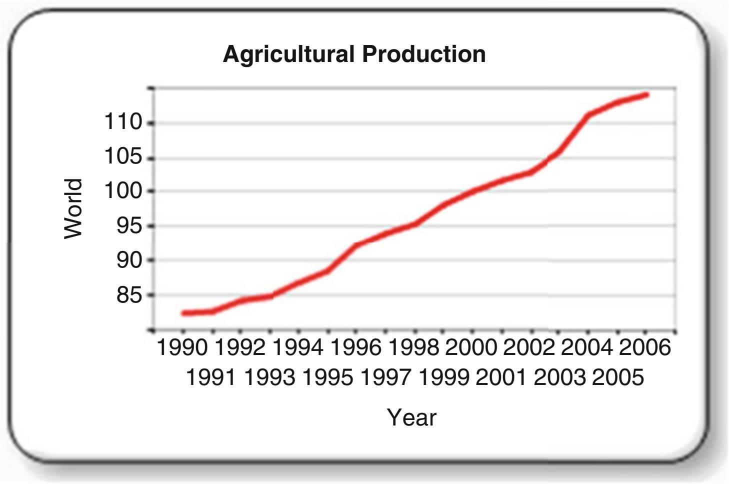


**Fig. 4.1** Linkages between policies, driving forces, and therefore the state of the environment relevant to water. *Source*: OECD Secretariat (2010)



FAO 2012

**Fig. 4.2** Global trend in agricultural production for different years

The global trend in agricultural production as per FAO statistics (FAO 2012) for different years is indicated in Fig. 4.2.

India is an agriculture-based country and development in agricultural sector is of prime importance for economic stability. The green revolution in the late 60s initiated the development in agriculture. High yielding varieties were introduced and there was increased usage of chemical fertilizers and pesticides. India thus achieved self-sufficiency and became an exporter of food grains. Increased food demands led to overusage of fertilizers and pesticides (Sharma 2011, p. 1). The study conducted by UNEP (1996) compared different sources of pollution, domestic, industrial, and agricultural, from the coastal zone of Mediterranean countries and reported that agriculture was the leading source of phosphorus compounds and sediment. The results of various surveys in India and Africa have shown that 20–50% of wells contain nitrate levels greater than 50 mg/L to several hundred milligrams per litre. Nutrient enrichment may cause destruction and eliminate species with higher oxygen requirements affecting the diversity of ecosystems. Nitrate is the commonest chemical contaminant within the world's groundwater aquifers. Mean nitrate levels have risen by an estimated 36% in global waterways since 1990, especially within the Eastern Mediterranean and Africa (Spalding and Exner 1993; Ward et al. 2018).

### 4.1.1 Nonpoint Sources of (Diffuse) Pollution

Soil, air, and water environments get polluted as a result of farming activities. The primary agricultural nonpoint source pollutants include nitrogen and phosphorus nutrients, pesticides, animal wastes, salts, and sediment. Various farming activities end in the erosion of soil particles. Pesticides used in agricultural activities can contaminate surface as well as groundwater resources. The sediment produced by erosion may transport excess agricultural chemicals and the runoff in turn damage aquatic habitat. Excess nutrients in surface water result from chemical fertilizers and manure used in agriculture and may lead to eutrophication. Return flows, runoff, and leachate from irrigated lands and improper grazing practices indirectly cause water quality degradation which in turn harm the environment (Tilman et al. 2002).

### 4.1.2 Usage of Agrochemicals and Its Impact on Environment

Overusage of agrochemicals has severe negative effects on water resources, biodiversity, and ecosystem functioning. Agrochemicals can contaminate soil, water, and vegetation. Pesticides can be toxic to many organisms, including birds, fish, beneficial insects, and non-target plants. Insecticides are generally the foremost acutely toxic class of pesticides, but herbicides also can pose risks to non-target organisms. The impact of agrochemicals on the environment can be classified based on health issues, pollution of water and soil, socioeconomic problems, biodiversity, etc. (Zhang et al. 2018).

#### 4.1.2.1 Health Issues

Storage, handling, and disposal of chemical agricultural inputs can cause serious negative health effects like cancer, negative influence on reproduction, or even disrupt the endocrine system. Farmers, their families, and consumers are exposed to dangerous synthetic pesticides. Pesticide residues in food and drinking water can cause severe health issues.

#### 4.1.2.2 Social and Economic Problems

The use of synthetic pesticides often is connected to a vicious circle of monetary dependency, leading to increasing indebtedness among farmers. There are several reported cases of suicides committed because of debts. Social and economic problems also include loss of land and migration. The unrestricted use of pesticides destroys beneficial organisms and induces resistance, creating the need for new and more expensive pesticides. Farmers lack choice of crops, choice of seeds, and even the choice of agricultural production system.

#### 4.1.2.3 Contamination of Water, Air, and Soil

Agricultural pollution can contaminate soil, air, and water environments. Diffuse agricultural pollution is associated with soil particles, pesticides, and other potentially toxic chemicals, nutrients, and pathogens. The study conducted by the U.-S. Geological Survey on major river basins across the country in the early to mid-90s reported the presence of pesticides and transformation products (USGS 1999; Savonen 1997). Also, quite 90 percent of water and fish samples from many streams contained many pesticides (Kole et al. 2001). The survey conducted in India found that 58% of beverage samples drawn from various hand pumps and wells around Bhopal were contaminated with Organochlorine pesticides above the EPA standards (Kole and Bagchi 1995). Over the past two decades, presence of pesticides was reported in the groundwater of more than 43 states (Waskom 1994). Overuse of pesticides in soil can cause populations of beneficial soil microorganisms to decline. According to the soil scientist Dr. Elaine Ingham, “If we lose both bacteria and fungi, then the soil degrades” (Ingham et al. 1985).

### 4.1.3 Pesticides

In India, production of pesticides started in 1952 with the establishment of a plant for the assembly of BHC near Calcutta. India was the second largest manufacturer of pesticides in Asia and ranked twelfth globally (Mathur 1999). Production of technical grade pesticides in India was 5000 metric tons in 1958 and increased to 102,240 metric tons in 1998. In India, 76% of the pesticide used is insecticide and the use of herbicides and fungicides is correspondingly less heavy (Fig. 4.3). The pattern of use of pesticides in India is different from that for the world. Pesticides are mainly used in India for cotton crops (45%), followed by paddy and wheat (Aktar et al. 2009).

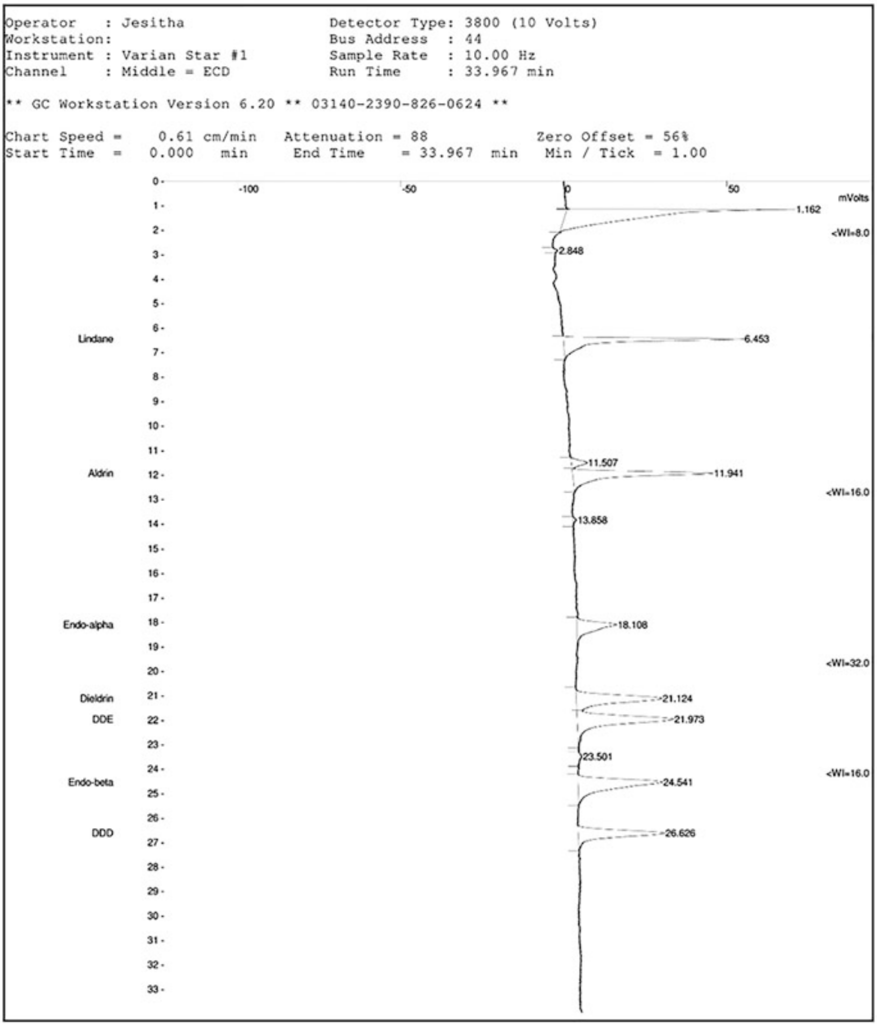
Kerala agriculture contributed 17.2% to Kerala’s economy (as of 2002–2003). The State’s agriculture sector contributes only 10.88% of the entire GDP (at current prices in 2013–2014) compared to 34.2% in Madhya Pradesh, 29.3% in Utter Pradesh and Rajasthan, and 27.4% in Punjab. High labour cost has forced many of the farmers to keep away from agriculture (Govt. of Kerala 2016). The agricultural sector requires a sizeable amount of pesticides (roughly 656.5 tonnes per annum), of which fungicides account for 73%. (Indira Devi 2010).

Environmental pollution not only causes serious health issues, but is a wider social issue and has the potential to destroy homes and communities. Pollution problems are also closely related to the mode of development in developing countries. Many developing countries have not developed environmental pollution control measures and not provided adequate implementation structures to ensure that related policies are effective (Aktar et al. 2009; PAN 2007; Cassou 2018).

Pesticide sprays can contaminate air, soil, and non-target plants since they can drift or volatilize from the treated area. Chlorpyrifos, the common contaminant found in urban streams, is highly toxic to fish. Herbicides can also be toxic to fish. Studies reported that trifluralin, a lively ingredient within the weed-killer, is very toxic to both cold and warm water fish (U.S. EPA 1996; Koyama 1996).

### 4.1.4 Agriculture Pollution in Kerala, India

The systems of ‘Pokkali’, ‘Kuttanad’, and ‘Kole’ are samples of purposeful human interventions, whereas irrigated, also as rain-fed, rice cultivation is widely practiced in valleys of midlands and highlands (Kerala State Land Use Board 2006). The peasants of Kerala evolved sorts of rice culture over the centuries to suit every



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Operator    : Jesitha                 Detector Type: 3800 (10 Volts)
Workstation:                          Bus Address   : 44
Instrument : Varian Star #1           Sample Rate   : 10.00 Hz
Channel     : Middle = ECD            Run Time      : 33.967 min

** GC Workstation Version 6.20 ** 03140-2390-826-0624 **

Chart Speed =    0.61 cm/min   Attenuation = 88          Zero Offset = 56%
Start Time  =   0.000   min     End Time    = 33.967  min   Min / Tick  = 1.00
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**Fig. 4.3** Gas chromatogram indicating the pesticides lindane, aldrin, dieldrin, DDD, DDE, endosulphan alpha, and endosulphan beta

conceivable agronomic condition. Considering the variations in resource endowments, topography, soil, and abiotic factors, significant rice agro ecosystems like Midland and Malayoram ecosystems, Kuttanad agroecosystem, Onattukara agroecosystem, Pokkali agroecosystem, etc. were identified.

The fertilizer and pesticide consumption in the catchment area of Kuttand has increased significantly in the previous years. Transport of these hazardous elements into the estuaries is indicated partly by appearance of insecticide residues in the estuarine sediments (Swaminathan 2007; Muralidharan and Ajayakumar 2002).

A study undertaken by Indira Devi (2010) reported that toxicity level and dose of pesticides exert a significant effect on health. If the dose of the most toxic chemicals used is reduced by 25%, health costs decrease by 30%. If the dose of all pesticides is reduced by 25%, then expected average health cost decreases by 41%. Dose reductions are a feasible strategy for farmers in Kerala and can be achieved either by restricting the number of pesticide used or by diluting the quantity sprayed with more water. Low pesticide use with shift to bio-pesticides or integrated pest management should be promoted to reduce the pesticide pollution from crops like rubber and cardamom in the catchments of rivers and paddy in Kuttanad.

The problems, thanks to pesticides, started way back in 1958 following the death of quite 100 people within the year 1958 after consuming flour contaminated with pesticides during transportation. The state-owned Plantation Corporation of Kerala began the aerial spraying of Endrin (later Endosulphan) way back within the 1970s in their cashew plantations and native people became the victims of severe health problems (Indira Devi 2010).

#### 4.1.4.1 Pollution of Vembanad Backwater System Due to Agrochemicals

The agricultural developments resulted in the input of large quantities of agrochemicals and pesticides in the wetland bodies of Kerala, especially in Vembanad Lake. The application of fertilizers and biodegradation of organic wastes have also led to the enrichment of nitrogen within the lake waters; the extent of ammonia was also high near thickly populated habitations, especially near urban centres like Alappuzha.

The annual usage of pesticides/fungicides/weedicides in Kuttanad was reported to be 117 tons during Virippu season and 368 tons during the Mundakan and Puncha season (Nair and Unni 1993; Babu et al. 2008). Annual fertilizer consumption in Kuttanad was 8409 tons of nitrogen and 5044 tons of potassium. Pesticides, fungicides, and weedicides of about 500 tons/year were applied (James 2009).

#### 4.1.4.2 Aggressive Waterweeds and Water Pollution

The low salinity in Vembanad Lake and increased discharge of organic wastes and fertilizer residues into water bodies are promoting eutrophication.

The water and sediment quality data collected of the lake indicated that the eutrophication of the Vembanad Lake was mainly phosphorous-limited (Harikumar et al. 2009). Physico-chemical analysis of the water samples collected in different seasons gave an insight into the pollution level of Vembanad wetland system (Harikumar and Nasir 2011). The water quality is seriously impaired by many organic and inorganic pollutants of different origin (Harikumar et al. 2009). High nutrient level caused hypereutrophic stage in many parts of the system. The high concentration of phosphorus increased the amount of algal growth, making the situation worst.

Determination of nutrient concentration indicated hypereutrophic stage of lake with vertical increase in the rate of deposition of nitrate, sulphate, and phosphate. The source of ortho-phosphorous to the system was due to the agricultural runoff. The amount of phosphorous in sediments is so severe that, albeit the source of phosphorous to the system is banned, it contributes phosphorous to the water. Distribution and variability of nutrients in Cochin backwaters have been extensively studied by Lakshmanan et al. (1987). Bindu and Harikumar (2007) studied the nutrient concentration in Vembanad Lake employing a dynamic model. The lake was infested with phytoplankton growth, especially during pre-monsoon and beginning of monsoon months. The management of river basins in relation to Vembanad backwater has to take care of the irrigation and drinking water requirements of the area.

## 4.2 Pesticide Residue Analysis of Samples Collected from Various Parts of Kerala with Special Reference to Endosulphan Issue of Kasaragod, Kerala, India

### 4.2.1 Materials and Methods

#### 4.2.1.1 Sampling of Water, Soil, and Sediment from Selected Locations for Pesticide Residue Analysis

The sampling and analysis of pesticide residues were carried out following standard protocols (APHA 2005, 2012; USEPA 1989, 1994, 1995).

The water samples for the analysis of pesticides were collected in 1 L clean amber glass bottles with teflon stopper and labelled. Each sample container was clearly marked with the information such as date, time, place of collection, sample type, and sample identification code. The glass bottles were washed with detergent solution, tap water, distilled water, acetone, and finally with the working organic solvent, *n*-hexane. The collected samples were transported to the laboratory in cool box with ice packs and subsequently stored under refrigeration at 4 °C until further analysis.

The soil samples were collected by a systematic grid sampling method at a depth of 0–10 cm. Random samples were also collected from certain locations of the study area near agricultural, plantation, or industrial areas. In such cases, composite soil sample was taken by collecting sub-samples from 5 to 10 sites throughout the field and then these sub-samples were combined. The soil sample was obtained by screwing the hand-operated soil auger through the soil to the desired depth. The sample was mixed thoroughly, the one-quart sample jar was filled, and the remaining soil was discarded. The soil and sediment samples for the analysis were collected and stored in air tight, solvent-washed new glass jars, verified as pesticide-free, sealed with Teflon foil liner fitted with new screw caps. These sample containers were clearly marked with the information such as date, time, place of collection, sample type, and sample identification code. Samples were air-dried, grained using mortar and pestle, and then sieved (aperture 2 mm). The samples were stored carefully, avoiding any external contamination.

#### 4.2.1.2 Reagents and Standards

Technical grade pesticides: lindane, aldrin, dieldrin, DDD, DDE endosulphan (endosulphan alpha + beta), and its metabolites (endosulphan sulphate, endosulphan ether, endosulphan lactone, and endosulphan diol) required for the study were obtained from E. Merck (Germany). All the reagents used were of analytical grade.

#### 4.2.1.3 Extraction of Pesticide Residues

For the extraction of the pesticide residues from water, liquid-liquid extraction method was adopted. Extraction of pesticides from soil required a more polar solvent than hexane or dichloromethane. Hence, a mixed extracting solvent with added acetone was used.

One litre of water sample was taken in a separating funnel. An amount of 30 g of NaCl and 50 mL of *n*-hexane was added. The hexane layer was separated after shaking the sample. This process was repeated thrice and hexane portions were pooled together. The co-extractives were faraway from the concentrated extract by passing through an alumina column overlaid with 1 g anhydrous sodium sulphate to get rid of any remaining water molecules. The extract was concentrated to 10 mL by employing a rotary evaporator. The concentrated extract was transferred to airtight, amber-coloured GC vials and stored at 4 °C until analysis (APHA 2005; USEPA 1989).

For the extraction of soil and sediment samples, 10 g of sample was taken in 100 mL conical flask containing 25 mL acetone. The mixture was shaken well and the flask was kept overnight in the electric shaker. The supernatant was transferred into a separating funnel of 1 L capacity. Acetone (25 mL) was added to the sample and shaken well for about 10 min and kept for sedimentation. The supernatant acetone extract was transferred into the same separating funnel. To the separating funnel, 300 mL of deionized water, 15 g of sodium chloride, and 20 mL *n*-hexane were added. The mixture was shaken well for 10 min and kept for layer separation. The aqueous layer was collected using a beaker. The *n*-hexane layer was transferred to a typical flask from the separating funnel. Again 20 mL *n*-hexane was added to the aqueous layer and shaken well for 10 min. Then the aqueous layer was discarded, and the n-hexane layer was transferred from the separating funnel to 100 mL conical flask. Anhydrous sodium sulphate (3 g) was added into *n*-hexane layer for dehydration and left the sample undisturbed for 20 min and then concentrated to 10 mL. The clean-up was done on an alumina column overlaid with 1 g anhydrous sodium sulphate. The extract was stored in airtight amber-coloured vials at 40 °C until analysis (USEPA 1989).

#### 4.2.1.4 Analysis of Pesticide Residues

After processing the samples through the different extraction steps, the final concentrated and cleaned up sample was analysed using Gas Chromatograph with Electron capture Detector which is specific and highly sensitive for halogenated compounds. Varian make CP-3800 Gas Chromatograph equipped with Ni 63 ECD (electron capture detector) was used to analyse the pesticides. One microlitre volume of each extract was injected into the injection port using the micro syringe.

WCOT-fused silica capillary column of length 30 m, 0.32 mm internal diameter, and 0.25 μm film thickness was fitted and efficient temperature programs were used. Nitrogen was used as the carrier gas and the gas inlet pressure was 80 psi

**Table 4.1** Validation results: limit of detection and limit of quantification

| Pesticide | LOD (μg/L) | LOQ (μg/L) |
|---|---|---|
| Endosulphan alpha | 0.05 | 0.17 |
| Endosulphan beta | 0.05 | 0.17 |
| Endosulphan diol | 0.10 | 0.33 |
| Endosulphan ether | 0.10 | 0.33 |
| Endosulphan lactone | 0.10 | 0.33 |
| Lindane | 0.10 | 0.33 |
| Aldrin | 0.01 | 0.03 |
| Dieldrin | 0.01 | 0.03 |
| DDD | 0.10 | 0.33 |
| DDE | 0.10 | 0.33 |

corresponding to a flow rate of 2 ml min-1. The temperature for injector and detector were 250 and 300 °C, respectively. The temperature column was programmed from 130 (hold 1 min) to 200 °C at 5 °C (hold 10 min) and then from 200 to 232 °C at 1 °C min$^{-1}$ The chromatograms were recorded and integrated using Star Workstation software. External pesticide reference standards from E.Merck (Germany) were used to compare and quantify the sample concentrations. The pesticides detected were compared with that of the standards (Vidal et al. 2000). Chromatogram indicating the pesticides lindane, aldrin, dieldrin, dichlorodiphenyldichloroethane (DDD), Dichlorodiphenyldichloroethylene (DDE), endosulphan alpha, and endosulphan beta is shown in Fig. 4.3.

Accuracy within-day and between-day precision were assessed using Quality Control (QC) samples at four concentration levels including LOD, 50, 100, and 200 μg/L. The samples were all run in triplicate on three different days and the RSD and relative error (RE) were calculated for each. Acceptable precision here was an RSD $<$ 5%. The overall accuracy was assessed by subtracting the theoretical concentration of each QC sample from the mean concentration determined from the 3 days of analyses. Detection (LOD) and quantification (LOQ) limits were calculated relative to the values for the blank at the retention times of the analytes (10 injections).

Table 4.1 summarizes the results of validation, percentage recoveries of the calibration data, and the LODs and LOQs for the studied pesticides. Table 4.2 shows the average recoveries and relative standard deviations (RSD %) at four concentrations.

Recoveries at the LODs ranged from 96.5 to 106.4%. Average recoveries for all other concentrations varied between 90.2 and 102.4%. The uncertainties of the recoveries, reported as RSD% (precision), varied between 1.0 and 4.7%.

**Table 4.2** Average recoveries and relative standard deviations (RSD %) at four concentration levels ($n = 4$)

| | LOD | | 50 (μg/L) | | 100 (μg/L) | | 150 (μg/L) | |
|---|---|---|---|---|---|---|---|---|
| Pesticide | % R | % RSD | % R | % RSD | % R | % RSD | % R | % RSD |
| Endosulphan alpha | 97.6 | 1.9 | 97.7 | 2.0 | 93.6 | 1.5 | 92.5 | 1.0 |
| Endosulphan beta | 99.8 | 2.8 | 95.7 | 2.3 | 95.8 | 2.3 | 90.2 | 4.7 |
| Endosulphan diol | 96.8 | 3.2 | 94.6 | 1.2 | 93.4 | 3.4 | 91.6 | 2.6 |
| Endosulphan ether | 97.8 | 2.4 | 98.9 | 2.6 | 95.2 | 4.2 | 95.5 | 2.4 |
| Endosulphan lactone | 96.5 | 1.6 | 102.4 | 3.2 | 96.6 | 3.2 | 96.6 | 2.3 |
| Lindane | 98.8 | 3.2 | 98.6 | 2.6 | 96.8 | 3.6 | 96.4 | 2.4 |
| Aldrin | 98.5 | 2.6 | 97.4 | 2.0 | 97.2 | 2.4 | 95.6 | 3.2 |
| Dieldrin | 106.4 | 2.4 | 96.8 | 3.4 | 95.4 | 2.2 | 94.3 | 3.2 |
| DDD | 97.8 | 1.6 | 96.8 | 2.3 | 96.4 | 3.4 | 93.6 | 2.7 |
| DDE | 98.8 | 1.4 | 98.6 | 2.2 | 96.4 | 3.2 | 94.2 | 3.4 |

### 4.2.2 Monitoring of Pesticide Residues in Water Samples Collected from Different Parts of Kerala

Fresh water samples, which included groundwater and surface water, were collected from different places of Kerala (Fig. 4.4). Surface water samples were collected from Calicut (CLT 4) District, Anjarakandi (ANJ5) in Kannur district, and Karamana (KRM) in Thiruvananthapuram district. Details of sampling stations from different parts of Kerala are given in Table 4.3. The sampling sites were selected taking into consideration the chances of pesticide pollution from the nearby agricultural or industrial areas.

The results of pesticide concentration in different water samples are represented in Table 4.4.

Among the 20 samples analysed, 11 were found to be contaminated with organochlorine pesticides. Aldrin, dieldrin, and endosulphan beta were detected in the samples. The concentration of aldrin and dieldrin in many samples was higher than the permissible limit as per BIS. But the concentration of other pesticides in the samples was relatively low.

The concentration of lindane, endosulphan alpha, DDD, and DDE was found to be below detection limit in all the 20 water samples. Samples collected from Manikothuvayal, Idumba, Anjarakandy, Kottakal, Thrikkakara, Pathalam, Eloor, Paravoor, and Payyannoor was polluted with the pesticide aldrin. Concentration of aldrin in the sample collected from Manikothuvayal (0.04 μg/L) was above the permissible limit of BIS. Manikothuvayal in Kannur district is an agricultural area. Sampling sites at Idumba and Anjarakandy in Kannur district and Kottakal from Malappuram district were also near agricultural areas. The selected sampling sites Pathalam, Eloor, and Paravoor in Eranakulam district were industrial areas. Sample was collected from a cashew plantation area from Payyannoor in Kasaragod district.

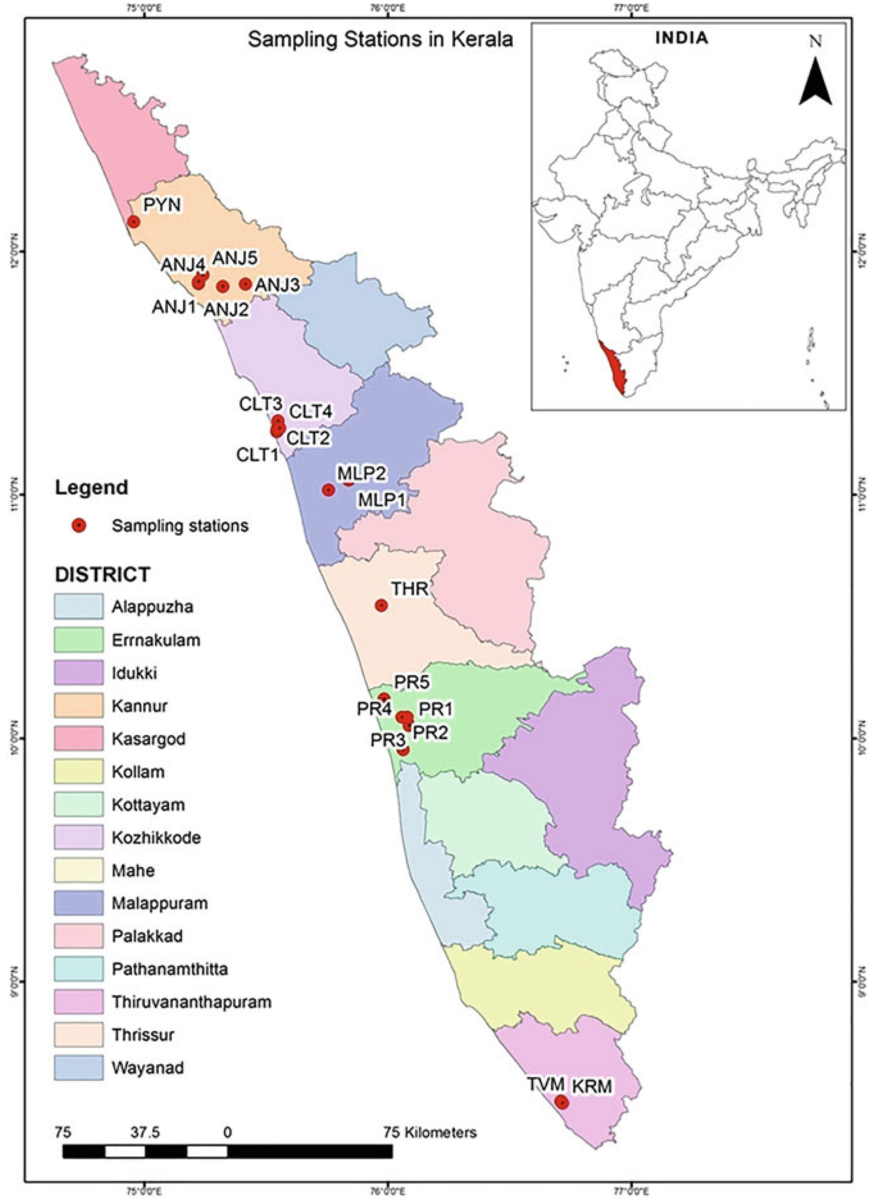


**Fig. 4.4** Map of Kerala showing the details of sampling stations for pesticide monitoring

Dieldrin was detected in the two samples collected from Kozhikode. Also, samples collected from Thrikkakara, Pathalam, Eloor, and Paravoor contained concentrations of dieldrin above the permissible limit. The highest concentration

**Table 4.3** Details of sampling stations in different parts of Kerala

| Sl. No | Sample code | Sampling stations | Latitude | Longitude |
|---|---|---|---|---|
| 1 | ANJ1 | Manikothuvayal | 11°50′56.4″N | 75°27′56.1″E |
| 2 | ANJ2 | Koothuparamba | 11°50′14.3″N | 75°33′57.2″E |
| 3 | ANJ3 | Kannavam | 11°50′47.2″N | 75°39′32.5″E |
| 4 | ANJ4 | Idumba | 11°51′25.2″N | 75°27′59.5″E |
| 5 | ANJ5 | Anjarakandi | 11°53′03.3″N | 75°29′00.5″E |
| 6 | CLT1 | Chalappuram | 11°14′21.5″N | 75°47′14.9″E |
| 7 | CLT2 | Thali Calicut | 11°14′51.1″N | 75°47′15.8″E |
| 8 | CLT3 | Calicut civil | 11°17′04.4″N | 75°47′29.6″E |
| 9 | CLT4 | Calicut SW | 11°15′15.6″N | 75°47′55.9″E |
| 10 | MLP1 | Malappuram | 11°02′28.9″N | 76°04′56.3″E |
| 11 | MLP2 | Kottakkal | 10°59′58.4″N | 75°59′55.5″E |
| 12 | PR1 | Thrikkakara | 10°02′05.1″N | 76°19′47.2″E |
| 13 | PR2 | Muttam | 9°50′41.1″N | 76°44′35.1″E |
| 14 | PR3 | Pathalam | 10°04′08.9″N | 76°19′19.4″E |
| 15 | PR4 | Eloor | 10°04′06.0″N | 76°18′04.5″E |
| 16 | PR5 | Paravoor | 10°02′35.9″N | 76°13′42.2″E |
| 17 | TVM | Thambanoor | 8°29′22.6″N | 76°57′11.7″E |
| 18 | PYN | Payannoor | 12°06′12.1″N | 75°12′02.4″E |
| 19 | KRM | Karamana | 8°28′51.5″N | 76°57′39.2″E |
| 20 | THR | Thrissur | 10°31′30.9″N | 76°12′58.0″E |

of dieldrin detected was 0.62 μg/L from the sample collected from Eloor. Eloor is a major industrial area in Kerala.

Endosulphan beta was detected only in one sample collected from Payyannoor in Kasaragod district. The sample was collected inside a cashew plantation where the usage of endosulphan has been reported previously before it was banned.

Samples collected from Koothuparamba and Kannavam in Kannur district, Chalppuram and Thali in Calicut district, and from Malappuram in Malappuram district, Muttam in Ernakulam district, Thrissur in Thrissur district Thambanoor, and Karamana in Thiruvananthapuram district were free from organochlorine pesticides.

### 4.2.3 Study on the Persistence of Pesticide Residues in Kasaragod District, Kerala

Organochlorine pesticides (OCPs) have been extensively used in India for agricultural purposes. Many pesticides are toxic and they persist in the environment for a limited period of time and later are subjected to some chemical processes of degradation, hydrolysis, oxidation, photolysis, etc. by the ecosystem (Ormad et al. 1997; Arias-Estevez et al. 2008).

Endosulphan is a persistent, toxic broad-spectrum organochlorine insecticide and acaricide used in food and non-food crops. In human health assessment studies,

**Table 4.4** Pesticide concentration in various water samples from different locations of Kerala

| Sl. No | Sample code | Lindane (μg/L) | Aldrin (μg/L) | Endosulphan alpha (μg/L) | Endosulphan beta (μg/L) | Dieldrin (μg/L) | DDD (μg/L) | DDE (μg/L) |
|---|---|---|---|---|---|---|---|---|
| 1 | ANJ 1 | BDL | 0.04 | BDL | BDL | BDL | BDL | BDL |
| 2 | ANJ 2 | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 3 | ANJ 3 | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 4 | ANJ 4 | BDL | 0.03 | BDL | BDL | BDL | BDL | BDL |
| 5 | ANJ 5 | BDL | 0.01 | BDL | BDL | BDL | BDL | BDL |
| 6 | CLT 1 | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 7 | CLT 2 | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 8 | CLT 3 | BDL | BDL | BDL | BDL | 0.01 | BDL | BDL |
| 9 | CLT 4 | BDL | BDL | BDL | BDL | 0.02 | BDL | BDL |
| 10 | MLP 1 | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 11 | MLP 2 | BDL | 0.03 | BDL | BDL | BDL | BDL | BDL |
| 12 | PR 1 | BDL | 0.01 | BDL | BDL | 0.04 | BDL | BDL |
| 13 | PR 2 | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 14 | PR 3 | BDL | 0.01 | BDL | BDL | 0.20 | BDL | BDL |
| 15 | PR 4 | BDL | 0.01 | BDL | BDL | 0.62 | BDL | BDL |
| 16 | PR 5 | BDL | 0.02 | BDL | BDL | 0.07 | BDL | BDL |
| 17 | TVM | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 18 | PYN | BDL | 0.03 | BDL | 0.22 | BDL | BDL | BDL |
| 19 | KRM | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 20 | THR | BDL | BDL | BDL | BDL | BDL | BDL | BDL |

*BDL* Below detection limit

endosulphan generally has been shown to have high acute oral and inhalation toxicity as well as slightly toxic dermal toxicity. It is an irritant to the eyes and primarily affects the nervous system (NIOH 2002; USEPA 2002). As per Bureau of Indian Standards (2012), the permissible limit of endosulphan in drinking water is 0.4 μg/L. Maximum permissible limit as per US Environmental Protection Agency for endosulphan in lakes, rivers, and streams is 74 μg/L (USEPA 2001a, b).

The use of organochlorine insecticides in India for agriculture and public health sector has been documented. Although the use of most organochlorine pesticides (OCPs) has been discontinued as a result of their environmental persistence, exposure to OCPs may continue during the coming years too. As a consequence, many OCPs may induce chronic toxicities through long-term exposure even if doses are relatively low (Leena and Choudhary 2011; Zhao et al. 2009; Ghadiri 2001).

Endosulphan is known to be an endocrine disruptor and also a genotoxin (Fernandez 2007). Because of its persistence in the environment for a long time and its toxicity, endosulphan contamination in the environment is of great concern. Endosulphan was aerially sprayed for many years in the cashew plantations of this area, though it has now been discontinued. Because of the reported cases of endosulphan problem and related health issues due to aerial spraying of endosulphan in Kasaragod district of Kerala, a study on the persistence of endosulphan was carried out in 11 selected Panchayats of Kasaragod district of Kerala in five phases.

#### 4.2.3.1 Materials and Methods

##### Description of Sampling Sites

The sampling sites were fixed with the help of concerned health inspectors and members of "Endosulphan Victims and Remediation Cell" formed under the coordination of District Medical Officer of Kasaragod district. Sampling locations are indicated in Fig. 4.5. All sampling points were geographically referenced with Global Positioning System. A total of 49 water/sediment/soil samples were collected for the analysis of endosulphan from 11 Panchayats. A total of 22 water samples were collected from the study area. The number of samples collected from each Panchayat is indicated in Table 4.5. The details of the water samples collected are given in Table 4.6. and Plates 4.1, 4.2, and 4.3 depict some of the water sampling sites. Soil and sediment samples were collected from the affected panchayats of Kasaragod district. A total number of 14 sediment and 13 soil samples were collected from 11 Panchayats of Kasaragod district. The details of sediment and soil sampling locations are described in Tables 4.7 and 4.8, respectively. Some of the sediment and soil sampling sites are depicted in Plates 4.4, 4.5, 4.6, and 4.7, respectively. In addition to this water, soil and sediment samples were collected from Cheruvathur Panchayat (N 12°11′34.5″, E 075°09′51.8″) of Kasaragod district as control where endosulphan spraying was not conducted. Additionally, four water and three sediment samples were collected from Nanjanparamba, Karadukka Panchayat of Kasaragod district and analysed for endosulphan.

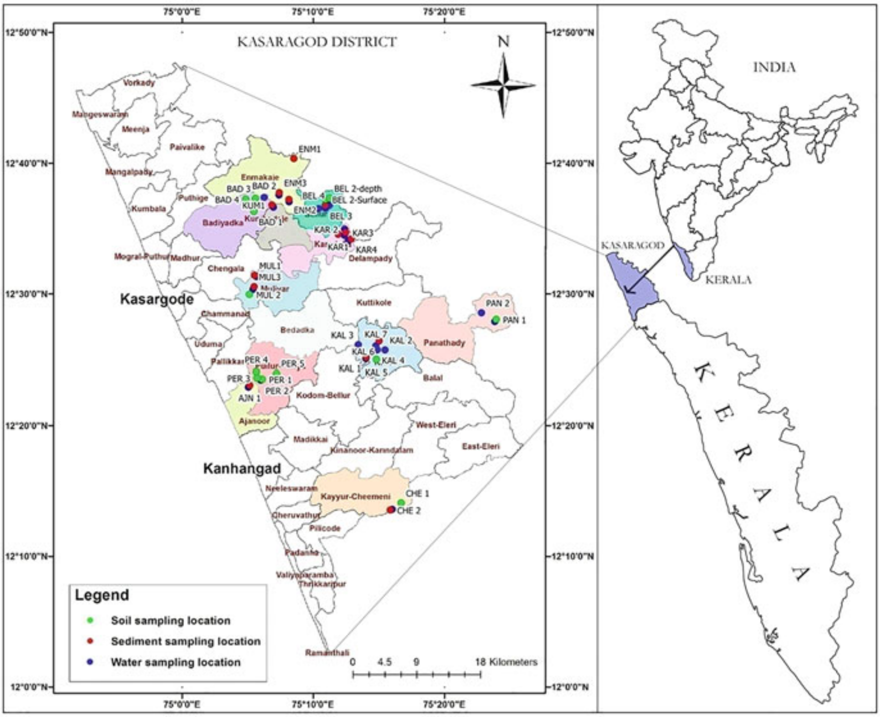


**Fig. 4.5** Map showing endosulphan sampling locations in Kasaragod district

**Table 4.5** Total number of waters, sediment, soil samples collected from 11 Panchayats of Kasaragod district

| Sl. No | Sampling area (Panchayat) | Number of samples | | | Total number of samples |
|---|---|---|---|---|---|
| | | Water | Sediment | Soil | |
| 1 | Kayyur cheemeni | 1 | 1 | 1 | 3 |
| 2 | Ajanur | 1 | 1 | Nil | 2 |
| 3 | Pullur periya | 1 | Nil | 4 | 5 |
| 4 | Kallar | 5 | 2 | 1 | 8 |
| 5 | Panathadi | 2 | Nil | 1 | 3 |
| 6 | Muliyar | 2 | 2 | 1 | 5 |
| 7 | Karadukka | 3 | 3 | Nil | 6 |
| 8 | Badiyaduka | 1 | Nil | 3 | 4 |
| 9 | Kumbadaje | 1 | 1 | Nil | 2 |
| 10 | Bellur | 3 | 1 | 2 | 6 |
| 11 | Enmakaje | 2 | 3 | Nil | 5 |
| | Total | 22 | 14 | 13 | 49 |

**Table 4.6** Details of water sampling locations in Kasaragod district

| Sl. No. | Sample code | Panchayat | Coordinates | Source of sample | Site description |
|---|---|---|---|---|---|
| 1 | ENM 2 | Enmakaje | 12°37′14.8″N<br>075°08′08.0″E | Surangam | Near house-near plantation |
| 2 | ENM 3 | Enmakaje | 12°37′45.8″N<br>075°07′23.8″E | Pond | Water from surangam |
| 3 | KUM 1 | Kumbadaje | 12°36′49.3″N<br>075°06′50.2″E | Pond | Clay mining area |
| 4 | PER 2 | Pullur Periya | 12°23′28.2″N<br>075°05′59.3″E | Pond | Abandoned pond |
| 5 | MUL 1 | Muliyar | 12°31′26.3″N<br>075°05′30.7″E | Surangam | Valley slope |
| 6 | MUL 3 | Muliyar | 12°30′01.9″N<br>075°05′08.9″E | Pond | Plantation area |
| 7 | CHE 2 | Kayyur Cheemeni | 12°13′35.5″N<br>075°16′00.6″E | Pond | Near temple |
| 8 | AJN 1 | Ajanoor | 12°23′04.4″N<br>075°05′09.0″E | Stream | Under bridge |
| 9 | BAD 2 | Badiyadukka | 12°37.327′N<br>075°06.279′E | Stream | Ukkinaduka, kangilla |
| 10 | KAL 1 | Kallar | 12°25′10.0″N<br>075°14′0.9″E | Pond | Pond near Kanhirathody-plantation area |
| 11 | KAL 2 | Kallar | 12°25′44″N<br>075°15′27.4″E | Open well | Well in private land- near plantation area |
| 12 | KAL 3 | Kallar | 12°25′17.7″N<br>075°13′57.0″E | Open well | Kanhirathody<br>Colony well -near plantation land |
| 13 | KAL 4 | Kallar | 12°25′44.5″N<br>075°14′51.8″E | Open well | Well near plantation quarters painikkara |
| 14 | KAL 7 | Kallar | 12°25′44.5″N<br>075°14′51.8″E | Open well | Well inside plantation area- |
| 15 | PAN 1 | Panathadi | 12°27′53.8″N<br>075°23′49.2″E | Plantation tank | Inside plantation area- near helipad site |
| 16 | PAN 2 | Panathadi | 12°28′34.4″N<br>075°22′48.3″E | Stream | Near Kallepalli plantation area |
| 17 | KAR 2 | Karadukka | 12°34.638′N<br>075°12.128′E | Open well | Well near Minchipadavu plantation office |
| 18 | KAR 3 | Karadukka | 12°34.571′N<br>075°12.031′E | Stream | Stream near Minchipadavu plantation office |
| 19 | KAR 4 | Karadukka | 12°34.717′<br>075°11.420′E | Pond | Pond in private land—near Minchipadavu plantation area |
| 20 | BEL 1 | Bellur | 12°35.289′N<br>075°10.396′E | Pond | Pond in private land (Megnamana) |
| 21 | BEL 3 | Bellur | 12°35.532′N<br>075°10.897′E | Pond | Near plantation area |
| 22 | BEL 4 | Bellur | 12°35.535’N<br>075°11.216′E | Pond | Pond near the plantation area |

**Plate 4.1** Temple pond—Kayyur cheemeni Panchayat

**Plate 4.2** Pond—Badiyadukka Panchayat

### Water, Soil, and Sediment Sampling

The sampling and analysis were carried out in three phases from 11 panchayats of Kasaragod district. The sampling covered 2 years and different months. The third phase of sampling was conducted during September 2012. Since endosulphan was found persistent in three soil samples during third phase of analysis, sampling was conducted in the fourth phase during April 2013. Fifth phase of sampling and

**Plate 4.3** Surangam—Enmakaje Panchayat

analysis was conducted in April 2015. Control samples were collected from Cheruvathur Panchayat during each phase.

### Extraction and Analysis of Samples

Extraction and analysis of water, sediment, and soil samples carried out as per standard protocol.

## 4.2.3.2 Results and Discussion

### Concentration of Endosulphan Residues in Water, Sediment, and Soil Samples Collected from Selected Panchayats of Kasaragod District

The chromatograms obtained indicating endosulphan alpha, endosulphan beta, and endosulphan sulphate during the analysis are indicated in Figs. 4.6, 4.7, and 4.8, respectively. The chromatogram obtained for control is indicated in Fig. 4.9.

Fifteen water samples were analysed during three phases of study and the results of the analysis are compared in Table 4.9. Endosulphan residues in water samples in the 15 sites were found to be below detection limit in all the three phases of sampling. The results showed that endosulphan was not present in the water samples. In addition to the 15 samples, seven new sites were identified where there was a chance of endosulphan persistence, and hence, water samples were collected from these sites and analysed during second and third phases of study (Table 4.10). Out of seven water samples, endosulphan was detected in two samples during the second phase (March 2012). During second phase of sampling, the concentration of endosulphan in water samples ranged from below detection limit to 1.11 μg/L.

**Table 4.7** Details of sediment sampling locations in Kasaragod district

| Sl. No. | Sample code | Panchayat | Coordinates | Source of sample | Site description |
|---|---|---|---|---|---|
| 1 | ENM1 | Enmakaje | 12°40′21.8″N 075°08′30.5″E | Pond | Valley |
| 2 | ENM2 | Enmakaje | 12°37′14.4″N 075°08′07.9″E | Surangam | Surangam near house |
| 3 | ENM3 | Enmakaje | 12°37′45.8″N 075°07′23.8″E | Pond | Near Galigopura Road |
| 4 | KUM1 | Kumbadaje | 12°36′49.3″N 075°06′50.2″E | Pond | Clay mining area |
| 5 | MUL1 | Muliyar | 12°31′26.3″N 075°05′30.7″E | Surangam | Valley slope |
| 6 | MUL3 | Muliyar | 12°30′01.9″N 075°05′08.9″E | Pond | Plantation area |
| 7 | CHE 2 | Kayyur Cheemeni | 12°13′35.5″N 075°16′00.6″E | Pond | Near plantation area |
| 8 | AJN 1 | Ajanoor | 12°23′04.4″N 075°05′09.0″E | Stream | Site under bridge |
| 9 | KAL 1 | Kallar | 12° 25′10.0″N 075°14′0.9″E | Pond | Pond near Kanhirathody plantation area |
| 10 | KAL 6 | Kallar | 12°25′85.1″N 075°14′60.4″E | Valley | Sediment from valley slope |
| 11 | KAR1 | Karadukka | 12°34.918′N 075°12.121′E | Pond | Sediment from Kaveri Temple pond |
| 12 | KAR3 | Karadukka | 12°34.571′N 075°12.031′E | Stream | Stream near Minchipadavu plantation office |
| 13 | KAR4 | Karadukka | 12°34.717′N 075°11.420′E | Pond | Pond in private land – Minchipadavu plantation area |
| 14 | BEL 3 | Bellur | 12°35.532′N 075°10.897′E | Pond | Near plantation area. Near Pallapady |

The maximum value for endosulphan in water was detected in sample PER 2 from Pullur Periya Panchayat followed by ENM 2 from Enmakaje Panchayat. The values were 1.11 μg/L and 1.01 μg/L, respectively. The sample with code PER 2 was collected from a pond adjacent to the plantation area and the pond remained undisturbed and was not cleaned for a long period. Sample ENM 2 was collected from a surangam, near the plantation area. During the third phase of water sampling, endosulphan residues were found to be below detection limit (Harikumar et al. 2014).

Eight sediment samples were collected and analysed during three phases of study and the results of analysis are shown in Table 4.11 and graphically compared in Fig. 4.10. Among the eight samples, endosulphan was detected in samples with sample codes MUL 3, KAL 6, KAR 3, KAR 4, and BEL 3. Endosulphan was completely degraded during the second phase. The endosulphan detected in sample KAL 1 was degraded only by 25% during second phase, but was found to be completely degraded during the analysis in third phase. In addition to the eight

**Table 4.8** Details of soil sampling locations in Kasaragod district

| Sl. No. | Sample code | Panchayat | Coordinates | Source of sample | Site description |
|---|---|---|---|---|---|
| 1 | CHE 1 | Cheemeni | 12°14′05.0”N 075° 16′41.0″E | Dry pond | Near plantation area |
| 2 | PER 1 | Pulloor Periya | 12°23′32.0”N 075° 06′05.6″E | Plantation area | Near plantation area |
| 3. | PER 3 | Pulloor Periya | 12°23′37.8”N 075° 05′42.4″E | Inside plantation area | Helipad site |
| 4. | PER 4 | Pulloor Periya | 12°23′39.9”N 075° 05′41.0″E | Inside plantation area | Helipad site |
| 5. | PER 5 | Pulloor Periya | 12°23′57.7”N 075° 07′11.1″E | Plantation area | Inside plantation area |
| 6. | MUL 2 | Muliyar | 12°29′59.0”N 075° 05′07.3″E | Dry pond | Dry pond |
| 7. | BAD 1 | Badiyadukka | 12°37′40.0”N 075° 06′03.8″E | Plantation-helipad site | Helipad site |
| 8 | BAD 3 | Badiyaduka | 12°37.327’N 075° 06.279′E | Near plantation area | Soil from a private land near plantation area |
| 9 | BAD 4 | Badiyaduka | $12^{0}$ 37.536 N $075^{0}$ 05.670′E | Near plantation area | Sacred heart church Compound |
| 10 | KAL 5 | Kallar | 12°25′0.796’N 075°14.794′E | Plantation compound | Soil from plantation compound |
| 11 | PAN 1 | Panathadi | 12°27′53.8”N 075°23′49.2′E | Plantation area | Soil and water from plantation tank |
| 12 | BEL 2-surface | Bellur | 12° 39.84’N 075° 12.45′E | Plantation area | Near Hosanamana – plantation area |
| 13 | BEL 2-depth | Bellur | 12° 39.84’N 075° 12.45′E | Plantation area | Near Hosanamana-plantation area |

samples, six additional sediment samples were analysed during second and third phases of study. Comparison of results of analysis of the six samples is indicated in Table 4.12 and graphically represented in Fig. 4.11. Out of 14 sediment samples, endosulphan was detected in seven samples during second phase of sampling. The maximum value of endosulphan was detected in the sample ENM-1 (6.24 μg/kg) from Enmakaje Panchayat. The source of sediment was a valley slope where the runoff water from the nearby plantation area was clogged and settled down. Beta-isomer was found to be in higher concentration than the alpha-isomer. Endosulphan sulphate was detected only in one sample collected from Kallar Panchayat (KAL

**Plate 4.4** Sediment sampling station—Karadukka Panchayat

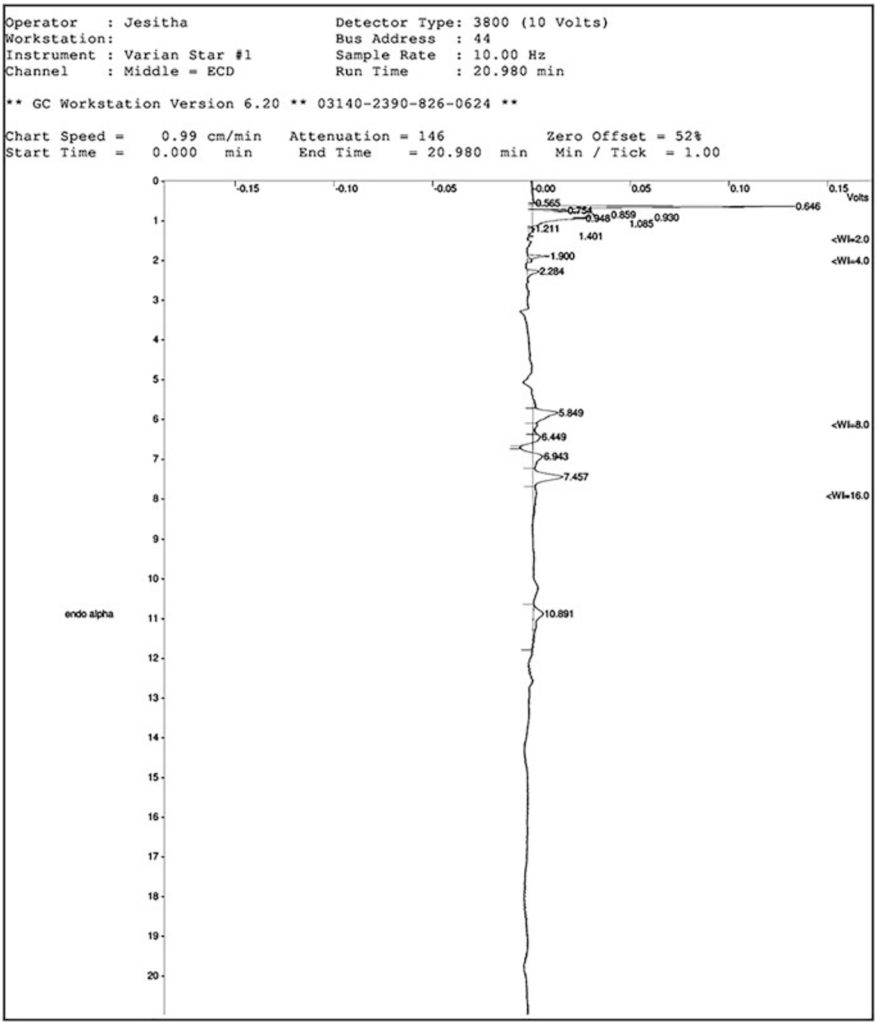
**Plate 4.5** Sediment sampling station—Bellur Panchayat

1 = 4.02 µg/kg). The concentration of endosulphan detected from the same site in 2011 was 5.37 µg/kg. During the third phase of sampling, endosulphan residues in sediment samples were found to be below detection limit. Comparison of results of

**Plate 4.6** Soil sampling station—Muliyar Panchayat

**Plate 4.7** Soil sampling station—Kallar Panchayat

endosulphan analysis of sediment samples indicated that degradation of endosulphan has taken place in majority of the samples. During 2010, traces of endosulphan were detected in selected samples. The comparative results show that the highest concentration of endosulphan (6.22 μg/kg) in sediment during 2010 was found in a sample collected from Kallar Panchayat. During the study conducted in



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Operator    : Jesitha                    Detector Type: 3800 (10 Volts)
Workstation:                             Bus Address  : 44
Instrument : Varian Star #1              Sample Rate  : 10.00 Hz
Channel     : Middle = ECD               Run Time     : 20.980 min

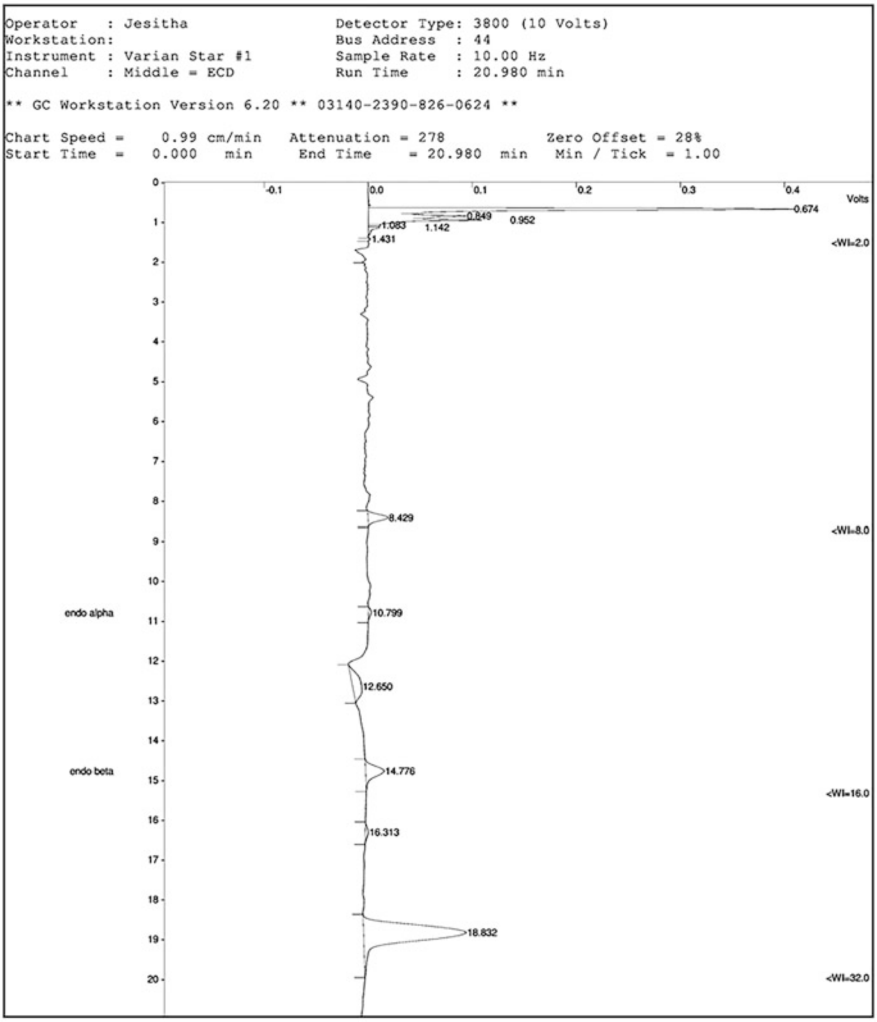
** GC Workstation Version 6.20 ** 03140-2390-826-0624 **

Chart Speed =    0.99 cm/min   Attenuation = 146          Zero Offset = 52%
Start Time  =   0.000   min     End Time    = 20.980  min   Min / Tick  = 1.00
```

**Fig. 4.6** Chromatogram indicating endosulphan alpha obtained during pesticide residue analysis

2012, endosulphan residues were not detected in any of the sediment samples (Harikumar et al. 2014).

Eight soil samples were collected and analysed during three phases of study and the results of analysis are compared in Table 4.13 and graphically represented in Fig. 4.12. The endosulphan present in soil samples with codes KAL 5, BEL 2, and BAD 4 degraded completely during second phase. The maximum concentration of endosulphan detected in Pullur Periya (PER 4) was degraded to 89% during second phase and complete degradation was found during third phase analysis. In the sample PAN 1, rate of degradation was found to be low; only 56% degradation



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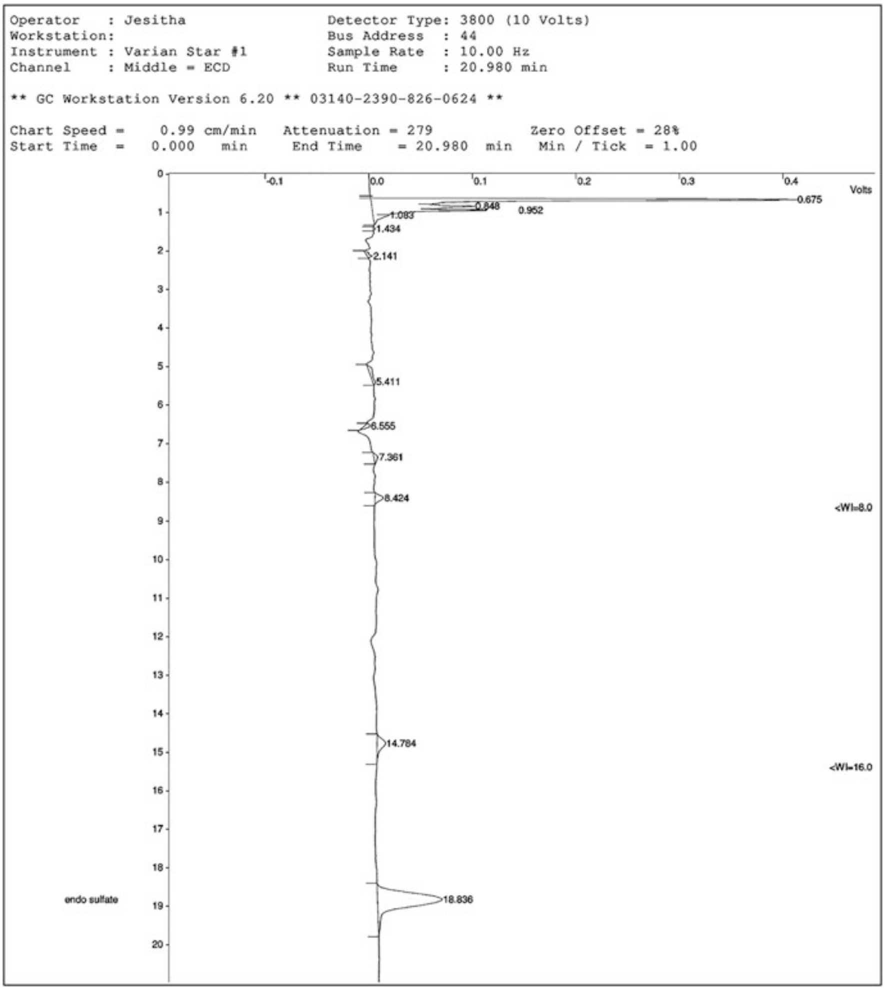
Operator   : Jesitha                    Detector Type: 3800 (10 Volts)
Workstation:                            Bus Address  : 44
Instrument : Varian Star #1             Sample Rate  : 10.00 Hz
Channel    : Middle = ECD               Run Time     : 20.980 min

** GC Workstation Version 6.20 ** 03140-2390-826-0624 **

Chart Speed =    0.99 cm/min   Attenuation = 278           Zero Offset = 28%
Start Time  =   0.000   min     End Time    = 20.980  min   Min / Tick  = 1.00
```

**Fig. 4.7** Chromatogram indicating endosulphan alpha and endosulphan beta obtained during pesticide residue analysis

during the second phase and 67% degradation during third phase were found. In addition to the eight samples, five additional soil samples were analysed during second and third phases of study. Results of analysis are shown in detail in Table 4.14 and indicated in Fig. 4.13. During the third phase of sampling, endosulphan was detected in three soil samples; PER 1 (from Pullur Periya Panchayat), PAN 1 (from Panathadi Panchayat), and MUL 2 (from Muliyar Panchayat). Sampling was continued in the fourth phase (April 2013) and fifth phase (April 2015) also to find out the persistence of endosulphan in soil samples (Harikumar et al. 2014).



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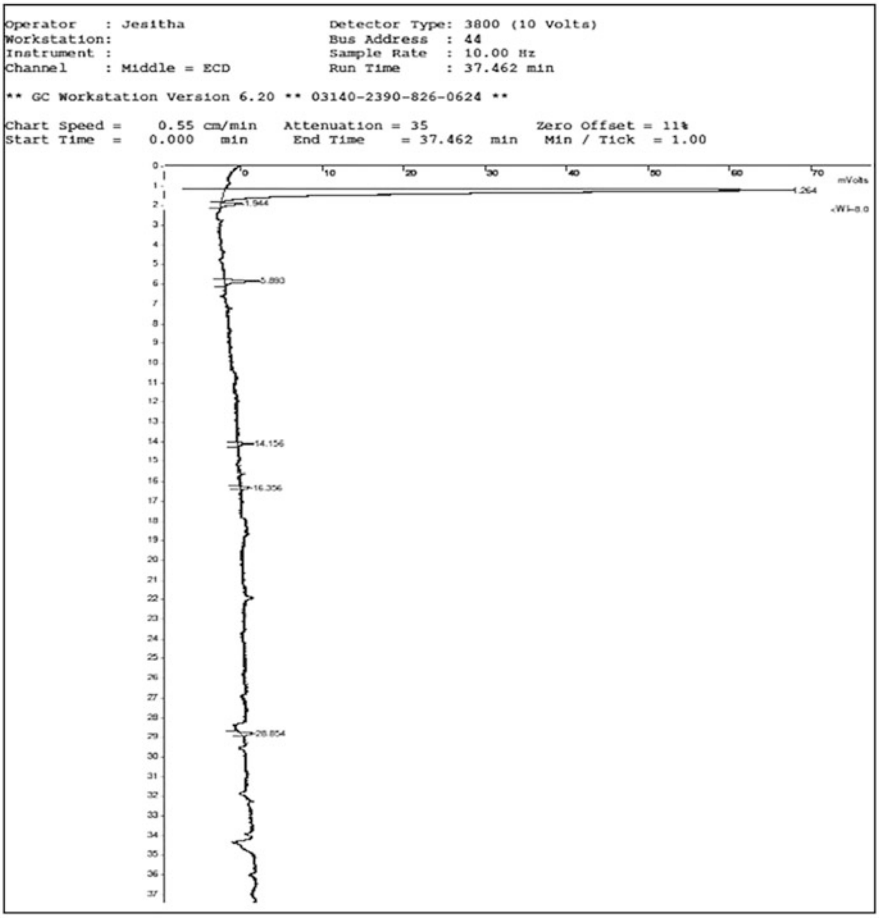
Operator   : Jesitha                 Detector Type: 3800 (10 Volts)
Workstation:                         Bus Address  : 44
Instrument : Varian Star #1          Sample Rate  : 10.00 Hz
Channel    : Middle = ECD            Run Time     : 20.980 min

** GC Workstation Version 6.20 ** 03140-2390-826-0624 **

Chart Speed =    0.99 cm/min   Attenuation = 279          Zero Offset = 28%
Start Time  =   0.000   min     End Time    = 20.980  min   Min / Tick  = 1.00
```

**Fig. 4.8** Chromatogram indicating endosulphan sulphate obtained during the pesticide residue analysis

The highest concentration of endosulphan (16.91 μg/kg) in soil was detected in Pullur Periya (PER 4) during 2010 (first phase of sampling). During second phase analysis, concentration of endosulphan degraded to 1.93 μg/kg and results of third phase analysis show that endosulphan was not present in PER 4. Comparison of results of endosulphan analysis of soil samples showed that out of eight samples, endosulphan was detected in five samples during first phase of sampling. During second and third phases of sampling, the number of samples where endosulphan was detected was three and two, respectively. Rate of degradation was found to be



```
Operator    : Jesitha                    Detector Type: 3800 (10 Volts)
Workstation:                             Bus Address  : 44
Instrument :                             Sample Rate  : 10.00 Hz
Channel     : Middle = ECD               Run Time     : 37.462 min

** GC Workstation Version 6.20 ** 03140-2390-826-0624 **

Chart Speed =    0.55 cm/min   Attenuation = 35          Zero Offset = 11%
Start Time  =   0.000   min     End Time    = 37.462  min   Min / Tick  = 1.00
```

**Fig. 4.9** Chromatogram obtained for control during pesticide residue analysis

different in different areas. Endosulphan released to the soil is subject to biodegradation. The biodegradation of endosulphan in soil and water is dependent on climatic conditions and type of microorganism present. Both biotic and abiotic processes are expected to decrease endosulphan concentrations in soil environments. PAN-1 was the only one soil sampling location where endosulphan sulphate was detected. The sample was collected from Rajapuram plantation area near the helipad. The site was primarily used for cleaning as well as filling pesticide into the sprayers of helicopter for aerial spraying. This might be the reason for the presence of comparatively high concentration of endosulphan in the area. The concentration of endosulphan detected from the same site in 2011 was 14.85 µg/kg. The reduction in the concentration may be due to degradation of endosulphan (Harikumar et al. 2014).

During the fourth phase, analysis concentration of endosulphan was degraded in three samples (Table 4.15). In the sample PER 1, endosulphan was completely

**Table 4.9** Comparison of endosulphan residues in water samples during the first, second, and third phase of sampling

| Sl. No. | Panchayat | Sample source | Sample code | Total endosulphan (μg/L) 1st phase | 2nd phase | 3rd phase |
|---|---|---|---|---|---|---|
| 1 | Ajanoor | Stream | AJN 1 | BDL | BDL | BDL |
| 2 | Muliyar | Pond | MUL 3 | BDL | BDL | BDL |
| 3 | Kallar | Open well | KAL 2 | BDL | BDL | BDL |
| 4 | Kallar | Open well | KAL 3 | BDL | BDL | BDL |
| 5 | Kallar | Open well | KAL 4 | BDL | BDL | BDL |
| 6 | Kallar | Open well | KAL 7 | BDL | BDL | BDL |
| 7 | Panathadi | Plantation tank | PAN 1 | BDL | BDL | BDL |
| 8 | Panathadi | Stream | PAN 2 | BDL | BDL | BDL |
| 9 | Karadukka | Open well | KAR 2 | BDL | BDL | BDL |
| 10 | Karadukka | Stream | KAR 3 | BDL | BDL | BDL |
| 11 | Karadukka | Pond | KAR 4 | BDL | BDL | BDL |
| 12 | Bellur | Pond | BEL 1 | BDL | BDL | BDL |
| 13 | Bellur | Pond | BEL 3 | BDL | BDL | BDL |
| 14 | Bellur | Pond | BEL 4 | BDL | BDL | BDL |
| 15 | Badiyadukka | Stream | BAD 2 | BDL | BDL | BDL |

*BDL* Below detection limit

**Table 4.10** Endosulphan residues in seven water samples during the second and third phase of sampling

| S. No | Panchayat | Sample source | Sample code | Total endosulphan(μg/L) 2nd phase | 3rd phase |
|---|---|---|---|---|---|
| 1 | Enmakaje | Stream | ENM 2 | 1.01 | BDL |
| 2 | Enmakaje | Pond | ENM 3 | BDL | BDL |
| 3 | Kumbadje | Open well | KUM 1 | BDL | BDL |
| 4 | Pulloor Periya | Open well | PER 2 | 1.11 | BDL |
| 5 | Muliyar | Open well | MUL 1 | BDL | BDL |
| 6 | Kayyur Cheemeni | Open well | CHE 2 | BDL | BDL |
| 7 | Kallar | Plantation tank | KAL 1 | BDL | BDL |

*BDL* Below detection limit

degraded during fourth phase. In the sample MUL 2, concentration decreased from 5.21 to 3.91 μg/kg. Also in the sample PAN 1, the concentration decreased from 4.88 to 4.12 μg/kg. The half-lives for the combined toxic residues of endosulphan (alpha endosulphan and beta endosulphan plus endosulphan sulphate) as reported by the EPA range from 9 months to 6 years (USEPA 2002). During the fifth phase of analysis, soil samples were collected from Muliyar and Panathadi Panchayats, where endosulphan was detected during fourth phase of analysis. The results (Table 4.16) showed that the endosulphan was completely degraded in the soil samples.

**Table 4.11** Comparison of concentration of endosulphan residues in sediment samples during the first, second, and third phase of sampling

| S. No | Panchayat | Sample code | Total endosulphan(μg/kg) | | | Rate of degradation during second phase | Rate of degradation during third phase |
|---|---|---|---|---|---|---|---|
| | | | 1st phase | 2nd phase | 3rd phase | | |
| 1 | Muliyar | MUL 3 | 3.39 | BDL | BDL | 100 | 100 |
| 2 | Kayyur Cheemeni | CHE 2 | BDL | 2.25 | BDL | – | – |
| 3 | Kallar | KAL 1 | 5.37 | 4.02 | BDL | 25.13 | 100 |
| 4 | Kallar | KAL 6 | 6.22 | BDL | BDL | 100 | 100 |
| 5 | Karadukka | KAR 1 | 1.48 | 1.7 | BDL | – | 100 |
| 6 | Karadukka | KAR 3 | 1.29 | BDL | BDL | 100 | 100 |
| 7 | Karadukka | KAR 4 | 1.37 | BDL | BDL | 100 | 100 |
| 8 | Bellur | BEL 3 | 1.33 | BDL | BDL | 100 | 100 |

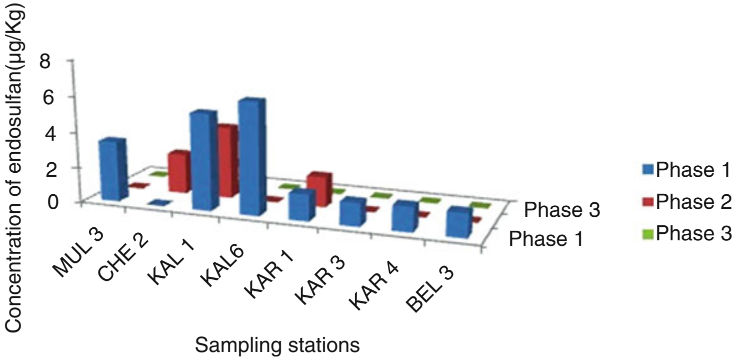


**Fig. 4.10** Comparison of endosulphan residues in sediment samples during first, second, and third phase of sampling

Figures 4.14 and 4.15 indicate the chromatogram obtained during the analysis of the samples from Muliyar and Panathadi Panchayats.

The results of endosulphan analysis of control samples from Cheruvathur Panchayat did not indicate the presence of pesticides.

During the third phase of sampling, endosulphan was detected in three soil samples with sample codes PER-1, PAN-1, and MUL-2. Sampling was continued in the fourth and fifth phases also to find out the persistence of endosulphan in soil samples. Results of endosulphan analysis of soil samples during the fourth phase of sampling are given in Table 4.15. In all the three samples analysed, a decrease in the concentration of endosulphan was observed, though at different rates.

**Table 4.12** Results of endosulphan analysis of six sediment samples of Kasaragod district during second and third phase of sampling

| S. No. | Sample code | Panchayat | Second phase |  |  |  | Third phase |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Endo-alpha (µg/kg) | Endo-Beta (µg/kg) | Endosulphan sulphate (µg/kg) | Total endosulphan (µg/kg) | Endo-Alpha (µg/kg) | Endo-Beta (µg/kg) | Endosulphan sulphate (µg/kg) | Total endosulphan (µg/kg) |
| 11 | ENM1 | Enmakaje | 1.23 | 5.01 | BDL | 6.24 | BDL | BDL | BDL | BDL |
| 22 | ENM2 | Enmakaje | BDL | 5.23 | BDL | 5.23 | BDL | BDL | BDL | BDL |
| 33 | ENM3 | Enmakaje | BDL | 1.51 | BDL | 1.51 | BDL | BDL | BDL | BDL |
| 44 | KUM1 | Kumbadaje | 0.82 | 0.36 | BDL | 1.18 | BDL | BDL | BDL | BDL |
| 55 | MUL1 | Muliyar | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 66 | AJN 1 | Ajanoor | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |

*BDL* Below detection limit

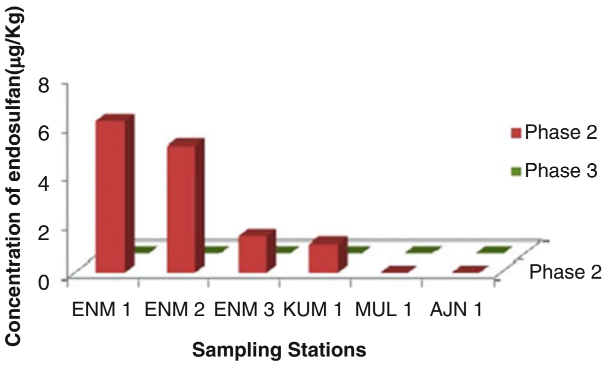


**Fig. 4.11** Endosulphan residues in six sediment samples during the second and third phase of sampling

**Table 4.13** Comparison of concentration of endosulphan residues in soil samples during the first, second, and third phase of sampling

| S. No. | Panchayat | Total endosulphan (μg/kg) | | | | Rate of degradation during second phase | Rate of degradation during third phase |
|---|---|---|---|---|---|---|---|
| | | Sample code | 1st phase | 2nd phase | 3rd phase | | |
| 1 | Pullur Periya | PER 1 | BDL | 1.37 | 1.91 | – | – |
| 2 | Pullur Periya | PER 4 | 16.91 | 1.93 | BDL | 88.59 | 100 |
| 3 | Kallar | KAL 5 | 1.64 | BDL | BDL | 100 | 100 |
| 4 | Panathadi | PAN 1 | 14.85 | 6.47 | 4.88 | 56.43 | 67.13 |
| 5 | Bellur | BEL2 (surface) | BDL | BDL | BDL | BDL | BDL |
| 6 | Bellur | BEL2 (depth) | 3.61 | BDL | BDL | 100 | 100 |
| 7 | Badiyaduka | BAD 3 | BDL | BDL | BDL | BDL | BDL |
| 8 | Badiyaduka | BAD 4 | 1.96 | BDL | BDL | 100 | 100 |

*BDL* Below detection limit

### Sampling and Analysis of Samples from Nanjanparamba, Karadukka Panchayat of Kasaragod District

Persistence of endosulphan was monitored from some sites identified at Nanjanparamba of Karadukka panchayat of Kasaragod district. A total number of four water and three sediment samples were brought to the laboratory (on 21 May 2013) for analysis of endosulphan residues. The results of analysis of water and sediment samples are shown in Tables 4.17 and 4.18, respectively. Endosulphan was not detected in the analysed water and sediment samples. The chromatogram obtained during the analysis of a sediment sample KAR 7 from Nanjanparamba is given in Fig. 4.16.

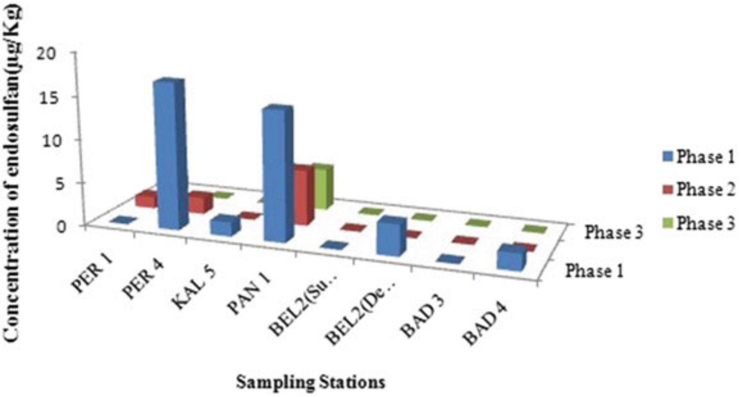


**Fig. 4.12** Comparison of endosulphan residues in soil samples during first, second, and third phase of sampling

The endosulphan case of Kasaragod district, Kerala, India, is considered by many experts in the field of community health and toxicology as one of the worst pesticide disasters. This extended tragedy occurred due to a constellation of reasons that included the recommendation of the use of the pesticide in a populated, water body-rich, and hilly area. Also, the application procedure was conducted by aerially spraying endosulphan over the cashew plantations, which was done for a period of 20 years by the Plantation Corporation of Kerala, without monitoring its collateral impacts.

A detailed study on the persistence of endosulphan was conducted in 2011 in Kasaragod district. Water, soil, and sediment samples were collected from different panchayats of Kasaragod district (KSCSTE 2011). Water samples did not report any pesticide residue.

As per the results obtained by the analysis of endosulphan in water, soil, and sediment samples collected from 11 Panchayats of Kasaragod district, it can be concluded that endosulphan persists only for a limited period. The degradation rates of both endosulphan isomers are greatly affected by environmental conditions. The study proved that combined toxic residues of endosulphan in the sediment and soil samples of selected areas of Kasaragod district are found to be persistent for a maximum period of 1.5–2 years from the beginning of this study. But the persistence showed variations depending upon the climatic conditions and physico-chemical characteristics like pH, organic matter content, and particle size of the soil in the area. The results also indicated greater persistence of endosulphan in soil and sediment samples than water samples because of greater adsorption of endosulphan in the sediment and soil than water. Comparatively high concentration of endosulphan detected in the soil is because of the fact that endosulphan is immobile in soil and is highly persistent.

**Table 4.14** Results of endosulphan analysis of five soil samples of Kasaragod district during second and third phase of sampling

| | | | 2nd phase | | | | 3rd phase | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sl. No. | Sample code | Panchayat | Endo-alpha (µg/kg) | Endo-beta (µg/kg) | Endosulphan Sulphate (µg/kg) | Total EEndosulphan (µg/kg) | Endo-alpha (µg/kg) | Endo-beta (µg/kg) | Endosulphan sulphate (µg/kg) | Total Endosulphan (µg/kg) |
| 1. | CHE 1 | Cheemeni | BDL | 1.70 | BDL | 1.70 | BDL | BDL | BDL | BDL |
| 2. | PER 3 | Pulloor Periya | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| 3. | PER 5 | Pulloor Periya | BDL | 1.47 | BDL | 1.47 | BDL | BDL | BDL | BDL |
| 4. | MUL 2 | Muliyar | BDL | BDL | BDL | BDL | 5.21 | BDL | BDL | 5.21 |
| 5. | BAD 1 | Badiyadukka | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |

*BDL* Below detection limit

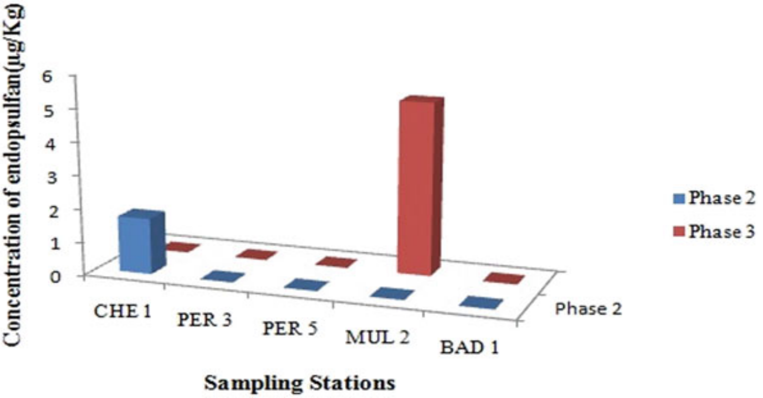


**Fig. 4.13** Endosulphan residues in five soil samples during the second and third phase of sampling

**Table 4.15** Results of endosulphan analysis of soil samples during the fourth phase of sampling

| | | | 4th phase | | | |
|---|---|---|---|---|---|---|
| Sl. No. | Sample code | Panchayat | Endo-alpha (µg/kg) | Endo-beta (µg/kg) | Endosulphan sulphate (µg/kg) | Total endosulphan (µg/kg) |
| 1 | PER 1 | Pulloor Periya | BDL | BDL | BDL | BDL |
| 2 | MUL 2 | Muliyar | 3.91 | BDL | BDL | 3.91 |
| 3 | PAN 1 | Panathadi | 4.12 | BDL | BDL | 4.12 |

*BDL* Below detection limit

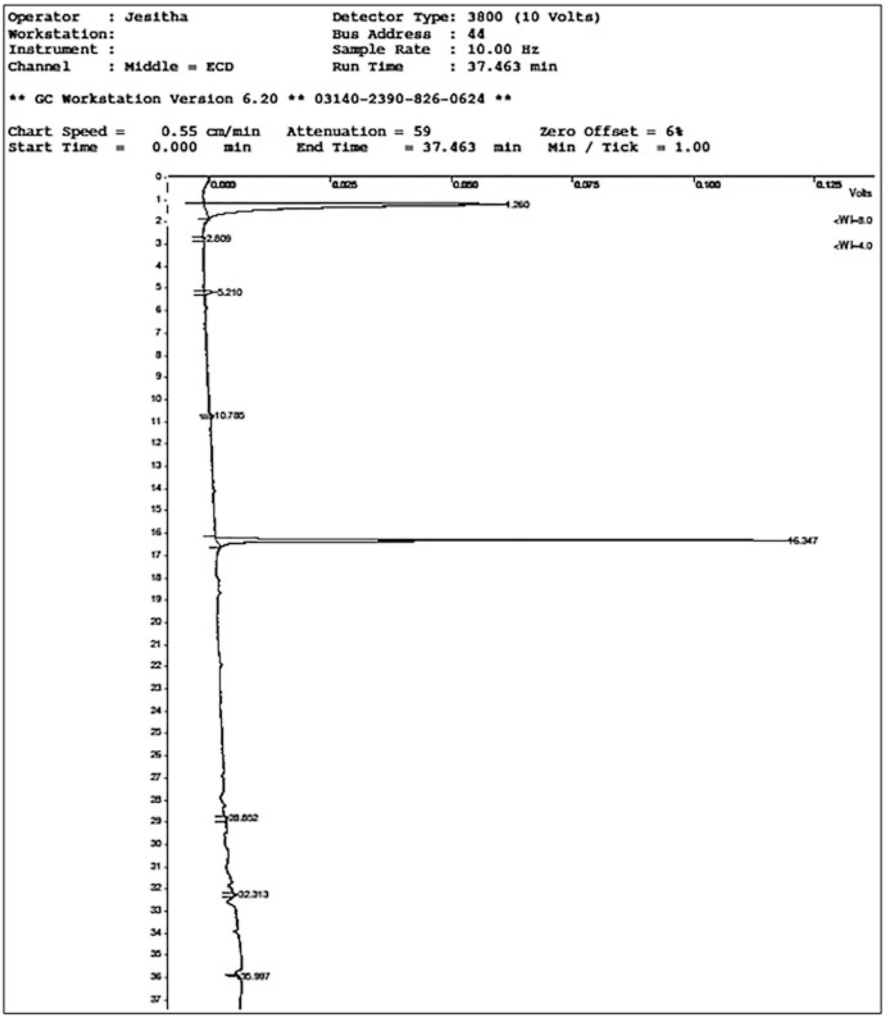
**Table 4.16** Results of endosulphan analysis of soil samples during the fifth phase of sampling

| | | | 5th phase | | | |
|---|---|---|---|---|---|---|
| Sl. No. | Sample code | Panchayat | Endo-alpha (µg/kg) | Endo-beta (µg/kg) | Endosulphan sulphate (µg/kg) | Total endosulphan (µg/kg) |
| 1 | MUL 2 | Muliyar | BDL | BDL | BDL | BDL |
| 2 | PAN 1 | Panathadi | BDL | BDL | BDL | BDL |

*BDL* Below detection limit

## 4.2.4 Monitoring of Pesticide Residues in Muthalamada Panchayat of Palakkad District

Water, sediment, and soil samples were collected from mango plantations of Muthalamada Panchayat of Palakkad district, Kerala, India for pesticide residue analysis. Details of sampling locations in Muthalamada Panchayat of Palakkad district are given in Table 4.19. Map of Muthalamada Panchayat of Palakkad district showing the sampling stations is given in Fig. 4.17.



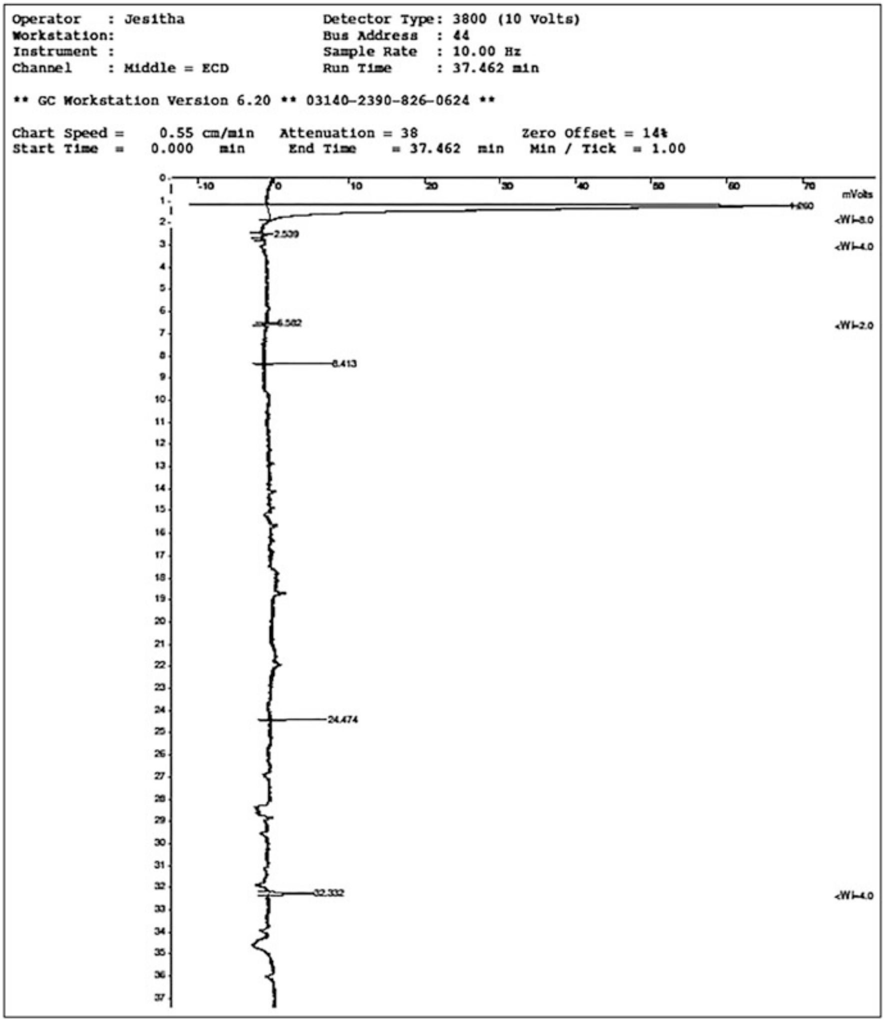
```
Operator    : Jesitha                  Detector Type: 3800 (10 Volts)
Workstation:                           Bus Address  : 44
Instrument :                           Sample Rate  : 10.00 Hz
Channel     : Middle = ECD             Run Time     : 37.463 min

** GC Workstation Version 6.20 ** 03140-2390-826-0624 **

Chart Speed =   0.55 cm/min   Attenuation = 59         Zero Offset = 6%
Start Time  =  0.000   min     End Time    = 37.463  min  Min / Tick  = 1.00
```

**Fig. 4.14** Chromatogram obtained for fifth phase analysis of sample from Muliyar Panchayat

Results of analysis of pesticide residues showed that lindane, aldrin, dieldrin, DDD, and DDE were not present in any of the samples. Endosulphan was detected only in one soil sample (EPKDS-8) collected from mango plantation area in Muthalamada panchayat. The concentration of endosulphan alpha detected in the sample was 0.18 μg/kg. The pesticide detected might be due to the earlier use of endosulphan in the mango plantations.



```
Operator    : Jesitha                  Detector Type: 3800 (10 Volts)
Workstation:                           Bus Address  : 44
Instrument :                           Sample Rate  : 10.00 Hz
Channel     : Middle = ECD             Run Time     : 37.462 min

** GC Workstation Version 6.20 ** 03140-2390-826-0624 **

Chart Speed =    0.55 cm/min   Attenuation = 38           Zero Offset = 14%
Start Time  =   0.000   min     End Time    = 37.462  min   Min / Tick  = 1.00
```

**Fig. 4.15** Chromatogram obtained for fifth phase analysis of sample from Panathadi Panchayat

## 4.3 Management Measures

### 4.3.1 Degradation of Pesticide Residues by Different Methods Based on the Study Conducted by CWRDM

Several experimental studies were conducted by CWRDM regarding the degradation and management of pesticide residues in water and soil. The remediation of organochlorine pesticides, particularly endosulphan, was studied by different chemical and

**Table 4.17** Concentration of endosulphan in water samples collected from Nanjanparamba, Kasaragod district

| Sl. No | Sample code | Coordinates | Sample type | Source of sample | Site description | Concentration of endosulphan (μg/L) |
|---|---|---|---|---|---|---|
| 1 | KAR 1 | N 12°35′98.6″ E 075°12′31.7″ | Water | Pond | Near temple | BDL |
| 2 | KAR 3 | N 12°34′56.7″ E 075°12′01.4″ | Water | Surangam | Near plantation area | BDL |
| 3 | KAR 5 | N 12°33′85.3″ E 075°11′28.2″ | Water | Well | Near anganwadi | BDL |
| 4 | KAR 6 | N 12°34′44.9″ E075°12′05.7″ | Water | Pond | Near plantation area | BDL |

*BDL* Below detection limit

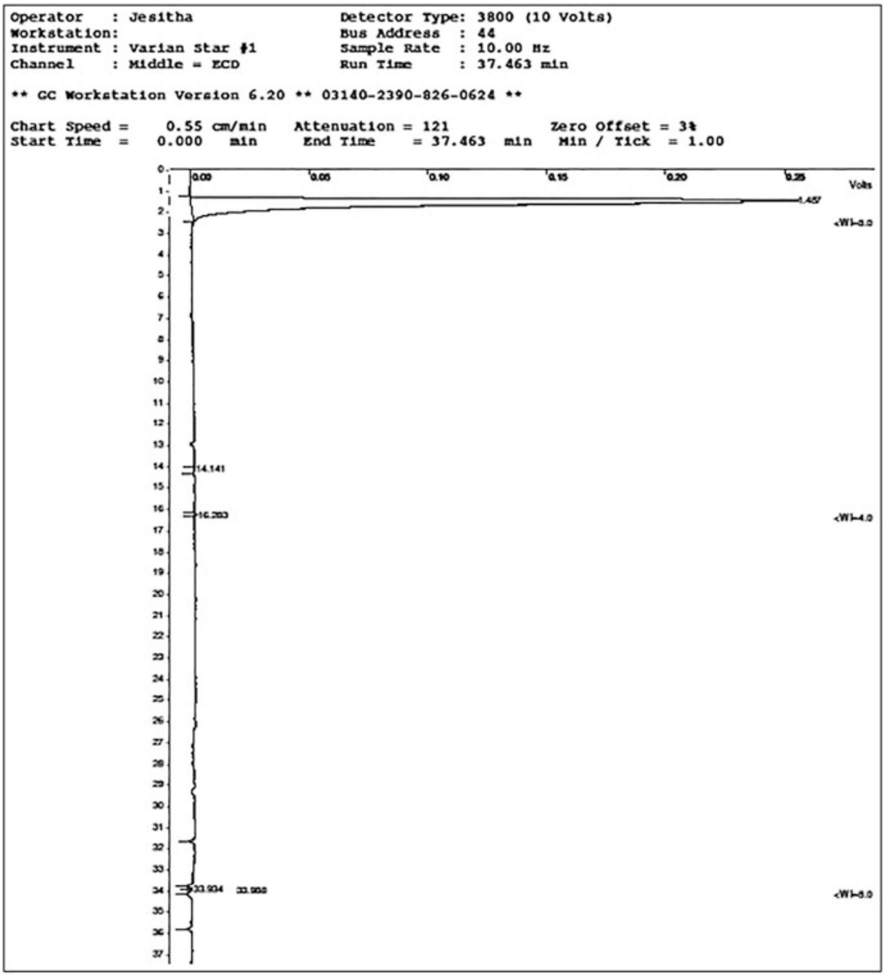
**Table 4.18** Concentration of endosulphan in sediment samples collected from Nanjanparamba, Kasaragod

| Sl. No | Sample code | Coordinates | Sample type | Source of sample | Site description | Concentration of endosulphan (μg/kg) |
|---|---|---|---|---|---|---|
| 1 | KAR 2 | N 12°35′98.6″ E075°12′31.7″ | Sediment | Pond | Near temple | BDL |
| 2 | KAR 4 | N 12°34′56.7″ E 075°12′01.4″ | Sediment | Surangam | Near plantation area | BDL |
| 3 | KAR 7 | N 12°34′44.9″ E075°12′05.7″ | Sediment | Pond | Near plantation area | BDL |

*BDL* Below detection limit

biological methods. Toxic isomers of endosulphan (endosulphan alpha and endosulphan beta) were effectively degraded by passing the test solution containing endosulphan through a photocatalytic reactor with $TiO_2$ photocatalyst-entrapped calcium alginate beads. Endosulphan from the soil was recovered by the application of Tween 80 before passing through the reactor. A concentration of 1 g/L Tween 80 released 83.89% ± 1.22% of endosulphan from the soil within 24 h. The photocatalytic degradation of endosulphan was more efficient when Fe-doped $TiO_2$ nanoparticles were used as photocatalyst. A pathway was suggested based on the study in which endosulphan was converted to endosulphan diol.

Phytoremediation uses plants to clean up contaminated environments. The potential of aquatic plant species, Giant salvinia (*Salvinia molesta*), and the terrestrial plant species, Spinach (*Spinacia oleracea*) and Tomato (*Solanum lycopersicum*), to remove endosulphan from contaminated water and soil, respectively, was studied.



```
Operator    : Jesitha                   Detector Type: 3800 (10 Volts)
Workstation:                            Bus Address  : 44
Instrument : Varian Star #1             Sample Rate  : 10.00 Hz
Channel     : Middle = ECD              Run Time     : 37.463 min

** GC Workstation Version 6.20 ** 03140-2390-826-0624 **

Chart Speed =    0.55 cm/min   Attenuation = 121          Zero Offset = 3%
Start Time  =   0.000   min     End Time    = 37.463  min   Min / Tick  = 1.00
```

**Fig. 4.16** Chromatogram obtained for sediment analysis of sample from Nanjanparamba Panchayat

Within 30 days of observation in the experimental plot, a percentage removal of 98% (with an initial concentration of 123 μg/L endosulphan) was observed with *Salvinia molesta* species. Thus, *Salvinia molesta* proved to be the best variety among the different plant species selected for the study. Among the selected terrestrial plant species, Spinach and Tomato, percentage removal of endosulphan was found to be higher with Tomato. On day 21, complete removal of pesticide (with an initial concentration of 140 μg/kg endosulphan) occurred in the soil in which phytoremediation was done with Tomato, while Spinach took about 28 days for complete removal of endosulphan. Isomers of endosulphan (endosulphan alpha and

**Table 4.19** Details of sampling locations in Muthalamada Panchayat of Palakkad

| Sl. No. | Sampling stations | Type of sample | Details of sampling site | Latitude-N | Longitude-E |
|---|---|---|---|---|---|
| 1 | EPKD-1 | Water | Near Chulliyar dam | 10°35′8.35″ | 76°45′51.64″ |
| 2 | EPKDSD-1 | Sediment | Near Chulliyar dam | 10°35′8.35″ | 76°45′51.64″ |
| 3 | EPKD-2 | Water | Vellaramkadavu-Well water | 10°34′27.57″ | 76°46′12.04″ |
| 4 | EPKDS -2 | Soil | Vellaramkadavu soil inside plantation area | 10°34′27.57″ | 76°46′12.04″ |
| 5 | EPKD-3 | Water | Vellaramkadavu<br>Opposite plantation area<br>Well water | 10°34′27.67″ | 76°46′9.78″ |
| 6 | EPKD-4 | Water | Near Vellaramkadavu | 10°34′26.88″ | 76°46′20.48″ |
| 7 | EPKDSD-5 | Sediment | Near Vellaramkadavu | 10°34′26.88″ | 76°46′20.48″ |
| 8 | EPKDS-5 | Sediment | Near Vellaramkadavu | 10°34′26.88″ | 76°46′20.48″ |
| 9 | EPKD-5 | Water | Vellaramkadavu stream | 10°34′34.16″ | 76°45′56.97″ |
| 10 | EPKD-6 | Water | Abandoned well near plantation | 10°34′45.41″ | 76°45′46.65″ |
| 11 | EPKDS-7 | Soil | Inside plantation | 10°35′2.66″ | 76°45′47.57″ |
| 12 | EPKDS-8 | Soil | Inside plantation | 10°35′25.60″ | 76°45′53.2″ |
| 13 | EPKDS-9 | Soil | Inside plantation | 10°35′25.81″ | 76°45′52.99″ |
| 14 | EPKDS-10 | Soil | Inside plantation | 10°35′38.55″ | 76°46′28.11″ |

endosulphan beta) and endosulphan sulphate were detected during the analysis of the samples. Phytoremediation is an attractive clean-up method. But the sites selected for phytoremediation should be properly protected with fences and other barriers to keep wildlife or domestic animals from feeding on contaminated plants. The experiments also showed the ability of some edible plant species to take up and concentrate the pollutants inside the plant biomass. The use of such plants has to be controlled, and after remediation, those plants should be destroyed properly (Harikumar et al. 2013).

Nano-phytoremediation, a combined technology, was employed to investigate the capability of combined effect of phytoremediation and nanoscale zero valent iron (nZVI) for the removal of endosulphan from contaminated soil. Chittaratha (*Alpinia calcarata*) was found to be very effective for the remediation of endosulphan and was transplanted to the pots containing soil artificially spiked with endosulphan and nZVI. The nano-phytoremediation method completely removed endosulphan (initial concentration: 1139.84 ± 0.93) from artificially spiked soil within 1 month. The results indicated that nano-phytoremediation was more effective than either nano-remediation or phytoremediation for degradation and removal of endosulphan. The advantage of the method was that only a small amount of endosulphan was hyperaccumulated in different parts of plant species since nanozerovalent iron particles promoted reductive dechlorination of endosulphan (Harikumar and Jesitha 2016).

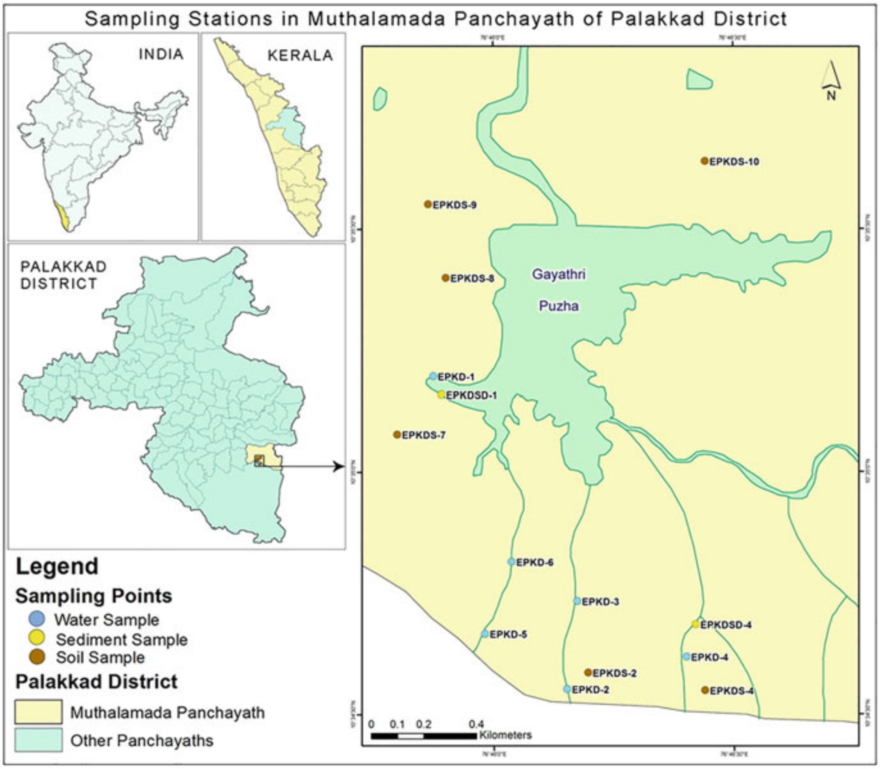


**Fig. 4.17** Map of Muthalamada Panchayat of Palakkad district showing the sampling stations

Bioremediation is emerging as an effective innovative technology for treatment of a wide variety of contaminants including pesticides. The degradation of organochlorine pesticides was studied using single bacterial cultures and mixed cultures which consisted of *Delftia tsuruhatensis and Bacillus thuringiensis.* The mixed bacterial culture was found more efficient to completely degrade the test solution of a mixture of organochlorine pesticides. Uninoculated test solution was maintained as control in order to compare the difference in degradation of mixed organochlorine pesticides. In soil experimental studies using mixed culture, the complete removal of pesticides (initial concentration: 120 ± 1.56 μg/L) happened within 2 weeks which proved that mixed culture can be utilized effectively for the degradation of organochlorine pesticides in contaminated soil.

Bioremediation of endosulphan was studied with two bacterial species, *Pseudomonas* and *bacillus,* isolated from the soil. *Pseudomonas fluorescens* was found effective for removal of endosulphan. *Pseudomonas* species degraded 98.02 ± 0.18% (initial concentration: 119.48 ± 0.53 μg/L) endosulphan after 14 days of incubation. *Bacillus* species could degrade only 50 ± 0.08% and uninoculated controls retained >50% of the substrate. The results of monitoring of endosulphan residues on the 16th day revealed that complete degradation of endosulphan had occurred on bioremediation using *Pseudomonas* species. Since the isolated *Pseudomonas fluorescens* proved effective for degradation of endosulphan, the study was further continued to find out the pathway for degradation and also to develop a basic design of a bioreactor for remediation of endosulphan (Jesitha et al. 2015).

### 4.3.2 Sediment/Erosion Control

Delivery of sediment from agricultural lands to receiving waters is to be minimized. The practices such as conservation tillage, strip cropping, contour farming, and terracing or a combination of these practices can help to remove sediment in runoff.

### 4.3.3 Confined Animal Facility

Animal waste contaminates many of our water bodies with pathogens and nutrients. These discharges from confined animal facilities to water should be avoided. This can be achieved by proper design and implementation of systems that collect solids, reduce contaminant concentrations, and reduce runoff management. Proper waste utilization and use of disposal methods can minimize the impact.

### 4.3.4 Management of Nutrients

Introduction of a nutrient budget for the crop, identification of the types and amounts of nutrients necessary for a crop, identification of the environmental hazards of the site, soil tests, and other tests to determine crop nutrient needs are some of the measures that can be introduced.

### 4.3.5 Management of Pesticides

Reduction of pesticide usage, improving the efficiency of application and spray equipment, and preventing backflow of pesticides into water supplies can reduce the entry and pollution into the nearby water bodies. Integrated pest management (IPM) strategies such as pest control measures, evaluating current pest problems considering the cropping history, and applying pesticides only when needed can be introduced.

### 4.3.6 Livestock Grazing

Livestock access to sensitive areas such as wetlands, estuaries, ponds, lake shores, etc. should be restricted. This restriction reduces the physical distance and direct loading of animal waste and sediment can be avoided

### 4.3.7 Effective Irrigation System

Effective irrigation system delivers necessary quantities of water and reduces non-point pollution to surface water and groundwater. The system requires an accurate measurement of crop water needs and the volume of irrigation water.

### 4.3.8 Control of Phosphorus from Point and Diffuse Sources

Phosphorus entry route into water bodies from land areas is as surface runoff and with erosion. Creation of artificial wetlands that collect water and remove nutrients through aquatic plants can be constructed for the control of phosphorus. Basins can also be constructed to collect runoff water and allow settling of suspended sediment rich in phosphorus.

## 4.4 Summary

Many of the pesticides are highly persistent in the environment and the complete environmental fate of such pesticides is still to be explored. Among the 20 samples analysed from different parts of Kerala, 11 were found to be contaminated with organochlorine pesticides. Aldrin, dieldrin, and endosulphan beta were detected in the samples. The concentration of aldrin and dieldrin in many samples was higher than the permissible limit as per BIS. But the concentration of other pesticides in the samples was relatively low. The low level of OCPs, although within the prescribed limit of national regulatory agency, may cause severe health disorders if there are chances of consumption or exposure for longer durations.

Water, soil, and sediment samples were collected from 11 selected panchayats of Kasaragod district in five different phases to assess the contamination by endosulphan applied on the cashew plantations. Endosulphan was detected only in two samples out of 22 water samples analysed during the second phase of sampling. Concentration of endosulphan was below detection limit in all the 22 samples analysed. During the third phase. A total of 14 sediment samples were analysed, and during the third phase, the concentration of endosulphan was below detection limit in all the samples. Out of 13 soil samples, endosulphan was detected in five samples during the second phase, and during the third phase, endosulphan was detected in three samples. Endosulphan was detected in two soil samples from Panathadi and Muliyar panchayats during the fourth phase. In addition, the comparison of results of analysis of endosulphan during third and fourth phase showed decrease in concentration in the three soil samples. The study conducted during the fifth phase in Panathadi and Muliyar panchayats has shown that endosulphan has been completely degraded. The findings from the study provide information on the residue levels and persistence of organochlorine pesticide endosulphan in water, sediment, and soil in selected areas of Kasaragod district in Kerala. The study indicated that combined residues of endosulphan in the sediment and soil samples of selected areas of Kasaragod district would be persistent for a period of 1.5–2 years from the beginning of the study. The persistence showed variations depending upon the climatic conditions and physico-chemical characteristics like pH, organic matter content, and particle size of the soil in the area. Based on the type of pollutant and extent of pollution, proper remediation or treatment techniques have to be adopted for protection of environment.

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# An Intergenerational Community-Based Approach to Safe Farming and Environmental Health

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## Abstract

Knowledge of and interest in organic farming have grown in recent years. Although the health and environmental benefits outweigh increased production that might occur with conventional farming, use of synthetic chemicals remains the most widely used method. A number of barriers prevent farmers from full conversion to organic methods. To overcome these barriers, an intergenerational, community-based approach is needed to fully implement organic farming. Such an approach addresses the farmer's full social ecology (i.e., farmer, community, children, trainers and monitors, greater society). Key to success is understanding and holding in reverence the knowledge of indigenous community members who can teach about the old, traditional ways and combine these with new knowledge.

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By working together in unity, the ecology can support farmers to be a part of the world's solution to advancing food security.

**Keywords**

Organic farming · Indigenous farming · Community-based farming · Social ecology

## 5.1 Introduction

Knowledge and science of organic farming practices are growing and methods are increasing in sophistication. Many low-income countries have an agrarian-based economy and could easily spread organic farming. Indeed, small rural farmers, rather than large-scale corporate farms, produce a good bit of the world's food and stand to make a strong positive impact on food security (Leakey 2020). Good Agricultural Practices (GAP) have been specified through individual country and global standards to guide safe farming (e.g., USDA 2020; Ghana Green Label 2021). However, despite these standards and the growth of scientific knowledge in organic farming, implementation is lagging behind among the small rural farmers who could have the greatest impact. Agrochemicals continue to have a foothold as a primary method of farming (Nishimoto 2019). In fact, the trends in the crop protection industry show a growth in agrochemical use since 2006. There was a downward trend in growth from 2014 to 2016 followed by recovery and growth (Nishimoto 2019). In a sense, the lack of uptake of organic farming is not surprising. Even with the most rigorous research establishing effectiveness of an innovation, studies indicate that it takes 17–20 years to get innovation to practice. Less than 50% of innovations ever make it out into the world for general use (Balas and Boren 2000; Bauer and Kirchner 2020; Grant et al. 2003; Morris et al. 2011). At a practical level, even when farmers have knowledge of organic methods, there are barriers to engaging in such practice.

At the present time, there is a dearth of research on implementation of organic farming in the real world of practice—rural communities around the world. Understanding barriers to organic practice implementation and how to overcome these barriers among rural farmers in low resource areas is critical to shifting the world to healthy food production. This chapter addresses the issue of implementation. First, we consider barriers rural farmers in low-income countries face that reduce or prevent implementation of organic methods. Next, we consider the importance of the indigenous culture to environmental health. Third, we advocate strongly for an intergenerational, community-based approach to implementation that involves the farmers themselves, the community, the children, trainers and monitors, and greater society (Swenson et al. 2018). Last, we discuss what is needed way forward to help farmers and communities implement and sustain organic farming as a way of life. Our focus is primarily on small rural farms in low resource areas.

## 5.2 Barriers to Implementation of Organic Farming

In rural areas of low-income countries, traditionally, farming has been approached with natural methods. Knowledge was passed down in families and seeds from previous harvests were used and shared. Over time, farming practices changed to agrochemical use primarily to increase food production (Zhang et al. 2017). Agrochemical use has benefited farmers in that it has increased food production (Carvalho 2006; Majeed 2018). However, the costs have been vast. The degradation of soil and biodiversity loss have contributed to low safety in foods and climate change (Zhang et al. 2017). In turn, changes in climate and weather have resulted in lower food production and higher food prices (Ndukwe et al. 2017). Food security is uncertain, especially for people who are vulnerable due to low incomes.

Agrochemicals are also being shown to have the additional cost of serious health conditions (Magauzi et al. 2011). Economically disadvantaged farmers, in particular, are at high risk of contamination from agrochemicals as they may not be able to afford personal protective equipment to reduce direct exposure. Agrochemicals enter the blood stream through the mouth, nose, skin, and eyes. Exposure has been associated with severe health problems such as reproductive and developmental disorders and cancer. In addition, central nervous system effects may be experienced as restlessness, loss of memory, or convulsions. Respiratory paralysis occurs in some cases and can turn to be fatal (Magauzi et al. 2011).

An understanding of the risks to the land and the health risks to themselves and their families from agrochemicals is fueling farmers' interest in a transition to natural, organic farming. The barriers to converting to organic methods deserve a closer look as low-income nations are at high risk of food insecurity (FAO 2015), yet stand a great chance of being a solution to world food insecurity. These barriers may be found in the areas of community norms and support, knowledge/training, level of effort and resources, farmer beliefs and attitudes, marketability, and involvement in misguided schemes.

Community norms and support are essential to farmer's uptake of organic methods (Niemeyer and Lombard 2003). When the community is comprised of organic and conventional farmers, there may be drift of agrochemicals to organic farms and drift of ideas. Conventional farmers may view high yields as only possible through agrochemicals and perceive that organic farming does not really benefit the environment. Instead, they may view organic farming as being sold dishonestly through media hype (Darnhofer et al. 2005). These perceptions can spread to organic farmers. A negative assessment of organic methods by credible peers has been shown to prevent farmers from converting to organics (Xu et al. 2018). Instead, support and encouragement from the local community and politicians contribute to farmers' motivation to farm organically (Koesling et al. 2012). Moreover, when organic farming becomes the norm in a community, farmers have a higher degree of satisfaction (Xu et al. 2018).

Organic farming requires a high degree of competence and skill. Many farmers who may wish to covert to organics will have varying degrees of knowledge of the methods. There are important core skills needed to be successful and not lose crops and money. The research and knowledge are available to teach farmers and there are many effective training programs around the world (Dubey and Srivastava 2016; Swenson et al. 2021; Tiraieyari et al. 2017) and manuals available (e.g., Weidmann and Kilcher 2011). Many training programs are based on "train and hope." That is, there is an underlying assumption that when people are trained in a method, they will implement it. There may also be an underlying assumption that publication equals implementation or that people who read about organic farming can and will implement the methods. Yet, despite the knowledge of risk and availability of training, it is exceedingly difficult for farmers in low-income countries to move away from agrochemicals (Carvalho 2006; Majeed 2018). More than training is needed.

Level of effort and available resources are important to whether organic farming is implemented or not. Organic farming may take more time and work than agrochemical farming, especially when farmers do not have machines. It takes longer to prepare land for weeding. Farmers may see more value in less time on the farm. In addition, and especially in low-income countries, farmers may not have the resources to put knowledge into practice (Swenson et al. 2021). Without equipment and supplies, many farmers cannot take the first step to fully convert to organic farming.

Farmers' attitudes and beliefs may be a barrier to implementation. Some may have a stronger day-to-day survival focus that prevents them from having nature in mind. Perhaps the survival focus is due to barely making it in life. Some may also have little confidence in their ability to meet new farming standards. Other farmers may feel fully satisfied with conventional farming and thus have difficulty with a desire for change or understanding a reason to change (Xu et al. 2018). A short-term, survival focus prevents farmers from considering the long-term implications of land degradation and chemical exposure to health. As such, a short-term survival focus may actually threaten survival.

Marketability can make or break a farmer's success. If organic produce costs more for the consumer, the farmer may not have a ready market to sell their goods. Local markets may be more supportive of chemically grown produce because buyers don't understand health risks and have a limited supply of money to spend. When the norms of a community are agrochemical farming, buyers may not choose organic over agrochemically grown produce because they are cheaper. In some areas, agrochemicals may be cheap because they have not been FDA-approved. People may be accustomed to using some medications that are not FDA-approved and so the lack of approval on chemical inputs does not feel essential.

In our own work, we have seen situations where farmers who cannot read or write become involved in misguided schemes in which they are taken advantage of. For example, a group may come into rural areas and offer farmers a "great deal" where the farmer buys chemically laden seeds and agrochemicals from the group. The great deal part of this is that when vegetables are ready for harvest, the group buys the vegetables from the farmers with the expressed intent of making the farmer an "international exporter." The farmer does not know what the chemical is and cannot read the can or bottle because it is in a language they do not know or because "they don't know book," they are unable to read. So, they have no idea of the risk, but are proud to be an international exporter. The purchasing of the crops happens for a couple of harvests and then the group tells the farmer they cannot buy the crops because they have not grown them properly. The farmer has spent all they have on seeds and chemicals and now they cannot get any money back through sales. These types of schemes are far too common and take advantage of hard-working farmers who want to find a way out of poverty. In effect, they sink the farmer deeper into poverty and hopelessness. Sometimes the barriers seem insurmountable, but with comprehensive interventions, they can be overcome.

## 5.3 Overcoming Implementation Barriers

As noted earlier, the barriers to organic farming implementation are multiple and across several systems (farmer, community, peers, markets, greater society). As such, the strategies to overcome the barriers must address all the systems. Each of these systems comes under the umbrella of local culture. Understanding the relationship of indigenous culture to environmental health is a critical step in implementation and overall sustainability. Indigenous culture underlies all work that is done in a community and influences every intervention to facilitate implementation. These cultures have been in place and in practice for generations and have many lessons to offer. As much as 80% of the world's biodiversity is protected by a mere 5% of the human population of indigenous people (Garnett et al. 2018). The positive environmental impact of these cultures is felt worldwide. Indigenous people can be found in each of the primary biomes across the planet, particularly in areas with the most intact ecosystems. Many indigenous cultures practice oral traditions rather than using written records, yet the cultural conservation is pervasive, preserving their native lands through generations globally. Indigenous cultures call us to keep in mind the old traditional ways that are important to sustainability and implementation in organic farming. They represent groups with extensive history and practice with organic farming in every major environment in the world. The research and implementation are already in practice. Each generation is brought up learning these practices and working within the ecosystem they inhabit, valuing and protecting it from childhood forward (Garnett et al. 2018). The major gaps in knowledge and practice in modern organic farming can be filled through methods developed by indigenous people and their understanding of the local ecosystems.

## 5.4 An Intergenerational Community-Based Approach to Implementation of Organic Farming

An intergenerational approach involves recognizing, respecting, training, and attaining buy-in from all members of the ecology that surrounds the farmer. In this approach, we apply Bronfenbrenner's (1979) theory of social ecology to farming. Figure 5.1 demonstrates this ecology as what we will call various systems. The influence is not one way. Each of the systems influences the other. In the center is the

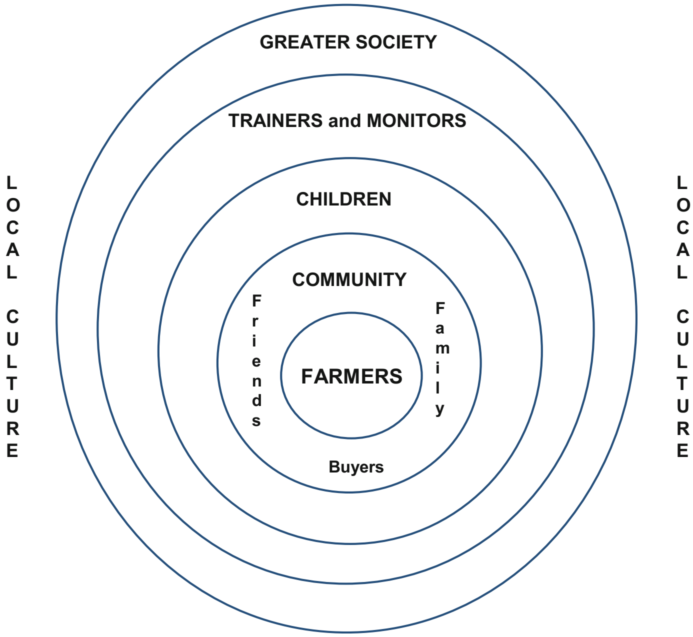

**Fig. 5.1** The social ecology of farmers

farmer who will carry out the bulk of the organic farming work. The circles surrounding the farmer are arranged according to the greatest level of influence on the farmer. The first system surrounding the farmer and that has the greatest level of influence is the community, which sets and follows the norms for how farming is carried out and supported. By shifting to organic methods, the farmers also bring their influence onto the community. The community includes the farmer’s friends, family, and buyers. As noted earlier, credible peers and supports influence whether farmers uptake organic methods and sustain this type of farming (Xu et al. 2018). The buyers may be from the community or beyond. Their view of organic foods is central to whether they purchase organic and support the farmers, but they could not change their buying practices without the availability of organic foods. The next circle of influence is the children. They will grow up as the next generation carrying on their family and community traditions. As we will explain later, children can have a strong influence on the adults in a community, but community members and farmers also influence children. Whether these children practice sustainable agriculture depends on the information and family role models they grow up with. The third circle of influence is comprised of trainers and monitors. This role is very important to educating and conveying knowledge and helping farmers maintain the integrity of organic methods. However, trainers and monitors spend less time with farmers than does the community. The outer circle of influence is the greater society system that may be comprised of local political leaders (in some communities Chiefs as traditional rulers) and government. They have a role to play in supporting the work of farmers in the community and farmers can influence their views. Overlying all systems and deserving great respect is the local culture. The indigenous culture flavors every system as the work gets carried out in local ways. Next, we discuss ways to intervene with each of the systems.

## 5.5 Farmers

To convert to and sustain organic farming methods, multiple needs must be met for farmers, including training, supplies, equipment, and ongoing monitoring and support (Swenson et al. 2021). From a position of cultural respect, before training is started, farmers should be interviewed to understand their existing knowledge of organic methods, understanding of benefits, attitudes towards change in their existing practice, and what they want to make sure they learn. Importantly, the trainer should assess the farmer's understanding of the impact of agrochemicals on health and especially when no PPE is used. Finally, farmers should be invited to reflect on how their grannies farmed and what traditional methods they learned from family that they practice now or would like to use. This pre-assessment can allow the trainer to make sure that farmers are offered the latest information on organic methods with emphasis on what farmers feel they need to learn most, along with their family history and values for the environment. If the trainer does not speak the local language or does but is not from the area, it will be important to have a local co-trainer if feasible or at least a local bilingual, interpreter. Also, training should include a didactic component, but demonstration and hands-on practice will be extremely valuable.

Training should introduce farmers to Good Agricultural Practices (GAP) in their country and Global GAP, a set of principles that evolved from concerns of a wide range of stakeholders (e.g., government, food producers, NGOs) about food production, safety, quality, and environmental sustainability. GAP principles guide food production, processing, transport, and protection of the health of workers and the environment (Burrell 2011; Hobbs 2003). Farmers must follow the GAP infrastructure to respect the standard of healthy growing.

Among farmers that participated in our Nkabom Organic Farming Project in rural Ghana, 92.9% successfully converted from agrochemical to organic farming (Swenson et al. 2021). Our training approach focused on core organic methods and transformative agriculture that included a combination of traditional farming practices and safe agricultural advances. The goal of training was for farmers to use methods that were free of synthetic chemicals and that focused on prevention. When a crop pest reached its threshold, or the crop was at risk of not being viable, botanical chemicals such as neem oil could be used. As a last resort and if nothing else was working, synthetic chemicals could be used in a controlled amount and only through safe practices such as wearing personal protective equipment (PPE). The next phase of this project moved to solely organic methods and the farmers stopped all use of synthetic chemicals. This is our current standard.

Farmers should be respected and viewed as small business owners. As such, it is critical to make sure they follow business practices such as record keeping. If farmers have not had the opportunity for education, they may have challenges with record keeping. Farmers can be shown that, without record keeping, they have no true idea of how much money they are making. They should record expenses and sales, but also it will be important to record insects they have dealt with and diseases their crops have experienced and how they managed them.

Several specific topics will give farmers core competencies. First is seed and planting stock practices. Many farmers will purchase seeds from suppliers due to low availability of organic seeds. They may also receive seeds from family members or save them from their own previous crops. It is essential to teach proper storage methods for seeds (Bishaw et al. 2012) and especially those techniques that will allow farmers to select the most disease-resistant plants. Rather than saving seeds from plants left in the field, they can begin to save seeds from selected plants.

The second topic is integrated pest, weed, and disease management. This is a critical knowledge area as farmers may be currently using some level of agrochemical means to manage pests, weeds, and diseases and these will need to be replaced. Farmers will learn about biological (e.g., natural pesticides and herbicides, companion planting), mechanical (e.g., tillage, hoeing), physical (e.g., burning), and cultural (e.g., crop rotation) methods to improve the health of the soil. It should be noted that in some parts of the world, the availability of organic products is limited. This is an issue that must be considered and a solution found.

The third topic is harvest and postharvest practices. Farmers may not think about the importance of sanitation practices such as hand washing before work on the farm or harvesting in addition to hand washing when work is done. Additionally, it is important for them to wash produce before sale and to wear gloves during harvest.

The fourth topic is soil fertility practices. Farmers may not be accustomed to using organic inputs such as chicken or cow manure, green manure, black soil, composting, and crop burning. In addition, they may not use crop rotation consistently or at all. These practices can be taught didactically and shown through practice.

The fifth topic is safe practice. Even when using botanicals such as neem oil, farmers should use PPE such as gloves, face masks, goggles, long sleeves, and boots. PPE may not be used due to inability to afford some product, or the product may not be available.

As noted earlier, hands-on experience through demonstration as part of training will help farmers see the methods taught in practice. To provide experiential training, it may be necessary to demonstrate techniques on farms of some of the trainees. In the Nkabom Organic Farming Project, we took the time to develop a half-acre demonstration garden 1 year before the farmers were trained in organic methods. The garden then provided a site for experiential instruction and for farmers to follow up training (Swenson et al. 2021).

In low-income countries, farmers may not use organic products because they are not readily available or they cannot afford them. As part of basic training on organic farming, providing a package to farmers that includes PPE and botanicals such as neem oil and a sprayer can get farmers started on converting to organics right away. Other important resources are finding no-cost or low-cost opportunities for farmers to engage in ongoing training, product availability, and consultation/monitoring to prevent drift from proper practice.

As farmers move forward on community-wide use of organic methods and away from agrochemicals, another option to consider is taking farmland not being used for organic farming and making it the site of rehabilitation. Methods such as conservation agriculture/agroforests have shown promising results for food production (Shepard 2013). Perennial farms can be grown and maintained in a manner that mimics the native permaculture, using native plants and the results will benefit the local community as a whole. Examples can be found in Africa, where tropical food forests are helping locals maximize yields, produce foods that are more nutrient-dense, and have a proven record of success in the environment (Leakey 2020). This practice reduces or eliminates the use of agrochemicals and even stimulates the local economy by creating small industries and local businesses to process the foods, which also adds value. Growing food in this way helps bridge the gap in food insecurity. The dependence on monocrops is reduced and the food yields can be increased up to 300–600% in just one agroforest as compared to a monocrop in the same space. (Leakey 2020) Growing food in this method also helps restore the local soil nutrient parameters.

## 5.6 Community

As noted earlier, training farmers to implement organic methods will meet with challenges to success if the community does not see value in organic methods and if they continue to view agrochemical as the norm. As such, training and intervention must be extended to the community. The start of a community campaign to support organic farming might begin with interviews with a sample of residents to assess community knowledge and attitudes towards organic farming. Training can be offered through gardening classes, community meetings, and small discussion groups. Community not only includes residents of the community and family of the farmers, but also potential buyers. If farmers try to sell in local markets but buyers do not support the sales, farmers will either have to seek out other markets or go to lower cost production methods. Potential buyers may not be aware of the health and environmental risks of agrochemically grown products. If they get sick from what they eat, they will surely experience costs for medical care if they can afford it. Learning the risk may move them towards growing organically in their own gardens and purchasing organically grown produce (Niemeyer and Lombard 2003). The community should be challenged to support health, soil fertility, and environmental cleanliness.

## 5.7 Children

Teaching children organic gardening and related academics is an essential component of an intergenerational community approach. It has been our experience that in communities where parents were unable to receive an education, but their children and grandchildren are being educated, there is a tendency to respect the educated child's point of view. For example, in our work in Ghana (Swenson et al. 2018), a safe water system was developed by drilling to find water and pumping it to the marketplace where taps were installed. The water was treated. Many adult residents felt unsure about the water because it tasted different from river water. The children being taught about clean and safe water and its importance to health allowed them to facilitate their parent's use of the treated "pipe" water. The same strategy is being used in our village Montessori school where children as young as age three are being taught the importance of organic gardening to health and food security directly in the garden setting. Educating young children in holistic organic gardening promotes a higher capacity to educate older generations in the community (Ramirez and Ketron 2021). Research on school gardens has shown that children involved their parents who then became more involved with the school (Thorp and Townsend 2001).

In addition to sharing lessons learned about organic farming with their parents and family, when organic gardening is taught in the schools, the learning is at a deeper level than what farmers may be taught. A holistic outdoor education will combine science, language, culture, math (measurements), and art. When children grow food organically and work in the garden regularly, they learn that connections exist between the environment, food, community, their body, and health.

Studies on organic gardening with school children indicate a benefit across the age range. School gardening has been shown to increase science scores and positive school behavior (Blair 2009). Additional benefits are increased analytical and problem solving skills, critical thinking, and integration of math, science, language arts, and social sciences (Bartosh et al. 2006). Research indicates that elementary children who are exposed to a school garden show more positive attitudes about environmental issues, increased interest in eating healthy, and increased interpersonal skills (Miller 2007). Even at the preschool level, through experiences in the garden, children show improvements in academic skills (math, science, and language concepts) and environmental awareness. Garden work helps young children understand their role in care of the environment (Miller 2007).

Organic gardening training as a child can impact a person across the lifespan. Adults who had positive experiences with nature in childhood were more likely to be environmentally sensitive, concerned, and active (Chawla 1998). In addition, children's involvement with plants may affect attitudes and behavior in adulthood (Blair et al. 1991). Active gardening as a child is a predictor of whether an adult views trees as having value (Lohr and Person-Mims 2005).

Due to the benefit, in the United States, school gardening has been established as a national movement that has been in development over 20 years (Blair 2009). Curricula have been developed by state departments of education, universities, nonprofits, and privately. Children's guides have been written to offer garden-related activities that can be done at home (e.g., Spohn 2007) and books are available that show activities that link gardening to math, science, literacy and art. Organic gardening can also be a way to teach children diverse culture. For example, in a book on Native American gardening, Caduto and Bruchac (1996) illustrate traditional ways of gardening through stories and cultural teachings. Earth Heart Growers in Charleston, South Carolina, connects children in hands-on organic gardening at Fields Farm on a barrier island. The Fields family are Gullah Geechee farmers with roots reaching back to West Africa. Children in the area who also have West African roots learn about their heritage of farming.

Recently, and especially important during the COVID-19 pandemic when outdoor education was more possible than indoor education, Earth Heart Growers joined with the Medical University of South Carolina to train teachers in organic gardening education. Prior to COVID 19, Earth Heart Growers traveled to Ghana and worked in our Montessori school to teach the same to teachers there. Their local curriculum in Charleston was designed to be in sync with South Carolina education standards and Good Agricultural Practices (Ramirez and Ketron 2021). Instruction meets the developmental level of children.

In the Flower Empower and Healthy Beans curriculum (Ramirez and Ketron 2021), children from pre-kindergarten through eighth grade are first taught basic gardening such as planting and the need plants have for water, sun, and nutrients. Garden tools are presented, and the names and functions are learned. Children learn when to weed and ways to manage pests and diseases organically. Teachers will develop actual gardens with the children for experiential learning. In keeping with education curriculum standards, lessons cover seed saving, parts of plants and flowers, garden shapes and colors, the water cycle, the cycles of life, the human skeleton and digestive system, the muscular system, the circulatory system, parts of a tree, the solar system, phases of the moon, recycling, garden helpers (insects and pollinators), life cycles and parts of insects, composting, earthworms in the garden, renewable and nonrenewable energy, layers of the earth, and cooking. Finally, children are taught record keeping with regard to the name of the plant they planted and how many seeds were planted. The individual that is teaching the children must be trained in education and organic gardening or the course could be offered by a teacher/farmer team. The reader will note that many of the topics in the children's curriculum are consistent with those offered to farmers in basic training in organic methods.

The value of the presence of an organic garden in schools or in the community cannot be understated. Children need direct, hands-on access to organic gardening. When children put their hands in soil, the micro particles and living organisms help improve health and invigorate the immune system (Hirt 2020).

In low resource communities where efforts are being made to widely convert to organic methods, having farmers come to the school to deliver a guest presentation will provide an opportunity for farmers to be role models for children in sustainable agriculture and will also sharpen the farmer's confidence in their work. In rural communities, many children go to the farm with their parents and doing so offers an opportunity to learn and to view organic farming as a way of life, the norm.

## 5.8 Trainers and Monitors

Above, we have noted important topics that provide farmers with the skills and competence they need to practice organically. After providing a core education on organic methods and assuring that farmers have needed supplies, trainers and monitors can still play a role. Their role becomes teaching additional skills didactically and in situ (the farm, garden) and reinforcement of skills taught through monitoring the work to help make sure farmers do not "drift" to environmentally unfriendly or unhealthy practices.

As farmers embrace GAP and standards required in their country to be able to expand their markets, they must have a business and production plan. Trainers and monitors can help farmers organize their record keeping and develop a biodiversity and conservation management plan. Farmers must determine how to prevent erosion and environmental destruction and protect crops from naturally occurring animals, birds, insects, and worms. They must plan how they will irrigate crops and assess the quality of the water. A waste management plan will be needed to determine: (1) how to use organic waste to aid in soil fertility; (2) how to dispose of plastic waste; (3) how to deal with waste water; and, (4) how to manage nonrecyclable waste such as metal containers. Trainers and monitors can assist farmers with making record keeping a habit. They will need to record crops planted and dates, pests and diseases observed, and how they were managed. As some pests are present certain times of the year, it will be important to record date/time of year and weather. Finally, harvesting records should be kept that include date of harvest, weight, and amount of produce. In addition to recordkeeping, as part of their production plan, farmers will need to keep track of all expenses (e.g., seeds, supplies, tools, transportation) and all sales. Monitors can assist farmers with determining net profit and how to plan to increase profits.

## 5.9 Greater Society

Greater society, including government, has a role to play in the areas of policy and implementation. Many governments throughout the world set policy for organic farming and develop schemes to provide strong standards that help lead to healthy food production and environmental protection. Importantly, regulations on the use of agrochemicals are needed. In low-income countries, farmers will need assistance in attaining resources to meet the healthy food production standards. Assistance may be in the form of subsidies to help farmers get their organic production off the ground. In addition, government can be instrumental in creating a market for organic produce through advertising and public education on the benefits. Government-funded research and development activities are also an important form of assistance. When a population is using few agrochemicals (and only as a last resort) and eating healthier, the government should see a reduction in expenditures for medical services. An example of significant government support is in the country of Denmark, the first country to enact a specific law on organic farming in 1987

(Daugbjerg and Svendsen 2011). This law on organic farming sets up a state certification and labelling system for organic farming and supported marketing and distribution. Costs were covered by the state rather than by farmers. For the first 3 years, Denmark introduced farm subsidies to help farmers convert. In 1994, permanent subsidies for organic farming were introduced. To be eligible, farmers agreed to farm organically for 5 years. In 2004, the permanent organic subsidies were abolished, and farmers were then paid an environmental subsidy in which organic farming was given first priority. In addition, the government provided organic extension services and state-funded research into organic farming. In 1995, the government introduced a pesticide tax that was then doubled in 1998. The revenue from the pesticide tax was used to fund subsidies for organic farming. The government of Denmark is an example of not only supporting organic farming, but also using creative funding to assure that organic farming could be successful and sustainable. Daugbjerg and Svendsen (2011) studied the success of organic produce in the market versus wind energy. Both had significant government support. Even with the level of government support noted above, organic food consumption lagged somewhat behind. The Danish government made significant efforts to increase wind energy demand and it has shown greater growth. The difference between the two government schemes is that, for wind energy, the government focused on increasing demand, whereas for organic farming the focus was on increasing production. The outcomes of the difference in government schemes in Denmark have provided a lesson learned for governments elsewhere that are seeking to support organic farming.

## 5.10 Way Forward

Successful implementation of organic farming goes far beyond giving farmers the skills needed to change practice from agrochemical. Intervention at a community-wide, intergenerational level is needed. In this chapter, several lessons have emerged regarding important factors in each of the key systems to facilitate implementation and sustainability. Each system (farmer, community, children, trainers and monitors, greater society) must be fully addressed:

- Before attempting organic farming conversion in a community, the desires of the community must be clear. The farmers should desire conversion to organics and there should not be staunch community opposition. If there is opposition, sorting this is the first line of intervention. Work should be conducted to understand the reason for opposition and how to shift it.
- Before an organic farming program begins, all trainers and monitors must develop an understanding of the local culture and the local ways. And the culture should be respected and revered in every step of the program.
- Trainers and monitors should take the time to develop a relationship with the community for purposes of trust.

- Farmers should have an opportunity to express what they know about organic farming and where they believe their gaps in knowledge lie and those gaps in knowledge should be addressed to satisfaction.
- Training should teach good agricultural practices (GAP) for the specific country and globally.
- Training should cover core competencies of seed and planting stock practices, integrated pest, weed, and disease management, harvest and postharvest practices, soil fertility practices, and safe practices such as use of PPE.
- As part of training, farmers should be equipped with a starter kit including at least organic seeds, PPE, and botanicals.
- Farmers must participate in ongoing technical training and monitoring.
- Farmers should be guided to approach their farming as a business rather than from a subsistence point of view. As such, a business plan should be created that includes how they will keep records related to crop production, earnings, and expenses. When farmers have not had the opportunity for education and cannot read and write, provisions should be made to give assistance in understanding record keeping and in recording.
- Farmer training should include didactics presented in ways that make the content clear to nonreaders. Training should also include an in situ portion where demonstrations are conducted on a trainee's farm or in a community garden.
- Post-training, farmers would benefit from the presence of a consultant or learning coach to advise them until organic farming comes natural to them. After that, quality assurance checks will help prevent drift to agrochemicals.
- Farmers should be educated on how to avoid misguided schemes that take advantage of them, exploit their desire for success, such as "international trade," and lead them on a path to unknown agrochemicals.
- Community and peer buy-in are critical to farmers implementing and sustaining organic methods. As such, significant work should be conducted to rally support, provide a strong information base on methods and benefits, and support community organic gardening on an ongoing basis.
- Communities and farmers should be reminded of "the old ways," of how their grannies worked on the farm without agrochemicals. They may have an interest in returning to natural ways their families originally farmed.
- Community information sessions will be a form of marketing, but farmers and community would benefit from additional assistance on marketing. Even buyers outside the community will need to be educated as to the short-term and long-term benefits of eating organic produce.
- Educating children in organic gardening is an essential component of an intergenerational approach as they convey what they learn to their parents and get their parents involved in their education.
- Education in organic gardening and providing a garden for experiential learning has been shown to improve cognitive, academic, and social skills in children across the developmental lifespan.
- Children who experience organic gardening are more likely to be adults who are concerned about the environment and active in environmental activities.

- An organic gardening curriculum for children should include many of the same skills taught to farmers with the addition of academics such as garden shapes and colors, the water cycle, cycles of life, the human skeleton, the muscular system, circulatory system, solar system, phases of the moon and life cycles, and parts of insects.
- Children should be taught to keep records of their work early on so that they can continue this practice as adults.
- School gardening should be a way to appreciate diversity and cultural learning.
- Government can play a significant role in providing guidelines and standards that help farmers stay true to organic methods.
- Government schemes that offer financial support to farmers, especially during start-up, can help facilitate success. However, it must be noted that government support should focus on increasing demand rather than just production.

## 5.11 Conclusion

In this chapter we have presented information from the scientific literature and our own work to offer an ecological and intergenerational conceptualization of organic farming implementation, especially in low resource, rural areas. Our experience is that training of farmers in key areas of competency is important, but is not enough for implementation and sustainability to occur. The decision to convert to organics is important as well but the support of peers, community, and even small children is essential for farmers to maintain the hard work of organic farming. Farmers and their community should be educated well on the short-term and long-term benefits of organic farming to their health and the land. They can be proud of their contributions to the environmental health of their community and the health of their neighbors and family. This pride and appreciation for their contribution can be a motivating factor in continuing to farm organically. Children can play a role in helping the community view organic methods as beneficial and even necessary. Their own experience in a school garden can impact them positively in academics and social skills and encourage their parents to get involved. Trainers, monitors, consultants, or coaches should be available to help farmers set up and follow a business plan and for long-term quality assurance. If government commits to organic farming in their country, they must follow the spoken commitment with financial assistance to farmers and significant work to market and help in developing demand so that farmers can sell their produce. The benefit back to the government may be seen in environmental protection and medical care savings. Finally, it takes everyone working together in unity to implement organic farming in practice and sustain it. The combined efforts will improve health of the environment and people, climate issues, and ultimately, food security.

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# Part II

# Pesticides/Insecticides/Herbicides in the Soil Environment

# 6

# Guidance on Pesticides Handling in Farming

Tandra Mondal and Pranab Kumar Nag

## Abstract

Farmworkers around the world continue to be poisoned or killed because of exposure to different categories of pesticides. The health effects of pesticide exposure include carcinogenic, immunologic, neurotoxic, and reproductive effects. Whereas acute poisoning may appear to have dramatic health effects, systematic health surveillance is a primary requirement to monitor any possible chronic poisoning. The illiterate farmers lack awareness of the potential risks in pesticide handling and application. The local government, agricultural associations, and pesticide manufacturers have a collective responsibility to educate community leaders, farmers, and healthcare workers about health and safety concerns regarding practices of pesticides handling. This contribution embodies a general-purpose modular framework of a checklist comprising 116 checkpoints in 14 modules. A local government-designated inspecting teams (evaluators) may examine and quantitatively evaluate pesticide handling, storage, transport and disposal practices, and record-keeping of events and incidents at the farming level. The inspecting team may compare the relative effectiveness of the enforcement of regulations, education, and training on safe practices, the efficacy of PPE, and access to healthcare facilities in crop-specific locations.

## Keywords

Pesticides · Health and safety · Pesticide poisoning · Farming

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## 6.1 Introduction

Global concerns are vivid as regard pesticide hazards among people in agriculture and other applications. Pesticides are complex chemicals; these include insecticides, fungicides, herbicides, rodenticides, molluscicides, nematocides, and other plant growth regulators. Protection of farm crops and livestock from insects and diseases requires specific synthetic pesticides, such as DDT, BHC, Aldrin, dieldrin, endrin, chlordane, parathion, captan, and 2,4-D. The organochlorine and organophosphate insecticides, carbamates, pyrethroids, and other formulations have selective restrictions on use. On the one hand, systematic pesticides' application perceives enhanced economic potential through increased food and fibre production and control of vector-borne diseases, such as malaria, dengue, and Japanese encephalitis.

Many of these chemicals are recognized to cause carcinogenic, immunologic, neurotoxic, and reproductive effects. The Prior Informed Consent (PIC) is a voluntary procedure to help national governments to be aware and assess the risks of hazardous chemicals and make informed decisions on their import. Estimated 200,000 deaths occur every year from pesticide exposures worldwide, mainly in underdeveloped countries with low income (Foodtank 2017). Notably, the farmworkers, including the rural residents in low-income countries, are high-risk groups for exposure to pesticides. Reports are available from Australia (MacFarlane et al. 2008), Brazil (Recena et al. 2006), cotton and cashew nut farmers in India (Srinivas Rao et al. 2005; Embrandiri et al. 2012), cocoa farmers in Nigeria (Tijani 2006; Oluwole and Cheke 2009), and vegetable farmers in the Philippines and Nepal (Lu and Cosca 2011; Ghimire 2014).

The toxicological syndrome of pesticide poisoning (Fig. 6.1) might appear within a short while of exposure (Peter et al. 2014), depending on the compound toxicity and amount absorbed through the skin, inhalation, and ingestion. The organophosphorus (OP) compounds have been reported to cause the highest number of poisoning among all agricultural pesticides; each compound has a unique biochemical affinity and receptor-specific outcomes (Peter et al. 2010). The well-defined muscarinic symptoms are salivation, lacrimation, urination, defecation, gastric cramps, and emesis. On the other hand, the nicotinic responses are fasciculation, muscle weakness, paralysis, tachycardia, and hypertension. The CNS receptor manifests as anxiety, convulsions, and respiratory depression. Certain pesticides are endocrine disruptors; even a low-level exposure for a prolonged period can elicit adverse effects by mimicking natural hormones in the body. Long-term exposure at a low concentration might link to serious health effects such as immune suppression, hormone disruption, reproductive abnormality, and carcinogenicity (Nag and Gite 2020).

The farming community is unlikely to be well-versed about the potential risks associated with pesticide handling and application. Understandably, illiterate farmers are unaware of the risks and grossly constrained to self-educate themselves on the correct handling of pesticides. The local government, pesticide manufacturers, and distributors, including agricultural associations, must recognize the critical issues about (a) the specific usage of pesticides, (b) the climate

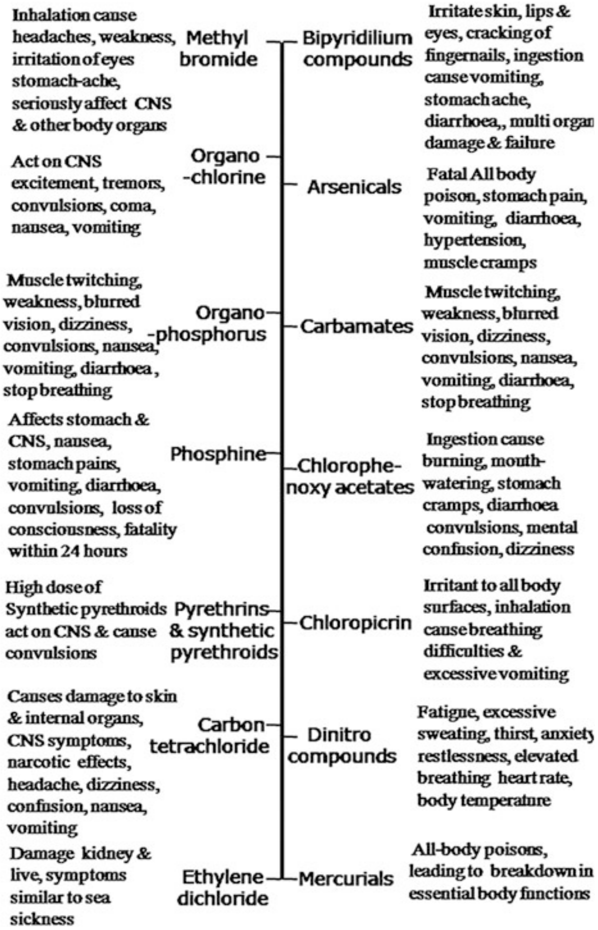

**Fig. 6.1** Toxicological syndrome of pesticide poisoning

conditions, (c) site and timing of application, (d) appropriateness of spray equipment, and (d) avoidance of pesticide contamination of the application areas and watercourse (Damalas and Eleftherohorinos 2011). They have a collective responsibility to educate community leaders, farmers, and healthcare workers about pesticide-related health hazards. This contribution embodies a checklist for local authorities and inspecting teams to examine and evaluate pesticide handling practices at the farming level. The quantitative approach to the checklist is helpful to evaluate different critical issues and compare the relative efficacy of crop-specific locations.

## 6.2 Guidance on Safety and Health of Pesticide Handling

The farmworkers have a wide geographical distribution in different land holdings, self-employment, and landless labourers. The health and safety concerns are vivid regarding practices of pesticide handling by farmers. The stated objective is to designate local inspecting teams (evaluators) acquainted with good practices of pesticide handling covering distribution, formulation, storage, disposal, and systematic record-keeping of unwarranted events and incidents. The checklist given herewith covers modules that the inspecting team may quantitatively evaluate a local farming area and compare locations of relative efficacy.

A general-purpose modular framework (Table 6.1) comprises a total of (116) checkpoints specific to (14) pesticide handling-related sections. These include public records, chemical safety data sheets (CSDS), spraying, and the like. A systematically constructed checklist facilitates studying multiple pesticide handling issues and forming a database for comprehensive evaluation of different farming locations. The structured checklist can be customized based on the provisions of applicable standards and regulatory jurisdictions. Depending on primary comprehension of the type of crop harvested and pesticides used, the inspecting evaluators may restructure the checklists with minor modifications. The checklist so designed takes account of multiple checking of desired items for situation-specific evaluation. The inspecting team (one or more persons) interviews the concerned individuals to make an apt judgement on each checkpoint. They assign a single-digit score on a standard 5-point agreement/disagreement scale, with (1) indicating strong disagreement to (5) strong agreement. The cumulative score of a specific module would stand as a relative agreement of compliance. For instance, the labelling and relabelling module consists of nine checkpoints, i.e. the lowest to highest score would be 9 (9 × 1) to 45 (9 × 5). With the cumulative scoring of 45 by the evaluator (with scoring all checkpoints of the respective module), the relative agreement/disagreement would be 45 out of 100. The numbers can also be normalized at a 100 percentage point for equating the scoring across modules. The final analysis of all modules would indicate the levels of compliance. The overall points established by the modules may be further graded as *Good*, *Fair,* and *Poor*. If the allocation of the modules exceeds two thirds of the available points, it is rated as *Good*, about half of the available points is rated as *Fair,* and below the level rated *Poor*. Accordingly, the evaluator would take measures of corrective and preventive actions. A single evaluation can include multiple farmhouses in a region, subject to the similarity of the crop harvested and the size of the farm holdings. The researchers may extend the analysis using a suitable statistical treatment of data for clustering of checkpoints.

## 6.3 Functions of the Inspecting Team

Use of the checklist would require a basic understanding of pesticides like about (a) the enforcement of regulations, (b) education and training on safe pesticide handling practices, (c) availability and efficacy of PPE for handling pesticides, and

**Table 6.1** Checklist on safe and effective handling of pesticide

| Checkpoints | | Likert score: strongly disagree (1); strongly agree (5) |
|---|---|---|
| *1. Labelling and relabeling* | | |
| 1 | The pesticide package contains the trade name and the chemical name (active ingredient) of the product | |
| 2 | The pesticide package has details of the manufacturer or distributor (including contact details) | |
| 3 | The package contains details of the quantity of the active ingredient and the weight or volume in the container | |
| 4 | The package displays well-defined hazard symbols, as per the classification of hazards | |
| 5 | The package includes the purpose and directions of its use, including wearing protective clothing | |
| 6 | The label of the package indicates application regulations (e.g. registration, compliance) | |
| 7 | Precautionary safety instruction contains guidance for storage, mixing, application of pesticides, and disposal of used containers | |
| 8 | The labelling includes instructions to health personnel for first-aid and other requirements in the case of pesticide contamination and poisoning | |
| 9 | The labelling describes instructions of the time interval between pesticide application and harvesting | |
| *2. Packaging* | | |
| 1 | Pesticides are packed *(glass, metal, plastic, or paper containers)* to ensure that the materials do not spill during handling (storing, stacking, loading/unloading) | |
| 2 | The packages are resistant to pressure, adverse climate, and corrosion | |
| 3 | Pesticide comes in the sealed package; the local vendors did not repackage pesticides locally | |
| 4 | The fastening device of the container is robust that allows repeated refastening at the user level | |
| *3. Transport* | | |
| 1 | Pesticides are not transported along with food items | |
| 2 | Transport vehicle pesticides do not have any sharp edges that can damage containers | |
| 3 | The driver should avoid harsh driving that can weaken containers and cause spillage | |
| 4 | The driver is well-trained about the basics of chemical safety data sheet of pesticide being transported and carry a copy of the same | |
| 5 | Containers of liquid products are not subject to excessive pressure for possible bursting during transport | |
| 6 | Cardboard or water-soluble packages are transported in vehicles with waterproof roofs | |

(continued)

**Table 6.1** (continued)

| Checkpoints | | Likert score: strongly disagree (1); strongly agree (5) |
|---|---|---|
| 7 | The driver must avoid the practice of carrying pesticides alongside the driver's seat | |
| *4. Transfer* | | |
| 1 | Transferring of pesticides from one container to another is discouraged | |
| 2 | In case of requiring transfer of pesticide, manufacturer's original container of same product and quality could only be used | |
| 3 | The container is clean and empty and properly labelled | |
| 4 | Containers of liquid products are not overfilled to avoid spillage due to volume expansion by temperature variation | |
| *5. Storage* | | |
| 1 | Storage is away from the dwelling area | |
| 2 | Floors are non-slippery to help cleaning of spillage or leakage | |
| 3 | All walls are impervious to liquids, and surfaces are smooth and washable | |
| 4 | The roof of the storage site is constructed with non-combustible material | |
| 5 | Entrance and exits are of adequate size for easy access and transfer of pesticides to farm vehicles | |
| 6 | The storage site is not shared with areas of storage of flammable materials, foodstuffs, and cowshed yard | |
| 7 | The storage area has a drainage system directly to a containment tank of adequate capacity | |
| 8 | Storage areas are not vulnerable to flooding or close to underground water supply sources | |
| 9 | Oxidizing products and fumigants are stored in dry conditions | |
| 10 | Flammable products are isolated and placed in the fire-resistant part of the store | |
| 11 | The storage area has adequate natural or artificial lighting, but no direct sunlight should fall onto pesticides | |
| 12 | The storage area has well-ventilated rooms to remove stale or contaminated air | |
| 13 | There is a sufficient distance between electric lamps and locations of stored pesticides to avoid transmission of heat | |
| 14 | Storage area and shelves are well demarcated and labelled to store, shelve, and stack pesticides promptly | |
| 15 | Appropriate security arrangement is made, to restrict the entry of unauthorized persons in the storage area | |
| 16 | Concerned local authorities, including the fire brigade and farm inspectors, are informed regarding the pesticide storage sites and quantities stored | |

(continued)

**Table 6.1** (continued)

| Checkpoints | | Likert score: strongly disagree (1); strongly agree (5) |
|---|---|---|
| 17 | A water supply facility should be present near the storage area but not in the store | |
| 18 | First-aid facilities are present at a known location for treating minor injuries and contamination of eyes and skin | |
| 19 | The fire extinguisher is present within the store | |
| 20 | Smoking or use of a naked flame is not allowed | |
| 21 | Washing facilities are available close to the store | |
| 22 | Ventilated accommodation at the separate area is present (cupboard or locker) for keeping protective clothing and personal clothing | |
| 23 | Empty containers of pesticides are not used to store food | |
| 24 | All containers are washed thoroughly and securely kept in a dry area | |
| 25 | To avoid polluting the surrounding environment, an isolated preparation area for application equipment is present | |
| *6. Dispensing* | | |
| 1 | Correct ratios for dilutions and doses are used | |
| 2 | Wearing protective clothing and gloves is advised | |
| *7. Pesticide application* | | |
| 1 | Equipment for pesticide application are checked for proper functioning | |
| 2 | Safety equipment, including personal protective clothing, are used as required | |
| 3 | Applicators are well-conversed about safety precautions at different stages of pesticide application | |
| 4 | Washing and safe disposal of empty containers and tanks with surplus pesticides are ensured | |
| 5 | The applicators are familiarized with applicable laws and guidance, as per code of practice | |
| *8. Pre-spraying precautions* | | |
| 1 | The operator understands the instructions about pesticides, application equipment, and protective clothing | |
| 2 | The operator ensures that application equipment is functioning satisfactorily without leaking or spilling | |
| 3 | To avoid excessive wind speeds and spray drift, the operator determines whether weather conditions are satisfactory | |
| 4 | The operator should warn nearby people if they were affected by the pesticide application | |
| *9. Precautions during application* | | |
| 1 | The sprayer wears prescribed protective clothing | |
| 2 | The correct way of application and dilution rate of pesticides is ensured for the intended farming task | |

(continued)

**Table 6.1** (continued)

| Checkpoints | | Likert score: strongly disagree (1); strongly agree (5) |
|---|---|---|
| 3 | Ensured to obviate the risk of a chemical reaction when two or more pesticides are mixed | |
| 4 | Containers are handled with care during pouring into the spray applicator | |
| 5 | In case of spillage, everyone is instructed to stay away from the area until cleaned up and disposed of safely | |
| 6 | The sprayer nozzle should not be blown by mouth to clear the block | |
| 7 | During applying pesticides, it is strongly discouraged to eat, drink, or smoke | |
| 8 | At the time of spraying pesticides, other workers or children are not be allowed to enter into the sprayed area and in close vicinity | |
| 9 | While spraying pesticides, changing weather conditions are monitored | |
| *10. Post-spraying precautions* | | |
| 1 | Take bath to wash hands, face, neck, and other body parts again | |
| 2 | Unused and surplus content from the application equipment is safely disposed off and are stored content | |
| 3 | Application equipment is thoroughly washed | |
| 4 | The washings are drained into a soak-away area to minimize risk to the environment | |
| 5 | Decontaminate protective clothing and work clothing is washed every day after spraying | |
| *11. Re-entry to the field* | | |
| 1 | A hazard sign and chart of the minimum re-entry periods are displayed on field entry points and footpaths | |
| 2 | The re-entry period is increased if entry into sprayed areas develops skin allergies and adverse symptoms on exposure to chemicals | |
| 3 | Protective clothing is worn when entry into a sprayed area is required before the re-entry period | |
| *12. Disposal* | | |
| 1 | The disposal site is located significantly away from land drains or watercourses | |
| 2 | Empty pesticide containers are not reused for storing water and food staff | |
| 3 | Empty containers are used to transfer an identical product from a deteriorated container | |
| 4 | Waste is disposed off by the persons trained to handle waste disposal | |
| 5 | Pesticide handlers wear protective clothing appropriate for the hazardous product | |

(continued)

**Table 6.1** (continued)

| Checkpoints | | Likert score: strongly disagree (1); strongly agree (5) |
|---|---|---|
| 6 | Ensured that liquid containers are first drained out and duly cleaned before disposal | |
| 7 | After cleaning, containers are crushed and stored for disposal | |
| 8 | Containers of pesticides carry the risk of reaction with water to produce hazardous gases if not cleaned with water when empty | |
| 9 | Containers are buried at least 1 m below the surface to eliminate risks of seepage from the site | |
| 10 | Records are maintained of dates and materials buried | |
| 11 | Burning of disposal items takes place in an open space away from the locality | |
| 12 | Fire is extinguished after use | |
| 13 | Fire is carefully monitored to avoid breathing of smoke produced | |
| 14 | Residues after the burning operation are buried | |
| *13. Personal protective equipment* | | |
| 1 | Any discomfort one experiences working with PPE is recorded | |
| 2 | PPE should be comfortable to the wearer, so that body movement is not restricted | |
| 3 | PPE is person-specific to the wearer and is not interchanged between individuals | |
| 4 | PPE worn is in good condition (sewn or repaired where necessary) | |
| 5 | Soiled items of clothing are properly cleaned separately and not mixed with the family wash | |
| 6 | Work clothes completely covering the body are worn under protective clothing to avoid exposure to accidental contamination | |
| 7 | PPE is resistant to pesticides | |
| 8 | Decontamination of PPE and items of clothing is done after use | |
| *14. Knowledge level of farmers* | | |
| 1 | Farmers understand national laws and regulations on the use of pesticides | |
| 2 | Farmers understand and follow the appropriate procedure to calibrate pesticide application equipment | |
| 3 | Farmers follow the procedure correctly for diluting concentrated products and mixing pesticides | |
| 4 | Farmers understand correct procedures to store pesticides safely and to dispose of empty containers and surplus products | |
| 5 | Instructions given on the pesticide containers are in easy local language | |

(continued)

**Table 6.1** (continued)

| Checkpoints | | Likert score: strongly disagree (1); strongly agree (5) |
|---|---|---|
| 6 | Mass media advertisement indicates potential health risks of toxic pesticides | |
| 7 | The first-aid facility is present in the locality in case someone becomes ill and need medical attention | |
| 8 | Farmers are aware that pesticides typically purchased are highly concentrated and to be diluted according to instructions | |
| 9 | Farmers take precautions to avoid breathing in or swallowing or skin absorption during handling of pesticides | |
| 10 | The pesticide supplier, formulator, retailer, or farmer discharge their duties for safe disposal of empty containers | |
| 11 | The practice of selling loose pesticides, empty containers, and bags are not allowed | |
| 12 | Farmers clean used drums and containers, puncture them at several places, bury them, or send them for safe disposal | |
| 13 | Only the competent person who understands the labelled instructions on the container of the pesticides uses pesticide application equipment | |
| 14 | The farmers are required to adopt measures to avoid self-contamination | |
| 15 | Farmlands should display warning signs after pesticide spraying | |
| 16 | The farmworkers never breathe sprayed toxic substances | |
| 17 | Farmers do not eat or drink pesticide-contaminated food, including recently treated seed or sprayed crops | |

(d) access to healthcare facilities. The inspecting team is primarily responsible for making the farming community aware of health hazards in handling hazardous pesticides (Heiberger 2015). The toxicity classification of pesticides is briefly described in Table 6.2, and specific hazard symbols are shown in Fig. 6.2. The inspecting team can use this information in scoring the checklist and also acquainting farmers about the same. Lu and Cosca (2011) have elaborated on the risk factors associated with improper PPE, dermal contact with pesticides, spills of sprayers, and re-entering the recently sprayed farms. Users of a knapsack sprayer must wear a safety kit that includes an efficacious face mask, gloves, eye protector, and a suitable overall that protects penetration of pesticide droplets to the body area. The tropical climatic conditions might hinder people from working with protective clothing and equipment. Therefore, the inspecting team may advise sprayer operators about the appropriate selection of safety kits.

**Table 6.2** Toxicity classification

| Classification | Symbol | Affects |
|---|---|---|
| Very toxic (class Ia) | Hazard class | Severe, acute, or chronic health risks and even death |
| Toxic (class Ib) | | |
| Harmful (class II) | | Moderate health risks |
| Irritancy (class III, IV, V) | Non-corrosive substance | Skin inflammation; according to country classification |
| Corrosivity | Corrosion | Destroy living tissues on contact; skin and flesh burns |
| Flammability | Extremely flammable | The liquid may catch fire if exposed to a flame |
| | Highly flammable | a substance that may get hot and ignite in contact with the ambient air |
| | Flammable | a substance that would catch fire if allowed to exceed ambient temperature |
| Explosivity | Exploding bomb | a substance may blow up under the effect of a flame and be subject to shocks or friction |

Refer to Fig. 6.1, the symptoms of pesticide exposure include headache, vomiting, skin rash, respiratory problems, and convulsions, depending on the toxicity, dosage, and exposure time to a compound. Appropriate pesticides must be selected and applied depending on the cropping. The depression in plasma cholinesterase (PChE) level has been identified as an indicator to monitor pesticide intoxication. If the PChE levels exceed 20% of the baseline values in pesticide handlers, they should be removed from work until their level reduces (Furman 2006). In any such poisoning incidences, the evaluators decide on the local support system to mitigate the situation.

Using pesticides is pragmatic on the judgment that the risks of long-term concomitant exposure to multiple pesticides may jeopardize the margin of safety. The inspecting team must recognize that repeated pesticide application can kill pests, but the resistant variety passes on to the next generation. The Codex Alimentarius Commission (2000) has provided the analytical approach to quantify the pesticide residue level in the crops. The guidance covers (a) the design of residue trials and sampling, (b) the application of the plant protection product, and records of (c) climate and soil data, and (d) plant growth and development data. Method validation and quality control for pesticide residues analysis depend on the acceptable levels of specific analytical parameters (Buschmann 2013).

The epidemiological database on the incidence of severe pesticide poisoning is lacking. Surveillance of outbreaks and accidental exposure to pesticides is valuable information that the evaluators notify pesticide poisoning to hospitals and local medical practitioners. The evaluators also coordinate with authorized analytical facilities for pesticide monitoring in human body fluids and tissues to examine the likely impacts of exposure to pesticides. Judicious use of the suggested checklist will

**Fig. 6.2** Hazard symbols

help the farming community recognize the potential risks associated with the toxicity of pesticides and quantitatively evaluate the prevailing situation in a farming zone.

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# Impact of Pesticides on the Ecosystem

7

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## Abstract

In the present time, pesticides have very serious impacts on the environment. Soil and air pollution are caused by the use of industrial pesticides, and some of the substances in the pesticides take years, if not decades, to degrade. The welfare of animals, microorganisms, trees and human is harmed by these chemicals. However, many natural pesticides (biopesticides) are also good at controlling pests. People must prefer biopesticides over toxic pesticides as the former are easily degradable either in soil or by sunlight. The soil will turn back to its natural state as soon as the chemicals degrade. Biopesticides are also non-toxic for humans and livestock. They vanish faster from eatable products, such as fruits and vegetables, thereby enabling us to consume them quickly. In this chapter, main emphasis is given to the impact of pesticides on the ecosystem in various ways.

## Keywords

Pesticides · Herbicides · Insecticide · Ecosystem · Pollution

## 7.1 Introduction

Due to the rapidly growing population and limited land area for farming, it is important to reduce the damage as well as spoilage and increase the yield of crops to provide food to every individual. Every living organism needs food for survival, and humans are the only creatures who cultivates their own food, according to their

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convenience and needs. They use many chemicals to enhance the quality as well as the yield of crops. Insecticides, fungicides, herbicides and fertilizers are also known as agrochemicals or agrichemicals. These chemicals are used as a boon in the agriculture sector. They are generally used to prevent diseases, control pests and control and promote growth. Agrichemicals are introduced in the 1960s. They are mainly responsible for the beginning of the "Green Revolution" (Unsworth et al. 2010).

As far back as 4500 years ago, Sumeria used sulphur as a chemical to kill insects in ancient Mesopotamia. About 3200 years ago, China used mercury and arsenic compounds to treat body lice. In Rigveda (written about 4000 years ago), some evidence of using poisonous plants to protect crops from pests is also found (Unsworth et al. 2010; Carvalho 2006).

## 7.2 Pesticides

The term pesticide can be defined as a chemical compound that is used to control or halt the reproduction process of insects, mites, fungi, rodents, weeds, algae, etc., which prevents the crops from being damaged or destroyed (Gilden et al. 2010). In other words, pesticides can be defined as toxic substances, biological agents or a mixture of different compounds that are liberated into the environment to control harmful pests. The main role of pesticides is to control pests and disease-causing vectors. Pesticides are the result of human efforts to control crop damage, increase crop yield and control diseases caused by pests (Helweg et al. 2003). Pesticides can be derived naturally or can be obtained synthetically. There are different classes of pesticides such as pyrethroids, neonicitinoids, organochlorines, carbamates and organophosphates.

Pesticides are also categorised based on their chemical structure, viz. organophosphate, organochlorines, carbamate and pyrethroids. They are also divided into various groups: copper-containing compounds, phenol and nitro-phenol derivatives, hydrocarbons, ketones, aldehydes and their derivatives, organochlorines (endosulfan, hexachlorobenzene), carbamic and thiocarbamic derivatives, organophosphates (diazinon, omethoate, glyphosate), fluorine-containing compounds, metal-organic and inorganic compounds, natural and synthetic pyrethroids, carboxylic acids and their derivatives and heterocyclic compounds such as benzimidazole and triazole derivatives (Bolognesi 2003; Franco et al. 2010; Katagi 2010).

Pesticides are extremely beneficial substances that help to prevent crop loss as well as crop diseases. Due to the overuse of commercially available pesticides, pests are developing immunity against them. Pesticides that are developed recently can target multiple species at a time (Speck-Planche et al. 2012; Gupta et al. 2021).

The extensive use of pesticides led to harmful and severe consequences to the environment as well as other species present on this planet (Agrawal et al. 2010). Pesticides have toxic nature due to their chemical properties, they are heat soluble, water-soluble and polar in nature. These properties made pesticides more lethal.

**Table 7.1** Pesticides and their target pests

| S. No. | Categories of pesticides | Target pests | References |
|---|---|---|---|
| 1. | Insecticides | For insects and arthropods | Kumar et al. (2018) |
| 2. | Fungicides | For fungi like moulds, mildews, rust and blight | Halo et al. (2018) |
| 3. | Bacteriocides | For bacteria | Scala et al. (2018) |
| 4. | Herbicides/ weedicides | For unwanted plants or weeds | Guerra-García et al. (2018),<br>Kaur et al. (2018) |
| 5. | Acaricides | For mites on plants as well as animals | Dekeyser et al. (2003) |
| 6. | Rodenticides | For rats and other rodents | Hoque et al. (1988) |
| 7. | Algaecides | For algae | Crafton et al. (2018) |
| 8. | Larvicides | For larvae | Henrick (2007) |
| 9. | Repellants | Repels pests by smell and taste | Nelms and Avery (1997) |
| 10. | Ovicides | For eggs of insects and mites | Egbuna and Sawicka (2019) |
| 11. | Viricides | For viruses | Egbuna and Sawicka (2019) |
| 12. | Molluscicides | For molluses | Egbuna and Sawicka (2019) |
| 13. | Nematicides | For nematodes | Mohamed et al. (2016) |
| 14. | Avicides | For birds | Egbuna and Sawicka (2019) |
| 15. | Piscicides | For fishes | Egbuna and Sawicka (2019) |
| 16. | Termeticides | For termites | Egbuna and Sawicka (2019) |

They release toxic substances that affect not only agricultural products but also people involved in the agricultural sector (Rashid et al. 2010). Categories of pesticides and their target pests are described in Table 7.1.

## 7.3 Insecticides

Insecticides are chemical substances that belong to a group of pesticides. They are used to kill/control the specific target. They can be further classified based on the growth stages of the insect's life cycle.

**Examples:**

1. Ovicides for eggs of insects.
2. Larvicides for the larval stage of insects.

These insecticides are widely used in the medicinal as well as agricultural sectors by consumers. They are the main reason for the increment of agricultural productivity in the twentieth century (van Emden and Peakall 1996).

## 7.3.1 Mode of Action of Insecticides

The mode of action is basically defined as the process by which any group of pesticides comes into action or prevents the crops from damaging. The mode of action of insecticides was given by Brown (1951), who classified them into two categories for a better understanding of their toxicity to related species (Table 7.2):

### 7.3.1.1 Modern Insecticides (Mode of Action)

Modern insecticides include all categories of insecticides based on their mode of action. These insecticides are divided into five groups for better understanding (Matsumura 1975; Brown 1951):

- Protoplasmic poisons
- Physical poisons
- Respiratory poisons
- Nerve poisons (most modern insecticides)
- Poisons of a more general nature

### 7.3.1.2 Non-expert Insecticides (Mode of Entry)

The non-expert insecticides are classified based on their mode of entry. These insecticides are divided into three groups (Matsumura 1975; Brown 1951):

- Stomach poisons
- Contact poisons
- Fumigants

## 7.4 Herbicides

Herbicides are chemical substances that belong to a group of pesticides. They help to control or destroy specific groups of unwanted plants called weeds that grow in crop fields (Tu et al. 2001).

On the basis of their mode of application, they are generally classified into two types:

1. Pre-emergent herbicides
   These are generally applied to the crop field before the germination of weeds. They either kill the germinating seeds or hamper the germination.
2. Post-emergent herbicides
   These herbicides are applied directly to unwanted plants or in the soil.

Some herbicides can be used in both pre-emergent and post-emergent application methods (Tu et al. 2001).

**Table 7.2** Classification of different insecticides and their mode of action

| S. No | Name of insecticides | Mode of action on primary site | Group of insecticides |
|---|---|---|---|
| 1. | Heavy metals, e.g., Hg, acids | • Protoplasmic level | • Protoplasmic poison |
| | Alkyl halides, chloropicrin | • Inhibitors of multiple miscellaneous non-specific sites | • Regulation of growth |
| | Fluorides, Tetronic and derivatives of Tetramic acid | • Acetyl CoA carboxylase inhibitors | • Synthesis of lipids |
| 2. | Heavy mineral oils, inert dust, Earth mineral oil (diatomaceous) | • Unspecified physical and mechanical disruptors | • Physical poison |
| | | • Surface level action | |
| 3. | HCN, CO, HzS, rotenone, dinitrophenol, pyrroles | • Electron transport inhibitors | • Respiratory poison |
| | | • Metabolic inhibitors | • Energy metabolism |
| | | • Disrupts the proton gradient through uncoupling of oxidative phosphorylation | |
| | | • Destroys energy metabolism | |
| 4. | Pyrethrin synergists | • Modulators of sodium channel | • Respiratory poison |
| | | • Inhibitors of mixed-function oxidase | • Nerve action |
| 5. | Sodium fluoroacetate | • Inhibitors of carbohydrate | • Respiratory poison |
| | | • Metabolism | |
| 6. | Chlordimeform | • Inhibitors of amine | • Respiratory poison |
| | | • Metabolism | |
| 7. | Juvenile hormone analogues | • Mimics juvenile hormone | • Respiratory poison |
| | | • Responsible for regulation in growth insect hormones | • Growth regulation |
| 8. | Organophosphorus compounds, organophosphates, carbamates | • Inhibitors of acetylcholinestrase (AChE) | • Nerve poison (neuroactive agents) |
| | | | • Nerve action |
| 9. | DDT analogues, pyrethroids, cyclodiene compounds, BHC (organochlorines) | • Sodium channel modulators | • Nerve poison (neuroactive agents) |
| | | • It interacts with the gated chloride channels of GABA-g-aminobutyric acid | • Nerve action |
| 10. | Nicotine analogues | • Competitive modulators in nicotonic acetylcholine receptor (nAChR) | • Nerve poison (neuroactive agents) |
| | | • Agents for nerve receptors | • Nerve action |
| 11. | *Bacillus thuringiensis* toxin and the insecticidal proteins produced by them | • Insect midgut membranes disrupted by microbial activities | • Poison of more general nature (stomach poison) |
| | | • Stomach poisoning | |

### 7.4.1 Mode of Action of Herbicides

The mechanism of action of herbicides is basically based on biochemical or physical methods. These methods are helpful in either controlling or killing the undesired plants. Following are the modes of action of herbicides on the basis of their chemical structure:

1. Herbicides mimic the growth hormones of plants and cause disorganized growth, which leads to the death of the susceptible plants. This mode of action is known as the auxin mimic mode of action. Some examples of auxin mimics are clopyralid, picloram, 2,4-D and triclopyr.
2. Lipid biosynthesis inhibitor is the process in which the herbicide halts the lipid synthesis in plants, which leads to the wilting followed by the death of plants. Lipid is necessary for the maintenance as well as the growth of the cell membrane. Some examples are sethoxydim and fluazifop-*p*-butyl.
3. Mitosis inhibitors are also known as dormancy enforcers. In this process, herbicides generally block the re-budding process in plants during the spring season and also halt the new growth in the summer season. Fosamine is a common example of this category.
4. Amino acid synthesis inhibitor: As the name itself indicates, the work of these herbicides prevents the synthesis of the amino acid in plants, which further leads to no protein formation as amino acids are required for protein construction. Some examples of amino acid inhibitors are imazapic, imazapyr and glyphosate.
5. Photosynthesis inhibitors are responsible for the halting of some of the specific reactions which lead to photosynthesis, and this causes cell breakdown. Hexazinone is the major example of this category (Tu et al. 2001).

## 7.5 Benefits of Pesticides Usage

There are many benefits of pesticides other than controlling and killing pests. They can be described as the primary and secondary benefits of pesticides: primary benefits are to kill or control pests and their population to save crops and the secondary benefits are to increase the crop yield. Many types of primary and secondary benefits are described in Tables 7.3 and 7.4, respectively (Cooper and Dobson 2007).

Total 40% of the crop yield worldwide is lost due to pests, plant diseases, weeds, rodents, etc. This damage can be more if there is no pesticide available. Due to the use of pesticides, an increase in agricultural production was recorded, and in the same report, it was mentioned that if there was no use of pesticides, the damage would be increased many more times and economic losses are also unbearable. In a study, due to the usage of herbicides and insect pollinators, an increase of 70% in the yields of crop production was also recorded (Webster et al. 1999). The protection of agricultural farms means the protection of all forms of life. Forests and other wildlife habitats are protected by invasive species of plants, pests and other non-native

**Table 7.3** Primary benefits of pesticides with examples

| S. No. | Primary benefits | Examples |
|---|---|---|
| 1. | Controlling pests to prevent human activities and human creations | (a) Protects grounds, pitches and golf courses |
| | | (b) Furniture and other wooden structures |
| 2. | Controlling disease causing vectors | (a) Kill insect like mosquitoes, houseflies, etc. which causes many lethal diseases |
| | | (b) Save domestic animals from pests |
| 3. | Control and prevent plants from diseases and damage | (a) Control weeds |
| | | (b) Kills or control harmful pests |
| | | (c) Prevents the plant from fungi |

**Table 7.4** Secondary benefits of pesticides with examples

| S. No. | Secondary benefits | Examples |
|---|---|---|
| 1. | Global benefits | (a) Prevents historical monuments |
| | | (b) Prevents pest migration |
| 2. | National benefits | (a) Maintains agricultural economy |
| | | (b) Reduces moisture loss and soil erosion |
| 3. | Communal benefits | (a) Provides food safety and security |
| | | (b) It reduces the cost of maintenance |

insects. When crop yields are improved, farmers can produce more food without any further extension of their crop field, which helps in protecting biodiversity. Herbicides and insecticides are also used to prevent grass and the surface layer of earth in different grounds, pitches and golf courses (Aktar et al. 2009). Insecticides are also used to control the population of bugs and insects, which improves the safety and sanitary conditions of houses (Delaplane 2000).

### 7.5.1 Risks That Are Associated with the Use of Pesticides

The risks of using pesticides are much higher than their benefits. Pesticides influence and affect non-targeted species present in different ecosystems. They affect every organism in a food web whether they are part of a terrestrial or aquatic ecosystem (Majewski and Capel 1995). It has been approximately 70 years after "Silent Spring" has been published. The book is about the effects of pesticides on the world's ecosystem. The book was written by Rachel Carson and she gave a warning to the world about pesticide toxicity and the harm it is causing to the beneficial insects, birds and larger animals (Kegley et al. 1999). Some beneficial insects, which are helpful in pollination, are natural pollinators such as honey bees and butterflies; they are very sensitive towards pesticides. The use of insecticide in a large amount directly affects the population of bees which cause a low pollution rate. The loss of bees, natural pollinator species, causes colony collapse disorder in which bee workers form a beehive or colony abruptly disappears of western honey bee (Hackenberg 2007).

Organisms that are present in an ecosystem are dependent on one another for their survival either directly or indirectly. Such a type of association can be seen between the key stone species and other species in an ecosystem; it connects all the species with one another in a food web. The key stone also plays a vital role in the structure, organization and maintenance of an entire community. The loss of key stone species by the use of pesticides (or other reasons) is a major loss to the entire community; it will affect community dynamics, and the balance of the food web will be lost. It will also lead to the extinction of other species in a particular community. For example, the sea otter is a key stone species for a marine ecosystem that controls the number of sea urchins (al Mills and Doak 1993).

Volatilization of 80–90% of the pesticides can be seen after a few days of application. This is commonly seen when pesticides are applied through sprays or sprinklers. These volatilized pesticides mix with the atmosphere through the evaporation process and affect the non-targeted species. This example would help us to understand the effect of pesticides on non-targeted species when we use herbicides on a particular crop, and it volatilizes to the other non-targeted plants and causes severe damage to them (Majewski and Capel 1995; Straathoff 1986).

These pesticides mix with natural resources in different ecosystems such as aquatic and terrestrial by contaminating the air, water and soil of the ecosystem. The excessive use of pesticides is a severe threat to the most vulnerable, endangered and rare species such as peregrine falcon, osprey and bald eagle. This is common in all species of plants and animals whether they belong to the terrestrial or aquatic ecosystem because the level of toxicity of pesticides is affecting them equally (Helfrich et al. 2009).

On the level of toxicity, the most toxic type of pesticide is insecticides, then fungicides, and then herbicides. As we discussed earlier, these pesticides have different chemical nature in terms of their solubility as they are heat soluble, water soluble, fat soluble, etc. They are polar in nature. Due to these qualities of pesticides, they can easily enter into any ecosystem and disturb the balance.

Pesticides which are water soluble are easily absorbed by the soil or dissolved in water of different water bodies such as river, streams, lakes and wells, and they contaminate the underground water. These pesticides can harm many non-targeted species. The fat soluble pesticides can also be absorbed by the animals by the fatty tissues through the process called bioamplification.

Bioamplification, also known as biomagnification or biological magnification, is any concentration of a toxin, such as pesticides, in the tissues of tolerant organisms at successively higher levels in a food chain (Silvy 2012).

Hence, these pesticides absorbed by any organism present in any food chain or food web in any ecosystem can affect other organisms although they do not directly absorb them. Bioamplification process is described in Fig. 7.1; the process of bioamplification is shown in simple food chain, where P denotes the concentration of pesticides in different organisms.

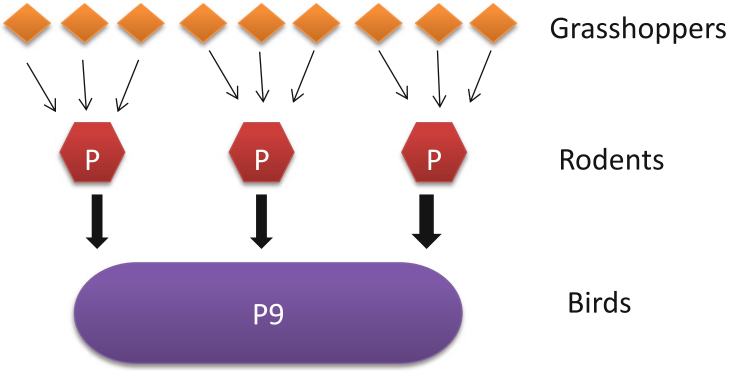

**Fig. 7.1** Depiction by bioamplification process of pesticides in the simple food chain

In Fig. 7.1, a small concentration of pesticides enters into the bodies of primary consumers (grasshoppers) through their food, which is generally plants. They are low-level organisms that depend on plants for their food and are the starting point for the food chain. The secondary consumer (rodent) in this food chain consumes the primary consumers (grasshoppers). By eating the grasshopper which has a small amount of pesticides, denoted by P in its body, resulted in an increase of pesticides. High-level predators, such as birds in this food chain, consume these rodents, who already have some concentration of pesticides in their bodies, and eventually increase the concentration of pesticides in their bodies, which is toxic to them.

This example of a simple food chain is best to understand the bioamplification of pesticides at different levels. “Higher the tropic level, greater the concentration of pesticides”. When the concentration of pesticides increases, which leads to an increase in toxicity in the bodies of higher organisms such as birds in the tropic level, this will lead to the death of all predators at the tropic level which further results in a massive increase in the population of secondary consumers like rodents, and this further leads to a decrease in the population of primary consumers such as grasshoppers. This whole process causes a disturbance in the ecosystem.

Insecticides have a broad spectrum such as carbamate, organochlorine and organophosphorus, these insecticides kill both harmful and beneficial pests indiscriminately, and this activity disturbs the natural balance between prey and predator insects. Many important roles are performed by these pests like pollination, nutrition cycling and soil aeration, and they control pests by maintaining a natural relationship between prey and predator. The harmful pests can recover rapidly because of their large population, and they also develop immunity or resistance from the previously used insecticides, but this is not the same for beneficial pests. Insecticides are intended to kill harmful insects, but they will be resurrected if this happens. In the future, the farmer will use more insecticides to kill these pests in order to protect his crops (Zacharia 2011).

### 7.5.2 Major Threats to Biodiversity

Pesticides, when used excessively, release toxins into the ecosystem, causing harm both to organisms and to natural resources, such as soil, water, and air. Pesticides affect plants, animals, and birds of different ecosystems such as terrestrial ecosystems and aquatic ecosystems. The increase in the concentration of pesticides in the food chain affects the population of predators and primary consumers directly, and this is a big reason to worry. Concentrations reduce the number of organisms that feed on weeds, shrubs, and insects indirectly.

Animals which are endangered, vulnerable and rare are also declining due to the spraying and sprinkling of different insecticides, herbicides and fungicides. In particular, the population of birds is highly affected by the use of pesticides. The long-term usage of these pesticides will cause the bioaccumulation of pesticides in different ecosystems. Other than pesticides, different types of chemicals are also present in this environment but they are present in very low concentrations that they do not harm any organism, but they may be responsible for other problems like genetic disorders, physiological changes and can show their effect in future by reducing the lifespan of organisms (Berg et al. 1999; Lourencetti et al. 2008; Durmaz et al. 2006; Van Wezel and van Vlaardingen 2004; Osano et al. 2002).

### 7.5.3 Harmful Effects of Pesticides on Ecosystem Level

An ecosystem is a collection of all types of living organisms as well as factors such as soil, air, and water (Zacharia 2011). In other words, we can say that the place where abiotic and biotic factors are the same in combination to support life. A few examples of ecosystems include ponds, a mountain meadow and rain forest (Fig. 7.2).

There are some events as well as processes that happen in an ecosystem or we can say these processes help to run an ecosystem in a balanced manner. These events go through days, seasons, years, decades and centuries. Birth, growth, reproduction, and death (this occurs in an ecosystem only with biotic agents) and interactions between species such as competition (intraspecific and interspecific) and commensalism and parasitism. All these events and processes are highly affected by the physical properties of the geographical environment. The ecosystem gains matter and energy from these processes and interactions for the exchange and cycles of nutrition and other different processes like water cycle and nitrogen cycle (Zacharia 2011).

A large amount of pesticides used in the environment will ultimately reach the soil where the nutrient cycle and soil formation process are taking place. Natural mechanisms can be affected by pesticides (Zacharia 2011).

These pesticides also hinder the process of nitrogen fixation which is required for the growth of higher plants, by causing a disturbance in the natural composition of the soil. The chemical signalling of legume-rhizobium is halted by many insecticides like methyl parathion, DDT and most importantly pentachlorophenol. This results in

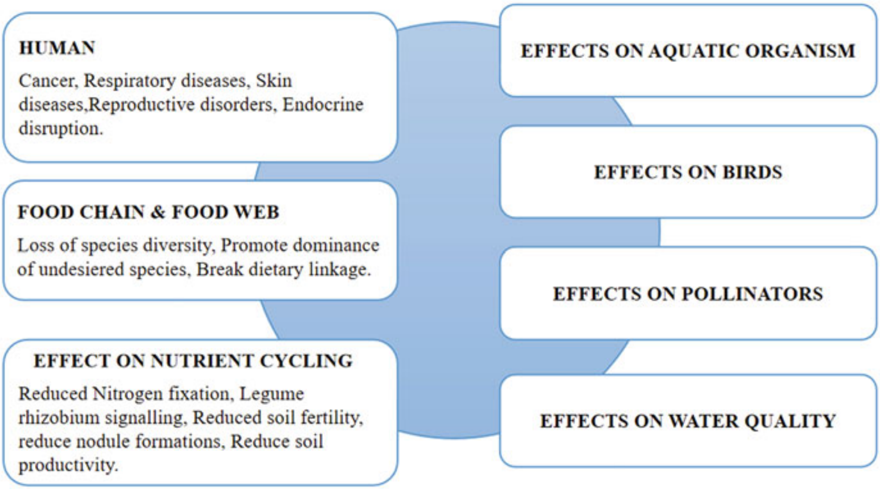

**Fig. 7.2** Harmful effects of pesticides on different organisms

the reduction of crop yield because the reduction of this symbiotic chemical signalling decreases nitrogen fixation (Rockets 2007). These microorganisms in legume plants fix nitrogen naturally, thereby saving $10 billion from being spent on fertilizers every year (Fox et al. 2007). When pesticides or other sources of pollution disturb the natural phenomena of nutrient cycling, this will lead to a decrease in soil productivity and soil fertility (Zacharia 2011).

### 7.5.4 Harmful Effects of Pesticides in Aquatic Ecosystem

There are many different ways by which the pesticides peculate in the aquatic ecosystem: they can enter by drift, leach through the soil, in runoff or sometimes directly on the surface of water bodies to kill or control insects like mosquitoes. Pesticides reach the water and contaminate it, which is a major problem for animals living in an aquatic ecosystem. These pesticides can also affect the nature of aquatic plants, behavioural and physiological changes in the population of fishes and also decrease the quantity of dissolved oxygen in the water. The drift method of pesticide application causes pesticides that are applied to agricultural lands to enter the aquatic ecosystem, where they can harm the fish and other non-targeted animals. The excessive use of pesticides leads to a decrease in the aquatic population and also encourages the growth of algae, which causes algal bloom (Scholz et al. 2012).

Following are the three methods by which these pesticides can enter into the bodies of aquatic animals:

1. Pesticides enter through drinking water in which pesticides are dissolved. This is called oral method.

2. By breathing contaminated air with some pesticides in it, pesticides enter the body through the gills. This is called breathing method.
3. Pesticides enter through the skin by direct absorption of toxic chemicals in it. This is called dermal method (Helfrich et al. 2009).

The aquatic plants provide 80% of the oxygen dissolved in water which is important to support life in the aquatic ecosystem. The toxic chemical of herbicides dissolved in the water can cause an extreme reduction in the dissolved oxygen level of the aquatic ecosystem, which suffocates the aquatic organisms to death. As a result, this will reduce fish productivity (Helfrich et al. 2009).

Pesticides that dissolve in the water bodies by runoff of the agricultural land and contamination by spray drift method will increase the toxicity of the water with the surface water containing more concentration of pesticide toxins than groundwater (Anon 1993). This does not mean that pesticides do not reach groundwater. The pesticides enter the groundwater through sewage contamination of surface water, accidental spills, leakages and improper disposal of pesticides.

Drifting of pesticides into water bodies like rivers, lakes and ponds causes high damage to the aquatic ecosystem and makes the aquatic ecosystem tougher to survive. Pesticides have a toxin named atrazine which is associated with the weakening of the immune system of some fishes and some amphibians (Forson and Storfer 2006; Rohr et al. 2008). It has been pointed out above that pesticides are toxic or concentrated more near the surface of the water; amphibians are organisms living on the surface of the water; contaminated water takes away their habitats and also reduces their population.

The herbicide glycophosphate harms the population of tadpoles and young frogs with the use of a highly toxic chemical named carbaryl, a pesticide compound that is particularly hazardous to amphibians (Relyea 2005). Similarly, the toxins named endosulfan and chloropyrifos also cause severe damage to the amphibian species (Sparling and Fellers 2009). Toxin named malathion in small concentrations causes harm or severe damage to the abundance and composition of periphyton and phytoplankton population which again affects the amphibian population indirectly (Relyea and Hoverman 2008).

The toxin present in the water reduces the reproductive capacity of aquatic organisms, and herbicides also damage the flora of the aquatic ecosystem by affecting aquatic plants. The reduction in the number of aquatic plants leads to the reduction of shelter and hiding places for the small fishes and fish nurseries from predators (Helfrich et al. 2009).

Quantifying the herbicide's toxicity is done by calculating the LC50, which is the amount of herbicide needed to kill half of the aquatic organisms within the study. LC50 is the measurement of pesticides present in 1 L of water in microgram (Tu et al. 2001).

The aquatic species are more susceptible against the ester-formulated pesticides than against acid- or salt-based pesticides because ester-based pesticides are fat loving or lipophilic in nature, and this property of these pesticides makes them pass through the gills and skin easily. Ester-based pesticides are not water soluble, which means they do not dilute in water in any case (Tu et al. 2001).

### 7.5.5 Effect of Pesticides on Terrestrial Ecosystem

Pesticides present in the soil and air cause sublethal effects on terrestrial plants and also kill the non-targeted plants. Volatilization and drifting of pesticides that are phenoxy based cause severe damage to the nearby non-targeted shrubs and trees (Dreistadt et al. 1994). Glyphosate-based herbicides make plants more susceptible to plant diseases (Brammall and Higgins 1988) and reduce the quality of seeds as well as their vitality (Locke et al. 1995). Herbicides like sulphonamides, imidazolinones and sulfonylurea cause severe damage to non-targeted plants, crops, natural plant communities and wildlife by affecting their productivity even in very low doses or low concentrations (Fletcher et al. 1993).

Harmful effects of pesticides are not only seen on plants but also on terrestrial organisms. It affects every group of organisms from small bees to large key stone species. Insecticides such as organophosphate, carbamates and pyrethroids are broad spectrum in nature and cause severe harm to non-targeted species like bees and beetles that are beneficial to the agricultural sector. In organic farms, the population of these beneficial insects is much more than in inorganic farms. Co-operative effects of fungicides and insecticides like triazole or imidazole and pyrethroids cause severe harm to the bee population (Pilling and Jepson 2006). Imidacloprid and clothianidin are neonicotinoid-based insecticides which are also toxic for bees. Even in very low doses, the imidacloprid can affect the behaviour of bees by causing difficulty in searching for food because insecticides affect their foraging behaviour (Yang et al. 2008) and also reduce their learning capacity (Decourtye et al. 2003). As we all know, bees are very important to the agricultural as well as the food industry. These sectors majorly depend on the bees for the pollination process as one-third of the total pollination is done by bees in this planet but the use of neonicotinoids is the reason for the disappearance of honey bees at the very beginning of the twenty-first century. A large amount of pesticides are found in the mixture with the commercially obtained honey and wax from the beehives. A report shows that these pesticides are neonicotinoid based. The use of these pesticides reduced 29–36% of the bee population each year since 2006.

There is a record declination of 20–25% in the bird population after 1962 because the use of pesticides in agriculture begins after that. Pesticides that are fat soluble are accumulated and absorbed by fatty tissues in birds which leads to their death. DDT and it metabolites are primarily responsible for the major decline in the bald eagle species of birds in the USA (Liroff 2000). Fungicides are responsible for the reduction of the earthworm population, which indirectly leads to a reduction of birds and mammals that feed on them. The granular form of pesticides confuses birds as food, leading to the direct consumption of pesticides by birds. Insecticides like organophosphate have poison raptors in crop fields which are highly toxic for the birds, and small quantities of these pesticides lead to behavioural changes in birds.

We all know that earthworms are farmer's friend. They increase soil fertility and make soil porous, which improves soil aeration. Earthworm also indicates soil pollution or contamination present in soil and also plays a significant role in the testing of soil toxicity. Pesticides that are present in soil are affecting the earthworm population, and their toxic effects were detected recently; pesticides contaminate the soil pores where earthworms are present. A study found that fungicides and insecticides are neurotoxic to earthworms and change their physiology after long-term use (Schreck et al. 2008). The long-term use of pesticides, chlorpyrifos and glyphosphate leads to deletion effects and cellular level damages in the DNA of earthworms. Glyophosphate also affects the viability and feeding capacity of earthworms (Casabé et al. 2007).

Different microorganisms are involved in the fixation of atmospheric nitrogen into nitrates called nitrogen-fixing organism. Fungicides like dinitrophenyl and chlorothalonil disturb the nitrification and de-nitrification processes which depend on nitrifying and de-nitrifying bacteria (Lang and Cai 2009). The soil bacteria involved in the transformation of ammonia into nitrite are also disturbed by the herbicide named triclopyr (Pell et al. 1998). Growth and activities of nitrogen-fixing bacteria are inhibited due to the presence of herbicides like glyphosphate (Santos and Flores 1995), and the transformation of ammonia into nitrates carried out by soil bacteria is also halted by the pesticide 2,4-D (Frankenberger et al. 1991). Herbicides and pesticides often damage many fungal species. Oryzalin and trifluralin are responsible for the inhibition of many symbiotic mycorrhizal fungi (Kelley and South 1978) that help in providing nutrition to the higher plants. A large number of fungal spores which are present in the soil are reduced due to the usage of pesticide oxadiazon (Moorman 1989). Triclopyr pesticides cause toxicity in some species of mycorrhizal fungi (Chakravarty and Sidhu 1987).

### 7.5.6 Effects of Herbicides on Birds and Mammals

The LD50 of herbicide is the dosage that kills half of the population of research animals when given orally (through the mouth) or dermally (through the skin). Adult male rats were used to assess the oral LD50s recorded here. For rabbits, dermal LD50s were calculated. The LD50 is normally expressed in grams of herbicide per kilogram of body weight of the species. Since LD50s are measured under a range of conditions, comparisons between herbicides can only give a rough indication of their relative toxicity. Herbicide applicators may find dermal LD50 values more useful because they are more likely to be exposed to herbicide through their skin rather than through oral ingestion. In either case, only a limited number of individuals, including applicators, are exposed to herbicide doses above the LD50.

The LD50 does not provide much detail about the chronic, long-term adverse symptoms that can be caused by lower doses. Sublethal doses can cause inflammation of the skin or eyes, headaches, nausea and, in the worst-case scenario, birth defects, developmental abnormalities, coma, cancer and even death. Since impurities obtained from herbicide formulation and adjuvants applied to the formulation can be more harmful than the herbicide compound itself, it is difficult to link elevated cancer risks or other side effects to a herbicide (Tu et al. 2001).

### 7.5.7 Harmful Effects of Pesticides on Humans

Pesticides are helpful in many ways and they also increase efficiency, but the harmful effects of pesticides are manifold than their benefits. The use of pesticides has increased in the past few decades, and the toxins of pesticides harm humans by entering into their bodies and causing toxicity in the body.

Following are the three major ways through which pesticides can enter into the body:

1. Through air by inhaling dust and vapours, aerosol.
2. Through oral by consumption of food and water having pesticides in it.
3. Through skin by direct contact of pesticides (Sacramento 2008; Spear 1991).

About 3,000,000 cases of pesticide poisoning and nearly 220,000 deaths are recorded per year in developing countries, according to a report of the World Health Organization (WHO) (Lah 2011). In developing countries, 2.2 million people are exposed to harmful pesticides and are at greater risk of poisoning from pesticides (Hicks 2013).

Different groups of people are more susceptible towards the toxicity of these pesticides like infants, kids, senior citizens, pregnant females and farmer, and person who work in the pesticide factory. Pesticides enter the human body by passing through many barriers and are finally stored in the tissues. This is mainly caused by the direct in-take of pesticides in food, and this is how the majority of the population is exposed towards pesticides toxins (Hayo and Werf 1996). The human body has a generalized mechanism of excretion of toxins, but in some cases, toxin reaches the circulatory system through absorption (Jabbar and Mallick 1994). When the concentration of pesticides present in the body is more than the initial concentration of pesticides present in the environment, the effect of pesticides is seen (Hayo and Werf 1996). Individuals can be exposed to harmful pesticides over a prolonged period of time, and their bodies are capable of metabolizing certain poisons at different rates, depending on the dose and duration of exposure they receive (Marer et al. 1988; Ware 1991). The effect of pesticides varies from person to person: weaker people are more sensitive towards small doses than healthier people (Marer et al. 1988). The effect of pesticides in human bodies is classified into two categories:

1. **Acute Effects of Pesticides:** It can be described as the exposure of humans to pesticides for the short term. It can cause blindness, headache, stinging of the eyes and skin, irritation of the nose and throat, skin itching, dizziness, diarrhoea, abdominal pain, nausea and vomiting, blurred vision, appearance of the rash and blisters on the skin.

2. **Chronic Effects of Pesticides:** This is the result of exposure to pesticides in the long-term period. Long-term exposure can cause hypersensitivity, asthma and allergies, and it also weakens the immune system (Culliney et al. 1992).

Pesticides when entered into the blood stream can cause blood cancer (leukaemia) and the presence of toxins in the body can also cause brain cancer, lymphoma, cancer of the breast, prostate, ovaries and testes.

The sensory organs if exposed to the pesticides can cause reduced visual ability and reduced motor signalling, loss of coordination and memory, etc. Organochlorines cause indigestion which leads to hypersensitivity to sound, light and touch, and also cause vomiting, nausea, confusion, dizziness, tremors, seizures and nervousness. Long-term exposure to pesticides can also damage vital organs like the kidney, lungs and liver and can also cause blood diseases (Lah 2011). There is an observation in which Parkinson's disease and Alzheimer's disease are related to long-term exposure to pesticides (Casida and Durkin 2013).

If pesticides are somehow entered into the human body and remain there for a longer period, they will affect the reproductive health of both males and females, and they interfere with levels of reproductive hormones. This will lead to infertility in both males and females, continuous abortions, stillbirth, birth defects, etc.

### 7.5.8 Effects of Pesticides on Soil

Many different types of pesticides are used in the agricultural sector which eventually contaminate the soil, and the impact of these pesticides we are using these days will affect the soil for decades. The use of pesticides also leads to a decline in the general biodiversity (Johnston 1986). To increase the soil quality we have to reduce the use of chemical pesticides; it also has many additional effects like the organic components of the soil develop a water retention mechanism in the soil itself, and this shows an increment in the yield for farmers in the drought season; this is the only reason why the yield of organic fields is 20–40% more than the field which used chemical fertilizers and pesticides. In soils with a high level of organic matter, pesticides are more likely to adsorb and present as bound pesticide residues. It happens due to the binding of organic matter with the pesticides and helps to break down pesticides (Lotter et al. 2003).

The moisture present in the soil, pH of soil, surface area of clay, the amount and quality of soil, the organic matter present in the soil and temperature of the soil are the primary factor that help to detect the presence of pesticides in the soil (Helling et al. 1971). Generally, the natural pH of the soil is measured between the ranges of 5.5 and 7.5. Leaching rates and rainfall majorly affect the value of soil pH strongly. In semi-arid and arid zones, the soil has more cations and becomes more alkaline in nature, whereas in rainy or wet areas, the cations present in the soil are leached out and result in the acidic soil (Tu et al. 2001).

### 7.5.9 Effect of Pesticides on Water Quality

Pesticides applied to crops in the agricultural field by direct over spraying, leaching, drifting, etc. can contaminate the water bodies and underground water (Taylor and Glotfelty 1988). Pesticides can also enter into water bodies by air. The four major routes by which the pesticides can enter into the water bodies are drifting, percolation, leaching and runoff or spilling.

The ability by which pesticides can contaminate the water bodies is they dissolve in the water and cause harm to aquatic as well as terrestrial animals. There are many factors that are responsible for contamination of water like soil type, methods that apply pesticides in the fields, weather, and the distance between water bodies and agricultural fields. All aquatic and terrestrial animals and plants require water to survive; therefore, when the water enters water bodies the harmful toxins and pesticides affect them all. They have very harmful effects even on humans. They can completely damage the aquatic ecosystem and also reduce fish production in streams and large water bodies; it will lead to major economic loss as well. Many communities living on the ocean banks are completely dependent on the aquatic animals for their survival (Zacharia 2011).

In the USA, a study conducted on the water showed that 90% of wells have pesticides in their water and every stream is polluted due to the presence of pesticides in them (Gilliom et al. 2007). Similarly, a study conducted in the UK showed that drinking water contains more concentration of pesticides, which is harmful to health (Bingham 2007).

## 7.6 Degradation Mechanisms of Pesticides

Through the photochemical, chemical or biological (microbial metabolism) reactions, a herbicide is decomposed into smaller component compounds, and ultimately $CO_2$, water and salts. For certain herbicides, biodegradation accounts for the bulk of the degradation (Freed and Chiou 1981). When a single herbicide degrades, it typically produces many compounds (called “metabolites”), each with its own chemical properties such as toxicity, adsorption ability and degradation tolerance. Some metabolites are poisonous and/or stable in comparison to the parent compound. Most of the time, the origin of the metabolites is uncertain.

Decomposition caused by sunlight is referred to as photodegradation. The strength of sunlight is influenced by a variety of factors, including latitude, season, and time of day, temperature, noise, and shading from soil, trees, and trash, among others. UV light is often used in herbicide photodegradation studies, but whether or not the majority of UV light enters the earth’s surface is a point of contention. As a consequence, photodegradation rates measured in the lab can exaggerate the significance of this process in the field (Helling et al. 1971).

Decomposition by microbial metabolism is referred to as microbial degradation. Multiple microbes can degrade different herbicides, so the rate of microbial degradation is determined by the microbial population present at the time. Warmth, precipitation and high organic content in the soil are suitable for microbial degradation (Voos and Groffman 1997).

Chemical decomposition is decay that occurs as a result of chemical reactions such as hydrolyzation (reaction with hydrogen, typically in the form of water), oxidation (reaction with oxygen) and disassociation (loss of ammonium or other chemical group from the parent molecule). It is unclear how important these chemical reactions are for herbicide degradation in the field (Helling et al. 1971).

## 7.7 Combating Toxicity of Chemical Pesticides by Using Natural Pesticides

Pesticides have proved a boon to the agricultural sector but it is also equally harmful to other living organisms. Overuse of pesticides by farmers results in severe environmental problems including loss of soil fertility, depletion of nutrient reserves, salinization, erosion, and pollution of water systems. These are the disease of ecotopes, and problems like animal genetic resources, elimination of natural enemies, pest resurgence and genetic resistance to pesticides, chemical contamination, and destruction of natural control mechanisms, loss of crop, pest resurgence come under diseases of biocoenosis (Saeedi Saravi and Shokrzadeh 2011). The main problem of civilization is that we search for safer pesticides that are being originated naturally. Alternatives are created or available in terms of pesticides which are a replacement, in the urge of biological pest control, and cover up the specific plant cultivation methods (such as pheromones and microbial pesticides), plant genetic engineering and methods for interfering with insect reproduction (Miller 2004).

There are other environmental friendly methods by which we can control the pests and diseases without harming other species and the environment (McSorley and Gallaher 1996): release of organisms that fight the pests; interfering with insects' reproduction; soil steaming; natural pesticides; biological pest control; plant genetic engineering; and interfering with insect breeding.

By using the method given above we can save the environment, and these methods do not have any side effects, and they can also help to create a balance between many organisms.

## 7.8 Natural Pesticides

Natural pesticides are not the product of chemical manufacturing, but they have a smaller environmental footprint and face a lower risk.

Botanicals, microbials, essential oils and mineral-based biopesticides are the most common types, with all of them derived from plants, insects or naturally occurring minerals. Insects and mites growth inhibitors, *Bacillus thuringiensis* (Kurstaki), horticultural oils, insecticidal soaps, entomopathogenic nematodes and neem products are some of the most widely used and effective natural pesticides. The use of biological materials has the advantage of having a smaller harmful effect on non-target species such as humans (Mordue and Blackwell 1993).

Derived pesticides are compounds present in nature and are the product of plants. Natural pesticides are an alternative to chemical formulated pesticide, but natural one also shows a negative impact on human health as they are toxic too in some amount, which are fast-acting toxins and cancer-causing agents (Regnault-Roger et al. 2005).

Natural pesticides are compounds harvested from plants and are useful in slowing down the growth rate of pests which harm or dormant the development of seeds, shrubs, trees, wood and natural vegetations favourable for humans. Ryania, nicotine, neem, pyrethrins, sabadilla, rotenone, fluoroacetate and carboxin are some of the natural pesticides.

1. **Advantages of Natural Pesticides**:
    - (a) The farmer is familiar with the plants that produce the above compounds since they seem to flourish in the same general location.
    - (b) Environmentally friendly, safer for the user/applicator and highly successful when used properly.
    - (c) These plants frequently have additional benefits, such as insect repellents in the home or medicinal properties.
    - (d) The active product's accelerated deterioration can be advantageous because it decreases the risk of contaminants on fruit.
    - (e) Any of these materials will be used even before being harvested.
2. **Disadvantages of Natural Pesticides:**
    - (a) Since all of these drugs are simply insect deterrents with a sluggish reaction, they are not true pesticides.
    - (b) They are quickly degraded by UV radiation, resulting in a brief residual effect.
    - (c) Plant pesticides are not always less harmful to other species than synthetic pesticides.
    - (d) They are not always available during the year.
    - (e) The majority of them do not have residue tolerances in place.

## 7.9 Nanopesticides

Nanopesticides tend to be an option since they can be used as "smart distribution systems" to unleash pesticides in a controlled and timely manner over a given time period. This will reduce the risk of contamination and the dangers that come with it. The physicochemical properties of nanopesticides, as well as their effectiveness against target and non-target species, must be investigated. Toxicological studies should be carried out because nanomaterials can cause non-specific toxicity in both targeted and non-targeted species (Pradhan and Mailapalli 2020).

Engineered nanomaterials (ENMs) are being more commonly known for use in agriculture due to their unique properties such as small size and high surface to volume ratio, increased permeability, thermal stability, solubility and biodegradability (Nair et al. 2008; Lin et al. 2014; Ranjan et al. 2019).

Because of the special properties of nanoparticles, they may be used to encapsulate agrochemicals in more compact and safer forms, resulting in increased crop production and productivity over time. Risk to the atmosphere and human well-being could be avoided if these nanoparticles were used more effectively (Yata et al. 2018).

There have been several studies on the use of ENMs in agricultural industries, such as the production of nanofertilizers and nanopesticides, as well as their use as an important remedial measure in pesticide identification (Zhu et al. 2008; Lin and Xing 2007; Noji et al. 2011; Pradhan et al. 2013a, b, 2014, 2015; Ghafariyan et al. 2013; Chandra et al. 2014; Kim et al. 2015; Servin et al. 2015; Dubey and Mailapalli 2016).

Nanopesticides are small molecules that are only used in pest control derivatives and/or encase the active ingredient in the pesticide in a protective nanocarrier (Kookana et al. 2014). They must ensure that precision farming is improved by “smart field management”. They have a higher surface-to-volume ratio and quantum effects due to their limited scale, peculiar phase transition and stabilization (Bakshi et al. 2015; Kuswandi 2019).

ENMs can reduce photo-degradation and improve the physicochemical stability of the materials (de Oliveira et al. 2014). As a result, a new diffusion-, erosion- and swelling-controlled nanodevice can be tailored to deliver active pesticidal components to the intended agricultural pest with increased longevity and efficacy while avoiding environmental contamination risks (Choudhury et al. 2012; Chowdhury et al. 2017).

## 7.10 Conclusion

More technological breakthroughs could be made in the future to aid in the production of healthier and safer food. Increasing the supply of food per capita, i.e. providing adequate food for the people, may be done by a range of technical means currently in existence.

Modern agribusiness employs a vast number of pesticides as a result of increasing food intake. This has resulted in major advancements in agricultural processing, but it has also resulted in a slew of environmental and health issues. The data on benefits and environmental-health risk management studies discussed in this study can be used as a tool for deeper understanding.

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# Pesticides and Their Effects on Plants: A Case Study of Deltamethrin

# 8

Zahid Hameed Siddiqui, Zahid Khorshid Abbas, Abid Ali Ansari, Mohammed Nasir Khan, and Wahid Ali Ansari

## Abstract

The current scenario of climate change and population explosion compels the humankind to device mechanism to meet the global food security. The application of chemical pesticides is one of the easiest and most extensive method to guard crop fields from pests and generate plenty yield. Although the pesticides have affirmative effects in increasing agricultural production, it harms the environment, especially soil and water. As a result of their usage, soil pollution by pesticides moves to higher trophic levels in the food chain. The WHO allowed the use of only three natural pesticide derivatives of the pyrethroid group, namely deltamethrin, permethrin and alpha-cypermethrin. Pyrethroids are the synthetic form of natural pyrethrins from the plant *Chrysanthemum cinerariaefolium*. These derivatives are more effective and toxic to insects as compared to vertebrates. Deltamethrin is classified as moderately hazardous insecticide and applied to a wide range of insect pests to protect the crops and animal health. It is a neurotoxic and acts when insect comes in direct contact to it or if they eat it. In case of plants, the use of pesticide generates oxidative stress to plants in a quantitative manner. The oxidative stress generates reactive oxygen species (ROS) and results in breakdown of proteins and chlorophyll pigments occur. This results in decreased photosynthetic efficiency and productivity of plants. The

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plant manages oxidative stress by activating the antioxidative defense system of plants, which contains enzymatic and non-enzymatic antioxidants. This system assists in neutralizing ROS and decreases the oxidative stress in plants due to pesticide toxicity.

**Keywords**

Pesticide · Deltamethrin · Sustainable development · Pyrethroids · Oxidative stress

## 8.1 Introduction

In the current scenario of climate change and boom in global population, humans are facing several challenges. The climate change brings floods, droughts, excesses of rains, and increase in global mean temperature. As result of population explosion an increase in supplies, enormous waste generation, pollution, and issues of food security are at alarming levels. In order to increase the global food production, application of pesticides becomes a key practice to check fungal, insects, or weeds growth in the agribusiness industry. It further brings out the associated issues of human and animal well-being as well as the dilapidation of the environment. These issues are extra rampant in emergent nations due to the extensive application of pesticides, and lack of good agricultural practice (Ecobichon 2001; Abhilash and Singh 2009; Albaseer 2019). The toxicity of pesticides compels the World Health Organization (WHO), the European Union (EU), and other countries to frame sustainable laws to govern their usage. The WHO allowed the use of only three natural pesticide forms of the pyrethroid group, namely deltamethrin, permethrin, and alpha-cypermethrin (EU Directive 2009; WHO 2014, 2015, 2016, 2017; CDC 2017). Pyrethroids are the artificial form of regular pyrethrins from the plant *Chrysanthemum cinerariaefolium*. These derivatives are thousand times extra poisonous to insects as compared to vertebrates. The high degree of toxicity is due to insect's lower body temperature, small size, and higher sensitivity to sodium channels (Bradberry et al. 2005; Chrustek et al. 2018; Hassaan and El Nemr 2020). The toxicity of pyrethroids to different types of water faunas such as shellfish (lobster, crayfish) and fish (Rainbow trout, Carp, Danio rerio) are reported by authors. They affect the ion channels in neuronal membranes as well as the mitochondrial membranes (Burridge and Haya 1997; Lutnicka and Kozínska 2009; Toynton et al. 2009; Lidova et al. 2016; Wang et al. 2017; Cárcamo et al. 2017). Pyrethroids are insect repellent suggested for combating insects, spreading infectious microorganisms to humans and animals. They are commonly use in households, agriculture, horticulture, and forestry as well as in medicine and veterinary medicine (Bradberry et al. 2005; Soderlund 2012; WHO 2014; Glorennec et al. 2017; Touzout et al. 2021). Although the pesticides have affirmative effects in increasing agricultural production (Aktar et al. 2009; Palangi et al. 2021), it harms the environment, especially soil and water. As a result of their usage, soil pollution by pesticides moves to higher trophic levels in the food chain (Han et al. 2017). Deltamethrin (DM) is an insecticide belonging to the pyrethroid family. It is a potent neurotoxin making rapid attack on the insect's nervous system (Shirani et al. 2016). The US Environmental Protection Agency (EPA) due to its toxicity limits the use of deltamethrin (De la Cruz et al. 2014). Besides that, it is used as a pest control agent worldwide for over 30 years for several crops such as cotton, maize, soybeans, cereals, and vegetables (Cycoń et al. 2014). Over the year use of deltamethrin revealed that its residues persist in the environment, particularly in soil and water (You et al. 2009; Bragança et al. 2019). Although it is less toxic to human beings, its long-term usage at a dose of 0.25–1% poses risks of headaches, abdominal pain, diarrhea, vomiting, nausea, and other allergic reactions (Kumar et al. 2011; Tang et al. 2018). Therefore, it is very important to make a check of residual levels of synthetic pyrethroids in fresh fruits and vegetables as well as in other foodstuff made of fresh agricultural produces (Albaseer 2019). In the whole scenario, the usage of pesticides also results in toxicity of plants that pose negative effects on the growth and development of plants. The indiscriminate use of pesticide causes reduction of chlorophyll and protein contents, which decrease the photosynthetic efficiency of plants. Further, pesticide stress generates reactive oxygen species that results in oxidative stress to plants (Bashir et al. 2007; Parween et al. 2016; Sharma et al. 2017a; Shahzad et al. 2018). Recently, Karaismailoglu and Inceer (2017) evaluated the genotoxic and cytotoxic effects of DM on root cells of *Helianthus annuus* and reported its potential damaging effects. The objectives of this chapter are to arrange a comprehensive update of the use of DM in the agribusiness industry and its potential hazards on the plants. In short, this chapter will discuss the basics of DM, its effects on the environment, and usage on plants as a pesticide as well as its effects on the physiology of plants and its consequences.

## 8.2 Deltamethrin: Chemical Properties and Application

Deltamethrin (DM) was first described in 1974, came in market in 1978, and listed by the US EPA in 1994, and it was not considered as mutation agent, genotoxic, teratogenic, or carcinogenic (Johnson et al. 2010; WHO 2017; Chrustek et al. 2018; NPIC 2021). It belongs to type II pyrethroids with a chemical formula of $C_{22}H_{19}Br_2NO_3$ (Fig. 8.1). As per WHO, DM falls under the category of moderately hazardous insecticide and applies to control a wide range of insect pests for plant

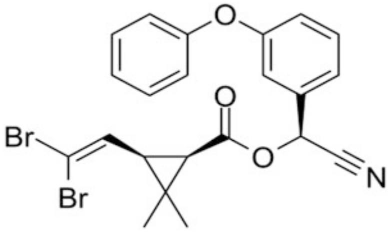
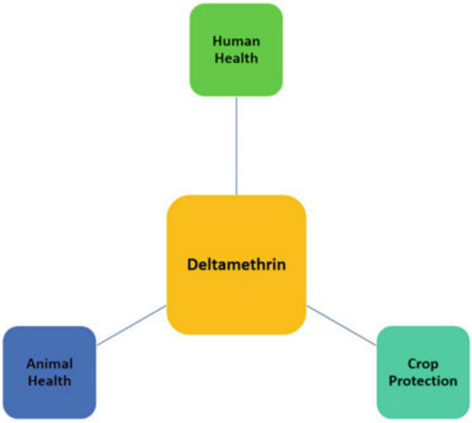


**Fig. 8.1** Structure of deltamethrin

**Fig. 8.2** General use of deltamethrin



protection animal health (Elyazar et al. 2011). It is used in crops as well as to control ticks, lice, fleas, whiteflies, tse-tse flies, aphids, spiders, bees, bedbugs, ants, and cockroaches (Shafer et al. 2008; NPIC 2021) (Fig. 8.2).

It also effectively controls the means of dengue and malaria like *Aedes aegypti* and *Anopheles gambiae* by soaking mosquito nets in DM solution (Kumar et al. 2011; CDC 2017). The marketing of DM is done in a variety of products ranging from wet powders, aerosols, granules, sprays, dust, and granules to kill an array of insects (NPIC 2021). In its variable form, DM is used to ensure harvest within the crop-field and in warehouses after season's growth to reduce yield loss.

## 8.3 Mechanism of Action

DM is a neurotoxic pyrethroid insecticide and acts when insect comes in direct contact to it or if they eat it. The neurotoxic action of DM is associated by the delayed opening of voltage-gated sodium channels which results in membrane depolarization of neurons, repetitive discharges, and synaptic disorders causing hyper excitatory indications of insects killing (Soderlund 2012; Costa 2015). Apart from sodium channels, DM also disturbs the role of the chloride and calcium channel of the neuron (Bradberry et al. 2005; Soderlund 2012). DM shows low toxicity to mammals owing to their large form, less perception to chemicals, and slightly higher body temperature (NPIC 2021). The DM can affect animals via digestive, respiratory, and skin system and cause nausea, vomiting, drooling, muscle tremors, headaches, dizziness as well as skin sensations like itching, tingling, burning, or numbness (Kumar et al. 2011; Chrustek et al. 2018; Zheng et al. 2020; NPIC 2021).

## 8.4 Effects of Deltamethrin on Environment

The application of different varieties of insecticides is responsible for pollution of water, air, soil, and overall ecosystem that leads to grave health risk for all living organisms. As stated earlier the use of synthetic pyrethroids are increasing day by day in agribusiness and associated pest control issues. The indiscriminate use of pesticide to control the infestation of insects, fungal, and weed growth has own environmental concerns. The pyrethroids' metabolites and their breakdown products impart cancerous and disturbing effects that result in pollution of different components of environment (Tsuji et al. 2012; Thatheyus and Selvam 2013). However, the harmful effects of pyrethroids to humans are less because of their rapid degradation. In areas of Mexico, where malaria is prevalent, environmental perseverance of DM was conducted. The mean half-life of DM was 15.5 days for outside samples and 15.4 days for inside samples (Ortiz-Pérez et al. 2005). In a long run DM traces were present in the environment, especially in water and soil (You et al. 2009). In the environment, DM is degraded by different hydrolysis process, depending on soil type and oxygen availability. The photolysis damage reduces DM and microbial activity with a half-life ranging from 11 to 72 days (Cycoń et al. 2014). In organic soil the half-life of DM is slightly longer as compared to non-organic soil (Ismail et al. 2015), whereas in sandy loam soils in anaerobic condition the half-life of DM was between 31 and 36 days (Tomlin 2006). In another report, Song et al. (2015) suggested that the improved lethalness of pyrethroids was antagonistic with its disintegration speed in soil and these pyrethroids may sustain for months in soils (Oudou and Hansen 2002). Therefore, we can decipher that the disintegration of DM is connected to the diverse organic component and soil type (Palangi et al. 2021). The impact of DM in a cabbage planted soil microbial community structure was evaluated by Bragança et al. (2019). The degradation half-life time of DM in soil was 8.8 days and the degradation rate was 0.079 day$^{-1}$. The author noticed that usage of DM enhances the 3-PBA metabolite and move in the soil microbial community structure was manifested after 30 days. The NGS data of the 16S rRNA of soil microbial community revealed that *Nocardioides* sp. and *Sphingomonas* sp. had a significant increase. These bacteria are known to weaken pyrethroid and 3-PBA.

## 8.5 Effects of Deltamethrin on Plants

In order to achieve the global food security for the increasing global human race, pesticides are widely applied in contemporary agribusiness industry, and it is an efficient and cost-effective method to increase the yield quality and quantity of the food crops (Tomer 2013; Sharma et al. 2019). The crop plants face a diverse array of insects such as leaf rollers, cut worms, soil insects, aphids, as well as fungal bacterial and viral infections, and pesticides are generally used to control them (Goh et al. 2011). It is a known fact that we have several new avenues such as use of biotechnology to develop transgenic varieties of pest resistant crops and use of biopesticides to control the pest menace. Despite that, the application of synthetic pesticides is one of the easiest and most extensive methods to guard harvests from pests and generate large produce. Mueller-Beilschmidt (1990) reported the accumulation of DM on the leaf of the investigational plants in one season. After frequent use, the authors recorded ten times more DM concentration as compare to the initial concentration. This rate of accumulation is much greater relative to the degree of DM degradation. Moreover, there are several reports that suggest pesticides residue are present on the crops, and the average recorded disintegration half-life for pyrethroids in plants range from 1.1 to 5 days (Fantke and Juraske 2013). It appears that differentiable disintegration of specific pyrethroids generally varies on the form of pesticides. The disintegration of DM on the silage and shells of chickpea happened at quicker speed relative to cypermethrin and fenvalerate (Srivastava and Sehgal 2015). For a detailed disintegration of DM on crop, a recent review by Albaseer (2019) can be consulted. Apart from the half-life of DM on crops, the effects of DM on the crop physiology are also very important to know. In general literatures are available suggesting that use of pesticides adversely disturbs the plant growth and development (Sharma et al. 2015; Shahzad et al. 2018). The use of pesticide generates oxidative stress to crops that resulted in the creation of reactive oxygen species (ROS) (Sharma et al. 2018; Touzout et al. 2021). The oxidative stress breaks down proteins and chlorophyll pigments and it ultimately results in decreased photosynthetic productivity of crops (Sharma et al. 2015). The plant manages oxidative stress by activating the antioxidative security arrangement of plants, containing enzymatic and non-enzymatic antioxidants (Sharma et al. 2015). This system assists with ROS scavenging and decreases the oxidative stress in crop plants due to pesticide toxicity (Sharma et al. 2015, 2017a, b). Bashir et al. (2007) evaluated antioxidative reaction system of *Glycine max* after using DM. The data was recorded after pre-flowering, flowering, and post-flowering phases and different aspects of Asc-Glu cycle were evaluated. The authors monitored a decrease in the total ascorbate content, whereas an increase in proline content, lipid peroxidation, and total glutathione content relative to control was noted. The antioxidants enzyme activities such as ascorbate peroxidase, superoxide dismutase, and glutathione reductase were significantly increased and decline in catalase was observed with increasing concentration of DM. The *G. max* was found as a delicate type where higher amount of DM create oxidative stress, which interrupts the Asc-Glu cycle. The use of DM on the potato tubers nutritional value was investigated and found an increased level of starch compared to control. However, the use of DM makes no change on the amylose percentage but the amount of total protein was decreased. Besides that, the level of free amino acids and ascorbic acid content was improved. Fidalgo et al. (2000) concluded that the nutritive worth of successor tubers of potato plants was not harmful after the treatments with DM.

Earlier, Fidalgo et al. (1993) described that the use of DM extends the life span of potato crops as well as enhanced the Rubisco activity; the possible reason that increased the starch in the potato tuber. In order to control the damage caused by onion thrips (*Thrips tabaci*) to cabbage crops, a block-design experiment was conducted (Trdan et al. 2007) by spraying DM. The leaf damage percentage was recorded on the outer leaves relative to the placement of the leaves from exterior to interior side. The authors concluded that one spraying was sufficient to control the damage of leaf caused by onion thrips.

Duran et al. (2015) examined the outcome of variable doses of DM on the germination, morphological, anatomical, and physiological changes on Maize. After 7 days of treatments the said aspects were evaluated; a 61% decrease in seedling growth with increasing DM levels (0.5 ppm) was observed. A reduction in stomatal density and stomatal dimension occurs with higher amount of DM. Furthermore, the photosynthetic pigments like chlorophyll a, chlorophyll b, total chlorophyll, and caretonoids were reduced with the surge in DM application. Inversely, anthocyanin and proline content were improved corresponding with DM application as compared to control. After the application of pesticides, the contamination of soil is inevitable and combined pollution of pesticide along with heavy metals is a new norm in agricultural fields. In a study by Touzout et al. (2021), the poisonous outcomes of DM and Cadmium (Cd) were examined singly and in grouping on tomato plants. The growth rate and concentration of photosynthetic pigments were significantly decreased on the application of DM and Cd. However, Cd application was more harmful as compared to DM but both deltamethrin and cadmium initiate $H_2O_2$ aggregation and lipid peroxidation. The upregulation of different anti-oxidative enzyme actions (APX, CAT, POD, and PAL) and non-enzymatic like reduced glutathione and proline was also recorded. The findings confirmed the part of oxidative stress induced by DM and Cd toxicity. Further, under a combination condition, deltamethrin and cadmium had collective effect on the photosynthetic pigments and growth of the tomato plant and an incompatible interface on antioxidant protection.

In case of sunflower, Karaismailoglu and Inceer (2017) recorded a decrease in root growth with increasing DM concentration as compared to control. The higher concentrations of DM compromised the root morphology in the form of blackout and show damaging effects on the root cells, they looked amorphous, with a friable cell wall, enhanced cell size and in many instances; cellular separation was detected in a light microscope. These assessments are the signals of cell death due to DM (Lerda et al. 2010). Besides that, burning and cloudiness in the roots occur after 48 h treatment of >2 ppm DM. Further, Karaismailoglu and Inceer (2017) evaluated the possible genotoxic and cytotoxic effects of DM on the chromosomes of sunflower root meristem. The Mitotic index was inversely related to higher DM concentration to each contact time. The mitotic irregularities were noticed as laggards, stickiness, c-mitosis, disturbed prophase, and chromosomal bridges. The micronucleus was present during interphase and its occurrence was measured in the test solutions. The micronucleus formation was greater at 2 ppm compared to variable DM consistency at all contact times.

## 8.6 Conclusion

Nowadays, among the pesticides, man-made pyrethroids are one of the conventional forms of pesticide used (Burns and Pastoor 2018). During the last 10 years, the high efficiency and reduced toxicity of DM in comparison to other insecticides make a significant increase in the application of DM. It is applied in agribusiness, residential consumer applications, and commercial pest control (Yoo et al. 2016; Albaseer 2019; Touzout et al. 2021). The use of DM is found to be very effective in terms of pest control; however, there are results reported by authors that give contrasting remarks about its degradation half-life in the environment. It was found that DM degradation is affected by several environmental factors including soil types, oxygen availability, and soil microbial community. The ramifications of DM on plant growth and development were dose dependent. At higher concentration DM results in loss of photosynthetic pigments, thereby decreasing photosynthetic efficiency or productivity of the plant. Further, it causes oxidative stress and results in a disturbed Asc-Glu cycle.

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# 9

# The Use of Glyphosate in Regions of Argentina and Colombia and Its Socio-Environmental Impacts

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## Abstract

The massive use of agrochemicals has made possible to increase food production on a global scale; however, it has also caused multiple impacts on the environment and human health. In several South American countries, currently predominates an agro-industrial production model based on a technological package that includes transgenic seeds resistant to the herbicide glyphosate (GLY), as well as specialized machinery and other inputs. Such is the case of Argentina, a country in which transgenic soybean, corn, and cotton monocultures occupy millions of hectares and represent a large part of foreign exchange earnings. This model implies the discharge of massive amounts of GLY and other agrochemicals into the environment, also affecting the health of rural populations. In contrast to its use in grain production, GLY and other herbicides have been widely used in Colombia in the control of illicit crops, in particular *Erythroxylum* spp. In the present work, different socio-environmental aspects of the use of GLY in Argentina and Colombia are analyzed, contributing to the discussion on the need to implement new production models that value biological diversity and guarantee the provision of ecosystem services.

## Keywords

Commodities · Agrotoxics · Ecotoxicity

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## 9.1 Introduction

In modern times the world food production system has been changing from the development of new technologies such as the application of chemical inputs and genetic engineering to agricultural work. Thus, a great variety of genetically modified (transgenic) seeds have been developed which are dependent on commercial inputs; they contribute to the so-called "homogenization of agriculture" that ends up promoting monoculture, drastically reducing biological diversity and environmental services in agroecosystems (de Groot et al. 2021).

The presence of pesticides in agricultural production is not something typical of today; the first reports of these practices can be found in Homer's Odyssey, where the use of sulfur to fumigate plants is mentioned. During the sixteenth century, in China, farmers applied small doses of arsenic and nicotine as insecticides (Carreño 2005). In the middle of the twentieth century, the use of agricultural inputs of biological and later on of chemical synthesis became popular, giving rise to the "green revolution." This framework has made it possible to attack plants, insects, and other undesirable organisms within the production system and at the same time add fertilizers to the soil artificially, thus accelerating the rate of world food production. Over the past decades, the farmers have been able to significantly increase world cereal production with little increase in the total area under cereal cultivation (Borlaug 2005). In this way, the availability of food has also increased for a human population that has been growing steadily worldwide, going from approximately 2500 M people in 1950 to 7800 M today.

In 1942, during the Second World War, Paul Hermann Müller, winner of the Nobel Prize in Medicine and Physiology in 1948, discovered in Switzerland the insecticidal properties of DDT ($p,p'$-dichlorodiphenyltrichloroethane). This compound was synthesized for the first time in 1874. In parallel, German laboratories began to produce organophosphate pesticides. In 1945, carbamates were discovered in England, and research into organochlorines led to new and more effective products. Starting in 1950, there was an exponential growth in the use of pesticides, until then, with unknown health and environmental consequences (Carreño 2005). In contrast to the economic benefits that bring greater food production in the same extension of land, the damage caused to the ecosystems and to the health of individuals who had direct or indirect contact with agricultural inputs of chemical synthesis began to be registered. At the beginning of the 1960s, it was already known that some synthetic chemicals could be found practically all over the planet, also affecting biota. In addition, it was observed that substances such as chlorinated pesticides could accumulate in living beings (bioaccumulation), increasing concentrations in tissues at higher trophic levels by predation, a process called biomagnification (Camps et al. 1989). These statements were a worldwide warning voice calling the attention to politicians and scientists who dedicated themselves to research the effect of chemical pollutants on human and animal health and on ecosystems.

According to FAO (2003), the term pesticide is defined as a substance or mixture of substances used to prevent or control any species of plants or animals harmful to other plants, animals, or humans; it also includes other substances or mixtures thereof used as plant growth regulators, defoliants, and desiccants. This term does not apply to antibiotics, fertilizers, or other chemicals supplied to animals for different purposes, such as stimulating their growth and reproductive behavior.

There is a wide variety of chemically synthesized pesticides, which are artificially processed. Some of these substances are not easily biodegradable and once applied can leave traces that take several decades to disappear. Other pesticides have high levels of toxicity whose effects can be difficult to quantify, since they can be evidenced immediately, in the long term or in the offspring of those who were exposed to these substances.

Glyphosate (*N*-(Phosphonomethyl) glycine) (GLY) is a non-selective, water-soluble, systemic herbicide of the phosphonate group. It is applied in post-emergence, especially for the chemical control of weeds in transgenic crops resistant to its toxic action: soybean (*Glycine max* L.), corn (*Zea mays* L.), and cotton (*Gossypium hirsutum* (L.) Merr.) and in the so-called “illicit crops,” among which *Erythroxylum* spp. stands out. The transgenic varieties are genetically modified to resist the action of the herbicide, which in non-genetically modified plants produces the inhibition of the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS), involved in the synthesis of the aromatic amino acids tyrosine, tryptophan, and phenylalanine (Carriquiriborde 2010). Currently it is also increasingly used as a desiccant, to favor the harvest of grains (Van Bruggen et al. 2018).

Some physicochemical characteristics of GLY allow it to be differentiated from other herbicides, for example its amphoteric character due to the presence of acidic and basic groups in its molecule, and its high polarity (Hernández 2010). Although it is a herbicide with relatively low toxicity for non-target organisms such as some species of native fish from South America (Carriquiriborde 2010), due to its widespread use in vast areas of this and other regions of the Globe, it is essential to study its behavior and effects in the environment.

The present work aims to analyze different aspects of the socio-environmental problem of the use of GLY in different regions of Argentina and Colombia, based on the review of relevant published works on the subject.

## 9.2 GLY Use in Argentina

Industrial agriculture is based on a technological package that includes genetically modified organisms (GMOs), specialized machinery, herbicides, and other pesticides. These chemical compounds are applied many times simultaneously and can contaminate soils, surface and groundwater, and sediments. In Argentina, industrial agricultural production uses massive amounts of the herbicide GLY, approximately 240,000 t/year (Ávila-Vázquez et al. 2018) for the production of soybeans, corn, and cotton, with approximately 23 M hectares destined for these crops (Berman et al. 2018). GLY is used at least four times a year in batches with continuous soybean crops or in soybean, corn, and cotton rotation (Berman et al. 2018; Scursoni et al. 2014). To put in context the importance of the cultivation of transgenic soybeans, the most important in economic terms, it can be mentioned that during the first 4 months of 2021, net exports of soybean-derived products (beans, flour, oils, pellets, biodiesel, and its mixtures) amounted to USD 6980 M, representing 32.4% of total argentine exports (USD 21,550 M) (INDEC 2021).

The Pampas of Argentina is the most relevant region in terms of agricultural and livestock production, and also is one of the regions where the use of GLY is more widespread. This practice derives from the productive changes in the last decade of the twentieth century, with the current predominance of direct seeding. This progressive conversion towards direct seeding implied a decrease in edaphic erosion problems but significantly increased the use of GLY and other agrochemicals (Binimelis et al. 2009). It should be noted that GLY's commercial preparations contain other substances including adjuvants, in particular surfactants such as polyoxyethylene amine (POEA). These substances are added to the mixture in order to increase the absorption and translocation of the active principle by plants (Van Bruggen et al. 2018). On the other hand, other herbicides and pesticides are often used together with GLY, for example, cypermethrin, chlorpyrifos, and endosulfan (Carriquiriborde 2010). Pérez et al. (2017) found 14 pesticides or their metabolites with detection frequencies greater than 40% in samples of surface water from a stream in an agricultural area in the south of the province of Buenos Aires, mainly destined to the cultivation of soybeans.

In Argentina, the use of GLY is not only widespread in the Pampas, but also includes other regions (Fig. 9.1) less suitable for agriculture, such as the Gran Chaco or the Yungas, located in the northern part of the country. In these regions, large areas were gradually destined to the production of transgenic crops through the technological, financial, and agronomic export of the Pampean model, in a process called "pampeanization," with an increase in the deforestation process (Pengue 2005).

The massive application of commercial GLY preparations involves effects of varying magnitude in the environment, which are usually not easy to foresee due to the complexity of the dynamics of this pollutant. Once released into the environment, GLY undergoes mainly biological degradation, its major metabolite being aminomethylphosphonic acid (AMPA). Although it is normally considered a low persistence herbicide, Primost et al. (2017) indicate that it could be considered a pseudo-persistent pollutant, since the application rate could be many times higher than its degradation.

In soils, the mobility of GLY is mainly affected by the content and type of clays and the cation exchange capacity (CEC), and in general it can be retained mainly in the most superficial layer of the soil (0–9 cm) (Lupi et al. 2019). Immobilization occurs by adsorption through the formation of surface complexes (dos Santos Afonso 2010). The concentrations of GLY + AMPA tend to decrease with the depth of the soil and can be strongly correlated with the concentrations of organic carbon (+ correlation) and pH (− correlation); however, there is also a risk of transport through the soil until reaching the groundwater (Lupi et al. 2015). In soils with a sandy texture, a higher content of organic carbon would limit the mobility and dispersion of GLY. On the other hand, although GLY has a relatively

**Fig. 9.1** Approximate limits of the main agricultural areas dedicated to extensive grain production in Argentina and of the most fumigated areas of Colombia during the 2008–2012 period to control illicit crops. (Source: prepared based on de Abelleyra et al. 2019 (Argentina) and Rodríguez 2020 (Colombia))

short half-life in soils, its degradation in other environmental matrices could be limited, for example in the sediments of water courses that receive surface runoff from fields where this herbicide was applied (Lupi et al. 2015). Another source of GLY in soils is its release by plants as root exudates or later from the decomposed biomass (Gill et al. 2018).

Due to the fact that GLY is strongly adsorbed by soil components such as clays, aluminum and iron oxides, and humic acids, its presence in surface and groundwater would not be foreseeable (Hernández 2010). However, it has been detected in a medium concentration of 0.60 μg/L in surface water samples in tributaries of the Paraná River (Ronco et al. 2016), one of the largest rivers in South America and the world. On the other hand, the authors of the aforementioned work highlight that

GLY and AMPA were detected in 17% and 37%, respectively, of the sediment samples extracted in the middle and lower reaches of the tributaries, with mean values of 742 μg GLY/kg and 521 μg AMPA/kg, confirming the preferential affinity of these substances for sediments. The detection of GLY and AMPA in sediments was correlated with the presence of sulfides and copper (Ronco et al. 2016). Lentic environments are also affected by the use of GLY in their drainage basins. Berman et al. (2018) found GLY in a large part of the sediment and water samples from shallow pampean lagoons, and to a lesser extent and concentrations in the suspended material, but found no remains of the herbicide in lakes in northern Patagonia, outside the Pampas region. However, authors emphasize that the process of transport and degradation of this toxin in the environment is very dynamic and complex, and depends on factors that operate at both a regional and local scale. For example, the appearance of pollution pulses is related on a regional scale to the time of application and the occurrence of rainfall. At a local scale, factors such as the type of crops, times of application of the herbicide, and fumigation machinery washing are probably relevant.

In a study on the presence of GLY and atrazine, the most widely used herbicides in Argentina, Alonso et al. (2018) detected these substances in more than 80% of the rainwater samples in GLY concentrations of 1.24–67.3 μg/L (medium to maximum) in urban areas of the Pampean region, with different degrees of land use and with extensive agricultural production. The results found highlight the importance of the wet deposition process in water, soil, and sediment contamination. In recent pioneering studies, Haberkon et al. (2021a, b) found GLY and AMPA in atmospheric particulate matter (PM10) associated with wind erosion and suspension of soil particles from unpaved roads in rural agricultural areas. The concentrations found in PM10 were higher than those determined in the soil. The occurrence and concentrations of GLY and AMPA in the soil and PM10 are related to the use and management of the soil, observing lower concentrations of these substances in areas with permanent pasture cover (Haberkon et al. 2021a).

Peruzzo et al. (2008) found GLY in concentrations of 0.10–0.70 mg/L in surface waters in a basin in the north of the province of Buenos Aires, while in sediments and soils the values fluctuated between 0.5 and 5.0 mg/kg. The temporal variation in GLY levels was directly related to the time and dose of herbicide application and the occurrence of rainfall events. Bollani et al. (2018) found the highest concentrations of GLY (2.38–13.6 μg/L) in surface waters of a stream in the province of Buenos Aires after copious rainfall. In this way, GLY can be transported from terrestrial areas to surface waters after rain events (Aparicio et al. 2013), while vertical transport to groundwater also increases. Lupi et al. (2019), indicate that the fraction of this herbicide that can reach surface waters through runoff is much higher than that which can reach groundwater by leaching. However, both transports depend on the type of soil, the presence of vegetation cover, and the slope (Borggaard and Gimsing 2008). The presence of GLY and AMPA in rainwater is associated with spray drift and indicates that precautions should be taken for the use for human consumption of rainwater collected in areas close to productive plots, especially in periods of herbicide application and after prolonged droughts (Lupi et al. 2019).

Bollani et al. (2018) found high concentrations of GLY in surface waters in coincidence with a high level of excreta from cattle. Krüger et al. (2014) reported that GLY concentrations in the urine of cows fed with genetically modified crops were higher than in cows without this management. This source of GLY should be considered taking into account that in Argentina, the balanced feed industry processes 320,000 t of soy annually (Ciani et al. 2018).

The implementation and regulation in the disposal of empty containers of GLY-based herbicides is a current environmental problem. The continuous generation of packaging, its waste, and the lack of management in its final disposal cause a great pollution of natural resources. In addition, it affects the health of the producer and the inhabitants of the area (UnIDA 2007). In Argentina, around 5700 t of GLY containers were used in 2007. Once discarded, these can contain up to 5% of remaining formulations, implying an impact on the ecosystem if these are not treated or disposed of properly (CASAFE 2009). The recycling of plastic containers implies their washing using different modalities: triple washing (washing by manual shaking with three determined aliquots of water), pressure washing (pressure equipment is used), and integrated rinsing (agrochemical application equipment to which container washing is integrated). In Argentina, the triple washing system is used in recycling plants, which is currently regulated by IRAM 12069 standards (CNIA 2009). Neder (2010) determined the remaining GLY concentrations after applying the triple wash on empty containers, obtaining the following results: first wash cycle 5742 mg/L, second wash cycle 118 mg/L, and third wash cycle 2 mg/L.

## 9.3 GLY Use in Colombia

GLY in South America is not only used for weed control in extensive grain crops, but also for the control of illicit crops, for example in Colombia. This country is located in the northern region of South America, has coasts in the Atlantic Ocean to the north, Pacific Ocean to the west, and crosses the Ecuador line to the south, and this geographical position provides thermal stability throughout the year and the mountainous complex of The Andes allow it to have great variability of thermal floors and ecosystems including jungles, forests, savannas, moors, and one of the rainiest spots in the world in the biogeographic Chocó (Bahamón 2012). The tropical Andes form ecological complexes where altitude differences shape a great variety of environments over relatively short distances, constituting one of the most important nodes of plant diversity in the world (Young et al. 2002). Small-scale coca (*Erythroxylum* spp.) cultivation is part of the cultural tradition of the original peoples in Colombia; however, in the last three decades it has increased in such a way that the country came to be the epicenter of world cocaine trafficking (Alfonso-Roa et al. 2020).

The production of plants with hallucinogenic properties receives in Colombia the colloquial name of “illicit crops” and its eradication has been one of the main objectives of public management through decades and governments of all political ideologies. The coca bush is easily cultivated in tropical and subtropical humid forests, areas of mountainous forest and Andean forest between 1000 and 2000 m above sea level; however, there are varieties that can grow and develop in much more extensive altitude ranges and in soils with low agricultural vocation, which facilitates the transhumance of crops which is reflected in the growth of coca activity in certain municipalities simultaneously with the decrease in other areas of the country, and this phenomenon does not allow the different eradication strategies to present acceptable advances and instead considerably increases deforestation (Alfonso-Roa et al. 2020) and violence against communities (Mejía and Restrepo 2013).

Faced with this uncertain panorama, and almost impossible to quantify panorama, since the 1980s in Colombia, different herbicides such as paraquat, triclopyr, imazapyr, GLY, and tebuthiuron have been used experimentally or within eradication programs, each of these substances associated with damage of different magnitudes on public health and the environment, GLY being chosen to fumigate coca and marijuana crops due to its "lower toxicity" (Hidrovo 2004). In 1999, the "Plan for Peace, Prosperity, and the Strengthening of the State," known as "Plan Colombia," was created, which seeks to reduce illicit crops in Colombia gradually until their eventual disappearance. Since that year, one of the main strategies of the Colombian government to combat illicit crops has been aerial spraying with herbicides (Fig. 9.1), a decision taken unilaterally without taking into account the participation of affected rural populations. As is to be expected, GLY is not a selective herbicide since it affects illicit crops but also other crops developed within the framework of legality, both commercial and subsistence crops (Rodríguez 2020).

Between 2000 and 2015, about USD 9.6 billion were invested in the implementation of Plan Colombia (DNP 2016). After more than 15 years of fumigations, it was evidenced that the eradication of crops by this means has a scarcely transitory efficiency since once the spraying period has passed, the areas are replanted with coca bushes (Rodríguez 2020) being necessary new sprays increasing thus the effects on health, the environment, and the economy.

The communities living in fumigated areas suffer economic losses by registering deaths of farm animals such as chickens and cows that drank water contaminated with GLY as well as considerable decreases in the production of corn crops (Espinosa 2009). Consequently, there are also job losses that are reflected in an economic crisis that in the long term tends to lead peasant communities to relapse into illicit crops as a source of survival (Osorio 2003).

Considering that GLY has been identified as an herbicide used in Colombia to eradicate illicit crops in rural areas and given the evidence of its toxicity, it is necessary to determine if anti-drug policies prevail in the face of the rights of human health and the healthy environment (Rivera 2005).

## 9.4 Health Issues

The massive use of GLY-based herbicides is not only associated with various environmental problems but can also have a direct impact on human health. Exposure occurs at the time of application or from spray drift. Other forms of exposure to the herbicide are through contact with contaminated soils and water and the ingestion of grains and foods containing traces of the herbicide and other substances present in commercial preparations (Coscolla 1993; Gill et al. 2018; Romano et al. 2009).

There is evidence of direct effects of GLY on early mechanisms of morphogenesis in vertebrates (Paganelli et al. 2010). In vitro studies in rodents published by Coullery and Rosso (2012, 2013) show a delay in development characterized by a decrease in axonal elongation and neuronal complexity. Although the commercialization of pesticides requires previous toxicological studies in rodents or other organisms, it was observed that in some cases the tests are weak because they do not cover the total life cycle of rodents, whose average life span is 24 months, questioning the validity of GLY safety (Rossi and Cabaleiro 2018).

High environmental exposure to GLY by rural populations has been associated with various conditions, including an increase in the frequency of reproductive abnormalities such as spontaneous abortions and congenital malformations (Ávila-Vázquez et al. 2018), although the authors highlight that it is not possible to establish a cause-effect relation and further research is required in this regard. In the long term, exposure to agrochemicals causes chronic and carcinogenic effects on human health and the life cycle of animals, with prolonged exposure (Rossi and Cabaleiro 2018). Mortality and cancer detection data in agricultural areas are worrying, as is the case in the southeast of the Province of Córdoba (Argentina). According to studies presented by Ávila-Vázquez et al. (2017), in these areas of the Pampas region, cancer diagnoses were evidenced in women, two or three times higher than the reference values, according to WHO data. Hoy et al. (2015) highlight that there may be a plausible causal relation between GLY exposure and higher rates of various conditions seen in children aged 0–15 years. These include facial abnormalities, lymphatic disorders, and abnormalities in newborns such as eye, blood, and skin disorders. Other effects in humans, both of the pure herbicide and of the most used commercial preparations, include cytotoxicity, genotoxicity, and endocrine disruption (Gill et al. 2018) among other multiple effects on human health (Rossi and Cabaleiro 2018; Moon et al. 2018).

## 9.5 Toxicological and Ecotoxicological Effects

There are multiple records of the acute and chronic toxic effects of GLY on a large number of species, both unicellular and multicellular organisms. These effects usually vary not only according to the species and the levels of concentrations or doses but also of the pure substance or commercial mixture used (Gill et al. 2018). The ecotoxicological effects of a substance can manifest itself through the affectation of one or more species, with potential repercussions at the level of populations and biological communities. The possible relation between the increase in agrochemicals, and in particular GLY, with higher rates of congenital abnormalities is well documented (Hoy et al. 2015).

In terrestrial environments, varied effects on nematodes, annelids, insects, amphibians, reptiles, birds, and mammals have been reported in response to exposure to GLY. Casabé et al. (2007) found deleterious effects on the activity of the soil fauna of GLY formulations when applied at the nominal concentrations recommended for soy crops. The density of earthworms was affected by GLY through the effects observed on the reproduction with the subsequent loss of their beneficial functions. In a review work, Gill et al. (2018) summarized the main effects on different taxa. In nematodes, the infectious capacity of the larvae decreased, while in annelids (earthworms) a decrease in weight, anatomical changes, and absence of cocoons and juveniles were observed in treatments with the herbicide. In bees, there is a lower sensitivity to nectar, a lower learning capacity, and a longer flight time to return to the nests, in addition to cytotoxicity to larvae. In wasps, one of the main preparations of the herbicide was toxic to the eggs. Toxic effects also developed in vertebrates. In amphibians, effects on swimming and cyto/genotoxicity were observed in *Rhinella arenarum* tadpoles and hepatotoxicity in *Leptodactylus latrans* (Gill et al. 2018). Lajmanovich et al. (2015) found neurotoxicity, oxidative stress, and immunological depression in *R. arenarum* exposed to the herbicide, although it should be noted that the toxicity of GLY was lower than that of chlorpyrifos and 2,4-D. In reptiles, commercial mixture of GLY was genotoxic to *Caiman latirostris*, also altering their immune system (Gill et al. 2018). In birds, toxicological effects such as changes in the reproductive system were recorded in male *Anas platyrhynchos*; however, there are also other indirect effects derived from the loss of bird biodiversity due to the elimination of vegetation after the use of GLY (Gill et al. 2018). Individuals of Wistar rats exposed to the herbicide suffered kidney and liver toxicity, sperm abnormalities, and low serum testosterone concentration in males. In pigs, effects were recorded at the level of the cardiovascular system (Gill et al. 2018).

Among the various modifications in agroecosystems in Argentina, associated with the massive and continuous use of GLY, the appearance of resistant weeds stands out. Groups of resistant species include herbicide tolerant species such as *Sorghum halepense* (Binimelis et al. 2009; Vila-Aiub et al. 2012) or *Brassica napus* (Pandolfo et al. 2016); species with late emergence, after the application of the herbicide and a third, very small group of species with varied life forms and growth cycles (Vitta et al. 2004). One of the secondary uses of GLY is its application in semi-natural pastures destined for livestock towards the end of the summer, with the aim of obtaining greater biomass of pastures for livestock in the subsequent winter and spring. This practice results in agroecosystems with less floristic richness and assemblages dominated by annual species to the detriment of native perennial species, and therefore can have negative consequences for the conservation of biodiversity, the functioning of the ecosystem, and the management of livestock (Rodríguez and Jacobo 2010). Reductions in honey yield and pollinators have been associated with the expansion of soybean monoculture, possibly due to the loss of melliferous species in response to massive use of herbicides and insecticides (de Groot et al. 2021).

In response to moderately low concentrations of GLY, effects on fish have been reported in aquatic environments, including structural cardiac abnormalities in *Danio rerio* (Roy et al. 2016) or metabolic abnormalities and severe kidney injury in *Carassius auratus* (Li et al. 2017). In *Cyprinus carpio*, exposure to high levels of GLY (205 mg/L or 410 mg/L, still below the range of commercial applications) induced changes in liver cells and mitochondria (Szarek et al. 2000). In contrast, the toxicity of the herbicide was low for two species of fish native to South America (*Cnesterodon decemmaculatus* and *Odontesthes bonariensis*), but it increased markedly with the joint application with endosulfan and chlorpyrifos, substances that are part of preparations used in soybean cultivation (Carriquiriborde 2010).

In addition to these direct effects on aquatic animals, GLY can affect interactions between fish and their pathogens or parasites. Exposure of *Rhamdia quelen* fish to sublethal concentrations of GLY (0.73 mg/L) in 96 h reduced the number of erythrocytes, thrombocytes, lymphocytes, and leukocytes in the blood, decreasing the phagocytosis of immune cells and increasing the susceptibility to the pathogen *Aeromonas hydrophila*, which resulted in a decrease in the survival rate. Similarly, environmentally relevant concentrations (0.36 mg/L) of GLY increased infection in freshwater fish *Galaxias anomalus* by the trematode parasite *Telogaster opisthorchis* (Zirena Vilca et al. 2018). Therefore, low levels of GLY in surface waters could alter the balance between hosts and their pathogens. This can cause unexpected changes in aquatic communities (Van Bruggen et al. 2018).

On the other hand, GLY transforms water bodies into turbid systems, with a great development of microalgae, small cyanobacteria. In this way, the whole system is modified and becomes more eutrophic. This change brings as a final consequence the deterioration of water quality (Camino and Aparicio 2010).

## 9.6 Remediation

In pioneering research on GLY degradation in the soil, it was observed that it occurred in a relatively short period, with a half-life of 20 days; however, after decades of application of the herbicide in different conditions, it is known that the degradation rates depend on the type of soil, the processing technique, and climatic factors, among others (Ermakova et al. 2010). Another important factor in the mineralization of the herbicide is its bioavailability for the microorganisms present, as well as the size and activity of the community of microorganisms capable of degrading this substance (Sterren et al. 2016). For this reason, bioremediation through bacterial strains with proven activity in the degradation of GLY, such as *Achromobacter* sp. KG 16 (VKM B-2534D) and *Ochrobactrum anthropi* GPK 3 (VKM B-2554D) and can be an interesting alternative for cleaning highly contaminated soils (Ermakova et al. 2010). After 1–2 weeks, from the introduction of the bacterial strains, the GLY content of the treated soil decreased as well as the toxicity and phytotoxicity, also contributing to the restoration of the biological activity of the soil (Ermakova et al. 2010). It was also found that potato crops treated with GLY and the addition of microorganisms *Lysinibacillus sphaericus* act as a bioremediation agent in cultivated soils sprayed by agrochemicals. *L. sphaericus* bacteria, as a plant growth promoter, together with its nitrogen fixation activity, can degrade GLY through the Carbon-Phosphorus (CP) pathway without affecting AMPA production. This treatment showed a 79% reduction in the GLY concentration in treated soils (Pérez Rodríguez et al. 2019).

GLY can be removed from water through physical-chemical and/or biological treatments. Vidal (2014) evaluated on a laboratory scale the treatment of wastewater generated in GLY storage and washing plants, through an advanced oxidation process that uses UV radiation and hydrogen peroxide. The degradation of GLY in water was observed, in addition to reducing the toxicity of the treated effluents on a series of organisms. In relation to biological treatments, López-Chávez et al. (2021) found high removals of the herbicide through the use of laboratory-scale artificial wetlands, vegetated with *Panicum maximum* (87% removal), *Typha domingensis*, and *Heliconia latispatha*. The importance of interactions between plants, rhizosphere microorganisms, and the wetland substrate is highlighted.

## 9.7 Conceptual Model

The main form of application of GLY is spraying, for which specialized agricultural machinery or fumigation planes are used. Although much of the herbicide falls directly on plants and soil, aerosols are also formed, which can be transported through the atmosphere and subsequently transported to more distant waters and soils via wet (precipitation) or dry deposition (Fig. 9.2). Likewise, weeds affected by the herbicide by dying, falling to the ground, and being decomposed can become a source of GLY and its metabolites.

In soils, GLY can be retained mainly in the surface layer and biodegraded, forming AMPA; however, water and wind erosion can remove soil particles that are later transported, contaminating other more remote sites or nearby water courses. Vertical transport by leaching through macropores is also possible, contaminating groundwater (Fig. 9.2). This process could be more important in soils with a sandy texture with little content of organic matter.

In humans, the toxic effects of GLY can occur from direct and repeated contact during herbicide application or through contact with contaminated soil, water, sediments, and food. It should be noted that agricultural workers and residents of areas neighboring fumigated plots often receive these products directly. Direct or indirect exposure can also produce toxicological effects on other species and even effects at the ecosystem level (Fig. 9.2).

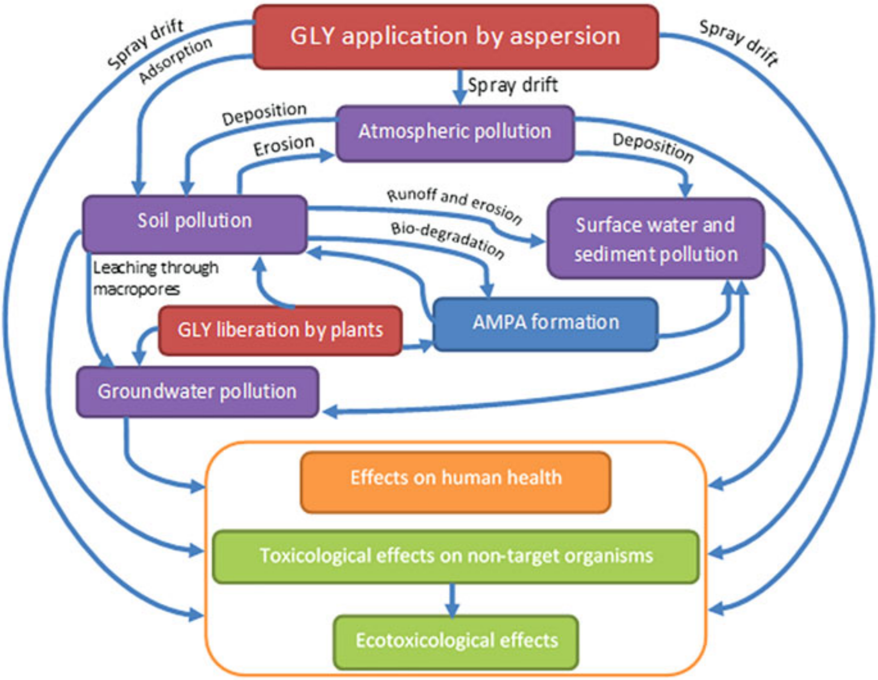

**Fig. 9.2** Conceptual model of GLY dynamics in the environment

## 9.8 Final Remarks

The use of glyphosate in Argentina and Colombia responds to different main objectives. In Argentina, its use is oriented to the production of commodities, especially transgenic grains, flour, and soybean oil, products that represent a significant volume of national exports. Meanwhile, in Colombia it is used more frequently in the control of the so-called illicit crops.

Despite the differences observed, the massive use of this herbicide results in multiple negative impacts on human health and the environment. In order to minimize these effects and value and preserve biodiversity and the services provided by agroecosystems, it is necessary to develop alternative modes of crop production or control not based on the use of massive amounts of pesticides.

Since 2009 in Argentina there has been a public debate about GLY use and its consequences on health (Skill and Grinberg 2013) based on studies showing malformations in amphibians (Paganelli et al. 2010). Previously, different socio-environmental NGOs had been mobilizing in this regard and the Argentine government commissioned a team of researchers to study the effects of GLY on human health (Decree 21/2009). This commission reviewed the scientific literature available to conclude that if agrochemicals are used correctly, the risk to human health is very low, alerting, however, to the need to promote pertinent studies due to the lack of published studies. Since then, there have been two positions based on opposing arguments: a pragmatic one that supports the use of GLY linked to good agricultural practices, and the precautionary position, defended by scientists, doctors, and social organizations that warn of the increase in cancer, spontaneous abortions, and birth defects in towns near the fumigated fields (Rulli 2009; Ávila-Vázquez et al. 2017). NGOs, residents of rural and peri-urban areas, doctors from these towns, and neighborhoods have formulated the National Plan to reduce the use of pesticides (https://reduas.com.ar/plan-nacional-de-reduccion-de-uso-de-agrotoxicos/). This proposal is based on the fact that at the national level the exposure to pesticides is 11.9 L per person per year. In rural areas it is 10 times higher. In an area where soybeans are grown (Monte Maiz, Córdoba), it rises to 121 L per person for all pesticides and 80 L for GLY. They propose incentives for non-use of pesticides, reduction targets in its use and local production, transfer collection center agrotoxics outside populated areas, and prohibit use of any pesticide around 1000 m of housing, schools, water resources, environmentally protected areas, and ecological or agro-ecological agriculture production areas. They also propose a National Program to Stimulate Agroecology, from which as the consumption of pesticides decreases, an agroecological-based agriculture will be developed in order to eliminate the use of agrotoxics.

The controversy over the use of GLY is a wicked problem. It is based on the discussion between both positions due to the diagnosis uncertainty. Its complexity increases because there are a lot of sociotechnical and political arguments around this issue as the debate transcends the GLY use, merging several actors, short vs. long-term risk and different relation between scientific knowledge. In addition, many questions remain open, such as the difficulty to evaluate the moment between the exposure and the appearance of diseases symptoms, who investigate these issues, who finance the research, who are capable of evaluating the relation between environmental damages and GLY application.

In addition, the debate is being hindered because it brings to the table two opposing models of development. While the pragmatic position that supports the use of the GLY is based on a model of intensive exporter development which contributes greatly to the country economy and tax collection based on an industrial agriculture and short-term profitability, the precautionary model takes the agroecology as a way to guarantee food security and sovereignty and blames globalized agriculture. Those who defend this discourse blame the transformations of the agrarian model for increased inequalities, discrimination, and rural depopulation (Palacios 2010; Skill and Grinberg 2013). As long as these antagonistic positions prevail, the shadow that tinges the use of the glyphosate will continue.

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# Impact of Insecticides on Soil and Environment and Their Management Strategies

# 10

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## Abstract

Now-a-days pesticides become an essential part of our up-to-date life and help us to preserve agricultural fields, stored grain, flowers beds, and exterminate pests that extend harmful infectious diseases. Insecticides are chemicals used to eliminate insects that attack, destroy, or injure plants. Insecticides are beneficial to crops but also have a significant harmful environmental impact. Excessive insecticide use may lead to the destruction of biodiversity. Insecticides enter into the food chain, where they bioaccumulate at a higher tropic level. Non-target organisms such as valuable soil microbes, plants, birds, fish, and insects exposed to insecticide residues in soil, water, and air worldwide possess major health and environmental risks. Novel scientific pest management approaches like integrated pest management (IPM), as well as laws prohibiting high-risk insecticides, limit the harmful consequences of insecticide contamination to the environmental habitat and soils. Based on such aspects, a national implementation plan (NIP) should be developed and implemented. Furthermore, new technologies viz. nano-biotechnology may contribute to the development of resistant genotype or insecticides with less undesirable repercussions.

## Keywords

Pesticides · Insecticides · Human health · Environmental impact

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## 10.1 Introduction

Pesticides are expected to cost over $38 billion per year globally. To accommodate worldwide demand, industries and researchers are rising new pesticide formulations. Pesticides should be dangerous only against target organisms, and must be biodegradable and ecofriendly enough (Carriger et al. 2006). Insecticides are the most toxic of all pesticide categories, followed by fungicides and herbicides. Organochlorines, carbamates, organophosphates, pyrethroids, and neonicotinoids are the major insecticide classes, with neonicotinoids accounting for the majority of currently used insecticides. Depending on their solubility, insecticides enter the environment in two ways. Water-soluble insecticides penetrate the groundwater, streams, lakes, rivers, and oceans affecting the advantageous organisms. Similarly, the concentration of fat-soluble insecticides buildup in the fat and tissues of animals via bio-magnification. They are absorbed by animal fatty tissues, resulting in their long-term persistence in food chains. Much of the species in elevated tropic levels will die as a result of amplified toxicity in their bodies, causing the whole ecosystem to be disrupted. Insecticides generally decompose into metabolites after being introduced into the environment. Furthermore, with the passage of time, various insects gain genetic resistance to insecticides (Meyers and Bull 2002). Insecticides are often classified based on their environmental persistence. Organochlorine group of insecticides are persistent, but organophosphates, pyrethroids, carbamates, and others are non-persistent group of insecticides. Non-persistent insecticides have substantially shorter environmental half-life than persistent insecticides and are less likely to bioaccumulate. However, existence of these compounds in the surrounding environment for longer duration raises concern because of extensive usage in agriculture sector (Barr and Needham 2002). Organophosphorous insecticides are less persistent in nature but their extensive use and slower degradation results in their accumulation in soil and eventually seepage in rivers and other water bodies. An example of carbaryl (carbamates group insecticide) and their breakdown by-product namely 1-naphthol has been reported to be present on water surface. 1-Naphthol, which is more toxic metabolite than carbaryl, has emerged in various parts of India. In comparison to other insecticides, pyrethrins and pyrethroids groups have excellent selectivity, specificity, and environmental bio-degradability, forming a popular alternative to synthetic organophosphorus compounds. The pyrethroids can readily bind to soil particles and can easily runoff with soil particles and reach sediment deposits, contaminating submerged amphibious habitats and destroying aquatic organisms such as invertebrates and fishes (Pérez-Fernández et al. 2017). The premier mechanism to control pest growth in plant crops is to understand the plant and insect pest well enough to develop a manageable plan maximizing the plant crop yield together with reducing the environmental hazards. Various combinations of cultural, physical, biological, and chemical approaches are frequently used for better management. Tillage, resistant varieties, crop rotations, and changing planting or harvest dates are examples of cultural controls. Physical control strategies include soil solarization, steaming, using light traps to attract various pests, and moisture management. Biological pest control includes promoting natural pest antagonists and manipulating the agricultural environment to the pest detriment. Chemical controls should include a strategy for selecting insecticide that provides the highest economic benefit at the lowest environmental cost (Llasera and González 2001).

## 10.2 Impact of Insecticides on Environment

### 10.2.1 Impact on Air and Water

Residues of insecticides in water are a significant source of concern since they harm biological systems and societies (including humans). There are number of methods by which insecticides penetrate the water streams including surface run off, over spillage, industrial sewage, accidental spills, washing of spray equipment after spraying, drift flow into lakes, ponds, streams, river, and oceans, aerial spraying to control water-suppressing pests, and volatilization from the handled surfaces. The amount of drift flow is determined by wind speed and droplet size, whereas the rate of volatilization is determined by the period following insecticides management, the site on which the insecticide targets, moisture, wind velocity, temperature, as well as the vapor pressure of the components. Insecticides and their active metabolites have been used indiscriminately, resulting in contamination of water bodies and surrounding air, potentially endangering aquatic organisms like fish, amphibians, and birds (Table 10.1, Singh and Mandal 2013).

#### 10.2.1.1 Surface and Ground Water Contamination

Water contaminated by insecticide runoff is the principle pathway that has ecological consequences. Bioconcentration and biomagnification are the two main pathways. Bioconcentration is defined as a process of transferring chemical components from the adjacent media into the living organism. For example, fat soluble insecticides like DDT and BHC accumulate in fatty adipose tissue (edible

**Table 10.1** Effect of insecticides on fishes, amphibians and birds

| Organisms | Effect of insecticides | References |
|---|---|---|
| Fish | Insecticides severely affect fish tissues, including the body cavities, liver, gills, and brain, affecting functions like mating, identifying prey, avoid predators, differentiating relative and migrating among others | Tierney et al. (2010) |
| Amphibians | Insecticide such as malathion, indirect effect aquatic communities by changing the development of aquatic habitat including fungus and invertebrates which leads to an enhance in phytoplankton, decline in periphyton, decline in frog tadpole development | Relyea and Hoverman (2008) |
| Birds | Insecticides influence bird behavior and reproduction. Due to their extreme toxicity, carbamates and organophosphates group insecticides have tendency to kill birds | Hunter (1995) |

fish tissue and human fatty tissue). Insecticide residues are volatilized, diffused, and carried over vast distances, resulting in an environmental recycling process between the air and the land (Sultana et al. 2014).

#### 10.2.1.2 Insecticides and Biomagnifications

Biomagnification refers to the increase in pesticide concentrations caused by their non-decomposing and persistent character in the tissues of living organisms at every consecutive level of the biological food chain. Organisms at the topmost level of the food chain suffer most of the harm as a result of this phenomenon in comparison to individuals who are at a lower level. The concentration of pesticides in tissue and other organs increases as smaller species are eaten by larger organisms. Accordingly, DDE-induced egg shell thinning, fish-eating birds have experienced reproductive failure and population reduction (Grasman et al. 1998). The range of biomagnifications increases with increasing amount of the persistence and fat-soluble properties in the insecticide. Those being the case, organochlorines have a greater biomagnification rate and are much more persistent in a broader domain of organisms compared to organophosphates. Before considering insecticides for agricultural use, it is essential to carry out risk evaluations based on their bioaccumulation and biomagnifications potential.

#### 10.2.1.3 Insecticides and Bioaccumulation

Organochlorines were restricted in agriculture and human hygiene sector due to the fact that it belongs to the class persistent organic pollutants (POPs). POPs being highly persistent tend to show high amounts of bioaccumulation in the food chain. These pesticides are insoluble in water but soluble in nonpolar and partially polar organic solvents, fats, and lipids and hence build up in fatty tissue and result in bioaccumulation as it can be ingested via fish, dairy products, carotene containing sea products, and other fatty foods (Kumar et al. 2018).

### 10.2.2 Impact on Biodiversity

#### 10.2.2.1 Impact on Aquatic Biodiversity

Insecticides penetrate in the water through drift, runoff, leaching, or, in some conditions, direct application into surface water, such as for mosquito control. Insecticide overuse can harm aquatic organisms and lower diffused oxygen levels in the water bodies, which can lead to physiological and behavioral modifications in fish populations. Malathion (OP's group insecticide) at low concentrations has been demonstrated to alter the quantity and constitution of plankton and periphyton populations, affecting frog tadpole growth. Amphibians are also severely harmed by chlorpyrifos (OP's group insecticide) and endosulfan (organochlorine group insecticide) (Relyea and Hoverman 2008).

#### 10.2.2.2 Impact on Terrestrial Biodiversity

The application of insecticides groups like organophosphates, carbamates, and pyrethroids can drastically decrease populations of valuable insects like beetle and bees. Birds die as a result of insecticide buildup in their tissues. For example, DDT and its metabolites were a major factor in the reduction of bald eagle numbers in the United States (Lupwayi et al. 2009).

## 10.3 Impact of Insecticides on Human Health

Insecticides are ingested, inhaled, or absorbed through the skin. When the concentration of insecticide in the body exceeds the initial concentration in the environment, toxic effects are produced. Insecticides have a wide range of consequences for human health (Hayo and Werf 1996). They can arise in a couple of days or are instantaneous, or might take months or years to emerge, and thus are referred to as chronic or long-term consequences.

### 10.3.1 Acute Effects of Insecticides

Headache, hurtful of skin and eyes, nuisance of throat and nasal passage, skin itching, emergence of rashes and blisters on skin surface, dizziness, abdominal discomfort, nausea, diarrhea, vomiting, blindness, blurred vision, and even death are instant consequences of insecticide consumption.

### 10.3.2 Chronic Effects of Insecticides

- Insecticide exposure can result in various neurological consequences, including decreased visual capacity, lack of coordination, cooperation and memory, and decreased signaling of motor neurons (Lah 2011).
- Insecticide intake over time weakens the immune system and can lead to increased production of IgE antibodies, asthma, allergies, and hypersensitivity.
- Insecticides accumulating inside the living body for a long time can have an effect on reproductive capacity by affecting the balance in male and female sex hormone. These conditions can result to stillbirths, deformities in fetal and newborn infants, abortions, and other complications. Infertility can harm the liver, lungs, and kidneys, as well as create blood disorders (Culliney et al. 1992).
- Organochlorine group insecticides poisoning produces touch, light, and sound hypersensitivity, seizures, tremors, dizziness, vomiting, diarrhea, nausea, anxiety, depression, and confusion. These insecticides disrupt nerve signal transmission, causing dizziness, fatigue, confusion, constipation, headaches, anxiousness, vomiting, and nausea as well as muscle and chest pain. Convulsions, difficulty in respiration, coma, and even death in severe conditions may occur (Lah 2011).

## 10.4 Impact on Non-target Organisms

Impact of synthetic insecticides on beneficial organisms has always remained to be a matter of extensive concern and research interest. Earthworms are essential indicators of soil quality in the agricultural ecosystem because they help to improve and maintain soil structure. Earthworms are harmed by indiscriminate insecticide usage, which can lead to decline in earthworm population. For instance, insecticides of carbamate groups are extremely poisonous to soil organisms like earthworms, whereas various organophosphate group insecticides have been reported as major cause for the continuous decline in earthworm populations. Insecticides outline dose-dependent effect on growth, development, and reproduction of earthworms (production of cocoon, number of hatchlings per cocoon unit, and incubation period of each cocoon). Earthworms subjected to several insecticides revealed cuticle rupturing, seeping of coelomic fluid, paling, and swelling of the anatomy, resulting in the body tissues softening (Kumar et al. 2012). Predators are key aspect while dealing with biological control method, being the part of IPM. For instance, studies showed that when brinjal was prayed with cypermethrin and imidacloprid resulted in the death of braconid wasps, coccinellids, and other predatory spiders as compared to the other treatments like application of biopesticides/botanicals (plant-based insecticides) such as neem (*Azadirachta indica*). Insecticides can have an impact on predator behavior as well as life-history factors such as development time intervals, growth rate, and other reproductive and generative processes (Ghananand et al. 2011). Plant pollinators are essential biological agents for pollination process. Insecticide overuse results in indirect disappearance of insect pollinators leading to indirect losses of crops owing to lack of appropriate pollinator populations. Pollinator foraging behavior, colony mortality, and pollen collection efficiency are all affected by insecticide application (Blacquiere et al. 2012). Insecticides can penetrate the human body through direct exposure to food, particularly fruits and vegetables, polluted water, chemicals, or contaminated air. Acute effect in people is usually caused by insecticide drift from agricultural fields, insecticide exposure while spraying, and intentional or unintentional poisoning. Insecticide poisoning can cause a variety of symptoms, including body aches, cramping, skin rashes, headaches, blisters, poor memory, dizziness, nausea, blurred vision, panic disorders, and, in severe cases, coma and even death (Singh and Mandal 2013). Humans develop chronic effects after being exposed to sub-lethal and toxic amounts of insecticides for an extended interval. Insecticide exposure is linked to the occurrence of human chronic disorders affecting the neurological, reproductive, renal, cardiovascular, and respiratory systems, according to accumulating data. Insecticides have also been linked to epigenetic changes such as DNA methylation, histone alterations, and non-coding RNA expression. Insecticide-induced oxidative stress has been connected to a variety of health concerns, including Parkinson's disease and glucose homeostasis disruption (Culliney et al. 1992). Insecticides severely destroyed various fish body parts/tissues, including the alimentary canal, liver, gills, brain of catfish, and carp. Another prominent consequence of toxic pollutants on fish is olfaction, which can impact behavior such as mating, food location, predator

**Table 10.2** Impact of insecticides on non-target organisms

| Non target organisms | Insecticidal effects | References |
|---|---|---|
| Earthworms | Insecticides affect earthworm development, reproduction (cocoon hatchlings percentage, cocoon formation, and incubation time), cuticle rupturing, pouring off coelomic liquid and bloating resulting in loosening of body cells | Kumar et al. (2012) |
| Predators | Predator performance and life-history factors like rate of growth, production time, and other mating processes are affected by insecticides | Ghananand et al. (2011) |
| Pollinators | Insecticide affects a variety of pollinator behavior, including feeding behavior, colony mortality, and pollen collection effectiveness. It also impairs bees learning and memory ability | Blacquiere et al. (2012) |
| Humans | Insecticide poisoning can cause various symptoms including dizziness, body pain, dermatitis, low memory, impaired eyesight, cramping, anxiety, and sometimes, coma, and death. Several health issues, including Parkinson’s disease and glucose homeostasis disruption, are related to insecticide-induced oxidative stress | Culliney et al. (1992) |
| Fish | High lipid concentration, persistence, low polarity, poor aqueous solubility, and result of their solubility they can bioaccumulate in fish and the food chain, hazardous effect on human health and the environment worldwide | Carter and Heather (1995). |

avoidance, relative discrimination, and homing (Carter and Heather 1995). Table 10.2 summarizes the examples of non-target organisms which are under negative impact of insecticides.

## 10.5 Impact on Vegetation

Insecticides interfere with the formation of legume rhizobium, impoverished root hair growth and development, yellowing of the shoots, and retarded plant growth. Insecticide like DDT, methyl parathion, interferes with legume rhizobium chemical signaling, nitrogen fixation is decreased, and reduced crop yields. Insecticides toxicity condensed chlorophyll and protein substance results in chlorosis, necrosis, stunting, distorting of leaves and burns, as well as the generation of reactive oxygen species (ROS), which causes oxidative stress and disbalance in plants. The deleterious impacts of oxidative stress are counteracted by activating the plant antioxidative defense system, which involves the enzymatic as well as non-enzymatic antioxidants (Sharma et al. 2015). Also, insecticides inhibit many biological processes of plant like mitosis, photosynthesis, enzyme activity, cellular division, root and shoot growth, and leaf and other floral parts development, as well as interfering with pigment, protein, and DNA formation, destroying cell membranes, and promoting uncontrolled growth.

## 10.6 Impact on Animals

Due to the persistence nature of insecticides they accumulate in animal tissues, resulting in the amount of human dietary intake via consumption of animal products (eggs, milk, and seafood). Insecticides can cause adverse health effects to humans and the environment, even at low doses and for long period of time. Residues in human food and livestock feed can result from direct implication of insecticide to food etymology, occurrence of pollutants in nature, and chemical transportation leading to biomagnification along a food chain. Endosulfan is commonly used in agriculture to manage a variety of pests in crops, which are identified in green fodders and feed concentrates as plant residues. Cancer, endocrine disruption, reproductive impacts, neurotoxic effects, kidney and liver damage, birth malformations, and developmental abnormalities have all been associated with it in a variety of animals (Deka et al. 2004).

## 10.7 Impact of Insecticide on Soil

### 10.7.1 Impact of Insecticides on Soil Enzymes

Insecticides entering into the soil can disrupt specific metabolism or change the enzyme activity of the soil. Soil can be termed as an enzymatic reservoir that includes immobilized extracellular enzymes, mobile enzymes, and enzymes processed using from and by microbes, all of which are measures of biological balance, such as soil fertility, nature, and quality. These enzymatic reservoir catalyzes the deterioration of both the insecticides and biological compounds present in the soil. As a result, monitoring changes in enzyme function are designated as a biological measure to determine the influence of insecticides on soil biological and physiochemical functions (Garcia et al. 1997; Romero et al. 2010). Several studies have already been conducted that show variations in the activity of soil bioenzymes including nitrogenase, phosphatase, and dehydrogenase (Chalam et al. 1996; Madhuri and Rangaswamy 2002). Furthermore, water is known as a universal solvent for insecticide migration and dispersion which is necessary for bacterial/ microbial action; moisture present in the soil is one of the essential components governing the insecticide bioavailability, processing, and degradation. The insecticides interacting with soil enzymes have been elaborated in Table 10.3.

### 10.7.2 Impact of Insecticides on Soil Microorganisms

Insecticides have the potential to change soil microbe's diversity and activity in the soil. Changes in soil microbial activity as a result of insecticide use eventually disrupt the soil ecosystem and soil loss; insecticides can affect the action of essential root colonizing microorganisms such as bacteria, fungi, algae, and arbuscular mycorrhiza in soil by disturbing their development, colonizing, and metabolism

**Table 10.3** Effect of insecticides on soil enzymes

| Enzyme (function in soil) | Examples | Effect of insecticide | References |
|---|---|---|---|
| Nitrogenase (fix atmospheric nitrogen) | Quinalphos, monocrotophos, carbamate insecticides, γ-HCH, endosulfan | Decreases nitrogenase activity | Chalam et al. (1996) |
| Phosphatase (hydrolyzesorganic P compounds to inorganic P) | Monocrotophos, methyl parathion, chlorpyrifos, phorate, quinalphos, cypermethrin, fenvalerate, and dichlorvos methomyl | Phorate decrease total bacterial population | Madhuri and Rangaswamy (2002) |
| Urease | Diazinon, profenofos, amitraz, cyfluthrin, imidachlor, tebupirimphos, profenofos, and pyrethrins | Increased urease activity, profenofos, and pyrethrins reduce urease and nitrate reductase activity | Abdel-Mallek et al. (1994) |
| Dehydrogenase (DHA) | Quinalphos, acetamiprid | Positive impact on the DHA, initially suppressed but activity was later restored | Andrea et al. (2000) |
| Invertase | Carbaryl | Invertase function is affected | Sannino and Gianfreda (2001) |
| Phosphomonoesterase | Quinalphos | Decreases the performance of phosphomonoesterase which recovers later | Mayanglambam et al. (2005) |

(Davies et al. 2012). Insecticides reduce microorganisms' functional structure and diversity and enhance the genetic variability of the microorganisms' population. Methamidophos decreases microorganisms' biomass while enhancing soil functional diversity, as evaluated by microbial biomass and society physiological benefits. Insecticides can interrupt several physiological behaviors in the soil (nitrogen fixation, ammonification, and nitrification by stimulating or inhibiting certain soil microbes/enzymes) (Hussain et al. 2009). Although insecticides, microorganisms, and soil qualities act together synergistically and additively in the determination of rates of soil biochemical processes. Insecticides have shown to affect the decomposition of organic matter in the soil, which is an important soil attribute that influences soil quality and production. Loss of useful micro flora in the soil results in low soil fertility, which leads to poor crop yield. As a result, it lowers farm profits and increases hunger and poverty (Wu et al. 2012). In addition to the durability, toxicity, and concentration of the sprayed insecticides, several environmental parameters affect the absorption, decomposition, and action of insecticides on soil micro flora. These factors include soil texture, organic carbon (C) content, biodiversity, and cultural practices. Even when treated at suggested dosage, insecticides begin to rise in soil by continual treatment over time and have negative harm in soil microorganisms. Carbamate group insecticide (e.g., methiocarb, carbofuran, and carbaryl) and OP's group insecticide (e.g., diazinon, quinalphos, dimethoate, malathion, and chlorpyrifos) have a diversity of negative possessions on the soil microbiological environment and enzymatic action, inhibiting the development and community of soil enzymes, bacteria, and fungi. As a result of their long-term residual effect and resistance in soil DDT, lindane and arsenic have a deleterious impact on microbial population, microbial activities, and enzymatic action (Van Zwieten et al. 2003).

#### 10.7.2.1 Impact of Insecticides on N-Fixing and Other Growth-Promoting Microorganism

The adverse relationship between insecticides and symbiotic N-fixers varies depending on the insecticides chemical group and the particular N-fixer group. Because of malathion, and parathion, fenthion, phosphamidon, Azotobacter growth and population are greatly suppressed. Number of N-fixing soil microbes is affected by monocrotophos and cypermethrin. Even at field approved doses/concentrations, several other insecticides (such as cypermethrin and phoxim) have inhibiting action on soil microorganisms. Monocrotophos, cypermethrin, and quinalphos have a favorable impact at small doses and inhibitory impact at high dosages. To soil microorganisms, cypermethrin and monocrotophos are more injurious, although fenvalerate is less harmful. Insecticides are toxic to soil microorganisms that are necessary for N conversion in soils, and the amount of toxicity varies depending on the kind and category of insecticide (Das and Mukherjee 2000). In addition, insecticide residues are less sensitive to ammonification. However, the ammonification process frequently decreases at higher doses.

### 10.7.3 Impact on Soil Properties

Insecticides can be absorbed, degraded, or leached into shallow ground water after being sprayed to soils. The soil properties that have the greatest impact on these processes are discussed below:

- **Organic matter:** Most insecticides bind strongly to the organic matter in the soil; increased organic matter content lowers the threat of insecticide runoff.
- **Clay:** Clay can bind a wide range of insecticides and can inhibit or slow the migration of percolating water. With increased clay content, these two mechanisms combine to decrease the risk of insecticide leaching.
- **pH:** Insecticides will leach less and degrade more quickly at lower pH levels.
- **Depth to ground water:** The longer insecticide residues have to leach to enter groundwater, the more likely they are to degrade biologically or chemically. Most insecticides decay slowly when they approach the groundwater table, despite the fact that degradation rates are rapid below the root zone.

- **Weather:** The weather has a major impact on the breakdown and mobility of insecticide in soil. Hotter and cooler temperatures will accelerate or delay degradation.
- ***Hydrologic loading:*** The introduction of water to the location of insecticide spraying regions is critical for insecticide transmission to groundwater. Precipitation or irrigation over evapotranspiration rates and soil water holding capacity can deliver insecticides deeper into the soil profile (Demanou et al. 2006).

## 10.8 Management Strategies

### 10.8.1 Cultural Control

Pests are eradicated or prevented from causing damage to plants utilizing cultural management measures. Several cultural management practices, like crop rotation, sanitation, timely growing and harvesting, use of certified seeds, allelopathy, resistant varieties, intercropping, use of farmyard manure, soil solarization, and organic mulches, have all been described as cost-effective and environmentally friendly methods to control different insects and nematodes (Amirkhanov et al. 1994). By synchronizing accessible activities with pest life cycles, more successful cultural management can be developed. As a result, the sensitive link in their life cycle is exposed to difficult environmental factors. Farmers eliminate huge insect number by subjecting them to severe climatic conditions by agricultural methods.

### 10.8.2 Physical and Mechanical Control

It is the process of managing insect populations by utilizing procedure that influence them physically or change their physical habitat. Sun exposure, heating, moisture control, and light traps are all physical control approaches for attract various types of beetles, moths, and other pests. Many unseen pests, including eelworms and bulb flies, are killed by hot water treatment of plant stored items like bulbs and corns. Superheating an empty grain storehouse to 50 °C for 10–12 h aids in the eradication of hibernating stored grain pests. During the summer exposing cotton seeds to the sun for 2–3 days can destroy pink bollworm eggs (Ahemad et al. 2009). The employment of manual equipment to manage insect populations is referred to as mechanical control. Exclusion through filters and barrier to prevent mosquitoes, house flies, and other pests away includes capturing, hand-picking, vacuum equipments, cutting, pruning and crushing infected shoots, and flower parts.

### 10.8.3 Host Plant Resistance

The genetic potential of the plant to optimize its growth and survival through a various modifications when comparison to several other cultivars and subjected to the same amount of pest infections. It is an important part of the IPM approach since it is the most successful, cost-effective, and environmentally acceptable method of pest control (Sharma and Ortiz 2002). The introduction of new molecular and biotechnology techniques has paved the road for the generation of pesticide-resistant genotypes that could help with IPM as well as reducing insecticide consumption. The use of biotechnology in crop production promotes rapid enhancement of pest-resistant varieties while also reducing the impact of linkage stress. Cotton is the most valuable examples of pest resistance transgenic genotype synthesis, with the genetic coding for Bt toxin as from bacteria *Bacillus thuringiensis* (Bt) being introduced, allowing cotton varieties to manufacture Bt toxin in their cells. Because the Bt toxin killed the lepidopteran larvae that feed on transgenic crops, the amount of insecticide used in the field was reduced. The usage of the RNA interference (RNAi) technology is another biotechnology and molecular approach that has been used to counteract biotic stressors. This method primarily employs transgenic plants that express dsRNA, which decreases the messenger RNA (mRNA) quantity of crucial gene in the target pest (with high specificity and fidelity) when the insect upon feeding (Kos et al. 2009).

### 10.8.4 Biological Control

Conservation, enhancement, and introduction of ecological natural predators are the three types of approaches used in biological control. In traditional system the significant biocontrol organisms are predator, pathogens, and parasitoids. Vertebrates arthropods (spiders, mites, and insects), nemathelminthes (flatworms and roundworms), and pathogens (viruses, bacteria, protozoa and fungus), including rickettsiae are all biocontrol agents that perform an active part in natural insect population management. The Vedalia beetle, *Rodolia cardinalis* (Mulsant), was brought to California (USA) from Australia for the suppression of cottony-cushion scale (*Icerya purchasi* maskell) on citrus trees (Pandey and Singh 2004).

#### 10.8.4.1 Bioinsecticides and Botanicals

In comparison to conventional chemical insecticides, bioinsecticides play an important role in insect management practices as effective and environmentally sustainable options to chemical insecticides, reducing pollution and contamination of soils while causing no harm to the environment or soil microbes. In view of such adverse effects, there is a need to develop environmental friendly pest control strategies for sustainable agricultural pest management. The essential oils and the extracts of the pesticidal plants ensure that the botanicals formulations that not only can act as a supplement to different plant protection practices but also can act as an environmentally benign substitute of synthetic pesticides (Kumar et al. 2019; Anjum et al. 2019; Rawat et al. 2021; Goswami et al. 2019; Thapa et al. 2020; Chauhan et al. 2011). So, for eco-friendly agricultural production, bioinsecticides encourage optimum soil health and environmental sustainability. *Bacillus thuringiensis* (Bt), Baculo viruses, Trichoderma, and *Azadirachta indica* are some of the most frequently used biopesticides. *Bacillus thuringiensis* is the most commonly used, and it is used to kill moth larvae on crops, with variants designed exclusively for mosquito and fly larvae. Baculo viruses, which target specifically viruses and kill disease-causing lepidopterous insects of rice, cotton and vegetables, are among the most significant microbial insecticides (Meena et al. 2015).

## 10.8.5 Chemical Control

Cultural and agro-technical approaches were not enough to maintain insect populations under the economic harm threshold indefinitely. To minimize insect harm, chemical control products are used as both preventative and therapeutic strategies. A good insecticide should be valuable against pests, safe for humans and non-target species eventually, degrade into harmless metabolites, so it does not stay in the environment. It's critical to understand spray particle size and density, as well as chemical dosage and exposure timing, to attain useful pest control. Research into the creation of appropriate packing, removal techniques, and refinement of application devices is also required (Rosell et al. 2008). During insecticide application, timing, dose, and persistence, as well as selective placement of insecticides, are all factors to consider, as described below.

### 10.8.5.1 Timing of Insecticide Application

The suitable time to apply insecticides is when the weather is favorable, when pests are most simply controlled, and when non-target organisms and their surroundings are least harmed. Most critical stage of an insect life cycle should have coincided with the application of insecticide. Insecticides cannot be used right before rain since they can be washed away by the rain and have no effect on the target pest. Insecticide drift raises the risk of harming pollinators, humans, domestic animals, and wildlife. Spraying in winds above 2.5 miles/s is not recommended since it can produce significant drift and contaminate nearby areas (Favari et al. 2002).

### 10.8.5.2 Dosage and Persistence

The amount of insecticide is determined by the insecticide manufacturer to provide an effective control, acceptable residue quantity, and maximum returns per unit of manufactured insecticide. In comparison to non-persistent insecticides, persistent insecticides have a greater durability on the target and hence requiring less frequently application (Sirotkina et al. 2012). When an insecticide is stable in nature, the possibilities of insecticide residues harming natural adversaries raise dramatically.

### 10.8.5.3 Selective Placement

Insecticides should be dispersed in the field in such a manner that they cover the maximum amount of target area possible. Only approximately 1% of insecticides sprayed are effective while the rest is lost. Studying pest physiology and behavior is serious because it can give knowledge on insect environment, reproduction, feeding, and other factors that should be taken into account when using insecticides. Because most insecticides are sprayed as liquids, the size of the droplets is important in determining their efficiency. Fine particles give better coverage and have a greater chance of reaching the target than bigger droplets, which can easily bounce off the plant surface. Insecticides can also spread from one region to another through the rain. Insecticide use should be kept to a minimum to avoid surface water contamination. Alternative pest management methods should be thoroughly investigated before resorting to chemical control.

### 10.8.6 Agronomic Practices

- Clean cultivation should be followed to reduce pest incidence. Pest/disease tolerant or resistant varieties should be preferred.
- To control pest infections, agronomic practices such as crop rotation should be used.
- Allow natural predators to control insect populations. However, it requires regular monitoring.
- Pest populations must be monitored regularly until they reach a certain economic threshold (ETL). There is minimal chance of yield impairment if the insect population is below the ETL. This requires scientific intervention to ascertain the ETL level of target pests in crops.
- To minimize pest levels, an integrated pest management (IPM) approach should be employed, with bioinsecticides and biological control being preferred.
- Trap crops and plants that have an allelopathic effect should be used.

### 10.8.7 Insecticide Selection and Application

- Insecticides should be chosen on the basis of low dose, low toxicity, target specificity, leachability, and fast degradation, leaving no or minimal residue on production.
- Controlled release formulations should be used whenever possible. Use suitable equipment for insecticide application.
- Apply insecticide when there is a low possibility of rain or strong winds, ensuring that less insecticide is lost by runoff, drift, or soil erosion. Prepare insecticide solution/mixture on a loading floor which ensures contamination due to spillage.
- Particle and vapor drift from insecticides can harm other plants, cause injury to people or animals, and pollute surface water. To reduce insecticide drift, follow the insecticide label's safe handling, storage, and disposal instructions, apply insecticides only when necessary and during suitable weather conditions, use the appropriate sprayer settings, and only spray after all other options have been explored (Brown and Brogdon 1987).

### 10.8.8 Use IPM Strategies to Minimize the Impact of Insecticides

- **Use crops resistant varieties to pests.** Insecticide applications are frequently reduced when resistant varieties are used.
- **Use crop rotation.** Crop rotations keep insect populations down by removing pest affected plants and enable insecticides to be applied to lower pest populations.
- **Biological controls.** It is critical to properly identify the pest and recognize beneficial insects. Choose an insecticide that is insect-specific to the insect and less toxic to non-target organisms. Pheromones were employed to monitor populations, prevent mating, and attract predators.
- **Use of cover crops.** Uses of cover crops to encourage water conservation and decreasing leaching, which leads to insecticide leaching into ground water.
- **Use of allelopathic characteristics of crops.** Some crops have the ability to naturally restrict insect population growth.
- **Use of timing of field operations** (planting, cropping, spraying, and harvesting) to reduce usage or runoff of insecticides.
- **Use of efficient application methods.** Insecticide spraying can be targeted when pest issues are discovered in a specific section of the field. The crop can be protected by banding rather than spraying the entire region (Guler et al. 2010).
- Using an Integrated Pest Management (IPM) strategy to pest control, which is designed to cause the least amount of environmental disruption? IPM is a method of attaining long-term, ecofriendly, and ecologically harmless pest control via the use a range of technology and other insect management strategies.

## 10.9 Conclusion

Insecticides were first used to enhance human life by increasing agricultural efficiency and preventive infectious disease, but the risks that insecticides cause harm to human life and ecosystem have raised question regarding their safety. Persistent nature of insecticides has such an impact on our environment that they have found their way into food chains and increasing tropic levels, including humans and other animals. Considering hazardous impacts of insecticides to human life and ecosystem, it is evident that a new agricultural theory is required. This new approach will be based on reducing the need of chemical insecticides, which can improve public health, the environment, and the economy. This is the time when sufficient insecticide application is necessary to defend our environment and, as a result, the health risks associated with it. Alternative strategies like IPM where all possible pest control methods are used in combination such as cultural methods, use of resistant genotypes, mechanical control, and reasonable use of insecticides could decrease the number and quantity of chemical insecticides required. Community development and different extension programs that can enlighten and support farmers to accept novel IPM practices are critical to minimizing the negative effects of insecticides on the ecosystem. Development of more effective, safe, and eco-friendly insecticide formulations may help to assist to offset the adverse impact on use of insecticide. The devastation can be remedied by using a less hazardous formulation or a moderate dose of a harmful formulation. Insecticides have significant negative influence on aquatic and marine ecosystems' biological integrity. To fully comprehend the primary and secondary effects of insecticides on ecosystem, it is essential to integrate studies from several disciplines like environmental chemistry, demographic biology, toxicology, conservation biology, community ecology, and landscape ecology.

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# Role of Insect Pest Management in Agriculture Conservation

# 11

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## Abstract

The Earth consists of life forms as pests that are classified into different species which are million in numbers. However, for foodstuffs, safe house, and the area just only 1% competes with human beings. Different practices of farming had been applied in managing pests or insects, but none of the practices have gained a fruitful result or control on pests till date. Controlling through chemical method is yet the dominating pest control measure; however, it causes environmental contamination and has side effects on human health also. The drawn-out manageability of agrarian society and common ecosystems relies on the protection of regular assets. Conservation agriculture uses innovative approaches and advances in technology to provide significant benefits along with enhanced levels of creation while at the same time saving the environment. It additionally enriches the biodiversity and ecosystem of vegetation, fauna and flora that assist with controlling insect pests; conflicting data induce worries in regard to diminished yields, expanded work prerequisites to reduce use of herbicides and insect pests issues. It is important to elaborate the natural, cultural, biological, mechanical, biotechnological and chemical control methods in managing the insect pests. The basic principle of integrated pest management is to develop a stable environment in between viable environmental practices and commercial farming. Using conservation agriculture technique for insect pest management will boost biodiversity and conserve native resources. It is based on similar fundamentals to the techniques that help increase biodiversity. In addition, the latest advancements in insect pest management like biotechnological approaches are also being used in the conservation management of insects. In management systems, sustainable

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pest management for crop production is possible by combining the latest technologies with IPM. In this chapter, we consider the advantages, disadvantages, and effects of conservation agriculture on pest management. The purpose of this chapter is to present the pros, cons, and impacts of conservation agriculture on managing pests, a discussion on plants and insect biodiversities, as well as different pest control methods.

**Keywords**

Integrated insect management · Pest management · Agriculture conservation · Biodiversity · Insect control

## 11.1 Introduction

As the twentieth century and early twenty-first century brought incredible advances in subsistence farming, technical revolutions, machinery and chemicals, humans have been able to clear land and grow crops faster than ever before. Humans were able to clear and cultivate land faster than ever before, improve the ability to grow plants and feed animals faster, and manage insects and infections. Subsequently, some issues were uncovered, for instance, compounds stored on animals and plants, land and water similarly as soil breaking down, salinity of soil, soil acidification as well as biodiversity loss. As the twenty-first century dawned, our inclinations towards the environment, individuals, plants and several other creatures' prosperity compelled us towards more organic farming (Mason 2003). From the past years, we have been doing different developmental programmes in agriculture. There has been evidence of improvements that are attainable and acceptable to farmers when the basic principles of good farming practices are applied to both mechanized and unmechanized farming as well as small- and large-scale farms. This structure is called 'conservation agriculture' (CA), and it is being practised on a greater scale of more than one million around the globe (Derpsch and Friedrich 2009).

More likely than not, recent and advanced technologies we are using in agriculture have passed through gigantic increments in food proficiency through concentrated cultivation. This expansion of agrarian practices brought normal, money-related and social concerns including health issues to individuals and biological defilement. In addition to ecological, economic, and social concerns, agricultural intensification has an impact on human and environmental health. As a result of this intensification, over 400 insects, mites, and plant diseases have acquired resistance to one or more pesticides (Gold 1999). Intensive farming impacts various plants and populations of insects which are present in this ecosystem by reducing their genetic diversity. The effect on local habitat and soil inhabitant relationships among organisms is termed as soil tillage (El Titi 2003). The soil tillage mechanism is insufficient for managing insect pests, that's why cultural, biological, physical, mechanical, and chemical control approaches are applied for it. The twenty-first century needs to be totally based on advanced techniques such as biotechnological approaches and technology which are in favour of the environment such as eco-technology.

## 11.2 Insect Pest Management

The advanced technology for managing agriculture defects is known as integrated pest management (IPM). IPM is a secure and an eco-friendly method of managing pests and diseases which is becoming popular in the area of production of crops across the globe (Jayasooriya and Aheeyar 2016). IPM is defined by the UN Food and Agriculture Organization as a process of considering all available pest control techniques and integrating appropriate measures that discourage the development of pest populations and keep pesticides and other interventions at levels that are economically justifiable and reduce or minimize risks to human health and the environment (FAO 2012).

Insect pest management isn't suitable with CA yet furthermore runs over alike postulates. Say, for example, insect pest management helps in improving geological cycles and broadens its work among pest management as well as crop management during the whole procedure of crop production. IPM practices develop the soil microbiota. Likewise, CA is dependent upon the improved natural development among the area that handles little creatures along with several types of soil biota that cause diseases. Plant associations and crop rotation practices along with agriculture chemicals are handled by IPM, to control the insect pests and diseases caused by them (FAO 2006). As time passed, enhancement in biological activity increased by conservation agriculture advances and pest management, which achieves low amount of agrochemicals used for crop protection. CA combined with IPM, which uses information about pest life cycles and their interactions with the environment, could be effective for pest control. Thus, IPM and CA are effective and address the most impossible threats to the environment and human prosperity and property.

In carrying out IPM practices, four approaches are used (Harford and Le Breton 2009):

- Setting action thresholds
- Observing and perceiving pests
- Countering
- Control

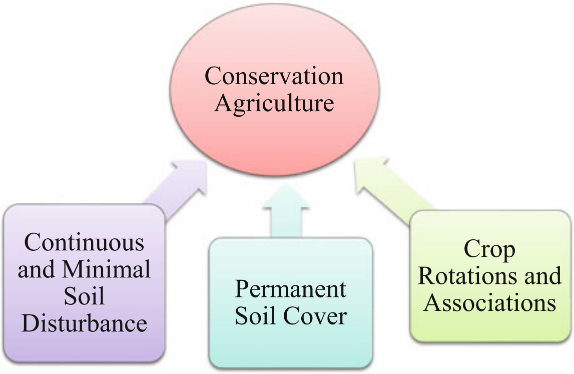


**Fig. 11.1** Major principles for conservation of agriculture

## 11.3 Conservation Agriculture

It is a management system of crop majorly based on three principles:

1. Minimum soil disturbance.
2. Soil surface must be covered by crop residues and crop covers.
3. Crop rotation must be followed by diverse species.

Conservation agriculture preserves the semi-everlasting *or* everlasting organic coverage of soil. This can be beaded mulch or can be a crop, which physically protects the soil from active soil biota, different climatic conditions and weather. The fauna and microorganisms in soil help in balancing the soil nutrient and tillage function. The mechanical process of tillage can disturb the soil condition. To avoid disease and pest problems, crop rotation is an important practice. Figure 11.1 shows the major principles of CA.

## 11.4 Conservation Agriculture and Insects

Insect pests are the predominant creatures on the planet, so it isn't astonishing that they cooperate with people in a bigger number of ways than some other gathering of organic entities. One million insect species or more than that have been portrayed. However 99% are generally beneficial or harmless to humankind, like bumble bees, silkworms, pollinators, parasitoids and predators. Just a small extent (1%) is our rivals making harm to our harvests (Grimaldi et al. 2005; Pedigo and Rice 2014). While the percentage of insect pest species is quite little in correlation with all the depicted species, they actually need critical assets, time and exertion to decrease their negative effect on crop production, crop assurance, human wellbeing and government assistance.

Insect pests offer significant biological types of assistance as predators, parasites, decomposers and consumers (Swift and Anderson 1989). Deterioration of crop plant or compounds by some maggots, parasites (muscid flies, blowflies, little compost flies), grubs and adult beetles (dermestid insects, scarab bugs, remains bugs) is used for reusing natural matter in environments (Castner 2010). Different predators (green lacewing, woman scarabs, predaceous plunging creepy crawlies, ground insects) and parasites (*Encarsias* sp., ichneomids) are assumed as significant species in controlling numerous phytophagous insect pests (Olembo and Hawksworth 1991). Insect pest management is separated into sections:

1. Regular section control mechanism
2. Practised or applied control mechanism

Control mechanisms incorporate factors according to the needs of the farm and are deliberately applied on abiotic and biotic factors, which include pests, parasites, and ill-health.

Most likely, by expanding bio-variety, CA is invaluable for controlling insect pests. Advancements are done through organic varieties by conservation agriculture, above the ground or beneath the ground by making an ideal cover (Jaipal et al. 2002), which assists in controlling insect pests. Predators and parasitoids are also seen in fields with the mulch and ground cover, by holding creepy crawly bothers within proper limits (Kendall et al. 1995; Jaipal et al. 2002).

## 11.5 Biodiversity Along with Insect Pest Management

### 11.5.1 What Is Biodiversity?

As we know, biodiversity itself is a complete framework presented by the degree for quality assortment or diversity inside the normal framework, both in number and recurrence. It is comprehended regarding the wide assortment of plants, creatures and pathogens, the properties they have and biological structure are made by them make them unique. In this current scenario, biodiversity or ecological habitat is the consequence of billions of long periods of advancement, formed by normal cycles and, progressively, by the impact of people. Small animals like creepy crawlies are recognized to be approximately 2.1 million in the species percentage. The existence of species on Earth is ranging from 9.0 to 52 million; this data is according to UNEP gauges (Mora et al. 2011). Biodiversity or ecological habitat additionally incorporates hereditary contrasts inside every species, for instance, between assortments of harvests and types of domesticated animals. Chromosomes, qualities and DNA, the structure squares of life, decide each and every species' rareness and the rareness of the individual. One more element of ecological habitat and biodiversity is the assortment of environments like deserts, timberlands, wetlands, mountains, lakes, streams and farming scenes. Each environment has their particular surroundings for living animals, viz. air, water and soil.

Biodiversity signifies three different levels:

1. **Hereditary variety:** This is the assortment of hereditary data that contain individual plants, creatures and microorganisms. Basically it is the variety of qualities found in the species and populaces.
2. **Species variety:** This is the assortment of species or the living beings. It is estimated regarding species extravagance (including species in a characterized region) and species abundance (relative numbers among species).

Species based on their functions are described below:

1. **Functionality sorts:** Those species, which perform distinctive natural capacities, come under functionality sorts.
2. **Functionality analogs:** Functionality analogs species have similar or very comparable natural capacities.

### 11.5.2 What Is Insect Biodiversity?

Across the world, a diverse group of animals are insects, which are making up a specific percentage in the global biodiversity (Foottit and Adler 2009). Insect pests are the world's most assorted gathering of creatures, making up over 58% of the known worldwide biodiversity. Insects are firmly connected with our lives and influence the government assistance of humankind in different ways. Simultaneously, huge quantities of creepy crawly species proceed to become terminated or extirpated from neighbourhood natural surroundings around the world. Our insight into insects' biodiversity is a long way from complete. Bugs are the most abundant sign of living things. Bugs can be gauged by numerous traits: their extensive capacities and security of their essential types, their collection of higher orders (with just about 30 species usually recognized), their abundance of species, as well as similar substances. Every one of these animal types has its person natural quirks, environmental job, appropriation and, also, connections inside the neighbourhood community. Each species may vary in propensity and appearance both from its nearest family members and furthermore across its reach to reflect nearby impacts conditions. Each species is in this way a mosaic of actual assortment and hereditary constitution that can lead to both ordered and natural vagueness in deciphering its honesty and the manners by which it might develop and persevere.

## 11.6 How to Control Insect Pests Through Different Mechanisms?

Insect pests are controlled as they are representing threats to humans, nature and economy. Creepy crawly bugs are presenting numerous dangers to crops which are implied in subjective and quantitative misfortunes of yields. On the off chance that bug irritations are not controlled successfully, then it will be hard for ranchers to get great yields from the harvest creation exercises. Bug control measures would give chance to the harvest makers or ranchers to control the bugs, before they cause financial misfortunes to the yield. Insect pests additionally should be controlled because they are the vectors of many harvest illnesses and result in moving infections to inaccessible regions via conveying with them the sickness side effects.

## 11.7 Methods for Insect Pest Control

Pest management can be carried out through various methods which are described in Fig. 11.2.

### 11.7.1 Pest Control by Cultural Method

It deals with preparation of soil and selection of plants that create an environment among the crop to make it less susceptible or make a resistance against the insect pest, e.g. use of resistant varieties, tillage of soil, planting of trap and rotation of crop. Planting of trap crops and many more practices are examples of cultural methods. Providing beneficial insects with a diversity of habitats by planting cover crops and nectar-producing plants is an important technique to use. Cover crops like grass species or vegetables stop retardation of weeds and soil disintegration. There are many cover crops which are utilized in the form of compost and green compost which always gives major nutrients and organic matter to the desired crop. If this same method of cover crops is done by a particular species like the *Brassica* family, it has the ability to cure infection through pests and smother wilting disease. The leftover crops like rye and wheat give in excess of 90% weed concealment. These cultural controls are chosen in view of the information related to pests' biology and their development. Cultural control strategies are describes in Fig. 11.3.

**Fig. 11.2** Methods of insect pest management

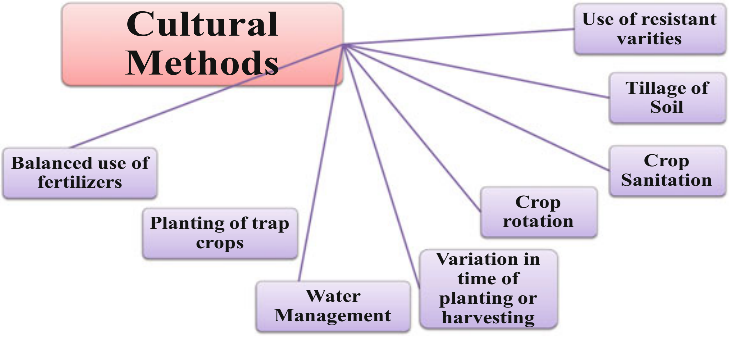


**Fig. 11.3** Cultural pest control strategies for the regulation of IPA

### 11.7.2 Physical or Mechanical Control

These depend upon the pests' behaviour. An example of physical method is majorly done in potato fields in the entrapment and relocation of *Leptinotarsa decemlineata*, a Colorado potato beetle, by forming a setup of lined channels of plastic. Some typical practices are done in developing regions for the pigeon pea plant in order to eliminate the hatchlings of *Helicoverpa*, and it is concluded by pigeon pea plant shaking. A straightforward strategy in control or in management of pest is the handpicking technique. Mechanical methods are used to create barriers and screens, as well as some exclusions, such as packaging with polymer films, screening through doors and windows, bird scaring, row covers, trenches, and particle barriers. Utilizing mulches to cover weeds and putting line covers to secure plants from pests are different models. Figure 11.4 shows mechanical and physical pest control strategies for the regulation of IPA.

### 11.7.3 Biological Control

This incorporates expansion and preservation of characteristic foes of nuisances like creepy crawly hunters, parasitoids, parasitic nematodes, organisms and microbes. In IPM programmes, local regular foe populaces are preserved, and non-local specialists might be delivered with the most extreme alert. The most important species of parasitoids is *Trichogramma*, which are continuously used in diversified desired crops. Various pathogens, for example, *Trichoderma* spp., *Verticillium* spp., *Aspergillus* spp. and species of *Bacillus and Pseudomonas* which assault or stifle the crops' microorganisms, have been misused as organic control specialists. Organic managing strategies are shown in Fig. 11.5. Figure 11.6 describes examples of predators which are used for pest control, and Fig. 11.7 describes various parasitoids used to control pests.

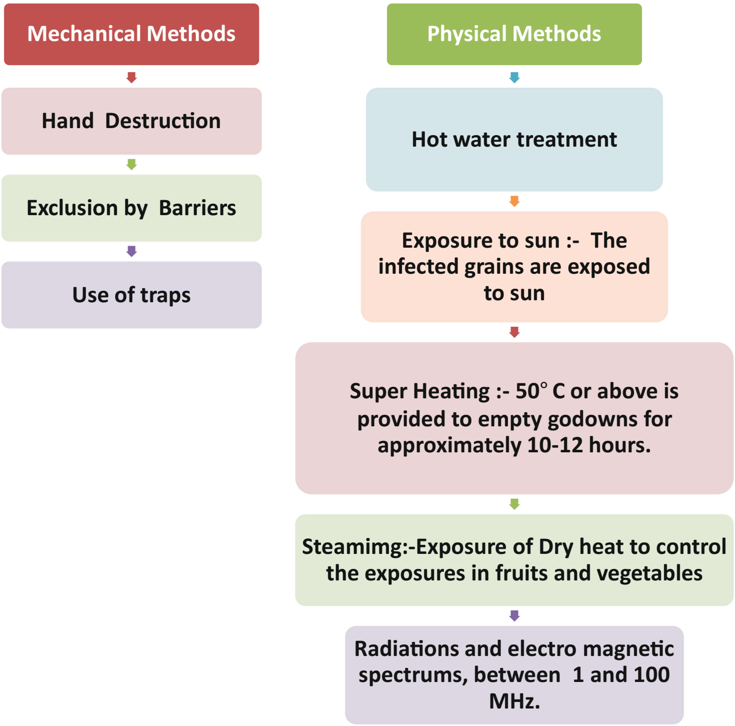


**Fig. 11.4** Mechanical and physical pest control strategies for the regulation of IPA

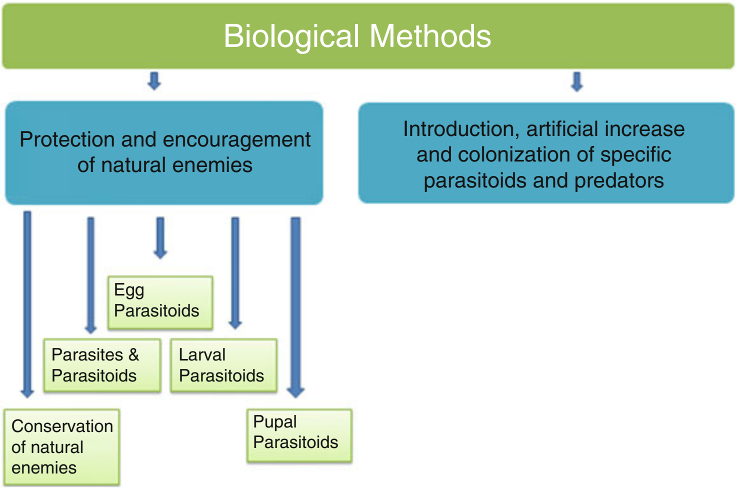


**Fig. 11.5** Biological strategies of pest control for the regulation of IPA

**Fig. 11.6** Predators used for pest control with example

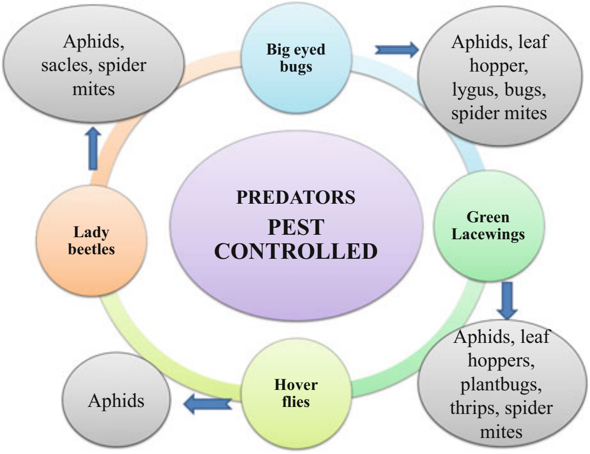
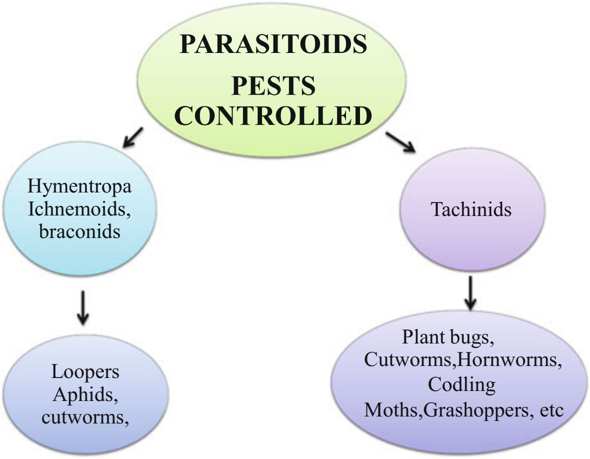


**Fig. 11.7** Parasitoids used for pest control with example



## 11.7.4 Chemical Controls

Pesticides are utilized to keep the irritation populaces beneath monetarily harming levels when the irritations can't be constrained by different methods. Pesticides incorporate one as well as other plant-inferred pesticides and engineered pesticides. Engineered pesticide incorporates man-made synthetic substances at a broad scale. These are comfortably being utilized, effective as well as moderately economical. Preferably, pesticides are ought to be utilized as a last resort in insect pest management programmes in view of their likely negative impact on the climate.

- Insecticides, herbicides and fungicides
- Acaricides; nematicides, which kill nematodes; rodenticides, for controlling rodents; and avicides which control birds (dark birds)

- Pheromones which usually disturb the mating behaviour of insects (exceptionally powerful, however not presently effectively available or affordable)
- Plant pesticides which are homebased
- Repellents which repel insects and pests
- *Bacillus thuringiensis* (Bt), biopesticide, neem-based pests sprays and so on

## 11.8 Control Methods Used for IPM

PM consolidates various methods to forestall bug harm without hurting the surrounding able environment. IPM can be executed in any place irritations are developed: in schools and on ranches, homes, medical clinics, cafés, greens and home nurseries. It additionally sets aside cash.

### 11.8.1 Natural Enemies

1. Avoiding pesticides ensures characteristic adversaries in home nurseries.
2. Natural foes incorporate hunters, parasites and infections of vermin.
3. Farming practices that secure common foes are utilized.
4. Predators, for example, ladybird creepy crawlies, are delivered in nurseries.
5. Pesticides made from bacteria are utilized with respect to vegetable and different yields.
6. Modification of habitats.
7. Food and water are needed by all bugs.
8. Managing techniques that keep retain bugs by this means essential requirements will surely diminish bug issues.

## 11.9 Procedures for IPM Execution

An incorporated methodology for the administration of significant nuisances and illnesses is conceivable by:

1. Reproducing new assortments that help in obstruction
2. Developing productive techniques for bother control through bug studies and checking
3. Natural control of bothers with the assistance of preservation and expansion of common foes like parasites, hunters and bug microbes

Financially reasonable management of pest has been created for the management of significant irritations in cotton, rice, sugarcane, beats and so forth. Control of top borer and Pyrilla of sugarcane, coffee mealybug, lepidopterous (moth pests) bugs which affect cotton, sugarcane, tobacco, coconut, and so forth, by releasing biocontrol agents, success can be achieved. A significant accomplishment has been the advancement of wide-ranging innovation for biological control specialists, for example, *Chrysoperla* spp., *Trichogramma* spp. and nuclear polyhedrosis viruses (NPV) of Heliothis and Spodoptera genera.

## 11.10 Basics for IPM Execution

- Availability of area explicit insect pest management modules, which are naturally reasonable, monetarily feasible and socially satisfactory.
- Degree of target gathering cooperation must be high.
- Spread methodology is area wide.
- In scattering of IPM, hindrances must be removed.
- Assessing, measuring and publicizing the effects of IPM.

Preservation of normal adversaries of nuisances and thus their increment has dominant significance. Furthermore, the inherent properties of inexhaustibility, reversibility and versatility of biopesticides/botanicals make them generally trustworthy instruments for practical IPM. Henceforth, to keep the natural equilibrium and to deal with the vermin, the utilization of bio-specialists and biopesticides/botanicals should get needed consideration. Supportable cultivating rehearses generally include:

- Crop turns that moderate weeds, sickness, bug and other vermin issues; give elective wellsprings of soil nitrogen; lessen soil disintegration; and decrease danger of water tainting by farming synthetic substances
- Pest control procedures incorporate coordinated bother the executives methods that decrease the requirement for pesticides by practices, for example, exploring/checking, utilization of safe cultivated species, planting time, and organic bother controls.
- Increment in weed control, mechanical/organic; more water and soil preservation rehearses; and key utilization of organic fertilizers
- Usage of common or engineered contributions to a system that represents no huge peril to people or on the other hand the climate

## 11.11 Procedures for Successful Management of Pest

To make IPM work, the imperatives should be tended to appropriately, and the gaps in information should be spanned through research and development. The following procedures could help improve appropriation of IPM:

- Training must be provided to the ranchers and expansion staff in insect pest management technique
- R&D institutions partnered with state officers and non-government organizations (NGOs) to organize aggressive demonstration campaigns.

- Improved or revamped accessibility of basic sources of bioagents, biopesticides and varieties which are resistant.
- Development of checking instruments and cautioning frameworks
- Utilization of more secure pesticides and proper application strategies
- Research on numerous infection- and irritation-safe assortments
- Holistic combination of all data to create bio-serious and financially savvy rehearses.

## 11.12 Advantages in Management of Insect Pest

1. More slow improvement of protection from pesticides.
2. Sprayed operators are less likely to suffer health problems.
3. Decreased substance tainting of food and also climate.
4. Decreased reliance on synthetic substances; henceforth insect pest management is a stage regarding maintainable farming.
5. Improved quality is obtained from the better wellbeing of plants.
6. Diminished crop plant misfortune.
7. Diminished utilization of compound application will diminish the danger of decay and deformation of possessions.
8. Diminished utilization of compound application may bring about a monetary reserve funds.
9. The natural enhancements made to the office to carry out an IPM programme will improve the drawn-out dependability of the property far beyond assurance against bugs.
10. IPM might be the lone answer for a few long-haul bug issues where substance application has no function.
11. Insect pest management at last permits the foundation to having much prominent command over and information on bother action in their office.
12. For major institutions, IPM is the most appropriate management strategy.

## 11.13 Disadvantages of Management of Pests

- Conventional management takes less staff time comparatively to insect pest management regardless of whether execution is contracted to a company which manages it in a better way.
- To execute IPM, the whole staff need to know about the planned exertion in an appropriate way.
- In the beginning, IPM may be more expensive than traditional pest management.

## 11.14 Futuristic Methods in Insect Pest Management

### 11.14.1 Biotechnological Approaches for Management of Insect Pests

Plant diseases and insect pests have an impact on plant yield; therefore, it is critical to managing those pests. Biotechnology and genetic design aid in the production of enhanced crop plants that are resistant to disease-causing insects, bacteria, or organisms. Globally, insect pests and plant pathogens cause crop losses of $30–50 billion annually (Cook 2006). In addition to other approaches of crop production, biotechnological and genetic engineering approaches have been used to support plant health, stabilized yields, and increment in the safety of food. Biotechnology utilizes living frameworks and creatures to create or make helpful items or (Jhon and Maria 2001) 'any innovative application that utilizes natural frameworks, living organic entities or subsidiaries thereof, to make or alter items or cycles for explicit use'. The significant executions of biotechnology in buildup or in creation by shielding crops from insect pests are the following:

The draining common asset base coupled with the blossoming populace requests a quantum bounce in our efficiency levels to meet the necessities. Biotechnology offers special freedoms to address environmental issues, some of which are caused by non-sustainable agriculture and mechanical practices, and has arisen as a significant tool in IPM, giving new methods of controlling plant obstruction to pests. Utilizing plant biotechnology, a few herbicide-tolerating crops have been created and marketed that permit the utilization of herbicides that are viable and prudent which are also favourable to environmental characteristics. Biotechnology gives the apparatuses to alter execution of significant organic components of pest control, like natural enemies and plant assortments. New yield-cultivated varieties with opposition to insects and pests and illnesses joined with biological control specialists should be prompted to decrease dependence on pesticides, consequently diminishing ranchers' yield insurance costs, while it is beneficial for both the climate and public wellbeing (Sharma et al. 2002). Transgenic protection against insect pests has been shown in plants conveying genes which are particularly insecticidal genes, such as those from *B. thuringiensis* (Bt) which have δ-*endotoxins*, protease inhibitors, some agrochemicals and metabolites of plants and their lectins. Protease inhibitors (PIs) are a type of plant defense protein that protects plants from insect pest infestation. Lectins are a broad family of carbohydrate-binding proteins discovered within and associated with organisms from all kingdoms of life and also have a defensive behavior against a vast range of organisms. However protease inhibitors and lectins do not show a highly poisonous effect in comparison to Bt poisonous proteins, and the collective use of these proteins is more effective (Hilder and Boulter 1999). Qualities presenting protection from insect pests can likewise be conveyed as multilines or engineered assortments. Encouraging outcomes came by the control of Bt-defence therefore less insect pests have been found in the research centre and in the working field, thus it is the earliest approach for commercial purpose which promoted the use of Bt-transgenic crops at large scale (Table 11.1). The utilization of

**Table 11.1** *Bt* gene which is used in opposition to the pest in desired crop

| Crop/ plant | *Bacillus thuringiensis* (Bt gene) | Used against the pest | References |
|---|---|---|---|
| Corn | cry1Ab | Heliothis zea | Koziel et al. (1993), Armstrong et al. (1995), Buschman et al. (1998) |
| | cry1Ac | *Pectinophora gossypiella* | |
| Cotton | cry1Ab | Pink bollworm | Jenkins et al. (1997), Perlak et al. (1990), Wilson et al. (1992), Artim (2003), Tohidfar et al. (2008), Khan et al. (2011), Bakhsh et al. (2012), Pushpa et al. (2013) |
| | cry1Ac | Cotton bollworm | |
| | vip3Aa | Lepidopteran, Homopteran insects *T. ni*, *H. armigera*, *H. zea*, *Pectinophora gossypiella*, *Heliothis virescens*, *S. exigua* | |
| | cryIIA | | |
| | cry1EC | | |
| | Potato inhibitor | | |
| | GNA | | |
| Potato | Cry3A | *Leptinotarsa decemlineata* | Perlak et al. (1993), Duck and Evola (1997), Ebora et al. (1994), Douches et al. (2004) |
| | Cry1Ab | Potato tuberworm | |
| | Cry1Ac | Potato tuberworm | |
| | Cry5 | Potato tuberworm | |
| Tomato | cry1Ab | Tobacco hornworm *M. sexta* | Delannay et al. (1989) |
| Brinjal | cry1Ab | Fruit borer | Kumar et al. (1998), Iannacone et al. (1997) |
| | cry3B | Fruit borer | |
| Chickpea | cry1Ac | Pod borer | Kar et al. (1997), Sanyal et al. (2005), Indurker et al. (2007), Acharjee et al. (2010), Mehrotra et al. (2011) |
| | cry2Aa | Lepidoptera | |
| | cry1A (c) + cry1A (b) | *H. armigera* | |
| Rice | cry1Ab | Yellow stem borer, striped stem borer | Datta et al. (1998), Shu et al. (2000), Ye et al. (2001), Nayak et al. (1997), Maqbool et al. (2001), Loc et al. (2002), Raina et al. (2002), Bashir et al. (2004), Bashir et al. (2005), Tang et al. 2006), Zhang et al. (2013a, b) |
| | cry1Ac | Yellow stem borer | |
| | cry2A-1Ac-gna | Rice weevil, rice hispa | |
| | cry1B-1Aa | Yellow stem borer | |
| | Cry1Ac-2A | Yellow stem borer, rice leaf folder | |
| | PinII | Lepidoptera, *Scirpophaga incertulas*, *Cnaphalocrocis medinalis*, *C. suppressalis* | |
| | cry1C | | |
| | sbk + sck | | |
| Sugarcane | cry1Ab | *Diatraea saccharalis* (shoot borer) | Arencibia et al. (1997) |
| Maize | Cry1 and Cry2 | Lepidoptera | (Schnepf et al. (1998) |
| | Cry3 | Coleoptera | |
| Soybean | cryIA (b) | *Holotrichia parallela* (dark black chafer) | Dufourmantel et al. (2005), Parrott et al. (1994), Qin et al. (2019), Dang and Wei (2007) |
| | cryIA (c) | Lepidoptera | |
| | Cry-8 like gene | | |

(continued)

**Table 11.1** (continued)

| Crop/ plant | *Bacillus thuringiensis* (Bt gene) | Used against the pest | References |
|---|---|---|---|
| Alfalfa | cry3a, Cry *1C* | Coleoptera, *Spodoptera littoralis* | Tohidfar et al. (2013) |
| Canola | cry*1Ac* | Diamondback moth | Stewart et al. (1996), Tabashnik et al. (1993), Ramachandran et al. (1998), Halfhill et al. (2001), Shelton et al. (2000) |
|  |  | Lepidoptera, *S. exigua*, *Helicoverpa zea* |  |

biotechnology strategies inside the horticulture area can conceivably improve foodstuffs by certainty raising yield resilience to unfavourable biotic and abiotic circumstances by upgrading flexibility of harvests to various environments and by improving yields, pest obstruction and, also, sustenance, especially of staple food crops.

## 11.15 Conclusion

The objectives of insect pest management and conservation agriculture are somehow similar, which seeks to enhance the conservancy of natural resources, sustainable productivity, reducing crop production cost, focusing on the environmental health, maintenance of biodiversity either of plants or insects and reduce the usage of chemicals in the production of crops as well as in the protection methods. Over the last few decades, there has been a massive flow of advancements in the agricultural area; technical developments are being used to shift traditional farming practices to modern farming practices. Conventional pest management practices harm our ecosystem in numerous ways than we realized. The IPM approach bring a positive change in the field of agricultural by understanding insect pest characteristics, crop rotation according to it and an enhancement in the monitoring techniques. Increment in the biodiversity that is of plant as well as insects is an effective task to keep insect pest population at an adoption level; in this wide diversity, only one method of pest control is not efficient, so we use multiple methods and recent advancements such as integrated pest management. Developmental conservation of agriculture is playing a vital role. However futuristic technologies are also being used such as biotechnological approaches, transgenics and usage of *Bt* genes.

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# Part III

# Sources of Agrochemicals/Contaminants and Their Impacts on Soil Health & Environment

# Mobility of Trace Elements in Agricultural Soils

# 12

Tamer A. Elbana

## Abstract

Numerous studies were published to quantify and model trace elements mobility in soils to understand their fate in the environment. The transport of trace elements is controlled by soil colloid properties, trace element characteristics, and environmental soil conditions. However, the diffusion process and the rate-limited sorption behavior control the retention and mobility of trace elements in soil, especially on the longtime scale. In this chapter, the role of solute transport mechanisms (diffusion and the hydrodynamic dispersion) and the principles of trace elements' reactivity in soils were reviewed and discussed. Besides, this chapter includes a concise review of using the advection-dispersion equation for quantifying and simulating the mobility of trace elements in soils. The literature review revealed that the combined effects of physical, chemical, equilibrium, and kinetic processes control trace elements mobility in soils. Several studies indicated the importance of considering the nonlinear and the sorption kinetic behavior for modeling trace elements' mobility in soils. Furthermore, brief discussions of Cd, Cu, Pb, Sn, and Se mobility in agricultural soils were presented. Based on the literature review, further research is needed to explore and model the competitive effect of multiple trace elements on the mobility of each other in the soil systems.

## Keywords

Heavy metal · Transport · Miscible displacement · Sorption · Kinetic

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## 12.1 Introduction

The soil is a porous system that allows water and chemicals to transport through it. Such a process enables the soil to regulate water supplies and control contaminants' fate in the ecosystem. The soil is a heterogeneous environment that consists of solid, liquid, gas, and biological phases. Each phase is a multifaceted compartment itself containing several compounds and chemical forms. For instance, the solid phase comprises organic materials and several minerals such as (hydr)-oxides of Al and Fe, silicates, carbonates, and phosphates. Each soil constituent interacts uniquely with the soluble chemicals (solutes) in the liquid phase. Sorption of the solute into the solid phase limits the mobility of chemicals in the soil profile. Besides, soil particles' size varies from microscopic dimensions to large visible particles creating different pore sizes that control water and solute mobility in soil. Furthermore, water content ($\Theta$) and aeration conditions induce factors where different mobility rates are anticipated under saturated and unsaturated conditions.

Trace elements are chemicals that occur at a concentration of less than 100 mg kg$^{-1}$ in uncontaminated soil. In agricultural soils, trace elements include metals, metalloids, and nonmetal such as Cd, As, and Se with an average of 0.5, 5.0, and 0.33 mg kg$^{-1}$, respectively (Kabata-Pendias and Mukherjee 2007). However, some trace elements such as Cu and Zn are essentials for living organisms; these elements are toxic at high concentrations. Anthropogenic sources of trace elements include the addition of biosolids, fertilizers, pesticides, reuse of drainage water and untreated wastewater, and atmospheric deposition (Adriano 2001; Elbana et al. 2019). The excess concentrations of trace elements in soils cause plant toxicity, animal and human health diseases, and environmental problems. For instance, pollution with Cd and $CH_3Hg$ cause Itai-Itai and Minamata diseases, respectively. The chemical reactivity of trace elements in soil directs its mobility and biological uptake. The sorption of trace elements on soil surfaces reduces its mobility in soils and the availability to plants. Numerous soil properties such as soil reaction (pH), redox potential (Eh), cation exchange capacity (CEC), and soil contents of $CaCO_3$, organic matter (OM), and Fe/Al (hydro)oxides control sorption of trace elements in soils (Adriano 2001; Chuan et al. 1996; Rouff et al. 2002; Sauvé et al. 2000; Shaheen et al. 2009; Sparks 2003). Moreover, soils exhibit different affinities to sorb various trace elements. For example, sorption of trace elements on different ten soils revealed that Pb and Cu showed higher sorption on soil than Cd, Zn, and Ni (Elbana et al. 2018).

In this chapter, the mobility of trace elements in the soils is discussed in terms of modeling trace element mobility, trace element reactivity, and soil/environmental factors that control these chemicals' fate in the soils. Besides, brief discussions on Cd, Cu, Pb, and Se mobility in agricultural soils are presented considering different soil properties and environmental conditions.

## 12.2 Solute Diffusion

Diffusion is the transport of solute due to the random molecular motions among soil liquid phase. The direction of solute motion during the diffusion process is indefinite at a particular time due to the random motion. Despite that, the average quantity of solute transfers through the system from high to low concentration can be quantified. In an isotropic medium, the rate of diffusing a chemical throughout the unit sectional area can be calculated according to Fick's law:

$$F_{\mathrm{e}} = -D_{\mathrm{e}} \frac{\partial C}{\partial x} \tag{12.1}$$

where $F_{\mathrm{e}}$ is diffusion rate per unit area (diffusion flux), $D_{\mathrm{e}}$ is diffusion coefficient (diffusivity, $\mathrm{L}^2\ \mathrm{T}^{-1}$), $C$ is a concentration of diffusing solute, and $x$ is transport distance. Here, the negative sign indicates that the diffusion process occurs in the opposite direction of increasing concentration. Thus, the vector notation of the general form of Fick's law in three dimensions can be written as:

$$F_{\mathrm{e}} = -D_{\mathrm{e}} \nabla C \tag{12.2}$$

where $\nabla C$ denotes the concentration gradient vector. Crank (1975) derived the differential equation in a Cartesian coordinates $x$, $y$, and $z$ as:

1. In isotropic-homogenous medium:

$$\frac{\partial C}{\partial t} = D_{\mathrm{e}} \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \tag{12.3}$$

2. In anisotropic medium:

$$\frac{\partial C}{\partial t} = D_{\mathrm{ex}} \frac{\partial^2 C}{\partial x^2} + D_{\mathrm{ey}} \frac{\partial^2 C}{\partial y^2} + D_{\mathrm{ez}} \frac{\partial^2 C}{\partial z^2} \tag{12.4}$$

   where, $D_{\mathrm{e}x}$, $D_{\mathrm{e}y}$, and $D_{\mathrm{e}z}$ denote the diffusion coefficients for the principal $x$, $y$, and $z$ axes, respectively.

   Simply, for one dimensional along $x$-axis, Eq. (12.3) can be simplified as:

$$\frac{\partial C}{\partial t} = D_{\mathrm{e}} \left( \frac{\partial^2 C}{\partial x^2} \right) \tag{12.5}$$

Differentiation of Eq. (12.5) by assuming diffusivity ($D_{\mathrm{e}}$) is constant. For thin-film geometry: At $t = 0$, $C(x, 0) = M\delta(x)$ where $M$ is diffusing solute per unit area and $\delta(x)$ is Dirac delta function. A numerical solution can be obtained by assuming solute is occurred on the surface of the sample (Mehrer 2007), as:

$$C(x,t) = \frac{M}{\sqrt{\pi D_{\mathrm{e}} t}} \exp\left(-\frac{x^2}{4D_{\mathrm{e}} t}\right) \tag{12.6}$$

Besides, the diffusion coefficient can be estimated successfully using empirical equations (Kemper and Van Schaik 1966; Dudek and Borys 2019). Modeling of diffusion is a valuable technique to quantify solutes' fate in the environment. Kirk (1990) successfully simulated the diffusion and the oxidation of iron in lowland rice. Specifically, Kirk (1990) considered the main reaction as:

$$4\mathrm{Fe}^{2+} + \mathrm{O}_2 + 10\mathrm{H}_2\mathrm{O} \leftrightarrow 4\mathrm{Fe(OH)}_3 + 8\mathrm{H}^+$$

Besides modeling the diffusion processes of $\mathrm{Fe}^{2+}$ and $\mathrm{O}_2$, they simulated acidity diffusion by Eq. (12.7):

$$\frac{\partial \mathrm{pH}}{\partial t} = D_{\mathrm{h}} \left(\frac{\partial^2 \mathrm{pH}}{\partial x^2}\right) \tag{12.7}$$

where $D_{\mathrm{h}}$ is a soil acidity diffusion coefficient. Such a successful simulation was obtained by considering several reactions (oxidation-reduction and acidification), environmental factors (moisture content), and the related parameters of the growing plant.

The diffusion of cationic trace elements in soils is minimal as a result of its reactivity. For example, Ellis (1970) reported that the diffusivity of Cu in water-saturated clay films of illite, montmorillonite, and vermiculite were $0.09 \times 10^{-5}$, $0.02 \times 10^{-5}$, and $0.01 \times 10^{-5}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$, respectively, whereas it was $1.09 \times 10^{-5}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$ for Cu in a pure aqueous solution. Bruemmer et al. (1988) concluded that the diffusion process controlled the longtime adsorption of Cd, Ni, and Zn by goethite with slow diffusion rates that ranged between $3 \times 10^{-20}$ and $20 \times 10^{-20}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$. Likewise, Shackelford and Daniel (1991) showed that nonlinear sorption and chemical precipitation enlarged the estimated values of the effective diffusion coefficients for Cd (ranged between $4.8 \times 10^{-6}$ and $10 \times 10^{-6}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$) and Zn (ranged between $8.2 \times 10^{-6}$ and $25.4 \times 10^{-6}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$) in compacted clay soils. Moreover, intra-particle diffusion controls the sorption rate of trace elements by biochar particles. Rees et al. (2014) found diffusion of Cd, Cu, Ni, Pb, and Zn in or from biochar particle-controlled immobilization in biochar-amended soils as a short-term effect. For an example of anionic trace element diffusion, Iida et al. (2011) found that the effective diffusion coefficient of Se was diminished as a result of lowering the salinity and increasing the bentonite content in bentonite/sand mixture with values that ranged between $9.7 \times 10^{-8}$ and $5.9 \times 10^{-7}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$. However, Ikonen et al. (2016) reported $7 \times 10^{-9}$ and $3 \times 10^{-8}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$ for the effective diffusion coefficient of Se in Kuru gray granite (fine-grained granitic rock) and Grimsel granodiorite (grained and slightly foliated granodiorite), respectively.

## 12.3 Solute Hydrodynamic Dispersion

Hydrodynamic dispersion or mechanical dispersion is another solute transport mechanism where flow velocity controls solute mobility. Soil is a heterogeneous open system that is characterized by its pore size variability. By comparing sandy and clayey soils, we observe different water flow rates due to the dissimilarities of pore space distribution associated with each soil. Even for one water flow pathway (e.g., capillary tube) in a soil, the highest discharge, water volume per time, occurs at the center of the tube, whereas the lowest discharge occurs adjacent to the boundaries of the capillary tube. Specifically, Poiseuille's law specifies that the discharge is proportional to the fourth power of the capillary tube radius (Hillel 2004). Therefore, the hydrodynamic dispersion coefficient influences solute transport and mobility of trace elements in soils. Then, the dispersion flux ($F_\mathrm{d}$) can be calculated according to:

$$F_\mathrm{d} = -D_\mathrm{s}\frac{\partial C}{\partial x} \tag{12.8}$$

where $D_\mathrm{s}$ is the hydrodynamic dispersion coefficient. Comparable to the diffusion equation for one dimension flow, the rate of the change in solute concentration ($\frac{\partial C}{\partial t}$) can be computed for one dimensional along the $x$-axis:

$$\frac{\partial C}{\partial t} = D_\mathrm{s}\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{12.9}$$

where $D_\mathrm{s}$ is the hydrodynamic dispersion coefficient. Because of the mathematical similarity, hydrologists use the term dispersion coefficient ($D$) to combine the total effect of hydrodynamic dispersion and diffusion coefficients, as shown in Eq. (12.10):

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{12.10}$$

The relationship between the dispersion coefficient and the average water velocity is positively linear, whereas the $D$ value decreased by increasing water content (Sato et al. 2003). Numerous factors affect solute dispersion in soils, such as scale effect (Pickens and Grisak 1981; Khan and Jury 1990; Gelhar et al. 1992), aggregate sizes (Anderson et al. 1992), anion exclusion (Gvirtzman and Gorelick 1991), and local permeability (Aggelopoulos and Tsakiroglou 2007). Solute dispersion is a reflection of soil heterogeneity and the native variability of soil systems. Aggelopoulos and Tsakiroglou (2008) concluded that high solute dispersion is associated with the occurrence of preferential flow as an indication of microscale soil heterogeneity. On a specific site and scale of up to 2.5 m, Godoy et al. (2019) emphasized the rule of the combined effect of soil physical properties on solute transport, where no strong correlation between dispersion coefficient and any individual soil physical properties (total porosity, effective porosity, macroporosity, microporosity, mesoporosity, bulk density, and hydraulic conductivity) was found. Here, measuring of dispersion coefficient takes place in modeling solute transport to quantify physical nonequilibrium. Moreover, other parameters related to chemical reactivity, such as sorption/desorption parameters, are significant to simulate trace element mobility in soils.

## 12.4 Trace Element Reactivity in Soils

Once a trace element occurs in a soil system, it is involved in chemical reactions or moves with soil water through diffusion and dispersion. Several chemical reactions can occur, such as adsorption/desorption, solubilization/precipitation, oxidation/reductions, formation of surface complex, and ion exchange. The relationship between the amount of the retained trace element on soil ($S$) and that concentration in soil solution ($C$) can be described as $S = f(C)$. Different mathematical functions were applied to simulate this relation which is commonly known as "sorption isotherm." For instance, linear isotherm (Eq. 12.11), Freundlich (Eq. 12.12), and Langmuir (Eq. 12.13) models are commonly practiced to describe sorption isotherms of trace elements in agricultural soils.

$$S = k_{\mathrm{d}}C \tag{12.11}$$

$$S = k_{\mathrm{f}}C^{n} \tag{12.12}$$

$$S = \frac{S_{\max}LC}{1 + LC} \tag{12.13}$$

where $k_{\mathrm{d}}$, $k_{\mathrm{f}}$ are linear and Freundlich distribution coefficients, respectively; $n$ is the nonlinearity parameter; $L$ is Langmuir coefficient; and $S_{\max}$ is the maximum sorption amount. Figure 12.1 shows a graphical representation of sorption isotherms where the sorbed amount on soil and the apparent equilibrium concentration in solution are plotted on the $y$-axis and $x$-axis, respectively. For the linear sorption isotherms, as Fig. 12.1 shows, increasing the slope (the linear distribution coefficient, $k_{\mathrm{d}}$) is an indication of increasing the sorbed amount on soil surfaces. Therefore, $k_{\mathrm{d}}$ of A-isotherm $<k_{\mathrm{d}}$ of B-isotherm $<k_{\mathrm{d}}$ of C-isotherm (Fig. 12.1).

The nonlinear isotherms (D, E, and F) were plotted in Fig. 12.1 using $n = 0.7$ for computing these three isotherms. The lowest $k_{\mathrm{f}}$ is associated with D-curve, whereas the highest $k_{\mathrm{f}}$ is associated with F-curve (Fig. 12.1). Therefore, in the case of the same $n$ value, the highest $k_{\mathrm{f}}$ designates the highest soil affinity. On the other hand, based on the Langmuir model (Eq. 12.13), comparing $S_{\max}$ can directly indicate the highest affinity of solutes on the soil. Moreover, linear sorption isotherm is not commonly observed for trace elements when a wide range of initial solute concentrations is applied. For example, Elbana et al. (2018) found that the sorption isotherms of Cd, Cu, Ni, Pb, and Zn on nine different soil series exhibited a nonlinear behavior. Specifically, the high retention behavior of those trace elements is

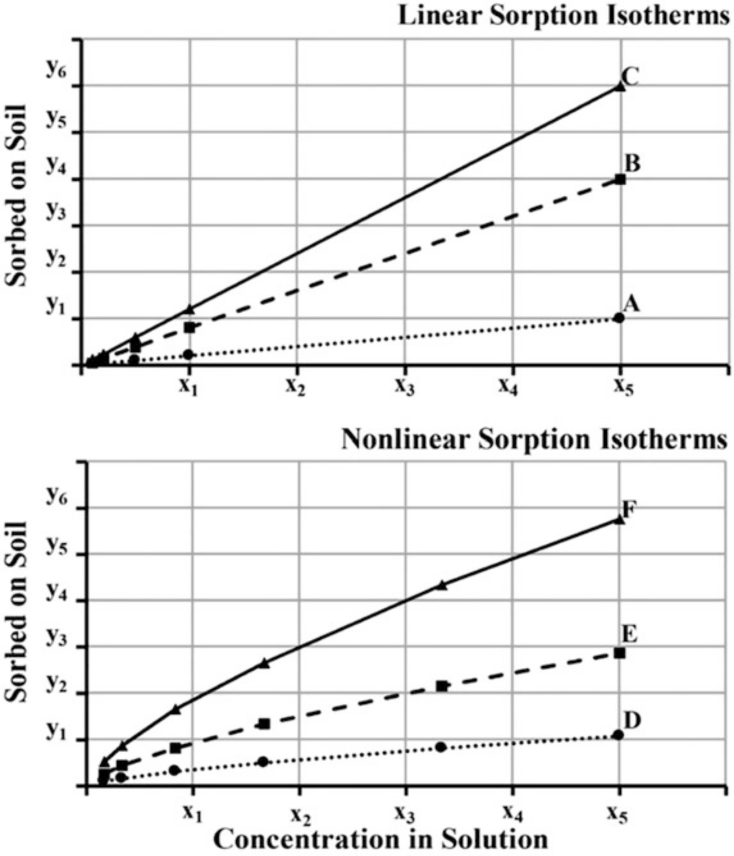

**Fig. 12.1** Linear sorption isotherms (top; A, B, and C) and nonlinear sorption isotherms (bottom; D, E, and F)

associated with soils that exhibited high CEC, high pH, and the existence of soil $CaCO_3$. Elbana and Selim (2010) explored the behavior of Cd sorption on two alkaline soils and an acidic soil, where high sorption was observed for all soils. Specifically, applying an initial Cd concentration of 0.890 mmol $L^{-1}$ caused sorption of 5.07, 4.22, and 4.91 mmol $kg^{-1}$ associated with surface alkaline, subsurface alkaline, and acidic soils, respectively. The respective desorbed percentages of Cd after 28 days were 3.4, 30.7, and 35.5% of the total sorbed amount. Such results signify the role of $CaCO_3$ and OM on the sorption/desorption process in soils.

The chemical behavior of trace elements in the soil varies in response to the variations in soil characteristics and the element reactivity itself under various environmental conditions. Based on X-ray absorption fine structure spectroscopy (XAFS), Mo et al. (2021) reviewed the different Cd sorption mechanisms and reported that four mechanisms were commonly observed:

1. Ion exchange such as the reaction with biotite and cryptomelane.
2. An outer-sphere surface complex that is a common Cd reaction with aluminosilicate minerals (e.g., kaolinite).
3. An inner-sphere complex that mainly associated with Fe/Mn (hydr)oxide systems.
4. Precipitation such as in Cd-Al-bearing minerals.

Based on analytical transmission electron microscopy studies, Sipos et al. (2019) attributed the high sorption of Cd to the presence of Fe oxyhydroxides in alkaline soil. In contrast, clay minerals exhibited a lower affinity to sorb Cd than Fe oxyhydroxides. Fontes and dos Santos (2010) found that iron oxides (hematite and goethite) positively correlated with the $S_{\max}$ of Pb, whereas the high contents of kaolinite and gibbsite were negatively associated with Pb sorption capacity in acidic soils. However, in calcareous soils, Jalali and Moradi (2013) showed that soils exhibited higher affinity to Cu and Pb than those for Cd, Zn, and Ni, where the highest sorption was associated with the high level of clay and $CaCO_3$ contents as well as the high pH. Sipos et al. (2018) reported that affinity of calcite to different trace elements was found in the order as Cu $>$ Cd $>$ Pb $>$ Zn, whereas the respective order for the clay affinity to sorb trace elements was found as Pb $>$ Cu $>$ Cd $>$ Zn. Despite the observation of strong sorption of Pb and Cu in calcareous soils, Martínez-Lladó et al. (2011) reported low and slow antimony (Sb) sorption on calcareous soils with $k_f$ of less than 1.5 (mol kg$^{-1}$) (mol L)$^{-b}$ and the nonlinear parameter "$b$" of 1.2–1.3. Martínez-Lladó et al. (2011) found the Sb sorption was negatively correlated to soil pH and $CaCO_3$ content and was positively associated with the contents of Al and Fe oxides. In fact, increasing soil pH can reduce the sorption of some trace elements such as arsenic when it is dominated as an anionic form (e.g., $HAsO_4{}^{2-}$), where increasing soil pH elevates the negative charge of Fe oxides and organic matter in soils that cause repulsion between anionic trace element and soil surfaces (Rahman et al. 2019).

The fate of trace elements in soils can be inferred and specified by interpreting the relation between the sorbed amount on soil and the solute concentration in solution precisely. Figure 12.2 shows examples of Cu and Pb sorption isotherms in different acidic soils allowing for 1 and 7 days equilibration sorption time (Elbana and Selim 2019). Maximum sorption capacity ($S_{\max}$) of Cu after 24 h sorption varied between 6.0 mmol kg$^{-1}$ (Candor surface) and 12.8 mmol kg$^{-1}$ (Crowley soil), whereas $S_{\max}$ of Pb varied between 13.1 mmol kg$^{-1}$ (Candor surface) and 16.9 mmol kg$^{-1}$ (Crowley soil). Such results illustrate the influence of soil properties and nature of trace element itself on the shape of sorption isotherm. Specifically, the lowest sorption was associated with the loamy sand Candor surface soil (pH $=$ 4.4 and CEC $=$ 5.3 coml kg$^{-1}$), whereas the highest sorption was associated with the silt loam Crowley soil (pH $=$ 5.2 and CEC $=$ 16.5 coml kg$^{-1}$) (Elbana and Selim 2019).

As shown in Fig. 12.2, Candor surface soil exhibited a significant increase of the sorbed amounts of Cu and Pb due to the expansion of equilibration time from 1 day to 7 days. However, Nada and Crowley soils revealed a limited increase of the sorbed Cu and Pb. Furthermore, Pb sorption on Nada and Crowley soils exhibited

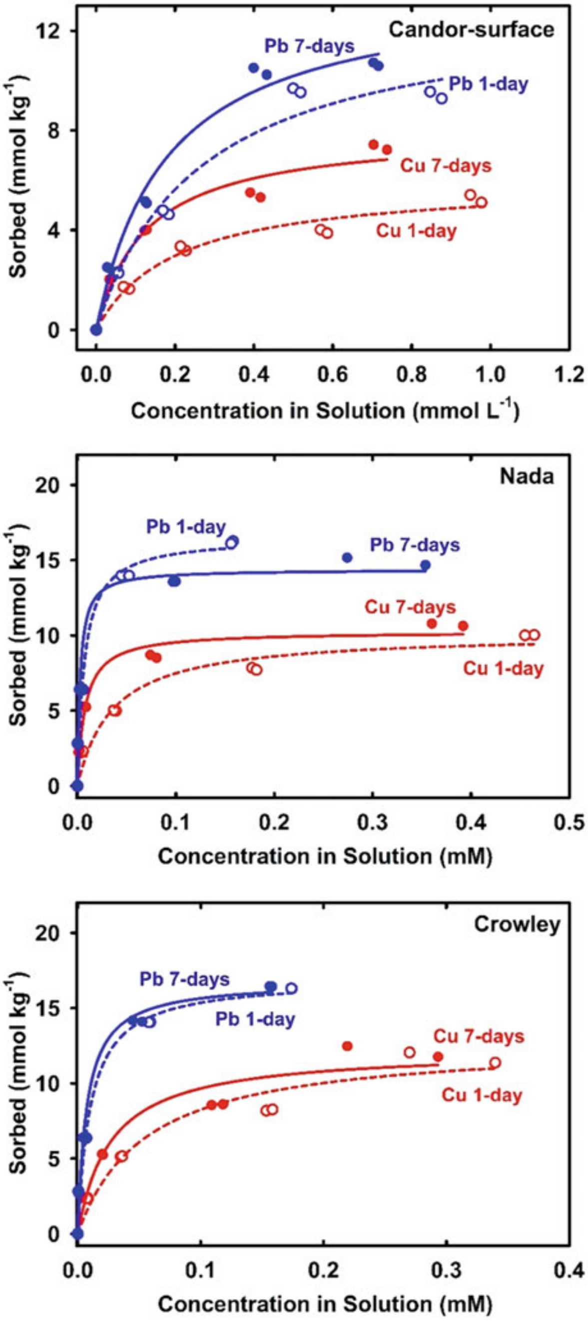

**Fig. 12.2** Examples of Cu and Pb sorption isotherms in three acidic soils (Candor surface, Nada, and Crowley soils) after 1 and 7 days. (Source: Elbana and Selim 2019; reproduction permission under the Creative Commons Attribution License)

limited kinetic comparing with Cu retention. Such results signify the role of the sorption kinetics of trace elements in soils that varied based on both soil characteristics and trace element properties. In short, the distribution of trace elements between solid soil particles and soil solution is controlled by soil colloids, trace element characteristics, and sorption conditions (Shaheen et al. 2013; Elbana et al. 2018).

In addition, the mutual competitive effect of trace elements explains the reduction of sorption behavior of trace elements in soils. For instance, the presence of 1.78 mmol $L^{-1}$ Sn in solution reduced the maximum sorption capacities, $S_{\max}$, of Pb for two acidic soils by 13.5 and 17.2% (Elbana et al. 2013a). The influence of trace element competition on sorption sites varied based on the chemical properties of the trace element and environmental conditions. Less competition on sorption sites can be anticipated in low concentrations of trace elements in solution where high availability of sorption sites is ensured. For instance, Sipos et al. (2019) showed that competitive effect decreased sorption of Cd and Zn than that one for Pb and Cu in soils when high initial concentration (10 mmol $L^{-1}$) was applied. Also, Jalali and Moradi (2013) concluded that the occurrence of Pb reduced the sorption of Cd, Cu, Mn, Ni, and Zn in calcareous soils.

Moreover, Sahraoui et al. (2015) reported that Aridisols Calcorthids soil exhibited a higher affinity to retain Cu and Pb than Co, Ni, and Zn, where higher sorption was associated with lower reversibility and lower release based on competitive sorption experiments. However, Li et al. (2013) investigated the sorption-competition between Cd and Pb in acidic paddy soils. They found a reduction of Cd-$S_{\max}$ by 42–48% in the presence of Pb in the binary solution system than $S_{\max}$ for a single Cd system. Additionally, a reduction of 36–41% was observed for Pb-$S_{\max}$ in the presence of Cd compared with the case of a single Pb solution system. Furthermore, Padilla and Selim (2021) conducted stirred flow experiments where single and binary pulses of Ni, Pb, and Zn were applied to acidic soil. Their results revealed that introducing a pulse of Zn released 31% of the sorbed Ni, whereas introducing Ni pulse did not cause Zn release from the soil. Besides, they reported that introducing a pulse of Pb released 26% and 37% of the sorbed Ni and Zn, respectively, whereas Ni and Zn exhibited the low potential to release Pb from this acidic soil.

Quantifying the rate of sorption/desorption of trace elements is a prerequisite to obtaining an accurate simulation of the mobility in soils. First- and second-order reaction models are commonly applied to describe the kinetics of trace elements sorption/desorption in soils. The pseudo-first-order rate equation can be written as shown in Eq. (12.14) to describe sorption kinetics.

$$\frac{\mathrm{d}S}{\mathrm{d}t} = k_{st}(S_{\max} - S_t) \tag{12.14}$$

where $S_{\max}$ and $S_t$ are the maximum sorption capacity and the sorbed amount at time $t$, respectively. $k_{st}$ represents the pseudo-first-order reaction rate. Considering the following conditions:

- The initial time = 0.
- Final time = $t$.
- Initial sorbed amount = 0.
- The sorbed amount at time $t = S_t$.

The integrated form of Eq. (12.14) can be written as:

$$S_t = S_{\max}\left(1 - \mathrm{e}^{-k_{st}t}\right) \tag{12.15}$$

The rate law of the second-order equation can be written as:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = k_{\mathrm{nd}}(S_{\max} - S_t)^2 \tag{12.16}$$

where $k_{\mathrm{nd}}$ represents the pseudo-second-order reaction rate. The integrated form using the aforementioned conditions can be written as:

$$\frac{1}{(S_{\max} - S_t)} = \frac{1}{S_t} + k_{\mathrm{nd}}\,t \tag{12.17}$$

The half-life time ($t_{1/2}$) of the pseudo-first-order reaction is independent of the initial reactant concentrations. However, the $t_{1/2}$ of the pseudo-second-order rate reaction is inversely proportional to the initial concentration.

A standard model applied to describe sorption/desorption and transport of trace elements in soil based on the first-order reaction is the multi-reaction transport model, MRTM (Selim 2016). Figure 12.3 shows MRTM simulations of Cu and Pb sorption/desorption kinetics in three acidic soils (Elbana and Selim 2019). Data in Fig. 12.3 represented the change in the sorbed amounts when two different initial concentrations were applied 0.966 and 1.473 mmol L$^{-1}$ of Cu as well as 1.483 and 1.823 mmol L$^{-1}$ of Pb. The best simulations were obtained by considering two reaction sites where reversible and consecutive irreversible sites were considered. The average Cu released from the soils ranged between 20% and 23%, whereas the respective range for Pb was from 8% to 14%. The results implied that sorption/desorption of Cu and Pb was concentration-dependent, and Cu exhibited less limited sorption/desorption kinetics compared with Pb (Fig. 12.3).

## 12.5 Advection-Dispersion Equation and Trace Element Transport

The classical advection-dispersion equation (ADE) is applied to predict trace element mobility in soils comprehensively (van Genuchten and Wierenga 1976; Sidle and Kardos 1977; Selim 1992; Toride et al. 1999; Elbana et al. 2014; Zhang et al. 2020). For modeling trace element mobility in one dimension, the ADE can be written as in Eq. (12.18):

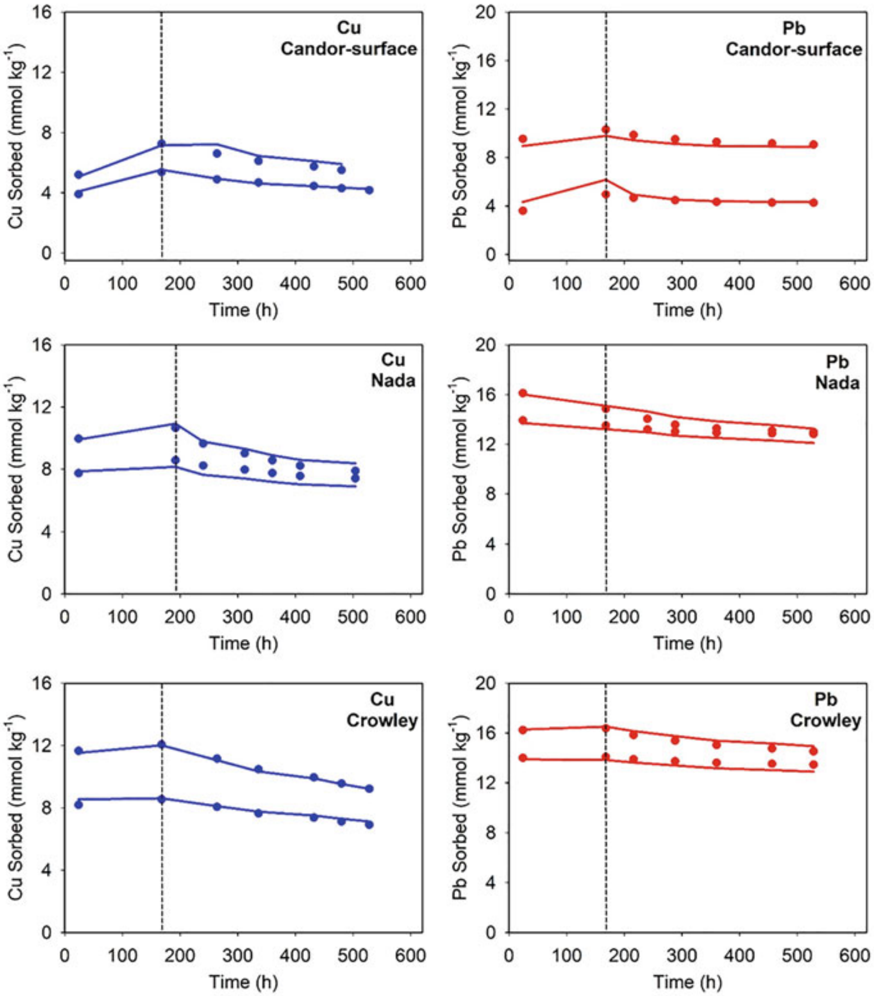

**Fig. 12.3** Sorption/desorption kinetics of Cu and Pb in three acidic soils (Candor surface, Nada, and Crowley soils). (Source: Elbana and Selim 2019; reproduction permission under the Creative Commons Attribution License)

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \nu\frac{\partial C}{\partial x} \tag{12.18}$$

$$R = 1 + (\rho k_{\mathrm{d}}/\theta) \tag{12.19}$$

where $R$ is the retardation factor for linear equilibrium sorption, $\rho$ is the soil bulk density, $\theta$ is the soil moisture content, and $\nu$ is the average pore water velocity. The term ($D\frac{\partial^2 C}{\partial x^2}$) refers to the spreading of trace element plume (dispersion, see

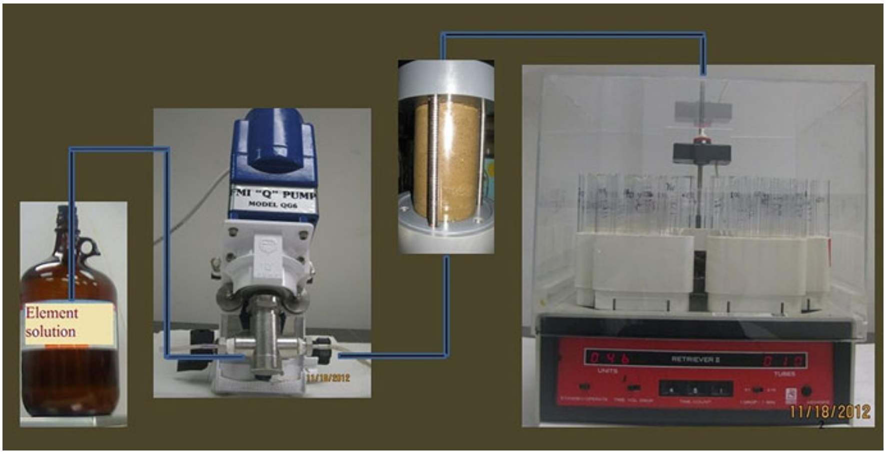

**Fig. 12.4** A miscible displacement experimental setup (from left to right: bottle of trace element solution, variable speed piston pump, acrylic soil column, and fraction collector; photos were taken by Elbana, T)

Eq. 12.10), and the term ($\nu \frac{\partial C}{\partial x}$) implies the mobility of trace element with flow velocity (advection).

Numerous analytical solutions (Selim and Mansell 1976; Van Genuchten and Alves 1982) and numerical solutions (Leij et al. 1991; Ataie-Ashtiani et al. 1996; Wallis 2007; Gurarslan et al. 2013; Yadav et al. 2016) were presented in the literature considering various initial and boundary conditions. Several software packages for simulating trace element in soils are available online that are based on ADE (Šimůnek et al. 1999, 2013; Selim 2016).

Quantifying trace elements mobility in soils can be accomplished through miscible displacement experiments on a laboratory scale. In this technique, a pulse of a trace element is introduced to the soil column for certain pore volumes (time) followed by a pulse of the background solution (Selim and Amacher 1997; Álvarez-Benedí et al. 2005; Elbana et al. 2014). Figure 12.4 shows an example of a miscible displacement experimental setup. In this experiment, soil column can be saturated, partially saturated, or unsaturated in advance of introducing the pulse based on the aim of the study (Nielsen and Biggar 1961). Then, the effluent solution is collected from the end of the column using a fraction collector and measuring the concentration of the trace element to produce a breakthrough curve (BTC). The BTC displays the relation between the relative concentration ($C/C_o$) of the applied trace elements and the relative pore volume ($V/V_o$) or a dimensionless time (Wang and Persaud 2004; Elbana and Selim 2010). It is environmentally and cost-effectively recommended to simplify the experimental setup for exploring trace element mobility in agricultural soils. Therefore, conducting laboratory column experiments is worldwide preferred than field scale to avoid environmental pollution and precisely control the experimental conditions such as saturation and oxidation statuses.

Mobility of trace elements in soils exhibited different shapes and trends based on the variation of soil properties, chemistry of the trace element, and environmental conditions. Long-term utilization of domestic wastewater in irrigation led to the accumulation of Cd, Cu, Ni, and Pb in sandy soils where considerable mobility of Cd > Ni > Cu > Pb was observed (Elbana et al. 2013b). The lower affinity of sandy soil to retain Cd than Cu and Pb can explain the extensive transport of Cd and the potential hazard as well as the high Cd availability in such soil. Tack et al. (1993) estimated that Cd would transport in sandy loam soil to a depth of 2.4 m without accumulation, whereas Cu and Pb would not transport to more than 0.2 m depth. In general, trace elements exhibit higher mobility under field conditions than in the experimental columns due to the preferential flow and the change in sorption behavior and element speciation (Tack 2010). In the following sections, a brief discussion of Cd, Cu, Pb, Sn, and Se will be presented as examples of trace element mobility in agricultural soils.

**Cadmium Transport in Soils** Cd is a toxic element that exhibits the potential risk of contaminating the agricultural ecosystem. Hamid et al. (2020) tested different amendments (lime, sepiolite, zeolite, biochar, manure, and mixtures of amendments) to reduce Cd leaching from three contaminated soils. They reported increases in soil pH and reduced Cd availability in the studied soils and observed a considerable reduction in Cd concentration in leachate. Although the addition of organic materials to soil could increase Cd sorption and subsequently reduce Cd mobility, incorporation of organic matter could increase the mobility of Cd in paddy soils due to the effect of dissolved organic matter and release of the organic acid over time (Yuan et al. 2021). Lamy et al. (1993) found that mobility of Cd increased in response to the addition of sewage sludge to loamy soil due to the influence of sludge soluble organic matter. Prokop et al. (2003) found that concentration of Cd in soil solution, Cd water-extractable fraction, and soil maximum Cd sorption capacity were good indicators for Cd mobility in soil.

Good simulation of Cd-BTC can be obtained by considering equilibrium linear sorption isotherm in soil with low affinities, such as acidic sandy soils (Gerritse 1996). However, counting for the nonlinear and the rate-limited sorption behaviors is essential for a proper description of Cd mobility in most agricultural soils. Notably, numerous studies indicated the influence of Cd time-dependent sorption on its mobility in soils (Selim 1992; Naidu et al. 1997). Based on a field study using a double ring ponded infiltration experiment, Lichner et al. (2004) found that Cd was detected in a 0.65 m depth after 110 min where more than 40% moved to a depth of 0.1 m due to preferential flow. Elbana and Selim (2010) explored the mobility of Cd in different soils (reference sand, alkaline surface sand soil with 2.8% $CaCO_3$, alkaline subsurface sand soil with 1.2% $CaCO_3$, and acidic loamy sand soil). The results for reference sand revealed that Cd exhibited behavior of nonreactive chemicals such as tritium, where 98% of the applied Cd was obtained. For the surface and subsurface alkaline soils, the obtained recoveries were <1% and 31%, respectively, whereas only 21% of the applied Cd was obtained from the acidic soil.

Elbana and Selim (2010) attempted to simulate Cd-BTC for each soil, considering a linear CXTFIT model and nonlinear MRTM model. The estimated Cd retardation factors (*R*) were found to be 1.95, 20.9, 14.5, and 6.8 for the reference sand, surface and subsurface alkaline soils, and the acidic soil, respectively. Their results revealed that Cd mobility could be simulated in reference sand using linear rapid, reversible reaction, whereas considering nonlinear slow kinetics and the irreversible reaction was required to simulate Cd mobility in the studied alkaline and acidic soils.

**Copper Transport in Soils** Cu is an essential micronutrient in plant nutrition. A high concentration of Cu causes plant toxicity and environmental problems. However, most agricultural soils exhibit high affinity to sorb Cu; a significant Cu mobility was observed in acidic soil that contains low OM contents (Mathur et al. 1984). Moreover, in alkaline soils exposed to repeated application of Cu fertilizers, Xiaorong et al. (2007) reported that 40% of the applied Cu during 17 years was transported below 0.6 m soil depth; and a labile Cu was detected at a soil depth of 4.0 m. Besides, Cu speciation affects its mobility and availability in agricultural soils. For example, He et al. (2006) reported that the exchangeable fraction controlled Cu release into the soil for the short reaction time, whereas carbonate-bound and exchangeable fractions governed Cu at long-term leaching in soils. Muyumba et al. (2019) examined Cu release from crushed rock-soil system using lysimeters at field experiment. Their results indicated an extensive Cu mobility at the end of a whole rainy season where soil properties, mineralogical composition, and Cu concentration elucidated Cu content in the leachate solution.

For single and competitive systems of Cu with Ni, Zn, and Pb, Buragohain et al. (2018) modeled Cu mobility in two soils considering ADE and the retardation factor (*R*) based on Freundlich and Langmuir sorption isotherms. They concluded that the value of *R* was sensitive to isotherm parameters that sometimes caused irregular behavior for fate predictions. Besides, using the Freundlich parameter estimated higher *R* values than that based on Langmuir isotherm for a high range of equilibrium concentration, whereas *R* values based on Langmuir were slightly higher than that based on Freundlich isotherm at the low range of equilibrium concentration. Moreover, the duration of Cu pulse affects the fate of Cu in soils. Elbana and Selim (2011) reported extensive Cu mobility in alkaline soils when long pulses were applied. The Cu recoveries varied between 27% and 60% of the applied Cu compared with less than 1% in short Cu pulses. They reported 11% and 86% recoveries for short and long Cu pulses for acidic Windsor soil, respectively. Elbana and Selim (2011) obtained the best Cu BTC simulation for a complete recovery from a reference sand column allowing for a nonlinear-one reversible kinetic site. However, they found that allowing for an irreversible sorption site and at least one kinetic reversible site was necessary to obtain the best simulation of Cu BTC for acidic and alkaline soils. Likewise, Vogeler (2001) proposed that Cu mobility in soils involved exchangeable and non-exchangeable reaction sites. Moreover, Chang et al. (2001) obtained better simulations of Cu BTC based on nonlinear Freundlich parameters than assuming linear sorption.

Copper was found to exhibit lower mobility in calcareous soils ($CaCO_3$ of 6–12%) than Ni and Cd (Lafuente et al. 2008) whereas higher mobility than Zn and Pb in soils with $CaCO_3$ of 35–38% (Sayyad et al. 2010). Elbana and Selim (2012) studied the influence of removing $CaCO_3$ from the soil on Cu mobility. They found that a recovery of 27% of the applied long pulse (59 pore volumes) was realized with a peak of relative concentration $C/C_o$ of 0.42 for soil with 2.8% $CaCO_3$. The respective recovery after removing $CaCO_3$ was found as of 87%, with a $C/C_o$ of 1.0. In fact, the reactivity of Cu in calcareous soils involves the formation of inner-sphere complexes on calcite and precipitation reaction (Elzinga and Reeder 2002; Rodriguez-Rubio et al. 2003). In agreement with that, Elbana and Selim (2012) recommended the use of the second-order-two sites model (SOTS) to predict Cu mobility in calcareous soils by considering kinetic reversible and irreversible sorption reactions.

**Lead Transport in Soils** Pb is known as a toxic element for living organisms that causes health and environmental problems. Limited mobility of Pb in soils can be ascribed to Pb reaction with OM (Vile et al. 1999) in peat soils as well as phosphate rock (Melamed et al. 2003) and calcite (Rouff et al. 2002) in mineral soils. Mobility of Pb in polluted soils decreases with the increase of clay contents but increases with rising Pb contents in soils (Kabala and Singh 2001). Elbana and Selim (2013) studied Pb mobility in reference sand columns where different input concentrations of 0.48 and 2.41 $mmoL^{-1}$ were introduced into column I and column II, respectively. Breakthrough curves (BTCs) of Pb arrived after 1 pore volume, where the recoveries of the applied Pb of 60% (with $C/C_o$ of 0.8) and 94% (with $C/C_o$ of 1.0) were obtained for column I and column II, respectively. They concluded the occurrence of kinetic reaction in these reference sand materials based on the shape of Pb BTC during flow interruptions in both columns. Such results indicate that the maximum sorption capacity of Pb was realized in these two sand columns and the mobility depended on Pb input concentration. Likewise, Yeboah et al. (2019) tested Pb mobility in intact soil columns of loamy sand soil, considering three different input Pb concentrations. They reported that early arrival and the highest $C/C_o$ were associated with the high input Pb concentration. Their results revealed that macroporosity and hydraulic properties influenced Pb mobility in agricultural soils, where the soils characterized with high porosity and saturated hydraulic conductivity exhibited elevated Pb mobility.

Soils exhibit a high affinity to retain Pb significantly reducing their mobility relative to most of the other trace elements. For example, Elbana et al. (2013a) obtained a recovery of less than 1% of the applied Pb, even though Cd and Cu pulses were introduced after the Pb pulse into alkaline sandy soils containing $CaCO_3 < 3\%$. Their results revealed that introducing Cu pulse following Pb and Cd pulses was able to release Cd, not Pb, where higher Cd recoveries of 46–53% were realized in comparing with a previous study, using the same soils in the absence of Pb when Cd exhibited immobile behavior (Elbana and Selim 2010). Such results indicate a limited influence of Cd and Cu on Pb mobility in soils. However, Sheppard and

Sheppard (1991) reported a recovery of only 33% of the applied Pb in the leaching solution from acidic sandy soil lysimeters. Thus, despite the limited Pb mobility in most agricultural soils, the occurrence and competition of other trace elements and applications of soil amendments can increase Pb mobility. For example, Elbana et al. (2014) showed increased Pb mobility in two loam soils due to introducing Sn pulse afterward Pb pulse. Specifically, higher recoveries of the applied Pb (52% and 96%) were obtained when Sn pulse was applied after introducing Pb pulse in compared with Pb recoveries of 37% and 58% when Sn pulse was applied before introducing Pb pulse. Besides, the early arrival of Pb was observed when a pulse of Pb followed Sn pulse. Such results indicated the combative effect of Sn on Pb mobility that caused a release of the sorbed Pb and caused the early arrival of Pb. However, Elbana et al. (2014) reported the immobility of Sn in loam agricultural soils, where the recoveries of the applied Sn in the effluent did not exceed 1% from the studied loam soils. In contrast, Sn recovery of 32% was realized for the reference sand column.

**Selenium Transport in Soils** Se speciation, pH, Eh, Fe/Al oxide contents, OM, and occurrence of ($SO_4^{2-}$) and ($PO_4^{3-}$) ions control Se mobility in soils (Fordyce 2013; Lopes et al. 2017). The primary mobile forms of Se in soils are selenate ($SeO_4^{2-}$) and selenite ($SeO_3^{2-}$). Selenate ions are readily mobile in alkaline soils under good aeration circumstances (Gebreeyessus and Zewge 2018). Guo et al. (1999) conducted miscible displacement experiments to assess Se mobility in sandy loam soil. They quantified very high mobility of $SeO_4^{2-}$ due to the anion exclusion effect. Specifically, under nonsparged ($O_2$: 6.9 mg $L^{-1}$), they obtained $R$ values of 0.989, 0.870, and 0.854 for untreated soil, soil treated with a compost dairy manure, and soil treated with gluten, respectively. However, under $O_2$-sparged ($O_2$: 32 mg $L^{-1}$), the respective $R$ values were 0.983, 0.937, and 0.895. Besides, they reported limited mobility for $SeO_3^{2-}$ with $R$ values that ranged between 1.69 and 5.54. Besides, based on total Se mass recovery, the soil treated with gluten-nonsparged retained 72% of the applied selenium. In contrast, untreated soil with $O_2$-sparged exhibited high Se mobility and retained only 4.6%. Moreover, Cong et al. (2011) studied the mobility of $SeO_3^{2-}$ in loessial soil columns and found that $R$ values varied between 4.028 and 4.886. They recommended the deterministic equilibrium ADE model to simulate selenite transport in the studied soil. On a large irrigated agricultural watershed scale, Neupane et al. (2020) modified the soil and water assessment tool (SWAT) to evaluate Se mobility and fate considering spatial variability of soil, climate, and irrigation management, where Se concentration in most of the area was $<20$ μg $L^{-1}$ except few hotspots with Se $>90$ μg $L^{-1}$. They found that Se mobility in soils was controlled by the ratio of S/Se in shale, autotrophic reduction rates of $NO_3$, sorption, redox reactions, the fraction of shale, and hydrologic parameters (available water capacity, delay time in groundwater recharge, hydraulic conductivity, overland flow, and runoff curve number). Besides, they concluded that $SeO_4^{2-}$ was the major dissolved species, and its mass flux included Se release from outcrop and bedrock shale, surface and groundwaters, soil percolation to the aquifer, and groundwater loading to streams.

## 12.6 Conclusion

Quantifying trace elements transport in agricultural soils is essential to preserving our environmental resources and for sustaining crop production. The mobility of trace elements varied in soils based on each soil's physical, chemical, and hydrological properties, the variation of environmental conditions, and the element's nature properties. All the circumstances that cause soil pH changes and oxidation-reduction properties can influence trace element speciation in soil and subsequently alter its reactivity and mobility in soil. Modeling trace element mobility revealed the importance of nonlinear-kinetic behavior and the need to include reversible and irreversible reactions to obtain proper mobility descriptions.

Most agricultural soils exhibit a high affinity to retain trace elements such as Cu and Pb under examination of a single system. However, sandy soils that are poor in OM, oxides, or contain low $CaCO_3$ exhibit a substantial trace element mobility, especially for Cd and trace elements that are dominant in soil solution in anionic form (e.g., Se). Moreover, studies based on competitive systems (involving more than single element) clarified extensive mobility and different reactivity of trace elements. However, the literature review revealed that numerous researchers explored and modeled a single trace element's mobility in soils, particularly on a small scale under laboratory conditions. In contrast, fewer studies considered trace elements' competitive mobility. Besides, few studies were conducted to simulate trace element mobility on the watershed scale, which are highly required for managing and remediating contaminated regions correctly. Therefore, the presented literature in this chapter revealed that further research based on competitive transport is needed to expand our understanding of trace elements' fate in the environment.

**Acknowledgments** The author would like to dedicate this book chapter to the soul of Prof. Dr. H.M. Selim, who has passed away in November 2020 at Baton Rouge, LA, USA.

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# The Effects of Nitrogen Enrichment on Low-Nutrient Environments: Insights from Studies of Serpentine Soil-Plant Relations

13

Thomas J. Samojedny, Jr., Mary Devlin, Rebekah Shane, and Nishanta Rajakaruna

## Abstract

It is widely known that anthropogenic inputs, particularly from modern agriculture and fossil fuel combustion, are severely altering the nitrogen (N) cycle. Humans have doubled the amount of reactive N ($N_R$) input into our environments, causing it to accumulate in ecosystems. However, N is anything but stationary. In various forms, $N_R$ enters the atmosphere where it can travel long distances and deposit back onto the biosphere. This chapter summarizes the process and effects of N deposition on low-nutrient environments (LNEs) which are significantly altered by nutrient addition. Using serpentine as a model environment, we conclude that primary effect of N deposition is an alteration in competition and invasion patterns. Excess N allows nitrophilous invasive plants to outcompete LNE-native plants. Other effects can further harm LNEs, including N deposition-caused soil acidification and toxicity that may be exceptionally detrimental to LNEs and their plants, animals, and fungi. To mitigate effects of N deposition on LNEs, certain strategies such as grazing and controlled burns have proven effective in the short term. However, it will take a dramatic reduction in anthropogenic $N_R$ input, particularly through changes to current agriculture methods, to protect Earth's unique and diverse LNEs from change.

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**Keywords**

Atmospheric pollution · Critical loads · Invasive species · Limiting factors · Nitrogen deposition · Serpentine soil · Sustainable agriculture

## 13.1 Introduction

Nitrogen is as essential to life as water. Without nitrogen (N), life's most crucial molecules—nucleic and amino acids—would not exist. Paradoxically, while N is abundant on Earth, making up 78% of the atmosphere, most of this is in the form of nonreactive $N_2$ gas which cannot be used by 99% of organisms (Galloway et al. 2003). The few organisms that can utilize $N_2$ by breaking its triple bond are a unique group of "nitrogen-fixing" bacteria and archaea that provide usable N for all other organisms. These N fixers are part of a larger N cycle that transfers N between its nonreactive form ($N_2$) and the reactive form ($N_R$) which can be used by the majority of organisms (Chapin et al. 2011). The cycle is governed by four major chemical processes all taking place within microbes. They are defined by Bernhard (2010) as (1) nitrogen fixation, the process previously described by which bacteria and archaea convert $N_2$ into ammonia ($NH_3$); (2) nitrification, the conversion of $NH_3$ into nitrate ($NO_3^-$) which is usable by plants; (3) anammox, the conversion of ammonium ($NH_4^+$) and nitrite ($NO_2^-$) back into $N_2$; and (4) denitrification, the conversion of $NO_3^-$ back into $N_2$. Under natural conditions, these processes provide enough $N_R$ for life on Earth to flourish without overburdening natural systems, because rates of N fixation and anammox/denitrification are roughly equal (Ayres et al. 1994).

However, like many of Earth's cycles, the N cycle is being disturbed by anthropogenic inputs. Humans have more than doubled the amount of $N_R$ in the environment (Fig. 13.1; Fowler et al. 2015) due to three major sources: the combustion of fossil fuels, cultivation-induced biological N fixation (C-BNF), and the widespread use of $NH_3$-based fertilizer (Fig. 13.1; Galloway et al. 1995, 2003). When fossil fuels are burned, both $N_2$ from the atmosphere and organic N stored within the fuels are converted into nitrous oxides ($NO_X$) (Galloway et al. 1995). Combined, these emissions account for roughly 15% of anthropogenic $N_R$ (Galloway et al. 2003). However, $NO_X$ emissions in many regions have declined over the past two decades (Fig. 13.2; Leip et al. 2011) due to the use of modern catalytic converters which convert $NO_X$ into $NH_3$ (Fenn et al. 2018). As a result, fossil fuel $NH_3$ emissions continue to increase in most countries, including an 11% total increase between 1990 and 2010 in the United States (Fig. 13.2; Xing et al. 2013; Fenn et al. 2018). C-BNF results from the ability of some of the world's most important crops, including legumes, rice, and sugarcane, to form symbiotic relationships with N-fixing microbes in root nodules or rhizospheres (Galloway et al. 2003; Smil 1999; Reddy et al. 2002; Baldani et al. 2002; Bernhard 2010). Widespread cultivation of these crops has led to increased rates of N fixation, contributing to an estimated 20% of anthropogenic $N_R$ (Galloway et al. 2003). However, the use of $NH_3$-based fertilizers dwarfs all other sources, comprising about 50% of anthropogenic $N_R$ input

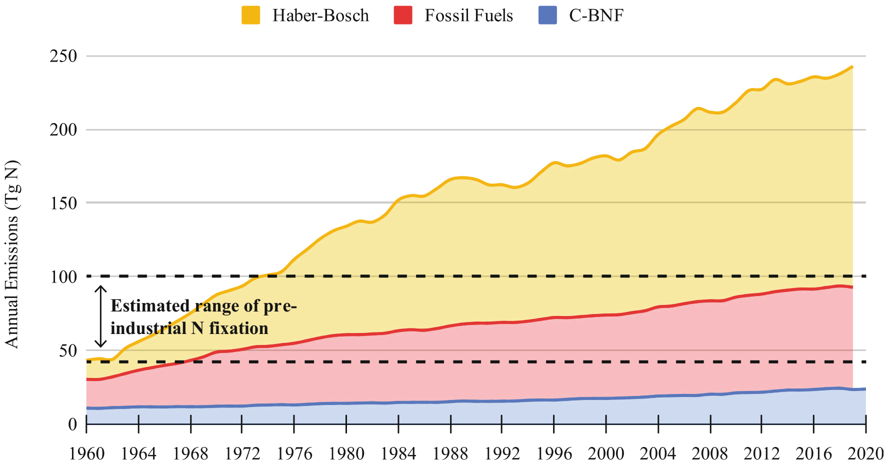

**Fig. 13.1** Stacked area graph of global emissions of the three greatest sources of $N_R$ (the Haber-Bosch process, fossil fuel combustion, and cultivation-induced biological nitrogen fixation) over the past 60 years. Haber-Bosch values come from USGS “Nitrogen Statistics and Information” (https://www.usgs.gov/centers/nmic/nitrogen-statistics-and-information). Fossil fuel values are from $NO_X$ emission data from EDGAR v.5 for 1970 to 2015 (https://edgar.jrc.ec.europa.eu/overview.php?v=50_AP; Crippa et al. 2019). Values for 1960–1969 and 2016–2019 were calculated by scaling $NO_X$ to fossil fuel carbon emissions (Friedlingstein et al. 2020). To convert to the mass of contained N, all $NO_X$ emissions were counted as $NO_2$ for molar mass. To calculate C-BNF data, the total area of N-fixing crops including legumes, rice, and sugarcane (FAOSTAT; http://www.fao.org/faostat/en/#data/QC) was multiplied by fixation rates from Smil (1999). Years without FAOSTAT data (1960, 2019, 2020) were scaled to population. Population data came from UN World Population Prospects 2019 (https://population.un.org/wpp/). The estimated range of pre-industrial N fixation is from Vitousek et al. (2013)

(Galloway et al. 2003). Production of $NH_3$-based fertilizers relies on the most widespread chemical process in the world—the Haber-Bosch (HB) process, a chemical reaction pioneered in the early twentieth century that converts $N_2$ into $NH_3$. About 80% of the $NH_3$ produced by HB is manufactured as fertilizer, with the rest utilized in pharmaceuticals, explosives, and industrial processes (Chen et al. 2019). Humanity relies so heavily on this process that over half of the N in our bodies comes from HB (Liu 2014; Howarth 2008). While these three sources account for about 85% of anthropogenic N, with 70% being related to agriculture, there are smaller sources such as biomass burning. Another source, which is of increasing concern to scientists, is the use of long-term fire retardants (LTFRs), such as *Phos-Chek*®, which are chemically similar to N fertilizers (Box 13.1).

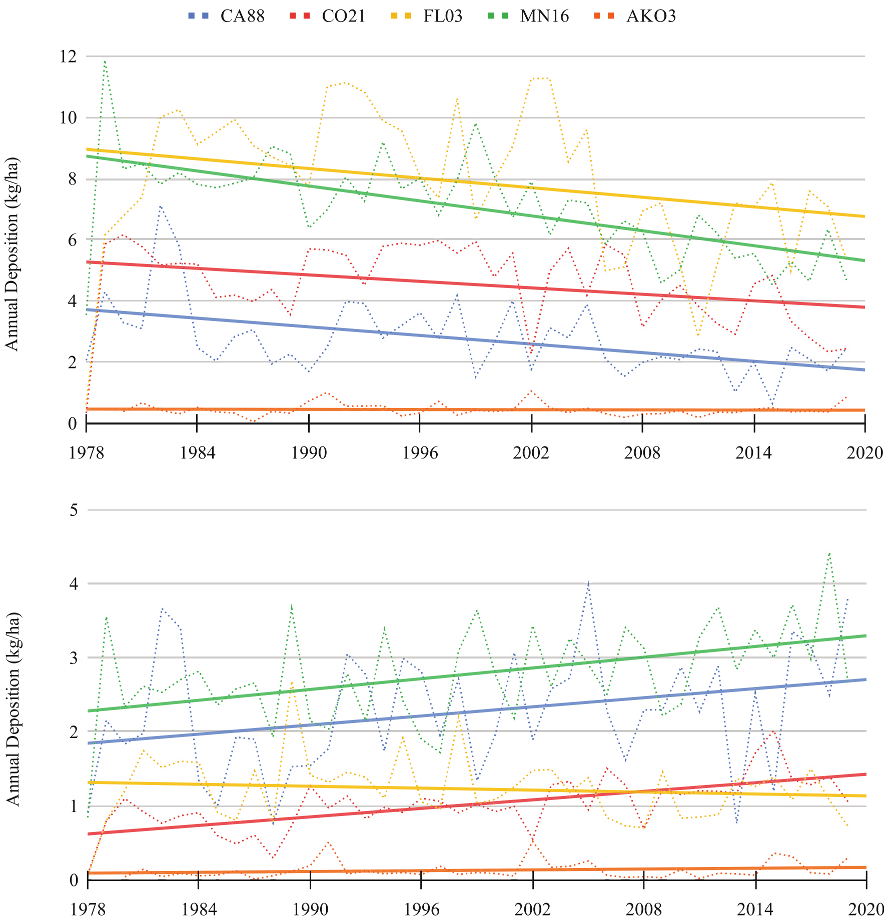

**Fig. 13.2** Deposition trends for $NO_3^-$ (top) and $NH_4^+$ (bottom) in the United States. Five sites from around the country were selected to cover a variety of elevations and latitudes. Data is sourced from the National Atmospheric Deposition Program (University of Wisconsin) National Trends Network (http://nadp.slh.wisc.edu/ntn/). The legend indicates site codes, which can be used to find more information about each site at the NADP website (http://nadp.slh.wisc.edu/data/sites/list/?net=NTN)

### Box 13.1 Focus study: effects of long-term fire retardants on the N cycle

Due to a combination of fire suppression and climate change, wildfires are increasing in intensity and frequency (Williams et al. 2019; Abatzoglou and Williams 2016; Westerling et al. 2006). In the past decade, California has repeatedly set new records for total area burned, with 2020 being the most

(continued)

**Box 13.1** (continued)

destructive year in modern history with around 1.7 million ha, or over 4% of the state, burned (CalFire 2020). As a result, fire suppression methods have intensified. One tool being used more frequently is the application of long-term fire retardants (LTFRs). LTFRs prevent combustion even after the water in them has evaporated (Marshall et al. 2016). LTFRs are mostly a mixture of water and ammonium salts, primarily diammonium phosphate and ammonium sulfate. They are typically dropped from airplanes in liquid or powder form to cover large areas. In the USA in 2013, over 100 million liters of LTFR were used at a rate of up to 200 kg N and 400 kg P deposited per hectare (Marshall et al. 2016).

LTFRs can stimulate plant growth because they are essentially a mixture of N fertilizer and water. Larson and Duncan (1982) found that treating a California annual grassland with diammonium phosphate LTFR doubled plant biomass from 6 to 12 t ha$^{-1}$. However, because LTFRs are applied in large quantities, treated areas will likely exceed their critical loads for N, and detrimental effects will occur. Z. Raposo et al. (unpublished data) compared serpentine soil treated with the widely used LTFR *Phos-Chek* with untreated serpentine soil. *Phos-Chek* treatment increased soil P and $NH_4^+$concentrations by 3430% and 1067%, respectively. Accompanying this was a lower Shannon diversity index value for the plant community growing on the treated substrate. Other studies support the idea that LTFR use can disrupt plant communities, reducing native plant diversity and increasing exotic plant abundance after application (Marshall et al. 2016; Bell et al. 2005; Besaw et al. 2011). At the extreme rate of up to 200 kg N ha$^{-1}$, N toxicity can also occur. It is widely confirmed that LTFRs are toxic to aquatic organisms and users are instructed to avoid spraying waterways (Giménez et al. 2004; Phos-Chek 2019). For plants, researchers have observed both immediate and gradual leaf and plant death, depending on the N sensitivity of the species (Bell et al. 2005; Bradstock et al. 1987). Luna et al. (2007) found that as the concentration of LTFR increases, seed viability and germination rates decrease. Mycorrhizae are also affected, with Marshall et al. (2016) observing decreased AMF abundance in both field and greenhouse studies after LTFR treatment. Because of these harmful effects on natural ecosystems, the success of LTFRs as a wildfire management tool must be balanced with their detrimental ecosystem impacts. Furthermore, LTFRs should be considered as another contributor to N cycle disruption.

But there is a facet of the N cycle that allows anthropogenic N pollution to affect environments far from sources: nitrogen deposition. However, it is important to first understand how anthropogenic $N_R$ enters the atmosphere. $N_R$ is released into the atmosphere in three main forms: $N_2O$ (about 5%), $NO_X$ (40%), and $NH_3$ (55%) (Krupa 2003). Agriculture is the largest source of $N_2O$, as it is a byproduct of denitrification processes in the soil as microbes decompose N fertilizers (Bhatia et al. 2013; Bernhard 2010). Most $NO_X$ released is a byproduct of fossil fuel combustion (Olivier et al. 1998). Because $NH_3$ is the largest source, it will be discussed here in detail. Again, agriculture is the main culprit, with 80% of the $NH_3$ released into the atmosphere coming from either N fertilizers or livestock waste (Reis et al. 2009; Li et al. 2016). Nitrogenous fertilizers are typically made from urea ($CO(NH_2)_2$) or ammonium ($NH_4^+$) salts (Dari et al. 2019). However, once these are applied to soil, they are converted into $NH_3$ gas by naturally occurring reactions (see Dari et al. 2019 for an overview of the reactions). Conversion into $NH_3$ gas also occurs for livestock excretions, which contain urea. Once in gaseous form, agricultural $N_R$ is lost through volatilization to the atmosphere. Another agricultural source is the cultivation of leguminous crops which increases the rate of microbial N fixation and thereby $NH_3$ production. This $NH_3$ can be volatilized if it is produced within a few centimeters of the soil surface (Bouwman et al. 1997). $NH_3$ is also produced by internal combustion engines with catalytic converters, as discussed previously. Based on these factors, gaseous $NH_3$ emissions are high in areas both with intense agriculture (particularly those areas that are hot, moist, and have alkaline soils; Ernst and Massey 1960; Overrein and Moe 1967; Dari et al. 2019) and industry/urbanization.

Once N enters the atmosphere in these three forms, it undergoes alterations and can be deposited back on Earth. While $N_2O$ is relatively inert and is not deposited back on Earth (Singh 1987), it is a potent greenhouse gas (Vitousek et al. 1997). On the other hand, $NO_X$ and $NH_3$ are highly reactive. These forms return to Earth through dry or wet deposition. Dry deposition occurs when gaseous or particulate molecules are adsorbed by leaves or soil, particularly if the air is turbulent and the surfaces are moist (Asman et al. 1998). $NO_X$ and $NH_3$ are commonly dry-deposited; however, dry deposition of $NH_3$ typically occurs closer to the source because once in the atmosphere most $NH_3$ is converted into $NH_4^+$ aerosols which can remain in the atmosphere for longer periods (Krupa 2003; Bouwman et al. 1997). $NH_4^+$ can also be dry-deposited, although it is often wet-deposited when aerosols are incorporated into clouds or are scavenged below clouds by precipitation (Aneja et al. 2008; Asman et al. 1998). $NO_X$ is oxidized in the atmosphere, forming nitric acid ($HNO_3$), a component of acid rain (Vitousek et al. 1997). Furthermore, gaseous $NH_3$ and $NO_X$ can even diffuse directly into plant stomata if the atmospheric concentration of the gas is higher than that in the leaf mesophyll (Asman et al. 1998; Campbell and Vallano 2018). Figure 13.2 shows US N deposition trends over the past few decades.

Because of $N_R$'s ability to convert to gaseous form, remain in the atmosphere for some time, and then deposit back on Earth, N pollution can occur even in remote areas. This is particularly true for $NH_4^+$, whose low deposition velocity allows it to remain in the atmosphere for days. Kros et al. (2008) found that over 20% of $NH_4^+$ could remain in the atmosphere after traveling 1000 km (for a comparison of $N_R$ deposition velocities, see Hanson and Lindberg 1991). Therefore, no terrestrial ecosystems are spared from anthropogenic N pollution. To quantify N deposition and determine which environments face the most risk, scientists typically use "critical loads" which are the levels above which detrimental effects occur (Pardo et al. 2011). Critical loads are typically expressed in kg N $ha^{-1}$ $year^{-1}$ and usually are in the 1–20 kg N $ha^{-1}$ $year^{-1}$ range depending on the environment. Table 13.1 outlines some of the many negative effects that can occur when critical loads are exceeded.

## 13.2 Effects of N Deposition on Low-Nutrient Environments: Overview

The diversity of Earth's landscapes is epitomized by low-nutrient environments or LNEs. For the purposes of this paper, LNEs are any terrestrial environment comparably low in plant essential nutrients. These environments are brought about due to extreme chemical, physical, or climate conditions that leave certain habitats devoid of nutrients such as potassium (K), phosphorus (P), and particularly N. The conditions (see Table 13.2, column 4) can be "limiting factors" for plant growth themselves or result in an N, P, or K deficiency that is a limiting factor. For example, the soil instability of coastal dunes reduces productivity and nutrient cycling, thereby reducing N/P/K availability. Likewise, in serpentine soils, the extreme chemical conditions reduce N fixation and cycling. But worldwide, N availability is one of the most common growth-limiting factors for terrestrial environments, particularly in temperate regions (Vitousek and Howarth 1991; LeBauer and Treseder 2008; Hou et al. 2012). Despite the abundance of atmospheric $N_2$, the LNE's extreme conditions cause breaks in the N cycle, preventing N fixers from completely reversing N limitation. Furthermore, natural disturbances such as fire can drastically reduce available N in environments (Vitousek and Howarth 1991). It is also important to know how plants are limited by nutrients. There are, however, conflicting explanations. One is the multiple limitation hypothesis (MLH) which asserts that plants will adjust growth patterns to optimize nutrient ratios so N, P, and C are equally limiting (Bloom et al. 1985; Ågren et al. 2012). But there is also Liebig's law of the minimum (LM) (Liebig 1840, 1855). This older law states that the one nutrient in least supply to the plant's requirements will limit growth (although there can be co-limitation at very strict ratios) (Ågren et al. 2012; Knecht and Göransson 2004). Neither explanation fits all plants, but, in the case of LNEs, most plants follow LM (Ågren et al. 2012).

To withstand LNE's nutrient limitations, some plants have evolved unique adaptations. The most direct adaptation to low-N environments is N fixation. Legumes (Fabaceae) are a prime example. The roots of legumes support nodules where N-fixing bacteria in the genus *Rhizobium* reside. Additionally, there are about 200 species of angiosperms that associate with N-fixing bacteria in the genus *Frankia*. This is called actinorhizal symbiosis (Franche et al. 2009; Stewart 1967). N-fixing plants are widespread, but some are native to LNEs such as certain species of the genus *Lupinus* which are native to California's sand dunes (Maron and Connors 1996). In another type of mutualistic relationship, many plants in LNEs gain nutrients by partnering with mycorrhizal fungi. While the majority of land plants partner with mycorrhizae, these partnerships are particularly valuable in LNEs

**Table 13.1** Harmful effects of N deposition in terrestrial environments, including plants, fungi, and animals. The relevant sources provide further detail on these harmful effects

| Harmful effect | Relevant sources |
|---|---|
| **Nitrogen toxicity**<br>While $N_R$ is a crucial nutrient for plants, high doses of certain forms can be toxic. Most toxicity has been observed with exposure to $NH_3$ and $NH_4^+$. $NH_X$ can be absorbed through the stomata or by roots, although it is rare for $NH_3$ to be taken up by roots. However, plants cannot store $NH_X$ in their tissues, meaning it all must be assimilated (converted into other forms). It is when $NH_X$ uptake exceeds assimilation capacity that it becomes toxic. Toxic effects can manifest directly as foliar injury; however, studies have also linked excess $NH_X$ to decreased drought, frost, pest, and pathogen resistance. This is likely due to the increased water and energy costs associated with $NH_X$ assimilation. Furthermore, excess $NH_X$ can alter the biochemistry of plants, changing amino acid ratios and disrupting photosynthetic processes | Goyal and Huffaker (1984), Krupa (2003), Díaz-Álvarez et al. (2015), Wang et al. (2019), Wu and Blodau (2015) |
| **Soil acidification**<br>While sulfur oxides were previously the largest source of soil acidification, that title now belongs to N oxides. As discussed previously, atmospheric $NO_X$ can form acid rain which falls to earth and acidifies soils. However, $NH_4^+$ is once again an antagonist. When $NH_4^+$ is deposited in soil, it is converted to $NO_3^-$ (by nitrification) or taken up by plants. Both processes produce excess $H^+$ ions and therefore reduce soil pH. pH changes affect nutrient availability, and extreme changes can kill plants and soil fauna. More specifically, soils buffer pH changes by releasing cations ($Ca^{2+}$, $K^+$, $Mg^{2+}$) which immobilizes excess $H^+$ ions. But in the long term, released base cations may leach out of the soil, decreasing the availability of these necessary plant nutrients. Additionally, soil acidification can form positive feedback loop with base cation availability: as pH decreases, so does base cation availability and the ability to buffer. At very low pH, soils buffer by releasing $Al^{3+}$ which can be toxic to plants and soil microbes | Tian and Niu (2015), Bowman et al. (2008), Horswill et al. (2008), Yang et al. (2018b), Lu et al. (2014) |
| **Decrease in mycorrhizae populations**<br>Many plants rely on arbuscular mycorrhizal and/or ectomycorrhizal fungi (AMF/EMF) for nutrient acquisition, particularly plants in low-nutrient environments. A plant invests in | Lilleskov et al. (2002), Wallenda and Kottke (1998), van Diepen et al. (2011), Phillips et al. (2019), Weber et al. (2019) |

(continued)

**Table 13.1** (continued)

| Harmful effect | Relevant sources |
|---|---|
| mycorrhizae by providing the fungi with sugar (C) in exchange for improved access to nutrients such as N and P. But when N becomes abundant in soil due to atmospheric deposition, plants allocate less C to mycorrhizae. Therefore, N addition can select for less mutualistic AMFs. Overall, N deposition can significantly alter mycorrhizae populations, often more rapidly than plant populations, since fungi are extremely sensitive to changes in soil chemistry | |
| **Altering interspecific plant competition**<br>While the factors mentioned above—direct N toxicity, soil acidification, and reduced mycorrhizal interactions—can all reduce plant diversity, a major cause is a change in interspecific competition. Chronic N deposition often favors nitrophilous and invasive species that grow quickly and outcompete native species. A common sign of excessive N deposition on a landscape is an increase in vegetative cover (total biomass) but a decrease in native plant abundance and diversity | Bobbink et al. (2010b), Yang et al. (2018a), Ren et al. (2019), Goldberg et al. (2017) |
| **Decrease in animal diversity**<br>N deposition affects animals through three pathways. The first is direct toxicity, which has the greatest impact on aquatic mussels and amphibians where it can hinder normal development and reproduction. N toxicity is thought to be one of the main contributors to the global decline of amphibian populations. The second is through eutrophication of aquatic habitats, leading to harmful algae blooms which can asphyxiate aquatic organisms. The third, which is the primary threat to terrestrial organisms, is more indirect. When N deposition decreases plant diversity, fauna is affected. Such is the case with the endangered Bay checkerspot butterfly of California, whose habitat is serpentine grasslands. N deposition has allowed invasive annual grasses to outcompete the checkerspot's native annual host plants, resulting in a decline of the butterfly populations | Hernández et al. (2016), Weiss (1999), Balangoda (2018), Campbell and Vallano (2018), Nijssen et al. (2017) |

**Table 13.2** Selected LNEs. The plant community column lists common plant types. Because these LNEs are broadly defined, not all examples worldwide will have the same plant composition or limiting factors; there may also be some overlap between LNEs. It is also important to note that limiting factors influence one another, with chemical, physical, or climate factors resulting in nutrient deficiencies. For information about how these LNEs are affected by N deposition, refer to the listed sources

| LNE | Distribution | Plant community | Limiting factors | N dep sources |
|---|---|---|---|---|
| Acid grasslands | Gravelly, sandy soils in Europe, especially Great Britain. Often associated with heathlands | Bedstraw (*Galium* spp.)<br>Bent (*Agrostis* spp.), *Festuca* grasses<br>Dwarf shrubs (*Calluna vulgaris*)<br>Bryophytes<br>Lichens | N/P deficiency<br>Acidic soils<br>Base cation deficiency<br>Aluminum, heavy metal mobilization | Stevens et al. (2011), BRIG (2011), Gaudnik et al. (2011) |
| Calcareous grasslands | Northwestern Europe on chalk and limestone, especially in Great Britain | *Festuca* spp.<br>Sedges<br>Wildflowers such as *Thymus polytrichus*, *Polygala vulgaris* | N/P deficiency<br>Alkaline soils<br>Shallow soils | Ridding et al. (2020), Van Den Berg et al. (2011), Smits et al. (2008) |
| Coastal dunes | Worldwide | *Ammophila*, *Elymus*, *Panicum* grasses<br>*Carex* sedges | N/P/K deficiency<br>Erosion, soil instability<br>Low soil organic matter | Remke et al. (2009), Jones et al. 2004, Maun (2009) |
| Fens | Temperate, boreal peatlands in N. America, Europe, and Siberia | *Carex* spp.<br>Orchids<br>Bryophytes<br>*Sphagnum* and *Drepanocladus* mosses | N/P deficiency<br>Often alkaline<br>Waterlogged<br>Low decomposition rates and low-N cycling | Kooijman (2012), Verhoeven et al. (2011), Wieder et al. (2020) |
| Fynbos | South Africa's Cape Floristic Region | Ericaceous taxa<br>*Aspalathus*, *Leucospermum*, *Protea*, shrubs<br>Bulbs | N/P deficiency<br>Acidic soils<br>Mediterranean precipitation patterns | Witkowski (1988), Manning (2018), Malan (2009) |
| Heath | Worldwide, but particularly common in Europe, Australia, California, and Chile | *Calluna vulgaris*<br>Ericaceous, other shrubs varying greatly by region | N/P/K/Mg deficiency<br>Acidic soils<br>Shallow soils | Aerts and Heil (2013), Bähring et al. (2017), Maskell et al. (2010) |
| Ombrotrophic bogs | Temperate, boreal peatlands in N. America, | *Sphagnum* mosses<br>*Carex* and *Eriophorum* sedges | N/P deficiency<br>Acidic soils<br>Waterlogged | Larmola et al. (2013), Bubier et al. |

(continued)

**Table 13.2** (continued)

| LNE | Distribution | Plant community | Limiting factors | N dep sources |
|---|---|---|---|---|
| | Europe, and Siberia | *Andromeda*, *Calluna*, *Erica* heaths<br>Carnivorous plants | | (2007), Aerts et al. (1992) |
| Serpentine | Worldwide, but particularly in New Caledonia, Cuba, California, and the Balkan Peninsula | Highly variable, ranging from fens/bogs to sparse outcrops. Specialized insectivorous plants including *Darlingtonia* spp. and *Nepenthes* spp. Vegetation often stunted or dwarfed | N/P/K deficiency<br>Low Ca/Mg ratio<br>Shallow soils<br>Low water retention<br>High heavy metal (Ni, Cr) content | Vallano et al. (2012), Huenneke et al. (1990), Pasari et al. (2014) |
| Tundra | Arctic, Antarctic, and alpine environments | Mosses<br>Lichens<br>Small ericaceous shrubs<br>Sedges<br>*Silene acaulis* (cushion plant) | N/P/K unavailability<br>Waterlogged soils or permafrost<br>Freezing temperatures | Choudhary et al. (2016), Zong et al. (2016), Burns (2004) |
| General sources | WHO (2000), Bobbink et al. (2010a) | | | |

where soil nutrients are scarce. For example, AMF association has been shown to reduce N and P loss in a sandy grassland LNE (van der Heijden 2010). Proteoid roots, or root clusters, are another adaptation common to LNEs. First discovered in the Proteaceae family of southwestern Australia and South Africa, these roots have tightly clustered lateral rootlets that extend out only a short distance from the main root (Watt and Evans 1999). Proteoid roots increase total root surface area and release large quantities of root exudates that can mobilize cation-bound P and organic N (Watt and Evans 1999; Lamont 2003; Lambers et al. 2006). Lastly, some of the most renowned LNE-adapted plants are carnivorous, such as the Venus flytrap (*Dionaea muscipula*) or the trumpet pitcher plants (*Sarracenia* spp.). Carnivorous plants have evolved worldwide in a variety of environments including bogs, fens, lakes, and serpentine soils (Jules et al. 2011; van der Ent et al. 2015). Elaborate leaf modification adaptations allow them to capture and digest insects: their primary N source. Generally, they reside in environments with plenty of water and sunlight but on soils lacking in N, P, and K (Givnish et al. 1984). Some carnivorous plants obtain up to 90% of their N from prey (Ellison 2006).

With these unique adaptations, plant life inhabits LNEs' unfavorable conditions with remarkable diversity (Table 13.2). For example, there are OCBILs, or old climatically buffered infertile landscapes (Hopper 2009). These landscapes are rare worldwide, found in a few unglaciated regions particularly in southwestern South Africa, southwestern Australia, and Venezuela. However, these regions boast remarkable plant diversity. Despite OCBIL rarity, at least 12 terrestrial biodiversity hotspots (out of 36 total; Myers et al. 2000) contain OCBILs (Hopper et al. 2016). But, in general, infertile soils worldwide boast high plant diversity. LNE-adapted plants must compete for nutrients which fosters diversity in morphological (i.e., phenotypic) traits such as different rooting depths or physiological traits such as N-fixing ability (Huston 1995). On the other hand, fertile environments have higher biomass so plants are generally competing for sunlight, which can be more restrictive to functional trait diversity (Huston 1995).

LNE-adapted plant species share a few other general characteristics. Since LNEs have reduced biomass, forbs, grasses, and shrubs dominate instead of large trees. These plants typically demonstrate slow growth, high resource use efficiency, and long-lived tissues (Funk 2013). This is supported by leaf economics spectrum (LES) data (Reich et al. 1997; Wright et al. 2004). At one end of the spectrum are plants with low leaf mass per unit area (LMA), short leaf lifespan, high rates of photosynthesis, and high foliar N content; at the other end are the LNE-adapted plants, with high LMA, long-lived leaves, lower photosynthesic rates, and lower foliar N content (Funk 2013). At this end of the spectrum, LNE-adapted plants use N more efficiently. With longer-lived, higher LMA leaves, a plant can achieve carbon gain (photosynthesize) at rates greater than or equal to plants in more fertile soils (Bloom et al. 1985; Bubier et al. 2011; Hiremath 2000). Without disturbance, these plants retain their niches by maintaining low-N conditions, since their litter is also low in N and decomposes slowly (Hobbie 1992; Santiago 2007).

Unfortunately, it is the very nature of these diverse LNEs that they are more susceptible to the effects of N deposition. LNEs have lower critical N loads than more fertile landscapes, meaning dramatic ecological effects can occur with relatively low levels of deposition. One of the biggest concerns about N deposition in LNEs is a resulting increase in invasive species. Typically, limiting factors of LNEs limit invasive species establishment and thus protect native plant diversity (Alpert et al. 2000). But under N deposition, limiting factors are altered. For example, the growth of peat mosses (*Sphagnum* spp.) was found to be limited by N in northern Sweden, but by P in southern Sweden where N deposition was three times greater (Aerts et al. 1992). Furthermore, as explained by the theory of fluctuating resource availability, "a plant community becomes more susceptible to invasion whenever there is an increase in the amount of unused resources" (Davis et al. 2000). Therefore, if an LNE is subject to N deposition, species that previously could not survive in the low-N conditions can now colonize and perhaps become invasive.

N-enriched LNEs are also particularly vulnerable to invasion because LNE-native plants have inherently lower productivity (growth rates/plasticity) and are slow to absorb excess nutrients. This gives invasive species more time to take advantage of them (Funk 2013). On the other hand, plants native to high-nutrient environments have inherently higher productivity (growth rates/plasticity) and can more rapidly assimilate excess N. While there are slow-growing invasive species, most belong to the end of the leaf economics spectrum characterized by fast-growing plants with short-lived, N-rich foliage (Ordonez and Olff 2013; Funk 2013). They are often larger than LNE-native species because as N availability increases, so does optimal plant size (Goldberg et al. 2017). Invasive species also generally have greater phenotypic plasticity, allowing them to better utilize excess nutrients (Davidson et al. 2011). Therefore, when there is excess N, these nutrient-loving plants invade and grow rapidly, blocking sunlight and outcompeting smaller LNE natives. If N deposition is accompanied by disturbance such as fire that creates unoccupied spaces, invasion intensity can further increase (Milbau et al. 2013; Boscutti et al. 2018; Alpert et al. 2000). Overall, the change in species composition associated with invasion can cause LNEs to accumulate more biomass and retain N, creating a positive feedback loop of rapid change from the original LNE (Maron and Jefferies 1999).

## 13.3 Introduction to Serpentine Environments

One of the most unique LNEs is serpentine. Serpentine landscapes are often described as otherworldly, appearing in stark contrast to nearby non-serpentine landscapes (Figs. 13.3 and 13.5; Kruckeberg 1986; Rajakaruna 2004). They are typically rocky with shallow soil tinted green by serpentine minerals or red by oxidized iron (Harrison and Rajakaruna 2011). As the serpentinite bedrock is weathered, it becomes soil characteristically high in trace and heavy metals Fe, Mg, Ni, and Cr and generally low in the nutrients N, P, K, S, Ca, and Mo (Kruckeberg 1984; Alexander et al. 2007). These extreme soil conditions reduce plant growth rates, leading to reduced organic matter accumulation and cation exchange capacity (Rajakaruna and Boyd 2008). Because the soil profile is often

**Fig. 13.3** The densely vegetated Buck Creek serpentine area of western North Carolina (left; credit Thomas Samojedny) compared to a more rocky, barren California serpentine outcrop in the foreground, sharply defined by the more vegetated marine sandstone and shale in the background (right; credit Ryan O’Dell)

poorly developed and shallow, serpentine soils commonly have low water holding capacity. Combined, serpentine's extreme conditions have been nicknamed the "serpentine syndrome" (Jenny 1980).

However, these common characteristics can manifest differently depending on the site. Most of the serpentine sites we discuss follow the less lush California (Mediterranean) model. But while the description of a rocky and sparsely vegetated landscape may fit some serpentine sites, including many California sites, it does not fit all. For example, the Buck Creek serpentine area in western North Carolina is densely vegetated with perennial forbs and shrubs and has a thin canopy of dwarf *Pinus rigida* (Mansberg and Wentworth 1984; Marx 2007). Buck Creek is much more productive than many of the California serpentine outcrops, but it still would be considered unproductive when compared to the lush Nantahala National Forest surrounding it (Fig. 13.3). Therefore, it is more useful to compare serpentine sites to their adjacent landscapes than to one another. While this chapter focuses on California serpentine, serpentine soils are present in small patches globally (Brooks 1987). For a review of other regions, see Galey et al. (2017) for South and Southeast Asia, Rajakaruna et al. (2009) for eastern North America, and Teptina et al. (2018) for circumboreal/temperate regions.

Serpentine's challenging edaphic conditions have contributed to high levels of plant endemism (Rajakaruna 2018). For instance, California serpentine outcrops harbor 14.7% of its endemic plants (Safford and Miller 2020). This accounts for about 250 taxa, a remarkably high number given serpentine soils cover less than 1.5% of the state (Safford et al. 2009). Due to their restricted ranges, many of these endemics are rare, and 192 (77%) are listed in the California Native Plant Society Inventory of Rare and Endangered Plants (Safford and Miller 2020). Many of these rare plants can grow well in more fertile soil; however, they are restricted from fertile substrates due to their low competitive ability (Anacker 2014; Sianta and Kay 2019). Therefore, serpentine acts as a refuge for them. In just the San Francisco Bay Area alone, serpentine grasslands harbor 14 federally listed endangered species including 13 plants and 1 insect, the Bay checkerspot butterfly (*Euphydryas editha bayensis*) (Elam et al. 1998). Rare plant alliances can also be found on serpentine, including the California pitcher plant (*Darlingtonia californica*) alliance in serpentine wetlands/fens (Jules et al. 2011) and the Sargent's cypress (*Hesperocyparis sargentii*) alliance found along ridges in California's Coast Ranges (Alexander et al. 2007). While these refugia are not abundant, the exclusive ecosystems serpentine soils support make them an ideal setting to study ecology, evolution, and conservation (Harrison and Rajakaruna 2011; Rajakaruna et al. 2014).

## 13.4 Insights from N Deposition on Serpentine

According to Fenn et al. (2010), the critical load for N deposition in serpentine grasslands is 6 kg N $ha^{-1}$ $year^{-1}$. But in California, many serpentine grasslands are experiencing deposition above this critical load (Fig. 13.4). As discussed in the introduction, N deposition varies by region, tending to be greater near urban areas

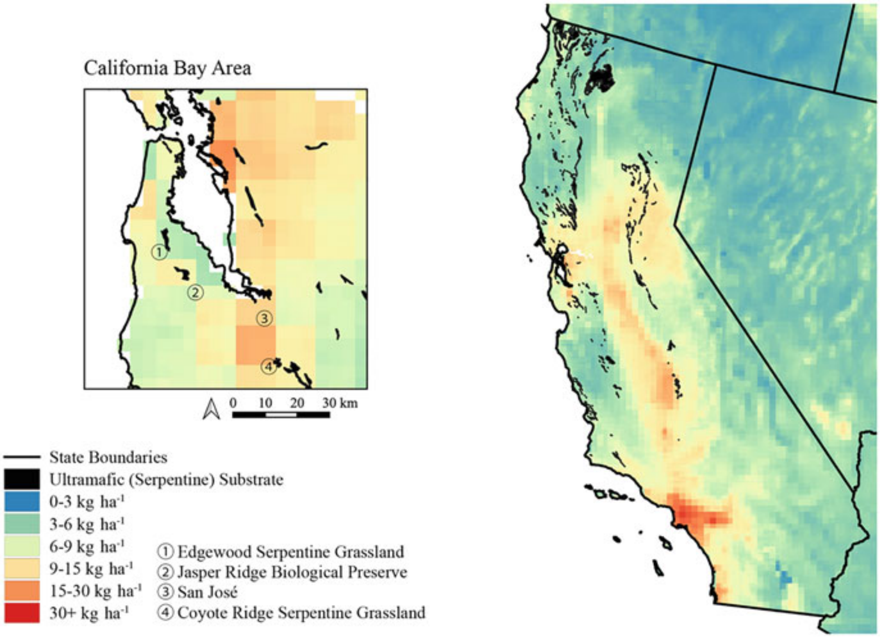

**Fig. 13.4** Map of 2019 total N deposition rates and locations of serpentine substrate across California. Areas with the greatest N deposition include the San Francisco Bay area, the Los Angeles area, and the heavily agricultural Central Valley. Zoomed area includes the location of the two serpentine grasslands mentioned in the chapter, the city of San José and the Jasper Ridge Biological Preserve. Deposition grid data from NADP Tdep (http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/). Serpentine substrate layers from USGS (https://mrdata.usgs.gov/geology/state/sgmc-unit.php?unit=CAum3)

with high levels of $NO_X$ and $NH_3$ emissions from automobiles and industry, or in heavily agricultural areas. For serpentine grasslands south of the heavily urbanized San Francisco Bay Area, a conservative estimate placed N deposition in the range of 10–15 kg N $ha^{-1}$ $year^{-1}$, greatly exceeding the critical load (Weiss 1999). More recently, Fenn et al. (2010) found similar deposition amounts at nearby sites, with one site exceeding 15 kg N $ha^{-1}$ $year^{-1}$. At another serpentine grassland, the Edgewood Natural Preserve upwind of San José but bordering busy highway 280 (Fig. 13.4), deposition was also around 15 kg N $ha^{-1}$ $year^{-1}$ (Fenn et al. 2010). For these sites near urban centers, dry deposition (mostly $NH_3$, $NO_2^-$, $HNO_3$) was much more substantial than wet deposition. However, since $NH_4^+$ and $HNO_3$ can remain in the atmosphere for long periods, wet deposition is still of concern, especially for remote serpentine sites.

Because these Bay Area grasslands are exceeding their critical loads, they offer important insights into the effects of N deposition. N deposition notably increases biomass in serpentine grasslands, as was observed in the Jasper Ridge Global Change Experiment (Fig. 13.5) which exposed a grassland to elevated $CO_2$, temperature, precipitation, and N deposition for 5 years. $NO_3^-$addition caused the largest

**Fig. 13.5** Jasper Ridge Biological Preserve in April 1981 (left; credit Bruce Bohm) and April 2009 (right; credit Nishanta Rajakaruna). In the 1980s, *Lasthenia californica* (yellow) and other serpentine-tolerant California native forbs create an abrupt demarcation between the serpentine and non-serpentine soil. However, due to environmental changes (which include N deposition; https://jrbp.stanford.edu/research/projects/nitrogenous-air-pollutant-monitoring), this pattern is no longer as striking, as the serpentine outcrop is increasingly invaded by non-native grasses such as *Lolium multiflorum* (annual ryegrass), *Bromus hordeaceus* (soft brome), and *Avena* spp. (wild oats)

increase in biomass among the four global change drivers tested (Dukes et al. 2005; Zavaleta et al. 2003). However, the primary detrimental effect of N deposition is an increase in invasive species establishment. When soil fertility increases, the habitat becomes accessible to plant species previously excluded from the area. It is important to note that serpentine communities, like other LNEs, are naturally resistant to invasion and are frequently dominated by native species even when neighboring substrates are heavily invaded (Harrison and Rajakaruna 2011; Gelbard and Harrison 2003). This is because serpentine's limiting factors (particularly low N availability) make it difficult for invasive species to establish themselves. For instance, California grasslands have experienced one of the most extreme global invasion episodes, with dozens of species from Eurasia invading after Spanish settlers arrived (Baker 1989). Some of the last remaining locations still dominated by native California grasses are serpentine environments (Huenneke et al. 1990).

Therefore, it is of particular concern that serpentine substrates are now being invaded (Fig. 13.5). This is primarily due to increasing N deposition which increases the fertility of serpentine soils, allowing non-native annual grasses and forbs to invade. Due to invasive plants' high phenotypic plasticity (Nielsen et al. 2019; Davidson et al. 2011; Harpole et al. 2007) and adaptability, they can overcome the remaining limiting conditions such as the extreme Ca/Mg ratios and make use of the excess N. Previous studies have identified the influence of N deposition on grassland species' competitive ability (Wedin and Tilman 1993; Lamb et al. 2007). However, only a few studies, such as Huenneke et al. (1990), have demonstrated the effects of N deposition on serpentine invasion. Huenneke et al. set up a fertilization field experiment in a serpentine grassland in Santa Clara County, California. Their study included two serpentine "clades," with half of the plots dominated by small forbs and the others by grasses. Plots were fertilized with N, P, non-NP fertilizer, or a mixture of all three. The first main observation was that during year 1 of fertilization, biomass increased to levels typical of non-serpentine grasslands. This provided evidence that low nutrient availability was the primary limiting factor at this site. However, during year 2, drastic community-level changes occurred. Total plant species richness decreased for all fertilizer treatments, from 12.3 to 9.5 species in forb plots and from 8.6 to 5.1 in grass plots. Unsurprisingly, non-native plant biomass increased, while native biomass decreased. Furthermore, forb plots became more similar to grass plots, highlighting the susceptibility of serpentine-native forbs, which contribute the most to serpentine plant diversity (Zavaleta et al. 2003). Based on this study, they concluded "increased nutrient availability, without physical disturbance of soil or of native vegetation, can favor the invasion and success of non-native species in an ecosystem where natural levels of resource availability are low" (Huenneke et al. 1990).

Other studies also support these findings. In a serpentine revegetation study by O'Dell and Claassen (2006), the effects of various nutrient amendments were tested. Nutrient addition increased native biomass at revegetation sites, but it also made sites more susceptible to invasion so they determined nutrient addition should be accompanied by invasion reduction strategies. M. Devlin et al. (unpublished data) found that N and P addition in a greenhouse study favored *Bromus hordeaceus* and *Avena fatua*, two non-native annuals, over *Festuca microstachys* and *Plantago erecta*, two serpentine natives. N and P addition increased seed mass and aboveground biomass much more significantly for *B. hordeaceus* and *A. fatua*, suggesting non-natives are better equipped to utilize excess nutrients (Fig. 13.6). In another greenhouse study simulating N deposition, Vallano et al. (2012) compared the abundance and competitive ability of five serpentine grassland native species, *Plantago erecta*, *Layia gaillardioides*, *Lasthenia californica*, *Vulpia microstachys*, and *Cryptantha flaccida*, against the most common invasive grass in the area—*Lolium multiflorum*. While all species showed a positive biomass response to N

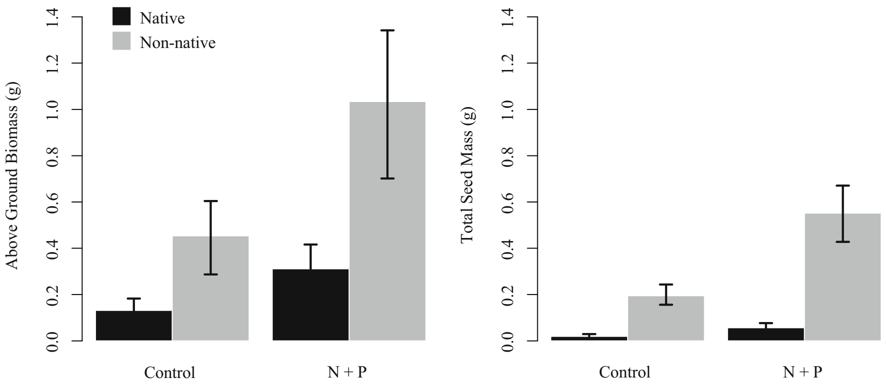

**Fig. 13.6** Results of M. Devlin et al.'s (unpublished data) greenhouse study. Left, aboveground biomass compared for serpentine-native and non-native plants with and without N + P fertilization (native vs. non-native, $p < 0.01$). Right, seed mass for the same groups (native vs. non-native, $p < 0.001$)

fertilization, *Lolium multiflorum*'s response was by far the strongest, suggesting it has a competitive advantage under N deposition. Weiss (1999) confirmed these effects in the field, noting areas once dominated by *P. erecta*, *Layia gaillardioides*, and *Lasthenia californica* are being overrun by *Lolium multiflorum*. This alteration has led to a rapid demise of the Bay checkerspot butterfly since *P. erecta* is its host plant (USFWS 2009) and *Layia gaillardioides* and *Lasthenia californica* are nectar sources (Weiss et al. 2007; Hernández et al. 2016). For instance, in the Edgewood Natural Preserve mentioned earlier, the butterfly's population decreased from 5000 in 1997 to zero in 2002 (Fenn et al. 2010). Cases like these demonstrate the severity of N deposition's influence on invasion and the accompanying ecosystem-level effects.

Once N deposition has occurred, the ecosystem-level effects are difficult to reverse. One reason is that the removal of invasive species is often very difficult. But another reason is that exotic grasses, such as *Festuca perennis* and *Bromus hordeaceus*, tend to have higher foliar N content (Franck et al. 1997) and produce more litter than natives (Huenneke et al. 1990). This can generate a positive feedback loop where high soil N levels are reinforced with each subsequent litterfall (Esch et al. 2013). Plus, since LNEs such as serpentine tightly recycle nutrients, the effects of N deposition can last longer (Elam et al. 1998). Another important factor is that many serpentine sites experience reduced or sporadic rainfall, including California serpentine grasslands, which occur in a Mediterranean climate with distinct wet and dry seasons. This may be a problem because N deposition can decrease the ability of LNE-adapted plants to withstand fluctuations in rainfall (Eskelinen and Harrison 2015; Fernandez-Going et al. 2012).

Additionally, California's Mediterranean climate allows deposited N to accumulate over the dry season in soil or on leaf surfaces and become available all at once after seasonal rainfall begins, leading to large pulses of N input (Ochoa-Hueso et al. 2011; Greaver et al. 2016). These pulses can lead to N toxicity, particularly for serpentine-native plants adapted to low N. While there are not any concrete examples of N toxicity for serpentine plant species, there is evidence it occurs. Huenneke et al. (1990) first suggested that N fertilization hinders germination and establishment of serpentine-native seedlings after documenting a dramatic decrease in native abundance during year 2 of fertilization, despite native seeds constituting the majority of seed rain. Vallano et al. (2012) also found that, for one serpentine-native grass *Vulpia microstachys*, N fertilization decreased stomatal conductance which can reduce photosynthetic capacity. Moreover, if N deposition is accompanied by changes in soil Ca/Mg ratios, toxicity may be worsened. Ghasemi et al. (2015) found that for the serpentine-endemic species *Alyssum inflatum*, higher Ca/Mg ratios increased mortality when exposed to $NH_4^+$, likely since $Ca^{2+}$ is known to stimulate $NH_4^+$ absorption (Fenn et al. 1995; Fenn and Feagley 1999). Since invasive species alter nutrient cycling on serpentine in general, it is possible that Ca/Mg ratios will be altered as well. N deposition may even have differing effects for the same species on and off serpentine. Watanabe et al. (2012) found that the growth of a hybrid larch was stunted by N addition on serpentine. Comparing effects between plants on serpentine and brown forest soils, larches grown on brown forest soil responded positively to N addition, while those grown on serpentine had decreased N allocation to the photosynthetic apparatus (Watanabe et al. 2012). While the mechanisms behind these effects are unclear, it is apparent that N deposition is responsible for unusual effects on serpentine plants.

An associated effect of N deposition on serpentine is soil acidification. As stated previously, there are a few N-cycling processes that decrease soil pH by releasing $H^+$, including nitrification and ammonium uptake by plants (Bolan et al. 2003; Yang et al. 2018b). The rates of these processes increase when more N is added to the system. Serpentine soils vary in their sensitivity to soil acidification. More developed serpentine soils with high clay and organic matter percentages will have a greater buffering capacity than less developed, sandy soils (Ryan O'Dell, Bureau of Land Management, California Department of the Interior, Region 10). But in all serpentine soils, acidification can alter nutrient cation availability since $Ca^{2+}$ and $Mg^{2+}$ are released for buffering and then are more prone to leaching. Moore and Zimmermann (1977) found that, in one laboratory study, acidification decreased the Ca/Mg ratio from 1:37 to 1:152. Acidification is also concerning because it can increase the availability of toxic metals: at low pH, Mn, Al, Cr, Cd, and Ni become more concentrated (i.e., bioavailable) in soil solution (Bolan et al. 2003). While many serpentine-adapted plants can tolerate low Ca/Mg ratios and high heavy metal concentrations (Ferrero et al. 2020), acidification may push plants past tolerance limits.

Nitrogen deposition also affects serpentine-associated mycorrhizae. Various studies have confirmed serpentine plants are strongly associated with mycorrhizae (Hopkins 1987; Moser et al. 2005; Gladish et al. 2010; Branco and Ree 2010). However, the fact that N deposition has been shown to decrease mycorrhizae populations (Lilleskov et al. 2002; Weber et al. 2019; Wallenda and Kottke 1998) may have stronger implications for serpentine plants since mycorrhizal associations can alleviate the effects of the serpentine syndrome. For example, mycorrhizae can reduce the toxicity of heavy metals found in serpentine (Southworth et al. 2014). In plants that do not tolerate high Ni concentrations, AMF inoculation was shown to decrease Ni uptake (Vivas et al. 2006; Guo et al. 1996), while it increased uptake in Ni-tolerant hyperaccumulators (Orłowska et al. 2011; Husna et al. 2017). Another study found AMF inoculation improved drought tolerance and increased P uptake for *Knautia arvensis* on serpentine (Doubková et al. 2013). Thus, with increasing N deposition and accompanying drops in mycorrhizae populations, certain serpentine plants may be less equipped to survive serpentine's harsh conditions.

These combined impacts of N deposition are causing drastic changes to serpentine plant communities and many other LNEs worldwide. From microscopic mycorrhizae to the charismatic Bay checkerspot butterfly, N deposition is disrupting serpentine environments. These changes affect the spatial ecology of the landscape; non-native species invasion and decline in native plant abundance decrease the heterogeneity of serpentine landscapes, as when diverse native annual forblands transition into less diverse non-native annual grassland (Harrison and Rajakaruna 2011). It is possible (although untested) that N deposition is also a contributing factor in the plant community shifts documented on serpentine outcrops in the mid-Atlantic, USA, where savanna-type native vegetation is being replaced by non-native conifer-dominated woodlands (Burgess et al. 2015). Thus, serpentine environments are not only losing their title as a refuge for rare and unique plants but also their charm.

## 13.5 Mitigation Strategies

Certain palliative strategies have proven helpful in lessening the symptoms of N deposition. Liming can be used to ameliorate N deposition-caused soil acidification (Huettl and Zoettl 1993; Bolan et al. 2003). Most other mitigation efforts target invasive species, using biomass reduction strategies such as livestock grazing. Livestock grazing appears to be particularly successful in California's serpentine grasslands, where it favors native forbs and reduces exotic grasses (Weiss 1999; Safford and Harrison 2001; Pasari et al. 2014; Jain 2015). Pasari et al. (2014) found that, in a serpentine grassland fertilization study, removal from grazing decreased native plant diversity slightly. Another study by Beck et al. (2015) found that, in ungrazed plots, native plant diversity decreased. They also found that grazing increased the temporal stability of native forb cover, meaning that native forbs were less susceptible to population fluctuations under grazing.

However, grazing does not appear to be as successful a strategy for non-serpentine grasslands. Harrison et al. (2003) found that grazing decreased native plant species richness for a non-serpentine grassland by 11.7% while increasing richness by 14.4% for a serpentine grassland. They hypothesized that since serpentine grasslands typically have smaller exotic populations, native plants may better utilize the space and light made available by grazing. But grazing cannot eliminate all invasive species such as ones inedible to livestock. At the Coyote Ridge serpentine grassland (Fig. 13.4), barbed goatgrass (*Aegilops triuncialis*) is a major invasive threat. Grazing increased its density, perhaps because livestock dispersed its seeds, and herbicides had to be used to reduce the numbers to hand-pulling density (Weiss et al. 2011). Therefore, grazing is not a foolproof solution for managing invasion in grasslands, particularly non-serpentine ones.

Another biomass reduction strategy is prescribed fire which has been shown to increase native species richness on serpentine grasslands (Harrison et al. 2003). Gillespie and Allen (2004) found fire increased native diversity in a serpentine chaparral habitat. But, like grazing, prescribed fire is not a perfect solution. Harrison et al. (2003) found that fire decreased native diversity in non-serpentine grasslands. Furthermore, fire may only be successful in regions where it is a frequent natural phenomenon, as fire reduced native plant diversity on serpentine in tropical New Caledonia and Cuba, where natural fires are not frequent (Gillespie and Allen 2004). Fire can also be detrimental to water quality because it can mobilize N, which can lead to eutrophication in downstream habitats. Because of these limitations, fire and grazing may need to be combined with other strategies such as mowing, which when timed properly, can thwart early-sprouting invasive grasses, and selective thinning, which can remove some stored N from forest ecosystems (Fenn et al. 2010).

However, these strategies are extremely costly and labor-intensive and only practical for small areas.

Due to the limitations of palliative strategies, preventing N deposition is likely the best solution. And the best way to do this is to limit the amount of $N_R$ added to the atmosphere and land each year. The first area to target is $N_R$ emissions from fossil fuel. Current estimates place global $NO_X$ emissions around 40 Tg N $year^{-1}$, of which 58% comes from fuel combustion (Jaeglé et al. 2005; Martin et al. 2003). Aber et al. (2003) concluded that eliminating $NO_X$ produced by fossil fuel combustion would decrease N deposition in northeastern US forests by over half. Many $N_R$ emission reduction strategies are feasible because they can be simultaneously used to reduce $CO_2$ emissions. And, as discussed in the Introduction, these strategies have worked to reduce $NO_X$ emissions, including a 40% reduction in the European Union between 1990 and 2009 (ETC/ACC 2015). However, fossil fuel $NH_3$ emissions are still increasing, with few attempts globally to regulate $NH_3$ aside from those in the Netherlands and Denmark (Fowler et al. 2015). Therefore, the threat of N deposition should be another impetus to switch to renewable energy sources and enact stricter pollution control policies.

The other prevention target, and perhaps the one with the most potential for change, is in agriculture. Livestock produces a lot of $N_R$, mostly urea in urine and feces. Therefore, changing the global diet to demand less meat would drastically cut $N_R$ emissions (Costa Leite et al. 2020). Farmers can also reduce the protein content of livestock feed to reduce excess livestock N excretion (Hou et al. 2016). Recent experiments with dietary additives, such as urease inhibitor, have proven effective in reducing livestock-produced $NH_3$ by nearly half (Ti et al. 2019). However, the most effective prevention strategies center on inefficient Haber-Bosch fertilizer use. 170 Tg $N_R$ was added to global croplands in 1995, the majority from HB fertilizer, yet only 12% of that $N_R$ ended up in humans (Smil 1999, 2002). A more recent (2010) estimate of nitrogen use efficiency (NUE), or the ratio between N actually incorporated into crops and that applied to crops, estimated a value of only 42% (Zhang et al. 2015b). Increasing the NUE must be prioritized, particularly since global fertilizer use will increase to satisfy the growing global human population's demand for food.

On average, 18%, and as much as 64%, of applied N is lost to the atmosphere through $NH_3$ volatilization (Pan et al. 2016). But fertilizer application techniques can reduce both the overall amount needed and the resulting volatilization. This can be accomplished temporally or spatially. One temporal strategy is splitting up fertilizer treatments into two or three smaller doses, which aligns nutrient availability better with plant need, rather than having a surplus after one large treatment. In a Hawaiian sugar cane plantation, spread-out smaller doses required one-third as much fertilizer total compared to a single treatment (Matson et al. 1996). Results from Shaanxi Province, China, showed that when splitting up treatments was correlated with low soil nitrate measurements, N fertilizer use could be reduced by 79% without yield loss (Zhao et al. 2006; Zhang et al. 2015a). Controlled release fertilizers are an alternative to multiple treatments, which in a meta-analysis by Pan et al. (2016) was calculated to reduce $NH_3$ volatilization by 68%. Spatial strategies concern the depth at which fertilizer is incorporated. When fertilizer is incorporated at depths >7.5 cm, $NH_3$ volatilization drops drastically, while NUE increases (Liu et al. 2015; Rochette et al. 2013). While these strategies are more labor-intensive, they are much more efficient than typical broadcasting.

There are a few other strategies that can reduce $NH_3$ volatilization. Amendments can be added, such as NBPT, a popular urease inhibitor that reduces the rate of conversion between urea and $NH_3$, thereby reducing volatilization by as much as 90% (Gioacchini et al. 2002; San Francisco et al. 2011; Rawluk et al. 2001). While not used in fertilizers, alum can reduce $NH_3$ volatilization by upwards of 80% when added to poultry litter ( 2016, 2011). Fertilizer choice is also extremely important. Urea is most commonly used because it is inexpensive and rapidly converts into nitrates for plant use. But compared to urea, many other fertilizers are more efficient. Bayrakli (1990) found using ammonium sulfate or diammonium phosphate reduced overall volatilization to 3.1% and 2.3%, respectively, compared to 32.6% for urea. Ti et al. (2019) found using ammonium nitrate, ammonium sulfate, and urea phosphate instead of urea reduced $NH_3$ emissions by 88.3%, 82.9%, and 76.2%, respectively. They also found switching urea fertilizer to ammonium nitrate was the single most effective strategy in reducing $NH_3$ emissions.

Alternatives to HB fertilizers may be an even better choice. Intercropping has been used for centuries in traditional agriculture systems. Intercropping can occur on a spatial scale, by alternating crops between or among rows, or on a temporal scale, by alternating crops between growing seasons or by staggering growth within a season (Lithourgidis et al. 2011). A popular form is alternating leguminous crops with non-leguminous crops, either spatially or temporally, so that the N fixed by the leguminous crops fertilizes the other. Thus, intercropping can greatly improve soil fertility and NUE. Another strategy called green manure often blurs the line with intercropping. Like intercropping, green manure crops can be grown during fallow periods or simultaneously with the main crop; however, they are not typically harvested for revenue (Hirel et al. 2011). Instead, their sole purpose is to fertilize the soil. After growing for a short time, the plants are incorporated into the soil or left on top as mulch. Typically, N fixers such as *Trifolium alexandrinum* or others such as rye are used (Reddy 2016). When grown during fallow periods, green manures also help reduce soil erosion, nitrate leaching, and weeds (Sullivan 2003). Organic amendments like compost and manure can also be used instead of HB fertilizer, with the added benefit of restoring valuable soil organic matter which has been depleted worldwide (Lal 2009; Karlen and Rice 2015; Ladha et al. 2011).

But the best option to reduce N pollution from agriculture is to combine these organic and chemical strategies. This has led to a method called integrated nutrient management (INM; Janssen 1993). INM is successful because practitioners begin with a thorough assessment of soil nutrients, follow with an evaluation of current practice efficiency, and then make recommendations to improve crop yield while reducing N losses (Wu and Ma 2015). Three principles guide INM: (1) using all possible sources of nutrient input including atmospheric deposition and organic sources, (2) matching nutrient demand with supply both spatially and temporally, and (3) reducing N losses while improving yields (Jat et al. 2015; Wu and Ma 2015).

While INM is certainly more time-consuming than simply broadcasting urea, it can prove to be cost-effective by reducing total fertilizer use, improving soil health, and increasing crop yields.

## 13.6 Future Directions

As in all other fields, there are discoveries to be made and methodologies to be improved. One of the primary concerns among N deposition studies is their emphasis on short time periods and high rates of deposition. The majority of simulated N deposition studies cited in this chapter are less than 5 years in duration and use very high deposition rates, often upwards of 10 kg N $ha^{-1}$ $year^{-1}$. While these may accurately represent certain sites such as serpentine grasslands along the side of a highway, they do not accurately account for environments with low deposition rates. Isolated environments where the majority of N falls as wet deposition, perhaps from volatilized agricultural $NH_3$, are not represented in these types of studies. In these environments, little is known about how chronic low-level deposition affects them over time. This imbalance among the research has led to an overemphasis on critical loads which are often determined by short-term/high deposition studies. Critical loads rely on the questionable principle that no ecosystem changes occur below a certain level of annual deposition. They are binary: either an ecosystem is safe from N deposition or it is not (Payne et al. 2020). This allows them to be practical in informing policies limiting new, point-source polluters (Payne et al. 2020). However, they are less effective for curtailing the effects of already established polluters and nonpoint-source polluters including agriculture.

Furthermore, studies show that critical loads are not always effective in halting ecosystem change. One reason is that certain species have lower N deposition thresholds than others; a critical load may protect one species, but a more sensitive species will be affected below the load (Payne et al. 2013; Wilkins and Aherne 2016; Wilkins et al. 2016). Payne et al. (2020) analyzed five European datasets surveying wet grasslands, acid grasslands, alpine habitats, coastal fixed dunes, and dune slacks. In all but the alpine habitat, ecosystem change occurred at deposition rates below the accepted critical loads. Due to these limitations of critical loads, a better N deposition metric needs to be developed, likely one that accounts for both cumulative and current deposition. Table 1 in Rowe et al.'s paper (2017) summarizes the pros and cons of critical load alternatives. One method is cumulative exceedance or CE which calculates the amount N deposition exceeds the critical load for a time period in a given environment. Rowe et al. (2017) propose time limits of 30 years ($CE_{30}$) and 3 years ($CE_3$) for soil-based and epiphytic habitats, respectively, to account for N that becomes unavailable to plants over time. While $CE_{30/3}$ still relies on critical loads, which likely need to be lowered, it does account for chronic effects and may better protect more habitats.

Mitigation strategies, ultimately the most crucial topic, also require some development. Because the field of integrated nutrient management is still relatively new, more research is needed to improve its efficacy and reduce its cost for farmers.

However, there are some signs of success. In Europe, agricultural $NH_3$ emissions have decreased by 26% between 1990 and 2011 (ETC/ACC 2015). On the other hand, $NH_3$ emissions from road transport have increased by over 300%, highlighting a desperate need for research and legislative action in this sector (ETC/ACC 2015). Since vehicular $NH_3$ emissions continue to increase, particularly in urban and urbanizing areas, nationwide $NH_3$ emission standards are desperately needed. Currently, the only standards in place are in Europe while the USA and China, the countries with the largest automobile populations, have severely unregulated $NH_3$ pollution (Sun et al. 2017). Research is needed on ways to reduce $NH_3$ emissions, particularly in automobiles. Additionally, more studies like those by Kelleghan et al. (2019) and Fenn et al. (2018) are needed to gather quantitative and qualitative data for worldwide $NH_3$ emissions and deposition.

## 13.7 Conclusion

Nitrogen's mobile nature, and its ability to volatilize and be deposited far from its source, leaves no environment spared from N pollution. Nuances among various forms of $N_R$ allow it to disrupt ecosystems by a variety of pathways including direct N toxicity, soil acidification, and perhaps most importantly, alteration of plant competitive fitness and invasion patterns. The effects of N deposition are most severe in low-nutrient environments (LNEs), where N limits plant growth in these often extremely biodiverse habitats. Here rare plants, fungi, and animals are at risk of extinction if N pollution continues to rise. One such LNE, serpentine, is an excellent environment for studying the impacts of N deposition, and studies to date provide evidence that N deposition above critical loads is altering community structure. Therefore, the major anthropogenic sources of $N_R$, including agriculture and fossil fuel combustion, require major curtailment to halt these ecosystem changes. Meanwhile, more research needs to be done on less-studied sources of N such as fire retardants (e.g., *Phos-Chek*). Overall, certain palliative strategies can mitigate the effects of N deposition; however, major ecosystem change cannot be avoided unless N pollution is reduced to manageable levels. Promising strategies such as integrated nutrient management (INM) provide routes to more efficient N use, but it is up to governments, policymakers, and individuals to execute them. The global N deposition crisis should be considered in league with anthropogenic climate change (Greaver et al. 2016) and will require global effort to address it. Hopefully, the inherent value of our beautiful, vulnerable, and diverse LNEs, ranging from South Africa's primeval fynbos to California's ruggedly diverse serpentine, will inspire immediate action.

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# Soil Erosion and Sediments: A Source of Contamination and Impact on Agriculture Productivity

# 14

I. Rashmi, K. S. Karthika, Trisha Roy, K. C. Shinoji, Anita Kumawat, S. Kala, and Rama Pal

## Abstract

Soil erosion is a multifactor threat to human beings and various ecosystem services. Accelerated erosion is a manifestation of soil degradation which can have severe soil and environmental impacts. In India, about 24.96% and 12.77% of total geographical area is infested with moderate (10–20 Mg $ha^{-1}$ $yr^{-1}$) and very severe (>40 Mg $ha^{-1}$ $yr^{-1}$) erosion rates respectively. Soil erosions have on- and off-farm effects, resulting in loss of economic and environmental benefits. On-farm effect includes the soil health deterioration and poor crop productivity. Whereas, off-site impact damages aquatic life by contaminating the water bodies with sediment, fertilizers and pesticides, causing siltation of rivers, shortening life of the reservoirs, contributing to loss of recreational activity, etc. During soil erosion process, runoff laden with soil nutrient losses results in deterioration of soil productivity. Soil erosion can cause extreme loss to the economy and

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environment, causing a negative effect to affected countries. Nitrogen, phosphorus, pesticides, heavy metals and some organic components are major contaminants accumulating in soil and received by water bodies. Nitrogen and phosphorus from agriculture runoff (from arable lands to rivers) cause eutrophication of water bodies and impair drinking water quality. Agricultural runoff is a dynamic and complex pollution process, in which controlling nutrient loss is difficult. The amount of nutrients and other contaminants carried by soil erosion depends upon the soil management practice and type of cropping system/land use pattern. There is a need to better understand the process of natural and anthropogenic soil erosion, at spatial and temporal scales, and to assess the impact of contaminants carried away with erosion on productivity and other environmental issues; better strategies are needed to prevent soil erosion and related contamination of water bodies especially from fertilizers and manures.

**Keywords**

Soil erosion · Contamination · Soil health · Water quality · Management

## 14.1 Introduction

Humankind is utilizing all ecosystem services more than nature can provide, creating a tremendous pressure on natural resources. Soil is a vital component of land, and its degradation will have deleterious impact on soil and related other systems like water ecosystem. Soil erosion is a global problem prevalent worldwide, and the quantity and damage caused is difficult to assess precisely (Lal 2020; Borrelli et al. 2020). Soil erosion is a continuous process, worsened by human beings in the quest for better life. Erosion is a natural phenomenon which occurs over several decades and produced the largely fertile (alluvial soil) and desert soils globally (Lal 2020). Globally, exploding human population, industrialization, intensive agriculture and other human activities contribute significantly to soil erosion processes (Ding et al. 2015; Leh et al. 2011). Earlier Holy (1980) classified soil erosion as both natural and an induced phenomenon, which keeps varying with the rate and occurrence intensity. Under normal conditions, soil erosion is a natural process that takes place for many years continuously from one site and forms new soils at the other site. However, accelerated or induced erosion is caused by anthropogenic activities like deforestation, overgrazing and improper farming practices resulting in more soil loss than its formation. As rightly mentioned by Lal (2020), increasing human activities have only accelerated the natural erosion rate which is critical with environment sustainability in the present and future centuries to come. Soil erosion from croplands is the major contributor for contaminating water bodies and polluting the environment. Agriculture is vital for many developing countries and a major contributor to national economy. To ensure food security with increasing population, the use of fertilizer and pesticide is indispensable to agriculture (Carvalho 2006). Among fertilizers, nitrogen (N) and phosphorus (P) are largely consumed for crop production worldwide. Recently, the FAO (2015) highlighted the use of N and P per hectare of land is 68.6 and 30.1 kg ha$^{-1}$, respectively. China is known for highest production capacity and use of chemical fertilizers in fields. India is after China and USA in production and consumption of fertilizers. It is well known the overuse of chemical fertilizers leads to greenhouse gas emission, eutrophication and groundwater pollution (Huang et al. 2017; Xia et al. 2020).

Soil erosion adversely affects the soil health and water quality with direct impact on agricultural sustainability. Soil erosion thus exacerbates soil degradation with decline in soil quality and vice versa (Lal 2020). Soil erosion is characterized by three major processes, detachment or loosening of soil particle, their transport and deposition. The process involves removal of nutrient-rich top fertile soil with on-site effect and further deposition of materials in drainage channels causing off-site effect (Issaka and Ashraf 2017). The major driving force behind detachment of soil particles is the energy sources like water and wind sources which are known as the most important factors of erosion. Other energy sources like gravity, chemical reaction and tillage operations play a significant role in accelerating erosion process. It is the rate and extent of the energy dissipation from all different energy sources that determines the erosion severity in any landscape. Beside the energy sources, other factors like soil type, topography, parent material, tillage, plant cover and climate significantly influence soil erosion (Guo et al. 2019; Singh et al. 2020). Soil erosion starts with raindrop splash which destroy soil structure, increasing runoff and the flow rate governed by rainfall diameter which has significant impact on the overland flow (Zheng et al. 2009; Han et al. 2010). The process of transportation of soil particles might cover a few millimetres to thousands of kilometres, and the time interval between transport and deposition might vary from few seconds to thousands of years (Lal 2001). Water and wind erosion are major soil erosion forms studied worldwide. Water erosion affects nearly 1.1 billion hectares of land worldwide (Oldeman 1994). Soil erosion displaces and deposits silt, clay and organic carbon associated soil particles at different sites. This soil fractions are the key indicators of soil quality and support numerous ecosystem services (Lal 2020). It is important to note that in many countries pollution of water bodies or wetlands, with decline in crop productivity, is directly associated with runoff or overland flow (Khan et al. 2018; Issaka and Ashraf 2017). Soil erosion by water is one of the major concerns of crop production in India and any country, given its impact on the environment and economic security. According to an estimate by NAAS-ICAR (2017), India suffers 15.7% production losses in cereals, oilseed and pulse crop. This calls for urgent need to reduce various land degradation processes and to create outlines for more sustainable land use system (FAO 2015). Furthermore, sustainable development goal (SDG) number 15.3 explains reducing land degradation which is necessary to support ecosystem services and functions. The chapter is divided into various sections of soil degradation with soil erosion; soil sediments as source of contamination; potential risk associated with this contamination on soil health and water quality; fate of contaminants like fertilizers, manures and pesticides; impact of soil erosion on productivity; and the contamination-reducing strategies.

## 14.2 Soil Degradation by Soil Erosion

It takes nearly 700–1500 years to form a thin soil layer of 0.017–0.036 mm thickness (Montgomery 2007), but with time and unsustainable agriculture practices, the same soil is lost through soil erosion (Lal 2009). Soil erosion by both water and wind is very severe in semiarid and subhumid regions of the world (Lal 2001). Using soil erosion models, Borrelli et al. (2020) predicted overall soil erosion rate could reach up to 4.3 Pg year$^{-1}$ with increase in agricultural land in developing countries such as Africa, India, Brazil, Myanmar and some parts of China. Asia is the largest producer of rice, various cash crops and tropical fruits (Narasimhan et al. 2019), having 663 Mha area under soil erosion (Lal 2001) and covering the highest area under soil erosion. Among Asian countries, China, India and Indonesia covering 0.47, 0.20 and 0.08 Mha, respectively, are severely affected by soil erosion (Ahmad et al. 2020). In India, inappropriate land management resulted in land degradation by erosion process which has severe impact on food security and economic crisis of farmers (Bhattacharyya et al. 2015). In India, nearly 120 million hectares is facing one or other forms of land degradation (NAAS-ICAR 2010). Of the total figure, approximately 82.57 Mha (68.4%) is under water erosion making it the most severe form of erosion resulting in removal of top fertile soil and creating undulating terrains (Bhattacharyya et al. 2015). Out of total geographic area of India, almost 126 Mha (39%) in different states have potential erosion rate of more than 10 ton ha$^{-1}$, whereas nearly 11% of area falls under severe erosion rate of 40 ton ha$^{-1}$ (Mandal and Sharda 2011). In India, water erosion occurs mainly during rainy season (June to September) when 45% of land is under cultivation (Sharda and Ojasvi 2016). Based on the first data on soil erosion by Dhruvanarayan (1983), the mean erosion rate of India was 16.4 ton per hectare per year, which is 5.3 billion ton of annual soil loss throughout the country. Of the total eroded soil, nearly 61% is displaced from one site to another, 29% is lost permanently into sea/oceans, and 10% reaches water bodies. North Indian rivers contribute for 68% of gross soil erosion rates, while southern rivers' contribution is 32% owing to more stable geological formation in later (NAAS-ICAR 2017). However, the permissible soil loss rate varies from 2 to 12.5 ton ha$^{-1}$ year$^{-1}$ calculated based on soil quality parameters and soil depth. Based on this range, Mandal and Sharda (2011) categorized nearly 69.5 and 13.3% of Indian land with soil loss tolerance limit of 10 and 2.5 ton ha$^{-1}$ year$^{-1}$, respectively. Based on river catchment dataset basis, Sharda and Ojasvi (2016), soil erosion rate varies between $<5$ and $>40$ Mg ha$^{-1}$ year$^{-1}$. They reported the mean gross erosion rate of India as $5.11 \pm 0.4$ Gt year$^{-1}$. Various erosion classes have been designated based on the severity of erosion risk for all Indian states. Of the total geographic area of the country (328.7 million ha), 25.72, 21.37, 27.96, 10.69 and 14.31% of area falls under very low ($<5$ Mg ha$^{-1}$ year$^{-1}$), low (5–10 Mg ha$^{-1}$ year$^{-1}$), moderate (10–20 Mg ha$^{-1}$ year$^{-1}$), severe (20–40 Mg ha$^{-1}$ year$^{-1}$) and very severe ($>40$ Mg ha$^{-1}$ year$^{-1}$), respectively, category of soil erosion classes (Mandal et al., 2020). Figure 14.1 explains the different erosion classes of Indian states, where total soil erosions from terrestrial land use are estimated as $4.87 \times 10^3$ Mg year$^{-1}$. Based on area, various erosion classes

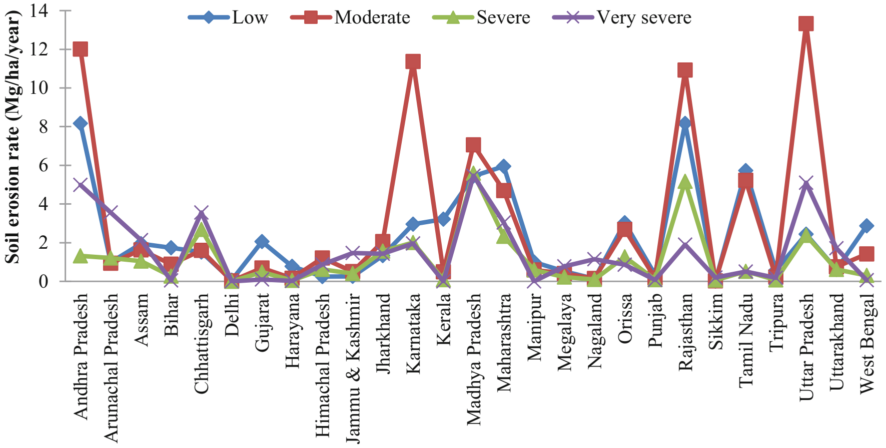


**Fig. 14.1** Mean erosion rates of different states of India (Source: Mandal et al. 2020)

followed the order, moderate (24.96%) > very severe (12.77%) > severe erosion (9.54%). In severe to very severe erosion class, the largest area is covered by Madhya Pradesh, Uttar Pradesh, and Andhra Pradesh, whereas Maharashtra, Gujarat and Orissa recorded the lowest erosion rate. However, all other remaining states showed low erosion rate between 0.001 Mha in Tamil Nadu and 5.47 Mha in Rajasthan. Climate change is likely to increase the risk for small and marginal farmers. It is predicted that by 2050, there will be an increase in amount and intensity of monsoon rainfall by 10% with changing climate scenario causing increased erosion rate (NAAS-ICAR 2017). As low as 1% increase in rainfall would increase rainfall erosivity by 2% (Sharda and Ojasvi 2006). In India, nearly 66 Mha of land falls under the category of 500–1000 ton km$^{-2}$ year$^{-1}$ which includes most of cultivable land but will be affected by high erosion due to climate change-induced rainfall patterns (NAAS-ICAR 2017).

Wind erosion is another form of soil erosion which is more prevalent in drier regions of the world in semiarid and arid areas. Wind erosion produces higher off-site impacts compared to on-site impact. It received less attention as compared to water erosion due to the larger impact of the latter (Uri 2000). Most of the damage caused by wind erosion mostly include higher cost of removing sand or dust particles from roads, ditches, higher maintenance cost of buildings, deterioration of machinery parts, respiratory or eye disorders, etc. Moreover, off-site damage also depends upon the location, population and climatic factors associated with wind parameters (Piper and Lee 1989). Subsequently, the impact of wind erosion from arable and other land systems cannot be distinguished easily nor it can be extrapolated to other areas (Uri 2000). Under arid conditions of India, Gupta and Raina (1996) reported a 5600 ton ha$^{-1}$ year$^{-1}$ soil erosion rate especially in Rajasthan state which has relatively strong winds during summer season.

## 14.3 Soil Erosion and Sediment Delivery as Source of Contamination

Soil erosion is exacerbated by several processes which directly influence the soil structure deterioration. Such process includes slaking or dispersion, compaction and crusting (Lal 2001). All these processes decrease soil structural stability and soil strength thereby accelerating erodibility and increasing vulnerability of soil movement through water, wind, gravity, tillage operations, etc. (Fig. 14.2). The various biophysical factors affecting soil erosion include climate, topography, ground/canopy cover, soil properties, etc. The two major aspects of soil erosion is soil erodibility and erosivity (Hudson 1971). Soil erodibility defines the vulnerability of soil towards erosion which include properties like soil texture, structure, consistency, aggregate stability, clay content, mineralogy, moisture content and transmission properties. On the other hand, soil erosivity is the climatic factor like rainfall parameters which include rain drop size, intensity, amount, runoff, velocity, wind velocity, etc. (Lal 2001). Topography or terrain is another important factor affecting soil erosion. The shape, length, slope gradient and aspect are the important terrain parameters which influence rate of soil erosion rate. Canopy or ground cover is a critical factor which determines the soil erosion rate for a given landscape. Beside these factors social, political and economic causes also impact soil erosion and directly influence soil degradation process (Lal 2001; Bhattacharyya et al. 2015).

Soil erosion results in soil loss nearly 20–40 times more than its rate of soil formation on a global level (Lal 2001). Soil erosion process degrades 30,000 ha of arable land and cause 30 kg and 15–20 kg per hectare loss of nitrogen and phosphorus, respectively (Pender et al. 2002; UNDP 2002). Soil erosion can be a major contributor for non-point source pollution as the contaminants move from different sources like fertilizers, manures, pesticide, etc. During runoff, fine and light soil particles loaded with the nutrients are preferentially lost during runoff and leaching (Lal 2001). As the runoff occurs, it picks up both natural and human-made contaminants and deposits in streams, reservoirs, groundwater, etc., later becoming a polluted site. Not all the field sediment enters reservoirs, but a significant portion of fine or chemically active particles reaches the water ecosystem. Once these particles enter the water system, the resulting poor water quality and related monetary losses show a severe impact on water bodies. Thus the off-site impact of soil erosion can be very significant as compared to on-site effect on productivity (Uri 2000). Improving soil properties with fertilizers and organic amendments could decrease the effect of soil erosion and improve soil fertility, for sustaining crop production.

Fertilizers and manures are nutrient sources for crops which increase nutrient use efficiency and agronomic yield. Fertilizers are inorganic sources that supply essential nutrients, easily available to crops, whereas manures are bulky in nature with slow release of nutrients. Long-term and indiscriminate use of inorganic fertilizers increases risk of soil and water pollution (Almasri and Kaluarachchi 2004). Soil erosion from long term or continuous applied fertilizers and manures are more susceptible to nutrient loss significantly reducing the soil fertility and productivity.

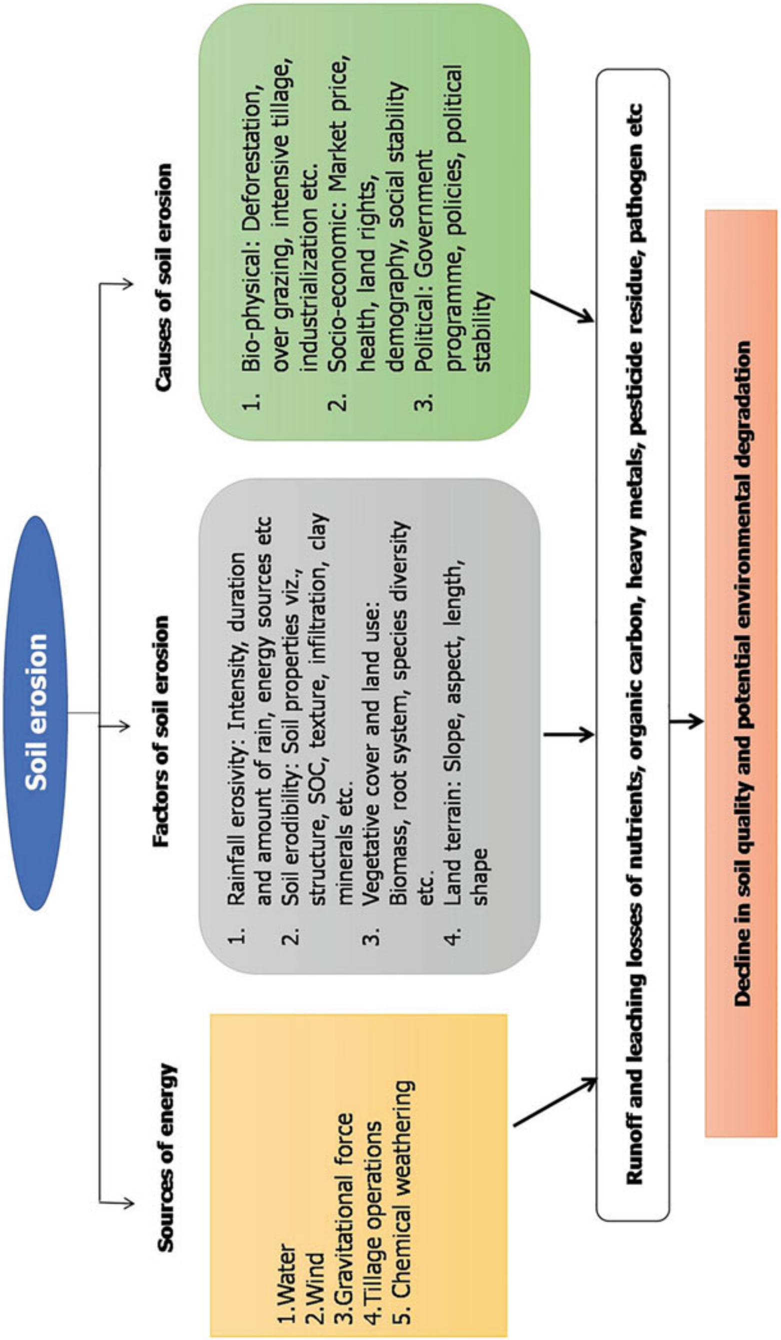


**Fig. 14.2** Soil erosion: energy sources, factors and causes

Soil erosion begins with detachment of soil particles caused by breakdown of soil aggregates due to the rainfall impact, shearing force of water and wind causing movement of soil (Lal 2001). Erosion as explained by Rose (1985) could be transport limited and detachment limited. Transport-limited phenomena occur when sediment is deposited at the site of origin, and detachment-limited phenomena occur when all the soil is transported downslope. The detachment-limited process occurs in well-structured soils where soil erosion is governed by rainfall impact or steep topography preventing soil accumulation. Soil erosion and sediment deposition is a selective process governed by Stokes' law, in which the size of the particle is directly proportional to the velocity and deposition directly depends upon concentration of sediment size (Lal 2001). The productivity effect of soil erosion have both on-site and off-site impact which can be explained in Fig. 14.5. On-site soil erosion effect directly influences soil and water quality. Soil quality refers to the removal of the topmost fertile layer with erosion exposing the subsurface layer. Movement of nutrients and pesticide with sediment (with water) during runoff or soil loss pollutes nearby water bodies. Soil erosion thus results in severe on-site and off-site impact on soil quality thereby affecting both long-term and short-term productivity losses (Lal 2001). Soil erosion delivers a large amount of sediments which gets washed off from the crop fields. Rainwater carries these sediments and deposits them either to the other site of the field or to the nearby streams and lakes. These huge loads of sediment can cloud the water, decrease sunlight penetration for aquatic plants and clog the fish gills. The sediments are laden with fertilizer, pesticide, heavy metals, etc. from croplands; thus depletion of oxygen accelerates algal bloom which is deadly for aquatic life forms. Therefore, farmers or policymakers can reduce 20–50% of such contamination with appropriate land management, control volume of runoff and soil erosion rate from fields thereby reducing soil transport (www.epa.gov/nps).

Sediment delivery and sediment transport are the major characteristics of soil erosion process. Sediment load during erosion process is dynamic in nature have direct role in reducing soil fertility, critical to food security and, therefore could adversely impact socio-economic condition of any region (NAAS-ICAR 2017). Both erosion and sediment redistribution highly influence landform formation and play a vital role in soil development. Sediment from land moves with or within water deposits in riverbeds. Rivers known to be sediment carriers determine the magnitudes of sediment loads directly influencing the ecosystem. Siltation of reservoirs often affect the irrigation canal and its efficiency, increase cost of water treatment from such rivers and are a major source of pollution and cause of aquatic habitat degradation (NAAS-ICAR 2017). Moreover, erosion, sediment load and hydrology of river are also influenced by land use/cover, climate change and human activities like deforestation, industrialization, dam construction, etc. (Walling 2009). In India, Sharda and Ojasvi (2016), reported sedimentation in rivers increased by 34% as compared to an earlier value of 10% reported by Dhruvanarayan and Ram (1983). Water erosion as overland flow carries soil sediments, nutrient, carbon and pesticides resulting in poor soil biodiversity, nutrient imbalance, compaction and pollution with contaminants, heavy metals, etc. Sharda and Ojasvi (2016) reported that the soil loss rate of India is 1535 ton/km$^2$/year resulting in nutrient loss (5.37–8.4 million tons), crop productivity loss, flood/drought occurrence, loss of biodiversity and siltation of reservoirs (annually 1–2%). Topsoil loss by erosion declines soil quality and decreases soil organic carbon (SOC). There are various views where SOC loss via erosion can act as sink or source of C emission (Mandal et al. 2020). Moreover, accelerated soil erosion is a major pathway that impacts $CO_2$, $CH_4$ and $N_2O$ emission (Lal 2020).

Generally, higher rainfall rate corresponds to higher runoff and loss of nutrients during soil erosion. During soil erosion, water carries dissolved nutrients in the runoff and the nutrient associated with soil particles. Both manure and chemical fertilizers are sources of contamination of soil and aquifers. Manures or fertilizers can improve soil fertility and crop production. However, indiscriminate use and improper handling and transportation can pose environment risk with direct influence on human health. Both nutrient sources can thus affect soil, air and water quality. Some of the major factors effecting the nutrient movement during soil erosion process are described below.

1. Topography or slope: Areas with steep slope are more prone to soil erosion and nutrient loss and vice versa. Erosion can occur even from a gentle slope depending upon the soil and climatic factors of a region.
2. Infiltration rate of soil: Runoff or nutrient loss occurs in any field when infiltrate rate is lower than rainfall intensity. This is directly affected by various other parameters like soil texture, compaction, surface crusting, etc. Finer soil texture has small pores resulting in slow infiltration rate and vice versa. Intensive tillage operations make soil compact due to heavy machinery, and soil crust formation in dry regions reduces infiltration of water causing overland flow with rainfall impact.
3. Climate: Soil erosion is directly related to climatic conditions of any place. Higher intensity rainfall increases the risk of runoff and erosion. Wet, humid weather conditions increase runoff and reduce water use efficiency of crops leading to poor yields.
4. Drainage: Subsurface drainage like tile drains reduces the runoff and nutrient loss.
5. Manure and fertilizer application: Application method and its rate are very important factors governing nutrient loss via runoff pathways. Manure or fertilizer application exceeding crop requirement often ends up in aquatic bodies causing algal blooms. Time of application of fertilizers, for instance, heavy rain soon after manure/fertilizer, leads to nutrient loss. Similarly, methods of application, for example, surface application of fertilizers/manures rather than incorporation, increase potential risk of nutrient loss and subsequently pollution of aquifers. Nutrient losses can be minimized if manures/fertilizers are applied in bands, incorporated or covered by soils.
6. Types of crops: Soil under perennial crop forage are less vulnerable to runoff and soil loss. Good canopy cover provided by perennial crops reduces the direct impact of rainfall, and efficient utilization of water by crops reduces soil erosion.

However, soil erosion risk is higher in seasonal crops like maize and cotton (erosion-permitting crops) and is less in canopy-spreading crops like soybean.

### 14.3.1 Some Other Mechanisms of Soil Erosion

Wind erosion is common in dry weather conditions with high temperature regimes. Soil particles are subjected to detachment, transport and deposition by wind energy. Thus, wind erosion drifts soil particles enriched with nutrients. Soil tillage operation is a major mechanism of soil erosion drifting particles from one place to other. Tillage operation leads to soil erosion resulting in downslope movement of soil particles from hilltop and its accumulation at the base of slopes. These soils are known to be very fertile lands for agriculture production. Tillage erosion results in significant movement of nutrients with soil particle and sometimes redistribution of nutrients within the field.

Fertilizers are the potential sources of heavy metal (HM) and radionuclide contamination. Chemical fertilizers contain numerous HMs such as cadmium (Cd), chromium (Cr), mercury (Hg), arsenic (As), lead (Pb), etc., and overapplication can reduce soil pH, which can increase its bioavailability affecting soil health (Huang and Jin 2008). For instance, phosphatic fertilizers produced from rock phosphate contain HMs like cadmium, chromium, etc. but also have radioactive components like uranium, thorium, radium, etc. (FAO 2009; Hassan et al. 2016). Crops or products from such soil provide entry of HM in food chain negatively impacting ecosystem, man and animal health (Nagajyoti et al. 2010). Additionally, organic manures and pesticides are also sources of HMs and other pollutants. Organic manures slowly release nutrients and improve soil health. The most commonly used organic sources in agriculture include compost, animal manure, sewage or sludge, municipal biosolids, industrial waste (fly ash, slag, distillery effluents), agri-wastes, etc. These organic amendments, however, have some disadvantages due to bulky nature, high transportation cost, land application and even presence of HMs, pathogens and toxic elements (Petersen et al. 2003). Besides, application of large quantity of animal manure in long term experiment showed higher buildup of HM in soils (Bolan and Duraisamy 2003; Zhang et al. 2012) and become the source of non-point water pollution (Mohammadi et al. 2009; Rees et al. 2011). Among various factors, rainfall plays a significant role in movement of nutrients, HMs, pathogen and other contaminants from the source to sink affecting environmental quality. Runoff or leaching pathways carry these HMs from fertilizer and manures, accumulating in plant biomass, entering food chain and polluting aquifers (Yargholi and Azarneshan 2014). Successive application of organic and inorganic fertilizers degrades soil quality and pollutes water bodies, disturbing various ecosystem services and functions. Eutrophication process is one such phenomenon occurring due to excessive loss of nutrients (especially P) from soil to water bodies, resulting in a sudden spike of phytoplankton accumulation, decreasing dissolved oxygen levels and severely affecting aquatic life (Pickney et al. 2001). Therefore, fertilizers and manures are inevitable resources for sustainable agriculture and at the same time are critical concerns, as contaminants from these sources cause potential risk to soil health and water quality.

## 14.4 Potential Risk of Contaminants Via Erosion to Soil Health

Overapplication of fertilizers especially N fertilizers like urea can increase nitrate content in soil susceptible to leaching and runoff loss. Overland flow during soil erosion process carries N and sediment and deposits on other places. This results in nutrient deficiency and affects soil properties. Frequent application of animal manures in Western countries leads to accumulation of sodium (Na) and potassium (K) ions resulting in saline soils. With continuous application, Na accumulation has a negative impact on soil aggregate stability (Manitoba 2013 report). Like N, P is an essential plant nutrient, and often soil is deficient in this nutrient. Unlike N, P is not easily available to crops due to its complex reaction with Fe, Al and Ca ions in soil solution. In most of the soils, adsorption and precipitation are the major mechanisms of P fixation. However, a small fraction of P known as labile P is very important because it supplies solution P by dissolution, desorption and mineralization. It is this P form which is agronomically and environmentally important as it is available to crop and equally vulnerable to erosion (Xia et al. 2020). Though P fixation capacity of soil is large, but not infinite, thus P fertilizer or manure application exceeding crop need often results in increased P loss via runoff or leaching.

Pesticides are the major contributors for improving crop yield during the Green Revolution to control pests and weeds which otherwise would have diminished crop productivity. These are the chemicals used for protecting crops against insects, weeds, diseases, etc. help to increase crop yield. In agriculture various forms of pesticide like insecticide (pests), weedicide (weed plants), fungicide (diseases), nematicide (nematodes), etc. are generally used to increase crop yield and income. However, pesticides are toxic to human beings and cause chronic health issues once they enter water and are ingested by animals and humans (Mansouri et al. 2017). Pesticide can remain in soil and water for a thousand years and can have toxicological effects depending upon its properties. Pesticides such as DDT and 2,4-D have high residual time in soil and water, and excessive use of these have shown deleterious affects on human health (Agrawal et al. 2010). Interestingly pesticides have a large impact on soil health, water quality and environmental consequences. Therefore, proper pesticide use is extremely important for protecting soil and water quality for future use.

## 14.5 Potential Risk of Contaminants Via Erosion to Water Quality

Quality of water is severely affected by point and non-point source (NPS) of pollution. Soil erosion by NPS is caused by runoff moving above and through the ground. Excess fertilizers and pesticides applied to agriculture field are sources of

NPS. This is also caused by nutrients and bacteria and other pathogens from manured plots which move with runoff and accumulate into water bodies (Fig. 14.3). Application of fertilizers and manures exceeding crop requirement often leads to contamination of water bodies. The most common problem associated with water pollution is due to excessive use of N, P, manures, pesticides, etc. Among nutrients, $NO_3^-$ is easily soluble and mobile susceptible to leaching and runoff losses causing groundwater contamination and river pollution. Phosphorus on the other hand is strongly adsorbed by soil colloids; therefore leaching is not a major loss pathway. However, accumulation of soil P leads to runoff losses of P to surface water bodies causing eutrophication. Potassium is not a limiting nutrient, and therefore most of the agriculture contamination is associated with N and P (Khan et al. 2018). The NPS by agricultural runoff results in excessive accumulation of N and P leading to loss of biodiversity, algal blooms, fish kills, etc. Lack of proper control of nutrient losses via runoff has made the NPS from agriculture field a global problem (Xia et al. 2020). Such a situation is common in many developed and developing countries. In China, almost 50% of major lakes are polluted and eutrophic, while others are deteriorating at faster rates (Sun et al. 2012). In the USA, more than 50% of lakes are in critical condition, and 60% of river beaches are damaged by contaminants (Smith 2003). In Canada, N and P enrichment in Lake Winnipeg is detrimental for water quality (Tiessen et al. 2010).

Nitrogen fertilizers are the easy source of water contamination due to solubility and mobility in soil body. Nitrate easily soluble in water leaches down or is carried with water during runoff and contaminates water bodies. Nitrate movement occurs with excess water (rainfall) and overuse of nitrate fertilizers occurring simultaneously in field. Though the fate of nitrate is uncertain, it potentially damages the environment and human health. Nitrate form when enters drinking water sources increases the potential risk of methemoglobinemia and other gastrointestinal disorders in humans (Khan et al. 2018). Methemoglobinemia or blue baby syndrome is caused by nitrate (10–45 ppm $NO_3^-$) pollution of water bodies. Water when consumed from such aquifers by infants and pregnant women results in reduced ability to transport oxygen in their bloodstreams resulting in blue baby syndrome. Soil erosion by water carries away dissolved N and $NH_4$ forms from organic manures associated with soil particles. Moreover, conventional tillage resulted in high N and sediment losses over reduced tillage practices in Manitoba (Tiessen et al. 2010).

Organic manures are known to release nutrient gradually and improve soil properties and soil health. Organic manures appropriately used are an excellent source of nutrients and improve fertility and physiochemical and biological properties of soil thereby improving crop yield (Eghball et al. 2002; Gomiero et al. 2011; Mellek et al. 2010). However, large quantity application to soil may result in a negative effect which can interfere with soil biodiversity, water quality, nutrient uptake, etc. Frequent application of animal manure and biosolids can thus enhance surface and groundwater pollution (Rees et al. 2011; Khan et al. 2018). Huge loads of organic manure application significantly increased bacterial counts and nutrient loss in a rainfall simulation experiment via runoff (Hill et al. 2005). Similarly, time

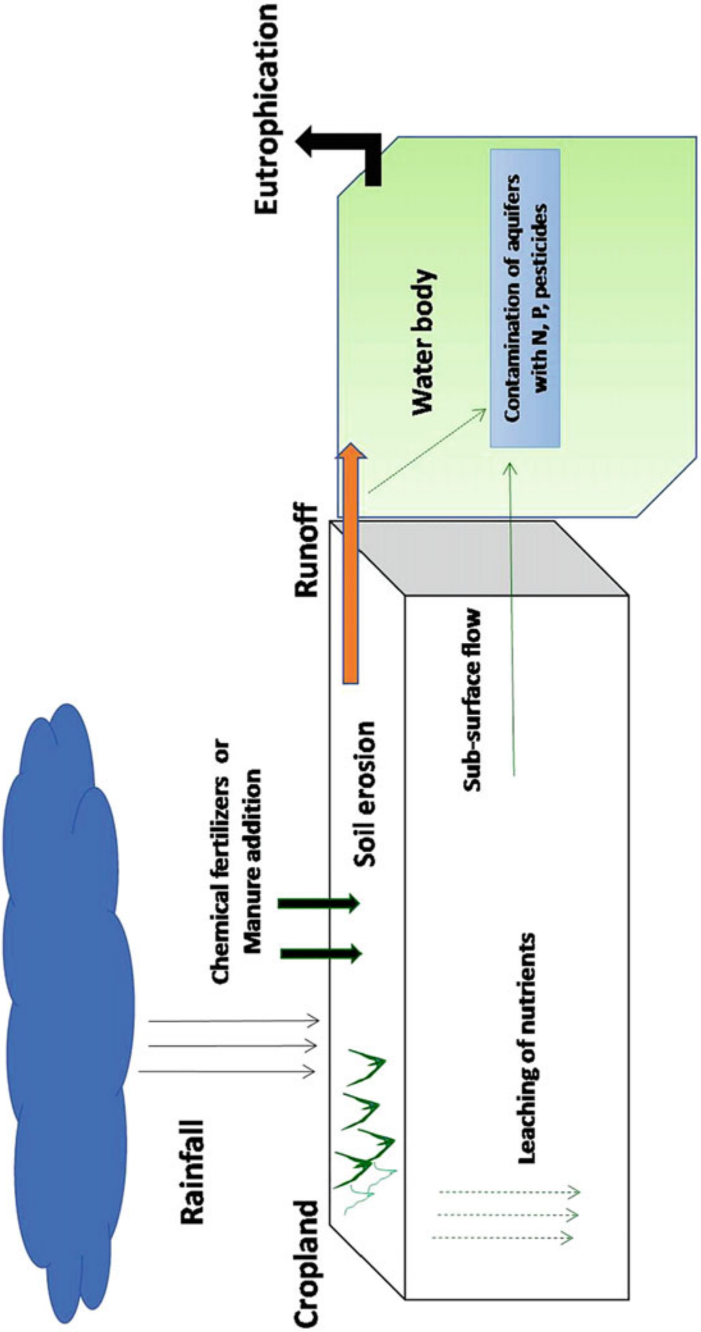


**Fig. 14.3** Nutrient movement pathways during erosion process

of application is also significant for nutrient loss. An experiment by Rees et al. (2011) reported fall period application of manures significantly increases runoff nutrient loss from 8% and 11% slope. Their study reported high concentration of *E. coli* pathogen from manure applied treatments. Sinton et al. (2007) highlighted that during soil erosion, rainfall plays an important role in transporting pathogen from fields applied with manure or biosolid to surface and shallow water bodies. Thus organic manures are likely to pollute surface water by erosion process as compared to groundwater. Pathogens present in manure can easily find its way to water bodies like in fine-textured soil or manure applied in fields near any aquifers, animals moving in such fields, etc. (Khan et al. 2018).

When manures are applied in large quantities exceeding crop N requirement, it often results in nitrate accumulation in soil after crop harvest which might increase risk of leaching or runoff losses of N from fields. On the contrary, applying insufficient N can also increase $NO_3^-$ leaching either by reducing crop development or significantly reducing nutrient uptake (Sharpley 2007). Both surface runoff from soil and vegetation and subsurface leaching reaching the surface water lead to total runoff of N. Thus minimizing runoff and erosion losses of N from fertilizers/manures can increase nutrient use efficiency and crop yield and protect water bodies. Nitrate pollution is a major concern in groundwater as it is directly related with human consumption. Similarly, even a small increase in ammoniacal N can also be toxic to aquatic life (Manitoba 2013 report). Like N, P is easily lost by soil erosion when associated with soil particles and dissolved P forms in runoff, leaching to groundwater. Continuous application of animal manures builds up high P levels in soil also results in incidental losses of P (Manitoba 2013 report; Walters et al. 2002). In many fields of nearly levelled topography, P enters surface water bodies in dissolved forms because runoff occurs in snowmelt process over frozen soil (Tiessen et al. 2010). Such dissolved P forms once they enter water bodies are difficult to intercept and therefore reach long distances unlike particulate P.

Another major concern is the increase in soil erosion from fields applied with high load of manures results in transmission of pathogens into nearby streams polluting water bodies. This condition can occur in coarse texture soils, with high water table. Similarly, agricultural runoff containing nutrients or pathogens is crucial to affect surface water quality. Nutrients transported through runoff from fertilizer or manure amended soils cause eutrophic water bodies, and its excess application could severely impact aquatic life forms. Among nutrients excess P entering water bodies from runoff can result in increasing algae biomass or algal bloom. These algal blooms significantly deplete oxygen levels in water causing negative impact on aquatic animals. Even blue green algal blooms can release toxin components harmful to aquatic life and other animals if they drink the water. Soil erosion accelerated by human activities causes eutrophication of water bodies impacting life forms.

## 14.6 Fate of Contaminants Lost by Soil Erosion

Chemical fertilizers and organic manures are considered a major contributor of water pollution in many countries. Non-point source (NPS) of pollution from fertilizers and manures affect soil and water quality. In China, agriculture NPS contributes to 52% and 54% of total N and P load, respectively, in Taihu Lake Basin (Zhang et al. 2004). Similarly, in the USA, NPS from croplands is a dominant source of polluting streams and reservoirs (Jabbar and Grote 2019). Therefore, suitable management strategies to control runoff losses from fertilizer/ manures /biosolids amended arable lands are of primary concern under United States Environmental Protection Agency (USEPA). The USEPA (1986) had recommended the critical limit for total phosphates as 0.5 mg/L in lakes and 0.1 mg/L in streams, above which, increases the risk of eutrophication due to nutrient enrichment. Inorganic and organic fertilizers are responsible for surface water eutrophication and groundwater contamination and are difficult to quantify (FAO 2015; Xia et al. 2020). Nutrient movement via runoff from crops like maize used as pasture is common in many countries due to large quantity of fertilizer application and extensive use of organic manures in pasture, farms, etc.

Some major effects of eutrophication of water bodies include:

1. Increased biomass of algae, phytoplankton and microphytes.
2. Changes in aquatic plants cause a shift in habitats.
3. Decrease in dissolved oxygen levels called deoxygenation killing aquatic life.
4. Replacement of desirable fishes by undesirable ones.
5. Release of toxic materials into water by some species of algae.
6. Weeds like water hyacinth rapidly cover water surface clogging canals and drainage channels.
7. Loss of recreational value of stream and rivers due to change in aquatic habitats and organisms, bad odour, weed infestation, etc.
8. Economic value of reservoirs reduces with less fish population and recreational purpose.

### 14.6.1 Fate of Essential Nutrients Lost by Erosion

Global consumption of three major nutrients, i.e. N, P and K, required for enhancing soil fertility and sustaining crop production is increasing at a rate of 1.5%, 2.2% and 2.4%, respectively, every year (FAO 2015). Use of fertilizers levies a high economic cost on-site for sustaining crop production and significant off-site environmental problems (Xia et al. 2020). Phosphorus is an essential plant nutrient, usually adsorbed/sorbed by the soil components, and reduced crop availability requires application of P amendments as fertilizers and manures. Phosphorus is nontoxic; however, continuous addition of fertilizers or manures enriched with P often finds its way to water bodies and accelerates eutrophication destabilizing aquatic life (Sharple 2007). This damages water quality of streams or rivers converting them into unhealthy water bodies. Indiscriminate use of P fertilizer thus results in not only water pollution but phosphorus shortage for crops. According to National Geographic (2020), 40% of the Earth's surface is polluted by P from various sources. An estimated loss of $2.2 billion per year in the USA is reported due to damage in ecosystem and water quality due to N and P loss. Phosphorus loss as runoff from fertilizer and manure application mostly depends upon parameters like method, rate and time of application, form of P, rainfall intensity, soil type, crop cover, etc. At the watershed level, severe loss of P with runoff has been reported by Smit et al. and Edward and Owen soon after one or two severe rainfall events contributing to 90% P loads. Unlike N, P loss is mainly through runoff pathway during water erosion. Generally, groundwater contains less amount of P, because of lower solubility of fertilizer P or native P and higher P retention on soil surface, retarding downward movement. Strong bond of P with metal oxides and clay minerals and involvement in biological cycle reduce P concentration in groundwater (Matthess 1982). Earlier due to high P fixation capacity of soil, downward movement of P was given little importance. However, Heckrath et al. (1995) reported increased vertical P movement in long-term fertility experiments at Rothamsted, UK, stating the significant impact of fertilizer/manures on P in drainage water from the fields with 100 years of fertilization. In India, low concentration of P in groundwater of Palar and Cheyyar River Basins of Tamil Nadu was observed by Rajmohan and Elango (2005). Phosphorus applied by fertilizers in the field was the main source of P leaching to groundwater with irrigation water. Phosphorus lost through runoff per year is insignificant from an agronomic point of view (Hart et al. 2004). Nevertheless, from water quality aspect, small amount of P is sufficient to impair water quality to make it eutrophic. For instance, in New Zealand, threshold for dissolved reactive P (DRP) is 15–30 $\mu g\ L^{-1}$. This P loss from grasslands is common in recently applied fertilizers and manures costing pollution and environmental losses. Ma et al. (2016) and Wang et al. (2011) highlighted total P loss in China through runoff, leaching and soil erosion pathways was 10% higher than total P added to the soil. Numerous studies have shown with increase in erosion, runoff P loss also increases (Hart et al. 2004; Sharpley 2007). Phosphorus movement (leaching) in tile drains is reported in many studies (Heckrath et al. 1995; Hesketh and Brookes 2000; Li et al. 2011), which can increase P movement into streams. Various P forms lost include inorganic and organic phosphate, dissolved reactive P (DRP) or particulate P (PP) fractions (Hart et al. 2004). Proportion of P in DRP or PP fractions via runoff depends upon the slope, soil erosion rate, time of application, etc. As the sediment load increases in overland flow rate, PP will increase compared to DRP forms and vice versa. Many researchers have reported that DRP is the common P lost from field via runoff from reduced till system over conventional tillage (McIsaac et al. 1995; Torbert et al. 2005). Soluble P concentration ranged from 270 to 572 $\mu g\ L^{-1}$ from a corn-soybean field of watershed region of central Illinois, USA (Algoazany et al. 2007). Increased sorption of P on suspended particles increases lowering dissolved P forms (McDowell et al. 2003). Another important aspect is direct P losses from recently fertilized field known as "incidental losses" (Haygarth and Jarvis 1999) which explains the coincidence of fertilizer/manure application followed by heavy rainfall events. This results in significant nutrient losses, known to be event-specific losses. This loss of P is directly correlated with available soil P levels. Overfertilization of fields with P fertilizer/manure loads is the potential contributor for runoff P losses and eutrophication (Cox and Hendricks 2000; Sharpley et al. 2000; Hart et al. 2004).

Nitrogen in the form of nitrate derived from fertilizers, manures and human and animal waste is the major source of N pollution. Nitrate being soluble easily leaches into groundwater polluting drinking water sources. However, diffusion is the major mechanism of N and P fluxes which differs in soil types. The diffusion coefficient of orthophosphate ion is one thousandth that of nitrate ion that effects the runoff losses of N and P from soil (Cookson et al. 2000). In a study by Harmel et al. (2009), addition of fertilizers at the rate of 196 kg N $ha^{-1}$ $year^{-1}$ and 87 kg P $ha^{-1}$ $year^{-1}$ resulted in runoff of 9.5% and 3.3% of N and P, respectively, from croplands. However, in another study by Zhang et al. (2011), addition of 210 kg N $ha^{-1}$ $year^{-1}$ and 36 kg P $ha^{-1}$ $year^{-1}$showed a runoff rate of 5.9% and 0.52%, respectively. This clearly indicates that loss of nutrients was low, but varied from place to place, crop type, management practices, month or time, etc. For example, in China high runoff loss of nutrients was observed during the months of June, July and August (Gao et al. 2005); this also corresponds to higher eutrophication losses (Xia et al. 2020). Agricultural runoff varies spatially and temporally based on rainfall, vegetative cover, soil factors, etc. making it difficult to control nutrient loss via agricultural runoff.

### 14.6.2 Fate of Manures Lost Via Soil Erosion

Organic manures are used as nutrient source and soil conditioner traditionally since a long time ago. However, continuous and indiscriminate addition of manures is found to increase metal accumulation in soils (Khan et al. 2018). Bolan and Duraisamy (2003) reported that overapplication of organic manures not only increases HM concentration but also changes metal availability and its uptake by crops. In the present scenario, intensive animal production requires the use of feeds or supplements which can be loaded with essential and nonessential elements. As a result the manure obtained from animals is the direct source of contamination to both soil and water resources. Animal manures contain several HMs (Zn, Cu, Ni) and alter the availability and uptake by crops. Czarnecki and During (2015) observed increased uptake of metals, higher SOC and cation exchange capacity of soil after long-term addition of organic fertilizers. Decreased soil pH also increased the metal uptake by plants even after omission of inorganic fertilizers for 8 years. Organic manure like sewage sludge is a storehouse for many HMs like Cd, Cr, As, Ni, Hg and Fe and other disease-causing pathogens and organic components. Higher use of such manures can lead to accumulation of HMs in soil and increase their transport to water bodies via runoff and soil erosion (Elliot et al. 2002). Saha et al. (2018) reported higher content of Ni, Pb, Cu and Cd in municipal sewage sludge of Kolkata, India, and recommended restricted use in agriculture. However, Mondal et al. (2015) reported the use of sewage sludge improved crop yield and soil quality without any risk to soil contamination. Nutrient content in animal manures is low and unbalanced, usually applied to the soil on N basis. This results in the accumulation of nutrients particularly P in soil. Consequently, excess P accumulated, moves beyond root zone via leaching on one hand, and on the otherhand lateral movement with runoff and soil loss during erosion is common (Azevedo et al. 2018). This not only adds to economic loss of farmers but is a critical potential environmental risk for contamination of surrounding water bodies (Khan et al. 2018).

### 14.6.3 Fate of Pesticides Lost by Soil Erosion

Pesticides have some major benefits in controlling and managing insects, weeds and diseases, but its improper use has led to undesired consequences. Pesticide is a product which is lethal to targeted pests and not to non-target organisms like humans and animals. However, disproportionate use of pesticide adversely affects flora and fauna of the ecosystem (Agrawal et al. 2010). Almost all pesticides have toxic effects (Ongley 1996; Mansouri et al. 2017). There was tremendous increase in usage of pesticides during the last 15 to 20 years for increasing food production. The major categories of pesticide include herbicide (85%) accounting for the largest form, followed by insecticide (13%) and fungicide (2%) as reported by Cumhur and Porca (2004). The long residual time of pesticide in soil and water disturbs the soil biodiversity, aquatic life and habitat affecting living beings. Among chemicals, herbicides occupy 85% of pesticide application, thus increasing the entry into groundwater which is used for irrigation purposes and negatively impacting crop quality and soil health (Cumhur and Porca 2004). Indiscriminate application of pesticide to soil increases the concentration of chemicals in soil. Rainfall encourages soil erosion, which carries the toxic chemicals with water and deposits in surface water and via leaching to groundwater. These contaminants vary in their turnover rate or degradation process depending upon several factors like active ingredient of chemical, chemical composition, concentration, climatic factors, organisms' activity, etc. Extremely toxic components in pesticides can kill fishes in water bodies and other microorganisms helpful in degradation of toxic components (Agrawal et al. 2010). However, groundwater contamination from such mechanisms is even more dangerous. In a ground with depleted oxygen levels, the turnover rate of pesticides is delayed, and breakdown of chemicals become less effective leading to water pollution. Moreover, replacing such groundwater aquifers is a challenging task and will take decades or many years. The ecological criteria for toxicity of water (soil) with pesticides are explained in Fig. 14.4.

#### 14.6.3.1 Various Factors for Pesticide Pollution in Water

1. Active ingredient of pesticide.
2. Impurities present in the active ingredient.
3. Different additives like wetting agents, solvents, adhesive, preservatives, emulsifiers, etc. mixed with active ingredients of pesticides.

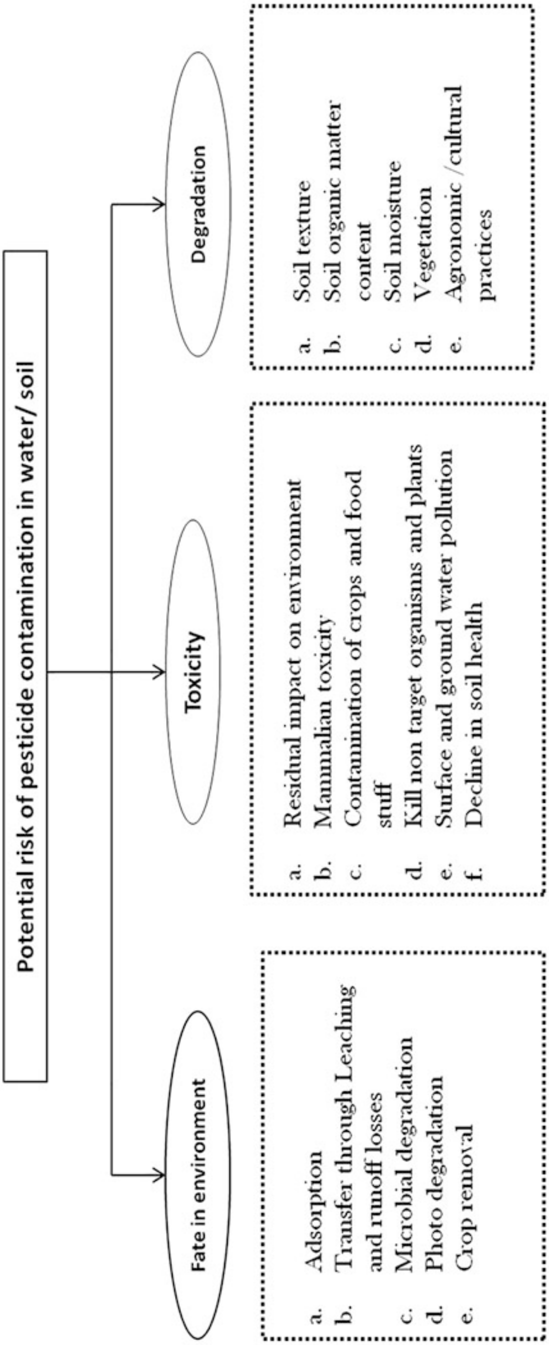


**Fig. 14.4** Ecological aspect of pesticide toxicity in the environment

4. Chemicals formed during biological, chemical or photochemical degradation of pesticide.
5. Half-life of pesticide is an important criteria deciding the fate of contaminants in water. Longer the half-life period to breakdown, higher will be persistence of chemical in environment and vice-versa. This also means, highly stable pesticide take longer time for disintegration resulting in higher residual effect in soil or water. This can be measured by decay constant in terms of half-life period. Half-life period is unique for individual chemicals which can vary depending upon climatic factors and rate of application.
6. Beside these factors climatic conditions like rainfall play a significant role in pesticide movement with soil erosion process. Increase in rainfall increases the risk of pesticide contamination in water bodies. Soil erosion from recently applied pesticide increases with overland flow, replaces pesticide from absorption sites and increases its movement into reservoirs.

Contamination of water bodies with pesticide increases the health risk in humans and animals. Some chemical groups like carbamates and organophosphates severely impact the nervous system. Some others are carcinogenic, and others might affect hormones or the endocrine system of the body. The toxicity of pesticides depends on its function and other characteristics; for example, insecticide is more toxic than herbicide (Nicolopoulou-Stamati et al. 2016). In 2003, the European Union (EU) imposed a ban on atrazine due to safety, health concern and non-point source of pollution (Sass and Colangelo 2006).

## 14.7 Impact of Soil Erosion on Agricultural Productivity

Soil erosion from arable land results in decline in crop yield, surface water pollution, siltation of drainage channels, etc. (Issaka and Ashraf 2017). Soil erosion by water or wind results in loss of fertile productive soils. India and China together have world's 13% of arable land and with the sustaining agricultural management practices almost thousand of years, estimated soil loss of 75 billion tons each year (Pimentel and Burgess 2013). Almost 50% of the world's area is under agriculture, 20% under forest, of which croplands are highly vulnerable to erosion due to frequent cultivation and removal of vegetative cover before crops are planted (Pimentel and Pimentel 2008). According to an estimate, erosion from such crop lands is 75 times higher than natural forests (Myers 1993). Among the several constrains associated with soil erosion, runoff is a major problem which reduces water availability and water infiltration into soil. Additionally soil erosion removes nutrient required by crops, carries away organic carbon and reduces soil biodiversity showing a severe impact on agricultural productivity (Lal 2020).

### 14.7.1 Effect of Erosion on Soil Properties and Nutrient Loss

Soil erosion either by water or tillage operations can create long-term changes in soil profile, subsequently affect nutrient availability and water holding capacity and cause OM loss with loss in grain yield. Soil erosion exposes the subsurface layers, usually low in SOC and nutrients, with lesser aggregate stability which directly influences crop growth and development. Soil characteristics, like rooting depth, plant available water content and physical and chemical properties of subsoil, determine the effect of erosion on crop yield (Lal 2001). During soil erosion, runoff increases overland flow thereby decreasing infiltration of water and thus reducing water availability of crops. Soil eroded from field carries away essential plant nutrients like N, P and K and micronutrients from field resulting in deficiency of nutrients. According to Young (1989) eroded soil contains almost three times higher nutrients as compared to residual soil left after erosion. Top fertile soil contains 0.1–0.6% N, 0.1–0.3% P and 0.2–3.0% eroded soil; however the remaining soil will have only 0.01–0.05% of N (Langdale et al. 1992). To reduce the effect of soil erosion, large quantities of fertilizers and manures are added to soil. Govers et al. (2016) reported soil erosion causes large nutrient loss of N and P with a corresponding significant economic loss almost equal to 34 billion and 80 billion US$ and food production at the world scale is almost 4000 billion US$. Such nutrient loss can be minimized by adding amendments, changing crop rotations, using soil and water conservation methods, etc., and high nutrient loss in sediment and runoff can be minimized with appropriate fertilizer and manure management practices. Addition of fertilizers improves crop above and below ground biomass, providing a good vegetative cover and reducing runoff velocity (Bashagaluke et al. 2018). However, indiscriminate use of chemical fertilizers, often end up in reservoirs polluting water bodies, killing aquatic life and causing a decline in recreational activities. The fate of nutrients as contaminants has been explained in the previous section. Phosphorus is tightly bound to the soil; therefore any factor increasing soil erosion will increase P losses to water bodies causing eutrophication (Khan et al. 2018; Xia et al. 2020). Application of manures exceeding crop requirements results in non-point source of pollution of water bodies. Therefore, soil nutrient management plays a significant role in both environmental and agricultural sustainability.

### 14.7.2 Effect of Soil Erosion on Carbon Dynamics

Soil erosion preferably removes the chemically active and fine soil particles laden with C resulting in redistribution of C at various geomorphic gradients and involves C mineralization which is important with changing climate scenario (IPCC 2007). Soil erosion removes the light C fraction with low density and dissolved organic carbon (DOC) fraction along the slope gradient (Berhe et al. 2012; Lal 2020). Transportation and deposition of this DOC leads to SOC accumulation in lower slope regions that can be stabilized by clay minerals, reducing C mineralization. Soil erosion influences C flux between soil and atmosphere by three mechanisms:

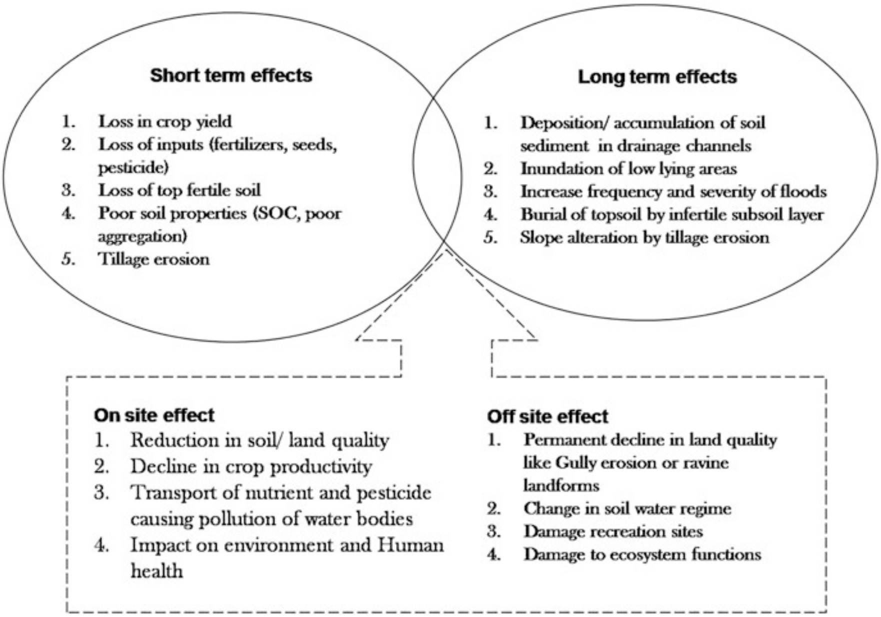
(a) dynamic replenishment of SOC at erosion sites, (b) deposition of SOC deeper off-sites and (c) increased decomposition of SOC with physical disintegration of soil during erosion (Lal 2003; Van Oost et al. 2007; Berhe et al. 2012). Moreover, there is uncertainty over erosion-induced C loss, as the C mineralization occurs during the aggregate breakdown with the rainfall impact on soil particles (Polyakov and Lal 2008; Lal 2020). Raindrop impact and flow intensity are major factors responsible for aggregate breakdown and release of encapsulated C (Berhe et al. 2012). Wang et al. (2014) reported that erosion-induced $CO_2$ represented 90.5% of C loss, and nearly considerable amount of C-rich sediment loss was laterally exported by runoff mechanism in a rainfall simulation experiment. This sediment-laden C has a significant role in terrestrial and aquatic ecosystems.

### 14.7.3 Effect of Soil Erosion on Soil Biodiversity

As mentioned, soil erosion removes the top fertile soil layer rich in soil organic matter which is directly associated with biodiversity of soil system. There is a profound effect of soil carbon on plants, animals and microbial biodiversity in soil system. Enriched microbial diversity in one cubic metre of soil consists of billions of microbes, lakhs of arthropods and ten thousands of earthworms. Also, 1 ha of soil may support 10,000 kg $ha^{-1}$ biomass of invertebrates and microbes (Pimentel and Burgess 2013). Application of manures increases microbial biomass and biodiversity in soil. Soil erosion indirectly effects soil flora and fauna. Erosion damages the plant productivity and removes SOC, nutrients which directly affect the microbial biomass. Pesticide carried away with runoff or overland flow reaching rivers can negatively impact aquatic life forms and water quality. The contaminants from pesticides affect the soil microcosms consisting of soil microfauna (Lo 2010) and also affect the soil biota (Hussain et al. 2009). The contamination of soils due to toxicity of agrochemicals resulted in decreased total microbial population due to indiscriminate use of herbicides (Milosevic and Govedarica 2002), decreased population of N-fixing bacteria due to excess application of Cu-based fungicides (Kyei-Boahen et al. 2001) and decreased population of symbiotic N fixers due to indiscriminate use of herbicides (Niewiadomska 2004). Soil erosion sometimes results in loss of keystone species; the loss of such species can have a cascading effect on the survival of other species in an ecosystem. For instance, loss of oak trees can severely affect biodiversity, pollinators of the area, habitats for biological N fixation, etc. (Sugden et al. 2004). Moreover, soil biota provides various beneficial activities for improving soil quality and health. Microbial activities include recycling of plant nutrients through mineralization of organic matter, tunnelling, burrowing activities of earthworms to increase air and water transmission in soil, etc. (Pimentel and Burgess 2013).

### 14.7.4 Effect of Soil Erosion on Crop Yield

Soil erosion is known to have both economical and environmental impact on society. Soil erosion removes topsoil layer resulting in nutrient disparity or exposure of subsurface layer with specific problems like hard or compact layer, high Al or Mn toxicity, high P fixation, etc. There many reports suggesting the improvement in crop yields from regions which receive soil deposits via erosion especially during a drought period or seasons with below rainfall levels (Fahnestock et al. 1995). However, few studies report a decrease in crop yield with soil erosion due to crop burial under sediments, waterlogging anaerobic conditions, pollution from pesticide with runoff, etc. (Lal 2001). Thus soil erosion can have short- and long-term effects as shown in Fig. 14.5. Sometimes yield loss might happen with loss of crop stand and arable lands in case of gully erosion-prone areas. However, with runoff the soil or water gets transported and might get deposited in the same field, which results in loss of water and nutrients which otherwise could have been used up for crop growth and development. On-site effect of erosion can be reduced by adding fertilizers and organic manures to increase crop production. On the contrary, off-site impact of erosion can be both positive and negative. Positive impact includes improvement in crop yield at depositional site, and negative effect includes sedimentation of reservoirs, pollution of water bodies, greenhouse gas emission, etc. (Lal 2020; Xia et al. 2020).



**Short term effects**

1. Loss in crop yield
2. Loss of inputs (fertilizers, seeds, pesticide)
3. Loss of top fertile soil
4. Poor soil properties (SOC, poor aggregation)
5. Tillage erosion

**Long term effects**

1. Deposition/ accumulation of soil sediment in drainage channels
2. Inundation of low lying areas
3. Increase frequency and severity of floods
4. Burial of topsoil by infertile subsoil layer
5. Slope alteration by tillage erosion

**On site effect**

1. Reduction in soil/ land quality
2. Decline in crop productivity
3. Transport of nutrient and pesticide causing pollution of water bodies
4. Impact on environment and Human health

**Off site effect**

1. Permanent decline in land quality like Gully erosion or ravine landforms
2. Change in soil water regime
3. Damage recreation sites
4. Damage to ecosystem functions

**Fig. 14.5** Effect of soil erosion on crop production (Modified from Lal 2001)

Though estimation of agronomic loss associated with soil erosion is difficult to make, due to the significant effect of climatic conditions, rainfall parameters and management practices are carried out. Few estimates from different continents depict the severity of soil erosion on crop productivity loss. An earlier study by Lal (1998) reported a global loss of 10% in cereals, 5% in soybean and 12% in root or tuber crops due to soil erosion. In North America, Den Biggelaar et al. (2001) estimated erosional losses in production of maize (234.5 × $10^3$ ton year$^{-1}$), soybean (60.2 × $10^3$ ton year$^{-1}$), wheat (75 × $10^3$ ton year$^{-1}$) and cotton (1.9 × $10^3$ ton year$^{-1}$).

In a report by the Chinese Academy of Sciences and the Chinese Academy of Engineering (2009), nearly 646 counties in China display significant soil erosion losses which is almost equivalent to 3.75 million km$^2$ land. Further a 2-year study predicted that if the present soil loss rate continues for another 50 years, it can result in a 40% reduction in food production in China (Jie 2010). In Africa, soil erosion causes a production loss of 2–40% with mean of 8% (Lal 1995). Mitiku et al. (2006) predicted a crop production loss of 9.2 billion tons in root and tuber crops by 2020 with accelerated soil erosion. Others, Khisa et al. (2002) and Nyawade et al. (2018) reported soil loss to the tune of 60–244 ton ha$^{-1}$ year$^{-1}$ in Kenya is largely due to water erosion. In India based on the estimate by Sharda et al. (2010) and Sharda and Dogra (2013), crop production and economic loss for cereals, oilseed and pulse crop was estimated. According to the report, crop production loss of 15.7% which equals to Rs 292.03 billion was estimated for cereals, oilseed and pulse crops combined. Among various crops, cereals, oilseeds and pulse crops accounted for a corresponding production loss of 66%, 21% and 13%, respectively. The most affected crop is paddy which accounts for nearly 4.3 Mt. of production loss followed by maize, soybean, groundnut and other pulse crops which corresponds to Rs 60.7 million monetary loss and is equivalent to an economic loss of 62% of due to soil erosion. These calculations were based on minimum support price (MSP) of India during 2015–2016. Similarly, crop productivity loss from rainfed crops is nearly 1.63 q ha$^{-1}$ equivalent to almost Rs. 3533 per hectare in India (Sharda and Dogra 2013).

## 14.8 Reduction Management Practices for Soil Erosion-Based Contamination

Increasing soil erosion and its environmental degradation is having cascading effects on human and other life forms. Overburgeoning population, climate change effect, intensive agriculture practices, industrialization, etc. are creating tremendous pressure on land, and erosion is the consequence of all these processes, independently or combined. Dissolved nutrients, pesticide and sediments by or in large through runoff cause various menaces like eutrophication, siltation, nutrient translocation, soil erosion, etc. In spite of that, during the last 30 years, a large area under erosion was restored by soil and water conservation technology at the watershed scale in

India. However, some technologies or interventions can also be used to mitigate contamination of natural resources, i.e. soil and water.

### 14.8.1 Tillage Practices and Soil Amendments

Soil erosion can be managed with sustainable land management practices to avoid erosion at the farm level. Tillage operation can be modified in such a manner to increase surface roughness so as to decrease runoff and sediment flow from fields, thereby reducing pollution load at the source (Xia et al. 2020). As per FAOSTAT (2019) nearly 11–14% (1.42 billion hectares) of arable land is under conservation tillage globally. Though tillage operation disturbs soil surface, reduced or no tillage protects soil from erosion. Conservation or reduced tillage manipulates soil properties by improving soil organic matter and increases infiltration thereby reducing overland flow during erosion (Issaka et al. 2019). Reduced or minimum tillage minimized runoff (30%) and soil (34%) in maize-wheat cropping system of slopy croplands of the Indian Himalayan region (Ghosh et al. 2015). Reduced tillage practices increase porosity that increases infiltration and reduces runoff and soil loss. Liang et al. (2016) observed a reduction in runoff volume by 25.9% with reduced tillage in rice-planted watersheds of China. Issaka et al. (2019) reported N losses reduced by 1.83 mg $L^{-1}$ under no or zero tillage in South China. Combining reduced tillage with residue retention or incorporation reduces detachment of soil particles under rainfall impact, intercepts the water movement down the slope, settles soil and enhances surface roughness, decreasing runoff and soil loss (Adimassu et al. 2019). Rotation tillage practices are another practice to reduce nutrient loss from croplands. This type of tillage is a better option to decrease loss of various P forms (dissolved, particulate P forms) and runoff duration. Liu et al. (2014) observed a reduction of 46% and 38% in total dissolved P and total P loss, respectively, in Canadian Prairies. Addition of gypsum, biochar, organic manures, etc. as soil amendments improves soil structure, indirectly helps to reduce soil erosion and pollutant contamination (Bashagaluke et al. 2018; Xia et al. 2020). Won et al. (2016) reported that application of paddy straw, polyacrylamide and biochar reduced suspended soil and total N by 87% and 35%, respectively, from a cabbage field. Combination of crop residues with organic manures and runoff hedges proved superior in reducing soil erosion from steep hillsides with shallow soils of Cabo Verde, Africa (Baptista et al. 2015). Rashmi et al. (2020) also reported application of gypsum and crop residue effectively reduced soil loss (29%) and runoff (26%) in soybean-mustard cropping system of tablelands of Western India.

### 14.8.2 Nutrient Management

Indiscriminate use of fertilizers and manures exceeding crop requirements leads to accumulation of nutrients in field soils which are easily removed by soil erosion causing nutrient deficiency for crops and toxicity for water bodies. Mean nitrogen use efficiency of rice, wheat and maize is 31%, 18% and 38%, respectively (Cassman et al. 2002). Xia et al. (2020) reported that among the world food crops, cereals' nitrogen use efficiency was found to be 36%. Therefore it is very crucial to manage fertilizers as excess N and P nutrients end up in reservoirs through runoff from arable lands. One important method is deep placement of chemical fertilizers which lowers N loss to water body. Total N and P loss was reduced by 64% and 43%, respectively, in band placement of fertilizers; however, corresponding reduction by hole placement was 77% and 54%, respectively (Ye et al. 2016). This is because of reduced contact between fertilizer and soil microorganisms and slow nitrification process. Controlled- or slow-release fertilizers are another efficient option to reduce nutrient loss via runoff. Moreover, application rate and timing are important points to be considered for efficient fertilizer management and to reduce nutrient loss. Model-based analysis can be used for studying long-term fertilizer effect on nutrient loss via soil erosion. Recently Press Information Bureau of India (PIB 2021), reported consumption of muriate of potash in India during kharif (July to October) seasons 2017–2018 to 2020–2021 was 54.38 million tons (urea, DAP, MoP) and 56.21 million tons, respectively. The Indian Council of Agricultural Research recommends soil test based balance and integrated nutrient management (INM) mechanism to reduce loss of nutrients, preventing soil health deterioration and contamination of groundwater. Additionally split application, band placement of fertilizers, slow-release fertilizers and resource conservation technologies are recommended for judicious fertilizer use and efficiency.

### 14.8.3 Water-Saving Techniques for Reducing Losses and Contamination

Heavy rainfall increases runoff and nutrient loss from fields. Zhao et al. (2012) reported 86% of cumulative N losses from paddy fields under runoff events. Xia et al. (2020) suggested that water-saving irrigation techniques like alternate wetting and drying method could reduce floodwater levels in fields, improve buffering capacity of soil and reduce runoff and nutrient loss. This alternate wetting and drying technique in paddy can reduce surface runoff by 30–37% compared to traditional flooding methods. Reduction in runoff will decrease nutrient loss and prevent contamination of reservoirs with N, P and pesticide residues.

### 14.8.4 Wetland Ditches to Control Soil Erosion

Wetlands can be constructed in densely populated areas for treating the runoff and sediments before reaching water bodies. This is also called ecological ditch system which can be used to reduce the contamination of agricultural nutrient via runoff through sorption, sedimentation, transformation, plant uptake, etc. These ditches have substrate, aquatic plant species and other facilities like drainage ditches by forming sediment-plant-microorganism system (Xia et al. 2020). Such systems are not common in India. However, such ecological ditches are performing in countries like China and the USA for controlling non-point source of contamination from fertilizer and pesticide before reaching streams, rivers, etc.

Some of the common designs are vegetative buffer strips, riparian buffers, land infiltration system, sediment control basin and constructed wetlands that can filter contaminants from overland flow. These techniques are the end treatment methods to control nutrient and pesticide contamination from fields reaching water bodies. Riparian buffers are transitional zones between farmland and nearby water bodies, with good sorption capacity and filtering capacity to retain nutrients like nitrogen and phosphorus, organic sediments, pesticide pollutants, etc. These technologies have numerous benefits like low cost, ease of operation and low maintenance. Another effective mechanism to control surface runoff and nutrient loss is source control technologies. In such methods, reducing the water volume and pollution load by adopting best management practices such as reduced tillage operation, nutrient management, water saving techniques are to be encouraged at field (source) level. These can be included in policy-making and can be popularized via government programmes at both rural and urban areas. However, such technologies can only be only successful depending upon their simplicity, cost-effectiveness, easy adaptability to local environment, higher degradation capacity of contaminants, etc.

## 14.9 Conclusion

Soil erosion is a severe form of land degradation and is omnipresent. Though 1 m of soil loss via water or wind erosion goes unnoticed by farmers, it might take a thousand of years to form. This can be added up to a loss of nearly 15 ton per hectare soil loss. Soil loss through erosion carries away the nutrients, organic carbon and fertile sediments which is a direct threat to soil and crop productivity. Similarly, another important aspect of soil erosion is nutrient-loaded pesticides and harmful contaminants that pollute the surrounding soil and drinking water. Thus soil erosion deteriorates soil health and associated ecosystem services causing long-term impact on the environment if left unnoticed. Soil erosion is a direct threat to food security and crop production at the same time. Beside this, shrinking land availability for agriculture and climate change have severe negative effects on crop productivity and global food production. Agricultural runoffs from arable land are the main sources of contamination of soil and water bodies. These runoffs have complex pollutant combinations including nitrates, phosphorus, heavy metals, pesticide residue, pathogen, etc. which get deposited downstream. Essential nutrients such as nitrogen and phosphorus are inevitable in crop cycle, but indiscriminate use of chemical fertilizers/ manures are the sources for non-point pollution source in lakes and rivers. Anthropogenic eutrophication is an important source of contamination via soil erosion which is having a strong potential effect on aquatic ecosystems and food chain. The severity of erosion on economic and environmental issues is still debatable. Therefore, controlling soil erosion will prevent non-point source of pollution of water bodies, reduce eutrophication of lakes and rivers and protect drinking water quality. Further research on reducing use of synthetic chemicals in agriculture and hybrid technologies to control pollutants at source and end levels is required for sustaining a clean environment.

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# Plastics in the Soil Environment: An Overview

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## Abstract

Contamination of soil by plastics is a global environmental issue. Plastics pollution has been detected and is showing a regular increase in both water and land ecosystems. There are many researches reporting the profound effects of plastics on soil quality parameters and its biota. This review provides information sources, abundance, distribution, toxic effects, and control measures of plastics in soil environment especially agricultural ecosystems. The use of plastics as sewage sludge, packaging material, plastic mulches, and compost is the major source of soil contamination. Soil environment may receive plastics directly or indirectly from different sources. When plastics accumulate in the soil, they may be combined with other soil contaminants such as heavy metals (HMs), persistent organic pollutants (POPs), antibiotics, and many other toxic substances, which have a greater harmful impact on soil quality, flora, and fauna. There are only few reports available on the biological effects of plastics on soil due to the lack of data from field and laboratory studies. More research data is required to understand completely the role of plastics as environmental contaminants and vectors of other contaminants which can enter the food chain. Gap of knowledge is still there on plastic pollution and its impact on soil environment which need to be fully revealed. This global environmental issue deserves more attention from the researchers and policymakers in the future.

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Soil · Plastics · Contaminants · Environment

## 15.1 Introduction

Plastics have recently shown a great impact on the environment and drawn the attention of scientists to its slow degradation or nonbiodegradable nature, small particle size, and various harmful impacts on the ecosystem structure and function (Scheurer and Bigalke 2018; Wright et al. 2013). However, some plastics can be recycled, but the majority of them exists in the environment due to its use in agriculture and as landfills. It is slowly shredded into small particles and enters into the soil environment (Wang et al. 2019). Due to continuous degradation process with the time, they may further break up into smaller particles which results into increased surface area and absorption capacity for hazardous substances like heavy metals (HMs) and persistent organic pollutants (POPs) which show long-term effects on the environment (Fendall and Sewell 2009). When ingested by polychaetes, echinoderms, bryozoans, and bivalves, they become more hazardous (Thompson et al. 2004). Plastics can enter into the circulatory system staying for many days in the intestinal tract (Browne et al. 2008). The agricultural environment is considered as the first entry point of plastics in the soil ecosystems (Rillig et al. 2017; Nizzetto 2016) (Fig. 15.1). In his study de Souza Machado et al. (2018) reported that the contamination of plastics is many times more in soil than that in waters which is one of the serious environmental risks. The plastic may also affect soil quality and food security.

According to the report published by Plastics Europe (2016), it has been estimated that the world production of plastics reached to 335 million tons in the year 2016 as plastics were required in different forms and in every aspect of humans' daily life. Although plastics provide a great convenience, they contribute a huge amount of nonbiodegradable wastes to the environment due to its improper waste management (Rochman et al. 2013; Thompson et al. 2009). Plastic wastes break down very slowly into the environment and can be transported from terrestrial to aquatic ecosystems or vice versa (Jambeck et al. 2015). Plastic materials under 5 mm are called microplastics, which are a more serious environmental issue than macroplastics and well known for their potential negative impacts on the living organisms (Galloway and Lewis 2016; de Souza Machado et al. 2018). Plastics originate from many sources such as mulching films, biosolid applications on soil, illegal dumping of plastic wastes and their littering, flooding, overland runoff, and transport through air (Chae and An 2018; Ng et al. 2018).

The world's oceans are receiving millions of tons of plastics, and this pollution by plastic is causing threat to the living organisms in water and on land. It is almost impossible to recycle the amount of plastic wastes that we are discarding every day. Most of it is ending into large landfills, where it can be decomposed in 1000 years. Leachates from these landfills contain toxic substances which enter the soil and

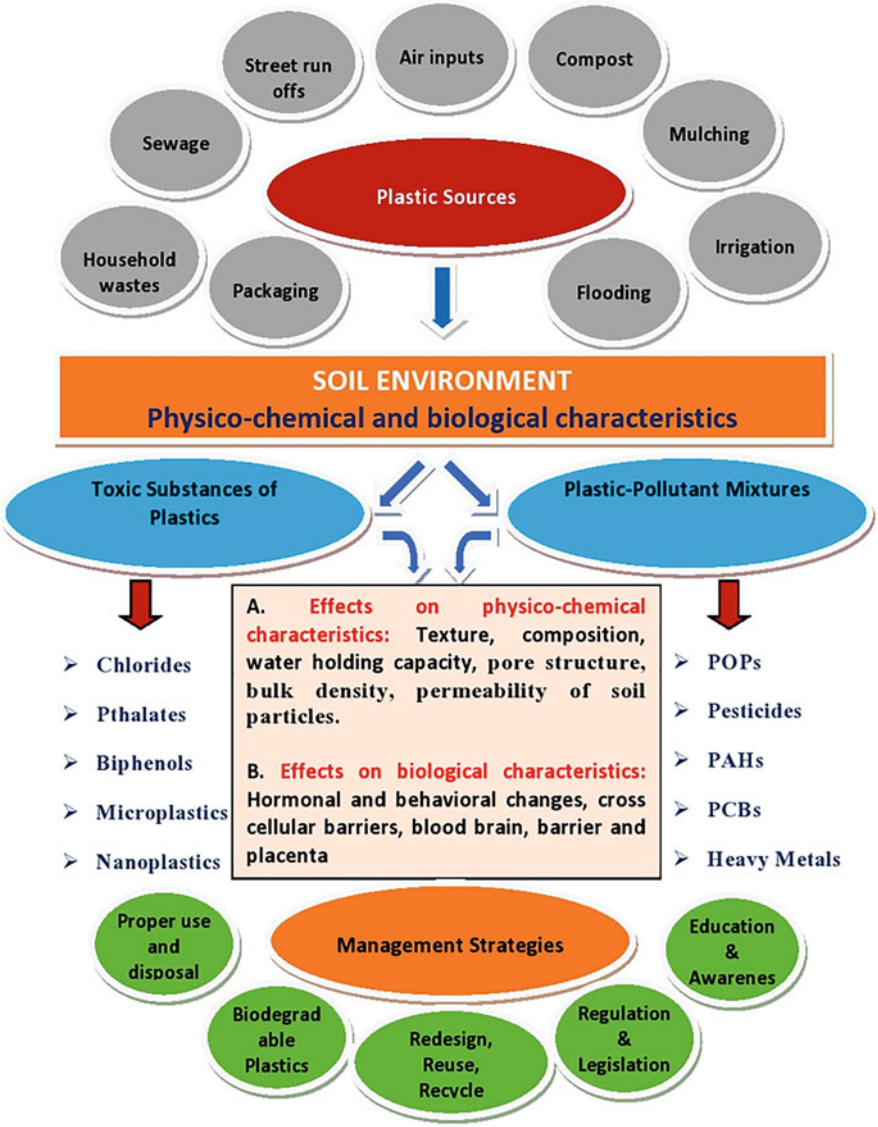

**Fig. 15.1** Plastics in the soil environment: an overview

waters and may cause long-term negative impact on the environment and the food chain (Paul Mocan 2018).

Plastic production began in the 1930s–1940s after synthetic polymers rose rapidly, which reached 622% in the year 2014 if compared with its production in 1976 (Thompson et al. 2009), and now plastics are abundant in the environment (Fuller and Gautam 2016). In the soil it becomes a part of a mixture of contaminants.

Due to its interactions with organic minerals, it makes the soil organic matter (SOM) very stable and can persist in the soil for hundreds of years (Kögel-Knabner and Amelung 2014). Plastics also accumulate many other toxic pollutants of the soil like polychlorinated biphenyls and heavy metals (Engler 2012; Velzeboer et al. 2014). Microplastic (below 1–5 mm) and nanoplastic (below 100–1000 nm) are more dangerous to the environment (Besseling et al. 2014; da Costa et al. 2016) as they can carry many other pollutants when taken up by living organisms (Thompson et al. 2004, 2005) through the food chain (Engler 2012; Teuten et al. 2007).

## 15.2 Plastics in Soil: A Global Issue

The plastic industry increased significantly in 1950s, and its light weight, low costs, durability, and malleability increased its demand for its multiple applications as it is the preferable material for packaging, car manufacture industry, construction, building, and agricultural use. Beside multiple uses and benefits of plastics are at the cost of huge amount of nonbiodegradable wastes and its leakage into the environment due to its low recyclability and reusability rates (Geyer et al. 2017). Global plastic production has reached exponentially to 322 million tons in 2015 (Plastics Europe 2016) contributing 6300 million tons of plastic waste. Out of which 79% was sent to landfills, 12% was incinerated, and only 9% was recycled. The accumulation of plastics in the environment will increase if the production and consumption has not stopped or decreased and proper waste management practices are not followed that may reach up to 12,000 million tons by the year 2050 (Geyer et al. 2017).

The presence of plastics in any form whether as microplastics or macroplastics has widely been considered as the world's challenging anthropogenic and environmental issue on the planet Earth and one of the important threats to biodiversity due to its potential entanglement and ingestion by living organisms. Plastic pollution is a well-known phenomenon in the freshwater and marine water ecosystems, but its contamination in the soil is still unexplored. Although plastics are more abundant in marine ecosystems, more than 80% of the plastics received in marine environments are produced, consumed, and disposed of on terrestrial ecosystems. Therefore, plastic pollution of soil is a major problem for both types of ecosystems, but its contamination on land is many times bigger than that on the marine environment (Horton et al. 2017; Machado et al. 2017).

## 15.3 Major Challenges

Various substances and chemicals of plastics are causing potential health hazards to the soil, water, and living organisms. Brominated flame retardants and polybrominated diphenyl ethers (PBDEs), bisphenol A (BPA), and phthalates are some of the toxic substances added to plastics later which accumulate in the environment (Lassen et al. 2015). Biodegrading capacity of plastics is an important environmental concern as they are widely used in agricultural practices (Adhikari et al. 2016; Horton et al. 2017). Polyethylene is commonly used in agriculture and shows a very slow degradation under a normal environment (Steinmetz et al. 2016). Recently developed bioplastics are considered biodegradable (European Bioplastics 2017). These bioplastics are polymers which are formed from the biomass resources of sugars, but their properties are not same as that of synthetic plastics (GESAMP 2016). The recycling due to the complex structure and ingestion by living organisms is another challenge associated with the use and production of bioplastics (Surfrider Foundation et al. 2017; EPA Network 2017). These plastics enter the food chain and food webs and finally reach to human food products causing potential health hazards (Weithmann et al. 2018).

## 15.4 Potential Sources of Plastics and Their Distribution

Primary microplastics has been considered an important primary source in terrestrial as well as aquatic ecosystems (Horton et al. 2017). Sewage sludge is the major source of primary microplastic contamination as it is very commonly used as a fertilizer in agricultural soils in many developed countries. Europe and North America process about 50% of sewage sludge to use as agricultural fertilizers. According to an estimation, 125 and 850 tons of microplastics/million inhabitants is being added to the agricultural land in Europe. It reaches up to 43,000–63,000 and 44,000–300,000 tons per year in European and North American agricultural lands, respectively (Nizzetto et al. 2017). Microplastics are released to the environment during municipal waste collection, transportation, processing, and landfilling. Air flow also contributes to the distribution and movement of plastics especially microplastics from land to water and vice versa. The use of plastics in agriculture as polytunnels, silage bailing, and plastic mulches are the sources in soil. Plastic containers, packaging, and netting are some other sources (Horton et al. 2017).

In plastic mulching plastic films are used on the crop plants for insulation and to protect seeds, seedlings, and delicate germinating shoots for better crop quality and production. It also protects the soil from erosion and controls pests. It is an important technique to create microclimatic conditions but it also has some limitations. Mulches are commonly made up of polyethyl ene (PE) which is a nonbiodegradable material and remains in the soil for years, and another issue is its recovery and recycling (Steinmetz et al. 2016). Mulches are also made with oxoplastics which also contribute to the contamination of soil (European Commission 2018a). China noticed a fourfold increase from 1991 to 2011 (319–1245 million tons) due to the common use of plastic mulching (Steinmetz et al. 2016). As a result, China improved its crop yield and quality; however, its extensive use resulted in soil contamination and reduced soil fertility. *Plastic pollution* is also known as *white pollution*. Actions are being taken by China to remove and recycle plastic residues, and they opted for a new type of biodegradable plastic films as a cost-effective alternative (Liu et al. 2014; Tiglu 2017; Sintim and Flury 2017).

The wide application of plastic mulch in agriculture in the form of polyethylene (PE) was started in 1938 which became the most important reason of its revolution and the commercial production of some selected crops (Steinmetz et al. 2016). In China it was recorded that in the last 20 years, the consumption of plastic mulch film increased up to four times from 319,000 to 1,245,000 tons (Liu et al. 2014). Plastic mulching showed a profound effect on soil quality, flora, and fauna. It affects the exchange of air and water in the soil, soil moisture, and biological activity and increases the soil temperature (Subrahmaniyan et al. 2006). In the soil the plastic mulch is crushed, undergoes some chemical reactions and degradation, and is converted to microplastics (Bläsing and Amelung 2018) which further contribute toxic substances of plastics added during manufacturing (Rillig 2012; Steinmetz et al. 2016).

The "Almeria" region of Spain is known as "Mar del plastico" which means "Plastic Sea" due to the large surface areas of lands (30,000 ha) covered with plastic greenhouses. Spain is the main exporting country of agricultural products (99.8%) in Europe. Most of the products are produced in the greenhouses of Almeria which is now well known as Europe's garden. But the use of plastics for greenhouses is becoming the major source of plastic remaining in the soil. Due to high temperatures, plastics are disintegrating into soils through strong winds and also transferring plastic residues to the sea. Plastic residues are also illegally burnt resulting in soil contamination (Balaguer Rosillo 2014; Gómez 2008; Husarova 2016). Fertilizers obtained from household organic wastes and industrial recycling of biowastes are applied to agricultural land and being considered as eco-friendly and beneficial for soil quality, but they are actually the strong sources of plastic contamination in terrestrial ecosystems (Weithmann et al. 2018). According to an investigation by the Italian Composting Council, the organic wastes in Italy are contributing 4.9% in soil contamination (Novamont 2018). Sieving and sifting are some known procedures to reduce use of plastics in fertilizers. However, due to its very small size, removing the plastic particles completely from the soil is a big challenge (Weithmann et al. 2018). Various soil amendments like compost and sewage sludge which are very rich in plant nutrients are commonly used to improve soil quality and crop yields (Bai et al. 2017; Cherif et al. 2009; Urbaniak et al. 2017). However, it is evident that these amendments contribute plastic inputs to the soil (UBA 2015).

Irrigation and flooding of agricultural lands by untreated wastewater which contains large amounts of plastic residues also contribute plastics to the soil. Household wastewaters from washing machines, shampoos, and peelings are the main sources of small plastic particles (Browne et al. 2011; Hartline et al. 2016; Napper et al. 2015; Ziajahromi et al. 2016). Soil may also receive plastics from littering and street runoffs (Kim et al., 2004, 2006). Plastic particles can also be received through the wind (Dris et al. 2015). Sewage sludge containing synthetic fibers of microplastics from households which are applied to the agricultural soil is one of the major causes of plastic pollution in soil (Horton et al. 2017; Browne et al. 2011). Also untreated wastewater which contains plastic particles is discharged into the marine waters which further accelerates its distribution (Kerstin and Fredrik 2014; Mintenig et al. 2017). When sewage is applied to agricultural lands in the form of biosolid fertilizer, they may enter the food chain (He et al. 2018)

Plastic packaging wastes also cause a serious contamination of soil and are difficult to be separated from the overuse of disposable plastic items which is one of the major applications (Jambeck et al. 2015). The data given by Li and Richter (2015) showed that more than 90 billion flimsy polybags are contributing as garbage and nonrecyclable plastic. The International Coastal Protection Association reported that they have removed 1,377,141 packaging bags from the environment in 2008 (Weinstein 2009). The durability of plastic material and its improper use and management resulted in massive accumulation of plastics in aquatic and terrestrial ecosystems.

## 15.5 Toxic Effects of Plastics

Chlorinated plastics release toxic chemical substances into the soil which reaches to the groundwater and other surrounding waters that may cause potential negative effects on the consumers of drinking water. The breakdown of plastic particles through chemical reactions changes them into a new substance with different physical and chemical properties and increases the risk of its toxic effects on living organisms and ecosystems. Plastics cause severe damage especially during its decomposition (Paul Mocan 2018). Some additives to plastics like phthalates and bisphenol are the important leachates from plastic particles which can cause hormonal effects on some vertebrates and invertebrates. Plastic nanoparticles cross the cellular barriers, selective membranes such as the blood-brain barrier, and the placenta and may cause inflammation of membranes. Intracellular effects of plastics include triggering changes in gene expression and biochemical reactions. The long-term effects of plastics are still underexplored. However, the Leibniz Institute of Freshwater Ecology and Inland Fisheries reported that the nanoplastics can cross the blood-brain barrier and cause behavioral changes in some fishes (Paul Mocan 2018).

## 15.6 Interactive Effects with Other Pollutants

Plastics also showed some combined effects with other soil pollutants. When microplastics absorb persistent organic pollutants (POPs), they cause a serious damage to terrestrial ecosystems (Bakir et al. 2014; Frias et al. 2010). Plastics are the carriers of various environmental contaminants (Hartmann et al. 2017). Some other organic pollutants, such as pesticides, herbicides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), with plastic mixture are also important factors affecting health of agriculture soils. Beside organic compounds microplastics can absorb heavy metals (Hodson et al. 2017) and increase the heavy metal uptake in terrestrial ecosystems which depends upon the chemical and physical properties of plastic material (Teuten et al. 2007; Brennecke et al. 2016). It has been reported that the rate of absorption of some heavy metals increased with microplastic mixtures (Massos and Turner 2017). Adsorption capacity of microplastics increased during its degeneration in the presence of UV light (Bandow et al. 2017; Brennecke et al. 2016).

## 15.7 Plastics and Soil Quality Parameters

Plastics amended in soil may change the quality parameters such as soil texture and composition due to the addition of various chemical substances to plastics. Plastics may alter the water holding capacity, pore structure, bulk density, and permeability of soil particles further affecting the evaporation process of soil (Machado et al. 2018), leading to cracks and shrinks especially in sandy and clay soils. The process of cracks and shrinks is a consequence of transport of water and other solutes in soil (Susanna Gionfra 2018).

## 15.8 Plastics and Soil Flora and Fauna

Healthy soil is the primary requirement to achieve the goal of sustainable food security, adapt to climatic and seasonal changes, and protect biodiversity. Plants play an important role as primary producers and in maintaining the health of soil ecosystem. But if the soil is contaminated by plastics, this may hinder the intake of nutrients and water absorption by plant roots and enzymatic reactions required for detoxification and conjugation (Verkleij et al. 2009). During this detoxification process, many enzymes and chemical compounds are released which may alter the plant biomass, elemental composition of cells and tissues, root characteristics, and physiology of soil microorganisms. It also affects the activities of some important small soil animals like nematodes, earthworms, ciliates, and mites (de Souza Machado et al. 2019). When plastics degrade into small particles, they are ingested by soil organisms affecting their growth, reproduction, immunity, and gut microorganisms. Furthermore, plastics release toxic substances and also act as a medium for the transport of other soil contaminants and increase the exposure of soil organisms to those contaminants (Wan et al. 2019).

Plastics may affect the growth, development, and reproduction of soil organisms and biodiversity of soil flora and fauna. However, in low concentrations, plastics may not influence soil organisms (Huerta Lwanga et al. 2016; Rodríguez-Seijo et al. 2017, 2019). When the animals get unconscious intake of indigestible plastics from soil, the plastic fragments choke their food passage (Peng et al. 2017; Huerta Lwanga et al. 2017). Some animals such as earthworms are capable of digesting the microplastics by crushing fragile small plastic particles (Rillig 2012; Rillig et al. 2017), but ingesting in large quantities may harm their intestine and cause them death (Rillig and Bonkowski 2018). Some reports concluded that the intake of microplastics may be harmful especially to filter feeders, flagellates, and ciliates (Jens and Hartmut 2002). Polystyrene plastics can cause damage to cholinergic and GABAergic neurons and oxidative stress kinase. Furthermore, the smaller the plastic particle size, the higher the risk to soil fauna (Lei et al. 2018). Oribatid mites also showed their capability to transport plastics (Zhu et al. 2018).

Plastic causes serious damage to mites and larvae populations which help in maintaining soil fertility. Soil fauna such as mites, roundworms, springtails, some micro-arthropods, and nematodes play an important role in nitrogen and carbon cycling. Plastic materials such as bags, cups, and fibers are the major sources of plastics in soil ecosystems affecting biodiversity of species below the soil surfaces. A significant decrease in abundance of some species of oribatid mites, arthropods, and nematodes was reported due to plastic contamination (Jonathan Watts 2020).

## 15.9 Management Strategies

### 15.9.1 Degradation of Plastics

The degradation of plastics in soil was studied by some workers who reported that the degradation of plastics in soil is a very slow process (Krueger et al. 2015; Restrepo-Flórez et al. 2014), while they found a negligible degradation of PVC (Ali et al. 2014). There are some degradation processes for plastics in the environment through UV radiation and physical abrasions (Song et al. 2017). Plastic materials such as polyethylene fragments coming from plastic mulching are degraded slowly and persist for many years in soil and after further degradation may change into even smaller plastic particles (Krueger et al. 2015; Briassoulis et al. 2015). To solve this important environmental issue, the so-called biodegradable plastics were introduced. However, they are not fully biodegradable, convert into nanoparticles, and may persist in the soil for years (Roy et al. 2011). Similar properties were observed for plastic films (Selke et al. 2015)

Microorganisms decompose the organic matter in soil and detoxify the soil plastics and harmful chemicals. Plastics serve as a substrate for soil microorganisms and are seen as the "plastisphere" (Oberbeckmann et al. 2016) which is important for the degradation process of plastics (Carson et al. 2013). Soil bacteria and fungi promote plastic degradation (Shah et al. 2008). The bacterium, *Brevibacillus borstelensis*, is reported to promote degradation of polyethylene (Hadad et al. 2005). The degradation process includes the production of extracellular enzymes excreted by microorganisms attached to the plastic surface. The polymer chain is then broken down into some water-soluble intermediates that are absorbed by the cells and enter into a particular type of metabolism, and finally, the end products ($CO_2$, $H_2O$ and $CH_4$) are released into the environment (Müller 2005)

### 15.9.2 Regulations and Legislations

A number of measurements have been taken worldwide to minimize the use of plastics and manage the disposal of its waste. Strategies are made to reduce the direct and indirect leakage of plastics into the environment. Reuse and recycle of plastic products should be promoted. The responsibilities of plastic producers should be extended, and modulation of fees based on plastic quality, design, and its recyclable property should be encouraged to support and promote secondary plastics (Watkins et al. 2017; Zero Waste Europe 2017; European Commission 2014). Bans and phaseouts are also one of the applied measures to control plastic products, use of small plastic particles in cosmetic products, and its other applications. Many countries have banned the use of microbeads (small plastic particles) in cosmetic products including the Ireland, New Zealand, Italy, the Netherlands, the USA, Canada, Australia, and the UK, which may help in reducing the concentration of microplastics in sewage sludge which is commonly applied as compost in agricultural soil (Beat the Microbead 2018).

Ban on single-use and nonbiodegradable plastic bags is one of the effective control measures applied across the globe. Various rules and regulations have been introduced to control the sale, use, and waste disposal of plastic bags. In addition, regulations on reducing litter and leakage can also reduce the plastic pollution in soil. Oxoplastics are so-called biodegradable plastics, but are also reported for contaminating soil when overused and should be restricted. The EU has made a strategy for such type of plastics (European Commission 2018a). There are hundreds of organizations and NGOs, businesses, scientists, and industrial associations that have agreed on proposing a complete ban on oxoplastic packaging (Ellen MacArthur Foundation 2017). Taxes and charges on manufacturing, use, and disposal of plastics may also support in reducing plastic pollution. Recycling, composting, and reuse are some of the alternative waste management strategies for plastics (CEWEP 2017). Poland imposed a landfilling tax on plastic waste materials (OECD 2018). Various environmental legislations for the use, manufacture, and waste disposal of plastics are also effective in many countries. The “EU Strategy for Plastics” is focused on improving the quality and economics related with recycling and reuse of plastics (European Commission 2018b). Manufacturing and use of plastic-containing fertilizers should be regulated. Germany has very strictly implemented the regulations on quality of fertilizers allowing only 0.1% plastics (by weight) in fertilizers (Weithmann et al. 2018). Strict regulations are also implemented on the applications of sewage sludge to agricultural soil as it is a commonly used fertilizer and may enter the food chain causing serious health hazards. Educating people at society, school, and university levels for proper use, disposal, and environmental and health issues related with plastic products can be a cost-effective measure to control the plastic pollution at the primary level.

## 15.10 Discussion

Plastics are produced, consumed, and disposed of on land, and more than 80% of which reach the marine environments. Plastic contamination in soil is estimated to be between 4 and 32 times higher than that in the waters. Improper use, disposal, and treatment of plastics and its bulk consumption for agricultural purposes allow them to reach our soils. A greater consideration of this issue and implications of policies and legislation is the need of the hour to overcome plastic pollution in agricultural soil.

Knowledge on plastic pollution is almost negligible due to the lack of education and awareness. Major sources of plastics in agricultural ecosystems are various soil amendments such as compost, sewage sludge, and use of wastewater for irrigation which may have a considerable amount of synthetic polymers of plastics. Plastic mulching serves as the route of entry of plastics into the agricultural soil and then to the food chain. Other inputs of plastics are through flooding, littering, and the atmosphere (Bläsing and Amelung 2018). The current data on plastics suggest that they are now equally contaminating the environment as the heavy metals. Plastic's macroparticles, microparticles, and nanoparticles are more likely to be dangerous for both water and soil. Their vertical movement and leaching may be a major cause of groundwater pollution (Bläsing and Amelung 2018). Therefore, regular monitoring of plastic accumulation in soil and research are urgently required. More researches may provide the data for a better understanding on the fate and effects of persistent and nonbiodegradable plastic materials in terrestrial environments.

There is an urgent need to reduce manufacturing, use, and dependence on plastics for industrial, agricultural, and household purposes. Burying plastics in soils must be avoided, as they are responsible for the adverse consequences on soil flora, fauna, and quality parameters and may also interfere in biogeochemical cycling in agricultural ecosystems (Jonathan Watts 2020). According to an estimation by Lebreton et al. (2017), more than 300 million tons of microplastics have been accumulated so far on the planet Earth posing a great threat to humans and the environment. For a more sustainable future, the use of plastic should be either stopped completely or reduced by avoiding unnecessary packaging and extensive agricultural use. Awareness and education on plastics should be more strengthened for its proper use, reuse, and recycling (He et al. 2013). Therefore, further investigations are urgently required to know the geochemical effects of plastics on soil ecosystems.

## 15.11 Conclusions

The issue of soil contamination by plastics received an attention in only the last few years. Plastics produced, consumed, and disposed on lands are the major sources of marine and soil litter. Plastics act as carriers for many other contaminants of the soil which enter the food chain. Moreover, data obtained from various researches showed that the use of plastics in agriculture is significantly increased. Further it is also evident from the data that plastics especially microplastics are potential health hazards to the soil and human beings. A number of control measures and management strategies are applied to tackle the plastic litter in marine waters. More emphasis is required to address issues such as use of plastics in mulching, control on fertilizer quality, overuse and treatment of plastics, and their disposal and leakage in the soil and groundwater. Information, knowledge and consideration of plastic pollution is the need of the hour in order to develop the policies and regulations to overcome this global environmental issue.

## 15.12 Recommendations

Microorganisms can be utilized for the adsorption and biodegradation of plastics. Microorganisms and the genes involved in the degradation should be investigated and identified for further use. Animals such as earthworms and other micro-animals and invertebrates can be an important tool for remediation of plastics from agricultural soil. However, uptake and excretion of plastics by these animals may have some uncertain impacts on soil and the animal itself. Toxic effects of plastics on soil fertility, flora, and fauna require more investigations. Macroplastic, microplastic, and nanoplastic pollutions have been considered as an important global environmental issue, especially in agricultural soils and food security. Still only few reports are available on degradation processes and the effects of toxic substances released from plastics. Another important issue is to control the migration of these toxic substances from soil to water and vice versa. The potential consequences of plastic pollution and sustainability of the environment and food security should also be analyzed. A strong cooperation between environmentalists and policymakers is the need of the hour for the mitigation of accumulation and contamination of terrestrial and aquatic environments by macroplastics, microplastics, nanoplastics, and the toxic substances added during manufacturing. Stopping or reducing the use of plastics as packaging and other materials, recycling, reuse, proper plastic waste management, bioremediation, legislation, and education can only be the important measures to control "plastic pollution" or the so-called white pollution.

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# Part IV

# Heavy Metals in the Soil Environment

# Cadmium Contamination in the Soil Environment: Impact on Plant Growth and Human Health

# 16

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## Abstract

Cadmium (Cd) is one of the common toxic heavy metals (HMs), having harmful effects on the environment and potential health hazards allied with food chain contamination due to higher mobility, easy integration capacity in ion channels, and prolonged persistence. At present, Cd toxicity has become a serious social issue, since the use of Cd has increased alarmingly owing to industrial development and advanced agricultural practices throughout the world. In the current chapter, we aim to summarize the latest research outcomes on the consequence of Cd toxicity on plants and human health. We discuss the sources of Cd and the mechanisms behind the contamination of agricultural soil along with the environment by Cd. The chapter also covers the exploration of Cd uptake, its transport and accumulation in plants, and the detrimental effects of Cd on seed

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germination, plant growth, photosynthetic efficiency, mineral nutrition, protein homeostasis, antioxidant potential, reactive oxygen species generation, oxidative damage, and relevant metabolic changes. The current knowledge of recent research advances would aid future research for developing new approaches in recovering the hazardous effect of Cd on plants and human health as well as benefit the farming societies and consumers, thereby mitigating concerns about food safety.

**Keywords**

Cadmium · Phytotoxicity · Human health · Food safety · Soil contamination

## 16.1 Introduction

The rapid growth of the industrial segment has unavoidably resulted in severe contamination of soil with a variety of pollutants. Among various pollutants, toxic heavy metals (HMs) pose the ultimate threat to both terrestrial and aquatic environments and ecosystems around the globe (Aziz et al. 2015; Jin et al. 2019; Peng et al. 2019). Considering all the biologically non-essential HMs, cadmium (Cd) is the most prolific and hazardous element for living organisms owing to its higher mobility, persistence with extended half-life, and toxicity to living systems (Wang et al. 2014; Zeng et al. 2018; Xu et al. 2019). Cd in general exists as divalent cations, complexing with other anions, and holds 7th position out of the top 20 recognized toxins (Hamid et al. 2019). The major source of Cd escalation in the environment is by many anthropogenic operations including mining and smelting activities, use of phosphate fertilizers, irrigation with industrial wastewater, waste incineration, fossil fuel combustion, and exploitation of Cd in various commercial products (Seshadri et al. 2016; Liu et al. 2019). More than 90% of Cd is released to the natural environment due to various anthropogenic activities (Bi et al. 2006); every year it accounts for around 13,000 metric tons of Cd escalation into the environment (Gallego et al. 2012). The British Geological Survey documented that by the year 2015, the total Cd production around the globe reached up to 24,900 metric tons (Brown et al. 2017), whereas the US Geological Survey (2017) reported that about 23,000 metric tons of Cd were generated globally excluding the USA in the year 2016. According to a report of Frišták et al. (2015), it is inferred that in China, roughly about 2.786 × $10^9$ $m^2$ of cultivable lands are completely contaminated by Cd; another report says that every year approximately 1.5 × 105 tons of farm products are found to be Cd contaminated (Xu et al. 2017). The Cd bioavailability differed from soil to soil, and the major influential determinants are the soil pH, clay particles, soil organic matter (SOM), cation exchange capacity (CEC), and redox potentials (Kirkham 2006; Alloway 2013a; Honma et al. 2016). Though it is not an essential element, Cd can easily be uptaken by the plant system growing in Cd-supplemented or Cd-contaminated environment (Clemens et al. 2013; Luo et al. 2019). Vigorous agricultural practices such as the application of chemical fertilizers and sludge materials to the agricultural soils and employing wastewater for irrigation are continuously adding toxic Cd in the agricultural soils, which might induce harmful effects via entering the food chain from the soil-plant-animal or human system (Anjum et al. 2015; Rizwan et al. 2016b).

The Cd toxicity in plants induces alterations in phenotypic, biochemical, physiological, and ultrastructural attributes of plants ( He et al. 2017a, b) witnessed by chlorosis, necrosis, reduced growth and biomass, impairment of defense mechanisms, metabolic changes, as well as disturbances in water and nutrient status of plant system (He et al. 2013; Chen et al. 2016a). The most harmful effect of Cd toxicity is the generation of reactive oxygen species (ROS) which cause impairment to macromolecules (proteins, RNA, DNA, lipids), pigmentation, and the cell membrane (Sidhu et al. 2017; Tian et al. 2019).

Since being one of the most staple foods, rice consumption contributes to the major route of Cd uptake globally, particularly in Asian countries such China, Japan, India, Bangladesh, and Pakistan (Mao et al. 2019). Also, as one of the typical metal accumulators, the rice (*Oryza sativa* L.) plant could easily uptake and accumulate Cd in its grains (Yang et al. 2016). In China, the Cd concentration is found to be higher in brown rice varieties, exceeding the prescribed national food contaminant standard limit (GB 2762-2017, Cd 0.2 mg $kg^{-1}$) (Zhou et al. 2018; Gu et al. 2019).

The long-term dietary exposure of Cd may result in severe health issues (Nordberg et al. 2007; EFSA 2012; Zhang et al. 2014) including renal failure, cardiovascular disease, skeletal damages, osteoporosis, and impairment of immune and excretory systems (Chunhabundit 2016; Deering et al. 2018). Moreover, Cd is a well-known human carcinogen (IARC 2018), and its chronic exposure results in lung, prostate, and renal cancer thereby increasing mortality rates (Pandey et al. 2016; Gu and Gao 2018). Recently, China and Thailand reported the renal dysfunctions caused by the consumption of Cd-contaminated rice (Honda et al. 2010; Hu et al. 2016). In order to reduce such effects, a monthly Cd intake of 25 mg $kg^{-1}$ body weight was established as a tolerable limit by the Food and Agriculture Organization (FAO) and World Health Organization (WHO) (Chen et al. 2018a).

This chapter, however, focuses on the sources, levels, and dynamics of Cd contamination in the soil environment. We have also tried to summarize the various factors and mechanisms behind Cd uptake, accumulation, and ROS generation in plants. In addition, potential human health risks from dietary intake of Cd have also been discussed.

## 16.2 Sources and Levels of Cd in the Environment

In nature, Cd rarely occurs as a pure metal, rather it is mainly associated with the zinc sulfide-based ores or as an impurity mixed with lead and copper ores (Ziemacki et al. 1989; UNEP 2010a, b; Roy and McDonald 2015). Like other metals, Cd is also generally extracted from the parent ore materials. However, the escalation of Cd into the environment is primarily by anthropogenic sources and sometimes by natural causes; for instance, only 10% of Cd contamination occurs due to natural processes (Khan et al. 2017b; Pan et al. 2016). On average, this metal in the earth's crust ranges from 0.1 to 0.5 mg $kg^{-1}$ (Morrow 2003); however different factors affect the Cd level either positively or negatively. The volcanic eruptions and the weathering of rocks contribute to its movement in the earth's crust; it is even equally contributed by sea sprays, windblown dust, and forest fires (Khan et al. 2017a, b). Since Cd is the typical component in the earth system, the weathering of parent material normally boosts its concentration in nature (Liu et al. 2013). Amidst all the parent materials, soil of volcanic tuff contributes the highest Cd escalation followed by alluvium and andesite lava. The level of Cd varies with different parent materials: igneous and metamorphic rocks normally have the Cd in the range of 0.02–0.2 mg $kg^{-1}$, whereas sedimentary rocks contribute higher levels of 0.1–25 mg $kg^{-1}$ (Cook and Morrow 1995). The Cd-rich mineral-like black shales have Cd up to 100 mg $kg^{-1}$ (He et al. 2015), siltstone and mudstone have 4.6 mg $kg^{-1}$, carbonate rocks contain 1.7 mg $kg^{-1}$ (Liu et al. 2013), and the fossil fuels have 0.5–1.5 mg $kg^{-1}$. The phosphate fertilizers have Cd in the range of 10–200 mg $kg^{-1}$ (Cook and Morrow 1995); in the marine phosphates, it is about 15 mg $kg^{-1}$ (EC 2000). The phosphate rocks of igneous origin typically incorporate lesser Cd contents of 15 mg Cd $kg^{-1}$ $P_2O_5$ (phosphate fertilizer), whereas the sedimentary counterparts have more than 20–245 mg $kg^{-1}$ (Çotuk et al. 2010). However, the usual range of Cd in the soil is reported to be 0.02–6.2 mg $kg^{-1}$, above which it is toxic to the environment; the soils with 5–20 mg $kg^{-1}$ of Cd are said to be highly contaminated and need immediate attention to overcome the toxic effects on biosystems (Adriano 2001). According to the European Commission (2000), the maximum limits of Cd in agricultural or horticultural soils should be 0.2–1.0 mg $kg^{-1}$ in countryside and 0.5–1.5 mg $kg^{-1}$ in municipal areas.

The Cd contamination in the soil is increasing gradually as a result of human actions and sometimes by natural causes (Adams et al. 2004; Fan et al. 2009). Altogether, the natural sources are projected to generate around 150–2600 tons of Cd into the atmosphere (Shahid et al. 2016); many areas of the world have been reported to have Cd in soil ranges from 0.07 to 1.1 mg $kg^{-1}$ which are intended to result from natural sources (Shahid et al. 2016). Many reports regarding the elevated levels of Cd in soil contributed by natural sources are available in various geographical locations (Khan et al. 2010; Liu et al. 2013, 2015). For example, in southwestern China, the soils of the Three Gorges Region are highly contaminated with Cd; this is attributed by the weathering action of Cd-rich sedimentary rocks over there. In these areas, the dietary exposure of Cd through food chain causes potential threats (Liu et al. 2015).

Some of the major anthropogenic inputs of Cd in agricultural soils are through the use of phosphate fertilizers, sewage sludges, wastewater irrigations, industrial and vehicular emissions, and mining activities (Roberts 2014; Rehman et al. 2015; Huang et al. 2017a, b).

Domestic sewages are the significant sources of Cd pollution in the environment; from the sewage, Cd ultimately enters into the water stream and contaminates the places it encounters. Sometimes, it also results in the contamination of groundwater

(Moradi et al. 2005). Industrial wastewater normally contains higher Cd concentration which ranges from 10 to 100 mM (Shuttleworth and Unz 1988). Besides, the element Cd is also constantly being used in numerous industrial processes including electroplating, as a stabilizer, nickel-Cd batteries, in automatic vending machines, as well as in cigarette manufacturing (Casalino et al. 2002; U.S. Geological Survey 2009; Mutlu et al. 2012). Due to the low melting point and anticorrosive effects, Cd is normally employed for many industrial purposes (U.S. Geological Survey 2015). In contrast, because of its high resistance to oxidation, Cd is widely employed for coating PVC and in shipbuilding. Further, it is generally employed as a coating material in most of household and industrial goods, automobiles and trucks, all types of tools, aircraft, and fasteners including nuts, bolts, nails, etc. Cd-associated sulfur is used as a coloring material in ceramics, plastics, glass, rubber materials, and even in paints (Scoullos et al. 2001; Wang et al. 2009). Cd is also necessary for photography and tire repairing (Kirkham 2006).

## 16.3 Cd Contamination of Agricultural Soils

Other than the pedogenic physical processes, various anthropogenic sources (Fig. 16.1) including aerial dispersion from mining industries and transport vehicles as well as non-judicial agricultural usage of pesticides, phosphate fertilizers, manures, sewage sludge, and industrial wastewater are the main causes of Cd contamination in agricultural soils (Wuana and Okieimen 2011; Rehman et al. 2015; Huang et al. 2017a, b). The Cd contamination in agricultural soils is of great importance because of its higher persistence and bioavailability to the plant systems (Kumar 2013). Particularly, the leafy vegetables and food grains tend to accumulate higher Cd levels, resulting in harmful effects on the food chain (Arora et al. 2008). Nevertheless, the agricultural soils with the concentration of Cd $<3$ mg kg$^{-1}$ are suggested to overcome the Cd accumulation in the edible parts of food crops (Lux et al. 2011). Globally, 5.6–38 × $10^3$ tons of Cd is getting released into the environment annually (Khan et al. 2017a, b). The calculated Cd concentration in France was 100 mg kg$^{-1}$ (Baize et al. 1999). China accounted for 743 metric tons of Cd emission in the year 2009, out of which 57% was solely contributed by the industrial sector (Cheng et al. 2014).

The nearby proximities of Cd mining/smelting and refining industries are in general highly contaminated by Cd (Lombi et al. 2000; Khan et al. 2017a, b). Besides, Cd in elevated levels is observed in limestone (Liu et al. 2013), coal (Galunin et al. 2014), and ultramafic rocks (Shah et al. 2010). While heating of non-ferrous metallic ores or leaching process, there is a higher chance of Cd release into the air and water, whereas irrigating crop lands with the wastewater released from mining and industries deposits loads of Cd. Further, the atmospheric deposition from the mining/smelting operations as well as combustion units also escalates the Cd even in the agricultural fields located far away from the source, although their contribution can be more difficult to quantify (Ghosh and Roy 2019). The mining/smelting of non-ferrous ores equally pollutes the agricultural crop land with Cd

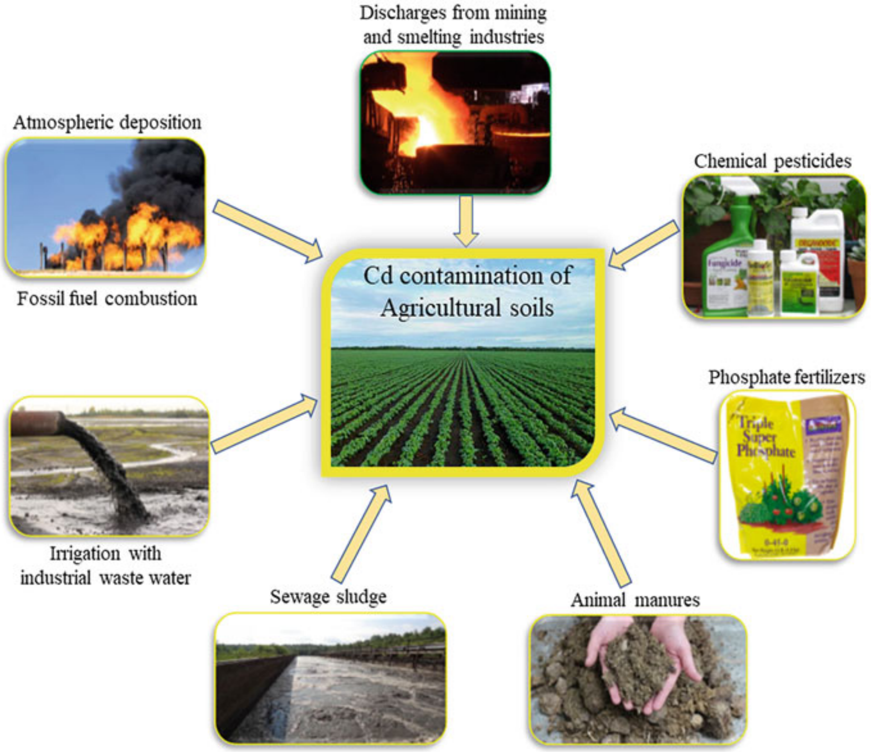

**Fig. 16.1** Anthropogenic sources of Cd contamination of agricultural soils

(Hu and Cheng 2013; Hu et al. 2013); inconveniently, the majority of China's non-ferrous metal deposits are in the regions of vigorous rice production areas. In addition to the industrial discharges, the application of phosphate fertilizers potentially contribute to Cd contamination in crop lands (Khurana and Jhanji 2014); for instance, many researchers reported the notable increase in Cd concentrations after prolonged application of phosphate fertilizers to the crop fields in New Zealand (Bramley 1990; Taylor 1997). Generally, phosphate rocks are used to produce phosphate fertilizers through various chemical processes; these rocks normally contain Cd at varying levels. The phosphate fertilizers produced in China normally have Cd in the ranges of 1.5–3.2 mg kg$^{-1}$ (Lugon-Moulin et al. 2006; Mar 2012), which contain very less Cd comparatively than those in North America (16–45 mg kg$^{-1}$ Cd) (Robarge et al. 2004) and European countries (0.1–120 mg kg$^{-1}$ of $P_2O_5$) (Nziguheba and Smolders 2008). Nonetheless, the exploitation of phosphate fertilizers causes the over-accumulation of Cd in agricultural soils; the Cd input not only depends on its concentration in fertilizer but also on the application rates and frequency to the soil (Roberts 2014; Murtaza et al. 2015). Having concern about increasing Cd concentration in agricultural lands, many countries like

Australia, Japan, and Canada have set up the limits of Cd concentration in phosphate fertilizers for agricultural use (Chaney et al. 2004; Roberts 2014).

Additionally, the deposition of Cd in the agricultural lands is also contributed by the application of contaminated manures and sludges (Nicholson et al. 2003). The concentrated confined-animal feeding operations (CAFOs) have increased the health impacts due to unsustainable animal production and manure utilization practices (Sims and Maguire 2005). The animal manures have a significant contribution to HM contaminations; this might be due to the presence of trace elements in animal feeds (Han et al. 2012; Wang et al. 2016). The steady usage of animal manures to croplands increases the soil toxicity and bioaccumulation of Cd and related HMs (Adesoye et al. 2014; Sakadevan and Nguyen 2017). Yanping et al. (2016) reported that in China, about 150,000–180,000 tons of trace metals are employed as food additive in animal feed; around 57–67% of these metals are flushed out of animal systems through manures, and applying these manures to crop lands ultimately increases the HM concentration in the soil. When compared with other HMs, the levels of Cd in domestic sewage sludge are found to be higher, which are mainly contributed from household products, car tires, cigarette butts, etc. Additionally, the composted sludge contains greater Cd concentrations; for example, by the use of composted sludge in the crop fields of Topeka, Kansas, 4.2 mg kg$^{-1}$ Cd was added (Liphadzi and Kirkham 2006). Further, the application of biochar amendment to the cropland also results in the increase of HMs in the soil. Biochar is normally considered as an excellent amendment that may help in improving soil fertility; however, the selection of feedstock decides its applicability to the soil. During the pyrolysis of feedstock, the metals present in the feedstock may also get intense due to the volatilization of syngases (Brown et al. 2015). Owing to the ability of controlled release, biochar consequently escalates the HMs from its structure into the soil. Sewage water is being utilized as an alternative to the usual fertilizers in three-quarters of the Asian cities (Gupta et al. 2008; Drechsel et al. 2010), which is also a potential source of HM contamination of agricultural soils (Minhas and Samra 2004).

## 16.4 Factors Affecting Cd Uptake by Plants

It is well known that the bioavailability of the Cd in the soil matrix is of more concern than that of the total Cd contents since the plants can only uptake the bioavailable portions; hence, the speciation and distribution of Cd are the major determinants affecting Cd availability to the plant system (Ok et al. 2004; Kirkham 2006) (Fig. 16.2). Notably, the addition of immobilizing agents can modify only the bioavailability of Cd but not the total Cd concentrations in the polluted soil (Bolan et al. 2003; Han-Song et al. 2010). Therefore, the factors associated with increasing or decreasing the bioavailabilities of Cd fractions are majorly determining the extent of Cd uptake by the plant systems and their consequent toxicities. Moreover, the behavior of Cd in the soil solutions mainly depends on its diverse chemical forms and is primarily controlled by the complex interactions with different soil matrices

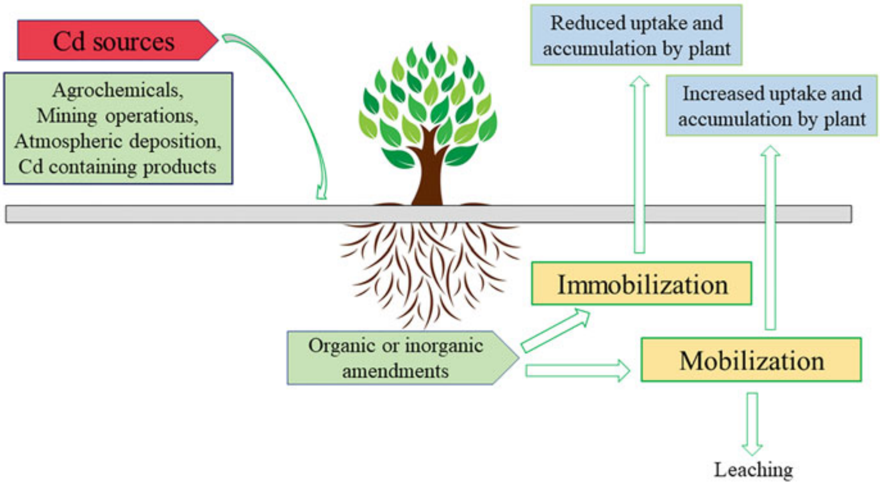

**Fig. 16.2** Cd contamination of soil from various sources and its probable fate in the environment

(Adriano et al. 2004). In general, the soil Cd exists in different forms including exchangeable free $Cd^{2+}$, complexations with carboxylic acid, amino acids, and Cd bonding with $SO_4^{2-}$, $Cl^-$, and other metal ions (Vega et al. 2010; Sammut et al. 2010). The bioavailability is also influenced by many physiochemical features of soil including soil pH, organic matter (OM) (Jung 2008; Usman et al. 2018), soil cation exchange capacity (Vega et al. 2010), Cd speciation (Sammut et al. 2010), chloride concentration (Kirkham 2006), and dissolved organic carbon (DOC) (Zhao et al. 2007). Besides, the bioavailability is also influenced by plant genotype, type of soil, other management practices (Perilli et al. 2010; Gao et al. 2011), plant nutrients (Sarwar et al. 2010), and microbial communities. The speciation of the metal ions and their distribution in soil medium are regulated by a number of reactions but not limited to adsorption-desorption, precipitation-dissolution, complexation, and ion exchange (Christensen 1984).

In general, the soil pH is very much influential for the metal bioavailability in soil medium (Jung 2008; Khaliq et al. 2016). The pH directly affects the rates of adsorption, desorption, sorption phenomenon, and complexations of metal ions which in turn result in the increase or decrease of Cd bioavailability (Naidu et al. 1997; Bolan et al. 1999). For instance, the Cd uptake prevails under acidic conditions (4.5–5.5) as it is less mobile in high alkaline conditions of soil (Jung 2008). Therefore, it is worth mentioning that soil pH and Cd content in plants have a linear relationship as the decrease in soil pH results in an increase of Cd contents in plant parts. In acidic soils, Cd occurs in the forms of $Cd^{2+}$, $CdSO_4$, and $CdCl^+$ in soil solution, whereas in alkaline soil, $CdHCO_3^+$, $CdCO_3$, and $CdSO_4$ predominate. In soils having pH above 7.5, Cd precipitation occurs as $CdCO_3$ and possibly $Cd_3(PO4)_2$ that are not easily mobilized (Kabata-Pendias 2010). In highly acidic soils, the higher concentration of $H^+$ ions tends to displace the adsorbed metals in the soil and hence their higher bioavailability (Alloway 2013b). Normally, a 1.5-unit increase in soil pH increases the Cd adsorption by 30% (Peijnenburg et al. 2000).

The Cd adsorption to the surface functional groups is strongly dependent on the pH of the solution where it exists (Lee and Davis 2001); for instance, a study reported the enhanced Cd sorption to the cork powder with increasing solution pH (Krika et al. 2016). The increased adsorption might be owed to the availability of negatively charged groups as at higher hydrogen ion concentration, the sorbent-metal interactions are hampered due to increased positive charges on sorbent surface (Ajmal et al. 2005). Recently, Chen et al. (2018b) assessed the effects of contact time, initial concentration, and solution pH for enhancing Cd adsorption and reported that the pH was found to be the most significant factor among all. The results implied that the Cd adsorption was less effective at pH $<6$, whereas it was higher at pH ($>9$). Jiang et al. (2012) reported the characteristic "S" pattern for Cd sorption-desorption as any changes in the solution pH affect the adsorption mechanism. In addition, the increment in the pH level affects the negative charges and improvements in the adsorption phenomenon (Jiang et al. 2012). Further, the application of biochar can positively influence the adsorption mechanism as it tends to increase the solution pH (Zhao et al. 2019). The increased metal adsorption associated with the biochar might also be due to the larger surface area and favorable adsorption sites of biochar as well as the hydrolysis by it. The increase in the hydrated ion protonation is also equally responsible for the enhanced metal adsorption. So, it can be concluded that the increase in pH increases the negative sites and induces the attraction of metal cations and ultimately the higher adsorption (Mouni et al. 2009). These above-said effects along with the increasing pH synergistically favor the enhancement of metal adsorption in alkaline conditions (Chang et al. 1997).

The increased soil pH may help the Fe/Mn oxide formation, which in turn also provides the extra sites for metal binding (Chen et al. 2016b). The addition of organic amendments in the contaminated soil thus regulates the translocation of Cd from soil-root-shoots; mostly, the organic amendments increase the soil pH and reduce the Cd bioavailability to plants (Eriksson 1989; Singh et al. 1995). Under field conditions, the uptake of Cd by plants may get affected by a variety of factors including the soil physiological properties and climatic parameters. In a study, Li et al. (2005) documented the Cd uptake in rice grains grown at acidic red soil of China; the accumulation of Cd in rice grains was found to be 0.36 mg $kg^{-1}$ at pH 4.95 and 0.43 mg $kg^{-1}$ at pH 6.54. According to Chaudri et al. (2007), the Cd accumulation in wheat grains is majorly determined by soil pH and organic carbon. In contrast, Singh and Myhr (1998) reported that there exist no significant correlations between the soil pH and Cd accumulation in the barley grains.

However, it is generally not easy to extrapolate the appropriate responses and results from the greenhouse studies as the same response might totally be different under field conditions. For instance, He and Singh (1994) reported the difference in effects of NPK application on Cd accumulation in crops; NPK fertilizers triggered the Cd concentration in crops under greenhouse conditions, whereas no such Cd increase was found with the crops growing under field condition with the same application rates. However, the genotype of plants also influences the extent of Cd accumulation (Li et al. 2005).

The SOM is also a significant factor in influencing the retention/availability of Cd to the plant systems. It has the capacity to change the exchangeable metal fraction to OM-bound fraction, thus preventing their entry into the plant systems (Pardo et al. 2014; Al Mamun et al. 2016). The sorption of Cd to the organic matter is by the binding to the different surface functional groups such as phenolic, carboxylic, and hydroxyl groups. Given below is the simple equation explaining the sorption of Cd with the functional group (R—OH) and ultimately increasing the $H^+$ ions.

$$Cd^{2+} + R\text{-}OH = Cd\text{-}RO + H^+$$

It is worth mentioning that adding of OM may also result in higher Cd immobilization by providing competing cations (Clark et al. 2007); however, sometimes the competing cations such as Ca may likely adsorb on the materials like clay minerals and increase the Cd availability, thereby inducing phytotoxicity (Degryse et al. 2009). Based on the different soil textures, the average Cd may differ; in general, the clay has 0.2–0.8 mg Cd $kg^{-1}$; in sandy soils, it is found to be in the range of 0.01–0.03 mg $kg^{-1}$, whereas in organic soils, it is 0.2–2.5 mg $kg^{-1}$ (Kabata-Pendias 2010).

The bioavailability of Cd also gets influenced by the type of plant species (Mench and Martin 1991). In soil, Cd predominantly exists in the form of $Cd^{2+}$, whereas in plants it is found in the form of chelates (Tudoreanu and Phillips 2004). The plants can secrete unique chelating materials such as phytosiderophores and other root exudates (Mench and Martin 1991). The phytosiderophores are in general secreted by many graminaceous varieties including wheat, barley, rice, etc. as well as by almonds under Fe deficiencies; these phytosiderophores are mainly secreted for mobilizing the Fe in solubilized form (Reichard et al. 2005). However, most of these phytosiderophores are reported to remain in complex with many metals including Cd and thus enhancing the entry of Cd to plant systems. Similarly, the root exudates also affect the bioavailability of metallic minerals especially in the rhizosphere (Dong et al. 2007). In addition to the routine chelation/complexations, the root exudates can influence the Cd bioavailability by modifying the rhizospheric pH as well as by modifying redox potentials (Eh). Numerous plant exudates are reported to be organic acids that are readily associated with the complexes of metal ions in the rhizospheric regions. Cieśliński et al. (1998) documented the increase in Cd uptake by plants mediated by solubilizing particulate-bound Cd into the soil solution. In a similar study, the organic acid exudates by *Zea mays* induce the Cd bioavailability, mobilization, and accumulation in the plant system (Nigam et al. 2001; Han et al. 2006). Further, coupling with the alteration in Cd behavior, the organic acids even alter the microbial community compositions of the rhizosphere which may also contribute to plant beneficiary functions (Shenker et al. 2001; Dong et al. 2007).

For instance, the microorganisms have the ability to exudate many chelating compounds or siderophores (Neubauer et al. 2000) which help in altering Cd behavior (Dimkpa et al. 2009). A bacterium could make many kinds of siderophores but not limited to carboxylic acids and hydroxomates (Klumpp et al. 2005); these are able to desorb the Cd (Hepinstall et al. 2005). Besides, microbes can further decrease the Cd solubility by forming insoluble metal sulfides as well as Cd sequestrations via cell wall, protein, or extracellular polysaccharides (Francis 1990; Dong et al. 2007).

The climatic changes may also be significant enough to bring changes in the Cd metal mobility and bioavailability. The climatic changes primarily influence the OM concentration which is a remarkable determinant for Cd bioavailability. Lower SOM and humid climate, which are the characteristics of arid climates, ensure high amount of OM. This OM may induce the binding of Cd to exchange complexes, especially in tropical climate conditions. Its presence associated with iron, manganese, and aluminum oxide minerals in soil profiles can limit mobility, along with the bioavailability of Cd. The temperature greatly influences the metal speciation since all the chemical reactions are highly sensitive to the changes in temperature (Elder 1988); a related 10 °C increase may influence biochemical reactions and enhance the system to reach equilibrium. Further, it affects the amounts of Cd uptake in organisms/biosystems (Prosi 1989). In addition, acid rain also affects Cd bioavailability; it directly induces the release of metals due to cation exchange with $Mg^{2+}$, $Ca^{2+}$, $H^+$, etc. (Probst et al. 2000; Hernandez et al. 2003).

## 16.5 Cd Uptake, Transport, and Accumulation in Plants

The concentrations, as well as the bioavailability of Cd, are the main determinants for its uptake by the plant system. Cd uptake by plants rather follows a similar mechanism as that of fluids and other essential nutrients like $Zn^{2+}$, $Ca^{2+}$, $Fe^{2+}$, $Mg^{2+}$, and $Mn^{2+}$ (Clemens 2006). As similar to other nutrients, Cd generally penetrates into the roots either apoplastically or symplastically or by vacuolar absorption (Benavides et al. 2005; Lux et al. 2011). In the cereal root system, the uptake of Cd is via various metal transporters including P-type ATPase heavy metal transporters (HMAs), natural resistance-associated macrophage protein (NRAMP), and Zrt- and Irt-like protein (ZIP), which have wide substrate ranges (Persans et al. 2001; Sebastian and Prasad 2014a, b, c). These transporters aid Cd uptake from apoplast and intracellular trafficking. The vacuolar transport is normally assisted by forming metal complexes; Cd-phytochelatin and Cd-organic acid complexes traffic to vacuoles with the aid of ATP-binding cassette transporter (ABC) family of proteins.

Based on the genetic makeup and the plant architectures, the Cd uptake and accumulation differ across different plants (Liu et al. 2003, Grant et al. 2008). In the same way, the accumulation by root systems differs widely with the root morphology, apices, and surface area as well as area of exposure/contact with Cd metal ions (Kubo et al. 2011). For instance, the fibrous root system of cereal plants could accumulate more Cd comparatively since their extra surface area favors more exposure and contact with metal ions. The number of the primary root differs between the cereals, thus in turn the metal uptake; rice, maize, and sorghum contain

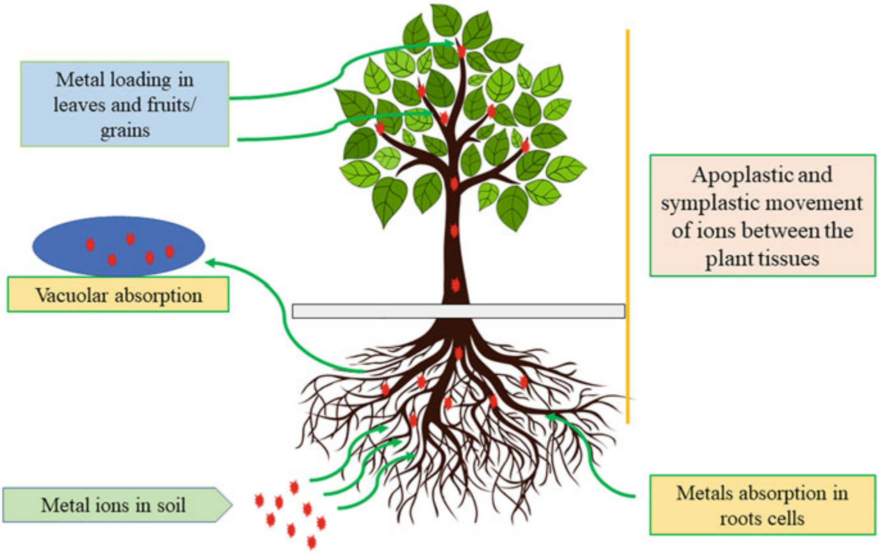

**Fig. 16.3** Scheme of metal uptake by plant roots from soil and transport to different parts of shoots

the single primary root, whereas the triticale and wheat have six to seven primary roots. Root hairs and lateral roots also play important roles in the Cd uptake by plants; the root hairs of maize and wheat can reach up to 1000 μm length. The lateral roots are generally of two types; L type (long and branching) and S type (short and non-branching). In comparison to all other cereals, the root system of maize is found to be very efficient in accumulating Cd metal ions (Rich and Watt 2013).

Further, the Cd ion competes with the other related mineral elements for plant uptake and subsequent accumulation (Roth et al. 2006) (Fig. 16.3). In general, Cd uptake decreases in the presence of Zn due to a strong competition in the uptake between Cd and Zn. This is because both are divalent cations and belong to the group II B transition metals with similar configurations (Nieboer and Richardson 1980); moreover, the presence of a saturable component suggests that $Cd^{2+}$ and $Zn^{2+}$ move via the saturable cation transporter in the plasma membrane. For instance, Hart et al. (2002) reported that in bread and durum wheat, $Cd^{2+}$ and $Zn^{2+}$ shared a common transport system at the root cell plasma membrane for their uptake.

In addition, the Zn deficiency may result in the damage of the plasma membrane thereby increasing membrane permeability (Cakmak and Marschner 1988), which may lead to the Cd uptake and accumulation in the plant system. Besides, the Zn deficiency may also increase the root exudation including amino acids, phenolics, and sugars in graminaceous and dicotyledonous plant systems which may also increase the Cd bioavailability by simply chelating the metal ions (Zhang et al. 1991). Also, the Zn-deficient conditions may increase the phytometallophore efflux in the cereal root system and increase the Cd bioavailability (Welch and Shuman 1995). The deficiency of certain elements like Fe or the presence of some toxic element like Al stimulates plants to secrete the metal chelators which in turn increases the Cd metal content in the roots (Sebastian and Prasad 2014a, b, c).

In general, the Cd ions tend to retain in the roots, and only a modest portion is actually translocated to shoots depending upon the plant types (Abe et al. 2008; Gill et al. 2011). The Cd distribution from belowground (roots) to aboveground (shoots/ leaves) plant parts is driven by means of plasma membrane transporters (especially diverse transporters like Fe) enabling xylem/phloem loading (Nakanishi et al. 2006; Ong et al. 2016; Ibrahim et al. 2017); further, it is an unaggressive method which is motivated by the process of plant transpiration.

However, the major transport and dislocation of Cd ions depend mainly on the Cd species and plant genotype (Dunbar et al. 2003). It has been suggested that the transportation of Cd from xylem to phloem occurs at the nodes of cereals. There are many earlier reports that proposed different mechanisms for Cd distribution inside the plant shoot tissues. For instance, Zorrig et al. (2010) reported the involvement of citrate molecule for engaging Cd transportation inside the xylem vessels, whereas Van der Vliet et al. (2007) observed that the Cd translocation was mainly occurred by the symplastic path in durum grain crop. Xylem-mediated loading of Cd was found to be the key process for Cd translocation from roots to shoots in many plants (Uraguchi et al. 2009). Jiao et al. (2004) postulated that Cd concentrations are normally very low in the edible portions like seeds and grains than the rest of the plant tissues as there is a necessity to cross many plasma membranes either through xylem or phloem. The Cd accumulation in the grains is mediated through the phloem-mediated transportation from leaves to the stalks during the maturation; however, Cd content in grains is directly proportional to the Cd concentration in leaves (Greger and Löfstedt 2004; Liu et al. 2007; Yoneyama et al. 2010). Uraguchi and Fujiwara (2012) reported that yellow stripe like phloem transporters were responsible for Cd accumulation in grains; further, they documented the remobilization of Cd to grains from leaves in cereal crops. The metal-chelating peptides like phytochelatin help in remobilization of Cd to grains (Yan et al. 2018).

The presence or absence of certain mineral nutrients directly influences the Cd uptake in plant systems. A study by Cheng et al. (2016) observed elevated Cd accumulation in wheat plants after amending with the nitrogen fertilizer, while Shao et al. (2018) found that the accumulation of Cd was lowered with the higher grain content of K, Mg, Cu, and Mn in rice plants. Corguinha et al. (2015) reported that among the cereals, the grains of maize plant were found to accumulate the higher Cd followed by wheat and rice.

## 16.6 Toxic Effects of Cd in Plants

Cd does not have a known role in biological functions, rather it is very toxic for plant systems (Marschner 1995). Among the known poisonous metallic elements, Cd is reported to create many problems in the living system as this element is highly toxic even in very low quantity, provided it is highly soluble in water (Benavides et al. 2005). Cd concentrations greater than 5–10 g kg$^{-1}$ dry matter are considered to be highly toxic to most of the plants (White and Brown 2010). The higher Cd concentration in the plants growing in Cd-polluted soil induces several problems, directly and indirectly, affecting the whole lifecycle of the plant from the seed germination till the withering (Shaw et al. 2004; Nagajyoti et al. 2010); it includes reduced germination, reduced pigmentation and photosynthesis, reduced hydration in plants, generation of ROS and obstruction in antioxidant cascades, enzyme inactivation, protein denaturation, damages to the lipids and cell wall, and ultimately plant necrosis (Bose and Bhattacharyya 2008; Guimarães et al. 2008). The overall damages that are induced by the Cd accumulation in the plant system are highly determined by two factors: (i) the concentration of Cd in the surrounding soil solution and (ii) the defense mechanisms developed by the plant system. However, in general, the concentration of Cd in the plant tissue is directly proportional to the presence of this element in the soil solution (Harangozo et al. 2012; Liang et al. 2013). Further, the mobility and bioavailability of this element used to be higher under the prevailing acidic conditions of the soil (Guimarães et al. 2008).

### 16.6.1 Effects on Seed Germination

Seed germination is the major event in the life cycle of a plant which is the determinant of plants' willingness to take environmental exposure to reach its reproductive maturity and bears its own seeds. The Cd toxicity affects the germination, reducing expression of α- and β-amylase activity, respiration, and cell division, thereby limiting the growth of the embryonic axis and radicle (Chugh and Sawhney 1996; Shaw et al. 2004; Nagajyoti et al. 2010). The Cd effects on germination depend on its concentration in the surrounding medium and plant genotype (Cheng et al. 2008; Kuriakose and Prasad 2008). Upon imbibition, the testa of the seed becomes more permeable leading to the increasing Cd accumulation in the inner tissues (Sfaxi-Bousbih et al. 2010); thus the genotypic variations of the seed coat and its permeability are considered to be the important factors that determine the Cd accumulation and directly seed germination (Ahmad et al. 2012; Liu et al. 2012). A study reported that the germination of *Trigonella foenum-graecum* seeds was strongly inhibited by Cd at 10 mg $L^{-1}$, the effect of which was comparatively higher than that of chromium (Cr) and lead (Pb) employed (Alaraidh et al. 2018). Similarly, the seed germination of *Triticum aestivum* was strongly inhibited by Cd even at lower concentration than that of the Pb (Titov et al. 1996). Adding 1 mM of $CdCl_2$ results in the complete inhibition of rice seed (*Oryza sativa* cultivar Hwayeong) germination (Ahsan et al. 2007). In contrast, the seeds of *H. vulgare* were found to be more tolerant to Cd; their germination rate was fully inhibited when Cd was applied at the concentration of 9.5 mM $CdCl_2$ (Munzuroglu and Zengin 2006). The Cd tolerance of germination mostly differs even within the plants of the same species (*T. aestivum* and *O. sativa* cultivars); some cultivars still stabilize to germinate vigorously even in higher concentrations of Cd, whereas others fail to germinate. Interestingly, under 0.5 mM $CdCl_2$, most of the tested *O. sativa* cultivars had better performance in germination compared to the control seeds (Cheng et al. 2008).

Similarly, Lefevre et al. (2009) observed the germination of *Dorycnium pentaphyllum* Scop. seeds in the presence of Cd at 10 μM $CdCl_2$; however, when exposed to higher concentration of Cd (1 mM $CdCl_2$ for 17 days), only 40% germination rate was recorded. This indicates that Cd at low concentrations stimulates seed germination.

There are several proposed mechanisms by which the Cd inhibits seed germination. For instance, by impairing the water uptake, Cd inhibits the germination in seeds of *Vigna unguiculata* (Vijayaragavan et al. 2011), whereas He et al. (2008) proposed that the inhibition in the germination was by the replacement of Ca ions and thus affecting the amylase activity and normal enzyme functioning. Furthermore, in radish seeds, direct competition for Ca-calmodulin binding sites occurred between Ca and Cd ions (Rivetta et al. 1997). The Ca-calmodulin interaction plays important role in metabolic activation during the early phase of seed germination (Cocucci and Negrini 1988). It also increases the malondialdehyde (MDA) content in *P. sativum* embryos causing lipid peroxidation and generation of ROS (Jalmi et al. 2018; Cuypers et al. 2016). In *P. sativum* seeds, the Cd-induced oxidative stress may be able to oxidize thioredoxins (Trx) isoforms, an important protein for monitoring redox states in both cereals and dicotyledons (Alkhalfioui et al. 2007). Further, the intracellular oxidative stress in seeds may ultimately lower the glutathione (GSH) levels and glutathione reductase (GR) activities (Smiri et al. 2011).

### 16.6.2 Effects on Plant Growth and Biomass

The Cd accumulation in the plant system affects its growth and biomass yield owing to its toxic effects on different physiological and morphological processes (Benavides et al. 2005; Sharma and Dubey 2007). Khan et al. (2013) observed the alteration of the plant nucleus under Cd stress due to the generation of ROS; ROS ultimately results from the plasma membrane-bound NADPH oxidase activity indicating the changes in the roots as the very first sign of Cd stress. Reduction in root length is primarily the visible indicator of Cd toxicity in plants (Lux et al. 2011). Elevated Cd levels in the root base multiply the development involving the endodermis of the roots and furthermore transform the relative size, along with proportion, of the root tissue (Seregin et al. 2004; Lux et al. 2011). The higher Cd exposure tends to retard the root group by inducing damages in the root tip (Zhan et al. 2017); it must be due to the loss of integrity of cells at the root tip. Further, the prolonged Cd exposure results in the browning of the main root and associated rigidity and twisting as well as inhibition of lateral root formations (Yadav 2010; Rascio and Navari-Izzo 2011). The Cd toxicity also brings the anatomical changes in the roots such as the callose deposition in the cortical and epidermal cells (Benavides et al. 2005; Piršelová et al. 2012). The Cd exposure also induces mucilage secretions in the roots (Benavides et al. 2005). It is imparted by the distorted divisions and abnormal cortical and epidermal enlargements in the root apices. Rascio et al. (2008) documented the inhibition of root growth and altered morphogenesis in the rice seedlings when they were exposed to Cd. In pea plants, the Cd stress induces abnormal mitosis and root elongation as well as chromosomal aberrations in the root tips (Siddiqui et al. 2009). Similarly, after 24-h exposure to Cd in *Allium cepa*, it causes the chromosomal and mitotic aberrations with the inhibition of mitotic index and micronucleus formation; further, DNA damages in the root tip was also notified (Seth et al. 2008). In contrast, a previous experiment reported that the lower Cd exposure and treatment increased the number of root hairs in rice plants by inducing the production of superoxide and nitrous oxide and inducing ethylene signal transduction pathway (Abozeid et al. 2017), while higher dosages of Cd treatment retarded the growth of root hairs (Lux et al. 2011). The Cd concentrations were found to be higher in the cortical region than that of pericycle and endodermis, hence the primary site of contact for Cd. The accumulation of Cd is normally higher in the fibrous root system (e.g., cereals), whereas it is relatively lower in the taproot system (dicotyledons) (Sebastian and Prasad 2019).

Various experiments on Cd toxicity in plant systems revealed a significant reduction of overall growth and biomass yield (Samardjieva et al. 2015; Hammami et al. 2016). However, the major hazardous effects of Cd depend on the plant species as well as the duration of exposure and concentration levels (Das et al. 1997; Di Toppi and Gabbrielli 1999). Chiraz Chaffei (2012) reported the reduction of tomato root and shoot biomass in a hydroponic media with increasing Cd concentrations. Wójcik and Tukiendorf (2005) documented the reduced biomass as a result of Cd toxicity in *Thlaspi caerulescens*. Shivhare and Sharma (2012) in their investigation of Georgina wild (*Dahlia* sp.) to Cd exposure noticed decreased shoot and root elongations and thus reduced growth and development. The disturbances of photosystems and photosynthesis leading to the reduced growth of maize due to the Cd were observed by Rizwan et al. (2017a, b). Similarly, the excess concentration of Cd reduced fresh weights of wheat leaves, shoots and roots (Azooz et al. 2012), and maize seedlings (Dresler et al. 2014), ultimately reducing growth and biomass yield. The Cd exposure may also cause stunted growth in many plants; the important reason behind this is the induced denaturation of important proteins mainly in the H–S (hydrogen–sulfur) bond by Cd metal ions.

### 16.6.3 Effects on Photosynthetic Pigments

The prolonged uptake and accumulation of Cd in the leaves results in the reduction of crop productivity by directly affecting photosynthesis (Sebastian and Prasad 2015a, b; Paunov et al. 2018). It may occur in many ways including net reduction of photosynthesis, chlorophyll, and carotenoids (Vijayaragavan et al. 2011; Chiraz Chaffei 2012). In the cucumber (*Cucumis sativus* L.) plant, the Cd exposure resulted in the damage of photosynthetic machinery and nitrate metabolisms (Feng et al. 2010). A similar result of reduced photosynthesis and nitrate metabolisms was also observed by Gill et al. (2012) in garden cress (*Lepidium sativum* L.) due to Cd exposure. The reduction in the stomata conduction and photosynthetic pigmentations was observed while treating the peanut (*Arachis hypogaea*) plants with Cd (Shi and Cai 2008). López-Millán et al. (2009) documented the exposure of

Cd on tomato plants (*Lycopersicon esculentum*); in the lower exposure levels (Cd $\leq$100 μM), the photosynthesis was not affected, whereas at higher levels (Cd $\geq$10 μM), it affected the photosynthetic pigmentation and complete photosynthesis. Recently, Chu et al. (2018) observed damages to the electron acceptor of photosystem II in *Schima superba* when they are constantly subjected to a higher concentration of Cd. The visual symptoms of chlorosis due to the reduced photosynthetic pigments (chlorophyll a, b, and carotenoids) were noticed by Dogan et al. (2018) while exposing aquatic plants (*Ceratophyllum demersum* L.) to Cd.

Baryla et al. (2001) observed chlorosis in oilseed rape on Cd exposure, but they claimed that the chlorosis is not due to the direct interaction of Cd with biosynthetic pathway rather as a result of decreasing chloroplast density. The decrease in pigment due to the Cd is primarily at the leaf surfaces (stomatal guard cells) rather than in the mesophyll. The Cd also causes changes in the cell size and reduction in stomatal densities of the epidermis; this implies that the Cd might reduce the stomatal conduction and directly interfere with the cell division and chloroplast replications. The Cd-induced retardation of photosynthesis might be due to the effect on linear electron transport and decreased RuBisCO activities. The blocking of light reactions is a well-known reason for photooxidative stress induction in plants, thus hindering the photosynthetic light reaction under Cd stress found to accelerate the photooxidative stress in plants, causing the bleaching of plant pigments like chlorophyll (Sebastian and Prasad 2019).

### 16.6.4 Effect of Cd on Mineral Nutrition

Cd has been shown to interfere with the uptake, transport, and use of several related elements such as Ca, Mg, P, K, and even water by the plant system (Das et al. 1997). However, the replacement with the minerals and associated harmful effects depend on the type of plants and nutrients as well as the intensity of Cd stress (Dong et al. 2006; Street et al. 2010). It was reported that the Cd caused deficiency of Fe in sugar beet (Chang et al. 2003), whereas the uptake of several minerals (P, K, S, Ca, Zn, Mn, and B) was inhibited in pea plants upon Cd exposure (Metwally et al. 2005). Guo et al. (2007) documented in their study about the Cd exposure to barley roots where exposure with 1.0 μM Cd decreased the minerals (P, K, Ca, Mg, Cu, Fe, Mn, Zn, Mo, and B) in roots; contrarily, their concentrations in the shoots were not affected corresponding to control plants. Alterations in the uptake of Ca and K by Cd were observed in a Cd hyperaccumulator, *Atriplex halimus* subsp. *schweinfurthii* (Nedjimi and Daoud 2009). Chiraz Chaffei (2012) reported the diminution in the uptake of $K^+$, $Ca^{2+}$, and $Mg^{2+}$ ions in shoots of tomato crops when they got exposed with higher Cd (50 and 100 μM). A study also revealed the reduced uptake of Cu, Zn, and Mn levels by Cd in soybean plants; however, it didn't have a major impact on the shoots (Dražić et al. 2004). In comparison, Zhang et al. (2002) reported that after exposure to Cd, levels of K, P, and Mn within the wheat grain increased and the translocation of Cd to shoots decreased. In the same way, it was also suggested that deficiency in essential elements might increase Cd level and toxicity in crop plants.

For example, Ca deficiency increases Cd toxicity in rice seedlings (Cho et al. 2012). Hernandez et al. (1996) reported that by inhibiting the nitrate reductase, the Cd reduced the uptake of nitrate and its transportation in the shoots. Similarly, a notable inhibition of nitrate reductase was observed in the plants of *Silene cucubalus* (Mathys 1975). Balestrasse et al. (2003) documented the reduction in the nitrogen fixation and primary ammonia assimilation in the root nodules of soybean when they are exposed to Cd.

However, it is not completely clear how the Cd inhibits the uptake of other elements in the living systems. In maize, Cd treatment induces an inhibition of $H^+$ATPase in root cells. $H^+$ATPase is an integral protein of plasma membrane found in epidermal and cortical cell layers of root tissues functioning as a major ion transporter across plasmalemma by electrochemical gradient; hence impairment of which resulted in the adsorption of some essential elements into the plant system (Astolfi et al. 2005). Solti et al. (2011) reported the inhibitory effect of Cd on mineral nutrition by exhibiting the competition with other related metal ions in poplar plants (*Populus jaquemontiana* var. *glauca*). It is well known that several plant nutrients have direct as well as indirect influences on the effects of Cd phytoavailability and associated toxicity. The direct effects include the decreased Cd solubility by inducing the precipitation/adsorption (Matusik et al. 2008), competing with the Cd by other plant nutrients for the same transport channels (Zhao et al. 2005), and Cd sequestration within the vegetative parts of the plant rather than edible parts (Hall 2002), whereas the indirect effects include diluting the Cd concentration by positively influencing the higher biomass production and alleviation of other physiological stresses.

### 16.6.5 Effect of Cd on Stress Proteins

The extremities in the environmental changes could cause the alteration in the plant gene expression by modifying the diversity of proteins in the cell. These protein-related changes in the plant system due to the stress can be used as the molecular markers for manifesting the stress responses in organisms. The proteomics approaches have been developed as the important methods for research on plant stress tolerances (Nanjo et al. 2011). Rodríguez-Serrano et al. (2009) observed the presence of pathogen-related proteins PrP4A and HSP71 in pea plants as a response for protecting cells against the damages induced by Cd treatment. A 51-kDa-soluble protein was found in wheat seedlings that were exposed to 50 μM $CdCl_2$ for 48 h, which might be the Cd stress-associated protein response. Further, this soluble protein was found below the plasma membrane and the outer periphery of the tonoplast of root tissues that were exposed to Cd (Mittra et al. 2008). In another experiment with poplar (*Populus tremula* L.) plants, the surge of stress-related proteins like HSPs, proteinases, and pathogenesis-related proteins was observed in the leaves with both short-term (14 days) and long-term (56 days) Cd exposures. Moreover, only the abundance of stress-related proteins was noticed, whereas the proteins involved in the primary metabolisms (glycolysis, tricarboxylic acid cycle, nitrogen metabolism, and sulfur metabolism) were seriously decreased (Kieffer et al. 2009). The exposure of Cd in the rice plants found to affect the synthesis of 36 different essential proteins (Lee et al. 2010); in roots, 16 proteins were synthesized with an absence of 1 protein, whereas in leaves 16 proteins were upregulated, and 3 were found to be downregulated. Similarly, Rodríguez-Celma et al. (2010) reported the exposure of tomato plants to 10 μM Cd concentration-induced changes in 36 different polypeptides, whereas the effect was still stronger with prominent changes in 41 polypeptides at the higher level (100 μM) of Cd exposure.

### 16.6.6 Generation of ROS, Responses of Antioxidant Molecules, and Oxidative Damage in Plants

The HM uptake in plants generally resulted in oxidative damages to the plant tissues either by directly or indirectly generating ROS. As Cd is not a redox-bivalent element, it does not directly take part in Haber-Weiss and Fenton reactions like copper and iron; but still it could indirectly generate ROS [superoxide anion ($O_2^{\bullet-}$), hydrogen peroxide ($H_2O_2$), hydroxyl radical ($OH^{\bullet}$), and singlet oxygen ($^1O_2$)] (Gratão et al. 2005; Wu et al. 2015). There are three proposed pathways by which Cd toxicity may induce ROS generation: (1) by deploying and replacing the Fe from proteins, Cd results in free redox-active elements which can generate ROS abundantly; (2) by inducing NADPH oxidase via electron derivation, it could generate $O_2^{\bullet-}$ from $O_2$; (3) by binding with the compounds having –SH group such as glutathione (GSH), it can decrease the scavenging of ROS (Cuypers et al. 2010). The Cd-induced ROS result in the interaction with proteins, lipids, and nucleic acids inducing membrane damages and lipid peroxidation and obstructing cellular metabolisms (Romero-Puertas et al. 2007). Hence, as an initiative to scavenge the generated ROS as well as to avoid oxidative stress-related damages, the plant system tends to activate the defense mechanisms by upsurging enzymatic and non-enzymatic antioxidants. It includes (i) enzymatic antioxidants: superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX), monodehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR), peroxidases (POD), glutathione reductase (GR), etc. and (ii) non-enzymatic antioxidants: glutathione (GSH), ascorbic acid (ASA), carotenoids, tocopherols, etc. (Gill et al. 2011; Etesami 2018).

However, antioxidants' efficiency is majorly determined by the type of plant species as well as by the amount of accumulated Cd inside the systems. The SOD normally catalyzes the dismutation of superoxide anion radicals into two molecules such as oxygen and hydrogen peroxides (Dixit et al. 2001). The reaction takes place in two steps including reduction and oxidation of metal enzymes in the catalytic center (Gill et al. 2011). SODs are of different types according to the metal element in their active sites; for instance, it may be of Cu/Zn–SODs (copper and zinc), Mn–SODs (manganese), and Fe–SODs (iron). Each SODs display distinct subcellular localization, expression regulation, and structural features including distinct protein fold. In plants, the Mn–SODs are found to localize in the mitochondria and Fe–SODs in chloroplasts, whereas Cu/Zn–SODs in the cytosol/chloroplasts (Gill et al. 2011; Miller 2012). The Cd exposure in many plants increased the SOD activities; for example, in pea (Sandalio et al. 2001), wheat (Milone et al. 2003), and bean (Cardinaels et al. 1984) plants, the SOD levels were found to increase after Cd exposures. Shah and Nahakpam (2012) documented the efficiency of SODs against the Cd stress in rice plants: six SOD isozymes were detected in the tolerant cultivar (*Bh-1*) varieties, and three isoforms were observed in the sensitive cultivar (*DR-92*) when compared to corresponding control plants. In another experiment, Yu et al. (2017) studied the genotypic expression of pak choi cultivars on Cd exposure; in a high tolerant variety (Baiyewuyueman), higher levels of expression of 10 different ROS-scavenging genes including Cu/Zn–SOD were observed than that of sensitive variety (Kuishan'aijiaoheiye).

The oxidoreductase enzymes such as CATs and PODs favor the protections against stress by dismutation of hydrogen peroxides to oxygen and water molecules (Vidossich et al. 2012; Yousuf et al. 2012). Almost in all eukaryotes, CATs exist as homotetramers comprised of an active heme group in the center and four subunits with NADPH molecules (Lukacová et al. 2013); moreover, it has three isomeric forms represented as CAT1, CAT2, and CAT3 (Dong et al. 2006). The CAT2 form was found to be dominant in places of significant production of hydrogen peroxide (cytosol, peroxisomes, and glyoxysome) (Gill et al. 2012), whereas the CAT3 form is predominantly seen in younger plant tissues catalyzing $H_2O_2$ decomposition resulting from fatty acids (Zhang et al. 2009). The variable activity of CAT has been observed under Cd stress. Yılmaz and Parlak (2011) reported that CAT offered higher tolerance to the Cd stress for *Groenlandia densa* plants.

A decrease in the POD activity with respect to the Cd exposure was observed in mustard (*Brassica juncea*) (Markovska et al. 2009), and an increased POD level was found in radish (*Raphanus sativus* L.), whereas no significant change was noticed in pea plants (El-Beltagi et al. 2010). APX is a crucial enzyme in the ascorbate–GSH cycle, where two molecules of ascorbate reduce the $H_2O_2$ resulting in water molecules and monodehydroascorbate (Meng et al. 2009). Gill and Tuteja (2010) reported that under Cd stress, an increased level of leaf APX activity was found in *Ceratophyllum demersum*, mustard, wheat, and black bean. In another similar study, the higher dose of Cd induced increasing levels of APX in *Phaseolus* (Dat et al. 2000). Markovska et al. (2009) found the increased activities of MDHAR and DHAR in mustard plants exposed to 10 μM Cd. The major role of GR is to offer protection against cellular damages during oxidation by scavenging the ROS (Verma et al. 2008). An increase in GR activity was found in cotton, *Arabidopsis*, blackgram, wheat, and mustard upon Cd treatment (Markovska et al. 2009; Gill and Tuteja 2010). Under Cd stress, increased GSH levels and antioxidant activities have been found in the leaves and chloroplast of *Phragmites australis* Trin. (Cav.) ex Steudel. The increasing GSH was found to be in direct proportion to the increasing Cd concentration in pea, *Sedum alfredii*, and black beans. Metwally et al. (2005) reported that the decreasing GSH levels weakened the antioxidant defenses against Cd stress in sensitive genotypes like pea plants. Ascorbate, a powerful antioxidant, was found to interact with singlet oxygen, organic peroxide radicals, hydrogen peroxide, superoxide, and hydroxyl radicals, occurring in the cytosol, vacuoles, chloroplasts, mitochondria, and peroxisomes in order to overcome Cd stress (López-Millán et al. 2009; Wahid et al. 2007). Another antioxidant, tocopherol, is a hydrophobic molecule that commonly resides in biological membranes and mainly encounters the reduction of peroxides and singlet oxygen (Redondo-Gómez et al. 2010); during their reaction with the radicals, sometimes it leaves behind the less reactive tocopherols which is further removed out of the system by other antioxidants like GSH and ascorbates (Meng et al. 2009). Carotenoids can quench the triplet chlorophyll, can help in preventing excessive production of ROS, and also can react with lipid radicals (Verma et al. 2008). Flavonoids in turn inhibit the activity of lipoxygenases and also the substrates for other enzymes including PRXs (Wahid et al. 2007). The antioxidant functioning in plants may also be attributed to substances like proline, mannitol, and sorbitol (Gomes et al. 2013). A study by Islam et al. (2009) reported the role of proline as an antioxidant in tobacco (*Nicotiana tabacum* L.) plants; it was documented that the elevated levels of proline under Cd stress were found to alleviate the inhibitory effects on cell growth.

Excessive ROS generations with subsequent oxidative stress appear to be major causes of Cd-mediated cytotoxic and genotoxic effects in plants (Verma et al. 2008; Xu et al. 2012). Lipid peroxidation was found to be the major effect of Cd-mediated oxidative stress (Ge et al. 2012), which leads to the disruption in the integrity of biological membranes; further, Cd was also found to alter the total lipid composition in plant tissues by inducing ROS-mediated lipid peroxidation. The ROS-mediated damages alter the membrane permeability and membrane lipid composition and result in increased metal uptake, obstruction in electron transport systems, and ultimately the cell metabolisms (Qadir et al. 2004; Zou et al. 2009). MDA, a product of membrane polyunsaturated fatty acid decomposition, serves as a reliable indicator for oxidative stress in tissues. Further, the Cd-induced oxidative damage results in the denaturation of lipid, DNA/protein, and ultimately plant death (Choppala et al. 2014; Liu et al. 2016). The DNA damage by Cd involves the destruction of nucleic acids, cell membrane, lipids, and proteins, resulting in reduced photosynthesis, protein synthesis, growth, and development of the whole organism. DNA damage has also been defined via the determination of the frequency of abnormalities such as fragments, precocious separation, laggards, single and double bridges, and stickiness (Gill and Tuteja 2010; Kranner and Colville 2011). In addition, the supplementation of $PO_4$ could boost up the oxidative damage of the membrane, proteins, and DNA since they are believed to be associated with the uptake of Cd by plant systems (Jiao et al. 2004).

## 16.7 Potential Health Risk from Dietary Intake of Cd

As per the Agency for Toxic Substances and Disease Registry (ATSDR), the metal Cd was ranked as the seventh highly toxic and dangerous element (ATSDR 2017). The most extensive exposure to this metal is via inhalation and ingestion from various sources including cigarettes, metal, and other industries employing Cd as well as some agricultural foodstuff (IARC 1990; Paschal et al. 2000). The workers in the mining, paint, and battery factories are constantly exposed to the dust and fumes containing Cd; they are the most vulnerable occupational groups. Second are the cigarette smokers since each cigarette contains approximately 1.5–2 μg and about 10% of it can easily go with the smoke (Järup et al. 1998); hence it is evident that compared to non-smokers, the levels of Cd used to be 3–4 times higher in smokers (Mortada et al. 2004; Galażyn-Sidorczuk et al. 2008). In general, the Cd exposure in non-smokers is mainly contributed by dietary input (Clemens et al. 2013). The amount of Cd from foodstuffs normally ranges from 10 to 25 μg, but it varies with different environmental Cd rates. For instance, in Japan, the Cd consumed from the foodstuffs is 28 μg day$^{-1}$ compared to 9.9 μg day$^{-1}$ in China and 9–10 μg day$^{-1}$ in Germany (Kikuchi et al. 2003). As the Cd leaching is a very slow process, the drinking water usually contains Cd in very low quantities ($\leq$1 μg L$^{-1}$) (Méranger et al. 1981; Lim et al. 2013). Since Cd is highly toxic, as per the standards by WHO, the provisional drinking water must not exceed 10 μg L$^{-1}$ (WHO 2017).

The increased Cd levels in the agricultural soil and their entry into the food chain through biological uptake cause toxicological-related problems in human beings (Islam et al. 2014; Roy and McDonald 2015; Rizwan et al. 2016a, c; Rizwan et al. 2017a) (Fig. 16.4). The Cd biomagnification in humans is generally through the staple food crops like rice and other cultivars (UNEP 2010a, b). For instance, rice grains in different areas account for various concentrations of Cd dietary intake; in the Europe population, it accounts for less than 27% (EFSA 2012), and in Japan, it is 44% (Watanabe et al. 2000), whereas it is as high as 56% in China (Song et al. 2017). The major reason for rice to contribute high dietary intake of Cd is that (i) it is recognized as the major staple food especially in Asian countries and (ii) uptake of Cd in rice grains is very high compared to other related cereals (Song et al. 2017). The dietary Cd intake of China was found to be doubled from 6.9 to 15.3 mg kg$^{-1}$ BW month$^{-1}$ over the last 25 years (from 1990 to 2015) (Song et al. 2017; Wang et al. 2017), and that clearly indicates that the limit exceeds above the Provisional Tolerable Monthly Intake (PTMI) values recommended by the ATSDR of the USA (3 mg kg$^{-1}$ BW month$^{-1}$) (ATSDR 2008) and the European Food Safety Authority (10.8 mg kg$^{-1}$ BW month$^{-1}$) (EFSA 2012). Leafy vegetables, tubers, nuts, and oil seeds especially account for the higher accumulation of Cd.

Various reports documented the exceeded dietary limits of Cd and their toxicological effects in human beings so far (Valko et al. 2007; Chen et al. 2008; Stasenko et al. 2010; Sughis et al. 2011; Costa 2016; Vickers 2017). Children are found to be more susceptible to Cd toxicity as compared to the adults since even a minor concentration of Cd leads to serious health issues (ATSDR 2017). In general, the toxicological effects are mainly due to the higher biological persistence, nonbiodegradability, and the ability to accumulate in various tissues and the inability to remove it out of human systems (Goering et al. 1995). Cd has a long biological half-life of 10–30 years, and their concentration in the human system tends to increase with age; the major organs that accumulate Cd in the human body are the kidney and liver (JECFA 2011).

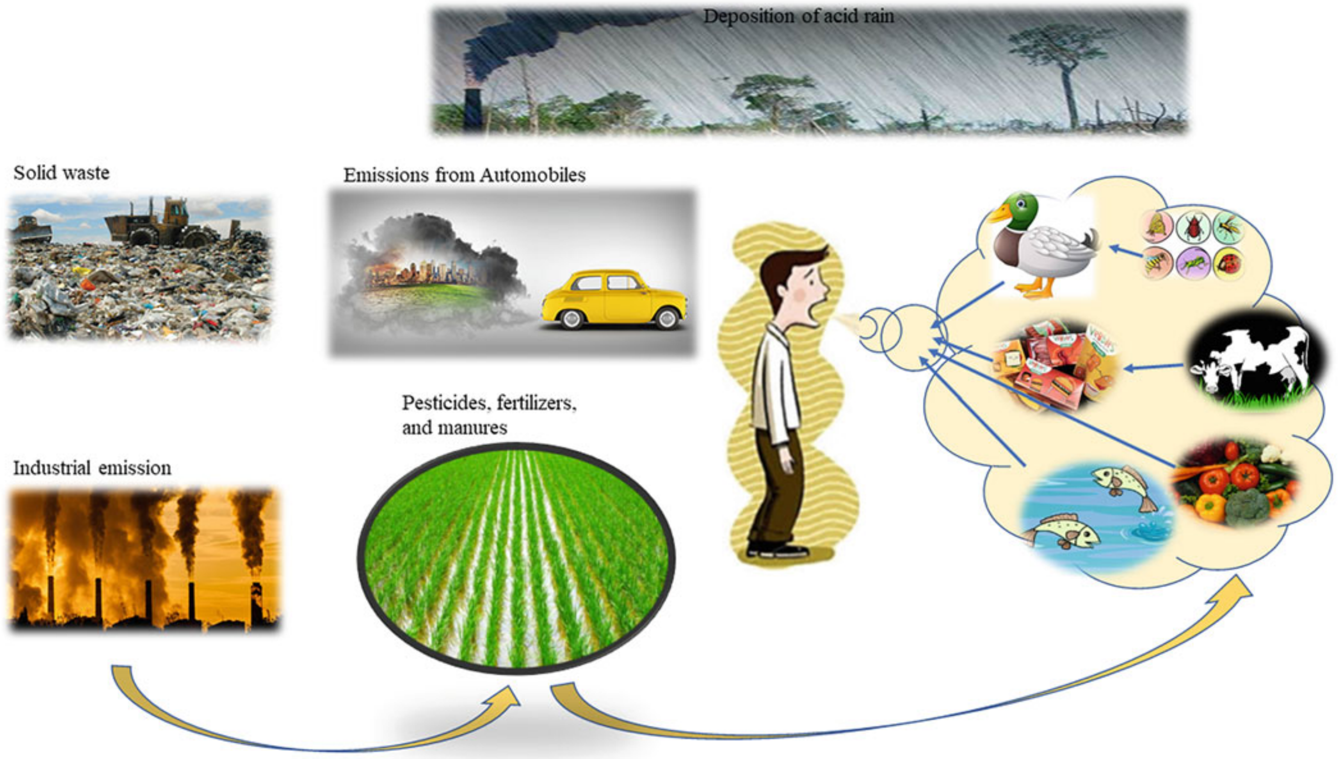

**Fig. 16.4** Schematic diagram of soil pollution by Cd and its accumulation in plants and entry in the food chain

The long-term exposure and accumulation of Cd result in irreversible kidney damages, osteoporosis, and demineralization of bone as well as low bone density as $Ca^{2+}$ is easily replaced by $Cd^{2+}$ (Hu and Cheng 2012; Zhang et al. 2014; Zhang et al. 2016). Furthermore, Cd has been designated as the Group I carcinogen by the International Agency for Research on Cancer. Prolonged exposure to Cd can result in lung, prostate, testicular, kidney, bladder, and breast cancer (Vinceti et al. 2007; Itoh et al. 2014; El-Kady and Abdel-Wahhab 2018). By inactivating the tumor suppressor genes, Cd can initiate the deterioration of cell adhesion, apoptosis, and suppression of DNA repair mechanisms as well as affect the antioxidant mechanism by generating ROS. By mimicking Ca, Cd can easily bypass the Ca ion channels and bind with the intracellular molecules, which get accumulated in the cell cytoplasm, thereby affecting metabolic functions (Bashir et al. 2016; Redza-Dutordoir and Averill-Bates 2016). Moreover, Cd replaces many essential nutrients and totally affects many biochemical reactions and body functioning (Yang et al. 2014); for instance, by replacing the Ca ions, Cd may damage Ca metabolism, resulting in Ca deficiency-associated bone and cartilage problems (ATSDR 2008). Similarly, it substitutes Zn and causes many metabolic-related problems (Campbell 2007). It also causes Fe deficiencies by binding with molecules such as histidine, cysteine, aspartate, and glutamate ligands (Castagnetto et al. 2002). The extreme case of chronic Cd poisoning in humans causes Itai-Itai, a bone disease causing several fractures and pains, which was first discovered in the 1950s along the Jinzu River basin in Japan (Wuana and Okieimen 2011; Uraguchi and Fujiwara 2012). The benchmark limits for Cd in rice causing Itai-Itai is 0.27–0.56 mg $kg^{-1}$ for women and 0.62–0.76 mg $kg^{-1}$ for men (Nogawa et al. 2017). For the above-discussed reasons, it is imperative to address the Cd poisoning and associated health problems and the route of biomagnifications of Cd in human beings so as to avoid the Cd entry into the food chain. Hence, selection of proper cultivars, improvement in the breeding technologies, as well as reduction in Cd escalation through anthropogenic activities are important to overcome the Cd poisoning in human beings and other higher animals (Uraguchi and Fujiwara 2012; Smolders and Mertens 2013).

## 16.8 Conclusions

Heavy metal pollution has been identified as a significant concern for both the environment and human health. Unlike the other organic contaminants, metals do not undergo any chemical or biological degradation and thus persist in the environment for a long run from the time of introduction. Especially, the non-essential element Cd, with its higher half-life and toxicity, negatively affects all the living systems. The contamination of the soil with Cd has gained much attention due to the major effects on agricultural crops, such as decreased biomass and yield, obstruction in pigmentation and photosynthesis, as well as deterioration of crop quality. Further, the risk of dietary Cd via the food chain poses a sturdy threat not only to humans and higher animals but also to crop productivity and food security. Cd escalates the environment through many natural and anthropogenic sources; however, in agricultural croplands, it is because of the use of excessive agrochemicals and irrigation with untreated municipal or industrial effluents. Further, due to the complications of remediation technologies for such highly contaminated agricultural croplands, it is imperative to take incumbent measures to control the further escalation of Cd into the environment. Quantification of Cd-soil-plant interactions and the factors affecting Cd phytoavailability is of utmost importance in order to intervene the pollution status and biomagnifications via food chains and to devise suitable remediation strategies.

Immobilization is one of the most popular remediation techniques gaining a lot of attention in recent days not only from scientific communities but even also from the innovative farming communities and municipalities for soil Cd remediation. A vast list of materials have been tested for their suitability in soil Cd remediation; however, organic amendments including but not limited to compost, manure, and biochar are found to be promising because of their higher availabilities, economic viability, and environmentally friendly aspects. Besides, they not only provide Cd-free foodstuff but also improve soil fertility and crop productivity thereby assuring food security. Various research experiments revealed that among the inorganic amendments, the use of lime, phosphate fertilizers, iron, and/or aluminum oxides, silicon, and nitrogen supported Cd decontamination as well as safer food production in small-scale experiments. Nonetheless, a field-scale verification is still needed for their efficacies in their lone and co-application along with other organic amendments supporting economic efficiencies for farmers.

Moreover, it is imperative to study the plants' response against Cd stress in order to develop Cd-resistant crop varieties. Effectively integrating the conventional breeding techniques with appropriate molecular markers can help to select the Cd-resistant/low-Cd-accumulating cultivars with desirable agronomic traits. Biological remediation, such as phytoremediation, can be an environmentally friendly and cost-effective strategy for moderately contaminated soils. In general, the highly contaminated soils are not only found to have a single metal contaminant like Cd but of multiple metals or other associated contaminants. Hence, it is imperative to study the exposure of plants to multi-metal-contaminated or real-life field pollutions, which could offer new insights into the metabolic adjustments of plants.

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# Heavy Metal Concentration in Farmlands in Crude Oil Exploration Area

# 17

Felix Aibuedefe Aisien and Eki Tina Aisien

## Abstract

Crude oil exploration and exploitation activities are one of the anthropogenic sources of metal contamination in farmlands. The polluted soils pose tremendous risks and hazards to plants, microorganisms, animals, and humans, distorting the ecosystem. The effect includes reducing food quality, reducing fertile land for agriculture, food insecurity, weak plant growth, reducing beneficial soil microorganisms, increasing man's sickness and diseases, etc. The soil characterization and remediation process are required to protect and restore heavy metal-contaminated soils, and remediation is an effective decontamination process. The potential of using phytoremediation, soil washing, and immobilization for remediation of heavy metal-contaminated soils is enormous.

## Keywords

Heavy metals · Farmlands · Remediation · Crude oil · Contaminated soil · Toxicity

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## 17.1 Introduction

The primary occupation of the people of the Niger Delta area of Nigeria is crop and fish farming. Also, there are a lot of crude oil exploration and exploitation activities in this area. These activities are one of the leading causes of crude oil pollution and result in heavy metal contamination of farmlands, sediments, and surface and ground water (Aisien et al. 2009). Hence, heavy metal contamination is one of the environmental problems in oil-producing communities in the Niger Delta area of Nigeria.

Besides, heavy metals are considered essential trace elements because of their crucial roles in different biological processes. Metal such as cobalt plays a crucial role in propionic acid fermentation (Stowers et al. 2014). Emamvedian et al. (2015) reported that heavy metals such as copper, nickel, iron, molybdenum, zinc, and manganese are required for growth and reproduction in plants. However, chromium, thallium, cadmium, lead, mercury, arsenic, etc. exhibit some level of toxicity even at low concentrations (Peralta-Videa et al. 2009).

Crude oil contains some heavy metals, and these metals exhibit metallic properties and have high atomic mass and high density of at least 5 g $cm^{-3}$, and they include transition metals, metalloids, lanthanides, and actinides (Sharma et al. 2014). Koller and Saleh (2018) reported that heavy metals are chemically bound in carbonate, sulphate, oxide, silicate rocks, or metallic elemental form. Several heavy metals are found in crude oil-polluted farmlands. These include nickel (Ni), lead (Pb), vanadium (V), cadmium (Cd), zinc (Zn), manganese (Mn), etc. (MEPPRM 2014). The heavy metal component of crude oil varies depending on where the crude is sourced (Nwadinigwe and Nwaorgu 1999).

Koller and Saleh (2018) reported that although heavy metals are naturally occurring elements found in the Earth's crust, anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal compounds lead to environmental contamination and human exposure when released in the process. Nworu et al. (2019) stated that crude oil exploration activities, sewage sludge, waste disposal, and fertilizer application are considered anthropogenic sources of heavy metals in soils. The pedogenic is another source of heavy metals, which is natural occurrence of heavy metals in soil (Kabata-Pendias and Pendias 2001).

In the Niger Delta area, farmlands are polluted with crude oil, contaminating crops and exposing people to heavy metals. Therefore, the soils posed health risks and hazards to man and the entire ecosystem because the contaminated groundwater and crops are water sources and food for man and the ecosystem. This leads to consumption of contaminated water and food, food insecurity, reduction in land usability, and food quality (Bhattacharyya et al. 2008). Besides, McLaughlin et al. (2000) reported that heavy metals in the soil could seriously inhibit the biodegradation of organic contaminants. Therefore, there is the need to protect and restore heavy metal-contaminated soils through soil characterization and remediation. Remediation or cleanup involves processes of excavation, stabilization, soil washing, and immobilization techniques. These processes can reduce or eliminate heavy metal pollutants from the soil and water environment such as farmlands, sediments, surface water, or groundwater. GWRTAC (1997) stated that phytoremediation, soil washing, and immobilization techniques are considered the best heavy metal contamination remediation techniques.

## 17.2 Sources of Heavy Metals in Farmlands

The two primary sources of heavy metals in contaminated soils are pedogenic and anthropogenic. Kabata-Pendias and Pendias (2001) reported that the pedogenic source involves the natural occurrence of heavy metals in soil resulting from the weathering of parent materials in the soil environment. The disposal of high metal wastes in improperly protected landfills, fertilizer applications, animal manures, biosolids (sewage sludge), metal mine tailings, coal combustion residues, petrochemicals, etc. is an anthropogenic source of heavy metals (Zhang et al. 2010). Also, heavy metal contaminants in soil can result from crude oil exploration and exploitation activities (Aisien et al. 2009). These activities result in crude oil spillage. The causes of crude oil spillage include accidental discharge, corrosion of pipelines, equipment and facility failure, vandalization, and sabotage (Aisien 2002). These heavy metals contaminate the farmlands and crops around borrow pits, flow stations, gas flaring sites, pipeline laying sites, oil wells, etc. Extreme quantities of heavy metals may occur in the soil due to typical geographical occurrences like the nature of ore formation, decaying/disintegration of rocks, and leakage (Osam et al. 2013). MEPPRM (2014) reported cobalt, vanadium, mercury, arsenic, nickel, thallium, cadmium, copper, lead, chromium, mercury, zinc, cobalt, tin, and manganese are some of the most common heavy metals found in crude oil-polluted farmlands. Besides, heavy metals are found at low soil concentrations depending on the soil's geological characteristics in limited areas (Shubhra et al. 2015). Heavy metal contamination can occur when soil particles are swept away by wind and rain from the initial pollution areas. Once these soil particles settle, the heavy metals may spread into the surroundings and pollute the soil environment. The reasons why heavy metals become contaminants in the soil environments are:

- Higher rate of generation via artificial cycles than natural ones.
- Higher concentration of heavy metals in the discarded products compared with those in the receiving environment.
- It becomes more bioavailable in the receiving environment (D'Amore et al. 2005).

## 17.3 Effect of Heavy Metals on Plants

Absorption is a necessary process used by plants to use the process to take up heavy metals from the soil. Nutrient availability, pH, organic matter, moisture, and temperature are essential for absorbing and accumulating heavy metals in plants (Tangahu et al. 2011).

Plants absorbed heavy metals from the soil as part of the soil solution's soluble component (Blaylock and Huang 2000). Sappin-Didier et al. (2005) reported increases in plant heavy metal uptake as the soil pH decreases. Low soil moisture content increases plant heavy metal uptake. Heavy metals tend to form complexes with organic matters and form tight chelates with humic acid, which increase adsorption (Lo et al. 1991). Some heavy metals are referred to as essential micronutrients and are very important for plant growth and development. They include zinc, nickel, copper, iron, cobalt, and molybdenum (Reeves and Baker 2000). However, the absorption and accumulation of these heavy metals in the plant beyond the plants' requirement lead to heavy metal toxicity (Monni et al. 2000). This can be directly or indirectly harmful to the plants. The direct toxic effects are inhibition of cytoplasmic enzymes and cell structure damage (Jadia and Fulekar 1999), while the indirect toxic effect is the replacement of essential nutrients at specific exchange sites of plants. Also, heavy metal toxicity in soil includes chlorosis, weak plant growth, low yield, disorders in plant metabolism, reduced nutrient uptake, etc. (Guala et al. 2011).

## 17.4 Effects of Heavy Metals on Soil Microorganisms

The changes in soil microorganisms' population size, diversity, and overall activity are some of the effects of heavy metal contamination in soil. The adverse effect of heavy metals on the growth and activities of soil microorganisms indirectly affects plants' growth. Turco et al. (1994) reported that pollutant degradation, cycling, and organic matter decomposition are essential for soil microorganisms. There is a reduction in beneficial soil microorganisms at high heavy metal concentration, decreasing the organic matter decomposition in soil, making the soil less fertile. The initial reaction of microorganisms as they contact crude oil in the soil is reduced activity. This is because of reduced soil air availability. Rasinussen et al. (2000) stated that depending on the heavy metal's bioavailability and the absorbed dose, the heavy metals in crude oil could cause detrimental effects on the soil organisms. Holderbrandt et al. (2007) and Gauthier et al. (2014) reported that the mechanism of heavy metal toxicity includes

- Reacting as a redox catalyst in the production of reactive oxygen species (ROS).
- Breaking fatal enzymatic functions.
- Breaking ion regulation.
- Directly affecting the formation of DNA and protein.

Heavy metals can also alter the biochemical and physiological properties of microorganisms. Booth et al. (2015) reported that aluminium could stabilize superoxide radicals responsible for DNA damage. Chromium, Cr (III), may change enzymes' structure and activity by reacting with carboxyl and thiol groups (Ceravantes et al. 2001). Besides, chromium and cadmium can induce oxidative damage and denaturation of microorganisms and weaken microbes' bioremediation capacity. Copper (Cu (I) and Cu (II)) could catalyse the production of reactive oxygen species (Osman and Caret 2008). Cadmium and lead cause deleterious effects on microbes, damage cell membranes, and destroy the DNA structure. They displace metals from the native binding sites or ligand interactions, causing harm (Olaniran et al. 2013). Bissen and Fummel (2003) reported that the metabolism, growth, and morphology of microorganisms are affected by high concentrations of heavy metals. This results from nucleic acid structure changes, leading to functional disturbance, inhibiting enzyme activities, disrupting cell membranes, and oxidative phosphorylation (Bissen and Fummel 2003; Fashola et al. 2016).

## 17.5 Effect of Heavy Metals on Man

The effects of heavy metals can either be acute or chronic toxicity. Micheal et al. (2018) stated that heavy metal toxicity refers to harmful effects from exposure or consumption of excessive heavy metals. The body's inability to metabolize heavy metals causes accumulation in soft tissues (Sobha et al. 2007). However, the uptake of heavy metals by plants and subsequent accumulation along the food chain is a threat to animal and human health (Singh and Kelamdhad 2011). Engwa et al. (2019) reported that the long-term exposure of the body to heavy metals could progressively lead to degenerative neurological processes, physical and muscular such as muscular dystrophy, multiple sclerosis, Alzheimer's disease, and Parkinson's disease (Engwa et al. 2019). Ihedioha et al. (2016) stated that ingestion or inhalation of Pb could damage the kidney, bone marrow, brain, and other system damage in children. Also, infants and children with low blood Pb levels (5 μg/dL) can lead to developmental problems, such as stunted growth, impaired hearing, and cognitive functions (Ihedioha et al. 2016). Teo et al. (1997) reported that acute arsenic poisoning could affect the heart and brain and destroy the blood vessels and gastrointestinal tissue, and chronic arsenic toxicity, termed arsenicosis, causes skin pigmentation and keratosis. A low concentration of chromium causes nausea and vomiting, reduced leukocyte and erythrocyte production, and damage to blood vessels, while at high concentration, chromium is carcinogenic (Achmad et al. 2017). Also, chromium courses painless erosive ulceration of the skin, which can lead to malignancy (Lewis 2004), and it can significantly damage the nasal mucosa and perforation of the nasal septum (Wilbur et al. 2012). Cadmium exerts toxic effects on the kidneys and the skeletal and respiratory systems. Previous studies have shown that chronic exposure to cadmium in humans can be associated with carcinogenesis (WHO 2019; Genchi et al. 2020). Besides, cadmium induces oxidative stress, which leads to oxidation and damage of biologically important macromolecules, such as proteins, DNA, lipids, and cellular membrane phospholipids. Cadmium lowers mitochondrial membranes' potential, disrupting oxidative phosphorylation and ATP synthesis (Wang et al. 2014).

Nickel on human health includes allergy, cardiovascular and kidney diseases, lung fibrosis, and lung and nasal cancer (Genchi et al. 2020). Cobalt is implicated in haematological and endocrine dysfunctions (Leyssens et al. 2017). Acute effects of copper ingestion are nausea and abdominal pain (Olivares et al. 2001). Symptoms such as muscle weakness, loss of deep tendon reflexes, cardiac arrest, and respiratory paralysis are some of the effects of rising magnesium levels (Krendel 1990; Turner 2010; Fung et al. 1995). The WHO (2019) reported that high sodium levels result in high blood pressure and increase heart disease and stroke risk.

## 17.6 Remediation of Heavy Metals in Crude Oil-Contaminated Soils

Remediation or cleanup or decontamination involves removing pollutants from the soil, sediment, surface water, or groundwater environment. Wuana and Okieimen (2011) reported that the remediation of heavy metal-contaminated soil would address food insecurity, unavailability of land resources for agriculture, and land tenure problems.

The remediation approach for heavy metal-contaminated soils depends on the form of the contaminants, whether physical and chemical. The knowledge of the site's physical characteristics, type, and level of contamination must be adequately evaluated to ensure an accurate assessment of site contamination and remedial alternatives (Wuana and Okieimen 2011). The first process in soil remediation is the characterization of contaminated soil. This is to establish the type, amount, and distribution of heavy metals in the soil. The second process involves the actual evaluation of the level of different metals in the soil. Remediation approaches aim to completely protect the environment and human health (Martin and Ruby 2004).

The remediation technologies for metal-contaminated soil are classified into three categories of hazard-alleviating measures. These are gentle in situ remediation, in situ harsh soil restrictive measures, and situ or ex situ severe soil destructive measures. The last two alleviating measures are to avert hazards either to man, plant, or animal, while that of the gentle in situ remediation is to restore the malfunctionality of soil for safe applications (Gupta et al. 2000). The USEPA (2007) defined in situ or place as treatment of contaminated soil in its original location or unmoved or unexcavated or in the subsurface. Also, ex situ means moving, excavating, or removing contaminated soil from the site or subsurface before treatment. Besides, remediation technologies for contaminated soils can be classified into source control and containment remedies. Immobilization, physical separation, isolation, extraction, and toxicity reduction are some of the remediation approaches for heavy metal-contaminated soil. Sometimes in practice, it will be required to combine two or more approaches for cost-effectiveness. The applicability and selection of the remediation technologies are based on long-term effectiveness/permanence, commercial availability, general acceptance, cost, toxicity reduction, volume reduction, mobility reduction, etc.

The GWRTAC (1997) reported that soil washing, immobilization, and phytoremediation techniques are the most appropriate heavy metal-contaminated remediation techniques. Phytoremediation is the treatment or decontamination using plants. The mechanisms involved include phytoextraction, phytostabilization, and phytofiltration. The benefits of phytoremediation are that it is relatively a low-cost and a natural treatment solution. Soil washing is a physical remediation technique that is widely used and leads to a volume reduction/waste minimization process. It can be done either by excavation (ex situ) or on-site (in situ). In the process, aqueous chemicals are used to remove contaminants from the soil. Cost-effectiveness, rapid cleanup of a contaminated site, and reducing or eliminating long-term liability are some of the benefits of the soil washing method. Immobilization techniques are practical methods that can be used to remediate heavy metal-contaminated soils. It can be applied ex situ and in situ, but in situ process is considered better because of its lower labour and energy requirements. However, the implementation of in situ will depend on specific site conditions. In cases where highly contaminated soil must be removed from its place of origin or high ecological risk (e.g., with radionuclides) connected with its storage, a high ecological risk (e.g., with radionuclides) is referred ex situ technique. Wuana and Okieimen (2011) reported applicability, relatively low investment, and operation cost-benefit in immobilization techniques.

## 17.7 Conclusion

There are several heavy metals present in farmlands in crude oil exploration areas. These heavy metals cause health risks and hazards to man and the entire ecosystem because of their adverse effects. It affects the growth, development, reproduction of microorganisms, plants, and man. Soil characterization and remediation can be used to protect and restore heavy metal-contaminated soil. Remediation is usually done through immobilization techniques, soil washing, and phytoremediation.

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# Effect of Trace Elements in Soils and Its Management

# 18

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## Abstract

Some trace elements are essential ingredients for plant progress as well as human and animal health, and they occur naturally in soils. At high concentrations, however, all trace elements become potentially hazardous. They are found in modest amounts (less than 1000 mg/kg) in organisms; however, they exert magnificent biological impact, as nutrients and environmental factor. In this chapter, we have discussed the various effects of trace elements in soils and their assessment and management via various methods, e.g. photostabilisation technique. The knowledge of trace element and its limitation will be essential for the management of the soil and environmental contamination. The present compilation of the data gives the information regarding its various techniques, which will be beneficial to maintain the ecosystem of the environment and the soils. The various research papers with the scientific explanation have been covered to get the concrete information to justify the title. Moreover, the chapter provides the limitation of the trace elements, which is directly related to clinical aspects as well as the phytomanagement of soil and its management. Similarly, related studies recently conducted on soluble as well insoluble trace elements and their soil extraction along with their clinical effects are summarised in the chapter.

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Trace elements · Photostabilisation technique · Essential nutrients · Environmental effect · Health management

## 18.1 Introduction

In today's scenario, trace elements (TEs) are seeking more and more attention for their nutrition value in plants as well as in animals. It is now well known that any type of deficiency or toxicity of these trace elements can alter or disturb the optimum economic yields of crops; also it can cause adverse effects on the other living things. The concept 'trace element' is helpful yet vague since it can apply to any element in the universal system, irrespective of its function (Herojeet et al. 2015). Initially, the word was used to describe a variety of elements detected in plants at concentrations so low that current analytical methods could only record them as 'a trace'. Substance material present as low as nanogram level can now be established using sophisticated analytical techniques, but still the limited concentration of trace elements in plant system and their utilisation. The soils are a matter of discussion (Singh and Kumar 2017). Because plants are the major source of trace elements for humans and animals, they are necessary nutrients for plant development and, in some cases, food and feed quality. Micronutrients are a suitable term for these trace elements. In spite of major one, some other trace elements that are found in plants but have yet to be identified as having a role are important for the growth of the living kingdom. Their trace present in the system can accelerate the metabolic process as well as act as negative catalyst in the process of development. Animals that have evolved a need on these tiny elements 'in terms of presence' could be classified as micronutrients as well. Animals have been proven to require a greater number of elements than plants. To achieve optimum productivity, micronutrients must appear in an adequate quantity in soil for plant-animal system. The phrase 'trace element' has the disadvantage of implying that even though an element is not required for plants or animals, it has no negative impact on them (Mazur et al. 2013). However, even trace amounts of particular metals can build up to hazardous levels in the plant or the animal that eats it. Plant growth can be harmed due to excessive presence of acidic minerals, e.g. nickel (Ni), cobalt (Co) and chromium (Cr) (Christou et al. 2017). Also human activities have elevated the soil contamination by increasing the limit of trace elements which may lead to give adverse effect to human health. They can be determined as crucial with their critical presence can be difference to plant to animal (Fronczyk et al. 2015).

## 18.2 Trace Element Resources

### 18.2.1 Soil Trace Elements

The native material from which soil is generally obtained can be used to analyse the quantity of trace elements present in that particular soil strata and also the quantity of trace elements in a particular soil can vary due to continuous leaching and following nutrient cycle via plant-animal ecosystem. Other sources through which soil can get TE are deposit dust, mainly found in dust storms prone areas, via adsorption from water draining system and pollution produced by human activities (Harvey et al. 2016).

#### 18.2.1.1 Total Contents Present in Soil

The integration of trace elements into silicate crystals can be done by determining their valency and ionic radii. Replacement can be done if the ionic radii of the two ions must not vary by more than 15%. Magnesium (Mg) has a 66 pm ionic radius (pm = 10–12 m) and may be substituted by Co (II) (72 pm), Cr (III) (63 pm), Ni (69 pm) and Zn (69 pm) (74 pm). This is the main reason soils formed of basic rocks have seldom micronutrient deficiencies and crop shortages are unusual (Sas et al. 2015). Indeed, toxicities can be an issue on such soils, e.g. serpentine-derived soils can contain high levels of plant-available chromium (Cr) and nickel (Ni) and a flora tolerant of high levels of these two elements can be discovered on these soils (Voběrková et al. 2017). Acid igneous soils, on the other hand, are often deficient in some micronutrients, causing plants and animals to suffer. Co deficiency is frequent in granite and rhyolite-derived soils, and when it comes to metallic micronutrients, there is a complicating factor (Adamcová et al. 2017).

Other major sources of TE for agricultural purposes are sedimentary rocks, which have covered around 75% of the earth's surfaces. In general, the transfer of metallic micronutrients into secondary or clay mineral lattice by mechanical invasion restores the alkali metal and converts its clumsy form to clay size form (Radziemska and Fronczyk 2015). It is feasible to make some generalisations about a soil's trace element content when its composition is nearly similar to that of the parent material, i.e. for young soils. For example, soils formed from shales frequently have a good trace element make-up (Kim et al. 2017). Small information is available regarding the effect of soil age to the element present, which can confirm the old soil contents more oxidising metal than the native one. The hypothesis is not well generalised so far (Anjum et al. 2015).

#### 18.2.1.2 Soluble Contents Present in the Soil

The presence of trace element in the soil is due to the mechanical aggression of silicate material from the source, which also governs by the various other factors. The ratio of ion charge to radius (in nm), commonly referred to as the ionic potential, determines whether trace elements precipitate or remain in solution (IP). B, Cr (VI), Mo (VI) and silicon are examples of oxyanions, which have ratios greater than 95 (Si). Elements with IP values below 30 generate soluble cations, which may become ‘imprisoned’ in complex precipitates generated ranging from 30 to 95. Cr (III), Fe (III), Mn (III), Mn (IV) and Mo are among the elements in this category (IV) (Cundy et al. 2013). These elements are generally obtained as they are found in a distinct form or they are coated on the scrap of the soil and around the cavity of the soil and come as a form of precipitation hydrous oxides. The presence of these hydrous oxide elements in small amount could be sufficient to exert their action, irrespective of their quantity (Radziemska et al. 2017). Other trace elements in the precipitate can be occluded as the hydrous oxides develop. As like, when the pH rises, the hydrous oxides showed improved affection with the trace cations at their surfaces, and the ions can migrate within the earthen lattice on which the oxide is bound through solid state diffusion after adsorption (Gil-Loaiza et al. 2016). Dissolution of hydrous oxides and following precipitation can alter the bioavailability of TE in plants and also modify pH of soil and redox potential. The availability of numerous micronutrients to plants is influenced by soil pH. B, Cu and Zn are widely accessible in a pH range of 5–7, whereas Fe and Mn are more readily available under the range of pH 6, while Ca and Mg are more readily available above pH 6.5 (Touceda-González et al. 2017).

## 18.3 Soil-Plant Trace Elements

Plants uptake and returning of trace elements in the form of leaf fall play a vital role in their dispensation in the soil. Trace elements are initially kept with the organic substance under these conditions, but when the humus decomposes, they can either travel down the soil or present in clay-rich layers. Micronutrient deficits can emerge when light-textured soils are recovered for agricultural use because soil cultivation speeds up the decomposition of humus and disrupts the natural cycle of these trace elements when they are taken from the produced food (Prasad and Freitas 2006).

### 18.3.1 Clinical Significance on Human Beings

Biological trace elements (TEs) are found in minute concentrations in organisms (1000 mg/kg), and also they impart a very strong effect on life as vital nutrients and also as environmental toxins. Various reports and surveys suggest that a large number of people are present around the globe who are either deficient of iron or suffering from anaemia (Gołda and Korzeniowska 2016), in which a percentage of children from the age group between 0 and 5 years old are about 35–40% and not only iron but they are also scarce of other essential elements like Se, Zn, etc. According to these survey and data, it is suggested that if the absorption of trace elements by plant will increase and again it is cycled in another form in soil which can be easily digestible to the human body system, then it will balance the concentration of TE in the human body especially in those areas where there is a scarcity of trace elements. However, in many circumstances, it is not a lack that causes harm to humans but rather the excessive use and exposure to TEs (Padmavathiamma and Li

2009). The main reasons of the increased volume of trace elements in our environment are excessive human activities including industrial pollutants. As a result, they build up over time under certain environmental circumstances because of the immobile nature of trace elements. All TEs, even those required for life, are hazardous to organisms at large doses; even plant growth is adversely effected by the increased volume of TE (Wong et al. 1994), and its uptake by plants may enable toxic element entrance into the food chain, thereby compromising human nutrition. Trace elements have contaminated 22 million hectares of soil around the world due to the increase in the rate of contamination which results in the reduction of food productivity as the population is growing vastly leading to shrinking of agricultural field (Yin et al. 2014). There are three detrimental effects of contaminated agricultural land. To begin with, its use produces food products that are hazardous to human health. Second, non-agricultural land, such as those beneath trees, may be destroyed for agricultural production, reducing biodiversity and eliminating a carbon sink (Labidi et al. 2017). Thirdly, agriculture will be expanded on non-contaminated farmland. Because TEs are undesired ingredients in many fertilisers and important components in many pesticides, this necessitates more fertiliser and pesticide application, which may cause soil contamination (Mills et al. 2005). Other types of land degradation, such as compaction, erosion and salinisation, may occur as a result of intensification (Kalenik 2014).

## 18.4 Assessment Techniques for Determination of Bioavailability of Trace Elements in Soils

### 18.4.1 Bioavailability/Bio-accessibility Related to Plants

Physical procedures, various leaching tests and chemical extractions are employed in risk assessment to estimate risks connected to contaminant behaviour under specific environmental conditions, supposing that its availability in the biological system is directly related to the solubility and consequent mobility (Radziemska et al. 2016a, b). Extracting the soil as pore water and analyzing it with spectrophotometry. Soil water that fills the pores or crevices between soil particles and is kept there by capillary forces is known as pore water (also called soil solution) (Bus et al. 2016). It is considered that TE uptake for plants and microorganism is more feasible in pore water. However, this is a theoretical viewpoint, as numerous TEs (e.g. Cu and Pb) can form binary or ternary complexes with other solution constituents, such as dissolved organic matter, altering TE availability for plant uptake (Gusiatin and Kulikowska 2016). Soil pore water can be retrieved using soil moisture samplers or centrifugation. In the first situation, the approach is only appropriate when only small amounts of soil solution are required. In the latter case, porous probes resembling plant roots are put into the soil, and the soil solution is retrieved using a suction system connected to the sampler (Jones et al. 2016). In this situation, samples can be taken repeatedly from the same location without disturbing the soil, with several days between each collection to account for soil reactivity. Soil moisture samplers are preferred for in situ pore water collection, as well as in potted soils, where the soil humidity and its effect on microbial communities may be regulated, due to the method's simplicity (Haloizyt 2017).

#### 18.4.1.1 Leaching Tests

Leaching tests are also reasonably easy and repeatable methods that can be carried out according to defined protocols based on the diffusion of the solid material to the liquid. In this process the leachants tend to dilute the soil solution, potentially changing TE chemical equilibria. As a result, the utility of leaching experiments in predicting the possible bioavailability of TE in soils is debatable (Sakiewicz et al. 2011). Leaching tests, on the other hand, are commonly utilised in environmental investigations, particularly on excavated polluted soils. Exhumed contaminated soils are classified as waste and must go through waste characterisation procedures, which include compliance tests. In such circumstances, the major method of a substance release, which poses a possible concern to the environment, is the breakdown of components in soils upon contact with water (Sakiewicz et al. 2016).

#### 18.4.1.2 Chemical Extraction Methods

One of the most known methods for evaluating bioavailability of TE is soil extraction technique. It generally includes diluted salt solution and various chelates and complexing agents either in joint form or independently. An exhaustive overview for the extraction techniques to recover potential availability of TEs in soils, by dividing seven groups of majorly used extraction protocols (Radziemska et al. 2013). Single solvent extractions are being used to estimate TE availability in soils, and single solvent extractions are among the most widely utilised procedures and methodologies in environmental legislation in the world. Sequential extraction methods are typically employed to measure TE fractions that can be mobilised in diverse conditions (e.g. acidified, redoxed), rather than TE bioavailability estimation (Radziemska et al. 2014).

### 18.4.2 Bioavailability/Bio-accessibility Related to Humans

Human health takes precedence in every risk assessment methods, and sanitary risk is identical with ecological risk. Metals are intensified in various body parts and are frequently an exacerbating point in a variety of acute and chronic disorders. In multidisciplinary efforts on geochemistry, epidemiology, spatial statistics and geographical aspects of public health, a human epidemiology of TECS (Tribal Epidemiology Centres) has long been developed and is constantly discussed (Radziemska et al. 2016a, b). At the moment, risk assessments for human exposure to pollutants are conducted using a software designed by the national or regional environmental protection authorities. Such softwares require site-specific soil and ambient parameter input, along with the estimations of the common pathways in the human body system, such as ingestion, inhalation, food intake and dermic absorption (Kabata-Pendias 2011). Although these assessments exceed the legal exposure limits, appropriate remedy methods or other measures are implemented to avoid human poisoning. In this case, it is obvious that the operationally defined TE fractions obtained in TECSs using the methods described above may not accurately reflect their potential toxicity to people. As a result, since the early 2000s, particular bio-accessibility assessments have been used to more precisely predict human toxicity in connection to environmental contamination and TECSs (Narendrula et al. 2012). In the health risk assessment method, the oral accessibility of the pollutant in soils is equivalent to the orally accessible contamination with the correlation with the toxic effect of the elements present in. Three factors combine to produce the orally accessible percentage of soil-borne contaminants: (1) bio-accessibility, (2) transport across the gastric and intestinal epithelia and (3) the first pass effect. Some metals, such as Pb, are not expected to undergo metabolism (Churchman et al. 1984).

Absolute bioavailability is defined as the amount of a pollutant that is absorbed in the organism as measured by the ratio of absorbed to ingested TE dosage in the context of human health risk assessment. However, because absolute bioavailability for humans is difficult to determine due to logistical and ethical considerations, the human health hazards associated with TECSs are calculated as a function of TEs' relative bioavailability. TE fraction is removed by digestive juices and can potentially be transported into the bloodstream. TEs formed from TECSs have lower bio-accessibility in humans than those derived from oral TE toxicity (Szczepanik et al. 2015). When pollutant concentrations marginally exceed guideline levels and the site has low priority for clean-up efforts, but humans are exposed to TECSs, determining bio-accessibility to humans can be informative. For both people and animals, there has been a link between RBA levels and the findings of in vitro bio-accessibility testing. When traditional remedial procedures are not workable and alternative strategies for in situ soil treatment do not diminish total soil TEs, then this methodology can also be used to estimate residual risks (Klute 1996).

### 18.4.3 Overview of Bioavailability Estimation by In Vitro Test

Chemical extractions permit for the determination of elemental concentration and speciation; however, the impression of polluted soils on live entities is complex and difficult to predict based solely on extracted elements. The harmful effects of TEs on organisms can be amplified or dampened depending on soil variables such as pH, salinity, DOM (Dissolved Organic Matter) and nutrient concentration. As a result, biological assays are frequently employed to determine the toxicity of soil (Enger and Riehm 1958). By detecting physiological changes in vital components, ecotoxicological assessment of environmental samples can be undertaken at any level of biological organisation, from molecular to whole organisms and communities. Three types of tests are available for assessing contaminated soils as per the reported research. Mammalian in vivo experiments to determine bioavailability are also carried out. Juvenile pigs, for example, could be utilised as a model for children. The area underneath the blood TE concentration-time curve and metal concentrations in target organs are used to calculate the biological response. The response is calculated as a function of the amount of soluble metal salt taken orally. This relative bioavailability is employed in the risk evaluation in the United States. These testing methods, on the other hand, are thought to be both expensive and unethical (Bremner 1965).

## 18.5 Management of Trace Elements and Their Human Health Effects

### 18.5.1 Phytomanagement: Impact on Environment

Phytomanagement term can be used when some modification or alternation is done in soil profile or in the process of utilisation of trace elements by plants to command TE differences in the ecosystems. As a result, phytomanagement may be used to address crucial TE deficiency or to mitigate the environmental danger caused by contaminated TEs. It should either be less expensive than alternative remedy or barricade techniques, or it should be a profitable activity that produces valuable plant biomass products. Rather than referring to a particular technology, the word phytomanagement refers to the optimum site-specific management alternative (Mocek and Drzymała 2010).

Phytomanagement refers to a collection of related technologies that includes phytomining, phytoremediation (phytoextraction and phytostabilisation) and biofortification. By collaborating with various type of technologies, phytomanagement also emphasises on the utilisation of herbage by reducing the cost of any environmental problems related to the location with the target of increasing the value of the land while also potentially reducing the negative impacts of soil pollution (Pueyo et al. 2004).

Phytoremediation aims to immobilisation of TEs in the soil, preventing them from leaching or entering plant shoots (phytostabilisation). Alternatively, the soil-plant system can be engineered or manipulated in such a manner that the contaminated TE will be absorbed and can be retained in its various parts in which phytovolatilisation or phytoextraction process can occur. Phytomining is generally used when the traditional technique of mining is not sufficient in low quantity of metals; therefore to gather the desired amount of metal from the parent material like ore bodies, this method is preferable (Adamcová et al. 2016). Phytoextraction of TEs from polluted soils might result in biomass with greater levels of vital TEs (biofortification) or sellable amounts of lucrative TEs (phytomining), all while reducing erosion and TE leaching (phytostabilisation) (Phytotoxkit 2004).

#### 18.5.1.1 Phytoextraction

Phytoextraction is generally used for those trace elements which contribute high amount of biomass. TE would be removed from the area with each cropping. Burning and fermenting help to reduce the quantity of trace element biomass, and for the recovery of the trace elements, it is further treated with residual materials or it is settled down in contained landfill. Conversion of soil contaminants into volatile substances which disappears in the air also occurs via phytovolatilisation method. Mercury, arsenic and selenium are the examples of such elements which get volatised by our ecosystems. Phytovolatilisation has two disadvantages: (1) the limited number of plant-microbial systems which helps the conversion of soil pollutants into volatise one and (2) the lack of control over the destination of the volatilised elements. Phytovolatilisation, on the other hand, offers the option of moving critical TEs like Se from locations where it is poisonous to downwind areas where it is deficient (Koda et al. 2013).

Phytoextraction via volatilisation has more advantages in comparison with other types of phytoextraction such as regular harvesting which is not needed until the level of TE reach to the standard ones. Phytoextraction is less cost-effective and utilise natural source of energy for the purification of the soil via following standard agronomic methods. In comparison with other extracting methods such as thermal desorption, incineration, etc., also they contribute less soil productivity (Minnikova et al. 2017). There are no effective phytoextraction field studies or commercial operations to speak of. One of the few effective field applications of phytoextraction is selenium volatilisation utilising genetically engineered *Brassica juncea* L. (Mustafa and Komatsu 2016).

#### 18.5.1.2 Phytomining

As per several reports, Ni is being extracted from low-grade ores; using plant-based extraction will be expensive and the quantity in soil will be less, which will enhance the productivity of soil. It has been found that low-grade Ni ores are widely found all over the world. For extracting up to 100 kg $\mathrm{ha}^{-1}$ of Ni (worth $550 ha at the time) when growing on ultramafic (serpentine) soils near Chinese Camp, California *Streptanthus polygaloides* (grey) was discovered (Benimeli et al. 2009).

The large-scale company with continuous crop incineration may generate energy of burning which would add an additional $219 ha. They concluded that a farmer farming a ‘crop of nickel’ would have a return that was equal to a farmer growing wheat. Crop cultivation is done for a short span of time, an incinerator used to generate steam for power generation has some drawbacks, and the power plant should be situated near a city where domestic waste can be used as a feedstock to keep the plant running for the rest of the year (Wyszkowski and Radziemska 2010). Growing two harvests every year would improve yield of Ni and also facilitate extra labour for a neighbouring incineration plant. Unlike phytoextraction for soil cleansing, the value of the TE extracted determines phytomining by many hyperaccumulator plants, such as *Alyssum* spp. and *Berkheya coddii*, which fulfils the necessity of high biomass construction (>10 t ha year) and nickel (>10,000 mg/kg).

The efficacy of Ni phytomining using *Berkheya coddii* is being affected by the presence of Ca in the form of hydroxyapatite. Nonetheless, it is unlikely the recovery of metal from bio-ore will prevent phytomining from being commercially viable (Sun et al. 2015).

As per reports, phytomining economics become more appealing when applied to a contaminated site as compared to natural site, because many recovered TEs will exceed the cost of site clean-up. In pits and trailing using high amount of target metal which might be too low for social exploitation to reduce the risk of residual TEs causing environmental harm, phytomining can be employed in combination with conventional mining (Friesl et al. 2003).

### 18.5.2 Biofortification and Their Relevance to Human Health

Biofortification focuses on improving human health and agricultural output by increasing the concentration of critical TEs in crops. Fe and Zn are the most typically deficient elements in human diets. Selenium and I both have deficiencies in a variety of areas. Rice and wheat are generally chosen for biofortification by the majority of people due its common use as a food source. Biofortification provides various benefits compared to adding critical TEs to the end product directly, such as fortifying flour with zinc compounds or adding nutritious substances (Sharaff et al. 2017). Plant portions with physiologically accumulated TEs are likewise more bioavailable to humans. However, because the efficacy of biofortification is dependent on conditions, genetic profile and environmental condition of soil, it may not provide a reliable source of TEs as standard fortification or dietary supplements. If the biofortification is achieved through crop genetic alteration, either through traditional breeding or in vitro gene manipulation, recurrent costs are modest, and the germplasm can be shared internationally, reaching those who do not have access to commercially fortified foods or supplements (Mazur et al. 2015). In the biofortification technique, the enhancement of the nutritious value of plant tissue remains a concern; however some of the detrimental effect producing element also elevated, which cause the major disadvantage of this technique. As a result, biofortified crops should be thoroughly checked for pollutants.

### 18.5.3 Phytostabilisation

If TEs in polluted soil remain immobile, the harm to the environment and human health is reduced. Some authorities have been using a risk-based method to evaluate the soil quantitatively, which takes into account TE solubility, mobility and concentration (Shutcha et al. 2015). Plant transpiration and root growth are exploited to lower the leaching and regulate erosion in phytomanagement to lower TE fluxes (phytostabilisation). Roots aid in the maintenance of an oxygen-rich space in the vadose zone, preventing the production of reduced TE species, which exerts high hazardous effect and mobility than oxidised counterparts. Phytostabilisation is the process of establishing vegetation on a contaminated site in order to increase the land's value. Ecological benefits or the development of non-edible economic products like bioenergy or timber can provide value. Phytostabilisation is particularly well adapted to low-value sites, when the cost of soil removal and landfilling outweighs the land value, which can refer to a variety of successful applications, including acidic mine tailings, wood waste piles and abandoned sheep-dipping sites (Nirola et al. 2015).

### 18.5.4 Phytomanagement Techniques

From the above discussion, it is now crystal clear that solubility, specificity of trace elements in soil, tolerance and plant absorption are the major criteria which controls phytomanagement techniques. To achieve maximum growth, plants must be able to tolerate TEs in the soil. Greater amount of absorption of trace elements by any specific part of plants (such as shoot) is favourable in the case of phytoextraction-related technologies, but successful phytostabilisation necessitates TE exclusion from the aerial sections; also it can become hazardous when huge numbers of TE enter our food chain via absorption by following all phytomanagement applications (Sinnett et al. 2011).

## 18.6 Conclusion

In the present chapter, the macronutrient deficiencies are addressed, and many researchers and scientists are focusing on the analytical technic of a plant's nutritional value calculation and its requirements with their availability in the soil. It is well reported that plant uptake is very much less than the real availability of nutrients present in soils, and also it was observed that by modifying soil pH and redox value, the concentration of micronutrients can be altered or enhanced. Thus it can conclude that various soil conditions can enhance or reduce the availability of micronutrients. The advancement in the analytical technics can be useful to estimate and minimise the hazardous trace material. The effect of the trace element is not the acute even, it aggrades the effect and express later. The bioavailability of trace in soil is a natural process, which occurs through the spontaneous process, which can be optimised with the advanced methods. In the report we discussed about the management strategy for trace elements in soil, phytomanagement is a technology that will last a long time. In view of the contaminated site, phytomanagement must produce useful biomass while also minimising environmental risk in order to compete successfully with alternative remediation strategies. Similarly, for biofortification and phytomining, useful biomass generation is the most significant criteria.

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# Part V

# Remedial Strategies, Utilization & Engineered Applications

# Remediation of Agrochemicals in Soil and Environment

# 19

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## Abstract

Agrochemicals play an important role in increasing crop yield. They have also been used for protecting the crops from insect-pests. However, only a fraction of agrochemicals are effective in killing insect-pests and preventing diseases, the remaining persist in soil and leach to groundwater causing potential threat to the environment and health. The prolonged existence of hazardous pesticide compounds in water, soil, and environment needs to be removed and detoxified. The breakdown rate of pesticide is affected owing to pesticide structure, pesticide concentration, temperature, degradation processes, soil types, and other factors. This chapter summarizes the current knowledge on various physical, chemical, and thermal methods of remediation and bioremediation including bacteria, fungi, and plants for removal and detoxification of agrochemicals from soil and environment.

## Keywords

Remediation · Soil · Contaminants · Bioremediation · Pesticides

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## 19.1 Introduction

Several chemical products used in agriculture against plant diseases and insects and for enhancement of plant growth are called as agrochemicals. The agrochemicals include pesticide, fungicides, insecticides, herbicides, rodenticides, and chemical fertilizers. The present-day agriculture greatly depends on many agrochemicals for the fulfillment of livelihood and food safety throughout the world (Nayak et al. 2020). The agrochemicals which are used for livelihood and food throughout the world and modern agriculture mostly depend on them. Majority of agrochemicals which are applied at excessive amount likely cause environmental risk when delivered into the soil, water, and air (Anwar et al. 2009). They also reduce the number and activities of soil flora and fauna. India reports about 3% utilization of pesticides for the protection of crops in the world, and it becomes the biggest pesticide user country. The organochlorine, organophosphate, and neonicotiniod pesticides are generally used in India (Parte et al. 2017). Only 0.1% amount of pesticides reaches the selected organism, and unused pesticides pollute the flora, water, and soil causing bioaccumulation in the first organism (Sivaramanan 2015). The advanced countries have minimized the use of pesticides due to its hazardous effects. To protect the environment, environmental awareness has been increasing among the people. Currently, in order to minimize pesticide effects on health and environment, to remediate polluted sites and for pesticide traces treatment, various techniques have been developed (Parte et al. 2017).

## 19.2 Harmful Effects of Agrochemicals

Many agrochemicals are persistent in soil and water posing serious hazards to human and environment. The increase in pesticide use causes poisoning to crop growers and agricultural laborers and they suffer from heart, lung, brain, and skin disorders, oligospermia, and fetal malformation (Rani and Dhania 2014). Pesticide toxicity also leads to neurotoxicity, human immune system disorders. Consumption of contaminated food and grains with pesticides causes diseases in human beings. Feeding of cattle with grains containing pesticide residue causes its accumulation in milk which is used by human beings. The vegetation, turf, soil, and water contaminated due to pesticides are toxic to fishes, birds, useful insects, and nontarget plants in addition to killing insects or weeds. Both the herbicide and insecticide compounds cause threats to nonselect life forms (Aktar et al. 2009). The contaminants occur in agriculture due to industrial applications, farming, and accumulation of natural pollutants, and they have harmful effects on the sustainability of the living forms (Kumar et al. 2019).

## 19.3 Beneficial Effects of Agrochemicals

The agrochemicals have been used in agriculture for assurance of plenty of food supply. The higher yields from plants, animal crops, and their reduced deterioration during storage were attained by using agrochemicals. These advantages are very significant, and along with crop species which are genetically improved, the agrochemicals have provided significant addition for the achievement of "green revolution" which helped to fulfill food demand for increasing human populations (Baishya 2015). The fertilizers and diverse pesticides are used for increasing yield of agricultural crops and soil fertility and for insect-pests management and to enhance food production (Majeed 2018).

## 19.4 Components Affecting Agrochemicals Breakdown

### 19.4.1 Pesticide Structure

Based on innate biodegradability and physical and chemical attributes of pesticide, pesticide structure is determined. The breakdown of pesticide compound is affected by addition by other groups on a benzene ring. Due to the addition of OH, $NH_2$, and COOH polar groups, which may be responsible for the change in the structure of pesticide, it becomes susceptible to the attack of microbes. Dichlorodiphenyltrichloroethane (DDT), dieldrin, and pentalene compounds are not held together by soil and also not dissolved in soil water. Therefore, the indicated chlorinated hydrocarbons for the process of decomposition are freely available (Rai et al. 2017).

### 19.4.2 Concentration

Pesticide concentration is the most vital criterion to determine the rate of decomposition process. The breakdown rate of butachlor was lowered in soil due to restrictions in the number of reaction sites and harmful effect of butachlor on microorganisms initially at higher concentrations (Prakash and Suseela Devi 2000). Pesticides having short half-lives may gather and persist less in the soils. On the contrary, those pesticides having long half-lives may increase the risk of environment contamination, and they are more persistent in nature (Raffa and Chiampo 2021).

### 19.4.3 Soil Types

The pesticides which degrade in the soils are influenced by clay mineralogy, pH, organic matter, soil types, etc. However, pesticides are firmly adsorbed to clay soils. However, they are weakly adsorbed to sandy soils. In coastal saline soil, the degradation rate of pencycuron fungicide was faster than alluvial soil. On the contrary, there was higher breakdown of pencycuron in alluvial soil when compared with coastal saline soil through the agency of microorganisms (Rai et al. 2017).

### 19.4.4 Temperature

Pesticide degradation rate increases when temperature increases. During rotary drum composing (full-scale), aldrin, endosulfan α, and endosulfan β compounds showed 85.67%, 84.95%, and 83.20% removal efficiency, respectively, at optimal temperature (Ali et al. 2014). The temperature influences the rate of degradation, rate constant (k) and half-life ($T_{½}$) which increased by three- to fourfold for 5–35 °C. This is because the increase in temperature enhanced the solubility and hydrolysis of atrazine and stimulated the activity of microorganisms in agricultural soil (Dong and Sun 2016).

### 19.4.5 Degradation Processes

The chemical reactions, sunlight, UV-rays, and microorganisms play a crucial role in the breakdown of pesticides. Depending upon pesticide characteristics and environmental conditions, degradation process requires hours or days to years. In photodegradation process, pesticides are degraded due to light energy absorption. The rate of degradation is influenced by light intensity, duration of light exposure, and pesticide properties. The photodegradation of chlorfenapyr insecticide was increased when exposed to UV rays and sunlight and recorded 90.07% and 61.93% degradation, respectively, after 48 h of exposure. The UV rays show more degradation of insecticide than direct sunlight (Kandil et al. 2011). In another experiment, exposure of glyphosate to UV-C light in potable water and groundwater containing inorganic and organic components showed greater toxicity reduction when compared to deionized water irradiation. Glyphosate concentration was reduced due to exposure to UV-C rays (Papagiannaki et al. 2020).

## 19.5 Physical, Chemical, and Thermal Remediation

The process of cleanup of contamination sites and the techniques to eliminate or remove it from water or soil is referred as remediation (Zhang 2009). Various processes/techniques play an important function in the cleaning of polluted sites. The following are various approaches to remediate contaminants with agrochemicals in soil, water, and environment.

### 19.5.1 Remediation by Physical Methods

Physical remediation allows the elimination of pesticides without changing their chemical structure, through physical methods like clay, activated charcoal, sodium zeolite, and polymers which work on the principle of adsorption wherein the contaminants are adhered to the surface of materials used. Mineral clays have a negative charge and hydrophilic to retain cationic pesticides. Activated carbon adsorbs pesticide and drug efficiently. The efficiency of activated carbon depends on pH, temperature, and other compounds dissolved in the solution. Heavy metallic elements and pesticides are removed by using zeolites. Polymeric materials (dendrimers) are used in the removal of pesticides in drinking water due to its low molecular weight but it has high cost of synthesis (Andres et al. 2019).

The contaminated soil is cleaned by thermal desorption (low temperature) which acts as a physical process. It is off-site remedial technique used for decontamination of pesticide-polluted sites. This requires a sophisticated facility and has high cost. In this technique, media is heated (300–1000 °F) to vaporize the dissolved sample without destructing the organic compounds. Organic compounds created in contaminated gas flow are treated by moving through device to condense or destroy pollutants entirely (Parte et al. 2017). By this method, pesticide and volatile and semi-volatile compounds are eliminated from the contaminated soil.

### 19.5.2 Remediation by Chemical Methods

Advanced oxidation and dissolved oxygen processes are used for the remediation of pesticides. Advanced oxidation processes are using hydroxyl radial generation, oxidation reactions on pesticides to degrade them in inorganic salts, $H_2O$, and $CO_2$. These processes may be catalytic or non-catalytic and with the use or not use of external energy. This chemical method requires expensive chemicals and has limitations in the treatment of water. Dissolved oxygen processes use dissolved oxygen as an oxidant for pollutants and are wet oxidation and supercritical oxidation methods. In wet oxidation, dissolved contaminants are oxidized using oxygen or air and carried out with or without catalysts. Use of catalysts improves the conversion of pollutants, with decrease of temperature and pressure conditions (Andres et al. 2019).

### 19.5.3 Remediation by Thermal Methods

Incineration is a waste treatment technology that is used for remediation of pesticide contaminant sites. The organic compounds are oxidized using oxygen and heat from polluted soils. The polluted soils/media are heated (1000–1800 °F) resulting in partial oxidation and also vaporization of organic compounds which destroy completely at temperatures between 1600 and 2200 °F (Parte et al. 2017).

Incineration technology causes complete destruction of contaminants. Open burning method may also be used as a thermal treatment.

## 19.6 Bioremediation

The process which uses green plants or their enzymes system and microbes (fungi and bacteria) to natural conditions changed due to contaminants found in original conditions is referred as bioremediation (Radhika and Kannahi 2014). Bioremediation showed the reduction in contamination of pesticide in agricultural soils by breakdown processes through the metabolic processes of microbes. This treatment is environmentally safe and economical (Raffa and Chiampo 2021). Bioremediation is applied in the elimination of soil and environment pollutants and therefore it restores original natural conditions. Bioremediation efficiency depends on temperature, water content, pH, microbial diversity of soil, and environmental condition. In general, bioremediation is categorized into in situ and ex situ. In in situ, treatment is done in zone of contamination and need to supply oxygen to the soil. In case of ex situ bioremediation, polluted soil is separated from main soil and transferred to the site of treatment. These techniques have low cost and effective.

### 19.6.1 Bioremediation Types

#### 19.6.1.1 In Situ Bioremediation

The major in situ types are as follows:

#### 19.6.1.2 Biostimulation

In biostimulation, the number and nutrient types are improved to assist the growth of native microbes (Raffa and Chiampo 2021). Due to this, the metabolic activity of microbes increases to degrade the pesticides.

#### 19.6.1.3 Bioventing

In this, the activity of microbes is promoted by supplying nutrients and air into contaminated soils through constructed wells for the degradation of the contaminants.

#### 19.6.1.4 Biosparging

This involves air injection into groundwater under pressure to enhance the level of oxygen and to degrade contaminants by microorganisms.

#### 19.6.1.5 Bioaugmentation

In bioaugmentation, the addition of cultured microbes into contaminated soil is done to biodegrade the contaminants zone. This involves indigenous microbes to degrade polluted soils.

#### 19.6.1.6 Natural Attenuation

This involves indigenous microorganisms to degrade polluted soils.

### 19.6.2 Ex Situ Bioremediation

#### 19.6.2.1 Bioreactors

In this, the raw materials in a vessel are transformed into particular products using a chain of biological reactions. The continuous, multistage and batch along with others are working methods of bioreactor. The capital expenditure determines the choice of the working method. Dry or slurry polluted samples are used in bioreactor. Use of bioreactor has many benefits over other ex situ techniques of bioremediation in the treatment of polluted soils (Maitra 2018).

#### 19.6.2.2 Landfarming

It is an aerobic bioremediation process. The contaminated soil is transferred to landfarming area and then mixed into the surface of soil and dig it to get aerated at regular intervals. This technique is applicable in the treatment of contaminated soils (Raffa and Chiampo 2021). This technique has low cost and requires less equipment.

#### 19.6.2.3 Biopiles

Biopiles are piling of polluted soil provided with pipe system for aeration. This was followed by amended nutrients for enhancement of activity of microbes. The contaminated environment (very cold) is effectively remediated by using biopiles (Maitra 2018).

## 19.7 Bioremediation of Pesticides

### 19.7.1 Bacterial Remediation

Many bacteria possess pesticide degradation capability. *Acinetobacter radioresistens* has exhibited great capacity to breakdown 38 % of chlorpyrifos and very low breakdown of malathion. *Pseudomonas frederiksbergensis* degrades endosulfan, chlorpyrifos, and malathion. *Bacillus pumilus* showed the efficient breakdown of dimethoate and malathion and partially degrades chlorpyrifos and IGEPAL C-210, while *Serratia marcescens* has shown degradation capability of diazinon, chlorpyrifos, IGEPAL C-210, and methyl parathion (Hussaini et al. 2013). Bacterial species such as *Flavobacterium*, *Arthrobacter*, *Azotobacter*, *Burkholderia*, and *Pseudomonas* degrade the pesticides. Moreover, *Pseudomonas* sp. and *Klebsiella pneumoniae* contain hydrolytic enzymes which are responsible for degrading s-triazine herbicide atrazine (Rani and Dhania 2014). The bacteria *Achromobacter spanius* and *Diaphorobacter polyhydroxybutyrativorans* isolated from farmland are useful for biodegradation of different pesticides (Rahman et al. 2018). Bacterial species such as *Mycobacterium*, *Alcanivorax*, *Cellulomonas*, *Sphingomonas*, *Micrococcus*, *Streptomyces*, *Bacillus*, *Haemophilus*, and *Enterobacter* could convert the aromatic hydrocarbons, azo dyes, and pesticides into inorganic forms and also change or eliminate the oxidoreduction condition of heavy metallic elements (Bhattacharjee et al. 2019). In the biodegradation process of pesticides, parent compound by its oxidation process is converted into $CO_2$ and $H_2O$ with liberation of energy which is utilized by microorganisms. The factors influencing the degradation of pesticides are extracellular or intracellular enzymes, pH, temperatures, nutrients, water content, types of pollutants, and the types of bacteria.

### 19.7.2 Fungal Remediation

Fungi are utilized in bioremediation as they produce many oxidative and hydrolytic enzymes. The ligninolytic enzymes produced by white-rot fungi are concerned with the breakdown of pesticides, aromatic hydrocarbons, waste munitions materials, artificial polymers and dye, polychlorinated biphenyls (PCBs), bleach plant waste, and wood preservers (Pointing 2001). Filamentous fungi such as *Trichoderma harzianum*, *Aspergillus fumigates*, *A. terreus*, and *Penicillium citrinum* have the capacity to degrade chlorfenvinphos and other pollutants found in water (Oliveira et al. 2015). *Metarhizium anisopliae* and *T. harzianum* strains isolated from the contaminated sites with insecticides showed the ability to degrade organophosphorus insecticides and could be beneficial for efficient biodegradation of insecticides (Abd El-Ghany and Masmali 2016). Entomopathogenic fungus *M. anisopliae* (Met.) degrades two agricultural insecticides, chlorpyrifos and cypermethrin, and thus, it plays function of soil bioremediation (Ong et al. 2019). The biodegradable pesticides in agricultural soils are remediated by using yeast, molds and filamentous fungi (Raffa and Chiampo 2021).

### 19.7.3 Phytoremediation

This bioremediation process uses various types of plants for removal of pesticide residues and agrochemical pollutants present in soil and groundwater. Plants are useful to control metabolic process of pesticides and pesticide-polluted water and soil. They are also useful to promote the activity of microbes in root zone to extract polluted water and to eliminate the accumulation of polluted water (Karthikeyan et al. 2004). The rhizospheric microbes degrade numerous organic contaminants efficiently. This microbial activity has favored the degradation power of plants. The enzymes isolated from sediment showed potentiality to degrade trinitrotoluene. These enzymes were of plant origin but not of bacteria (Cunningham and Ow 1996). *Kochia* sp. planted in pesticide-polluted soils has enhanced the degradation of trifluralin, atrazine, and metolachlor (Tripathy et al. 2014). The plant species like *Glycine max* and *Plantago major* are found convenient for the phytoremediation of soil contaminated with azoxystrobin. However, *P. major* with tween 80 could enrich the phytoremediation of azoxystrobin-contaminated soil (Romeh 2015). Aquatic plants such as *Eichhornia crassipes*, *Elodea canadensis*, and *Lemna minor* could uptake the pesticides, and its phytodegradation can be utilized as cost-effective method to eliminate pesticides from the water bodies (Chander et al. 2018). Sumiahadi and Acar (2018) have summarized several crop plants such as *Allium schoenoprasum*, *Brassica juncea*, *Brassica napus*, *Cicer arietinum*, *Cucumis sativus*, *Eichhornia crassips*, *Jatropha circus*, *Lantana camara*, *Lens culinaris*, *Lepidium sativum*, *Lactuca sativa*, *Medicago sativa*, *Oryza sativa*, *Pistia stratiotes*, *Pisum sativum*, *Rapanus sativus*, *Spinacia oleracea*, *Solanum nigrum*, *Sorghum bicor*, *and Zea mays* for their utilization in phytoremediation of heavy metallic elements. Usually, plants accumulate the pesticides and heavy metallic elements from soil and water for their growth and development. However, phytoremediation is restricted as the level of soil contamination should not go beyond particular depth. Due to this, the pollutants do not come in contact with the plant roots. Generally, plants have the capacity to eliminate pesticides from soil through the process of plant uptake, metabolic activity, enzyme release, and volatilization (Sun et al. 2018). However, these processes take a long time for decontamination of site owing to restricted growth of preferred plants (Anjum et al. 2012).

## 19.8 Conclusions

The agrochemicals are used to increase yield of agricultural crops, management of insect-pests, and enhancement of food production. However, their extensive use is responsible for the pollution of soil, water, and environment. Physical, chemical, and thermal methods of remediation are utilized for the elimination of contaminants from groundwater or soil. However, these methods are expensive and require sophisticated facility. On the contrary, bioremediation is efficient, environmentally safe, and less costly. It utilizes bacteria, fungi, and plant species for the elimination of pesticide contaminants from water and soil.

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# 20 Alleviation in the Toxicity of Heavy Metals in Crop Production by Metal-Resistant Bacteria

Bisma Shahzadi, Ayesha Sadiqa, and Muhammad Faisal

## Abstract

Agrochemical pollution is a serious issue for the environment. Exposure to such chemicals for long period of time has detrimental health effects, for example, neurotoxicity and cancer. Accumulation of agrochemicals in soil and plant system for long duration poses a serious threat to environmental safety and food chain. Runoff of the synthetic fertilizers and pesticides into water bodies can lead to water contamination. Moreover, long-term and excessive usage of agrochemicals may cause heavy metal environmental contamination. Toxic heavy metals have vital contributions in polluting the environment because they are nonbiodegradable and are accumulated in plants that are then consumed by humans and animals. Heavy metals are formed as a by-product in industries and are sent out in seas and the atmosphere; other natural sources of heavy metals are volcanogenic particles, wild forest fires, and windblown dust. Bacteria, plant growth hormone, and bioremediation alleviate heavy metal toxicity. Bacteria eliminate toxic effects of heavy metals by siderophore production and minimize metal bioavailability by forming complexes. Rhizobial microflora increases the ability of metal uptake from soils in plants. Endophytic bacteria play a major role in heavy metal stress. Plant growth-promoting rhizobacteria (PGPR) also deal with phytoextraction, mobilization, and phytoremediation of heavy metals from soil. Bioremediation is one of the cost-efficient methods to alleviate toxic heavy metals and its agents are microalgae, macroalgae fungi, and bacteria.

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Siderophores · Rhizobial microflora · Endophyte bacteria · Plant growth-promoting rhizobacteria (PGPR) · Bioremediation

## 20.1 Introduction

Agrochemicals are synthetic fertilizers or pesticides used for better and upgraded crop production technology. Optimum doses and balanced use of agrochemicals are very important for the increased crop yield (Vurro et al. 2019). Overuse of such kind of chemicals may result in immediate or long-term effects on the environment. Uncontrolled use of synthetic fertilizers or pesticides has become the cause of synthesis of significant amount of residues. This may lead to low-quality products and nutrient imbalance (Majeed 2018). Extensive use of such agrochemicals can result in heavy metal contamination of the environment and food chain. A wide range of impurities, contaminants, and chemicals have been added to the environment which is affecting our ecosystem such as air, soil, and water in unimaginable ways. Out of all these pollutants, heavy metals are having a serious concern to the ecosystem and to human health because of their low solubility in biome and elevated rate as contaminants.

### 20.1.1 What Are Agrochemicals?

Agrochemicals are also called as agrichemicals and are a name given to those chemicals which are used for agriculture purposes. Agrochemicals can be synthetic fertilizers, pesticides, soil conditioners, and growth hormones (Prasad 2020). Agrochemicals are not only used for agriculture purposes but also introduced to the wider environment through various spontaneous hydrological processes (Elahi et al. 2019). Such kinds of agrochemicals are made up of combinations of two or more chemicals. These chemicals are used to improve the crop production and for killing harmful insects or herbs. Agrochemicals help protect the crops, increase crop productivity, and maintain the product quality (Zhang et al. 2018).

### 20.1.2 Types of Agrochemicals

Agrochemicals are classified into following types:

1. *Synthetic fertilizers*: Synthetic fertilizers are inorganic and man-made fertilizers. These are made up of inorganic waste material and minerals. They are used to enhance the crop growth by providing with essential nutrients (Qaswar et al. 2020).

2. *Pesticides*: Pesticides refer to those chemicals which are used to control pests. These include all of the following: insecticides, fungicides, herbicides, bactericides, etc. (de Souza et al. 2020).

*Growth hormones* are used to increase the growth rate in crops (Ismail et al. 2021).

#### 20.1.2.1 Soil Conditioners

Soil conditioner is a substance that is combined with soil for the improvement of physical attributes of soil. They replenish and maintain nutrients for the plants (Liu et al. 2020).

### 20.1.3 Effects of Agrochemicals

Although agrochemicals are used for the betterment of crop's health, excessive use of such chemicals may lead to severe effects on the environment. Some agrochemicals have a serious impact on ecological and human health. Even small quantities of some chemicals can cause severe damage to human health and the environment. Lodgment of fertilizers and pesticides in soil and water can have negative effects, so the use of these chemicals is of great concern (Habib 2020). These chemicals are resistant to degradation and can be accumulated in water and soil. Agrochemicals are transported through water, air, or organisms and then accumulated far from the place where they were released. Some toxic agrochemicals, for example, persistent organic pollutants (POPs), organophosphate (Ops), rodenticides, and carbamate compounds, resulted in serious threats for the species that are present at the top of food webs (Meena et al. 2020). Long-term and excessive use of such chemicals is damaging for succeeding crops as they produce residues that may enter into the food chain and lead to deleterious effects. Unbalanced and overuse of these chemicals leads to the degradation of environment and poses many challenges to the soil's health. Degradation of soil due to excessive use of agrochemicals has endangered the food security and soil health conditions, which is a global issue. Killing of nontarget organisms such as beneficial and useful microbes has become the serious problem caused by excess exposure of pesticides (Singh et al. 2020).

#### 20.1.3.1 Effect of Agrochemicals on Soil

Long-term use of agrochemicals alters the pH of soil and results in increased nitrate level. Misuse of such chemicals may leave residual effects which cause nutrients imbalance and reduction in crop production. Accumulation of agrochemicals in soil can kill beneficial bacteria and other soil organisms. Deposition of these chemicals results in toxicity of soil and reduction of the quality of soil (Mandal et al. 2020).

#### 20.1.3.2 Effect of Agrochemicals on Water

Lodgment of agrochemicals in water leads to eutrophication due to the presence of excessive chemicals. It can promote the algal growth, which results in water pollution and leads to detrimental effects on aquatic life. Moreover, water becomes unfit for the consumption because of the accumulated nitrate. Large concentration of this poisonous compound is very damaging to human and aquatic life. The runoff of the synthetic fertilizers and pesticides into water bodies can have severe effect on the life cycle of life forms present in water (da Silva Santarossa et al. 2020).

#### 20.1.3.3 Effect of Agrochemicals on Air

Particles and agrochemical residues can lead to air pollution; it affects the health of organisms. Excess amount of the spray evaporation and pesticide drift can result in polluted air (Chandrappa and Das 2021).

#### 20.1.3.4 Effect of Agrochemicals on Human Health

Exposure of humans to agrochemicals results in various adverse health effects. This may be acute or chronic depending on time duration and extent of exposure and toxicity of the chemical as well (Sellare et al. 2020). Overuse of synthetic fertilizers may cause some serious diseases such as diabetes mellitus, Alzheimer's disease, or hemoglobin disorders (Warra and Prasad 2020). Excessive use of pesticides may result in rashes, skin problems, mild allergies, and reproductive abnormalities which lead to infertility. Exposure to agrochemicals for long duration can result in neurotoxicity, nerve damage, hormone disorders, and cancers (Pandey et al. 2020).

### 20.1.4 Heavy Metals

Heavy metals are the members of an imprecise set of elements that display different metallic properties. These consist of the metalloids, transition elements, lanthanides, and actinides. Some of the metals are essential for the plants in micro amount such as Co, Zn, Fe, Co, Ni, etc., but if their amount exceeds this will cause adverse effects. Heavy metals are those carrying weight more than 5.0 g cm and are normally classified into three classes (Nagajyoti et al. 2010):

a. Toxic metals, i.e., chromium (Cr), mercury (Hg), zinc (Zn), copper (Cu), lead (Pb), arsenic (As), tin (Sn), cadmium (Cd), cobalt (Co), etc.
b. Some precious metals, i.e., platinum (Pt), palladium (Pd), gold (Au), silver (Hg), ruthenium (Ru), etc.
c. Radionuclides, i.e., thorium (Th), uranium (U), americium (Am), radium (Ra), etc.

Many niches of our environment have been polluted by these heavy metals, and it is a crucial concern these days because these metals are difficult to degrade and their toxic effects stay longer if compared to the other pollutants (Etesami 2018).

### 20.1.5 Occurrence

Many heavy metals, e.g., magnesium, aluminum, and iron, naturally occur in the ecosystem. Many erosion factors, e.g., vegetation, physical characteristics of soil, and rainfall intensity, have affected the distribution of the heavy metals from the rocks to the environment (El-Kady and Abdel-Wahhab 2018). Heavy metals are mostly scattered in rock formations. Some heavy metals are found in the aquatic environment and in soil on a large scale and comparatively in smaller quantity in the atmosphere as vapors; urbanization and industrialization have elevated toxicity of heavy metals in the ecosystem (Nagajyoti et al. 2010). The anthropogenic contribution of these heavy metals in the wastewater is noticeable. Many industries send out the major heavy metals in the water as the result of their surface treatment activities (Karvelas et al. 2003). Availability of heavy metals in sediments is a considerable threat to marine environment (Christophoridis et al. 2009). There are a lot of anthropogenic contributors which are involved in the contamination of marine environment such ass melting of the metallic ores, industrial fabrication, and many commercial uses of heavy metals (Saher and Siddiqui 2019). The utmost cause of accumulation of these heavy metals in freshwater is automobile traffic (Haus et al. 2007). Some heavy metals can be attached with inorganic or organic molecule. Their presence has also been observed in air particles (Faweya and Babalola 2010).

### 20.1.6 Heavy Metal Toxicity from Natural Sources

Natural and anthropogenic sources can be the utmost causes of heavy metal pollution. Many harmful and toxic gases along with their high levels of Mn, Al, Cu, Ni, Hg, Pb, and Zn have been reported by the eruption of volcanoes. Data from natural sources on the release of heavy metals are specially limited. This data shows how much natural sources are globally produced and their annual emission of toxic heavy metals. Annual emission of Cd is greater in volcanogenic particles, emission of Hg is greater in forest wild fires, and emission of Co, Cr, Cu Ni, Mn, Zn, and Pb is greater in fluttered dust.

### 20.1.7 Effects of Heavy Metal Toxicity

#### 20.1.7.1 Microorganisms

Impact of heavy metals on microorganisms depends on consideration of microbial colonies, on specific environment, and particularly on the involved metal. For example, on the phylloplane, usually bacteria turn into a form which is more sensitive to the metal pollution as compared to fungi (Duxbury 1984). A famous American chemist Bewley revealed that oak leaves which are polluted contained low amount of bacteria than uncontaminated control. A highly negative correlation appeared between many bacteria and the concentration of lead on the hawthorn leaves (Bewley 1980).

#### 20.1.7.2 Animals

Ambient air concentration areas near heavy metal toxic emission sources or consumption of contaminated water or food affects the animals because these toxics get bioaccumulated in biological organisms. Carcinogenicity, immunosuppression, mutagenicity, impaired reproduction, and poor body condition are the effects usually associated with heavy metal toxics. The residues of Cd and Pb were found in dairy cattle, chickens, and swine. Pb deposits were found in bone but both Pb and Cd deposits were found in the kidney and liver. The consumption of the liver and kidney from these exposed animals should be avoided (Govind and Mashuri 2014).

#### 20.1.7.3 Plants

Similarly, like other organisms and animals, deficiency and excess of a few vital micronutrients and heavy metals are dangerous for plants. Cu is exclusively known to be an essential micronutrient for the plants but it can also behave as a contaminated metal and has harmful effects arise at tissue level when the amount of this toxic element slightly surges. Amount of Cu when in excess brings a variety of metabolic and biochemical effects in plants that are accountable for growth inhibition, often supplemented by anomalous development (Fernandes and Henriques 1991).

#### 20.1.7.4 Human

Human consumes heavy metals through edible parts of plants which are harmful for human health if consumed for a very long period of time. Numerous toxic heavy metals affect humans when consumed in surplus than their desired amount. All heavy metals based on the importance of human health are categorized into four main groups (Rajesh and Madhoolika 2005).

The recommended dietary allowance of Zn is calculated at15 mg for adults and 20–25 mg for lactating and pregnant women (Prasad 1999). Severe Zn toxicity in humans comprises of dehydration, lethargy, vomiting, drowsiness, abdominal pain, electrolyte imbalance, renal failure, and nausea (Athar and Vohora 1995). Prolonged consumption of zinc increases the risk of damage to the pancreas, causes anemia, raises the LDL cholesterol level and lowers down HDL cholesterol level, and increases the symptoms of Alzheimer's disease. Mental fume fever was found in workers who were exposed to zinc fumes from welding or smelting (Hajjami and Fouad 2013).

## 20.2 Agriculture

Excessive use of contaminated water in the agriculture sector has become a common practice in the areas with the water scarcity (Alghobar and Suresha 2017). Generally, this contaminated water contains considerable amount of some useful nutrients and heavy metals, which are causing opportunities and problems in the agricultural sector (Singh et al. 2010).

Therefore, regular use of municipal or industrial contaminated water in agriculture may result into absorption of toxic heavy metals in plants and soils. Some important toxic pollutants are the heavy metals which affect the use of water for industrial or domestic application (Petrus and Warchol 2005).

Because of their prolonged biodegradable process and half-life nature of heavy metals, these are enlisted as the major environment-related problem, as they contaminate agricultural crops and soils and accumulate in the organs of animals and humans (Radwan and Salama 2006). The heavy metal contaminants mostly found in vegetables are Cd, Zn, Cu, and Pb (Kachenko and Singh 2006).

Through contaminated water irrigation, vegetables and crops are accumulated with toxic heavy metals and are a threat to those who consume these vegetables or crops. The first and foremost food quality and safety is to check the heavy metal contaminations in edibles (Khan et al. 2010). One of the reasons for the decrease of immunological defenses, impaired psychosocial faculties, widespread gastrointestinal cancer rates, intrauterine growth retardation, and disabilities related to malnutrition is the contamination of edibles by heavy metals which have adverse effects on human health (Arora et al. 2008).

Several researches show that the major reason of severe impacts on human health is due to the deposition of heavy metals in plant. DIM (daily intake of metals), HRI (health risk index), HQ (health quotient), and TF (transfer factor) are different indices used to determine the level of health risks caused by contaminated water with heavy metals (Liu et al. 2005).

Carcinogenic effects are shown by heavy metals, for example, Cd and Pb. Cu and Zn are the essential micronutrients for humans but can affect human health when taken in excess concentrations than their daily required proportionate. For instance, Cu taken in excessive amount can result in acute stomach pain, liver damage, and intestine-related problems and Zn can affect the immune system (Gaetke and Chow 2003).

Regular use of contaminated water for agriculture has enhanced the amounts of toxic heavy metals in plant system and soil. Research shows that soils irrigated by contaminated water were supplemented with Pb, Cu, Cd, and Zn, and various crops displayed differences in data with respect to the World Health Organization (WHO) and Food and Agriculture Organization (FAO) allowed limits. Hence, the consumption of these crops or vegetables may lead to low level deposition of heavy metals over the long period of time and the result becomes visible after few years to exposure with heavy metals. HRI (the health risk index) greater than 1 showed that the contamination of Cd and Pb in vegetables or crops had a great impact on human health due to the deposition of these toxic heavy metals in plant system grown in that area (Chaoua et al. 2018).

### 20.2.1 Heavy Metal Interaction with Bacteria

In order to carry out various biochemical reactions, bacterial cell breakdown requires various metal cations. Metal ions in higher concentrations are toxic as they inhibit bacterial growth in microbial cells (Ahemad and Malik 2011). In bacterial cells several resistance mechanisms occur, by which they immobilize, mobilize, and transform and uptake of the heavy metals. By going through these mechanisms, bacteria decreases ion toxicity associated with heavy metals. Other vital mechanisms and processes by bacteria in reducing heavy metal toxicity are exclusion, complexation, detoxification, and physical sequestration. Extracellular and intracellular materials attach with heavy metals and inhibit them from entering in microbial cells (Ahmead and Kibret 2013). Bacteria eliminate toxic effects of heavy metals by production of siderophores and restrict the bioavailability of metals by producing complexes. The production of bacterial transporters and particular metabolites can detoxify the heavy metals (Ahmead 2012).

Microbes associated with plant enhance the process of phytoremediation directly by changing the metal deposition through biochemical reactions and enhance the parameters for the growth of plants. Arsenate-reducing bacteria increased the ability to remove arsenic from contaminated soils in plants. Endophytic bacteria have great potential to stress caused by heavy metals (Idris et al. 2006). Endophytic bacteria improve the growth of plants and inhibit metal stress by repressing their translocation in plants. It also enhances plant biomass, Cd accumulation, root tips, and surface area of roots. Cd toxic effects are alleviated by enhanced root secretion of succinic, citric acid, and oxalic caused by inoculation of bacteria (Chen et al. 2014). Amalgam of mushrooms and bacteria has been used to alleviate the level of heavy metals. Following endophyte bacteria increased the process of phytoremediation of toxic heavy metals (Babu et al. 2013).

### 20.2.2 Plant Growth Hormones Alleviate Toxicity of Heavy Metals

Industrial wastes or municipal contaminated water application as liming agent and fertilizers is a separate issue in agriculture. Microorganisms associated with plants, especially PGPR (plant growth-promoting rhizobacteria), play a key role in the remediating soils from organic pollutants and in plant growth by different mechanisms (Rajkumar et al. 2012). PGPR also deals in phytoextraction, phytoremediation, and mobilization of heavy metals from soil (Sessitsch et al. 2013). The following methods of PGPR enhance the mobilization of heavy metals (Rufino et al. 2008):

1. Acidifying the environment of rhizosphere
2. Solubilizing metal minerals
3. Phytohormones production
4. Salicylic acid exerts
5. Proline accumulation
6. Biosurfactants
7. Exopolysaccharides production
8. Siderophores production

## 20.3 Relation Between Hormones and Toxic Heavy Metal Treatment

**ABA (Abscisic Acid)**

ABA (abscisic acid) is one of the phytohormone that plays a vital role during numerous stages in a life cycle of a plant that includes seed development and seed dormancy (Nambara et al. 2010). This hormone in rice plants, potato tubers, *Typha latifolia*, and *Phragmites australis* treats Cd by increasing endogenous ABA levels in their roots (Finkelstein 2013). In wheat seeds, it treats Hg, Cu, and Cd by increasing ABA levels (Bartels and Sunkar 2005; Tuteja 2007; Danquah et al. 2014).

**Auxin**

Auxin is a vital mediator in several aspects of plant growth and development (Vanneste and Friml 2009). Inside the cell, auxin decreases the IAA/AUX transcriptional repressors that are related to auxin-responsive factor (ARFs) and inhibits the transcription of auxin-responsive genes ultimately modifying plant physiology (Ruzicka et al. 2007). Under B starvation, PIN1 changes auxin distribution and possibly inhibits root elongation. Cd induces NO accumulation, which represses auxin transport and reduces root meristem size. NO is also involved in the auxin signaling pathway in response to Cu exposure (Camacho-Cristobal et al. 2015). Under Cd stress, an auxin conjugate (IAA-Asp) modulates catalase and peroxidase activity and decreases hydrogen peroxide concentration. In the same condition, auxin (NAA) increases hemicellulose 1 content and more Cd is fixed in the roots (Besson Bard et al. 2009).

**Brassinosteroids (BRs)**

This hormone regulates cell expansion and elongation, flowering, photomorphogenesis, seed germination, male fertility, vascular differentiation, stomata formation, and plant architecture (Mandava 1988). According to the number of carbons, 60 BRs have been recognized until now (Vardhini 2014). BRs help in plant development and growth and protect against abiotic stress, including low and high temperatures (Abbas et al. 2013). BRs induce SOD, CAT, and POD activities, protecting plants against heavy metal toxicity (Sharma et al. 2011).

### 20.3.1 Bioremediation Alleviate the Toxicity of Heavy Metal

Reverse osmosis, electrochemical application, chemical precipitation, oxidation, ion exchange, evaporation, filtration, and reduction are few of the physiochemical mechanisms which have been adopted in developed countries. However, these methods are very costly and also cause toxic and harmful effects leading to environmental pollution (Ahluwalia and Goyal 2007).

Therefore, a need of new cost-efficient and ecological techniques is required to alleviate the toxicity of heavy metals, and bioremediation has grasped the attention of the researchers to alleviate heavy metals. Microbes can reduce the heavy metal toxicity without polluting the environment like that of traditional physiochemical methods (Kothe et al. 2005). Due to soil sediments and heterogeneity, bioremediation is a challenge because they require microbes which are well adapted for their remediation (Tabak et al. 2005).

Hence, there is requirement for innovative and advanced technologies to recognize the processes of toxic heavy metals on the living cells. Microbial models are useful to examine the oxidative stress at cellular, biochemical, and molecular levels because of oxidative stress caused by the toxic heavy metals. Bioremediation agents are microalgae, macroalgae fungi, and bacteria (Poljsak et al. 2010).

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# Bioremediation Strategies to Mitigate the Impact of Atrazine on the Environment: Recent Advances and Prospects

# 21

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and Elizabeth Agostini

## Abstract

Atrazine is an *s*-triazine herbicide widely used for the control of weeds, primarily in corn, sorghum and sugarcane crops. It is relatively persistent in the environment, moderately soluble in water and toxic to different organisms and humans. Its mobility through soil by leaching and runoff events frequently lead to contamination of sediments and water resources. Thus, atrazine has become a compound of public concern because it is frequently detected in surface, groundwater and rainfall samples in quantities exceeding the limit values set by regulatory agencies (the EU and the USA) for drinking water. In addition, several studies have shown its impact on the ecosystem and human health. For this reason, bioremediation strategies have been described to allow the removal of atrazine and avoid its dispersion in the environment. This chapter provides information on the behaviour and impact of atrazine in soil, aquatic ecosystems and non-target organisms and summarised current knowledge about bioremediation strategies for the clean-up of sites polluted with this herbicide. Recently, material-microbial-integrated technologies have been investigated in order to degrade atrazine, which will be also described. Finally, the bioremediation strategies are evaluated under laboratory and field conditions. Future advances

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related to atrazine degradation need to focus on an efficient removal and low environmental impact.

**Keywords**

Atrazine · Bioremediation · Phytoremediation · Organic pollutants · Environment

## 21.1 Introduction

Atrazine is the most widely used s-triazine herbicides to control broadleaf weeds for many crops in the world. However, the benefit of weed elimination in crops is offset by the negative impact generated by the application of herbicides on the environment and on living beings. In fact, the atrazine contamination has become a growing public concern because it is one of the most commonly detected pesticides in soil, surface water and groundwater, representing a serious risk for the environment and public health (Nguyen et al. 2014). To minimise the damage caused by this herbicide, it is necessary to find and apply processes that allow its removal from contaminated sites. A great number of technologies are developed, such as adsorption, biodegradation and photochemical catalysis. Among the different methodologies proposed, bioremediation appears as a promising alternative that takes advantage of the metabolic potential of microorganisms to degrade contaminants and it can be carried out in different media such as sediments, soils, surface and groundwater, and biological sludges. In addition, both microbial-assisted plant remediation and the use of immobilised microorganisms have been also proposed for atrazine degradation. In the present chapter information on the behaviour and impact of atrazine on soil and aquatic ecosystems will be discussed. Besides, the progresses of researches based on the abovementioned biological treatment technologies for atrazine removal will be reviewed and summarised as well as the future prospects of these approaches.

## 21.2 Atrazine: Main Characteristics, Behavior and Environmental Impacts

### 21.2.1 Atrazine: Properties and Uses

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is an important *s*-triazine herbicide. Its molecular formula is $C_8H_{14}ClN_5$; it is a solid crystalline powder and unstable at high temperature. Atrazine has a melting point of 175.8 °C, a water solubility of 33 mg $L^{-1}$ (20 °C) and is readily soluble in organic solvents (Lewis et al. 2016). Atrazine is highly persistent with a half-life of 32–128 days in soil and of 100 days in water (Krutz et al. 2008). However, their half-life is increased in subsurface environments due to the low natural microbial degradation potential (Singh and Jauhari 2017).

Atrazine has been commercially available for more than 50 years. It was registered in Switzerland in 1958 and is widely used since the early 1960s in the USA, Europe, Africa, Asia and South America to control broadleaf weeds and some grasses weeds that affect mainly on corn, sorghum and sugarcane crops (Viegas et al. 2012). Nowadays, atrazine is the second most extensively used herbicide globally with an annual consumption of about 70,000–90,000 tons (Cao et al. 2021). The United States (USA) applied about 33,560 tons every year (Gaffar et al. 2021), while China has consumed 23,000 tons (Liu et al. 2021). South America is one of the areas of the world where atrazine is massively applied in agriculture. In Argentina, about 10,000 tons of atrazine are consumed annually (Alonso et al. 2018). Atrazine can increase yields by 6–50% depending on the crop (Rajendran et al. 2021). Commercial atrazine formulations are different and depend on each country: flowable, wettable powder, water-dispersible granules and soluble concentrate (Viegas et al. 2012). The main advantages of using atrazine are the versatility of its application and facility to mix it with other herbicides, such as *S*-metolachlor, alachlor, paraquat and linuron for broad-spectrum weed control (Rajendran et al. 2021).

Atrazine is used as a non-selective herbicide on both fallow and non-farmland land (He et al. 2019). It acts on the target weeds by blocking electron transport in photosystem II. This blocking occurs because atrazine inhibits the plastoquinone binding site (QB) of the D1 protein in chloroplasts and consequently suppressing the electron flow between photosystems (de Albuquerque et al. 2020). Therefore, electrons are not stored as chemical energy and chlorophyll molecules are heavily loaded with energy leading to lipid peroxidation in the membranes, inhibition of carbohydrate synthesis, decrease of the carbon (C) stock and accumulation of carbon dioxide ($CO_2$) within plant cells and damage of leaf chlorophyll (Marchi et al. 2008). In the pre-emergence application, atrazine is first absorbed by the roots and then transported to the leaves, where its action produces chlorosis, necrosis and death. In post-emergence application, this herbicide is absorbed by the leaves (Souza et al. 2012; de Albuquerque et al. 2020). The action time of atrazine varies between 2 and 6 months, due to its stability in neutral and slightly alkaline or acid soil conditions (CASAFE, Cámara de Sanidad Agropecuaria y Fertilizantes 2013). The accumulation of atrazine in soil is prone to phytotoxicity to sensitive crops, such as soybeans, rice, oat and wheat (Chen et al. 2019).

The application of atrazine has been discussed due to its persistence and mobility in the environment, and consequently it is detected in the soil, surface water, groundwater, pastures, streams, lakes, sediments, foods and even glaciers in remote areas (Barchanska et al. 2012; Hansen et al. 2013; Sun et al. 2017; Pan et al. 2019; Wang et al. 2020). Consequently, the European Union (EU) banned its application in the year 2004. The USA and Canada have adopted restriction policies to minimise its potential environmental impact. However, it is still used extensively in agricultural practices in numerous countries, highlighting Argentina, China, Brazil and India (Sun et al. 2017; Montoya et al. 2019; de Albuquerque et al. 2020).

Massive application, mainly coinciding with rainy seasons, the high persistence and mobility are the main reasons for the atrazine detection in soil, surface water and groundwater at concentrations exceeding the limit established by normative values

(Bachetti et al. 2021; Rajendran et al. 2021). The US Environmental Protection Agency (US EPA) has established the maximum atrazine concentration limit values in drinking water at 3 μg $L^{-1}$ (US EPA 2007). However, the EU (EU 2004) and the World Health Organization (WHO 2011) have established the permissible limit to 0.1 and 2 μg $L^{-1}$, respectively. The persistence of atrazine on environmental compartments poses a serious threat to human health. Furthermore, the US EPA has classified atrazine in toxicity class III and as an endocrine disruptor herbicide (Morales-Pérez et al. 2016; Singh and Jauhari 2017). The International Agency for Research on Cancer (IARC) has categorised atrazine in the list of carcinogenic herbicide (Mahler et al. 2017).

### 21.2.2 Behaviour and Impact of Atrazine on the Environment

After being applied, only 0.1% of the herbicide reaches the target organisms (weeds). The remainder can interact with the different environmental compartments through complexes biological, physical and chemical reactions. The environmental behaviour of atrazine depends upon several factors, including retention, transformation and transport processes, as well as by the interaction between them (Fig. 21.1) (Sun et al. 2019). These interactions are complex, being controlled simultaneously by biological, physical and chemical reactions. After being applied and before it reaches the soil, the herbicide may undergo photolysis, volatilisation and/or may be adsorbed or absorbed by the plant or by the stubble on the surface. Once in the soil, the xenobiotic is partitioned into solid, gas and liquid phases; in the latter, chemical and microbial degradation occurs, these processes being the most important for the dissipation of most herbicides. It is well known that the natural attenuation and fate of atrazine in soil environments are strongly related to adsorption, desorption and mineralisation processes (Liu et al. 2021).

The transformation of atrazine can be due to photochemical or biochemical processes, producing simpler molecules with different properties from that of the original compound (Mudhoo and Garg 2011). In fact, atrazine can be degraded in more than 15 metabolites, and each transformation product varies in its persistence (months to decades) and toxicity (Xue et al. 2021). The major atrazine degradation products are hydroxyatrazine (HA), deethylatrazine (DEA) and deisopropylatrazine (DIA). Due to their mobility, they have been frequently detected in many surface and groundwater of the world (Jablonowski et al. 2011; Nödler et al. 2013). Formation of HA occurs through different (biotic or abiotic) degradation mechanisms leading to the hydrolysis of atrazine molecule, and the microbial mediated process of atrazine N-dealkylation produces the mobiles metabolites DEA and DIA (Mudhoo and Garg 2011). The HA is the most important metabolite, with a higher retention in soils compared to other products (Chokejaroenrat et al. 2020).

A comprehensive understanding of the herbicide behaviour in the environmental compartments is extremely important to implement appropriate environmental management strategies to reduce its impact on human and animal health in the vulnerable areas.

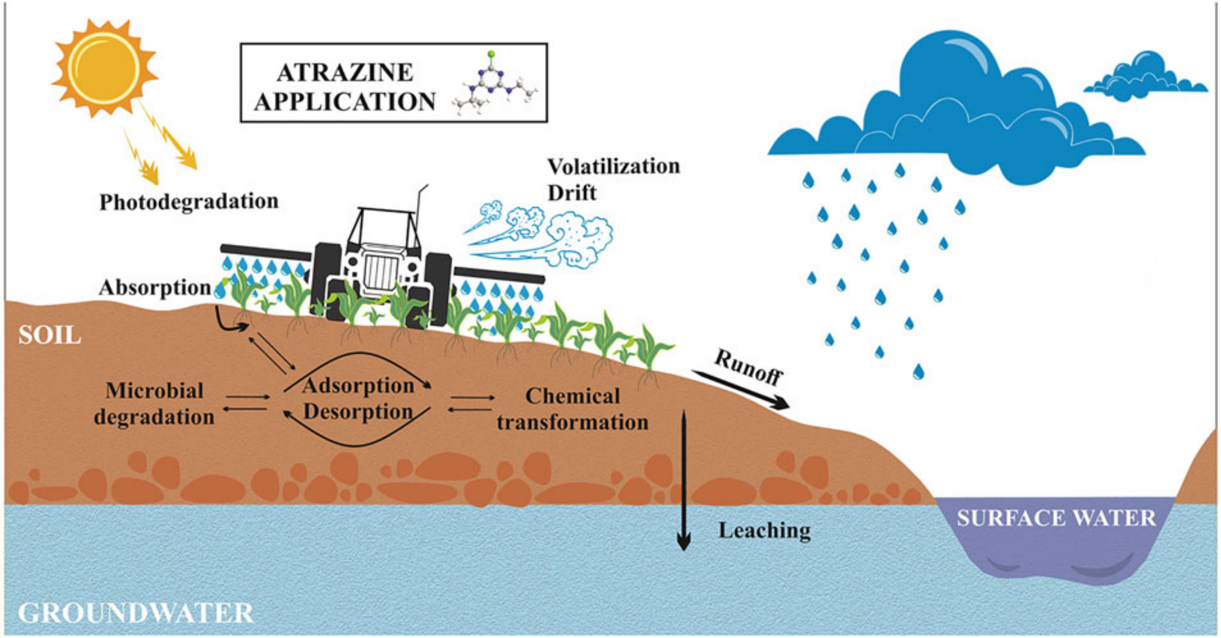

Fig. 21.1 Environmental behaviour of atrazine

### 21.2.3 Soil Contamination and Effects in Terrestrial Ecosystems

Soil is an important life-supporting system and plays a critical role for primary production, the regulation of biogenic gases, biogeochemical and hydrological cycles as well as the biodiversity preservation (Sun et al. 2017). However, soil pollution has become a worldwide concern because it acts as an important reservoir for numerous organic pollutants such as herbicides (Ali et al. 2019). In the soil, atrazine is distributed between aqueous and solid phases. Two different but coexisting processes are proposed for the atrazine movement in soils. One of them, is the rapid movement of the herbicide corresponding to a preferential flow through the soil macropores and the other one is a slow transport due to the sorption and degradation processes in the soil matrix (Mudhoo and Garg 2011).

The main processes that determine the persistence of atrazine in the soil environment are the physicochemical and microbiological properties (organic matter content, pH, texture, cation exchange capacity, microbial abundance and metabolic activity) of the soil, climatic characteristics (temperature, humidity, precipitation) and other parameters (mode and rate of application, prior history use, plant cover, topography) (Hernández et al. 2008; Prado et al. 2014). Atrazine breakdown in soil occurs mainly by chemical and microbial aerobic degradation (Viegas et al. 2012). Chemical degradation can occur by hydrolysis or by photodegradation. Atrazine is stable at room temperature, in the dark, at neutral pH and in the absence of microorganisms and organic matter (Prosen and Zupančič-Kralj 2005). This herbicide atrazine can be extremely persistent in soil environment due to its ability to bind to soil colloids (organic matter and clays) and become non-extractable residues (Martins et al. 2018). Recent studies have been dedicated to evaluate the behaviour and fate of atrazine in soils (Salazar-Ledesma et al. 2018; Sun et al. 2019; Liu et al. 2021), especially the adsorption and desorption processes between this herbicide and soil which influence its mobility and availability for weed control (Martins et al. 2018; Piratoba et al. 2021). Adsorption of atrazine seems to be positively correlated with organic matter and clay content and negatively with pH (Aparicio et al. 2015; Yue et al. 2017). It is reported that soil organic matter contains a variety of functional groups such as hydrophobic, hydrophilic and free radicals that can strongly entrap atrazine (Barriuso and Houot 1996). The pH is a factor affecting the adsorption of atrazine in soils, because when the pH increases, the soil surface tends to be negatively charged and organic molecules also tend to be ionised and negatively charged (Huang et al. 2013). This generates a repulsion of same-sign charges, which will be detrimental to the adsorption of organic molecules on the soil surface (Wang et al. 1999).

The accumulation of atrazine in soil (either dissolved or bound to colloids) is considered a long-term source of the compound leading to its possible occurrence to surface or groundwater. Numerous studies also reveal an accelerated degradation of atrazine due to the prolonged exposition of emergent native microbial populations capable to utilise the herbicide as a C (carbon) or N (nitrogen) source (Jablonowski et al. 2011; Sun et al. 2017). The exposure to some pesticides may change the resources that soil microorganisms use to obtain energy and nutrients, especially in soils with low levels of organic matter (Fernandes et al. 2020). Specific microorganisms are able to detoxify atrazine by N-dealkylation or dehalogenation reactions, and this may imply the development of microbial communities that can utilise the N in the triazine ring (Cycoń et al. 2017; Esquirol et al. 2020). Atrazine microbial degradation will be explained in Sect. 21.3 of this chapter. Soil macrofauna can also directly or indirectly affect the degradation and ultimately the fate of atrazine. In point of fact, the presence of earthworms in the soil may also affect the transport of atrazine. This is due to earthworms, which are keystone organisms that can ingest and transport the atrazine residues to deeper soil layers, enhancing the formation of non-extractable residues, thus reducing the leaching potential of this herbicide (Mudhoo and Garg 2011; Viegas et al. 2012).

Several studies have reported atrazine residues in soils and sediments from all over the world. Atrazine residues (19.5 g ha$^{-1}$) and their degradate products were still found in agricultural soils a long time after the last herbicide application (more than 20 years), as well as in soils with no history of atrazine application (Jablonowski et al. 2010). Sun et al. (2017) showed that atrazine concentrations ranged from 1.0 to 113 ng g$^{-1}$ dry weight, with a frequency of detection of 57.7% in soil samples of China ($n = 241$) and reported a close association between contamination and land use type. In Pakistan, Ali et al. (2019) evaluated the concentrations of 30 endocrine disrupting pesticides in soil and vegetable samples. Atrazine concentrations ranged from 1.7 to 120 μg kg$^{-1}$ in soil samples, while no residues were detected in the vegetables studied. Alonso et al. (2018) showed atrazine residues (4–66 μg kg$^{-1}$) in soil samples ($n = 58$) from the provinces of Córdoba and Buenos Aires (Argentina), an important corn producing area of Argentina. In addition, Mac Loughlin et al. (2017) detected atrazine in sediments of Carnaval creek ($n = 10$) (Buenos Aires, Argentina) at concentrations ranging from 5.1 to 32.7 μg kg$^{-1}$, causing lethal and sublethal effects on benthic fauna.

The most susceptible group to the deposition of atrazine residues in the soil environment are non-target crops that may receive atrazine by spray drift, accidental spills or carryover. As a consequence of atrazine exposition, target and non-target plants often undergo oxidative stress because of an enhanced reactive oxygen species (ROS) production. Beker Akbulut and Yigit (2010) determined that ROS caused negative effects on peroxidase, ascorbate peroxidase and lipid peroxidation in *Z. mays* plants with postemergence atrazine application. Gao et al. (2011) reported that exposure to 10 μg L$^{-1}$ atrazine significantly reduces plant fresh weight and total chlorophyll concentration. The authors also revealed a high plant mortality (up to 86.7%) at 100 μg L$^{-1}$ concentration. Çanakci-Gülengül and Karabulut (2020) investigated the biochemical effects of atrazine concentrations (0, 200, 500 and 1000 μM) on wheat (*Triticum aestivum* L.) seedlings. The results indicated a decrease in reduced glutathione/oxidised glutathione (GSH:GSSG) ratio and catalase activity (CAT) in leaf and root and an increase in superoxide dismutase (SOD) activity. Gao et al. (2019) showed that seagrass *Zostera marina* L. exposed to high concentrations of atrazine (1, 3 and 10 μg L$^{-1}$) significantly inhibited photosynthetic efficiency and reduced shoot sugar levels.

Atrazine also affected soil invertebrates, especially earthworm, mites, nematodes and collembolans species (Singh and Jauhari 2017). Lammertyn et al. (2021) exposed earthworms (*Eisenia fetida*) to different concentrations of atrazine to evaluate possible sublethal harmful effects. The results showed that atrazine (2 mg kg$^{-1}$) affected the rate of cocoon production and increased lactate dehydrogenase and, especially, acetylcholinesterase activity. On the other hand, Dani et al. (2018) showed that earthworms exposed to sublethal concentrations of atrazine (362.4, 181.2, 90.6 and 45.3 ng cm$^{-2}$) caused a general suppression in their metabolism, reduced ATP synthesis and had a negative impact on general health.

### 21.2.4 Water Contamination and Effects in Aquatic Ecosystems

Atrazine properties, such as low vapour pressures, moderate water solubility and low soil adsorption coefficient ($K_{OC} = 100$ cm$^3$ g$^{-1}$), indicate its high leaching potential, particularly in well-structured soil profiles (de Albuquerque et al. 2020). Most atrazine movement occurs in the soil aqueous phase. Therefore, precipitation contributes to its dispersion in aquatic systems near the application zone (Jablonowski et al. 2011; Bachetti et al. 2021). Another, but less common, transport mechanism is adsorption of atrazine to eroded soil particles (Alonso et al. 2018). Atrazine is a frequently detected pesticides in groundwater and surface runoff from around the world (Table 21.1). Peng et al. (2018) identified the diversity and complexity of organic pollutants at 28 sampling sites in the Yangtze River Delta, finding an atrazine concentration of 1726 ng L$^{-1}$. The authors concluded that this concentration exceeded the annual average environmental quality standards of Europe. In fact, the value was 9.4 times higher than the concentration reported by Battaglin et al. (2016) in seven US states for atrazine in surface water (183 ng L$^{-1}$). These authors analysed a total of 86 water samples and atrazine was one of the most frequently detected herbicide (18% of the samples). In Europe, researchers collected 314 groundwater samples from the Júcar River European Union Pilot Basin (Spain), and the study showed that atrazine was frequently detected after terbuthylazine and bromacil (Menchen et al. 2017). Fingler et al. (2017) obtained samples from different surface and groundwater resources in Croatia, finding atrazine residues in all of them in concentrations of around 68 ng L$^{-1}$. Almasi et al. (2020) founded atrazine concentrations from 0 to 2,175,800 ng L$^{-1}$ in aquifers from Iran. In South America, atrazine is a common herbicide detected in various surface water and groundwater (De Gerónimo et al. 2014; Montagner et al. 2019; de Albuquerque et al. 2020). Particularly in Argentina, Montoya et al. (2019) reported its occurrence in 26% of groundwater samples ($n = 95$) with concentrations between 0.3 and 16.1 ng L$^{-1}$. The values detected in this study were lower than those informed by Mas et al. (2020) in aquifers from Santiago del Estero (Argentina), where concentrations ranged from 1 to 7921 ng L$^{-1}$. Recent studies performed in the Ctalamochita river basin (Córdoba, Argentina) showed the high ubiquity and persistence of the herbicide in surface water courses and at concentrations reaching 5000 ng L$^{-1}$. The results revealed that atrazine residues in surface waters increased

**Table 21.1** Atrazine residues detected in water resources around the world

| Continent | Country | Sites | Water resource | Concentration (ng L$^{-1}$) | | | Reference |
|---|---|---|---|---|---|---|---|
| | | | | Min | Max | Mean | |
| Europe | Croatia | Zagreb | Surface water<br>Lakes<br>Groundwater<br>Drinking water | 8.0<br>5.0<br>5.0<br>5.0 | 18.0<br>6.0<br>61.0<br>68.0 | – | Fingler et al. (2017) |
| | France | | Bottled waters | 2.0 | 4.0 | – | Le Coadou et al. (2017) |
| | France | South | Groundwater | 1.0 | 109.0 | 14.0 | Sassine et al. (2017) |
| | Greece | Epirus | Surface water | 75.0 | 77.0 | 13.0 | Kapsi et al. (2019) |
| | Portugal | South | Surface water | 2.0 | 3.0 | – | Gonzalez-Rey et al. (2015) |
| | Spain | Catalonia | Sea water | 0.0 | 3.8 | 1.1 | Köck-Schulmeyer et al. (2019) |
| | Spain | Mancha Oriental | Groundwater | 1.1 | 380.0 | – | Menchen et al. (2017) |
| America | Argentina | Córdoba | Surface water | – | 5000.0 | – | Bachetti et al. (2021) |
| | Argentina | Santiago del Estero | Groundwater | 1.0 | 7921.0 | 260.0 | Mas et al. (2020) |
| | Argentina | Pampean plain | Rainwater | 500.0 | $6.7E^4$ | 5490.0 | Alonso et al. (2018) |
| | Argentina | La Pampa | Groundwater | 0.3 | 16.1 | - | Montoya et al. (2019) |
| | Brazil | São Paulo | Surface water<br>Tap water<br>Groundwater | 1.0<br>1.0<br>2.0 | 611.0<br>687.0<br>5.0 | 30.0<br>36.0<br>3.0 | Montagner et al. (2019) |
| | Brazil | Rio Grande do Sul | Tap water<br>Surface water | 5.0<br>5.0 | 37.0<br>49.0 | 16.0<br>19.0 | Caldas et al. (2019) |
| | Brazil | São Paulo | Surface water<br>Groundwater | 5.2<br><1.7 | 516.0<br><1.7 | – | Acayaba et al. (2021) |
| | Canada | Quebec | Tap water | 30.0 | 195.0 | 69.0 | Montiel-León et al. (2019b) |

(continued)

**Table 21.1** (continued)

| Continent | Country | Sites | Water resource | Concentration (ng $L^{-1}$) |  |  | Reference |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Min | Max | Mean |  |
|  | Canada | Trois-Riviéres | Surface water | 4.0 | 666.0 | 29.2 | Montiel-León et al. (2019a) |
|  | Canada | Ontario | Lakes | – | 754.0 | – | Metcalfe et al. (2019) |
|  | Chile | Central | Surface water | – | – | 45 | Climent et al. (2019) |
|  | USA | Rocky Mountain Nacional Park | Surface water | – | 12.0 | – | Battaglin et al. (2018) |
|  | USA | Florida | Sea and surface water | 5.0 | 21.0 | – | Fernandez and Gardinali (2016) |
|  | USA | Tifton | Surface water | – | 1650.0 | – | Glinski et al. (2018) |
|  | USA | Ohio | Tap water | 0.0 | $1.6 \times 10^4$ | – | Almberg et al. (2018) |
| Asia | China |  | Tap water | 10.0 | 1441.0 | 1.7 | Wang et al. (2020) |
|  | China | Baima River | Surface water | 10.0 | 1120.0 | – | Sun et al. (2019) |
|  | China | Guangxi | Tap water, groundwater and surface water | 70.0 | 585.0 | – | Li et al. (2018) |
|  | China | Jiaozhou Bay | Sea water | 20.3 | 174.0 | – | Ouyang et al. (2019) |
|  | China | Liaodong | Surface water | 21.3 | 1726.1 | 191.4 | Peng et al. (2018) |
|  | China | Liaodong | Surface water | 8.7 | 64.8 | 23.3 | Xie et al. (2019) |
|  | Iran | Shadegan Wetland | Surface water | 0.0 | $2.2 \times 10^6$ | – | Almasi et al. (2020) |
| Africa | Egypt |  | Groundwater | 0.0 | 5000.0 | 2000.0 | Masoud et al. (2018) |
|  | South Africa | Gauteng | Surface water<br>Groundwater | <5.0<br>100.0 | 1570.0<br>180.0 | – | Rimayi et al. (2018) |

during the warm and rainy season as a consequence of atrazine application but also due to differences in textural and compositional characteristics of soil (Bachetti et al. 2021). Besides, atrazine has also been detected in rainwater from the Pampean plain of Argentina with detection frequency >80%, at concentrations from 500 to 67,280 ng $L^{-1}$ (Alonso et al. 2018). The detection of atrazine in water resources, in concentrations above the maximum acceptable levels for drinking water, is of concern as it represents a direct risk to human health through drinking water consumption. To minimise the damage caused by this herbicide, it is necessary to apply processes that allow its removal from *s*-triazine-contaminated sites.

Aquatic ecosystems are complex environments as they contain a great diversity of organisms (algae, bacteria, fungi and protozoa) that play important roles in primary productivity, decomposition of organic compounds and nutrient cycling (Mauffret et al. 2017). Aquatic environments receive direct and indirect inputs of different compounds such as herbicides, causing qualitative and quantitative changes on microbial communities. These effects can impact on higher trophic levels and on processes that contribute to overall water quality (Verrhiest et al. 2002; Ensz et al. 2003). In this context, environmental impact on aquatic organisms associated with the application of atrazine has been widely reported (Bai et al. 2015; Baxter et al. 2016; Singh and Jauhari 2017). In addition, atrazine can be absorbed by algae and aquatic plants through cell walls, exerting toxic action mainly through inhibition of photosynthesis (DeLorenzo et al. 2001). For instance, Esperanza et al. (2017) evaluated the impact and action mode of the atrazine on the cellular senescence process of *Chlamydomonas reinhardtii*. The results indicated an increase in intracellular calcium levels, alterations in nuclear and cell morphology, as well as in the activity of biochemical and molecular markers, suggesting that short-term exposure to atrazine can promote death of microalgae, which are the basis of aquatic food webs. Zhao et al. (2018) showed that atrazine inhibited the growth of the microalga *Selenastrum capricornutum*. Sun et al. (2020a) observed acute toxicity of atrazine in the microalga *Chlorella* sp. because atrazine damaged the reaction centre of photosystem II. Religia et al. (2019) demonstrated that phytoplankton (*Raphidocelis subcapitata*) exposed to sublethal doses of atrazine affect the population dynamics of its predator, *Daphnia magna*, due to the production of non-viable broods. Simultaneously, atrazine toxicity can change water quality, due to increased concentrations of C, N and/or inorganic phosphorus (P), pH modifications and increased electrical conductivity (Viegas et al. 2012; de Albuquerque et al. 2020) and decreased dissolved oxygen ($O_2$) concentration due to reduced primary productivity (C fixation) by photosynthetic organisms (DeLorenzo et al. 2001).

### 21.2.5 Effects on Higher Organisms

Toxicity effects of atrazine on other non-photosynthetic organisms (honeybees, birds and mammals) is lower in comparison to plants and algae. However, several works have demonstrated the effect of atrazine exposure on different higher organisms (Hirano et al. 2019; Soltanian 2016). Atrazine mainly affects the endocrine system

(Mukherjee et al. 2019; Graceli et al. 2020), and it also causes oxidative stress due to the formation of reactive oxygen species, leading to reduced semen quality and infertility in fish, crustaceans and mammals (Gely-Pernot et al. 2015; Owolabi and Omotosho 2017; Stara et al. 2018). In aquatic species, the exposure to atrazine ($<5$ μg $L^{-1}$) resulted in transgenerational reproductive dysregulation in *Oryzias latipes* (Cleary et al. 2019), disrupted immunity in *Cyprinus carpio* (Wang et al. 2019) and induced oxidative stress, reproductive dysfunction and neuroendocrine impairments in *Danio rerio* (Adeyemi et al. 2015). In addition, Hedayatirad et al. (2020) exposed *Danio rerio* to 0, 5 and 50 μg $L^{-1}$ atrazine and observed that it increased cortisol level and decreased total immunoglobulin and lysozyme, affecting reproduction, thyroid function, stress reactivity and immunity of mature female zebrafish and subsequently their offspring. Abdulelah et al. (2020) demonstrated that exposure to atrazine ($>10$ ppb) causes significant DNA damage in crayfish lateral antennal cells, including olfactory sensory neurons, leading to impaired chemosensory abilities. Because crayfish rely on chemoreception for survival, changes in their ability to perceive odours following exposure to atrazine may have detrimental effects on their population size. Blahova et al. (2020) showed that common carp (*Cyprinus carpio* L.) chronically exposed to a range of atrazine concentrations (0.3; 300; 1000 and 3000 μg $L^{-1}$) for 12 weeks negatively influenced many health status indicators, such as oxidative stress indices, immune system response, haematological and biochemical profile and organ histopathology.

In mammals, Komsky-Elbaz and Roth (2017) indicated that bovine spermatozoa exposed to atrazine (0.1–3 μg $L^{-1}$) negatively affected sperm membranes, sperm viability, acrosome reaction and mitochondrial function. In females it produces imbalances in sex hormones and interferes with androgen or oestrogen receptors, altering instinctive abortion, ovarian cycles and defect in birth development (Bohn et al. 2011). It was suggested that the negative effects of atrazine on the neuroendocrine system are caused by altered hormone levels, mainly follicle-stimulating hormone (FSH) and luteinising hormone (LH) (Song et al. 2014). Altered LH levels contribute to prolonged prolactin secretion and subsequent stimulation of mammary gland changes and increased incidence of mammary fibroadenomas and adenocarcinomas (Jowa and Howd 2011; Simpkins et al. 2011). Foradori et al. (2009) exposed ovariectomised female rats to several atrazine doses (0 and 200 mg $kg^{-1}$ $day^{-1}$) for 4 days and reported that this herbicide reduced the number of activated gonadotropin-releasing hormone (GnRH) neurons. However, after 4 days of atrazine withdrawal, LH levels and GnRH activation markers returned to normal levels in treated animals. Although the negative effects could be reversed, it is unknown what may occur after longer exposure with the herbicide. Finally, Foradori et al. (2018) concluded that atrazine activates the hypothalamic-pituitary adrenal axis centrally and requires corticotropin-releasing hormone receptor activation. Atrazine also causes liver damage, the main metabolising organ of atrazine in mammals (Xing et al. 2015; Sagarkar et al. 2016). Cardiovascular system functioning is also affected by atrazine exposure (Cosselman et al. 2015). Besides, a possible association between atrazine contamination and a greater effect of several types of cancer in human cells, leukaemia and lymphoma has also been proposed (Thueson et al. 2015; Kirsten et al. 2017; Li et al. 2017; Brasil et al. 2018). There is limited epidemiological evidence on the adverse effects of prenatal atrazine exposure in humans. Consumption of drinking water with atrazine residues has been associated with an increased risk of preterm birth in Kentucky (Rinsky et al. 2012) and in four Midwestern states from the USA, where $<10\%$ of the population uses private well water (Stayner et al. 2017). In France, Chevrier et al. (2011) demonstrated that atrazine residues in maternal urine were associated with alterations in the babies, such as lower birth weight, head circumference and height. Xie et al. (2021) exposed human SH-SY5Y neuronal cells to 0.3, 3 and 30 $\mu g\ L^{-1}$ atrazine, showing alterations in neurite outgrowth and SNCA pathology, which leads to epigenome changes and an increased risk of Parkinson's disease. Previous epidemiological studies on the effect of atrazine on newborns are based on ecological estimates obtained from environmental monitoring data. Thus, a more reliable and accurate presence of atrazine is essential to ensure the safety of biota, human health and the environment.

## 21.3 Bioremediation of Atrazine-Contaminated Environments

Bioremediation involves the utilisation of microorganisms, plants or their enzymes for the partial or complete transformation of organic pollutants present in environments, in order to protect the natural ecosystem and prevent further pollution (Viegas et al. 2019). This biotechnological tool has several advantages compared to the physicochemical treatments, such as lower operational costs, in situ application, efficient elimination and minimum disturbance of the treated site (Hernández et al. 2008). Due to this intensive method which must be adapted to site-specific conditions, small-scale pilot experiments are necessary before they can be carried out in the contaminated field. However, bioremediation sometimes has limitations, which will affect the efficiency of microbial degradation. Therefore, it is necessary to search microorganisms with better performance and environmental tolerance. Besides, the use of genetic technologies to improve the degradation properties of microorganisms is also receiving increasing attention (He et al. 2019).

Biostimulation and bioaugmentation are natural attenuation methods that allow in situ microbiological remediation of atrazine. Natural attenuation involves physical, chemical or biological processes in the environment to dissipate the contaminant, being a very slow process. Biostimulation involves treating the contaminated soils to increase the pollutant bioavailability or adding a co-substrate or nutritional compound to increase the population of indigenous (or introduced) bacteria that degrade contaminants (Tyagi et al. 2011). In this case, the elimination of atrazine depends on its initial concentration, the pH of the medium, the inoculation time and the type of stimulant (Rajendran et al. 2021). On the other hand, bioaugmentation involves the inoculation with microbial strains or consortia (indigenous or not) to improve the system's biodegradation capacity of a specific organic pollutant in contaminated soils or water (Philp and Atlas 2005; Hernández et al. 2008). Furthermore, bioaugmentation may be required when indigenous degraders cannot degrade the pollutant rapidly or the degrading microorganisms are not present (Gentry et al.

2004). Both biostimulation and bioaugmentation are the most efficient methods of converting a pesticide into a less-harmful end product.

### 21.3.1 Bacterial Remediation

Bacteria are able to remove, degrade or breakdown xenobiotic compounds in less toxic or non-toxic ones by a process usually called bioremediation. This is a promising technology that includes different processes such as (a) pollutant transformation, (b) degradation to simple molecules, (c) mineralisation into inorganic compounds (such as $CO_2$, $H_2O$, $H_2$, $NH_3$, etc.), (d) cell surface sorption and (e) intracellular accumulation, among others (Krastanov et al. 2013). It is a profitable and increasingly popular technology to restore the environment quality (Lyon and Vogel 2013). In this process, microorganisms employ the contaminants as a source of nutrients or energy for their growth (Benimeli et al. 2008). However, at the time of its application, it is important to consider the susceptibility of the contaminant to microbiological transformation, the biological activity (bioactivity) to promote microbial growth and activity and the affordability of the contaminants to microorganisms (bioavailability) (Niti et al. 2013).

Numerous bacterial strains (Gram-positive and Gram-negative) have been described with the capability to use atrazine as a substrate (C and/or N source) for their growth (Udiković-Kolić et al. 2012). Among them, *Pseudomonas* sp. ADP has been the bacteria used for the study of the metabolic pathway of *s*-triazine degradation and its regulation (Cao et al. 2021). The two catabolic pathways of atrazine degradation, one upper and one lower, involve the *atz*ABCDEF genes located in the pADP-1 plasmid (Martinez et al. 2001). The enzymes encoded by these genes catalyse six successive hydrolysis: one dechlorination, two dealkylations, biuret deamination, ring cleavage and an allophanate hydrolysis (Fig. 21.2). Thus, the upper catabolic pathway transforms atrazine to cyanuric acid, and the enzymes responsible for these transformations are coded by the *atz*A, *atz*B and *atz*C genes (Mandelbaum et al. 1995; De Souza et al. 1996, 1998; Sadowsky et al. 1998). An initial hydrolase different from *atz*A, but with identical function, called *trz*N, has also been described, mainly in Gram-positive bacteria, such as *Arthrobacter aurescens* TC1, *Nocardioides* sp. C190 and *Nocardioides* sp. SP12 (Topp et al. 2000a; Piutti et al. 2003; Sajjaphan et al. 2004; Smith et al. 2005). However, its presence has also been demonstrated in Gram-negative genera such as *Sinorhizobium* and *Polaromonas* (Devers et al. 2007). Thus, atrazine dechlorination results from the activity of *atz*A (atrazine chlorohydrolase) or *trz*N (triazine hydrolase), both aminohydrolases, which produce HA. It is known that *atz*A and *trz*N possess different substrate ranges: *atz*A hydrolyses *s*-triazine compounds whereas *trz*N hydrolyses radical groups (–$OCH_3$, –$SCH_3$, –CN, –F, –Cl) of both *s*-triazines and pyrimidines (De Souza et al. 1996; Seffernick et al. 2000, 2002; Strong et al. 2002; Shapir et al. 2006). Subsequently, HA is transformed into N-ethylammelide or N-isopropylammelide by hydrolysis of the N-ethyl or N-isopropyl side groups. Then, the transformation to N-isopropylammelide is encoded by *atz*B

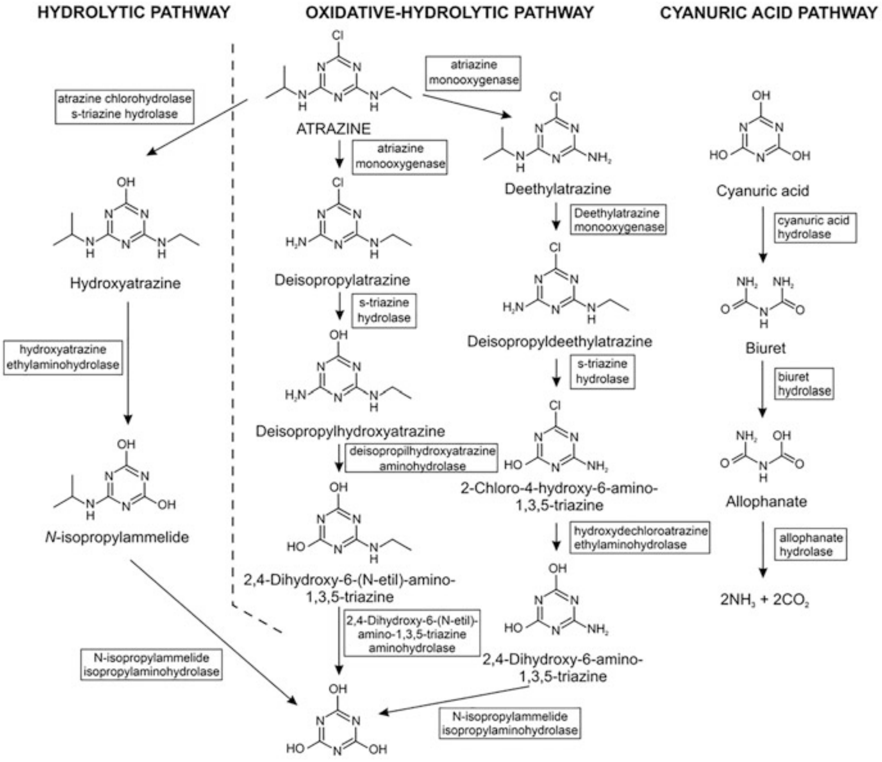

**Fig. 21.2** Pathways of atrazine mineralisation

(hydroxyatrazine hydrolase) (Boundy-Mills et al. 1997) which is capable of catalysing the hydrolytic deamination of N-ethylammelide to cyanuric acid (Smith et al. 2005), an intermediate in the catabolism of *s*-triazines (Cook 1987). However, N-isopropylammelide is transformed to N-isopropylamine and cyanuric acid by the enzyme *atz*C (N-isopropylammelide hydrolase) (Sadowsky et al. 1998). These intermediates freed from the *s*-triazine ring by *atz*B and *atz*C can be used as sources of C, N and/or energy for the growth of the microorganism itself or others present in the environment (Strong et al. 2002; Kolić et al. 2007).

The lower pathway is carried out by three enzymes coded by the *atz*D, *atz*E and *atz*F genes (Cao et al. 2021) and leads to the final mineralisation of cyanuric acid to $CO_2$ and $NH_3$. It begins with ring cleavage in cyanuric acid catalysed by the enzyme cyanuric acid hydrolase (*atz*D) resulting in the production of the intermediate biuret carboxylate, which rapidly decomposes to biuret and $CO_2$ (Seffernick et al. 2012). Alternatively, the *trz*D gene, with homologous function to the *atz*D gene, which encodes an enzyme involved in the cleavage of the *s*-triazine ring of cyanuric acid, has been identified in several *s*-triazine-degrading bacterial genera such as *Pseudomonas*, *Paenarthrobacter*, *Arthrobacter*, *Aminobacter*, *Nocardioides*, *Klebsiella*, *Alcaligenes* and *Ralstonia* (Cheng et al. 2005; Arbeli and Fuentes 2010; Yang et al. 2010; Fernández et al. 2013; Li et al. 2020). The hydrolysis of biuret to allophanate is mediated by biuret hydrolase (*atz*E) (Martinez et al. 2001; Cheng et al. 2005), and this deamination releases ammonium, which can be used by bacteria as a N source for growth. Finally, allophanate hydrolase (*atz*F) produces $CO_2$ and $NH_4$ from allophanate (Martinez et al. 2001; Cheng et al. 2005; Shapir et al. 2005, 2006). Comparisons among known degradative strains reveal substantial heterogeneity in the organisation and location of these catabolic genes in the genome. Thus, they may be located in (a) a single plasmid (Piutti et al. 2003; Aislabie et al. 2005; Devers et al. 2007), (b) several plasmids of varying size in the same host (Topp et al. 2000b; Rousseaux et al. 2002; Devers et al. 2007) and (c) occasionally in the microbial chromosome (Cai et al. 2003; Devers et al. 2007; Vaishampayan et al. 2007).

Bacterial strains that use partially degraded *s*-triazine as a N source were obtained from wastewater and soil from Switzerland and identified as *Klebsiella pneumoniae* strain 90 and 99 and *Pseudomonas* sp. (strains A, D and F) (Cook and Hütter 1981). *Pseudomonas* sp. YAYA6 was the first pure strain capable of mineralising atrazine and using it as a C source (Yanze-Kontchou and Gschwind 1994). A year later, Mandelbaum et al. (1995) identified from the US soils with a previous *s*-triazine herbicide application the bacterium *Pseudomonas* sp. ADP capable of growing with atrazine as C and N source, which was used for the characterisation of the enzymatic mechanism of atrazine mineralisation, as was previously described (De Souza et al. 1995, 1996; Mandelbaum et al. 1995; Boundy-Mills et al. 1997; Sadowsky et al. 1998; Martinez et al. 2001). Since then, numerous bacterial isolates capable of degrading *s*-triazines, either totally or partially, belonging to phylogenetically diverse groups have been isolated worldwide (Table 21.2). There are several parameters that influence the efficiency of the degradation process. The effect of N sources on the regulation of the atrazine catabolic pathway has been the subject of numerous studies (García-González et al. 2005). The external addition of N has shown a negative effect on atrazine biodegradation in most of the bacteria studied (García-González et al. 2003). High water salinity affected atrazine degradation in an industrial wastewater bacterial community (Udiković et al. 2003). Atrazine degradation efficiency both in the presence of $O_2$ and in anaerobiosis showed no differences in both conditions, so that $O_2$ would not influence the metabolism of this herbicide (Mandelbaum et al. 1995). Atrazine residues have a very ubiquitous distribution and can be found in different compartments of the environment, so these contaminated sites are the most appropriate for the isolation of tolerant microorganisms with the capacity to degrade them (Ortiz-Hernández et al. 2001). Although there is a great diversity of atrazine-degrading isolates obtained worldwide, most of them have been isolated from agricultural soils with a previous history of atrazine application (Fernández et al. 2013; Li et al. 2020; Cao et al. 2021) and only a few from effluents of agrochemical manufacturing industries (Li et al. 2008; Yang et al. 2010).

New investigations are being carried out to improve biodegradation of atrazine, including the use of bacterial consortia, immobilised cells on different natural or synthetic materials, among others, as will be described later.

**Table 21.2** Main characterised bacterial isolates with atrazine-degrading capability described to date

| Strain | Final products of degradation | Catabolic genes | Origin | References |
|---|---|---|---|---|
| *Gram-negative bacteria* | | | | |
| *Agrobacterium radiobacter* J14a | $CO_2 + NH_3$ | *atz*ABCDEF | Soil (USA) | Struthers et al. (1998)<br>De Souza et al. (1998) |
| *Agrobacterium* sp. NEA-D | $CO_2 + NH_3$ | *atz*ABCDEF | Soil (France) | Devers et al. (2007) |
| *Alcaligenes* sp. SG1 | $CO_2 + NH_3$ | *atz*ABC, *trz*D | Industrial waste (USA) | De Souza et al. (1998) |
| *Aminobacter aminovorans* | $CO_2$ | *atz*C, *trz*D | Soil (France) | Rousseaux et al. (2001) |
| *Ancylobacter* sp. T10A11 | *ND* | *atz*ABCDEF | Soil (Colombia) | Arbeli and Fuentes (2010) |
| *Chelatobacter heintzi* Cit1 | $CO_2 + NH_3$ | *atz*ABC, *trz*D | Soil (France) | Rousseaux et al. (2001) |
| *Chelatobacter heintzi* Sal1 | Hydroxyatrazine | *atz*A | Soil (France) | Rousseaux et al. (2001) |
| *Ensifer* sp. CX-T | $CO_2 + NH_3$ | *atz*ABCDEF | Soil (China) | Ma et al. (2017) |
| *Klebsiella ornithinolytica* ND2 | *ND* | *atz*A | Soil (USA) | Siripattanakul et al. (2009) |
| *Polaromonas* sp. NEA-C | Cyanuric acid | *trz*N, *atz*BC | Soil (France) | Devers et al. (2007) |
| *Pseudaminobacter* sp. C147 | $CO_2$ | *atz*ABC | Soil (Canada) | Topp et al. (2000b) |
| *Pseudaminobacter* sp. C150 | Hydroxyatrazine | *atz*AC | Soil (Canada) | Topp et al. (2000b) |
| *Pseudomonas* sp. ADP | $CO_2 + NH_3$ | *atz*ABCDEF | Soil (USA) | Mandelbaum et al. (1995)<br>De Souza et al. (1996) |
| *Pseudomonas* sp. MHP41 | $CO_2 + NH_3$ | *atz*ABCDEF | Soil (Chile) | Hernández et al. (2008) |
| *Pseudomonas* sp. YAYA6 | $CO_2$ | *atz*A | Soil (Switzerland) | Yanze-Kontchou and Gschwind (1994) |
| *Ralstonia brasiliensis* M91-3 | $CO_2 + NH_3$ | *atz*ABC, *trz*D | Soil (USA) | Radosevich et al. (1995)<br>De Souza et al. (1998) |
| *Rhizobium* sp. PATR | Hidroxyatrazine | *atz*A | Soil (France) | Bouquard et al. (1997) |
| *Schlesneria* spp. | $CO_2 + NH_3$ | *atz*BC | Soil (USA) | Douglass et al. (2017) |
| *Shewanella* sp. YJY4 | Cyanuric acid | *atz*ABC | Soil (China) | Ye et al. (2016) |
| *Sinorhizobium* sp. NEA-B | Cyanuric acid | *trz*N, *atz*BC | Soil (France) | Devers et al. (2007) |

(continued)

**Table 21.2** (continued)

| Strain | Final products of degradation | Catabolic genes | Origin | References |
|---|---|---|---|---|
| *Stenotrophomonas maltophilia* | Hydroxyatrazine | *atz*A | Soil (France) | Rousseaux et al. (2001) |
| *Variovorax* sp. | *ND* | *atz*BC | Soil (USA) | Douglass et al. (2016) |
| *Gram-positive bacteria* | | | | |
| *Arthrobacter aurescens* TC1 | Cyanuric acid | *trz*N, *atz*BC | Soil (USA) | Strong et al. (2002) |
| *Arthrobacter crystalopoietes* Cit2 | Cyanuric acid | *trz*N, *atz*BC | Soil (France) | Rousseaux et al. (2001) |
| *Arthrobacter nicotinovorans* HIM | Cyanuric acid | *atz*ABC | Soil (New Zealand) | Aislabie et al. (2005) |
| *Arthrobacter* sp. FD; MD; SD | Cyanuric acid | *trz*N, *atz*BC | Soil (Argentina) | Fernández et al. (2013) |
| *Arthrobacter* sp. 3A; 2B | Hydroxyatrazine | *trz*N | Soil (Croatia) | Devers et al. (2007) |
| *Arthrobacter* sp. AD1 | *ND* | *atz*A | Waste water (China) | Cai et al. (2003) |
| *Arthrobacter* sp. AD26 | *ND* | *trz*N, *atz*BC | Waste water (China) | Li et al. (2008) |
| *Arthrobacter* sp. AG1 | Cyanuric acid | *trz*N, *atz*BC | Soil (China) | Xian-Zhu et al. (2007) |
| *Arthrobacter* sp. AK-YN10 | Cyanuric acid | *trz*N, *atz*BC | Soil (India) | Sagarkar et al. (2016) |
| *Arthrobacter* sp. C2 | Cyanuric acid | *trz*N, *atz*BC | Soil (China) | Cao et al. (2021) |
| *Arthrobacter* sp. C3 | Hydroxyatrazine | *trz*N | Soil (China) | Wang et al. (2016) |
| *Arthrobacter* sp. CMU6 | Cyanuric acid | *trz*N, *atz*C | Soil (USA) | Vibber et al. (2007) |
| *Arthrobacter* sp. DNS10 | Cyanuric acid | *trz*N, *atz*BC | Soil (China) | Zhang et al. (2011) |
| *Arthrobacter* sp. FM326 | Cyanuric acid | *trz*N, *atz*BC | Soil (China) | Li et al. (2020) |
| *Arthrobacter* sp. MCM B-436 | Biuret | *trz*N, *atz*ABCD | Soil (India) | Vaishampayan et al. (2007) |
| *Arthrobacter* sp. T12B12 | *ND* | *trz*N, *atz*BC | Soil (Colombia) | Arbeli and Fuentes (2010) |
| *Arthrobacter* sp. T3AB1 | Cyanuric acid | *trz*N, *atz*BC | Soil (China) | Yang et al. (2021) |
| *Arthrobacter* sp. TES6 | Cyanuric acid | *trz*N, *atz*BC | Soil (Egypt) | El Sebaï et al. (2011) |
| *Arthrobacter* sp. ZXY-2 | Cyanuric acid | *trz*N, *atz*BC | Pesticide plant (China) | Zhao et al. (2017) |
| *Arthrobacter* spp. | *ND* | *trz*N, *atz*BC | Soil (USA) | Douglass et al. (2017) |

| | | | | |
|---|---|---|---|---|
| *Bacillus licheniformis* ATLJ-5 | Hydroxyatrazine and N-isopropylammelide | *ND* | Soil (China) | Zhu et al. (2019) |
| *Bacillus megaterium* ATLJ-11 | Hydroxyatrazine and N-isopropylammelide | *ND* | Soil (China) | Zhu et al. (2019) |
| *Clavibacter michiganese* ATZ1 | N-ethylammelide | *atz*AB | Soil (USA) | De Souza et al. (1998) |
| *Nocardia* sp. | Cyanuric acid | *trz*N, *atz*C | Soil (USA) | Smith et al. (2005) |
| *Nocardioides kribbensis* CMU5 | Cyanuric acid | *trz*N, *atz*BC | Soil (USA) | Vibber et al. (2007) |
| *Nocardioides panacihumi* | Cyanuric acid | *trz*N, *atz*C | Soil (USA) | Vibber et al. (2007) |
| *Nocardioides* sp. 1D | Hydroxyatrazine | *trz*N | Soil (Croatia) | Devers et al. (2007) |
| *Nocardioides* sp. C190 | N-ethylammelide | *trz*N | Soil (Canada) | Topp et al. (2000a) |
| *Nocardioides* sp. C1S | *ND* | *trz*N, *atz*CDEF | Soil (Colombia) | Arbeli and Fuentes (2010) |
| *Nocardioides* sp. NEA-A | Cyanuric acid | *trz*N, *atz*BC | Soil (France) | Devers et al. (2007) |
| *Nocardioides* sp. SP12 | Cyanuric acid | *trz*N, *atz*BC | Soil (France) | Piutti et al. (2003) |
| *Nocardioides* sp. V3A16 | *ND* | *trz*N, *atz*BC | Soil (Colombia) | Arbeli and Fuentes (2010) |
| *Paenarthrobacter ureafaciens* AAC22 | Cyanuric acid | *trz*N, *atz*BC | Surface water (Argentina) | Bachetti et al. pers. communication |

### 21.3.2 Phytoremediation

The use of plant species for in situ treatment of contaminated sites is called phytoremediation. Pesticides can be transported across plant cell membranes and removed from the environment. Phytoremediation of pesticides involves several processes: pesticides in the soil can be absorbed by plant roots (rhizofiltration) or adsorbed by plant tissues (phytoextraction); pesticides in plant tissues can be transformed by plant enzymes (phytotransformation) or volatilised into the atmosphere (phytovolatilisation); and pesticides in the soil can be degraded by microorganisms in the rhizosphere (rhizoremediation) (Morillo and Villaverde 2017). Afterwards, incineration removes the compounds sequestered in the plant tissues (Gerhardt et al. 2009). Several studies have shown that root exudates of some plants significantly increase the desorption of organic pesticides in contaminated soils, increasing their bioavailability (Kidd et al. 2008; Muratova et al. 2009). Physical-chemical properties of the compounds and environmental and plant species characteristics are some of the causes that determine the rate of pesticide uptake (Singh and Jauhari 2017). Phytoremediation technology has many advantages: reduced costs compared to other remediation technologies; reduced erosion rate; improved physical, chemical and biological properties of the soil; aesthetic improvement; and environmentally friendly. However, it also presents some inconveniences such as longer restoration time of the contaminated site, extent and depth of the contaminated area, high dependence on climatic conditions, concentration and bioavailability of the contaminant and plant tolerance to contaminants (Morillo and Villaverde 2017; He et al. 2019). In addition, phytoremediation species can act as environmental filters at strategic water recharge points. For example, tree species capable of enhancing pesticide degradation in agricultural fields can be planted in alternating rows or as riparian forests to reduce or prevent their transport to rivers or groundwater (de Araújo et al. 2019). *Inga striata* and *Caesalpinia ferrea* are species that have shown their high tolerance to the atrazine herbicide (de Araújo et al. 2019; Aguiar et al. 2020).

Phytoremediation application is suitable in sites with low contamination and spread over large areas (Bini 2009). Several dicot and monocot species have been characterised as having high herbicide tolerance and some genotypes degrade herbicides in soil (Singh and Jauhari 2017). Herbicide removal is mainly attributed to the enzymes secreted by plant roots, such as peroxidases, polyphenol oxidases and invertases, followed by the uptake and transformation of the plants themselves (He et al. 2019). Merini et al. (2009) found that *Lolium multiflorum* had a higher atrazine removal capacity than natural attenuation in soil and water. Sui and Yang (2013) studied different rye grass genotypes, finding three genotypes capable of accumulating and degrading atrazine. Sánchez et al. (2017) investigated the phytoremediation of atrazine with *Lolium perenne*, *Festuca arundinacea*, *Hordeum vulgare* and *Zea mays*. The results showed that all plants had the ability to degrade atrazine, but *Z. mays* was the most efficient. Zhang et al. (2017) employed a genetically modified rice containing a metabolic enzyme glycosyltransferase 1 (ARGT1) capable of transforming atrazine. Cao et al. (2018) showed that the interaction between *Pennisetum americanum* and atrazine-contaminated soil influenced microbial communities and enhanced rhizosphere bacterial diversity by reshaping some soil physicochemical properties (urease activity, catalase activity, water-soluble organic carbon content and pH). In addition, some specific bacteria that could facilitate the degradation of organic pollutants or soil nutrient cycling were only identified in the rhizosphere of *P. americanum*. Aguiar et al. (2020) evaluated the remediation potential of *Inga striata* and *Eremanthus crotonoides* in atrazine-contaminated soils. They found that atrazine modified the physiological variables of these plants (photosynthetic rate, $CO_2$ consumption and transpiration) but without compromising their development. *Eremanthus crotonoides* and *I. striata* were able to reduce atrazine residues even in soils with high concentrations, allowing their use in polluted sites. More recently, the electrokinetic-assisted phytoremediation (EKPR) is also used in the atrazine removal for improving the effect of phytoremediation, in soil mesocosms using ryegrass (*Lolium perenne* L.) (Sánchez et al. 2020).

### 21.3.3 Plant Microbial Remediation

Plant microbial remediation is a technology that uses plants and microorganisms to remove pollutants. Synergistic treatment between soil microorganisms and plant roots can promote the degradation of persistent organic pollutants in contaminated sites (Zhang et al. 2014; Asemoloye et al. 2017). Rhizodeposition and root exudation provide a source of nutrients for microorganisms present in the soil. Evidence suggests that organic acids, sugars, amino acids, tannins, phenolic compounds and vitamins found in root exudates have an important role in root-microbe communication (Tanimoto 2005). In addition, P solubilisation and N fixation occur in the rhizosphere, so bacterial populations benefit from increased availability of P and N (Shimp et al. 1993). Therefore, plants benefit from rhizosphere microorganisms through their metabolic detoxification of contaminants that can affect growth and these microorganisms, in turn, benefit from root exudates (Asemoloye et al. 2019). The detoxification mechanism may include three aspects: plants absorb organic pollutants to metabolise or accumulate them in their tissues, enzymes produced by plants favour the elimination of pollutants and microorganisms favour mineralisation.

A wide variety of plant species have demonstrated efficient degradation of organic pollutants present in the rhizosphere (Abhilash et al. 2012). Dong et al. (2016) combined *Canna indica* with *Funnelliformis mosseae* (arbuscular mycorrhizal fungi) to remove atrazine. They found that *F. mosseae* could reduce the inhibition of atrazine on photosynthesis and growth of *Canna indica*, while the combination of *C. indica* with *F. mosseae* increased the degradation rate to 95.7% compared with phytoremediation alone (68.1%). Bazhanov et al. (2017) used *Arthrobacter ureafaciens* DnL1-1 in combination with alfalfa and wheat to degrade atrazine and the results showed that DnL1-1 strain could help crops from the negative effect of the herbicide. The degradation rates of atrazine by the DnL1-1-

alfalfa and DnL1-1-wheat combinations were 75.6% and 99.8%, respectively. James et al. (2018) isolated *Pseudomonas* strains from the roots of *Typha latifolia*, *Acorus calamus* and *Phragmites karka* and employed them in combination to remove atrazine. The results showed that *A. calamus* and *Pseudomonas* strains presented the highest degradation rate of atrazine, and the combination of plants-microbes could enhance the herbicide removal as compared with the use of single microorganisms or plants. Qu et al. (2018) evaluated the atrazine degradation and its detoxification by *Myriophyllum spicatum* in combination with the bacterial community present in the lake sediments. The results of the study indicated that *M. spicatum* and possibly the predominant sediment bacteria (*Nitrospirae* and *Acidobacteria*) degraded atrazine to biuret over a 60-day incubation period. Jiang et al. (2020) investigated the effects of *Pseudomonas chlororaphis* strain PAS18, a type of plant growth-promoting bacterium (PGPB), on the growth and physiological responses of *Pennisetum americanum* (L.) K. Schum seedlings under three different levels of atrazine (0, 20 and 100 mg $kg^{-1}$) in a pot experiment. The results suggest that strain PAS18 could alleviate atrazine-induced growth and stress in *P. americanum* by enhancing photosystem II repair and antioxidant defence capacity, as well as balancing $Ca^{2+}$ influx. Yang et al. (2021) showed the influence of co-inoculation of *Trichoderma harzianum* LTR-2 and *A. ureafaciens* DnL1-1 on wheat treated with atrazine. Strains LTR-2 and DnL1-1 caused significant increases in shoot biomass, root biomass and root/shoot ratio and significantly decreased the amount of atrazine and its degradation products.

Plant microbial remediation presents a wide range of application and research prospects, due to the low cost of application, low energy consumption and possible large-scale application to remediate contaminated environments (He et al. 2019).

### 21.3.4 Material-Microbial Remediation

Microorganisms used in bioremediation processes constitute an attractive methodology for the recovery of contaminated environments. Some of the strategies used to achieve that goal include on-site introduction of nutrients and $O_2$, which stimulate native microbial strains (biostimulation) or on-site inoculation with competent microorganisms (bioaugmentation) (Nzila et al. 2016). However, an important factor to be considered in a bioaugmentation process is using the correct inoculation system to ensure the successful adaptation of the inoculated microorganisms. Immobilisation on biological or polymeric supports can be an appropriate inoculation strategy during bioaugmentation. The advantages of microbial immobilisation are (a) microbial protection from adverse environmental conditions or possible predators (protozoa, parasites, etc.) that threaten microbial survival, (b) nutritional stress prevention by allowing the exchange of nutrients and waste products, (c) the introduction of a higher density of degrading bacteria to the environment, (d) a major stability of microorganisms in sites with high concentrations of contaminants, (e) cell viability preservation in the long term by offering the possibility of repeated inoculation of cells, (f) allows microbial metabolism to remain relatively constant over time and (g) the easy recovery of the already decontaminated solution (Hsieh et al. 2008; Khondee et al. 2012; Angelim et al. 2013). In addition, immobilised cells are easier to handle, thus minimising the risks of contamination during transport, application and storage (Park and Chang 2000).

There is a wide range of substrates used as cell immobilisation matrices, which usually show an appropriate ability to be applied for removing organic pollutants. Synthetic polymers include polyacrylamide, polyethylene glycol, polyvinyl alcohol and polyurethane (Wang et al. 2012; Tong et al. 2014; Zhang et al. 2020) whereas natural substrates include alginate, carrageenan, agar, collagen, chitin, chitosan and biochar (Morgante et al. 2010; Banerjee and Ghoshal 2011; Lu et al. 2012; Sun et al. 2020b; Yu et al. 2020). Desitti et al. (2017) encapsulated *Pseudomonas* sp. strain ADP in core-shell electrospun microtubes and then used it for atrazine removal in a reactor. Besides, the sol-gel process was employed to immobilise ADP strains in thin silica layers, which were coated onto carrier materials (Pannier et al. 2014). Currently, there is an increasing focus of interest to find low-cost, more efficient and easier-to-handle support matrices. Khatoon and Rai (2018) investigated the potential of sugarcane bagasse as an immobilising support for *Bacillus badius* strain ABP6 for atrazine biodegradation. The results showed that the cells were strongly adsorbed and completely dispersed on the bagasse surface after immobilisation, removing 85.3% of atrazine at 14 days of assay.

Biochar produced from biological sources is an important source of C and with high stability to chemical and microbial degradation (Kupryianchyk et al. 2016). The biochar has been studied for remediation of pesticide-contaminated sites, due to its multiple advantages including the possibility of trapping bioremediation bacteria in the biochar micropores (Morillo and Villaverde 2017). Yu et al. (2019) evaluated the immobilisation of *Arthrobacter* sp. strain ZXY-2 on mushroom pellet biochar (*Aspergillus niger* Y3). The self-immobilised biomixture was capable to remove 50 mg $L^{-1}$ of atrazine in 1 h. Tao et al. (2020) evaluated the immobilisation of four phosphate-solubilising bacteria and one atrazine-degrading bacterium (*Acinetobacter lwoffii* DNS32) on BC550 straw-based biochar. The results indicated that the combined immobilisation showed 49% higher capacity to degrade 100 mg $L^{-1}$ atrazine in 24 h and 27% higher capacity to degrade 20 mg $kg^{-1}$ atrazine after 3 days in liquid and soil, respectively.

## 21.4 Strategies for Bioremediation of Atrazine Under Laboratory and Field Conditions

As was previously highlighted, atrazine is a persistent herbicide frequently found in agricultural areas, surface water as well as groundwater (by infiltration through soils) (Alonso et al. 2018; Bachetti et al. 2021), and different alternatives have been proposed for its remediation. Among them, microbial degradation is one of the most efficient strategies from an economical and environmental point of view. However, increasing the efficiency of biodegradation processes is a challenge that researchers have to solve. Selection of suitable microorganisms, the increase of pollutant uptake and degradation, the immobilisation of microorganisms in adequate matrices and/or performing an appropriate bio-formulation are some of the approaches used to improve tolerance and atrazine removal (Desitti et al. 2017; Chen et al. 2019; Zhu et al. 2019; Herrera-Gallardo et al. 2021). More recently, computational models have been used to make simulations in order to design proper media not only for growth optimisation but also for enhancing atrazine biodegradation (Ofaim et al. 2020). Other strategies include optimisation of certain agronomic factors; the management of soils and microbial communities, including rhizospheric bacteria, fungi and endophytic microorganisms; and their selection and improvement through different techniques to generate a beneficial effect on plants or modify atrazine bioavailability (Liu et al. 2021; James and Singh 2021). For instance, it was reported that an epiphytic root bacteria *Pseudomonas* spp. strains AACB and TTLB and *Arthrobacter* spp. strain PPKB isolated from emergent hydrophytes could decontaminate atrazine at different pH and temperatures. Due to these strains also exhibiting PGP properties, they could be successfully applied as bioinoculants, for the phyto/rhizoremediation of terrestrial and aquatic ecosystems (James and Singh 2021). In the same way, intracellular crude enzyme extracts from these *Pseudomonas* strains were applied for atrazine detoxification and could be proposed as an alternative remediation technique (James and Singh 2021).

Despite several bacterial strains being able to display a great catabolic potential under laboratory conditions, they could fail to behave similarly in natural surroundings. This could be due to suboptimal growth environmental conditions, such as variations in pH, temperature and nutrient sources; the competition with well-adapted indigenous organisms and, also, the possible presence of environmental traits that might repress the genes responsible for the catabolic activities. These aspects are often not taken into account and are causes of failure of strains in the fields because to date, a high number of available results of atrazine decontamination by different microorganisms have been carried out under controlled laboratory conditions. On the other hand, it is interesting to consider that the experimental design should not only include synthetic solutions but the results must also be validated using more complex matrices such as soil, sediments, surface waters, etc. since many times certain microorganisms can degrade atrazine with high efficiency in a simple matrix but not in more real environments. In this sense, although it is widely recognised that *Pseudomonas* sp. ADP is able to degrade atrazine with high efficiency in synthetic solutions, the same did not occur in bioaugmentation experiments carried out in a liquid phase of sediment slurries, as well as in water circulating in columns filled with sediments. Besides, concomitant biostimulation with Na-citrate did not affect atrazine degradation in these experimental conditions (Liu et al. 2020). This and many other examples have been described in the literature showing diverse experimental devices for bioremediation studies. Such preliminary tests are fundamental to address in an appropriate way this highly complex subject. However, assays at microcosm and mesocosm levels are also needed. These systems constitute experimental devices that are interesting to make an approximation to reality, since they allow evaluating bioavailability and the effects of temperature, radiation, etc., which may have a decisive role on the observed responses. In addition, they allow to study the optimal conditions for implementing a biotechnological process. Microcosms can also be used to analyse certain specific target genes, related with degradation activities, and these studies could serve to predict the results of certain bioremediation strategies (Sagarkar et al. 2013). The literature provides many examples of studies related to bioremediation of atrazine using microcosms and mesocosms as experimental systems that were performed in the last years (Liu et al. 2021; Sagarkar et al. 2014, 2013; Urseler et al. 2021). For instance, bioaugmentation with *Arthrobacter* sp. strain AAC22 improved atrazine removal avoiding its lixiviation, being almost complete (>99%) after 8 days of treatment in a microcosm system using an agricultural soil. A bioassay indicated that toxic by-products were not detected after this treatment, demonstrating that AAC22 could be an efficient biotechnological tool for remediating atrazine-polluted soils (Urseler et al. 2021). Other research works suggest the existence of complex regulatory pathways for atrazine degradation in agricultural soils, which may be affected by the presence of N (Govantes et al. 2009).

Simulating field conditions, several bioremediation strategies have been proved at mesocosm level, in order to scale-up the process. For instance, a bacterial consortium with atrazine-degrading capabilities was used and this process was monitored at biochemical and genetic level (Sagarkar et al. 2014). Nonetheless, it is very important to follow a gradient of work scales and finally to confirm the behaviour of these systems on a larger scale, for example, in contaminated sites, since atrazine bioavailability as well as climatic traits could generate greater discrepancies between laboratory and field conditions. As it can be easily deduced, one of the main challenges is still the utilisation of these technologies to larger extensions, in the field and/or in the aquifers. In this sense, an analysis of the actual situation shows that there is some experience at the level of basic studies but its implementation in the field is very limited. Thus, future studies should be focused on reducing the gaps between atrazine bioremediation at laboratory and at field scales to find a proper and adaptable strategy to remediate extensive polluted sites.

## 21.5 Conclusion and Perspectives

Pollution caused by herbicides, such as atrazine, is considered among the top ten environmental hazards, which require the contribution of several disciplines to find strategies that allow mitigating its effects on ecosystems and also on human/animal health. As it was highlighted in this chapter, bioremediation is a cost-effective, efficient and clean strategy as against other common detoxifying methods, which has to be continuously improved. In the last years, several microorganisms have demonstrated to be efficient for atrazine removal. However, microbial consortia frequently showed more advantages because they can better withstand different environmental conditions. Despite an extensive knowledge now available in this regard, the continuous selection of more suitable and effective microorganisms is still an area of great interest.

Another key aspect is the understanding of the complex biodegradation processes of atrazine in natural environments. In this context, the use of new computational platforms together with the integration of different omic approaches (genomics, metagenomics, proteomics, metabolomics, etc.) is likely to strongly contribute to this aim and will promote the progress and the improvement of novel bioremediation strategies to enhance atrazine remediation applicability. Besides, the study of microbial communities by molecular tools could provide new knowledge related on catabolic potential and diversity of microorganisms. Thus, this information could improve treatments against pollution in addition to encouraging a better comprehension of these complex biological communities and opening new ways for biotechnological advances. Surely, some of these powerful approaches could help for the development of eco-friendly and efficient strategies for atrazine biodegradation.

On the other hand, a well-formulated and designed strategy is needed in order to implement an efficient bioremediation technology, by taking into consideration several aspects that influence the process. In this sense, the search and selection of new and low-cost matrices and nanomaterials would be useful to make this process more economical and environmentally viable. In fact, the development of new biomaterials, which possess good performance, is a new and promising research line in the area of pollutant remediation. However, they sometimes have certain disadvantages related to the entrapment material, the preparation of the biomaterial and the toxicity of certain components, among others. These and other aspects have to be solved previous to their large-scale application and constitute the aims of future research lines related to the use of such new technologies.

It is expected that atrazine bioremediation at different environments can be improved in the coming years not only by integrating recent findings but also by combining various strategies simultaneously in a safe way, by means of a synergistic action. This is one of the approaches that require more investigation in the future to test the efficiency. It should also deepen all those aspects related to the successful application of these technologies on a larger scale and with low environmental impact, which constitutes a challenge for the scientific community.

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# *Aspergillus*-Mediated Bioremediation of Agrochemicals: Current Progress and Future Perspectives

## 22

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**Abstract**

In modern agriculture, several synthetic chemicals are used to achieve higher crop production and to mitigate biotic stresses in plants. Crop productivity has increased over the last few decades as a result of the use of newer technologies and stress control measures but due to excessive use of agrochemicals to tackle the problem of crop damage during the pre- and post-harvest period, it has become a significant threat to the productivity and sustainability of the ecosystem. Bioremediation technique has been used for degradation/removal of agrochemicals from the environment. Microbial bioremediation is utilizing the potential of microorganisms to remove the toxic materials from the environment. The role of several strains of *Aspergillus* in bioremediation of agrochemicals is well understood, and due to its cosmopolitan distribution, it has a great potential for in situ bioremediation. A diverse array of secondary metabolites, bioactive peptides, enzymes and lectins secreted by *Aspergillus* strains are reported to aid in breaking down the complex agrochemicals. In this review, we have discussed the role of the fungal genus *Aspergillus* in the bioremediation of the agrochemicals.

**Keywords**

Bioremediation · *Aspergillus* · *Agrochemicals* · *Atrazine* · *Glyphosate* · *Endosulfan* · *Monocrotophos*

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## 22.1 Introduction

Humans are engaged in agricultural practices since time immemorial. Rapid increase in population has led to the decrease in cultivable land and increase in food demand. With the onset of Green Revolution, age-old agricultural practices were modernized by introducing high yielding crop varieties, well-planned irrigation system, use of modern farm machineries and use of synthetic agrochemicals. Although the Green Revolution has mitigated food shortage to a large extent in the last few decades, the productivity of the agricultural land has been continuously decreasing. Rampant use of hazardous synthetic chemicals to combat pest, insects, weeds, etc. has increased manyfolds. Excessive use of agrochemicals has led to the contamination of the environment (Gagic et al. 2017), and as a result residues of these chemicals are reported from different components in the ecosystem (Cencelj and Dorer 1974; Brar 2020). Toxicity of these synthetic chemicals has not only affected their target crops but also many non-target organisms (Ware 1980; Thiour-Mauprivez et al. 2019) including the humans (Weisenburger 1993). This rise in usage of the agrochemicals is a serious threat to the ecosystem sustainability and hence cannot be overlooked.

Different remediation and management strategies have been applied to attenuate the effect of pollution caused due to the use of agrochemicals by employing physical (Díez Aida et al. 2018), chemical (Sebastian et al. 2020) and biological methods (Singh 2008). Among the available techniques, bioremediation is the most eco-friendly approach towards cleaning the environment from pollutants. Research on bioremediation is predominantly focused on bacterial degradation of the agrochemicals. A diverse group of bacteria including *Bacillus* sp. (Guo et al. 2010; Pujar et al. 2018; Zhang et al. 2020a, b, c), *Pseudomonas* sp. (Gilani et al. 2016) *Arthrobacter* sp. (Wang et al. 2015) and *Ralstonia* sp. (Wang and Liu 2016) were reported for effective bioremediation of agrochemicals. However, a limited number of studies on degradation of agrochemicals by fungi (Bujacz et al. 1995; Mitra et al. 2001) have also been reported. Among these few studies, the genus *Aspergillus* is found to have a significant potential towards bioremediation.

The genus *Aspergillus* includes approximately more than 340 species which has been a fascinating area of research for their ecological significance (Abdel-Azeem et al. 2019). Many species of the filamentous fungi *Aspergillus* are reported to be a potent agrochemical degrader. It has the ability to break down agrochemicals into simpler nontoxic end products by utilizing their carbon and phosphorus as limiting resources for nutrition. It is found to be an active microbe secreting a wide array of secondary metabolites, bioactive peptides, enzymes and lectins, which makes them potential microbial agent with potential application in bioremediation. Numerous studies have also been reported on the role of *Aspergillus* in food production (Mojsov 2016), biotechnology (Maitan-Alfenas et al. 2016) and ecosystem services (Nayak et al. 2020). For sustainable agriculture, *Aspergillus* can be used as biofertilizer, as they are capable of cycling of nutrients such as carbon, nitrogen and phosphorus and some species are able to secrete plant growth-promoting hormones (Lubna et al. 2018). It also has the ability to solubilize insoluble compounds on soil and make it available for plant uptake (Chuang et al. 2007).

Studies were also conducted on the antagonist effect of *Aspergillus* on plant pathogen of the genus *Fusarium*, *Rhizoctonia* and *Macrophomina* in chickpea (Dolar 2002).

This chapter aims to provide an overview on the current status of our understanding on *Aspergillus*-mediated bioremediation of agrochemicals and its future potential.

## 22.2 Agrochemicals Used in Agriculture

Use of agrochemicals has become an inevitable part in the modern agricultural system as it offers high yield of crops and requires less labour. For the sake of producing enough crops for the ever-increasing world population, several million tons of agrochemicals are applied in the agricultural fields. Two most important categories of agrochemicals are pesticides and fertilizers. According to the reports published by the Food and Agricultural Organization (FAO), approximately 4.2 million tons of pesticides and 188.52 million tons of fertilizer were used worldwide in the year 2019. Agrochemicals are both synthetic and natural (organic). Nitrogen (N), phosphorus (P) and potassium (K) are the primary nutrients in the synthetic fertilizers. Single Super Phosphate is extensively used as a source of phosphorus (Plotegher and Ribeiro 2016), while urea has been used as a source of nitrogen in agriculture (Majewski and Capel 1995). On the other hand, pesticides are categorized based on their chemical compositions (Singh et al. 2020a, b), i.e. organophosphates, organochlorides, carbamates, pyrethroids, trazine etc., under different trade names. Use of chemical pesticides commenced after World War II with the discovery of aldrin and dichlorodiphenyltrichloroethane (DDT) in 1939 (Mahmood et al. 2016). Likewise, in the 1960s, organophosphate (OP) insecticides were introduced for the first time, carbamates in the 1970s and pyrethroids in the 1980s (Aktar et al. 2009). In India, production of pesticides started in the year 1952 with the production of benzene hexachloride and DDT (Gupta 2004). Out of the total pesticides used in India, 76% are used as insecticide, 13% as fungicide, 10% as herbicide and the remaining 1% is the other pesticides. India is the fourth largest producer of pesticides (Nayak and Solanki 2021) and lowest user of pesticides consuming 291.2 g/hectare (Devi et al. 2017).

According to the IPCC special report on climate change and land, synthetic agrochemicals are reported to be the key factor for global warming and disturbances in the ecosystem. Moreover lack of awareness among the farmers regarding the appropriate use of these agrochemicals is also one of the primary reasons for making these chemicals a threat to the environment. Most of these synthetic agrochemicals are toxic and persist in the environment for a longer period of time. Even the exposure of these agrochemicals to human skin can cause several abnormalities such as irritation to skin, blurred vision and difficulty in breathing, nervous system damage and cancer (Sharma and Singhvi 2017). Hence a holistic bioremediation approach is much required to remove the deleterious agrochemicals from the environment. Considering the scenario of hazardous effects of synthetic agrochemicals, natural agrochemicals have been started to be used as an alternative. Organic manure and vermicompost can be used as a substitute for chemical fertilizers. They provide the nutrients needed for agriculture and also have the ability to restore the fertility of the soil. Secondary metabolites of plants and microbes are also being used as green pesticides. Various essential oils, e.g. limonene, pulegone, citronellal, etc., are reported to show a broad spectrum of insecticidal, antifeedant and growth regulatory activity against insects and plant pathogenic fungi (Mohan et al. 2011). Although green pesticides are more compatible and eco-friendly than synthetic agrochemicals, it is challenging to overcome the massive damage caused by pre- and post-harvest diseases just by applying only natural agrochemicals. Moreover, farmers prefer synthetic agrochemicals over natural ones for their cost-effectiveness, availability and longer self-life.

## 22.3 Impact of Agrochemicals on the Ecosystem

### 22.3.1 Residues in the Environment

#### 22.3.1.1 Soil

Aggravated use of pesticides for a very long period of time has caused accumulation of its residues in the soil and also results in imbalance in the ecosystem. Due to the small particle size and large surface area of soil colloids, pesticides get easily absorbed by it. These residues remain bound to the clay matter or organic particle of the soil and thus cannot be extracted. Pesticides are absorbed either by physical absorption or by chemical reactions (Calderbank 1989). Binding and aggregation of the residues vary with the nature and chemical structure of the pesticides. Ionic pesticides such as atrazine get attached to the organic component of the soil by various mechanisms such as hydrophobic partitioning, ligand exchange, ionic exchange, cation or water bridging and charge transfer and is highly influenced by the pH of the environment while the absorption of neutral pesticides is least affected by pH (Kah and Brown 2006). A study conducted on the soil chemical profile of the Cardamom Hill Reserve, in Kerala, India, revealed the presence of 17 organochlorine pesticides residues (Joseph et al. 2020). Pesticide residues interact with the soil and its environment and are reported to cause negative effect to the soil. Residues of atrazine are found to reduce soil microbial diversity and thus affect the fertility of the soil (Chen et al. 2015). Several researches have also reported the uptake of agrochemical residues by plants from the soil (Hwang et al. 2018). Through plants these agrochemical residues also enter the food chain and affect the higher organisms.

#### 22.3.1.2 Water

Groundwater and waterbodies near crop fields are reported to be highly contaminated with agrochemical residues. Agrochemicals used in the crop fields may enter the water ecosystem by several ways such as surface run-off, drifting away from the treated area, leaching through the soil and accidental spilling (Ansari et al. 2014). As a result of the presence of these agrochemicals, many different organisms belonging to different trophic levels are disturbed and an imbalance is created in the ecosystem. Several studies are conducted on the presence of pesticide residues on surface water (Fadaei et al. 2012; Gao et al. 2009) and groundwater (Shukla et al. 2006; Hallberg 1989; Cerejeira et al. 2003). Almost all the rivers of India are reported to contain invariable amount of organochloride agrochemicals such as HCN and DDT (Mohapatra et al. 1995) including the river Ganga in Kanpur which showed the presence of malathion, dieldrin and γ-HCH (Sankararamakrishnan et al. 2005). In the USA, waterbodies are found to be contaminated with agrochemicals almost throughout the year (Gilliom et al. 2007). Atrazine, metolachlor, chlorpyrifos, carbendazim and tebuconazole are some of the common agrochemicals frequently detected in surface water (De Souza et al. 2020). Biomagnification of the agrochemicals causes their accumulation in the food chain and causes hazardous effects to the ecosystem. Considerable amount of DDT, DDE, endosulfan and carbofuran was estimated in the flesh of *Catla catla* of the Ravi River, in Pakistan (Akhtar et al. 2014). Nohara and Iwakuma (1996) reported the presence of simetryn residues in the lamina of *Nelumbo nucifera* at a concentration of 300 $\mu g\ kg^{-1}$. These pesticides present in waterbodies may even find their way out to contaminate the drinking water. In a study conducted on the detection of pesticides in the drinking water of the Dutch, residues of 15 pesticides were reported including two neonicotinoids and predominant among them are the acetamiprid (1.1 mg/L) and thiamethoxam (0.4 mg/L) (Sjerps et al. 2019). In the agricultural regions of Southern Ontario, Canada, thiamethoxam was detected in the drinking water with a concentration which is above the prescribed limit of the European Union directive on pesticide levels (Sultana et al. 2018).

#### 22.3.1.3 Air

Residues of agrochemicals are also detected in the atmosphere. Pesticides sprayed on the agricultural field may drift away from the target crop or it may be evaporated to the atmosphere (Ansari et al. 2014). About 15–40% pesticides applied in the agricultural field are found to be dispersed in the atmosphere. The extent of air contamination by agrochemicals depends on the chemical properties of the agrochemicals, method of their application in the field, concentration used and weather conditions of the area like wind speed, temperature, precipitation, etc. While investigating agrochemical concentration in the atmosphere of three Canadian Integrated Atmospheric Deposition Network (IADN) sites, high concentration of atrazine was observed (Yao et al. 2007). Another study reported DDT, dieldrin and endrin as commonly detected pesticides in the atmosphere of China (Zhang et al. 2011). Agrochemicals in the atmosphere are carried away by wind and deposited in different places either in the form of gases or particles (dry deposition) or in the form of rain or snow (wet deposition) (Majewski and Capel 1995). In a comparative study conducted on the air and rainwater samples of urban and agricultural region along the Mississippi river, residues of pesticides, viz. glyphosate, atrazine, propanil, etc. were detected (Majewski et al. 2014). Study of rainwater from Hisar, India, also reported the presence of several insecticides of organophosphorus and organochloride groups (Kumari et al. 2007). Detection of the pesticide residues of endosulfan, chlorpyrifos and trifluralin both in the air and ice core of arctic region indicates their long-distance transmission via the atmosphere (Vorkamp and Rigét 2014). Pesticides in the atmosphere act as a major source of pollution and drastically affect the ecosystem.

### 22.3.2 Effects on Non-target Organisms

Agrochemicals seem to exert its effects parallelly on both target and non-target organisms. The positive impact of the agrochemicals used in our agricultural practices is surpassed by the negative impact it causes on the non-target organisms. Most of the agrochemicals are reported to adversely affect the growth of non-target microbial communities. Agrochemicals are shown to alter the biochemical and metabolic pathways of microbes, thereby causing a decline in their growth (Meena et al. 2020). Santos and Flores (1995) conducted a study on the effect of glyphosate on *Azotobacter* and observed that the herbicide halts protein synthesis in the bacterial cells and thus reduces their growth. Similarly, considerable variation was observed in the growth of microbes in the presence of insecticides such as chlorpyrifos, imidacloprid, cypermethrin, endosulfan and carbofuran. Among the tested pesticides, chlorpyrifos and malathion show negative effect on the microbial population (Shan et al. 2006). In contrast monocrotophos, quinalphos and cypermethrin have a positive effect on microbial growth when present at a lower concentration (Gundi et al. 2005). Most of the agrochemicals are reported to have a negative effect on the microbes while some may stimulate their growth or have no effects. Pesticide residues are also found to interrupt the life cycle of the valuable invertebrates like earthworm, centipede, mites, etc. present in the soil (Iyaniwura 1991). DDT is found to be toxic to the mites (Davis 1952) while the earthworms are reported to be adversely affected by the pesticides such as chlordane, endrin and heptachlor (Edwards 1973). Alteration of the population of organisms residing in the soil also causes alteration in the soil properties which affects its fertility and thus the growth of the plants. Agrochemicals may also affect plants directly. It generally seems to cause stunt growth, necrosis, chlorosis, reduced photosynthesis and oxidative damage by generating reactive oxygen species (ROS) in plants (Sharma et al. 2018). In a study conducted by Shakir et al. (2016), it was observed that the application of pesticides has caused reduced germination in tomato seeds. Pesticides may enter and translocate through the non-target crops and accumulate inside the plant body. Inside the plant cell they either alter the plant metabolism or be transformed to toxic or nontoxic metabolites (Norris 1974). A study by Liu et al. (2021) demonstrated the uptake of 11 pesticides by *Triticum aestivum* and has developed a model describing its uptake kinetics which would further help in studying its accumulation in the plant.

From the environment, harmful agrochemicals enter the food chain and cause toxicity to the higher organisms of the ecosystem such as fish, birds, reptiles and mammals. Chlorpyrifos, which is the second largest selling organophosphate pesticide, is reported to cause disruption in the metabolism of fishes by inhibiting the enzyme acetylcholinesterase (Deb and Das 2013). Ingestion of sublethal dose of organochloride pesticides was reported to affect the reproductive rates of insects and birds (Matsumura 1985). Several toxicological studies of agrochemicals on humans are also conducted and it is reported to cause several life-threatening diseases. Approximately, 385 million cases of unintentional pesticide poisoning occur annually across the globe (Boedeker et al. 2020). In India, the first pesticide poisoning is reported in 1958 in Kerala which occurred due to the consumption of parathion-contaminated wheat (Karunakaran 1958). Effects of pesticides on humans are both acute (short term) and chronic (long term). The toxicity could be due to skin contact, inhalation or ingestion of the agrochemical residues. Dizziness, nausea, allergy, headache and difficulty in breathing are some of the symptoms that occur after the exposure to the harmful pesticide residues. Prolonged exposure of these residues could result in chronic diseases (Kumar et al. 2012). The herbicide atrazine is reported to cause disruption of the reproductive process in humans and cause several birth defects (Wirbisky and Freeman 2015). Farmers and agricultural workers are the first targets of toxic agrochemicals. About 44% of the total farmers in the world are found to be poisoned by pesticides (Boedeker et al. 2020). Considerable amount of residues of glyphosate and its metabolites are detected from the blood and urine of agricultural workers (Peillex and Pelletier 2020). Hayat et al. (2010) estimated the amount of pesticide present in the blood of pesticide-spraying workers from Vehari, Pakistan, and reported the presence of chlorpyrifos and pyributicarb at a concentration of 0.009 mg/L and 0.001 mg/L, respectively. Organochloride pesticides are also reported to cause non-Hodgkin's lymphoma (NHL), leukaemia and cancers of the lung and breast (Dich et al. 1997; kettles et al. 1997).

## 22.4 Bioremediation of Agrochemicals: Its Significance

Bioremediation is the method where living organisms such as plants and microbes are utilized for degradation/removal of environmental pollutants. It is the most ideal method for removal of agrochemicals from the ecosystem. Cost-efficiency and eco-friendly nature of bioremediation process make it a better choice over other remediation methods. Both plants and microorganisms have the ability to remove contaminants from the environment. However, the unique nutritional strategy of the microorganisms to first digest their food and then consuming it makes a way out for efficiently degrading the complex polymeric substrates (contaminants) and thus possesses excellent potential for bioremediation. Microbes convert the toxic agrochemical residues present in the environment into less toxic end products (Singh et al. 2020a, b). The choice of microbes for bioremediation depends on the nature of contaminants and the physical nature of the environment where it is present. The microorganisms may already be present in the soil or it may require to be provided by isolation from a different site, i.e. bioaugmentation. Sometimes additional substrates such as carbon, electron donor and buffers must be added to accelerate the degradation process, a process known as biostimulation (He and Su 2015).

Bioremediation may be carried out on the site of contamination, i.e. in situ, or by extracting the contaminants from the original contaminated site and then carried to the laboratory, i.e. ex situ. Remediation cost in addition to the cost of excavation and transportation of the contaminants in ex situ bioremediation makes it a less preferred technique in comparison to in situ bioremediation. Both bacteria and fungi are reported to play a significant role in bioremediation. Bacterial species belonging to the genus *Pseudomonas*, *Bacillus*, *Flavobacterium*, etc. are reported to degrade a wide range of pesticides such as chlorpyrifos, aldrin, endosulfan, monocrotophos, atrazine, methyl parathion, etc. (Sviridov et al. 2015; Huang et al. 2018). Actinomycetes are observed to degrade pesticides such as organochlorines, *s*-triazines, triazinones, carbamates, organophosphates, acetanilides and sulfonylureas (De Schrijver and De Mot 1999). Liu et al. (2012) reported the degradation of chlorpyrifos by *Bacillus cereus*. Mixed consortium of bacterial species proves to be more efficient in the degradation of pesticides. Olawale et al. (2011) compared the glyphosate degradation potential of mixed consortium of *Pseudomonas putida*, *P. aeruginosa* and *Acetobacter faecalis* with their single isolated cultures and observed that the mixed consortium is a better degrader with a relatively shorter lag phase. *Trichoderma harzianum* is reported to degrade DDT, dieldrin, endosulfan, pentachloronitrobenzene and pentachlorophenol to less toxic end products (Katayama and Matsumura 1993). The fungi *Fusarium oxysporum*, *Aspergillus oryzae*, *Lentinula edodes*, *Penicillium brevicompactum* and *Lecanicillium saksenae* were reported to efficiently degrade terbuthylazine, which is the most persistent triazine herbicide on the surface environment (Pinto et al. 2012).

## 22.5 *Aspergillus* as Potent Degrader of Agrochemicals

*Aspergillus* can survive in wide range of environmental conditions and can grow in diverse types of substrates. Their survival in varied conditions is favoured by their competitive nature, reproductive potential and unique metabolism. *Aspergillus* produces many rare toxins and enzymes that make them both industrially and ecologically significant. In the last few decades, considerable amount of work on fungal strains belonging to the genus *Aspergillus* indicated its potential as an efficient agrochemical degrader, which is discussed in the following section.

### 22.5.1 Atrazine

Atrazine is a widely used herbicide that targets broadleaf weeds like pigweed, velvetleaf, cocklebur, etc. It has been extensively used in the USA during the last 30 years, mostly for corn production. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) belongs to chlorinated s-triazine class of herbicide that inhibits the photosynthesis mechanism in higher plants (Shimabukuro and Swanson 1969). It is found to be one of the most commonly detected herbicide on surface water. It has a long half-life and is reported to adversely affect the nervous system, endocrine system and immune system in some mammals (Fan and Song 2014).

Studies showed that *Aspergillus* spp. has the ability to degrade atrazine residues present in the environment. The successful growth of *Aspergillus* on media containing atrazine as substrate has provided evidence that *Aspergillus* can utilize atrazine for its survival (Islas-Pelcastre et al. 2015) by breaking it down into simpler forms and utilizing it as a nutrient. A positive correlation between the mycelial growth of non-toxigenic *Aspergillus* section *Flavi* strains and their atrazine removal ability is established by Barberis et al. (2019). In a study conducted by Lu et al. (2021), strains of *A. oryzae* growing on atrazine are found to have the ability to efficiently absorb more than 70% of atrazine. Further analysis on the optimal condition (pH = 5–7, and 20–30 °C) for the biosorption process was also carried out by HPLC analysis of the fermentation products. *A. flavus* and *A. parasiticus* are found to grow on maize meal extract agar (MMEA) media supplemented with different atrazine concentration (5, 10, 50, 100 mmol $L^{-1}$). In the atrazine concentration of 100 mmol $L^{-1}$, they show the lowest lag phase and highest mycelial growth (Benito et al. 2019). Gajendiran et al. (2017) reported that *A. alliaceus* isolated from paddy field of Vellore shows a considerable growth by utilizing atrazine as the sole source of carbon. Using analytical techniques such as GC-MS, HPLC and FTIR, it was found that *A. alliaceus* strain was capable of degrading atrazine at a concentration of 1500 mg/L completely within 6 days of incubation. On the other hand, *A. niger* is reported to be an efficient degrader of atrazine (Olu-Arotiowa et al. 2019). *A. niger* AN400 was found to degrade atrazine from wastewater and can degrade almost 40% of atrazine (30 mg $L^{-1}$ concentration) within 8 days of time, which can be enhanced to 72% by supplementing with glucose (Marinho et al. 2017). Herrera-Gallardo et al. (2020) have reported about 75% degradation of atrazine by *A. niger* when cultured with 10% w/w of co-substrate (glucose and *Opuntia ficus indica* residues) under 80% humidity and a temperature of 40 °C. Similarly, Olu-Arotiowa et al. (2019) have performed several assays regarding the biodegradation of atrazine through bioaugmentation and biostimulation using *A. niger* and has attained a considerable success. Other species of *Aspergillus*, viz. *A. fumigates* and *A. flavipes*, are also found to degrade atrazine. *A. fumigates* is reported to metabolize atrazine via dealkylation reaction of either of the two groups of atrazine which leads to the formation of 2-chloro-4-amino-6-isopropylamino-s-triazine or 2-chloro-4-ethylamino-6-amino-s-triazine or both which may subsequently break down into carbon dioxide and ammonia (Fig. 22.1) (Kaufman and Joan 1970; Oliveira et al. 2015). On comparing the growth of two strains of *A. niger*, namely, AN251 and AN384, on three different pesticides, i.e. glyphosate, chlorpyrifos and atrazine, the lowest growth was observed in the presence of atrazine. Thus it was concluded that atrazine is more difficult to be degraded than the other two pesticides (Carranza et al. 2014a, b). In contrast, a study conducted by Barberis et al. (2019) reported atrazine to be more rapidly degraded by *A. oryzae* (over 90% in the first 2 days of incubation) in comparison to endosulfan and chlorpyrifos. These studies clearly depict the capability of different *Aspergillus* spp. in degrading atrazine.

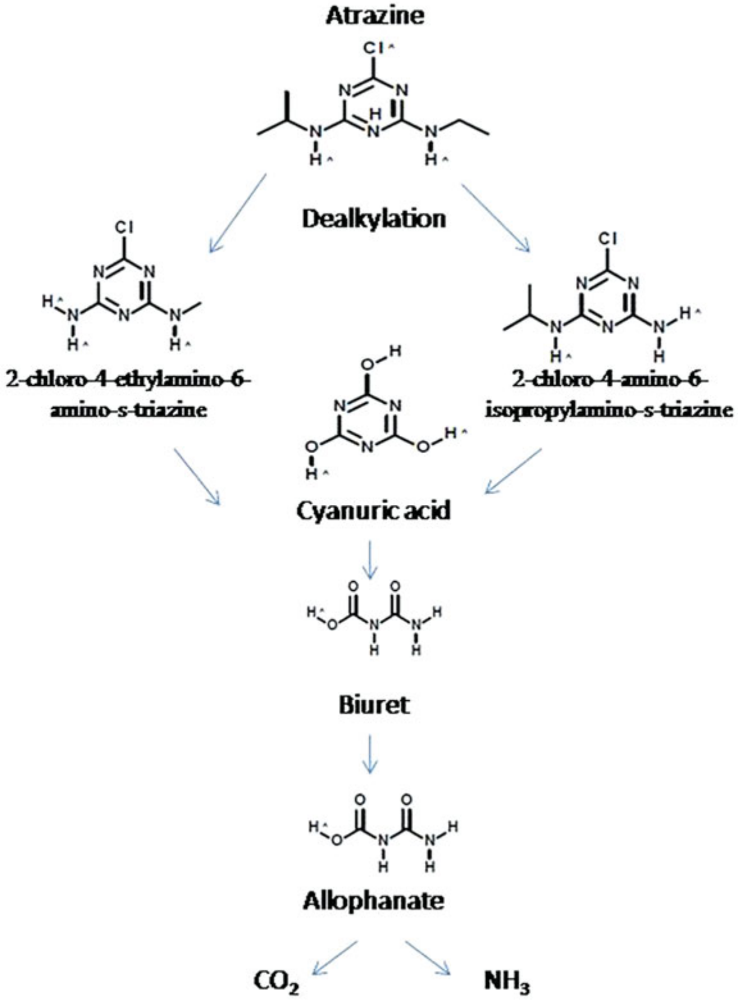

**Fig. 22.1** Atrazine degradation pathway

### 22.5.2 Glyphosate

Glyphosate [N-(phosphonomethyl)glycine] was first introduced as an herbicide and tested for the first time by John E Franz of Monsanto Co. in the year 1970 (Franz et al. 1997). Commercially, it is sold as Roundup by Monsanto since 1974 (Duke and Powles 2008). Initially, the use of glyphosate was limited as it can kill weeds and crops indiscriminately and thus can only be used as post-harvest herbicide. However, glyphosate-tolerant genetically modified rice, wheat and soybean were developed at the beginning of the twenty-first century, which increased the demand of glyphosate across the globe. Glyphosate acts as an analogue of phosphoenolpyruvate which is a substrate for the enzyme ESPS thus inhibiting the action of this enzyme (Valavanidis 2018). Suppression of the activity of ESPS leads to halt in aromatic amino acid production which further affects in protein synthesis of the weed and affects their development. Glyphosate has become the most popular herbicide worldwide due to its wide range of action and low toxicity to the environment. However, recently glyphosate toxicity on farmers and other agricultural workers are noted. In 2015, the International Agency for Research on Cancer (IARC) classified glyphosate as a group 2A carcinogen (Valavanidis 2018). The poisonous effects of glyphosate raised concern and so several studies are conducted on biodegradation of glyphosate from the environment. *Aspergillus* is reported to play a major role in degradation of glyphosate which is discussed in the following section.

The ability of the strains of *Aspergillus* to tolerate and grow on glyphosate-contaminated media is considered as a sign for its inherent potential of glyphosate degradation (Sebiomo and Banjo 2020; Njoku et al. 2020). Many studies are conducted on such *Aspergillus* spp. regarding their ability of bioremediating glyphosate. A study carried on the fungal species present in the soil samples from Indonesia illustrated the potential of *Aspergillus* in bioremediation of glyphosate (Arfarita et al. 2014). Carranza et al. (2019) identified two strains of *A. oryzae* (AM1 and AM2) having the ability to efficiently degrade glyphosate. Using glyphosate as a sole source of phosphate or nitrogen, both strains of the filamentous fungi were found to degrade more than 50% of the herbicide. In a similar study conducted by Carranza et al. (2016) on three strains of *A. oryzae* (AM 1, AM 2, AM 3), one strain of *A. flavus* (GM 4) and two strains of *A. niger* (AN 251, AN 384), it was observed that the strains of *A. oryzae, A. flavus* and *A. niger* (AN 384) have a longer lag phase in comparison to *A. niger* (AN 251), when grown on media containing glyphosate. Longer lag phase found to help in better acclimatization of the fungus to glyphosate and prepare it for inducing degradation process. Further study on the growth rate of the fungus shows that they can grow efficiently by using glyphosate as a sole source of phosphorus or nitrogen. In addition, the enzyme laccase, which is effective in removing pesticide residues, can be extracted from *A. niger* (Swe et al. 2020). Similarly, several studies are conducted on the growth of *A.* section *Flavi* strains on media supplied with different concentration of glyphosate under different water activity ($a_w$). In most of the studies, considerable growth was observed under different $a_w$, but no inhibitory effect of glyphosate on the fungal strains was observed (Carranza et al. 2014a, b; Benito et al. 2021; Barberis et al. 2013; Carranza et al. 2016; Abdel-Megeed 2013). Fu et al. (2017) have investigated the mechanism of degradation of glyphosate using *A. oryzae*, by analysis of the metabolites in the glyphosate fermentation medium of *A. oryzae*. The metabolites detected were identified as aminomethylphosphonic acid (AMPA), which is formed by breakage of the C-N bond of glyphosate by the enzyme glyphosate oxidoreductase and methylamine which is formed by breakage of C–P bond of AMPA by C–P lyase (Fig. 22.2). On the other hand, sarcosine, which is formed by breakage of the C–P bond of glyphosate by C–P lyase, was obtained as a major metabolite during the degradation process by *A. niger* and also by other fungal species. Thus the major pathway of degradation of glyphosate is reported to be the C–P lyase pathway

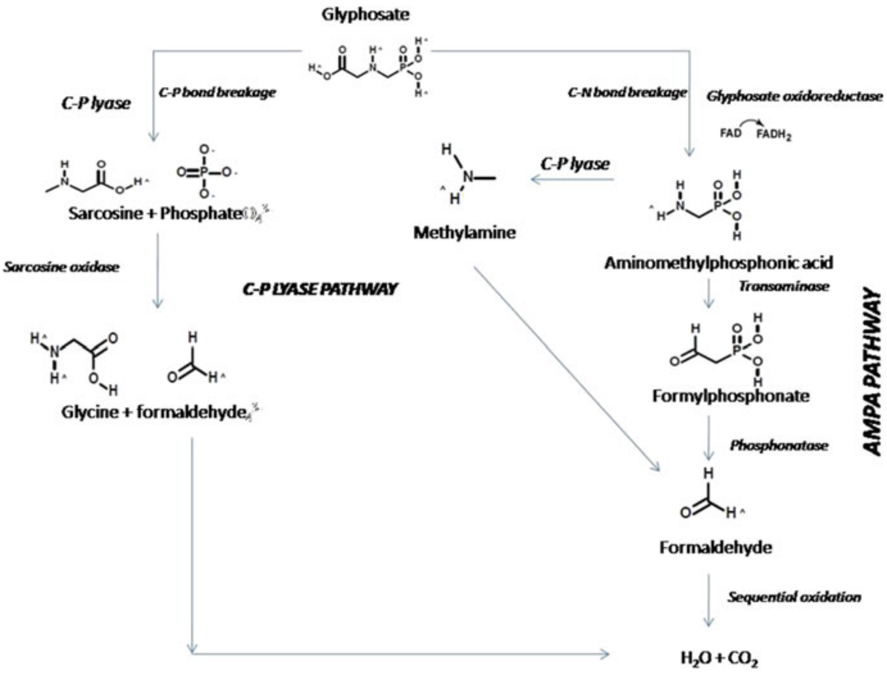

**Fig. 22.2** Metabolism of glyphosate by *Aspergillus* sp.

(Adelowo et al. 2014). Hence, glyphosate is used as a source of nitrogen and phosphorus by the fungus and degrade it into simple nontoxic products.

### 22.5.3 Endosulfan

Endosulfan is an extensively used organochloride insecticide belonging to cyclodiene group. It was first made in the mid-1960s by Farbwerke Hoechst and is sold commercially as Thiodan which is a mixture of α-endosulfan and β-endosulfan in the ratio 7:3. Due to its cost-efficiency and non-selective properties, endosulfan is widely used around the globe. India was considered as the largest producer of endosulfan, producing about 5.4 kMT annually (Ayres and Ayres 2000). However, it is banned in many countries due to its high persistence in the environment especially in waterbodies. It is reported to be highly toxic to the non-target organisms including the humans. An unforgettable example of endosulfan toxicity is the endosulfan tragedy in Kerala, India, where at least 10,000 residents were affected by diseases and more than 4000 people died (James and Emmanuel 2021). Thus, several initiatives were taken for the removal of the persistent residues of this poisonous chemical from the ecosystem.

Several strains of *Aspergillus* are found to tolerate and degrade endosulfan to less toxic or nontoxic metabolites. The different metabolites obtained during the

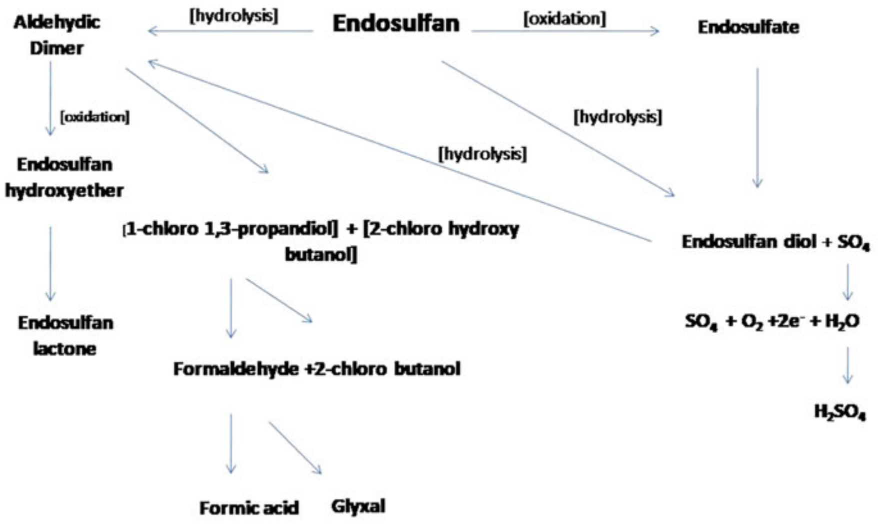

**Fig. 22.3** Degradation routes of endosulfan

degradation process were identified as endosulfan diol, endosulfan sulphate, endosulfan ether, endosulfan hydroxyether, endosulfan lactone and endosulfan dialdehyde. Two degradation routes of endosulfan are proposed based on the analysis of the intermediate metabolites obtained during the degradation process (Fig. 22.3). The metabolite endosulfan sulfate is found to be the product of oxidation reaction while the endosulfan diol and endosulfan ether are the intermediates of hydrolysis reaction. The filamentous fungus, *A. niger*, is found to play a significant part in bioremediation of endosulfan. In the presence of the fungus, 98.6% of β-endosulfan was found to be degraded compared to control which is only 78.4% (Mukherjee and Gopal 1994). Similarly, strains of *A. niger*, isolated from the cotton fields of Pakistan, were also reported to degrade 98.6% of endosulfan within 4 days of incubation (Mukhtar et al. 2015). Ahmad et al. (2020) has analysed the intermediate metabolites of degradation process of *A. niger* and *A. flavus* by GC-MS analysis and identified endosulfan diol, endosulfan ether, endosulfan hydroxyether, 1,2-benzenedicarboxylic acid, diisooctyl ester and endosulfan lactone. Thus, the degradation route is predicted to be hydrolysis reaction. In another study conducted on endosulfan bioremediation by *A. niger*, a considerable decrease in pH (3.6) and an increase in chlorine content were observed with the progression of degradation process. The free chloride ions might form hydrochloric acid which probably has led to decrease in pH. In contrast to the previous study, here the degradation product was identified as endosulfan sulfate and hence it seems to follow the oxidation reaction (Bhalerao and Puranik 2009). Decrease in pH and evolution of $CO_2$ were detected at the end of the degradation process. However, other studies that analysed the metabolites of endosulfan bioremediation by *A. niger* have reported it to show both oxidative and hydrolysis reaction (Bhalerao and Puranik 2007; Bhalerao

2013a, b). *A. terricola* and *A. terreus* were reported to degrade both α-endosulfan and β-endosulfan. On studying the effect of variation of pH and temperature in the process of degradation, it was found that the optimum pH of 6 and temperature of 30 °C were required for degradation. Maximum degradation of up to 74% of endosulfan was observed when inoculated in broth media and kept under agitated condition (Hussain et al. 2007). Similarly, Mukherjee and Mittal (2005) have also studied the ability of *A. terreus* to detoxify endosulfan within 15 days of inoculation. The major metabolite obtained was endosulfan sulfate, which was also later degraded by the fungi. A fungal strain *A. tamarii* JAS9, isolated from *Abelmoschus esculentus* grown in the agricultural field of Vellore in Tamil Nadu, was found to degrade endosulfan along with its metabolites α-endosulfan, β-endosulfan and endosulfan sulphate within 10 days of inoculation (Silambarasan and Abraham 2013a, b). A study was conducted by Goswami et al. (2009) on endosulfan bioremediation potential of *A. sydoni* both in broth culture and soil microcosm. It was reported that the maximum degradation was observed in broth culture (95% degradation of α-endosulfan and 97% of β-endosulfan), and both oxidation and hydrolysis reactions take place for the transformation of endosulfan into its metabolites. From the above studies, it can be concluded that many *Aspergillus* spp. possess the enzymes required for degradation of endosulfan and thus can be used as an effective tool for its degradation.

### 22.5.4 Monocrotophos

Monocrotophos (dimethyl (E)-1-methyl-2-(methylcarbamoyl)vinyl phosphate) is an organophosphorus insecticide used to protect cash crops such as cotton and sugarcane from common mites, ticks, spiders, etc. Chemically, they possess a P-O-C linkage and amide bond. It has been widely used in the agricultural fields of developing countries like India. The residues of this agrochemical are easily soluble in water and show considerable toxicity to aquatic organisms. Along with the insects, it also affects the nervous system of the non-target organisms.

One *Aspergillus* sp. was found to completely degrade monocrotophos in 8 days of incubation to some volatile fatty acids and intermediate compounds (Anitha and Das 2011). Jain and Garg (2015) have screened the ability of *A. Niger* JQ660373 and *A. flavus* in degrading monocrotophos in soil. After 30 days of incubation of the fungal strains in monocrotophos-enriched media, 99% degradation was estimated. HPTLC and FTIR analysis has shown that hydrolytic cleavage of the vinyl bond has led to breakage of chemical to inorganic phosphorus, carbon dioxide and ammonia The degradation kinetics is reported to follow first-order kinetics, and half-life of monocrotophos in the presence of *A. niger* and *A. flavus* was observed to be 7.35 and 9.23 days, respectively. Hence, it was concluded that *A. niger* is a more efficient degrader compared to *A. flavus*. Another experiment conducted using *A. flavus* reported similar results, i.e. more than 75% degradation of monocrotophos within 15 days of inoculation (Jain and Garg 2015). However, *A. niger* is reported to degrade 90% of the monocrotophos within 10 days of inoculation under optimal

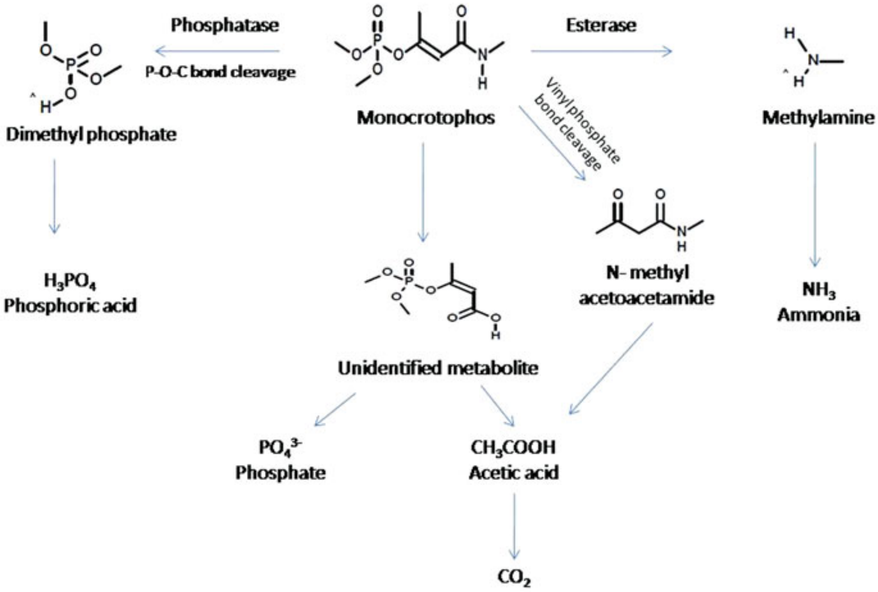

**Fig. 22.4** Degradation pathway of monocrotophos

conditions, i.e. pH 8, temperature 25–30 °C and monocrotophos concentration of 150 mg $L^{-1}$ (Jain et al. 2012, 2014; Thirugnanam and Senthilkumar 2016). Monocrotophos (500 mg $L^{-1}$) was found to be degraded by *A. sojae* strain JPDA1 in about 72 h of incubation (Abraham et al. 2016). The extracellular enzyme organophosphate hydrolase was extracted from *Aspergillus* sp., which is reported to aid in degrading monocrotophos (Jain and Garg 2013). Similarly, *A. oryzae* ARIFCC 1054 was isolated as monocrotophos-tolerant species by Bhalerao and Puranik (2009), and the fungal isolate was reported to possess phosphatase activity which helps in metabolizing monocrotophos into carbon dioxide, soluble inorganic phosphates and ammonia (Fig. 22.4). Thus, the neurotoxic chemical can be successfully detoxified by the fungal strain belonging to the genus *Aspergillus*.

### 22.5.5 Bioremediation of Other Agrochemicals

Apart from the above-mentioned agrochemicals, several other agrochemicals are also reported to be degraded by *Aspergillus* sp. Fungal species *A. sydowii*, *A. viridinutans* and *A. niger* were reported to degrade the organophosphate pesticide chlorpyrifos (Da Silva et al. 2015; Tamim and El-Hamid 2016; Mukherjee and Gopal 1996). Chlorpyrifos metabolite 3,5,6-trichloro pyridine-2-phenol (TCP) was also found to be completely metabolized in soil by *A. terreus* JAS1 after 24 h of incubation (Silambarasan and Abraham 2013a, b; Maya et al. 2012). *A. sydowii* metabolized methyl parathion, which is a widely used organophosphate insecticide, by utilizing it as a sole source of carbon (Abd-Alrahman and Ashraf 2014). *A. sydowii* was also reported to degrade the agrochemical profenofos and 71% of it was found to be degraded after 20 days of incubation (Silva et al. 2013). Soares et al. (2021) have deduced the pathway of degradation of the three agrochemicals, viz. chlorpyrifos, methyl parathion and profenofos, by *A. sydowii*. Enzymes such as phosphoesterases, methyltransferases, ethyltransferases and cytochrome P450 were reported to aid in the conversion of the three agrochemicals into phenolic end products. Fungi *A. niger* secretes enzymes such as carbaryl hydrolase, pyrethroid hydrolase and phytase which break down carbaryl, pyrethroid and other organophosphate pesticides (Zhang et al. 2003; Liang et al. 2005; Shah et al. 2017; Cycoń and Piotrowska-Seget 2016; Hamad 2020; Adelowo et al. 2015). It also has the ability to degrade 3-methyl-4-nitrophenol which is the main metabolite produced during fenitrothion degradation (Kanaly et al. 2005). *Aspergillus* strain PYR-P2 has the ability to degrade up to 500 mg $L^{-1}$ of pyrethroid mixture (cypermethrin (CYP), cyfluthrin (CYF), cyhalothrin (CYH)) in minimal salt media (Kaur and Balomajumder 2020). Beta-cypermethrin was found to be broken down by *A. niger* YAT strain through a pathway which converts beta-cypermethrin into permethric acid and α-cyano-3-phenoxy benzyl alcohol by the enzyme esterase. Being unstable, α-cyano-3-phenoxy benzyl alcohol is converted to 3-phenoxybenzaldehyde, which undergoes dehydrogenase and dioxygenase reactions and is converted to straight chain olefin which finally oxidize to $CO_2$ (Deng et al. 2015). Likewise, M-4 strain of *A. oryzae* can degrade 80.62% of 3-phenoxy benzoic acid within 5 days of incubation (Zhu et al. 2016). *A. niger* was found to be effective in degrading λ-cyhalothrin to acceptable maximum residue level (Sanyaolu 2018; Birolli et al. 2018). Considerable amount of β-cyfluthrin is reported to be degraded by the strains of *A. niger*, *A. terricola* and *A. nidulans* var. *dentatus* (Saikia and Gopal 2004; Mukherjee and Mittal 2005). *A. niger* and *A. terricola* are reported to effectively degrade the pesticides pyrethroid and dimethoate (Lone and Mohd 2012; Yin and Bin 2012). *A. niger* secretes a dimethoate degrading enzyme, which seems to aid in the process of its bioremediation (Liu et al. 2001). *A. fumigatus* can also detoxify the residues of dimethoate and methomyl in aquatic environment (Derbalah et al. 2021). Zayed et al. (1983) have reported the aerobic degradation of trifluralin by *A. carneus*. Fungal strain *A. sydowii* is reported to degrade an important organophosphate pesticide trichlorfon by utilizing it as a carbon-phosphorus source. By analysing the metabolites, a degradation pathway of trichlorfon is proposed. Initially the P–C bond of trichlorfon is hydrolysed to form dimethyl hydrogen phosphate (dominant) and chloral hydrate. Dimethyl hydrogen phosphate is later deoxidized and degraded to phosphate radical, carbon dioxide and water (Tian et al. 2016; Zhang et al. 2019; Zhang et al. 2020a, b, c). Carbamate pesticides such as carbofuran were found to be metabolized by *A. niger*, and 3-hydroxycarbofuran was detected as the major metabolite (Das et al. 2003; Salama 1998; Suzuki and Takeda 1976). In another study conducted on the soil from Sudan, 77.8% of oxyfluorfen herbicide is found to be degraded by *Aspergillus* sp. at 40 °C after 45 days of inoculation (Hussein Adil et al. 2011). Sulfonylurea agrochemicals such as orthosulfamuron, chlorsulfuron, metsulfuron-methyl, nicosulfuron and pyrazosulfuron-ethyl are reported to be metabolized by *A. niger*. The fungi cleaves the sulfonylurea bridge which results in nontoxic end products (Pandey and Choudhury 2021; Boschin et al. 2003; Yang et al. 2008; Sondhia et al. 2013). Neurotoxic insecticide imidacloprid was found to be degraded by *A. terreus* strain YESM3, isolated from wastewater and *A. oryzae* and isolated from the soil of Uttarakhand (Mohammed and Badawy 2017; Gangola et al. 2015). Commonly used herbicides like 2,4-dichlorophenoxyacetic acid (2,4-D) and diuron were reported to be degraded by *A. penicillioides*, *A. brasiliensis* G08 and *Aspergillus* sp. G25 (Vroumsia et al. 2005; Lopes et al. 2016). Metolachlor was reported to be metabolized by *A. flavus* and *A. terricola* through hydrolytic dechlorination, *N*-dealkylation and amide bond cleavage (Sanyal and Kulshrestha 2002). *A. flavus* can degrade 100% of malathion (5 mg $L^{-1}$) after 36 days of incubation at 30 °C (Derbalah et al. 2020). Fungicides isopyrazam and metalaxyl were reported to be effectively biodegraded by *A. niger* (Ahmad and Gul 2020; Massoud et al. 2008). Similarly agrochemicals like paraquat, lindane, omethoate, triclosan, terbuthylazine, thiencarbazone 1 methyl, alachlor and pentachlorophenol are also reported to be degraded by *Aspergillus* sp. (Ahmad et al. 2020; Hussaini et al. 2013; Chun et al. 2004; Taştan and Dönmez 2015; Pinto et al. 2012; Ahmad et al. 2020; Massoud et al. 2017; Wongputtisin et al. 2021; Mathialagan and Viraraghavan 2005). From the discussion above, it can be concluded that *Aspergillus* sp. can be an effective candidate in the remediation of diverse harmful agrochemicals from the environment (Table 22.1).

### 22.5.6 Strategies for Amplification of the Bioremediation Process

*Aspergillus* sp. can be used as a promising tool for bioremediation of agrochemicals from the ecosystem. However, this process of bioremediation can be further amplified by using certain approaches which creates a suitable environment for the enhanced metabolism of the fungi. Adaptation of the fungi in the soil environment, difficulty in attaining nutrition, overgrowth of other indigenous microbes and low availability of the chemicals for metabolism are some of the hurdles in the process of efficient bioremediation of these agrochemicals. Some of the researchers have deduced some strategies to enhance the bioremediation by *Aspergillus.*

Marinho et al. (2017) have reported that the addition of glucose to the media can elevate the degradation of atrazine by *A. niger* to 72% in comparison to control condition which is only 40%. It was observed by adding different concentration of glucose (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 g $L^{-1}$) to the reactor, and the highest degradation was found to be attained at 3 g $L^{-1}$ concentration of glucose. This concludes that an addition of carbon source to the fungus helps in its better metabolism of the chemical or degradation. However, increasing the glucose concentration above 3 g $L^{-1}$ led to decrease in the rate of degradation which could be due to substrate competition kinetics.

In another study conducted by Bhalerao (2013a, b), biostimulation of *A. niger* culture by 1% glucose proves to increase the rate of degradation of another pesticide

**Table 22.1** List of *Aspergillus* spp. participating in the process of bioremediation of agrochemicals

| Sl No. | Agrochemicals | Class | *Aspergillus* sp. having bioremediation potential | References |
|---|---|---|---|---|
| 1. | Atrazine | Triazine | *A. niger* | Olu-Arotiowa et al. 2019 |
| | | | *A. oryzae* | Barberis et al. 2019 |
| | | | *A. flavus*<br>*A. parasiticus* | Benito et al. 2019 |
| | | | *A. alliaceus* | Gajendiran et al. 2017 |
| | | | *A. fumigatus* | Kaufman and Joan 1970 |
| | | | *A. flavipes* | Oliveira et al. 2015 |
| 2 | Glyphosate | Organophosphate | *A. niger* | Adelowo et al. 2014 |
| | | | *A. oryzae* | Carranza et al. 2019 |
| | | | *A. flavus* | Carranza et al. 2016 |
| 3 | Endosulfan | Organophosphate | *A. niger* | Mukherjee and Gopal 1994 |
| | | | *A. flavus* | Ahmad 2020a, b |
| | | | *A. terricola* | Hussain et al. 2007 |
| | | | *A. terreus* | Mukherjee and Mittal 2005 |
| | | | *A. tamari* | Silambarasan and Abraham 2013a, b |
| | | | *A. sydoni* | Goswami et al. 2009 |
| 4. | Monocrotophos | Organophosphate | *A. niger* | Jain and Garg 2015 |
| | | | *A. flavus* | Jain and Garg 2013 |
| | | | *A. oryzae* | Bhalerao and Puranik 2009 |
| 5 | Chlorpyrifos | Organophosphate | *A. terreus* | Silambarasan and Abraham 2013a |
| | | | *A. sydowii* | Soares et al. 2021 |

(continued)

**Table 22.1** (continued)

| Sl No. | Agrochemicals | Class | *Aspergillus* sp. having bioremediation potential | References |
|---|---|---|---|---|
| | | | *A. viridinutans* | Tamim and El-Hamid 2016 |
| | | | *A. niger* | Mukherjee and Gopal 1996 |
| 6 | Carbaryl | Carbamates | *A. niger* | Zhang et al. 2003 |
| 7 | Fenitrothion | Organophosphate | *A. niger* | Kanaly et al. 2005 |
| 8 | Dimethoate | Organophosphate | *A. niger* | Liu et al. 2001 |
| | | | *A. terricola* | Lone and Mohd 2012 |
| | | | *A. fumigates* | Derbalah et al. 2021 |
| 9 | Beta Cyfluthrin | Pyrethroids | *A. niger*<br>*A. terricola* | Saikia and Gopal 2004 |
| | | | *A. nidulans* var. *dentatus* | Mukherjee and Archana 2007 |
| 10 | Cypermethrin | Pyrethroids | *A. niger* | Deng et al. 2015 |
| 11 | Cyhalothrin | Pyrethroids | *A. niger* | Sanyaolu 2018 |
| 12 | Methyl Parathion | Organophosphate | *A. sydowii* | Alvarenga et al. 2014 |
| 13 | Profenofos | Organophosphate | *A. sydowii* | Silva et al. 2013 |
| 14 | Trifluralin | Dinitroaniline | *A. carneus* | Zayed et al. 1983 |
| 15 | Oxyfluorfen | Diphenyl ether | *Aspergillus* spp. | El Hussein et al. 2011 |
| 16 | Carbofuran | Carbamate | *A. niger* | Salama 1998 |
| 17 | Orthosulfamuron | Sulphonylurea | *A. niger* | Pandey and Choudhury 2021 |
| 18 | Chlorsulfuron | Sulphonylurea | *A. niger* | Boschin et al. 2003 |
| 19 | Metsulfuron-methyl | Sulphonylurea | *A. niger* | Boschin et al. 2003 |
| 20 | Nicosulfuron | Sulphonylurea | *A. niger* | Yang et al. 2008 |
| 21 | Pyrazosulfuron-ethyl | Sulphonylurea | *A. niger* | Sondhia et al. 2013 |
| 22 | Imidacloprid | Neonicotinoids | *A. terreus* | Mahmood et al. 2016 |
| | | | *A. oryzae* | Gangola et al. 2015 |

(continued)

**Table 22.1** (continued)

| Sl No. | Agrochemicals | Class | *Aspergillus* sp. having bioremediation potential | References |
|---|---|---|---|---|
| 23 | 2,4-dichlorophenoxyacetic acid (2,4-D) | Chlorophenoxy | *A. penicillioides* | Vroumsia et al. 2005 |
| 24 | Diuron | Urea derivatives | *A. brasiliensis* G08<br>*A.* sp. G25 | Lopes et al. 2016 |
| 25 | Metolachlor | Chloroacetanilide | *A. flavus*<br>*A. terricola* | Sanyal and Kulshrestha 2002 |
| 26 | Malathion | Organophosphate | *A. flavus* | Derbalah et al. 2020 |
| 27 | Isopyrazam | Ortho-substituted phenyl amides | *A. niger*<br>*A. flavus*<br>*A. terreus*<br>*A. fumigatus* | Ahmad et al. 2020 |
| 28 | Metalaxyl | Phenylamide | *A. niger* | Massoud et al. 2008 |
| 29 | Paraquat | | *A. niger* | Smith et al. 2006 |
| 30 | Omethoate | Organophosphorus | *Aspergillus* sp. | Chun et al. 2004 |
| 31 | Lindane | Organochlorine | *A. niger* | Hussaini et al. 2013 |
| 32 | Triclosan | Polychloro phenoxy phenol | *A. versicolor* | Taştan and Dönmez 2015 |
| 33 | Terbuthylazine | Chloro-s-triazine | *A. oryzae* | Pinto et al. 2012 |
| 34 | Thiencarbazone-methyl | N-sulfonylurea | *A. terreus* | Ahmad et al. 2020 |
| 35 | Alachlor | Chloroacetanilide | *A. niger* | Ahmad and Gul 2020 |
| 36 | Pentachlorophenol | Organochlorine | *A. niger* | Mathialagan and Viraraghavan 2005 |
| 37 | Diazinon | Organophosphorus | *A. niger* | Hamad 2020 |

endosulfan. Similarly, addition of glucose also hastened the degradation of methyl parathion by *A. niger*. The kinetic constant of the process was 0.063 ± 0.005 $h^{-1}$ which increased to 0.162 ± 0.014 $h^{-1}$ in the presence of glucose (Rodrigues et al. 2011). The process of degradation was found to be accelerated by using the residues of *Opuntia ficus indica* as a co-substrate for the reaction. *O. ficus indica* provides the traces of nutrients which are required for beginning the growth of *A. niger* from lag phase and it helps in activation of the enzymes required for degradation of atrazine

(Herrera-Gallardo et al. 2020). Addition of the Tween 80 helps in degrading monocrotophos by *A. fumigatus* (Pandey et al. 2014). However, instead of a single isolate, using consortia of microorganisms helps to further increase the efficiency of degradation process. Enhanced bioremediation of endosulfan was achieved when a combination of *A. oryzae* and *Trichoderma longibrachiatum* was applied to it (Bhatt 2015). Similarly, consortium of *Aspergillus fumigatus* and *Penicillium citrinum* was also reported to stimulate the process of degradation of atrazine (Bravim et al. 2020). Degradation process can also be enhanced by microbial cell immobilization technique which prevents their contact with the inhibitory substance in the soil environment and increase their catalytic activity. A self-immobilized biomixture (SIB) is formed by fixing the cells of *Arthrobacter* with the cell pellets of *A. niger* Y3. This SIB is found to be a stable mixture and can efficiently remove atrazine. It was reported to degrade 57.3 mg/L of atrazine in 10 h (Yu et al. 2019a, b). However, this experiment was repeated again by adding *Agrobacterium* strain to the SIB which was found to further enhance efficiency of the bioremediation process (Yu et al. 2019a, b). Immobilized *A. sydowii* cultures on magnetically separable chitosan beads are reported to show enhanced removal of trichlorfon (Zhang et al. 2020a, b, c). Enzymes are reported to play a predominant role in bioremediation. Microorganisms possess a wide array of enzymes which directly helps in the degradation of the xenobiotics. Cell-free enzymes are extracted from potential strains for bioremediation and are reported to be utilized for degradation of agrochemicals. Enzymes such as carbaryl hydrolase and pyrethroid hydrolase were extracted from *A. Niger*, which has a role in bioremediation of the pesticides (Zhang et al. 2003; Liang et al. 2005). Using UV mutagenesis, strains of *A. oryzae* with maximum glyphosate degradation enzyme activity were obtained. The mutated strains were observed to confer almost twofold increase in their enzyme activity and could be successfully utilized in the removal of glyphosate from the environment (Fu et al. 2016). However, these enzymes responsible for degradation can also be immobilized on biosorbents which increases its stability and activity. In a study conducted by Chen et al. (2019), the enzyme laccase extracted from *Aspergillus* sp. was immobilized on biosorbents developed with peanut shell and wheat straw and were used in the successful degradation of nine pesticide residues from water.

## 22.6 Future Perspectives and Conclusion

Several strains of different *Aspergillus* spp. are found to be capable of degrading the noxious agrochemicals. Being a filamentous fungi, *Aspergillus* possesses a strong hyphal system which can penetrate complex substrates and a well-developed enzymatic system that aids in breaking down the xenobiotics. Although several studies are found to be carried on bioremediation of pesticides, their application in situ are comparatively scanty. More experimentation should be carried on this aspect in the future and initiatives must be taken for their in situ applications. *Aspergillus* sp. is reported to be pathogenic to both plants and humans (Pawar et al. 2008; Paulussen et al. 2017), and therefore strict precautions and monitoring are required for their use in bioremediation. The process must also be carried on in a controlled manner so that partial degradation of the agrochemicals does not take place, which may leave behind more harmful metabolites to the environment. Research work should be carried out on the use of modern technology such as genetic engineering in escalating the process of degradation. Proteomics- and metabolomics-assisted study for understanding the mechanism of toxicity of the agrochemicals and physiochemical pathways of degradation must hasten for effective use in bioremediation.

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# 23

# Implications of Phytohormones as Agrochemicals in Dynamic Environmental Conditions

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## Abstract

A number of anthropogenic activities being practised worldwide cause serious threat to the natural ecosystem. Industrialisation and urbanisation have affected the agriculture sector significantly by shifting the climate and weather pattern. Plants being sessile living beings have to adapt to changing environmental conditions in its own habitat but certain devastating factors prove lethal to the plant life as well. Therefore, to ensure the normal crop productivity and maintain ecological stability at the same time under such conditions, eco-friendly chemicals must be employed for improving agricultural crops. Phytohormones are such chemicals which are produced endogenously within the plant and are known to regulate vast array of physiological and developmental processes in the life cycle of a plant. Exogenous application of such chemicals in minimal quantities has proven valuable to crop plants by maintaining their growth in stressful habitats. This book chapter mainly addresses the utilisation of different plant hormones, i.e. auxins, gibberellic acid, cytokinin, ethylene, abscisic acid, brassinosteroids, jasmonic acid, salicylic acid and strigolactones, for improving the crop productivity and their use as potential agrochemicals.

## Keywords

Agrochemicals · Phytohormones · Crop productivity · Abiotic stress

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## 23.1 Introduction: Phytohormones as Agrochemicals

Food is an essential and vital needs for endurance of life on the planet earth. Agriculture is one of the most vital sectors which not only provides food across the globe but also adds to economy of the nation. That is why the agriculture sector holds an indispensable share in the worldwide domestic production. Also, cultivation of crop plants is environmentally friendly as it provides oxygen as well as clears toxic pollutants. It is the source of earnings of large population especially in rural areas. But this sector is no longer protected from the harmful effects of cruel anthropogenic activities. Pollution of soil and water is of major concern as it directly as well as indirectly hampers the crop productivity. Not only this, these activities are also responsible for disturbance in natural climatic conditions which may act as stress to the plant growth. Hence, crop's production in natural habitation formulates them very prone to numerous confronts of dynamic environmental circumstances. These diverse conditions pose various threats to the plant survival in this manner manipulating on the whole productivity. Thus, this is the need of hour to offer healthy food with financial security to people across the world (Rodríguez et al. 2020). To cope with these adversities in order to maintain normal crop productivity, a number of products are being employed for application to different parts of crop plants. These products which are applied to agricultural crops for their proper growth and development under adverse conditions are referred as agrochemicals. Most frequently used agrochemicals include fertilisers and pesticides and these are synthetic in nature. These chemicals are not only toxic for the environment but also lethal to the human health. Therefore, the use of eco-friendly and non-toxic agrochemicals must be practised in order to avail the required benefits to the plants.

Phytohormones are one of such plant growth regulators which are produced naturally within the plants, and their exogenous application promotes the metabolic activities of plants, thus ensuring the survival of plants under imbalanced environmental conditions. Auxins, gibberellins, cytokinin, ethylene, abscisic acid, brassinosteroids, salicylic acid and strigolactones are the phytohormones which independently as well as in coordinated manner regulate various aspects of plant development. These are applied to plant in different forms as through seed treatment or foliar application. The positive effects of these hormones utilised as agrochemicals are discussed in detail in different sections of the chapter.

## 23.2 Auxins

Involvement in controlling the plant tropism towards light and gravity led to the recognition of auxins as phytohormones which later was discovered to regulate wide array of plant growth and development responses like embryogenesis, development of shoot, rhizogenesis, vascular differentiation, development of fruit and many more (Miransari et al. 2014; Estelle 2011). Indole-3-acetic acid (IAA) is the most abundant naturally occurring form of auxin which controls and regulates many physiological processes in plants till senescence (Çakmakçı et al. 2020; Tivendale and Cohen

2015). Auxins are reported to enhance the plant growth and productivity under the dynamic environmental conditions that enable them to occupy position as potent agrochemicals. Auxins were reported to support the hypocotyl elongation under low light and high temperature stress that drastically regulated the hypocotyl elongation. The endogenous levels of IAA and indole-3-pyruvate (IPA) along with gibberellins were found to increase during hypocotyls elongation. The results were further confirmed by exogenous application of auxin or auxin biosynthetic inhibitors. The transcript levels of genes involved in auxin synthesis were also enhanced under low light and high temperature stress (Bawa et al. 2020). The exogenous application of indole-3-butyric acid (IBA) was found to be essential in adventitious root formation in olives (*Olea europaea*) that hold great market value where the auxin homeostasis and distribution across root and stem helped in adventitious root formation (Velada et al. 2020). Another study on *Carica papaya* was reported where the exogenous treatment of auxin (IAA) at concentration of 37.5μM $L^{-1}$ aided in amelioration of salt stress (Sá et al. 2020). Different studies have analysed the effect of auxin-type compounds on the growth of plants under different stress conditions. For instance, auxin-type compounds 1-[2-chloroethoxycarbonyl-methyl]-4-naphthalenesulfonic acid, calcium salt (TA-12) and 1-[2-dimethylaminoethoxicarbonylmethyl] naphthalene chlormethylate (TA-14) were exogenously applied to water-stressed pea plants (*Pisum sativum*). The auxin analogues helped in protecting the plant against drought stress by maintaining the levels of ROS and uplifting the antioxidants (Sergiev et al. 2019). Microarray profiling was performed to unravel the role of microRNA (miRNA) under arsenic (As) toxicity in *Brassica juncea*, and different families of miRNA displayed alterations in their expression during As stress. Some of the upregulated miRNA resulted in enhanced levels of phytohormones like auxin, jasmonates and abscisic acid. The study suggested interplay of the phytohormones and miRNAs under stress that supported the growth of mustard. The same was approved by the growth enhancement on exogenous application of IAA and jasmonates (Srivastava et al. 2013).

The action of auxin and cytokinins (CK) has also been acknowledged in controlling the reactive oxygen species (ROS) which are harmful for the growth and development of the plants (Verma et al. 2016). Exogenous application of IAA (200 ppm) in *Vicia faba* enhanced its tolerance against salinity stress. The IAA foliar application maintained the water balance, reduced ROS and enhanced total protein, free amino acid, sugars, activity of antioxidants, nodules and root-shoot traits (Abdel Latef et al. 2021). Inhibition of the expression of YUCCA (YUC) pathway of the auxin biosynthesis resulted in the mail sterility in *Arabidopsis thaliana* and *Hordeum vulgare* during high temperatures which was reversed by exogenous IAA (Sakata et al. 2010). The drought-resistant phenotypes have been related to the enhanced levels of auxin which helps in uplifting the activities of antioxidants, mitigating the ROS, enhancing the expression of stress-related genes in order to support the growth at fullest during drought conditions (Bielach et al. 2017). Shi et al. (2014) reported the drought-alleviating effect of auxins by modulating the root architecture of the plants. Moreover, the crosstalk of auxin with other stress-related hormones like abscisic acid, salicylic acid, jasmonates and ethylene has been

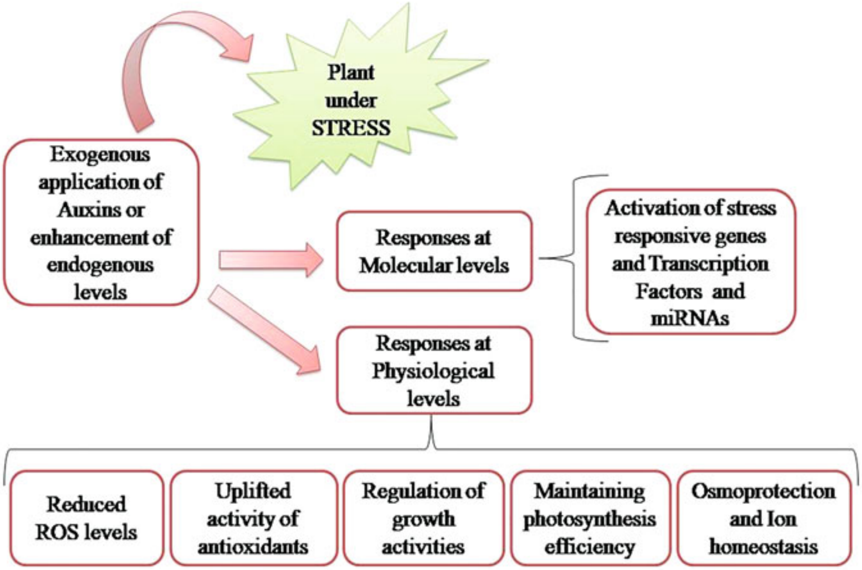

**Fig. 23.1** Response of auxin on encountering stress conditions in plants

reported, where auxin regulated the growth of the plants during stress. In silico analysis depicts that a large number of stress-related motifs are associated with the regulatory regions of the *SlARF* (auxin response factors) in *Solanum lycopersicum* (Bouzroud et al. 2018). The role of *SlARF* has been well acknowledged under various biotic and abiotic stress conditions which open up new field of research for the manipulation of ARF genes to enhance the tolerance of plants against stress. Small auxin-upregulated RNAs (*SAUR*s) are auxin-regulated genes which are also under environmental regulation. A *SAUR* gene in *Triticum aestivum* was identified, namely, *TaSAUR75*, which when overexpressed induced salt and drought tolerance in wheat (Guo et al. 2018). Bashri and Prasad (2015) reported IAA application of high dose and low dose in *Trigonella foenum-graecum* exposed to cadmium (Cd) stress resulted in improving the growth parameters as compared to Cd-stressed plants. The photosynthetic efficiency, carbonic anhydrase activity and antioxidants were found to enhance in the aforementioned study. Therefore, it can be well suggested that auxin is an essential plant hormone with its role in stress conditions (Fig. 23.1). The exogenous application of hormone or enhancement of the endogenous levels through genetic manipulations helps in producing appropriate growth responses under conditions of stress.

## 23.3 Gibberellic Acid

Gibberellic acid or gibberellins (GAs) are weakly acidic tetracyclic diterpenoid phytohormones with gibbane ring-like structure and are known to cause conspicuous effects on leaf and stem elongation in intact plants by regulating cell elongation and division (Hashimoto and Rappaport 1966). GAs are distributed in all parts of the plant with the highest concentration being reported in the immature seeds and young leaves. Depending upon a slight variation in structure and biological function, more than 136 forms of GA have been identified with $GA_3$ being regarded as the most commonly occurring gibberellic acid (Hashimoto and Rappaport 1966). The biosynthesis of GA occurs inside plastids with acetyl-CoA as its precursor, which forms mevalonate as the first product which is further acted upon by various enzymes to yield kaurene which is then stepwise changed to $GA_{12}$ and other forms of GA (Hedden and Thomas 2012).

In the twentieth century, green revolution is attributed to an enormous increase of rice and wheat yield which was achieved by the development of semi-dwarf varieties. This semi-dwarf habit was later confirmed to be controlled by *semidwarf1* (*sd1*) in rice and *Rht* in wheat which is a GA biosynthetic and GA signalling gene, respectively (Gao and Chu 2020). The *semidwarf1* (*sd1*) is used as a modern rice cultivar since the 1960s due to its semi-dwarf nature (Tu and Wang 2019). Since its discovery, GA is reported to actively participate in diverse growth and developmental processes like the induction of hydrolytic enzymes in seed germination, leaf expansion, induction of bolting in long-day plants; elongation of stem and development and maturation of flowers, pollens, fruit and seeds (Piskurewicz et al. 2008; Arnaud et al. 2010; Hauvermale et al. 2012; Sakata et al. 2014). Thus, due to its diverse roles in plant growth, development and stress tolerance mechanisms, GA is long been exploited as an agrochemical for crop production with an estimate global use of around 100 tons of $GA_3$ annually for plant production (Table 23.1).

The direct seed dressing application of $GA_3$ marketed under the name Release® is a common treatment during rice cultivation under suboptimal temperatures which improves the germination percentage, seedling height and stress tolerance of the crop (Dunand 1992). AlTaey (2017) used poultry and gibberellins as manure to alleviate salt tolerance in pepper (*Capsicum annuum* L) and observed it to mitigate salt stress by increasing growth parameters like dry weight of shoot, root and fruit weight and NPK contents in leaves. A comprehensive transcriptomic study of $GA_3$-treated plants of sugarcane reported an increase in the activity of genes regulating metabolic pathways, synthesis of metabolites, photosynthesis and signal transduction of phytohormones in the internodal region of the treated plants, thereby regulating gibberellin-induced plant growth (Chen et al. 2020).

Recently, a report showed an increase in the fruit quality and marketability of "Washington Navel" orange trees by foliar treatment of $GA_3$ at 50 ppm plus Sytofix (CPPU) at 10 ppm or $GA_3$ at 50 ppm plus cytokinin-BA (6-benzylaminopurine) at 50 ppm to obtain an increased fruit size and weight with a reduced fruit splitting percentage (Elmenofy et al. 2021). Further, Sudradjat and Purwanto (2021) have delineated that exogenous treatment of 25 ppm $GA_3$ on oil palm (*Elaeis guineensis*

**Table 23.1** Implications of gibberellins in agriculture

| S. No. | Form of application | Method of application | Intended use | Reference |
|---|---|---|---|---|
| 1. | $GA_3$ release® | Seed priming | • Enhanced germination rate<br>• Improved seedling height<br>• Stress tolerance | Dunand (1992) |
| 2 | Gibberellic acid | Foliar application of soluble form | • Induce hydrolytic enzymes for seed germination<br>• Bolting in long-day plants<br>• Leaf and stem elongation<br>• Maturation of flowers and fruits<br>• Mesocarp firmness and enhanced free fatty acids (FFA) in oil palm<br>• Increase in height of sugarcane orchid (*Grammatophyllum speciosum*) | Arnaud et al. (2010), Sakata et al. (2014), Sudradjat and Purwanto (2021), Ria et al. (2021) |
| | $GA_3$ mixed with poultry manure | Solid manure mixture | • Salt tolerance in pepper (*Capsicum annuum* L.)<br>• Increase dry weight<br>• Increase fruit weight<br>• Upregulate NPK content in leaves | AlTaey (2017) |

Jacq.) retained mesocarp firmness in the fruit and enhanced fruit weight and quality of fresh fruit bunches (FFB). These fresh fruit bunches (FFB) when processed within 24 hours of harvesting yielded premium quality palm oil with an elevated level of free fatty acids (FFA) and a reduced amount of crude oil (Sudradjat and Purwanto 2021). Ria et al. (2021) studied the effect of the exogenous application of $GA_3$ on the growth of sugarcane orchid (*Grammatophyllum speciosum*) and observed an increase in the height of in vitro grown plant 12 weeks after culture. Since gibberellin metabolism directly targets many vital growth and development-related genes of plants, their large-scale agricultural and horticultural manipulation as agrochemicals would open new doors to the science of crop improvement.

## 23.4 Cytokinin

Cytokinins (CK) are adenine derivatives with an aromatic or isoprenoid side chain attached with N-6-position of adenine, and out of the two, isoprenoid side chain derivatives are more common in plants. CKs are known to play pivotal role in inculcating stress tolerance in the plants under both abiotic and biotic conditions (Table 23.2). *Verticillium longisporum* is a soil-borne fungus that affects the trans-zeatin levels upon disease incidence. It was observed that protection against *V. longisporum* can be induced on maintaining the levels of CKs in *Arabidopsis* (Reusche et al. 2013). *Spinacia oleracea* faces stress during pre-transplantation from the plug cell volume which hinders the root and shoot growth of the crop and results in loss of the yield. However, the spray of 6-benzyl amino purine (BAP) helps in removing any root restrictions and enhances the green leaf area along with the photo-assimilates (Geraci et al. 2018). CKs are reported to shorten the breeding season of *Vicia faba*, and the supplementation with BAP enhanced the pollen viability and led to early seed set during cold stress conditions (Mobini et al. 2020).

Another study in *V. faba* reported that application of 6-benzyladenine under salt stress maintained the cellular homeostasis and enhanced mineral nutrition of the plant thereby improving the growth parameters (Latef et al. 2021). High temperature and drought stress lead to huge economic loss in wheat. However, application of BAP led to the enhancement of the photosynthetic attributes along with improving the biomass of the plant along with controlling the ROS produced under stress (Kumari et al. 2018). CK application during silking stage in maize produced low retrograde tendency grains under post-silking drought stress (Wang et al. 2021). Zaheer et al. (2019) reported that combined treatment of *Rhizobacteria* and zeatin helped in ameliorating drought stress in wheat. The seed inoculation with rhizobacteria and spray of zeatin in a combined way was more beneficial rather than independent treatments (Zaheer et al. 2019).

The role of CKs in alleviating drought stress has also been reported in *Agrostis stolonifera* where the contents of isopentenyladenine (iP) and zeatin content in leaves and shoots during water stress maintained the photosynthetic efficiency and osmotic potential of the drought-stressed plants (Merewitz et al. 2011). It was further reported that the root growth was highly supported when the CK content in the roots was enhanced during water-deficit conditions which was achieved on enhancing the expression of the isopentenyl transferases (ipt) and the enhanced levels of CKs help in ROS scavenging and activating antioxidants (Xu et al. 2016). The research conducted in *A. stolonifera* demonstrated that the turf quality was significantly improved on exogenous CK application with higher amount of nitrogen under drought stress along with enhanced activity of the antioxidants (Chang et al. 2016). In case of *Arabidopsis*, it was observed that the CKs were associated with the heat stress alleviation and helped in enhancing the photosynthetic efficiency under high temperature circumstances (Skalák et al. 2016).

Another report suggested similar results where the higher endogenous levels of CKs, achieved by overexpressing ipt, helped in mitigating the heat stress (Černý et al. 2013). It was observed in case of maize if the *IPT* gene was overexpressed in

**Table 23.2** Potential applications of cytokinin in agriculture

| S. No. | Treatment | Plant | Stress | Response | Reference |
|---|---|---|---|---|---|
| 1. | 6-Benzyladenine (200 ppm) | *Vicia faba* | Salinity | Enhanced biomass, mineral absorption and reduced ROS | Latef et al. (2021) |
| 2. | Cytokinin (0.1 g/L) | *Zea mays* | Drought stress | Grains with low retrograde tendency | Wang et al. (2020) |
| 3. | 6-benzyl amino purine ($10^{-5}$) | *Vicia faba* | Cold stress | Enhanced pollen viability and early seed set | Mobini et al. (2020) |
| 4. | Cytokinins (bacterial transformations or exogenous application) | – | Osmotic stress | Delayed senescence, maintaining osmotic potential, reduced ROS and improved growth | Gujjar and Supaibulwatana (2019) |
| 5. | Zeatin (25 mg/L) + r*hizobacteria* | *Triticum aestivum* | Drought stress | Improved yield and mineral nutrition | Zaheer et al. (2019) |
| 6. | BAP<br>Foliar application | *Spinacia* oleracea | Plug cell volume (pre-transplantation) | Enhanced leaf area, photo-assimilates and productivity | Geraci et al. (2018) |
| 7. | BAP (10 ppm) | *Triticum aestivum* | High temperature and drought | Enhanced photosynthetic efficiency, relative water content and other growth parameters | Kumari et al. (2018) |
| 8. | Cytokinins (150 mg/L) | *Zea mays* | Drought stress | Enhanced yield parameters | Akter et al. (2014) |

maize exposed to water-deficit conditions, the grain yield obtained was comparable with the well-watered conditions. The stomatal conductance, photosynthetic rate, biomass, number of grains, grain weight and total productivity were maintained by stress-dependent CK synthesis under drought stress (Oneto et al. 2016). Overall, CKs play essential role in the growth of the plants under normal and unfavourable stress conditions which is of greater interest for their manipulation and use as agrochemicals in a commercial way in order to drive maximum benefits.

## 23.5 Ethylene

Ethylene, the simple hydrocarbon ($CH_2 = CH_2$), is a gaseous phytohormone known to be active at even as low as 0.006 ppm and is recognised to stimulate transverse or isodiametric growth in plants. This gaseous phytohormone is known to have some crucial roles in plant growth and development, viz., fruit development, leaf and fruit abscission, growth and maturation of tissues, reproductive success, organ longevity, etc. (Iqbal et al. 2017). The 5-carbon amino acid methionine is regarded as the precursor of ethylene, where methionine reacts with ATP (adenosine triphosphate) to form 5-adenosylmethionine which in turn forms ACC (1-aminocyclopropane1-carboxylic acid) that is finally converted to ethylene by action of enzymes on the tonoplast (McKeon et al. 1995). Under dynamic environmental conditions, ethylene production is accelerated in plants by altering the step in ACC formation thus playing a central role in plant survival and adaptation (Ravanbakhsh et al. 2018).

Ethylene is defined as a multifarious plant hormone which serves pleiotropic roles in both plant growth and senescence (Iqbal et al. 2017; Ravanbakhsh et al. 2018). Over the years ethylene is reported to orchestrate diverse functions of plant growth and development including development of leaves, flowers and fruits and is also known to promote or inhibit senescence, promote germination and inhibit root elongation in plants (Pierik et al. 2006, Mattoo 2018). Thus, ethylene is known to regulate two contrary responses of growth and senescence in plants. Apart from being recognised as an aging hormone, ethylene also orchestrates cell expansion and proliferation and aids in plant defence mechanisms under abiotic and biotic stress (Table 23.3). Thus, regulation and agronomic exploitation of this phytohormone could provide indispensable outputs on crop yield and serve as a major growth regulator in agriculture and horticulture sector (Depaepe and Van Der Straeten 2020).

Ethylene is regarded as the master regulator of fruit ripening process in plants where it is reported to regulate the ripening process by complex interplay between ethylene signalling and ripening-related transcription factors (Liu et al. 2020). In tomato, the most explored model of fruit ripening, it was reported that the downregulation of *SlAP2a* transcription factor of family AP2/ERF increased ethylene biosynthesis and thereby accelerated carotenoid accumulation turning the fruit colour to red (Karlova et al. 2011). Fleshy fruits are a vital source of various essential vitamins and fibre in human diet. Ethylene is reported to aid fruit ripening at molecular level by speeding up the fruit softening process, accumulation of sugars

**Table 23.3** Implications of ethylene in agriculture

| Form of application | Method of application | Intended use | Reference |
|---|---|---|---|
| Ethephon (2-chloroethylphosphonic acid) | Aqueous or concentrated foliar spray | • Ripening of fruits like tomato and apple<br>• De-greening of citrus fruits<br>• Boll opening and de-foliation of cotton crop<br>• Abscission in apple<br>• Promote female flowers in *cucumber* | Depaepe and Van Der Straeten (2020) |
| Ethylene ($CH_2 = CH_2$) | Foliar spray of aqueous solution | • Cell expansion and proliferation<br>• Tomato fruit ripening by carotenoid accumulation<br>• Increase sugar metabolism in grape berry<br>• Upregulates fructose, glucose and quinic acid in kiwifruit<br>• Fibre accumulation in cotton<br>• Stem elongation in maize<br>• Alleviates abiotic stress | Depaepe and Van Der Straeten (2020), Karlova et al. (2011), Chervin et al. (2006), Lim et al. (2017), Qin and Zhu (2011), Dubois et al. (2018) |

and altering the acidity, thereby increasing the market value of the fruits (Liu et al. 2020). Exogenous application of ethylene to grape berry was observed to increase sugar metabolism and sugar content in the ripening process (Chervin et al. 2006). Application of ethylene to kiwifruit showed an upregulation in the fructose, glucose and quinic acid of ripened fruits and thereby increased the consumer acceptance of the fruit (Lim et al. 2017). Post-harvest treatment of ethylene and 1-methylcyclopropene (1-MCP) on cold-stored apricot (*Prunus armeniaca* L.) fruits was reported to delay fruit ripening and softening process by supressing the action of pectin-degrading enzymes and effectively enhanced the sensory quality and consumer value of the fruit (Fan et al. 2018). Similarly, ethylene is also reported to improve fruit ripening of peach (Gong et al. 2015), fibre elongation in cotton (Qin and Zhu 2011), stem elongation in maize (Zhang et al. 2019), photo-oxidative stress

(Guo and Ecker 2004) and many other physiological responses in plants. Also, over the years many evidences had unravelled the molecular connection between ethylene, growth and cell expansion explaining the organ growth and yield under abiotic stress conditions (Dubois et al. 2018). Thus, the wide array of ethylene responses had further opened the way for its agricultural use to enhance yield and quality of crops (Kuroha et al. 2018).

Along with the idea of direct use of ethylene in agriculture, recently the use of some chemical-based artificial derivatives and ethylene-inducing compounds has also been encouraged (Depaepe and Van Der Straeten 2020). The 2-chloroethylphosphonic acid or ethephon, marketed under the name Cerone or Ethrel, is researched to induce many ethylene-related responses like flower development and fruit maturation in pineapple fruits. Further, the pre-harvest application of ethephon is reported to synchronise and stimulate the process of fruit ripening and maturation in tomato and apple (Depaepe and Van Der Straeten 2020). Ethephon is also reported to enhance effective harvesting of cotton crop by stimulating the opening of cotton balls and defoliation of harvest-ready crop (Smith et al. 1986). Thus, a further research on ethylene and its related compounds as agrochemicals could open new prospects of ethylene-based agriculture and horticulture attempts to improve crop yield by modulating the physiology and phenotypic traits of crops of interest.

## 23.6 Abscisic Acid (ABA)

Environmental stress management is vital for increased plant production as biotic and abiotic stressors severely limit crop growth and development. Agrochemicals produced for crops have mostly been used to managing biotic stresses, although both biotic and abiotic stressors produce many reactions in plants, contributing to decreased yields. Plants produce and release abscisic acid (ABA) in response to a variety of biotic and abiotic stresses (Hewage et al. 2020). ABA, for example, protects plants from severe temperatures, high salinity, high concentrations of heavy metals, radiation, low or abundant water supply and cold (Fig. 23.2). ABA also aids in the regulation of several key plant developmental processes, including root growth, seed development, vegetative-reproductive phase transitions and senescence (Rajagopalan et al. 2016). As a result, the application of ABA-based agrochemicals may aid agricultural plants in dealing with environmental stress while maintaining adequate output. Thus, in addition to their potential utility in ABA signalling pathway studies, the creation of novel ABA analogues or agonists may have major agricultural uses (Dejonghe et al. 2018).

Plants adjust their transpiration rates by altering stomatal aperture, thus ABA receptors have emerged as intriguing targets for optimising water consumption; nevertheless, ABA agonists agreed for this purpose have yet to be developed. We reasoned that the agrochemical manage of plant water consumption might be achieved in transgenic plants expressing an engineered ABA receptor that reacts to an obtainable agrochemical, a technique based on orthogonal ligand-receptor

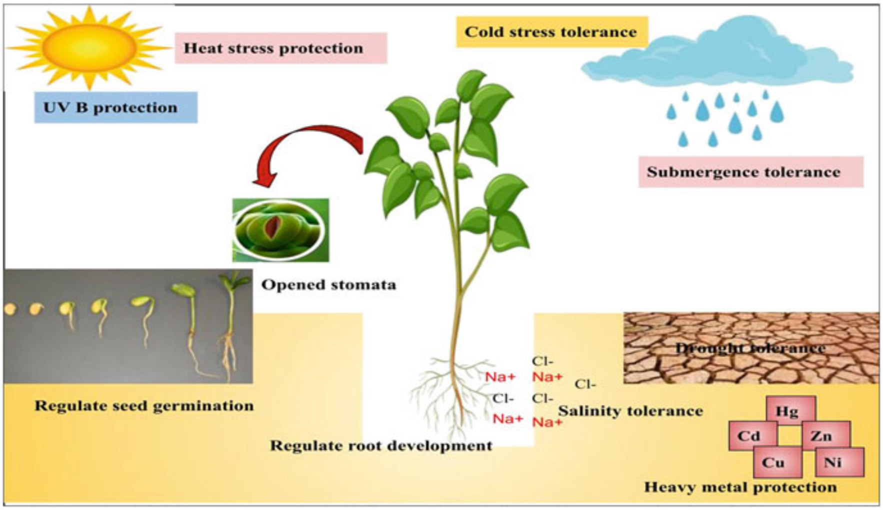

**Fig. 23.2** Involvement of ABA in plant growth and stress tolerance

systems that have permitted selective chemical control of various targets (Ma et al. 2018). The core ABA signalling components have now been identified, which include ABA receptor proteins (pyrabactin resistance/pyrabactin resistance-like/regulatory component of ABA receptors (PYR/PYL/RCAR) (referred to as PYLs), sucrose nonfermentation-1-related subfamily of kinases (SnRK2s), downstream interacting proteins as well as type 2C protein phosphatases (PP2Cs). Furthermore, in vitro restoration of the core ABA signalling system verified the sequential processes of ABA perception and phenotypic responses (Qin et al. 2019). Foliar injection of ABA and ABA agonists boosted the water usage efficiency (WUE) of wheat (*Triticum* sp.) and barley (*Hordeum vulgare*), whereas greater ABA sensitivity improved drought tolerance in *Arabidopsis* and rapeseed (*Brassica napus*) was enhanced by the downregulation of a farnesyltransferase (Cao et al. 2017). The ABA signalling components mainly involved in the suppression of root cell development, with the ABA receptor protein PYL8 playing a specific function (Belda-Palazon et al. 2018). The ABA receptor genes *AtPYR1*, *AtPYL1*, *AtPYL2*, *AtPYL4*, *AtPYL5* and *AtPYL8* in *Arabidopsis* enhance ABA-mediated regulation of root development. PYL8 acts together with the transcription factors MYB44, MYB73 and MYB77 directly. PYL8 promotes lateral root development after ABA suppression in the absence of ABA-SnRK2 signalling. As a result, the PYL8 protein, an ABA signalling component, is identified as employing a non-cell autonomous method in root ABA sensing (Belda-Palazon et al. 2018).

Both agonists and antagonists of ABA perception have shown potential as agrochemicals. Agonists that target subfamily III PYLs and augment or improve ABA-like activity (e.g. cyanabactin, AMF4, opabactin and quinabactin) are promising drought protectants (Vaidya et al. 2019). They decrease transpiration by shutting stomata and activating a set of ABA-responsive genes. The antagonists reported either inhibit PYL-PP2C contacts or maintain non-productive ligand-PYL-PP2C interactions, limiting further downstream signalling processes (Gupta et al. 2020). Antagonists that inhibit ABA-mediated stress responses may be beneficial for chemical control of plant senescence. As demonstrated for the antagonist AA1, the inhibition of ABA-mediated stress responses by antagonists may be beneficial for the chemical control of plant senescence (Ye et al. 2017). Abscinazole-E2B and abscinazole-E3M, which specifically inhibited the CYP707A enzyme, were used to modulate ABA catabolism (Takeuchi et al. 2016). Among the current ABA catabolism inhibitors, these selective inhibitors appear to work without harming plant development. The development of such agrochemicals is a viable alternative to plant breeding for tolerance to biotic and abiotic stressors. Such breeding is frequently time-consuming and constrained by the characteristics of the plant genome. As agrochemicals, ABA signalling modulators are a far simpler answer to plant stress management than breeding. A chemical may be created in a very short period of time, and its usage can be restricted (Hewage et al. 2020).

## 23.7 Brassinosteroids

Brassinosteroids (BRs) are polyhydroxylated steroid plant hormones which is well acknowledged in enhancing the plant safety in opposition to the harsh surroundings of environment, thereby retaining the yield attributes (Ahanger et al. 2018; Ahammed et al. 2020). Application of BRs in enhancing the plants' tolerance in opposition to harsh environmental conditions and upholding the quantity as well as quality of productivity puts emphasis on the application of BRs as agrochemicals in increasing the productivity with expanding plants' survival to various conditions of stress (Table 23.4). BRs have already been well-known crucial components of commercially accessible plant growth stimulants such as growth "Tianfengsu" (Ikekawa and Zhao 1991) and "Epin2" (Moiseev 1998). Implication of such eco-friendly natural substances that display promising potential in improving agriculture may be of greater interest to plant breeders, researchers, industrialists and agriculturists. Out of various BRs, brassinolide (BL), 24-epibrassinolide (24-EBL) and 28-homobrassinolide (28-HBL) are the most active forms (Bajguz and Hayat 2009).

Crop yield is honestly associated with biomass, where increase in the biomass occurs with efficient cell proliferation and expansion (Evans and Fischer 1999) which is regulated by BRs (Xie et al. 2011). As a result, BRs verify yield of a crop. Besides this BRs also control the photo-morphogenesis and vascular differentiation (Nolan et al. 2020). BRs are also well known to participate and play fundamental roles in convalescing the activity of Rubisco enzyme, net photosynthetic efficiency and relative water content of plants all along with the carbon assimilation and improved PSII (photosystem) activity which helps and leads to the superior growth aspects of the crop plants (Lima and Lobato 2017; Siddiqui et al. 2018). BRs also control the stress-responsive genes which arbitrate diverse stress-related retorts (Zhao et al. 2016). Foliar spray of BRs has also shown their role in

**Table 23.4** Different roles of BRs with exogenous appliance

| Sr. No. | Name of the plant | Applications of BRs | Reference |
|---|---|---|---|
| 1. | Potato | Longer dormancy and delayed sprouting in tubers enabling long-term storage under application of 24-EBL | Korableva et al. (2002) |
| 2. | Cucumber | Production of parthenocarpic fruits | Manzano et al. (2011) |
| 3. | Pepper | 24-EBL improved flower and fruit number and overall yield per plant | Samira et al. (2012) |
| 4. | *Arachis hypogeal* | In the presence of BR, antioxidant enzyme activities were augmented and MDA content was progressively declined | Verma et al. (2012) |
| 5. | *Tomato* | Enhanced soluble sugars, respiration rate lycopene and ethylene synthesis and lowered chlorophyll content by BL | Zhu et al. (2015) |
| 6. | *Brassica napus* | BRs augmented the seed yield leading to amplified overall oil content per plant | Sahni et al. (2016) |
| 7. | *Gerbera hybrid* | Petal growth, expansion of basal and middle regions of petals | Huang et al. (2017) |
| 8. | *Rosa hybrid* (rose) | Protection against *Botrytis cinerea* | Liu et al. (2018) |
| 9. | *Brassica juncea* | HBL regulated gene expression and antioxidant enzyme activities in response to temperature-induced oxidative stress | Kaur et al. (2018) |
| 10. | *Linum usitatissimum* | BRs supported epigenetic modification all the way through cytosine methylation | Amraee et al. (2019) |
| 11. | *Lavandula intermedia* | Enhanced lavandin content, growth parameters and total phenolics | Asci et al. (2019) |
| 12. | *Glycine max* | BRs endorsed raise in the germination, length and dry matter of soybean seedlings, and further these results were clarified via growth in the root anatomy | dos Santos Ribeiro et al. (2019) |
| 13. | *Linum usitatissimum* | BRs application developed the fibre yield and quality for flax | Yuan et al. (2019) |
| 14. | *Carthamus tinctorius* | EBL significantly amplified the chlorophyll contents and oil percentage with extensive reduction in the malondialdehyde (MDA) content via raising the proline and carotenoids content under stress condition | Zafari et al. (2020) |

fruit and flower growth and development along with defeating post-harvest losses (Kang and Guo 2011). Nevertheless, the type of action of BR offers by plant may differ with plant species along with the mode of appliance of BR (root application, seed priming, inflorescence spray, foliar spray or addition to growth medium), quantity of applied concentration and stress intensity and also depends on the stage of plant during application (Ahanger et al. 2018).

Zhang et al. (2020a, b, c) finding showed the outcomes of soil drying under BR treatment on rice where BRs protected the spikelet of plants from degeneration. This observation was confirmed by adding BR synthesis inhibitor to the young panicle where BR synthesis gene knock down was done, and this leads to reduced adenosine triphosphate (ATP), ameliorated contents of $H_2O_2$ and also spikelet degeneration. Afterwards, it was also studied that BRs defend the plants from high temperature stress and also from water-deficient conditions in cereals. BR signalling components play crucial role to achieve rise in the productivity and yield in terms of grains, and this concern is of huge attention to the breeders (Kothari and Lachowiec 2021). BRs also play role in the protection of plants against several biotic attacks by maintaining the growth and development. 24-EBL treatment to barley (*Hordeum vulgare*) protected the plants from *Fusarium* pathogens (*Fusarium culmorum*) that affects grain quality and leads to head blight disease as mycotoxins found to be accumulated in the grain, and this poses harmful effects if consumed. Here, the exogenous application of 24-EBL upregulated the expression of genes related to parthenogenesis and thus protected the barley from disease damage. This appliance also enhanced the photosynthetic efficiency of plants (Ali et al. 2013).

In addition to BR effects associated with growth, a major plant defence signature, expectedly refereed by BES1/BZR1, was noticeable in the transgenic plants. All these results and outcomes established that BR can corporately and simultaneously develop biotic and abiotic stress tolerance and plant productivity. The capability to present pleiotropic favourable effects allied with diverse agronomic traits puts forwards that BR-related genes are imperative for increasing plant productivity and performance under different stress conditions. From an agricultural perspective, these BR-related genes could serve as reproduction targets for the crop improvement (Sahni et al. 2016). It is hypothesised that EBL can influence safflower biochemical properties, oil content and crop yield under water-deficit conditions (Zafari et al. 2020). Furthermore, Ariyoshi et al. (2016) observed that BRs regulated pod growth positively all the way through cell hypertrophy in soybean plants.

BRs proved to be a good agrochemical in agriculture industry as Huang et al. (2020) observed that supplementation of BRs to groundnut that was exposed to drought conditions sustained the yield of the crop as well as encouraged numerous differentially expressed genes (DEGs) which control stress responses for drought tolerance (Huang et al. 2020). BRs have also been reported to counter the damaging effects of metal-contaminated soils and herbicide in leguminous crops thereby sustaining their endurance and standard chemical composition under diverse conditions (Mota 2020). Moreover, the association of mycorrhizal arbuscular with some fungi amplifies the crop potential in uptake of different vital nutrients for better crop development. Such kinds of associations are also upregulated via BRs application (Wei and Li 2016; McGuiness et al. 2019). Asci et al. (2019) found that foliar appliance of 24-EBL on *Lavandula intermedia* improved the essential oil content which has wide use in the cosmetics and perfumes, and it also holds the medicinal importance.

Ever since the finding of BRs, they have been of superior notice to the researchers crosswise the world. The productivity of the crops like legumes, cereals, fruits, vegetable and oilseed etc. must be retain as BRs offer solution to the food challenge that happens due to growing population and harsh environmental conditions.

## 23.8 Jasmonates

Plants produced phytohormones such as jasmonic acid (JA) and its cyclopentanone derivatives. They are referred to collectively as jasmonates (JAs). These multifunctional hormones have been shown to reduce the harmful impacts of dynamic environmental conditions (Table 23.5) (Per et al. 2018). Various studies have shown that exogenous application of JA improves herbivore tolerance and induces the expression of defence-related genes (Awang et al. 2015). Furthermore, JAs are involved in a variety of physiological activities such as tuber formation, tendril coiling, seed germination, stomata opening, leaf senescence, fruit ripening and root growth, as well as playing critical roles in plant defence responses against damage caused by insects and microbial pathogen attack (Wasternack and Strnad 2018). The major source of salt stress in plants is excessive $Na^+$ and $Cl^-$ ion concentrations in the soil. Plants were severely harmed by $Na^+$ retained in woody roots and $Cl^-$ accumulated in the shoots. Salt stress reduces root/shoot dry weight and root length, but it also reduces $K^+$, $Ca^{2+}$ and $Mg^{2+}$ concentrations in plant shoots. Na uptake was

**Table 23.5** Mechanism of regulation of JA under dynamic environmental conditions

| Stress type | Plant species | Mechanism of regulation | Reference |
|---|---|---|---|
| Freezing | *Arabidopsis thaliana* | The C-repeat binding factor (CBF) transcriptional pathway was positively regulated, which increased the expression of cold-responsive genes downstream | Hu et al. (2017) |
| Chilling and freezing | *Zoysia japonica* | Upregulated *ZjCBF*, *ZjLEA* and *ZjDREB1* expression | Li et al. (2018) |
| Drought | *Oryza sativa* | OsJAZ1 acted as a negative regulator via the ABA-dependent and JA-dependent pathways | Fu et al. (2017) |
| Drought | *Glycine max* | Cell wall fractionation, saturated and unsaturated fatty acid, flavonoid, phenolic acid and sugar fraction levels have all increased | Mohamed and Latif (2017) |
| Salt | *Solanum lycopersicum* | ROS antioxidants, both enzymatic and non-enzymatic, were activated | Abouelsaad and Renault (2018) |
| Salt | *Zea mays* | Na + exclusion was improved by lowering Na + uptake | Shahzad et al. (2015) |
| Heavy metal (cadmium) | *Vicia faba* | Reduced oxidative stress by inhibiting the build-up of Cd, H2O2 and MDA and increasing osmolyte and antioxidant activity | Ahmad et al. (2017) |
| Far-red | *Arabidopsis thaliana* | The photoreceptor CRY1 and the JA-conjugating enzyme FR-insensitive 219/JAR1 interact | Chen et al. (2018) |
| Imazapic stress | *Brassica parachinensis* L. | Elevated antioxidant activity and phytohormone levels, as well as a reduction in MDA content | Kamran et al. (2021) |
| Circadian stress | *Arabidopsis thaliana* | Reduced the phenotype of cell death | Gao et al. (2020) |

reduced, resulting in a rise in Ca and Mg and a little increase in K as a result of JA application (Siddiqi and Husen 2019).

Various physiological investigations have also shown that when exposed to heavy metals and metalloids, endogenous JAs levels in plants rapidly increase (Lei et al. 2020). Cu- or Cd-treated runner bean (*Phaseolus coccineus*), Ni-exposed woody shrub *Daphne jasmine*, Cd-treated pea (*Pisum sativum*) and Cu-affected rice leaves all had higher amounts of JAs (Wiszniewska et al. 2018). Furthermore, Cd-induced JA synthesis in the hyperaccumulator *Noccaea* (*Thlaspi*) *praecox* is reliant on mechanical puncturing or fungal infection, showing that Cd-induced JA plays a beneficial function in metal hyperaccumulators under abiotic and biotic stressors. Exogenous JAs are widely used to relieve the plant growth inhibition induced by heavy metals and metalloids (Verma et al. 2020). Altogether, our findings suggest that increased JA caused by toxic metals is a widespread stress response mechanism across several plant species. Plants can stimulate the expression of JA biosynthesis genes such as *allene oxide cyclase* (AOC), *allene oxide synthase1* (AOS1) and *lipoxygenase 2* (LOX2) under low temperature conditions. To improve cold tolerance, JAs positively adjust downstream cold-responsive genes, which are also increased through the C-repeat binding factor (CBF) transcriptional pathway (Hu et al. 2017). Recent investigations on bananas have revealed that two *MYC2* TFs (transcription factors) are quickly activated by the exogenous application of MeJA during cold storage. Furthermore, MeJA substantially increases the expression of cold-responsive pathway genes that trigger CBF expression (ICE-CBF) (Wang et al. 2020). These findings show that the MaMYC2 transcription factor, in collaboration with MaICE1, plays a role in MeJA-induced chilling tolerance in banana fruit.

Furthermore, drought stress can cause oxidative responses that build up membrane lipid and further persuade antioxidant enzyme expression (Wang et al. 2015). In *Arabidopsis thaliana*, JA can reduce water loss by controlling stomatal opening and closure (Ruan et al. 2019). Endogenous JA concentrations increase hasty during drought stress and subsequently revert to baseline levels if the stress period is protracted. Besides, exogenous application of JAs might mitigate drought-related damage in *P. armeniaca* (Wang et al. 2020). MeJA foliar spray on soybean leaves can improve water stress tolerance, and subsequent research revealed improved levels of phenolic compounds, sugars and flavonoids (Mohamed and Latif 2017). Light has an important role in JA biosynthesis and signal transduction (Yadav et al. 2020). Radhika et al. (2010) discovered that both light and JA affected extra-floral nectar (EFN) secretion: JA reduced EFN secretion in the dark but stimulated it in the light. On the other hand, JA-Ile can increase EFN secretion in the presence of light but does not reduce EFN secretion in the absence of light. JA or its precursor, 12-oxophytodienoic acid, may rescue the growth of plants cultivated under both dark and red-light conditions in a JA-free hebiba mutant of *Oryza sativa* (Yadav et al. 2020). Robson et al. (2010) demonstrated that *A. thaliana* mutants with decreased JA production and signalling levels responded to high irradiance under far-red (FR) light at lower levels. The findings showed that coronatine-insensitive1 (COI1), a key component of JA signalling, affected FR light-induced transcription factor gene expression and that JA reduced the expression. Remarkably, phytochrome A(phyA) was needed for COI1-mediated degradation of JAZ1-glucuronidase (JAZ1-GUS) in response to JA treatment (phyA). In general, the data suggest that both phyA and JA signal through the degradation of the JAZ1 protein and that both are necessary in plant responses to light stress (Liu et al. 2019). According to Chen et al. (2018), exogenous MeJA application improves the interaction between FR-insensitive 219 (FIN219) and the C terminus of cryptochrome 1 (CCT1) under blue light. Further research found a mutually antagonistic connection between cryptochrome1 and FIN219, suggesting that the link between the JA signalling and blue light signalling pathways is important in seedling growth and stress responses. Liu et al. (2012) discovered that JA pretreatment significantly reduced the negative effects of UV-B on photosystem II function in wheat seedlings by increasing the effective photosystem II quantum yield, the photosynthetic electron transport rate and the capture efficiency of excitation energy in the reaction centre and as well as decreasing nonphotochemical quenching. These findings suggest that both endogenous and exogenous JAs take part in various stress tolerance in plants.

## 23.9 Salicylic Acid

Salicylic acid (SA) is a phenolic compound and is well known for its versatile roles in controlling several plant processes such as seed germination, photosynthesis, nutrient uptake and transport, flowering and fruit yield (AM). It is found in plants in both free as well as conjugated forms. The phenolic compound has been reported to act as plant protector, preventing them from dynamic fluctuations in growing environments and is also known to mitigate the harmful effects of high and low temperatures, drought, heavy metal, salinity and pathogen stress. The alleviating effects of SA on different agricultural crops grown under stressful environmental conditions has been listed in Table 23.6.

The exact mechanism of action of SA is yet to be discovered; however, in certain research findings, it has been unveiled that the compound shows synergistic cornstalks with auxins, GAs, cytokinin, ABA and BRs and hence improve the efficiency of various metabolic processes of plants. SA being natural and non-toxic compound can be used as potential agrochemical in future.

## 23.10 Strigolactones (SLs)

Strigolactones (SLs) are new class of phytohormones discovered from root exudates of *Gossypium hirsutum* and were found to stimulate the growth of *Striga lutea,* a parasitic weed (Cook et al. 1966). As many as 19 SLs have been isolated from different plant species till date. The basic structure of SL consists of three aromatic rings which are connected through enol ether bridge to the fourth ring. SLs are well known to enhance hyphal branching of arbuscular mycorrhizal fungi (AMF) which in turn assists plants to obtain optimum nutrients from the soil (Jamil et al. 2011).

**Table 23.6** Utilisation of SA as potent agrochemicals in adverse environmental conditions

| S. No. | Agricultural crop | Environmental condition | Protective effects of SA | Reference |
|---|---|---|---|---|
| 1. | Tomato | Pathogen attack: *Fusarium oxysporum, Botrytis cinerea*<br>Salt stress | Reduction in disease severity and incidence<br>Enhanced photosynthesis, transpiration rate and endogenous levels of ABA | Jendoubi et al. (2015), Li and Zou (2017), Horváth et al. (2015) |
| 2. | Pepper | Pathogen attack: *Ralstonia solanacearum*<br>*Fusarium oxysporum* | Recovery of seed germination<br>Enhancement of seedling growth<br>Decline in disease incidence | Chandrasekhar et al. (2017), Yousif (2018) |
| 3. | Rice | Pathogen attack: *Xanthomonas oryzae; Oebalus pugnax*<br>Drought, chilling stress, arsenic and chromium toxicity | Reduction in disease severity and pathogen infection rate<br>Increased nitrate reductase activity, protein content, membrane integrity and plant growth | Le Thanh et al. (2017), Stella de Freitas et al. (2019), Singh et al. (2017), Huda et al. (2016), Shatpathy et al. (2018), Theerakulpisut et al. (2016) |
| 4. | Black gram | Attack by mungbean yellow mosaic Indian virus | Decline in severity of disease | Kundu et al. (2011) |
| 5. | Groundnut | Pathogen attack: Peanut mottle virus | Decrease in disease severity | Kobeasy et al. (2011) |
| 6. | Pumpkin | Pathogen attack: *Zucchini yellow mosaic virus* | Lowered disease incidence and infection index | Radwan et al. (2007) |
| 7. | Wheat | Cold stress<br>Co, salt and drought stress | Increased quantum yield of PS II, photosynthetic pigments and ABA levels<br>Decline in lipid peroxidation rate, electrolyte leakage and $H_2O_2$ production due to improved ADS | Wang et al. (2018), Mohamed and Hassan (2019), Ulfat et al. (2017) |
| 8. | Sunflower | Arsenic toxicity | | Saidi et al. (2017) |

(continued)

**Table 23.6** (continued)

| S. No. | Agricultural crop | Environmental condition | Protective effects of SA | Reference |
|---|---|---|---|---|
| | | | Activation of enzymatic antioxidants for scavenging ROS | |
| 9. | Rapeseed | Cr stress | High biomass and activated ADS | Gill et al. (2016) |
| 10. | Brassica juncea | Nickel stress | Restoration of growth, photosynthesis, nutrient uptake & ADS | Zaid et al. (2019) |
| 11. | Maize | Cu, Pb and chilling stress | Less Cu uptake, $H_2O_2$ production & high activity of enzymatic antioxidants along with increase in overall biomass and endogenous osmolyte level | Moravcová et al. (2018), Zanganeh et al. (2018) |
| 12. | Pumpkin | Salt stress | Higher protein content and activity of nitrate reductase | Rafique et al. (2011) |

**Table 23.7** Applications of SLs in agriculture

| Agricultural crops | Environmental condition | Benefits of SL application | Reference |
|---|---|---|---|
| *Solanum lycopersicon* | Low-light | Increase in the content of photosynthetic pigments, quantum efficiency and activity of enzymatic antioxidants | Lu et al. (2019) |
| *Vitis vinifera* | Drought stress | Decrease in lipid peroxidation and ROS production along with significant enhancement in the RWC and photosynthetic efficiency | Min et al. (2019) |
| *Oryza sativa* | Salt stress | More plant growth, intracellular $CO_2$ concentration, photosynthetic and activation of ADS | Ling et al. (2020) |
| *Brassica rapa* | Chilling stress | Elevated levels of total proteins, photosynthetic efficiency, proline, expression of antioxidant enzymes and MAPKs | Zhang et al. (2020a, b, c) |

Owing to its versatility, a number of SL analogues such as GR24 have been synthesised which show fine potential in controlling physiological and developmental plant processes under changing environmental conditions. SLs act independently as well as in crosstalk with other hormones in order to reciprocate the harmful effects of stressful growth conditions. The important applications of SLs in different agricultural crops along with its beneficiary affects are listed in Table 23.7.

Alleviating effects of SLs have been reported in many crops under different abiotic and biotic stresses. The mechanism of action of SLs is yet not explored completely. However, it is found to show interactions with classical phytohormones and hence its effects are seen.

## 23.11 Conclusion

Phytohormones regulate multiple growth and development-related functions in the plants, and also, their role under environmental cues has been recognised since time immemorial and is still emerging. The aforementioned roles of plant hormones evidently signify their potential in ameliorating various types of stress encountered in the natural environment of the plants. Phytohormones are eco-friendly in nature that can produce wide multifarious responses of growth and development in plants under normal and unfavourable environment. They exhibit growth-stimulating and yield-promoting responses under dynamic environment. The exogenous mode of application or enhancing the endogenous levels of the plant hormones by genetic modifications protects the plants from any harsh abiotic condition or biotic attacks without compromising with the quality and quantity of the productivity thereby meeting the food and nutritional requirements. This enables the large section of population to enjoy economic profits along with deriving nutritional benefits. This clearly directs the attention to acknowledge their role as potential agrochemicals that promote the productivity of economically essential crops in an eco-friendly approach. Since they bring physiological or molecular level changes in plant at exceptionally low concentration, their exploitation as commercial agrochemicals will bring great economic benefits.

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# Genetically Modified Bacteria for Alleviating Agrochemical Impact on the Environment

# 24

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## Abstract

The intensification of agricultural sectors tend to have overuse and misuse of agrochemicals such as inorganic fertilizers (for increasing farm productivity) and biocides (for controlling of unwanted groups such as weeds, parasites, insects, pathogen and pests). Thereby, this has been resulted in pollution of water environments (rivers, lakes, aquifers and coastal waters) and land organism. This ultimately brings great impacts and conveys the loss of ecological functioning and threatening of life in the ecosystem. Consequently, there is the need to find effective methods for the detoxification of agrochemical residue from contaminated environments or reduction of agrochemical use via substituting eco-friendly options. Among various approaches, which are important to minimize agrochemical impact on the ecosystem, microbial remediation (especially the use of bacteria) is cost-effective, efficient, ecologically friendly, and important to transform and/or mineralize contaminants into carbon dioxide, water, energy and microbial biomass. The effectiveness of bacterial remediation, however, depends on their catabolic genes, diverse metabolic pathways, presence or absence of specific enzymes, physicochemical and biological factors and stress tolerance. The conventional application of bacteria in the agriculture for the detoxification of agrochemical waste or for the application of alternative biofertilizer and biopesticide was limited due several reasons. Therefore, supporting the conventional one with genetically modified bacteria to minimize the impact of agrochemicals on the ecosystem is the finest alternative. Therefore, via addressing the impact of agrochemicals residue in the ecosystem, this review

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focused on the mechanism of genetically modified bacteria to minimize the impact of agrochemicals in the ecosystem.

**Keywords**

Bioremediation · Agrochemicals · Biofertilizer · Genetically modified bacteria · Biopesticide

## 24.1 Introduction

Following the rapid growth of world population, the demand of food supply is increased. In order to supply enough amount of food, the agricultural sectors have been using agrochemicals (different fertilizers and pesticides) rigorously. Use of agrochemicals in agriculture has great roles for increasing crop productivity. Since cultivated crops are suffered by biotech factors (pest, weed and insect) and abiotic factor (low soil fertility) farmers are influenced to apply pesticides and fertilizer extensively. The usage of these fertilizer and pesticides has revealed the improvement of soil fertility and pest/insect management, which lead the busting of crop yields for the last 40 years (Lamichhane et al. 2016).

Several studies have confirmed that the use of agrochemicals continuously increased both in developing and developed countries (Gellings and Parmenter 2004; Carvalho 2017). However, there are rising global issues about the application of synthetic pesticides and fertilizers in the agricultural area due to their poisonousness to the environment, humans and the ecosystem. The key risks related with regular application of fertilizers and pesticides are soil and water pollution, occurrence of resistance varieties of weeds and pests for pesticides, ecological variability and harm to the human as well as other organisms (Lamichhane et al. 2016; Majeed et al. 2017). Different reports have elucidated that terrestrial and aquatic ecosystems are at starting risks because of the extensive use of pesticides and fertilizer.

In the last two decades, efficient and eco-friendly microbial pesticides from EPBs (entomopathogenic bacteria) were considered as good alternatives for harmful synthetic pesticides used to control crop damaging pests. The most significant challenge with EPB use is their inadequate field constancy. Furthermore, harsh environmental conditions can influence the pathogenicity of these bacteria. The stability of EPBs to harsh environment might be improved by genetic engineering (Karabörklü et al. 2018).

In order to reduce the influence of synthetic fertilizers on the environment, nature has given varieties of microbes, which can maintain soil quality and works with plants via acting as “biofertilizers” (Khosro and Yousef 2012). Biofertilizer found a crucial portion of eco-friendly agriculture. It contains capable microbial strains and organic products, which supply nutrients to soil. Then, gradually biofertilizer raises crop productivities via improving soil fertility. Microorganisms in the biofertilizer convert the accessible nutrients to the available form via increasing the number of microbes in the soil.

There are several complaints from agriculturalists about the efficiency of biofertilizer due to its long time requirement between preparation and field application of the product as well as its short shelf-life (Youssef and Eissa 2014). This limits their applicability as biofertilizer. Due to this reason, quick production system and enhanced life time are the bases for biofertilizer commercialization (Adesemoye and Kloepper 2009). Recently, different biofertilizers are available which fulfil maximum viability of microbes via the help of several mechanisms (Bhattacharyya and Jha 2012). Among these strategies using genetically modified bacteria is the best one. Different researches have been done to formulate capable biofertilizers via the help of genetically engineered techniques.

Therefore, to save the environment and human health, it is necessary to use biotechnological approach like using genetically modified bacteria as a bioremediation to treat agrochemical wastes in the environment and to minimize the application of synthetic agrochemicals in agriculture. This paper discussed the impact of agrochemicals, genetically modified bacteria for agrochemicals waste treatment, genetically modified bacteria for biofertilizer, and biopesticides as alternatives to chemical pesticides.

## 24.2 Impact of Agrochemicals on Waterbodies

At this time, the demand of agricultural products is intensively required to nourish the world population. As a result, the farmers are using agrochemicals (biocides and fertilizers) to increase yields and control weeds, pests, parasites and insects (Jimoh et al. 2013; Singh et al. 2019; Rani and Dhania 2014). Studies showed the most widely used agrochemicals and responsible for waterbody contamination are pesticides (for pests: 2P organophosphates, organochlorines, neonicotinoid dieldrin, aldrin, alpha-BHC, beta-BHC, delta-BHC, gamma-BHC (Lindane), heptachlor, endosulfan, methoxychlor, aroclor and dichlorodiphenyltrichloroethane), herbicides (for undesirable plants: atrazine, simazine, alachlor, metolachlor and trifluralin), insecticides (for insects: dichlorodiphenyltrichloroethane, diazinon and parathion methyl), fertilizers (urea, ammonium sulphate and N P K compound), fungicides (for fungal diseases), bactericides (for bacteria), rodenticides (for rats, mice and other rodents), nematocides (for nematodes), acasicides (for mites and spiders), veterinary drugs, feed additives, wood additives and fumigants (Aydinalp and Porca 2004; Sunitha et al. 2012; Al Hattab and Ghaly 2012; Ogbodo and Onwa 2013; Rani and Dhania 2014; Goodwin et al. 2017; Parte et al. 2017; Zhang et al. 2018; Itom et al. 2020; Syafrudin et al. 2021). The use of such diverse kinds of agrochemicals are likely associated with the overwhelming environmental and organisms' health concerns (microorganism, plants, pets, livestocks, people and wildlife) (Sunitha et al. 2012; Al Hattab and Ghaly 2012; Parte et al. 2017; Sadh et al. 2018; Singh et al. 2019; Briceño et al. 2020; Itom et al. 2020; Syafrudin et al. 2021).

Thus, the use of excessive agrochemical pollutants (viz. biocides and fertilizers) is the most noticeable source of pollution of aquatic environments (marine and fresh water forms) and finally leads to the deterioration of water ecosystems (biotic and abiotic components) (Mello et al. 2019; Shah et al. 2018), loss of aquatic physical habitats, destruction of biodiversity and decrease in productivity and quality of waterbodies and affects human and animal health (Briceño et al. 2020; Itom et al. 2020). It is stated that 0.1% of agrochemical substances address their targets while the remaining 99.9% can move into the aquatic environment (Mello et al. 2019) through direct application, atmospheric deposition and rainfall effects and bring surface water and underground water pollution (Shah et al. 2018; US Environmental Protection Agency 2005) and ultimately convey various devastating effects on the functioning of water ecosystems with immediate or persistent effects (Ogbodo and Onwa 2013; Syafrudin et al. 2021). This can cause the remarkable reduction and/or destruction of biodiversity of aquatic life such as vertebrates (amphibians, reptiles and fish) and macroinvertebrates (crustaceans, molluscs, crustaceans, insects and bryozoans) and macro- and microphytes and introduction of invasive alliance species (Itom et al. 2020).

### 24.2.1 Accumulation of Chemical Pollutants

It can be caused by the discharge of agrochemical substances in waterbodies which constitute biocides, fertilizers and toxic metals (Shah et al. 2018; Aydinalp and Porca 2004; Ogbodo and Onwa 2013). These pollutants from agricultural fields can be leached away and moved on the surface and/or groundwater and eventually accumulated in aquatic systems. Inorganic fertilizer and pesticides used for agricultural purpose contain trace toxic or heavy metals such as arsenic, cadmium, lead and mercury (Rani and Dhania 2014; Zhang et al. 2018; Singh et al. 2019; Syafrudin et al. 2021) and deposited through time in aquatic ecosystems (Shah et al. 2018).

The accumulation and bioavailability of heavy metals can lead to the threatening of life inhabiting the waterbodies and mankind too (Zhang et al. 2018; Shah et al. 2018). It is also indicated that 98% of the pesticides kill fishes and crustaceans, and 73% pesticides were also identified as notorious chemicals to kill amphibians in aquatic environment (Rani and Dhania 2014). In addition the massive use of agrochemical can contaminate aquatic environment and ultimately reach to higher organism including human kind through food chain and leading bioaccumulation (Rani and Dhania 2014).

### 24.2.2 Eutrophication

Eutrophication refers to a condition of ecosystem responses whereby there is large accumulation of phosphorus-, potassium- and nitrogen-rich fertilizer, frequently leading to changes in plant-animal populations and loss of water and territory standard. This has been happening by leaching of soil, rich with fertilizers, into waterbodies by anthropological or natural activities (Rani and Dhania 2014; Zhang et al. 2018). Consequently, eutrophication causes the occurrence of algal bloom, bad smell and taste for aquatic environment and leads to hypoxia (remove dissolved oxygen) and methemoglobinaemia (deadly disease for infants), killing aquatic organisms (fishes, tadpoles, aquatic plants and poisons seafoods) (Jimoh et al. 2013; Shah et al. 2018; US Environmental Protection Agency 2005).

In general, the introduction of agrochemicals directly or indirectly to aquatic ecosystem accounts for the poisoning of aquatic food sources, loss of trophic levels, unfriendly for recreation, obliteration of habitats and niches, death of organisms, eutrophication, bioaccumulation of heavy metals, increment of acidification, inhibition of nitrification, decrement of microbial community structures, removal of symbiotic mycorrhizal association, alteration of productivity, reduction of oxygen levels and impairment of water for human uses (Jimoh et al. 2013; Shah et al. 2018, Aydinalp and Porca 2004, Ogbodo and Onwa 2013; Mello et al. 2019; Itom et al. 2020).

### 24.2.3 Biomagnification of Agrochemicals

Biomagnification is the accumulation of toxic remains in the body of both animals and humans due to the application of agrochemicals. This can necessitate temporal delaying effects in organisms at the final trophic level in food webs. At large, the biomagnification can affect the biological and physicochemical features of living organisms, viz. changes in enzyme activity, reduced respiration, increased mortality, change in morphology, delayed development, change in behaviour, increased susceptibility to infections, reduced or failure of reproduction (some fish species and egg shell), changes in age structure and growth rate of population, changes in community composition, thinning of birds (peregrine falcons, sparrow hawk and eagle owls) and changes in ecological functioning (Al Hattab and Ghaly 2012; Mello et al. 2019; Syafrudin et al. 2021; Itom et al. 2020).

### 24.2.4 Depletion of Dissolved Oxygen

The discharging of various kinds of agrochemicals into waterbodies brings an immediate drop of dissolved oxygen (DO) thereby reducing the biological oxygen demand (BOD) (Rani and Dhania 2014). The low level of DO in waterbodies indicates the availability of organic wastes and other reducing agents. Consequently, the distribution and number of both fauna and flora have been affected by suffocation (Jimoh et al. 2013; Rani and Dhania 2014; Mello et al. 2019).

### 24.2.5 Effect on Biotic Interaction in Aquatic Environments

The impacts of agrochemicals, therefore, in aquatic environment are countless according to their type and nature of toxicity (Mello et al. 2019). Aquatic environment is known to harbour both free floating plant-like organisms (phytoplankton) and animal-like organism (zoo planktons). Agrochemicals can affect the distribution and availability of such aquatic biota and fauna groups. When there are the accumulation of fertilizers in the waterbody, it can cause stimulation of biomass of phytoplankton and positively affect the zooplanktons, and when there is the accumulation of herbicides, it affects the availability of primary producers and hence consumers are negatively affected (Mello et al. 2019).

In addition, the use of various kinds of agrochemicals can affect non-targeted aquatic organisms and bring destruction of the physical habitat (Itom et al. 2020). Hence, the agrochemicals in aquatic environment affect the interaction of biotic components by increasing biotic and abiotic stress (Singh et al. 2019).

### 24.2.6 Effect on Human and Animal Health

Unwise and misuse of agrochemicals bring substantial effect on organisms' health (Singh et al. 2019). For instance, pesticides show biological stability and higher degree of lipophilicity in aquatic and land food products and affect life in contaminated sites (Rani and Dhania 2014). In addition, an increased use of pesticides also results in cardiopulmonary disorders, eye irritation, neurological and skin disorders, cancers, foetal deformities and miscarriages (Ortiz-Hernández et al. 2011; Al Hattab and Ghaly 2012; Rani and Dhania 2014).

## 24.3 Bacteria as Agrochemical Waste Treatment

Excessive and improper use of agrochemicals contaminates aquatic ecosystems (water sources) (Ortiz-Hernández et al. 2011; Rani and Dhania 2014; Fang et al. 2018; Briceño et al. 2020). Hence, many efforts have been made for the removal of agrochemical hazardous pollutants and effective wastewater treatment. The efficacy of the wastewater depends on the types of treatment mechanisms used, i.e. physicochemical and biological methods.

The aforementioned method includes filtration, flocculation, adsorption, flotation, photocatalysis, volatilization, incineration, thermal desorption and electro-oxidation to remove solids, organic matter and nutrients (Al Hattab and Ghaly 2012; Parte et al. 2017; Aragaw 2021). However, it is labour-intensive, not cost-effective, prone to secondary pollution and ecologically unfriendly while the latter techniques (bioremediation or biodegradation) which include composting, biostimulation, attenuation and bioaugmentation are cost-effective and environmentally friendly (Al Hattab and Ghaly 2012; Rani and Dhania 2014; Parte et al. 2017; Aragaw 2021).

The bioremediation techniques are typically focused on the use of plants (phyto-remediation), microalgae (phyco-remediation), fungi (myco-remediation) and bacteria (microbial remediation) (Rani and Dhania 2014; Aragaw 2021). Studies indicated that organisms like bacteria, yeast, algae, protozoa and plants are identified for wastewater treatment in accordance with their genome and the enzymes that they produce (Parte et al. 2017). On the other hand, for effective application of biological treatment method, identification of type of contaminant, evaluation of the effect of the pollutants, determination of treatment sites (in situ or ex situ) and selection of best remediation techniques in terms of safe elimination, efficient and economical aspect (cost), containment ability, detoxification ability and time and size of contaminated site are mandatory (Ortiz-Hernández et al. 2011; Al Hattab and Ghaly 2012; Rani and Dhania 2014; Parte et al. 2017).

Accordingly, the bacterial degradation mechanism is selectively recommended because of its diverse enzymes, effective genes, efficient physiognomies and acclimatization potential, and it is cost-effective, withstands stresses in polluted environment and is able to remove (mineralization) or convert (biotransformation) pollutants into carbon dioxide, water, biomass and energy (Fang et al. 2018; Aragaw 2021). The most effective bacterial species are of *Stenotrophomonas* sp., *Pseudomonas* sp., *Mycobacterium* sp., *Thauera* sp., *Methyloversatilis* sp., *Hyphomicrobium* sp., *Allochromatium* sp., *Ralstonia* sp., *Plesiomonas* sp., *Bacillus* sp., *Klebsiella* sp., *Pandoraea* sp., *Mesorhizobium* sp., *Phanerochaete* sp., *Burkholderia* sp., *Chrysosporium* sp., *Enterobacter* sp., *Flavobacterium* sp., *Alteromonas* sp., *Agrobacterium* sp., *Ochrobactrum* sp., *Nocardia* sp., *Spingobium* sp., *Staphylococcus* sp., *Xanthomonas* sp., *Arthrobacters* sp., *Azotobacter* sp., *Burkholderia* sp., *Moraxalla* sp., *Acinetobacter* sp., *Paracoccus* sp., *Aerobacter* sp., *Alcaligenes* sp., *Burkholderia* sp., *Sphingomonas* sp., *Rhodococcus* sp., *Achromobacter* sp., *Alcaligenes* sp. and *Dechloromonas* sp. (Ortiz-Hernández et al. 2011; Rani and Dhania 2014; Parte et al. 2017; Fang et al. 2018; Briceño et al. 2020).

Microbial enzymes (intracellular or extracellular) play a great role to alter and decontaminate pollutants and to efficiently clean contaminated environments with noxious agrochemicals (Rani and Dhania 2014; Parte et al. 2017). Thus, autochthonous bacteria can adapt this agrochemical contaminates sites and able to produce various enzymes that enhance the removal of toxic agrochemicals and utilize them as the sole source of carbon, nitrogen, sulfur, and/or phosphorus (Singh et al. 2019; Briceño et al. 2020). The most identified kinds of enzymes for such applications are hydrolase, oxygenase (mono- and dioxygenase), isomerase, laccase, peroxidase, oxidoreductases, dehydrogenase, ligninase, phosphotriesterase, dehalogenase and organophosphorus acid anhydrolase (Rani and Dhania 2014; Parte et al. 2017; Fang et al. 2018). Several studies indicated that those enzymes are encoded with various encoding genes for the detoxification or degradation of specific agrochemical pollutants such as *ppo*, *hdx*, *dxnA-dbfA1*, *ppah*, *dxnA*, *dbfA1*, *naph*, *carA*, *boh*, *mheI*, *bphA1*, *p450*, *mnp*, *opd*, *opdA*, *opaA*, *adpB*, *pepA*, *hocA*, *pehA*, *phn*, *ophB*, *ophC2*, *opdB*, *imh*, *mpd*, *oph*, *mph*, *mpdB*, *opdE*, *lin*, *lip* and *benA* (Ortiz-Hernández et al. 2011; Parte et al. 2017; Fang et al. 2018) and are found on extrachromosomal, genomic or transposons (Table 24.1).

**Table 24.1** Agrochemical-degrading bacterial species with their catabolic genes and enzymes

| Bacteria | Catabolic genes | Enzymes | Pollutants | Citation |
|---|---|---|---|---|
| *Mycobacterium* sp. | *mheI* | Hydrolase | Carbendazim | Fang et al. (2018) |
| *Bacterial species* | *pobA*, *pytH* | Hydrolase | Beta-cypermethrin | Yang and Ji (2015) |
| *Bacterial species* | *libA* and *hylA* | Hydrolase | Linuron | Fang et al. (2018) |
| *Flavobacterium* sp. | | Phosphotriesterase organophosphorus hydrolase | Organophosphate compounds | Ortiz-Hernández et al. (2011) |
| *Variovorax* sp. | *libA*, HylA | Hydrolase | Linuron | Parte et al. (2017) |
| *Streptomyces* spp. | *feh* | Hydrolase; esterase | Lindane, methoxychlor, chlordane, pentachlorophenol and chlorpyrifos | Parte et al. (2017), Briceño et al. (2020) |
| *Thauera*, *Stenotrophomonas*, and *Methyloversatilis* | *ppo* | Laccase and polyphenol oxidase | Aromatic compound | Fang et al. (2018) |
| *Mycobacterium*, *Dechloromonas* | *mnp* | | Mono-aromatic compound | Fang et al. (2018) |
| *Pseudomonas* | *hdx* | | Metamitron | Fang et al. (2018) |
| *Pseudomonas* and *Alcaligenes* ssp. | | Oxygenases, hydroxylases, hydrolases and isomerases | 2, 4-D | Rani and Dhania (2014) |
| *Pseudomonas*, *Mesorhizobium*, *Ralstonia*, *Rhodococcus*, *Achromobacter*, *Brucella*, *Ochrobactrum* and *Bacillus* | *mpd* | Carbofuran hydrolase methyl-parathion hydrolase, organophosphorus hydrolase | Carbamate; organophosphate | Parte et al. (2017) |
| *Serratia*, *Pseudomonas* sp. | | Carboxyl esterase, phosphotriesterase | Pyrethroid | Parte et al. (2017) |
| *Pseudomonas* sp. and *Klebsiella pneumoniae* | | Hydrolase | Atrazine | Rani and Dhania (2014) |
| *Klebsiella* sp., *Alcaligenes* sp. *Staphylococcus* sp. *Pseudomonas* sp. | | Dehalogenases | Organochlorine | Parte et al. (2017) |

| **Bacteria** | **Gene** | **Species** | **Degradation substrate** | **Citation** |
|---|---|---|---|---|
| Atrazine chlorohydrolase | *atzA* | *Pseudomonas* sp. | Atrazine | Chen et al. (2014) |
| Oxygenase | *CndA* | *Sphingomonas* sp. *DC-6* | Acetochlor | |
| Organophosphates | *ophc2* | *Pseudomonas pseudoalcaligenes* | Methyl parathion | Gotthard et al. (2013) |
| Organophosphorus hydrolase | *mph* | *Burkholderia cepacia* | Organophosphorus | Liu et al. (2019) |
| Pyrethroid hydrolase | *pytH* | *Sphingobium* sp. *JZ-2* | Fenpropathrin | Duan et al. (2011) |
| Triazophos hydrolase | *tpd* | *Ochrobactrumsp.mp-4* | Triazophos concentration | Gu et al. (2006) |
| Glycerol-3-phosphate dehydrogenase | *glpA/glpB* | *Pseudomonas pseudomallei* | Glyphosate | Peñaloza-Vazquez et al. (1995) |
| Amidase | *cmeH* | *Sphingobium quisquiliarum DC-2* | Acetochlor | Li et al. (2013) |

However, the effectiveness of microbial bioremediation for agrochemicals depends on physicochemical and biological factors. The physicochemical factors include pH, moisture, temperature, dissolved oxygen, nature of contaminants and concentration of contaminants, nutrient availability and types of electron acceptors while biological factors include the bioavailability of contaminant, nature of degrading microorganism (single, consortium), effectiveness of catabolic genes (metabolic capability, physiology status), biodiversity of degrading microorganisms (microbial community), degradation mechanisms of microbes (aerobic or anaerobic), availability of targeting enzymes, etc. (Ortiz-Hernández et al. 2011; Al Hattab and Ghaly 2012; Rani and Dhania 2014; Goodwin et al. 2017; Parte et al. 2017; Singh et al. 2019; Briceño et al. 2020). By considering the above factors, agrochemical pollutants can be eliminated using single bacterial species, consortia and indigenous (autochthonous) or exotic (allochthonous) type. However, the use of indigenous and consortia (mixed population) is efficient than exotic and single bacterial species for the transformation and mineralization of agrochemical contaminants (Ortiz-Hernández et al. 2011; Singh et al. 2019; Briceño et al. 2020).

## 24.4 Genetically Modified Bacteria for Agrochemicals Waste Treatment

The extensive application of agrochemicals such as herbicides, pesticides and fertilizers in agriculture poses a serious problem in soil properties, water quality, air environment and extremely toxic to humans and other animals (Verma et al. 2014; Liu et al. 2019). Organophosphates, carbamates and pyrethroids are the most common pesticides applied in agriculture to control pests and poisoning of the natural environment (Lan et al. 2006). Approximately 3.5 million tonnes of pesticides are sprayed every year all over the world, where China, the USA and Brazil are the most user countries (Sharma et al. 2019). According to the European Union report, the use of pesticide is banned or restricted within the European countries due to its adverse impacts, and pesticide companies located within the EU exports over 42,636 tonnes of pesticides to developing countries (European Commission 2020). In developing countries like Africa where pesticide use regulations are less restricted, pesticides are widely used to control pests and crop-damaging desert locust invasion which recently occurred (Sarkar et al. 2021). Since pesticides are very toxic, they cannot be easily degradable by the living organisms. Using the recent advance of science and technology, the scientific communities are trying hard to find options to reduce the impact of pesticide in the environment.

Microorganisms are the primary organisms that undergo normal degradation of pesticides from soil and the environment. However, only some species of microorganisms can have the capability to degrade these agrochemicals and have limited degradation efficiency. The advancement of molecular biotechnology enables the manipulation of genes of microorganisms using genetic engineering tools to increase their degradation efficiency of pesticides in the environment. The use of genetically modified bacteria (*Pseudomonas diminuta*) to detoxify the most toxic pesticide, organophosphate pesticides, was demonstrated for the first time by Serdar et al. (1989). Shimazu et al. (2001) demonstrated simultaneous degradation of organophosphorus pesticides and ρ-nitrophenol by genetically engineered *Moraxella* sp. with surface expressed organophosphorus hydrolase. Similarly, Lan et al. (2014) have applied genetically modified microorganism *Sphingomonas paucimobilis* UT26 which has the capability to degrade both methyl-parathion and γ-hexachlorocyclohexane simultaneously. The rate of degradation was increased with rising temperature from 20 to 35 °C and optimal pH of 8.4. The recombinant bacterium UT26XEGM was constructed by introducing a parathion hydrolase gene into an initially c-hexachlorocyclohexane (γ-HCH)-degrading bacterium *Sphingomonas paucimobilis* UT26. Suicide system was designed by introducing suicide cassettes containing killing genes gef and ecoRIR from *Escherichia coli* controlled by Pm promoter and the xylS gene which is important to reduce the potential risk of gene escaping into the environment. In another study, engineered *Pseudomonas putida* KT2440 strain was used for simultaneous degradation of organophosphates and pyrethroids and its application in bioremediation of soil (Zuo et al. 2015). Although genetically engineered bacteria showed better efficiency in the degradation of agrochemicals, its application in the environment is limited due the biosafety concerns and low public acceptance (Azad et al. 2014). These causes a paradigm shift into bio-based products such as biopesticides and biofertilizers as an option to minimize the chemical pollution and promote sustainable agriculture (Meena et al. 2020).

## 24.5 Genetically Modified Bacteria for Biofertilizer

The long residual action resulting from excessive use of chemical pesticides and synthetic fertilizers has highly deteriorated the soil quality and resulted significant change of the microbial structure and diversity in the soil. The study reported by Chaudhry et al. (2012) has revealed the changes in microbial structure and diversity and even diminished microbial diversity in response to long-term application of chemical fertilizers in the soil. So, it is necessary to improve the soil quality via an eco-friendly way without affecting the soil microbial communities. Besides agrochemical degradation, genetically engineered microbes can be used as a fertilizer which could feed the poorest world. Globally, the use of microbial inoculants for crop improvements is rapidly increasing particularly in Africa and Asia where multiple strains can be developed from rhizosphere soil (Sudheer et al. 2020). Advancement in genetic engineering tools augment the current agricultural practices by providing eco-friendly biofertilizers using modified bacterial strains alternative to chemical fertilizer. According to Robert (2017), genetically engineered microbes can make fertilizer when added to soil and can improve plant growth 1.5 times larger than crops not treated with buds and synthetic fertilizers. Researchers in Harvard University developed a genetically engineered microbe called *Xanthobacter autotrophicus* which has hydrogenase enzyme capable of producing polyhydroxybutyrate (PHB) from ATP, $H_2$ and $CO_2$ and stored in the microbial bodies. Using their nitrogenase enzyme, the bacteria are able to fix atmospheric nitrogen and combine with the hydrogen from the stored PHB to synthesize ammonia, the starting material for fertilizer. This is a novel approach and a first of its kind in synthesizing ammonia without industrial process.

Nitrogen-fixing bacteria such as *Rhizobium* can be modified by genetic engineering tools and used as biofertilizers which can provide better nutrient accessibility to plants (Ali et al. 2020). Wang et al. (2020) have demonstrated the use of genetically engineered nitrogen-fixing bacterium *Pseudomonas protegens* CHA0-ΔretS-nif for biofertilizers and disease control for plants. The study evaluated the effects of the modified bacteria on garlic growth, disease control and soil microbial communities under different field conditions. The result revealed that the *Pseudomonas protegens* CHA0-ΔretS-nif inoculation enhanced the garlic growth and yields and showed 12.03% of production increase compared with the control (without inoculation). The study also indicated the inoculation of the modified bacteria enhanced the growth of bacterial diversity in the garlic rhizosphere and inhibits the garlic root rot disease. The conservation of new microbial inoculants in the rhizosphere, difficulty of monitoring the bacterial existence and persistence in the environment post application and expression of improvements in the target are mentioned as the current major challenges in the release of genetically modified microbial inoculants (Sudheer et al. 2020).

## 24.6 Biopesticides Alternative to Chemical Pesticides

Albeit efforts are being made to exploit genetically modified bacteria for pesticide degradation, its release into the environment raises question due to the biosafety concern and regulatory policies. The approaches of using bio-based pesticides and environmental-friendly alternative to chemical pesticides and better solution to minimize chemical pollution and contamination of soils without affecting the microbial communities are encouraged (Meena et al. 2020). Moreover, the emergence of resistant pests to synthetic pesticides derives to the production of biopesticides where production cost is low and takes less time compared with synthetic pesticides (Liu et al. 2019). Biopesticides are natural and biological occurring compounds produced by living organisms such as plants, algae and microorganisms to control pests through non-toxic mechanisms (Sharma et al. 2020; Kumar et al. 2021). The major advantage of biopesticides is they are species specific, attack pests only in the target environment and thus minimize the risk in non-pest species compared with chemical pesticides (Samada and Tambunan 2020). Besides pest control, biopesticides can augment plants by improving nutrient availability in the soil and can also promote drought resistance in plants (Sharma et al. 2020).

There are different categories of biopesticides such as microbial pesticides, plant-based pesticides, biochemical pesticides and GMO-based biopesticides. The review is focusing on microbial pesticides and GMO-based pesticides which constitute 90% of total biopesticides in the market (Koul 2011). Microbial pesticides are derivatives of bacteria, fungi and virus bioactive compounds (Kumar et al. 2021).

Entomopathogenic fungi such as *Trichoderma* species and family of baculoviruses are the main fungal and viral sources of biopesticides, respectively, which can destroy plant pests and promising biocontrol agents that can be directly applied to plants without affecting the non-targeted pest species (Kumar et al. 2019). Cry protein producing spore-forming bacteria such as *Bacillus thuringiensis*, obligate pathogens such as *Bacillus popilliae*, potential pathogens such as *Serratia marcescens* and facultative pathogens such as *Pseudomonas aeruginosa* are the main bacteria species used for biopesticides (Koul 2011). Among these, *Bacillus thuringiensis* has cry genes encoding for toxin proteins that can kill pests and widely used to control pests due to its stability, safety and effectiveness. Based on the recent information, more than one hundred *B. thuringiensis*-based bioinsecticides have been developed, most of which are used to target lepidopteran, dipteran and coleopteran larvae (Sarwar 2015). Many genetically modified plants have been developed through recombinant DNA technology by introducing Bt-genes to plants to make them capable of killing pests naturally.

Since biopesticides are effective, safe, target only specific pests and environmentally sustainable pest management option, there is a high demand of biopesticides in the global market (Ramírez-Guzmán et al. 2020). Consumer's attitude towards eating organic food with improved food safety promotes the commercialization of biopesticides (Samada and Tambunan 2020). Globally, biopesticides share a 5% of total production of biopesticide products in the commercial market (Damalas and Koutroubas 2018). Microbial pesticides derived from *Bacillus thuringiensis* species are dominating the market and cover approximately 90% of the available biopesticide in the current global market (Damalas and Koutroubas 2018; Arthurs and Dara 2019).

The recent developments in new techniques such as molecular biotechnology, genetic engineering and protein engineering would contribute in advance to increase the current production of biopesticides. Genetic engineering has plausible application to shorten the time to kill pests, enhance its stability in the field and reduce the lethal dose of the biopesticides. The advent of gene-editing technologies and synthetic biology could revolutionize the modification of important microbes to have new abilities to overcome the current challenges of agriculture and environmental pollution (Sudheer et al. 2020). The release of GMO-based biopesticides in the global market may raise question due to a biosafety concern and restriction by the regulatory authorities. The exploitation of CRISPR-Cas technologies and synthetic biology approach could overcome the current challenges in the production of safe and effective biopesticides to promote sustainable agriculture.

## 24.7 Genetically Modified Bacteria in the Detoxification of Pesticides Residue

Presently, pesticides are widely applied in agriculture to control and prevent plant from different pests and diseases for better productivity via minimizing crop damage (Damalas and Eleftherohorinos 2011). The excessive use of synthetic pesticides, however, in recent agricultural trends causes pollution of diverse media together

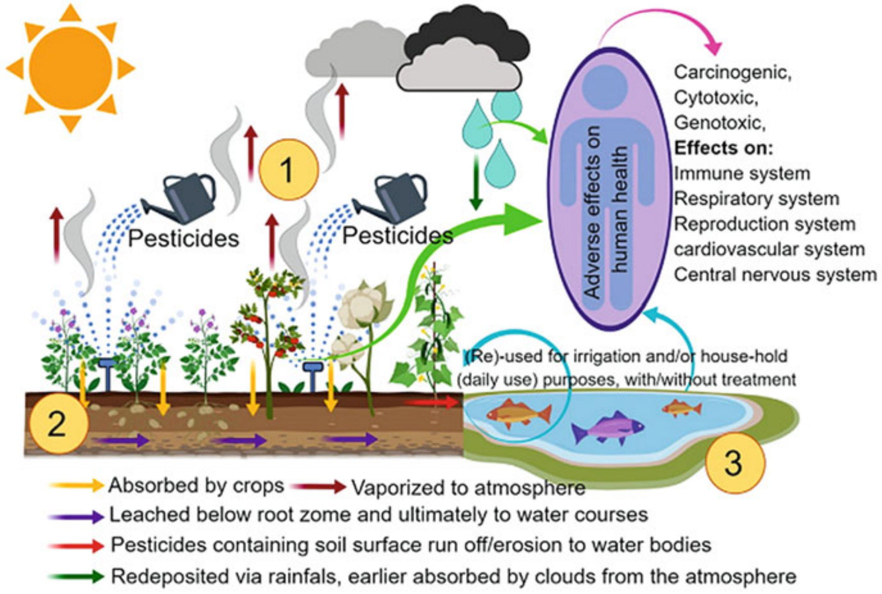

**Fig. 24.1** Consequences of agrochemicals in modern agriculture that lead to contamination of different media including (1) air, (2) land and (3) water (Liu et al. 2019)

with land, air and water (Craig 2019; Li 2018). As a result, it adversely influences the health of human and non-targeted organisms via numerous methods (Fig. 24.1). About 45% of the entire synthetic biocides used universally are organophosphorus pesticides, which potentially damage the ecosystem (Shabbir et al. 2018). Globally, per year 200,000 deaths happen due to organophosphate poisoning (Ojha et al. 2013). Numerous physicochemical methods have been established for the degradation of pesticides at polluted sites. However, these methods are not cost-effective and even prone to secondary. Consequently, biological treatment mechanisms take advantage of the use of bacterial biodegradation. Supporting this, several bacteria have been characterized, identified from various sources, and capable of detoxifying numerous pesticide wastes to non-harm output in the ecosystem (Rayu et al. 2017). Furthermore, the biodegradation potential of wild microorganisms for varied biocide pollutants is typically restricted. So, the creation of extremely effective genetically modified bacteria significantly increases the efficacy of contaminant degradation (Yuanfan et al. 2010).

Currently, numerous genes able to degrade pesticide residue were identified from diverse species as indicated in Table 24.1. These genes helped the chance of creating genetically modified bacteria. For instance, the gene atzA that codes atrazine chlorohydrolase has a great degradation potential to atrazine, a most frequently applied herbicide through a possible risk to living things (Neumann et al. 2004). Strong et al. (2000) show effective field-scale bioremediation in atrazine-contaminated soil via using transgenic *Escherichia coli* by atrazine chlorohydrolase.

Via upregulation of *tpd* gene that codes triazophos hydrolase from *Ochrobactrum sp.* in engineered *Pseudomonas putida* KT2440 biodegraded numerous aromatic hydrocarbons and organophosphorus pesticides (Gu et al. 2006). In a constant genetically modified BHC-A-mpd strain in *Sphingomonas* sp., overexpressed methyl parathion hydrolase gene (*mpd*) has shown very effective detoxification of methyl parathion and hexachlorocyclohexane (HCH) (Lu et al. 2008). In another study, the mixture of organophosphates (OPs) and organochlorines (OCs) pesticide has been simultaneously degraded by overexpression of OP-degradation gene (*mpd*) and OC-degradation gene (*linA*) in engineered *E. coli* strain (Yang et al. 2012).

Pyrethroid hydrolase coded by *pytH* gene from *Sphingobium* sp. JZ-2 was identified for the degradation of fenpropathrin. When this gene is overexpressed in engineered *Sphingobium* sp. BA3, pytH strain has shown a significant fenpropathrin degradation improvement (Duan et al. 2011). Therefore, for environmental stability and better growth between nature and humans, the application of genetically modified organism for the detoxification of pesticide has become a crucial trend in sustainable agriculture to safeguard human health.

## 24.8 Conclusion

Excessive use of biocides and fertilizers to increase agricultural products to feed human and animal populations leads to dangerous effects on both abiotic and biotic factors. This in due course needs to find appropriate treatment mechanisms to make the environment safe for all life forms. Therefore, bacterial metabolic pathways depend on effective enzymes codified in plasmid, stability of plasmids itself and the degrading potential of the microbes increased via genetically modified bacteria in wide range of environmental conditions. The use of bacterial remediation is recommended to remove or detoxify environments contaminated with agrochemicals. In addition to detoxification of agrochemical waste, it is also an advantageous minimization of agrochemical usage in the agriculture via a substitution with eco-friendly biofertilizers as well as biopesticides. Thus, for the functioning of the ecosystem, the use of genetically modified microorganisms plays a great role in the removal or reduction of hazardous agrochemicals.

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# Omics Perspective: Molecular Blueprint for Agrochemical Bioremediation Process in the Environment

# 25

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## Abstract

Global population outbursts and food security concerns have led to tremendous use of agrochemicals that majorly involve pesticides, herbicides or fertilizers in agricultural sectors. However, unrestrained uses of agro-based chemicals contaminate the environment and cause lethal toxicity in living organisms. Bioremediation process is powerful for intoxicating pollutants from the environment, but to evaluate it fully, different outlooks concerning microbial physiology and degradative pathways need to be envisaged. The advent of revolutionary tools of omics, namely, genomics, transcriptomics, proteomics and metabolomics, generates relevant information and validates processes like complex degradative pathways, protein identification, expression, interactions, characterization, molecular changes in response to stress and metabolites synthesized during biodegradation. This chapter describes the insight of OMICs and interdisciplinary bioinformatic tools to assess the progress of bioremediation process and microbial community shifts occurring at the contaminated zones.

## Keywords

Agrochemicals · Bioremediation · Genomics · Transcriptomics · Proteomics · Metabolomics · Bioinformatics

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## 25.1 Introduction

The term 'agrochemical' is defined as synthetic chemical products used in the agricultural sector including fertilizers, pesticides (herbicides, insecticides and fungicides), raw manures and plant hormones to enhance microbial diversity and organic matter and hence improve soil quality. Their implementation helps to improve the yield of crops; on the other hand, their tremendous uses lead to great risk to the environment, in particular soil biology (Bhardwaj and Kapley 2015; Sharma et al. 2016; Malik et al. 2017). Bioremediation of these contaminated sites thus remains a potential option and has become a practice with advantageous features when compared to other conventional techniques due to its proficient and eco-friendly nature. In the current situation, bioremediation through microbiological measures has the upper hand in metabolizing an enormous class of environmental pollutants including agrochemicals in terms of sustainability and unproblematic in situ applicability (Ghosh et al. 2019; Malik et al. 2021). The basic step of bioremediation is to appreciate the native microbiome, their collaboration with the ecosystem and the factors which assist in the expression of genotype. The bioremediation technique is as yet riddled with inconveniences that should be inscribed. In this respect, a multidisciplinary approach is needed to expose the pathways and biochemistry that remain hidden for making bioremediation a versatile method for monitoring contaminated environment (Purohit et al. 2016; Chandran et al. 2020). The advanced research in molecular techniques enabled a cutting edge to assess the unculturable microorganisms from their natural ecosystem (Gutleben et al. 2018). Techniques including genomics, proteomics, transcriptomics and metabolomics and other omics methods have disseminated our comprehension to explore and generate significant data related to genes and their encoding enzymes that participate in the degradation of agrochemicals, intermediate metabolites and the action of the cell against stress induced by the exposure of pesticide (Koenigsberg et al. 2005). Toxic effects and bioremediation of various pesticides such as DDT (dichlorodiphenyltrichloroethane), HCH (hexachlorocyclohexane) and ATZ (atrazine) have been explored to a great extent under different conditions using omics tools (Das and Osborne 2018; Jaiswal et al. 2019).

The underlying investigations for biodegradation processes of various agrochemicals were centred on the conventional microbiological techniques including isolation, identification and characterization of microbial strains (Qureshi and Purohit 2002; Rodríguez et al. 2020). However, only a few microbes and their genes involved in agrochemical degradation have been characterized. The study of their genetic constitution with identification of genes encoding enzymes involved in the pesticide degradation merged with new tools for investigating nucleic acid pool of soil microbes will develop unique perception into their genetic and molecular events. This would promote designing of advanced tools for monitoring pesticide degradation in natural habitats conserving the most important agricultural assets, i.e. soil (Ellis et al. 2003; Qureshi et al. 2009; Hernandez-Soriano and Carlos Jiménez-López 2014). Application of genomic tools to identify microbial communities has encouraged the revelation of remarkable microorganisms that were inconvenient by conventional tools. Extraction and amplification of coding segment of DNA from the targeted niches by using polymerase chain reaction (PCR) have demonstrated schematic characterization of the indigenous microbial community (Malik et al. 2008; Pal and Gardener 2006). However, the discovery of the conserved 16S rRNA gene sequence with variable nature in all bacteria describes the phylogenetic similarities between microbes within communities (Langille et al. 2013). The detailed knowledge of the genome organization of microbial communities and genes associated with various species of microbes involved in degradation can be obtained by genomics and metagenomics approaches (Malik et al. 2021). On the other hand, transcriptomics defines an expression of microbial genes that had taken importance in the bioremediation of agrochemicals. This technique utilized different microbes ranging from bacteria, cyanobacteria to fungus as a model and assess the impacts of agrochemical exposure on gene expression (Rodríguez et al. 2020). The study of the expressed gene product is called proteomics which helps to analyse the molecular mechanism of decoding, post-translational modifications and degradation pathways of cell system (Sharma et al. 2016; Pérez-Llano et al. 2018; Balakrishnan et al. 2019; Rodríguez et al. 2020). Once the degradation is completed, the qualitative and quantitative evaluation of the comprehensive profiles of metabolites in a microbial system is defined as metabolomics (Chandran et al. 2020). The tremendous potential of omics tools and their uses has generated significant biological data that enable schematic analysis of the microbial physiology during the bioremediation process. Therefore, the analysis, acquisition, organization and interpretation of this enormous pool of biological data set would not be practically impossible without the execution of bioinformatics tools (Fulekar 2009). This book chapter enlightens the multi-omics tools used in the bioremediation field which highlights the capabilities of the biological systems and its components using genomics (DNA), transcriptomics (RNA transcripts), proteomics (translated proteins) and metabolomics (metabolic intermediates/products) to give a deeper and vast idea of the whole bioremediation process and also discusses the applications of bioinformatics tools used to compile the data generated through omics approaches (Fig. 25.1).

## 25.2 Omics Approaches in Microbial Bioremediation of Agrochemicals

To understand a completely biological process involved in the degradation of agrochemical that is complex as microbial bioremediation, a single omics study is not always sufficient (Zhang et al. 2011). System biology is a versatile and integrative field of research to study the complexity in the living system, effectively explaining the underlying mechanism involved in the microbial-based management of agrochemicals. Current innovative postgenomic research approaches (omics) and molecular tools encompassing the study of genes (genomics), proteins (proteomics), mRNA (transcriptomics) and metabolites (metabolomics) have been broadly explored (Kookana 2010).

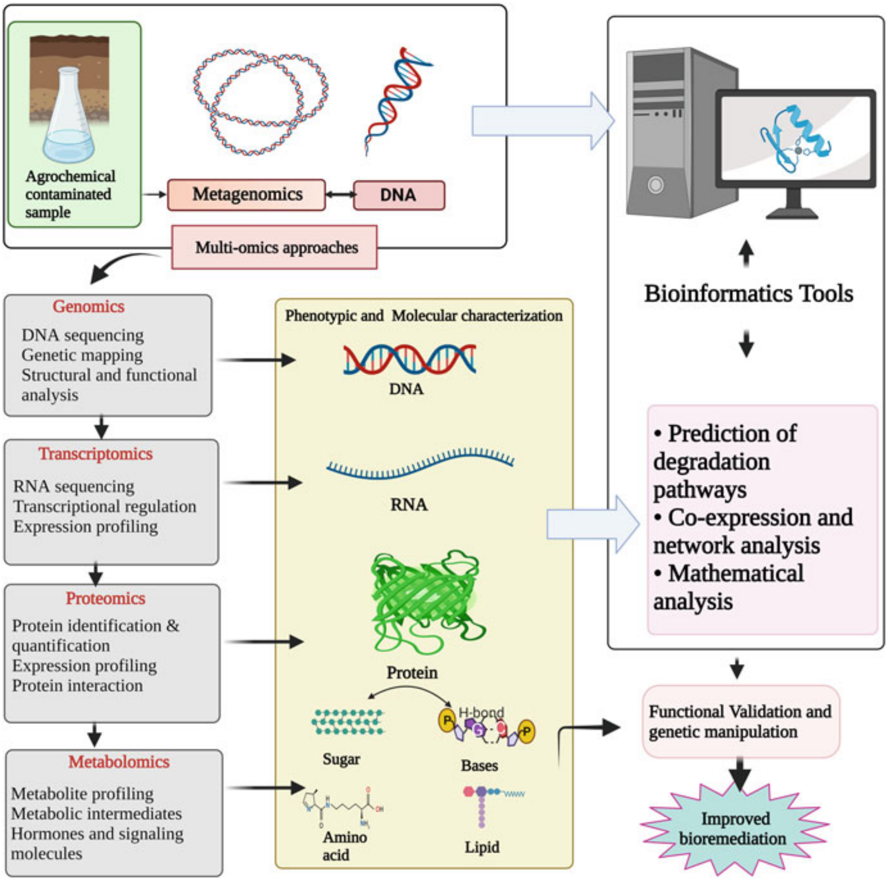

**Fig. 25.1** Omics techniques and associated components

## 25.2.1 Genomics in Bioremediation of Agrochemicals

Genomic approaches mostly used to assess the degradation of agrochemicals generally involve the study of the microbial population existing in contaminated environments, nature of microbial community, genetic diversity, functionality and characterization of the genome structure of microorganisms (Segata et al. 2013). Dr. Tom Roderick coined the term 'genomics' while working on the project of human genome mapping in 1986 (Ogbe et al. 2016). Genomics involves the use of recombinant DNA, genome sequencing procedures and bioinformatics tools for assembling, analysing and predicting the relationship between the structural and functional attributes of the genomes (Ogbe et al. 2016). Various research studies have investigated the ability of recombinant DNA technology in microbe-assisted degradation of toxic organic contaminants, like pesticides. The recent discoveries in genome and metagenome sequencing tools encourage the finding of the genes and regulatory proteins related to bioremediation in both culturable and nonculturable microbes (Bharagava et al. 2019; Rodríguez et al. 2020). Sequencing innovation, particularly next-generation sequencing (NGS), is ending up being fundamental in the advancement of genome sequence databases that generate high output genomic data at a low investment (Sharma et al. 2016). The concept of a functional gene array known as DNA microarray or a biochip was proposed, which targets more than 12,000 distinct functional genes and proved as the most promising approach (Liebich et al. 2009). Functional genomics gives a broad idea about the microbial metabolic and regulatory pathways that help to improve the perception of gene activity. The essential practice in functional genomics approaches is to broaden the range of biological study from evaluating a single gene or its encoding protein to investigate them all in a systematic pattern simultaneously (Ortiz-Hernández et al. 2013). Presently, whole-genome sequences of all the known organisms which actively participate in degradation are accessible through the public domain. Kaminski et al. (2019) analyse the genome of *Sphingopyxis lindanitolerans* WS5A3p which can degrade γ-hexachlorocyclohexane (γ-HCH). According to their analysis, the genome of *Sphingopyxis lindanitolerans* WS5A3p includes 4.3 Mbp in total containing one circular chromosome and two putative plasmids. When the genome of this organism was sequenced and analysed, 13 *lin* genes were identified that participate in the degradation of γ-HCH (Kaminski et al. 2019). *Burkholderia cenocepacia* CEIB S5-2 is a bacterium that can successfully hydrolyse MP and biodegrade the primary methyl parathion hydrolysis product, p-nitrophenol (PNP). The presence of the methyl parathion-degrading gene (*mpd*) and the gene cluster pnpABA'E1E2FDC, which includes the genes implicated in PNP degradation, is linked to the MP- and PNP-degrading capacity seen in *B. cenocepacia* CEIB S5-2, according to genomic data (Ortiz-Hernández et al. 2021). Genes involved in the degradation of different agrochemicals are listed in Table 25.1.

### 25.2.2 Transcriptomics in Bioremediation of Agrochemicals

The occurrence of agrochemicals and other pollutants, in the environment, regulates the expression levels of the gene in the microorganisms; such adaptive regulation in the expression of genes is also called as transcriptional regulation, which is associated with the presence of agrochemicals, its metabolism and mineralization processes (Rodríguez et al. 2020). Transcriptomics involves the study of gene expression at the mRNAs level in a defined cell population. Transcriptome, or a whole collection of RNA, is edited and transformed into mRNA, which transports information to the ribosome, which converts the message into protein (Fig. 25.2). Unlike the genome, the transcriptome is dynamic as it is being constantly varying with conditions and time. It essentially acts as a mirror of the active genes expressing at a particular time under specified conditions. Transcriptomics studies reveals how gene expression patterns vary in response to internal and external variables like biotic and abiotic stimuli. Thus, transcriptomics is a valuable tool for acquiring a better knowledge of biological processes. Next-generation sequencing (NGS) and

**Table 25.1** Microbial genes reported for the degradation of agrochemicals

| Sr. no | Genes identified | Source | Targeted agrochemical | Reference |
|---|---|---|---|---|
| 1 | *LinB* | *Sphingobium* sp. | Hexachlorocyclohexane (β and δ isomers) | Ito et al. (2007) |
| 2 | *AtzA* | *Pseudomonas* sp. ADP | Atrazine | Boundy-Mills et al. (1997) |
| 3 | *puhA* | *Arthrobacter globiformis* D47 | Phenylurea (herbicides) | Turnbull et al. (2001) |
| 4 | *atz*A, *atz*B, *atz*C, *atz*D | *Pseudomonas* sp. A02<br>*Achromobacter* sp. A01 | Atrazine | Fernandes et al. (2018) |
| 5 | *trzD* | *Enterobacter cloacae* JS08. Deg01 | Atrazine | Solomon et al. (2013) |
| 6 | *thcB* | Rhodococcus sp. strain NI86/21 | Thiocarbamates | Shao and Behki (1996) |
| 7 | *oph*B | Pseudomonas sp. BF1-3 | Chlorpyrifos | Barman et al. (2014) |
| 8 | *linA* | *Sphingobium japonicum* UT26 | γ-Hexachlorocyclohexane | Nagata et al. (1999) |
| 9 | *ophB*, *ampA*, *opdE*, *opd*, *opdA*, *mpd* | *Brevundimonas faecalis* MA-B12, *parafaecalis* MA-B13, *Citrobacter freundii* TF-B21, *Ochrobactrum intermedium* DV-B31, *Bacillus cereus* | Methamidophos<br>Trichlorfon<br>Dichlorvos<br>Dimethoate | Jiang et al. (2019) |

other transcriptomic approaches can help researchers to understand more about the genome's functional components (Valdés et al. 2013; Van Emon 2016). Transcriptomics is mostly applied in different microbial systems to discover the genome-guided transcriptional behaviour and define the controllers (regulators and inducers and inhibitors), draw the outline of operon structures, recognize binding sites of enzymes in DNA and perform comparative genotyping. Currently, microarrays, next-generation sequencing and RNA-Sequencing are majorly used for the transcriptional profiling of biological samples under varied conditions (Rodríguez et al. 2020). Bælum et al. (2008) investigated the expression of *tfdA* gene involved in the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) in contaminated agricultural soil by using m-RNA-based quantitative real-time PCR. The results show that the expression of class I *tfdA* genes was visible in the native microbial communities while class III *tfdA* genes expressed dominantly during incubation and degradation of MCPA in soil.

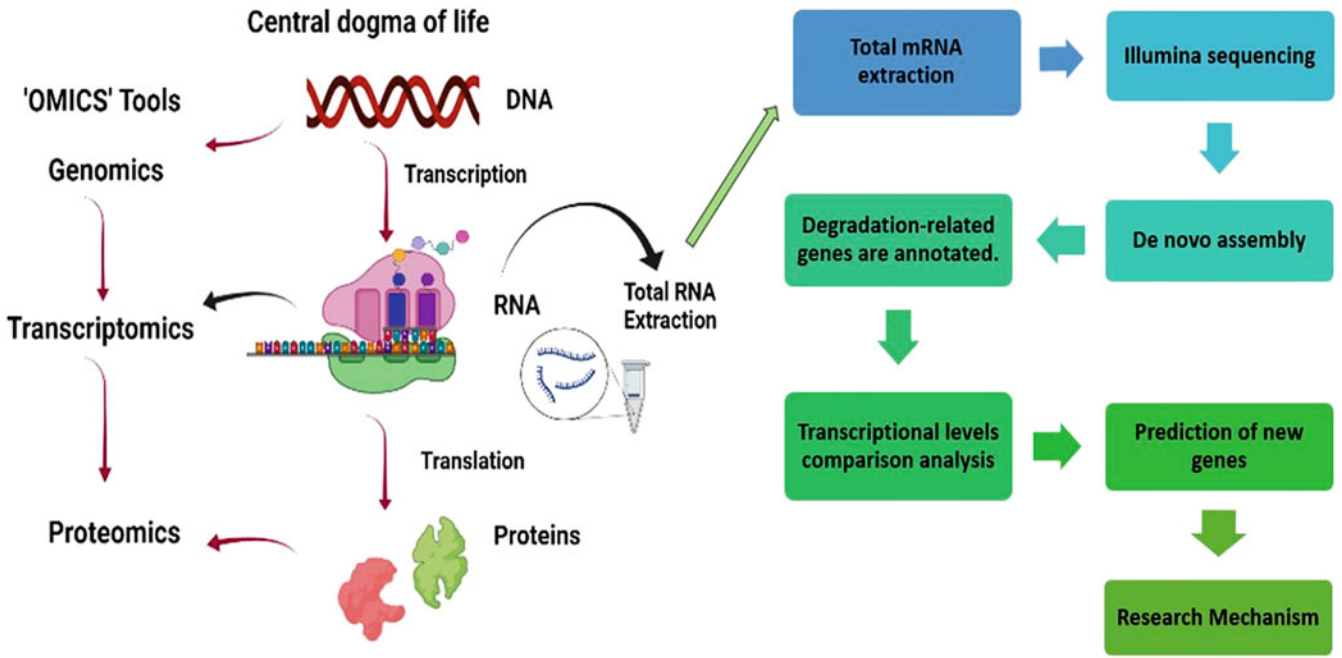

**Fig. 25.2** Schematic representation of transcriptomics

### 25.2.3 Proteomics Approaches in Bioremediation of Agrochemicals

Microbial enzyme machinery or proteins have a significant role in the degradation of agrochemicals. Application of proteomics in bioremediation of agrochemicals will help to explore the expression pattern of proteins within microorganisms and to build a map of all expressed proteins in a given environmental conditions (Ginsburg and Haga 2006; Yates et al. 2009; Jarnuczak et al. 2019; Chandran et al. 2020). In 1995, the term 'proteome' and its study named 'proteomics' were introduced for explaining a dominant post-genomic feature that evolved from the development of large and complex genomic data sequencing (Wasinger et al. 1995; Bhushan et al. 2011). Proteomics analysis provides information about how the proteins function and interact among them (Merchant and Weinberger 2000; Chandrasekhar et al. 2014) along with the changes in protein pattern and the network of protein-protein interaction (Baginsky et al. 2010; Aslam et al. 2017). It also involves the study of changes in protein abundance during a defined period of bioremediation process (Mishra et al. 2019). It revealed the post-transcriptional and post-translational modification in protein including their classifications that cannot be generated from genomic data (Bhushan et al. 2011).

The changes in environmental conditions drastically fluctuate the expression of cellular proteins. The identification of the specific proteins responsible for microbial response can provide support for understanding the genes and their regulations related to biodegradation (Merchant and Weinberger 2000). The pollutants are mineralized by the chain of metabolic enzymes, which are proteins by nature could be extracted, isolated and characterized through proteomics studies at different time points corresponding to different physiological states of the microorganism (Mishra et al. 2019). Jayaraj et al. (2016) investigated the expression of the proteins in a cypermethrin-degrading strain of *Bacillus thuringiensis SG4 by using* 2D electrophoresis. *In their study, they* account the expression of 223 proteins under normal conditions while 250 unique proteins under stress conditions. Based on their role in biological reactions, identified proteins were categorized as stress proteins, catabolic enzymes and translational enzymes. Classification of specific proteins involved in the degradation of cypermethrin will help in in situ bioremediation practices. The addition of proteomic approaches for studies on agrochemicals biodegradation is achieving importance in recent times. The proteomics approaches is now evolving which were traditionally based on highly efficient tools of separation two-dimensional polyacrylamide gel electrophoresis (2-DE) and modern tools of bioinformatics in combination with mass spectrometry (MS) (Chen et al. 2009). A new combined approach of proteomics and transcriptomics exposed a new pathway for anaerobic and aerobic biodegradation of agrochemicals which will definitely open the doors for identification and characterization of new signature proteins (Hochstrasser 1998).

### 25.2.4 Metabolomics Approaches in Agrochemicals Bioremediation

Metabolomics approach in agrochemicals bioremediation involves exposure of specific concentrations of xenobiotic compounds to model microorganisms and analyse the concentration change and path of the metabolic response in a particular time. This study allows risk assessment, diagnosis and monitoring of environmental pollution and biomarker studies in microbes as a response to xenobiotic stress (Chen and Kim 2013; Viant and Sommer 2013). The metabolomics approach has been widely applied for microbial biodegradation of various xenobiotic compounds especially PAHs (Parisi et al. 2009; Callaghan 2013; Keum et al. 2008). Metabolomics could be referred to as a comprehensive study of metabolite profiles in a biological system both qualitatively and quantitatively under specific conditions (Vignoli et al. 2019; Aliferis and Jabaji 2011). The metabolic profile of any biological system is integrated by several enzymatic reactions (comprised of intermediates and end products) that change with the environmental stimuli and provide insights into the biochemical state of the microorganism (Hernandez-Soriano and Carlos Jiménez-López 2014).

Metabolomics involves two strategies for analysing biological systems; the first strategy is untargeted, for analysing biological system for which no prior information for metabolic pathways is available. This involves metabolite identification over a broad range producing ample data that must be analysed and compared to different samples (Alonso et al. 2015). The second strategy is specific and targeted towards the identification of specific metabolites based on previous information, providing valid results for untargeted metabolomics studies (Malik et al. 2017). The metabolomics workflow is shown in Fig. 25.3. It initiates with a selection of biological samples and experimental designing following extraction and separation of metabolic intermediates by analytical techniques like liquid or gas chromatography. The following step in the work flow is data acquisition either by NMR or mass spectrometry. The analysis is then statistically carried out identifying the spectral data by comparing with existing libraries and database. The interpretation of biological information can then be performed (León et al. 2013; de Souza et al. 2017). Agriculture yields are commonly improved through the use of agrochemicals. These agrochemicals along with improving plant productivity are responsible for reprogramming plant metabolism especially secondary metabolism and therefore regarded as a xenobiotic, regardless of their other positive impacts. These agro-xenobiotic compounds impart silent effects on the plant genome and also on the microbial community residing with the plant rhizosphere. In agroecological systems, metabolomics provides with monitoring of metabolic flux within plants and microbial associations with abiotic agents like agrochemicals. Metabolomics of agrochemical-affected plant and their associated microorganisms would provide a better understanding of the complex interaction within the plant system. The emergence of metabolomics has added a new dimension to the field of functional genomics *with a broad perspective of multiple biological aspects enabling the exhaustive study of inclusive metabolic networks* (Vinayavekhin et al. 2010). Metabolomics deals with the quantification and identification of metabolites ranging

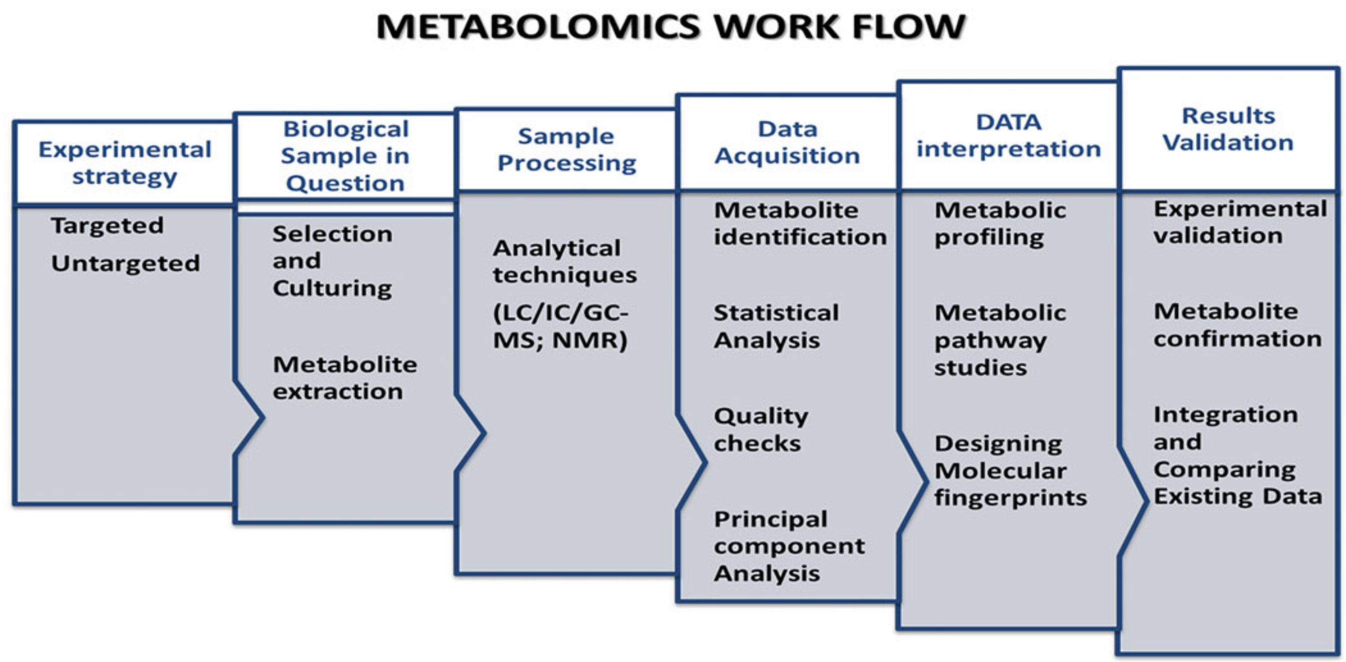

**Fig. 25.3** Schematic diagram showing the workflow of metabolomics

between 1500 and 3000 Da. The metabolites consist of several macromolecules including carbohydrates, amino acids, nucleic acids and secondary metabolites such as organic acids, polyphenols, alkaloids, vitamins and flavonoids (Aliferis and Jabaji 2011). Metabolomics study of microbial community can complement genomic studies and could be useful in the genetic improvement of crops from nutritional and functional point of view along with the plant response to several stresses including both biotic and abiotic.

Metabolomics can be considered as a valuable tool for studying the toxicologicalproperties of pesticide and its exposure effects on microorganisms during physiological processes. The biological information obtained from metabolomics profiling has various applications in agrochemical research studies like biomonitoring, understanding ecotoxicological and biodegradation processes, obtaining safety screenings for agricultural products and discovering new agrochemicals for sustainable development (Aliferis and Jabaji 2011; Wang and Wu 2015).

## 25.3 Analytical Platforms Used in Omics Approach

### 25.3.1 16S rRNA Approach

16S rRNA gene sequence technique can be utilized for a complete evaluation of microbial diversity through amplification and sequencing of the hypervariable regions of the 16S rRNA gene selectively. It is a highly competent and cost-effective method that can easily be accessed by a variety of bioinformatics tools and frequently used for characterizing complex microbial communities (Chandran et al. 2020). Nayarisseri et al. (2015) reported organophosphates degrading a strain of species of *Flavobacterium* species EMBS0145 by 16S rRNA gene sequencing. Bacterial isolates degrading chlorpyrifos were likewise identified by 16S rRNA gene sequencing as *Pseudomonas vesicularis*, *Pseudomonas pseudoalcaligenes*, *Pseudomonas stutzeri*, *Pseudomonas maltophilia* and *Enterobacter aerogenes*, respectively (Awad et al. 2011).

### 25.3.2 DNA Microarrays

DNA microarray is a promising approach in the research field of genetics. It gives a broad insight into microbial populations and dynamics in contaminated samples (Mishra et al. 2019). It permits the analysis of different genes at one time without amplification of the genes individually. It was also reported that the expression profile of catabolic genes and physiology of microbes isolated from polluted samples under numerous environmental conditions can be assessed by DNA microarrays (Hivrale et al. 2016; Chandran et al. 2020). Liebich et al. (2009) assessed the atrazine-degrading gene in the DNA from the groundwater samples of agricultural fields using GeoChip. In their study, they used 37 gene probes that are likely involved in atrazine degradation.

### 25.3.3 Next-Generation Sequencing

Next-generation sequencing (NGS) approaches have brought a factual revolt in the field of environmental biodegradation and biotechnology approaches. The commonly used method in next-generation sequencing includes preparation of library, sequencing, base calling, alignment to build the genome and annotation (Samorodnitsky et al. 2015; Jaiswal et al. 2019). The important platforms mostly used to study the microbiome in next-generation sequencing are pyrosequencing (Roche/454 sequencing), Illumina, Ion Torrent, SOLiD, PacBio RS, etc. (Hivrale et al. 2016).

### 25.3.4 Two-Dimensional Polyacrylamide Gel Electrophoresis (2-DE)

The two-dimensional electrophoresis promotes the evaluation of distinct protein expression in microorganisms growing on contaminated sites and contaminant-free sites (Wang et al. 2000; Kim et al. 2004; Kühner et al. 2005). It is designated as two-dimensional because the proteins here are separated by SDS-PAGE while in the first dimension the proteins are separated by isoelectric focusing. The immobilized pH gradient strips extremely enhanced the utility of 2-DE gels by making them more reproducible and comparable (Singh and Nagaraj 2006). However, due to very basic and hydrophobic membrane proteins in compartmental proteomics, 2-DE has been considered to have a very restricted approach. By introducing an alternate approach for multidimensional protein identification technology (MudPIT), there is improvement in the 2-DE technique (Shipitalo et al. 2004).

### 25.3.5 Mass Spectrometry (MS)

Mass spectrometry has transformed the proteomics application in the environment as the technique analyses small molecules from peptides and proteins and the time duration of the process has minimized from hours to minutes. This has raised the use of the MS technique in the identification of protein from several orders of magnitude (Aebersold and Mann 2003). The progression in MS techniques is coupled with database searching and paved a role in proteomics for protein identification. MALDI-TOF-MS (matrix-associated laser desorption/ionisation time-of-flight MS) is the mostly used method for protein identification (which is excised from the 2-DE gels) through the generation of peptide-mass fingerprinting (Aebersold and Mann 2003). SELDI-TOF-MS (surface-enhanced laser desorption ionisation time-of-flight mass spectroscopy) uses a chip for combining the sample fraction with MALDI-

TOF-MS analysis (Merchant and Weinberger 2000; Seibert et al. 2005; Singh and Nagaraj 2006; Hivrale et al. 2016).

### 25.3.6 NMR Spectroscopy

NMR spectroscopy delivers unique information on structural attributes on purecompounds and their complexes. The identification of compounds in a mixture is tremendously difficult and requires prior separation in one-dimensional (1D) proton NMR (1H NMR), two-dimensional (2D) analyses including proton-proton (1H–1H) 2D J-resolved experiments and correlation spectroscopy (COSY) (Viant and Sommer 2013; Krishnan 2005). The recent advances in composite techniques such as LC-NMR and LC-NMR/MS, Magic angle spinning (MAS) NMR spectroscopy technique has proven an immense potential in metabolomics studies (Nicholson and Lindon 2008). Various omics tools and their application in bioremediation of agrochemical are described in Table 25.2.

## 25.4 Applications of Bioinformatics Tools in Omics

Recently, bioinformatics has been utilized as a multidisciplinary approach in microbial biotechnology that applies computational innovative advances for the improvement of programming, software, algorithms, statistical and mathematical models for analysis and organizing of the wet-lab data, sequencing of the genome, identification of protein-coding segments and comparison of the genome to classify the functional genes, the improvement of genomics and proteomics databases and surmising phenotypes from gene-level functions (Azad and Borodovsky 2004; Zimin et al. 2013; Rodríguez et al. 2020). In the field of microbe-assisted bioremediation, bioinformatic-based study encourages the understanding of molecular mechanisms and metabolic pathways involved in the degradation of pollutants. A list of bioinformatics tools applied in different omics approaches is listed in Table 25.3.

## 25.5 Future Prospective

Analytical skills and bioinformatics tools have made it possible to combine data from different management levels and improve the understanding of mechanisms that influence biological processes and behaviours that occurs during the bioremediation process (Majumdar and Keller 2020). Despite this most of the genes discovered to have no comparable counterparts in databases and understanding the operational functions of uncultured organisms remains a difficult challenge. Many technical hurdles remain in the characterization of microbial communities using metagenomic, meta-transcriptomic and proteogenomic methods. The in silico tools are a collection of databases and software that can help diminish the ‘sequence-function gap’ and aid in the broad-spectrum research of soil microorganisms and their application to

**Table 25.2** Omics tools and their application in bioremediation of agrochemical

| Sr. No | Omics tools involved | Microbes involved | Agrochemical toxicant | Analytical/other sequencing technique | Remarks/specification | References |
|---|---|---|---|---|---|---|
| 1 | Genomics | *Pseudomonas spp. MR3* | Methyl parathion | In ion torrent (PGM), next-generation sequencer | Genes for phosphonoacetaldehyde hydrolase, salicylate hydroxylase, catechol 1,2-dioxygenase, 1H-3-hydroxy-4-oxoquinaldine 2,4-dioxygenase and monoamine oxidase found | Parakhia et al. (2014) |
| 2 | Genomics | *Alcaligenes spp. EGD-AK7 and Arthrobacter sp. AK-YN10* | Atrazine | Illumina mi seq (applied bioinformatics) sequencing<br>RAST<br>Prokaryotic genome automatic annotation pipeline (PGAAP)<br>NCBI | Atrazine-degrading gene *atzA*, *atzB*, *atzC*, *atzD*, *atzE* and *atzF* | Sagarkar et al. (2013) |
| 3 | Genomics | *Bacillus amyloliquefaciens YP6* | Organophosphorus pesticides | PacBio RS and Illumina sequencing platform | Phosphorus-solubilizing and OPs-degrading related genes (*phoD*, *phoA*) *phrC*, *phoE*, *ycsE*, *bcrC* and yvaK were identified | Meng et al. (2019) |
| 4 | Transcriptomics/ genomics | *Rhodococcus sp. CX-1* | Carbendazim | HPLC-MS/MS<br>KEGG and GO | Oxidation-reduction processes involved in the degradation of carbendazim | Long et al. (2021) |
| 5 | Transcriptomics | *Pigmentiphaga sp. H8* | 3,5-Dibromo-4-hydroxybenzoate (DBHB) (metabolite used in herbicide bromoxynil) | HTSeq v0.6.1 software | Flavin monooxygenases involved in the degradation | Chen et al. (2018) |

| | | | | | | |
|---|---|---|---|---|---|---|
| 6 | Transcriptomics | *Sphingobacterium multivorum* | Hexaconazole (triazole fungicide) | GO database<br>KEGG database | Degrade in 6 days aldehyde dehydrogenase and monooxygenase was upregulated | An et al. (2020) |
| 7 | Proteomics | *Burkholderia sp.* | N-Methyl carbamate | LC-MS/MS | Identified the key enzyme involved in the degradation of N-methyl carbamate | Seo et al. (2013) |
| 8 | Proteomics | *Rhodococcus sp.* | p-Nitrophenol | MALDI TOF/TOF-MS | The primary enzyme involved in 4-NP degradation was membrane-bound 4- NP MO | Sengupta et al. (2019) |
| 9 | Proteomics | *Escherichia coli* | p-Nitrophenol (PNP) | MALDI TOF/TOF-MS, microarrays<br>Proteome<br>RT-qPCR | *E. coli* cells grown in (14)C-labelled PNP indicated incorporation of (14)C carbon, and Orf306-dependent assimilation of PNP in *E. coli* cells | Chakka et al. (2015) |
| 10 | Proteomics | *Mycobacterium sp.* | PAHs (PYR-1) | Two-dimensional polyacrylamide gel electrophoresis | Six major proteins were significantly induced and overexpressed on 2-DE when *Mycobacterium* sp. strain PYR-1 was exposed to phenanthrene, dibenzothiophene and pyrene | Kweon et al. (2007) |
| 11 | Metabolomics | *Actinomycetes* | Aflatoxin B1 | High-resolution Fourier transform mass spectrometry (HR-FTMS)<br>MS2 fragmentation | Degradation studies at acidic pH 6 | Eshelli et al. (2015) |
| 12 | Metabolomics | *Citrobacter freundii CD-9* | Fenvalerate (pyrethroid insecticide) | 16S rRNA sequencing<br>HPLC, GC-MS | 10 metabolites identified<br>Localization of pyrethroid-degrading enzymes studied | Tang et al. (2020) |

(continued)

**Table 25.2** (continued)

| Sr. No | Omics tools involved | Microbes involved | Agrochemical toxicant | Analytical/other sequencing technique | Remarks/specification | References |
|---|---|---|---|---|---|---|
| 13 | Meta transcriptomics | *Synechococcus sp. (Cyanobacteria)* | Glyphosate (herbicide) | KEGG database | Sp. can utilize glyphosate as a source of phosphate, by reducing the toxicity to other organisms | Lu et al. (2020) |

**Table 25.3** Bioinformatic tools and their applications

| Sr. no | Bioinformatics tools | Application | Reference |
|---|---|---|---|
| 1 | BLAST (basic local alignment search tool) | Performs comparisons between pairs of sequences, searching for regions of local similarity | Altschul et al. (1990) |
| 2 | CLUSTAL-W | DNA or protein multiple sequence alignment program for *three or more* sequences | Chenna et al. (2003) |
| 3 | SWISS-MODEL | A fully automated protein structure homology-modelling server | Waterhouse et al. (2018) |
| 4 | Cn3d | Application for a web browser that allows you to view 3-dimensional structures from the GenBank entrez structure database | Wang et al. (2000) |
| 5 | Protein Data Bank (PDB) | Universal storage place of processing and distribution of 3-dimensional structure data of macromolecules. The information in PDB derived from a variety of tools and experiments like NMR, X-ray crystallography, microscopy, cryo-electron and theoretical modelling | Berman (2008) |
| 6 | NCBI Structure Database (MMDB) | The database provides biologists with broad information on the biological functions of proteins, on mechanisms related to their functions and on the relationship between biomolecules and their evolutionary history. NCBI also called MMDB (molecular modelling database) and includes the 3D structure of macromolecules and visualization tools for comparative analysis of proteins | Madej et al. (2014) |
| 7 | Mage and Kinemages | Used for protein structure visualization and rotation of the entire image in real time, displaying of parts by turning off and on them | Rastogi et al. (2008) |
| 8 | VAST (vector alignment sequence tool) | Tools produced by NCBI and provide identification of similar proteins with 3D structure | Gibrat et al. (1996) |
| 9 | DALI | Computational protein structure alignment tool used for comparison of protein structure in 3D | Holm and Sander (1995) |
| 10 | CDART (Conserved Domain Architecture Retrieval Tool) | For searching protein having similar domain architectures | Geer et al. (2002) |
| 11 | HMMER | Homologous protein sequences may be searched from the respective databases | Finn et al. (2011) |
| 12 | Prosite | Provides information on protein families, conserved domains and actives sites of the proteins | Sigrist et al. (2012) |

(continued)

**Table 25.3** (continued)

| Sr. no | Bioinformatics tools | Application | Reference |
|---|---|---|---|
| 13 | Pfam | Collection of protein families | Finn et al. (2011) |
| 14 | COMSPARI | COMSPARI (comparison to spectral and retention information) is a tool to visualize mass spectrometry data | Katz et al. (2004) |
| 15 | MassTRIX | Visualization of gene expression and metabolome | Suhre and Schmitt-Kopplin (2008) |

sustainable agrochemical bioremediation (Bhatt and Barh 2018). More advanced computational techniques are necessary to properly use omics-derived data for improved gene annotation, metabolic network comprehension and metabolite discovery. A single user-friendly platform with all bioinformatics tools and datasets for data analysis and metabolic pathway reconstruction models is required. This platform will incorporate all of the data, analytical methodologies and pipelines associated with bioremediation research. This demands collaboration among scientists from various laboratories to share data and update and maintain databases. Acceptable refinements have been witnessed for the degradation of agrochemicals by using gene tools. Implementation of TALEN, ZFNs and CRISPR Cas9 proves as promising gene-editing techniques for modifying the activity of microorganisms with specific genes and enzymes involved in agrochemicals bioremediation (Jaiswal et al. 2019).

## 25.6 Conclusion

Microbial communities have a significant role in the degradation of organic compounds, nutrient recycling and bioremediation of pollutants from the environment. Contamination of agrochemicals in elements of the environment brings changes in the diversity and novelty of the indigenous microbial communities. Moreover, flexible metabolic activity and genetic diversity of microbes allow them to survive in the presence of toxic pollutants. The effective execution of microorganisms in biodegradation of agrochemicals still needs to beat a few limitations, due to failure in the absolute degradation or their low efficiency to mineralize complex mixture of agrochemicals in a contaminated site. In such conditions, the in-detailed knowledge and understanding of the molecular events that occur during degradation are more essential. Omics technologies have the potency to predict molecular mechanisms, genes, protein and metabolic pathways that occur at the site of contamination within the microbial communities. Analysis through these approaches would assist in tracking suitable microorganisms for the efficient degradation of agrochemicals. Multi-omics tools and approaches will empower us to assemble new speculations, hypotheses and paradigms for the remediation of polluted environments. A complete database gathered from all available omics tools during bioremediation research will set a platform for researchers to interchange obtained data and investigation strategies. Collectively, these tools will allow interpreting 'omics' data precisely, leading to the invention of judicious prognostic models and strategies for the effective performance of bioremediation technology in the future.

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# Agrochemicals in Soil and Environment: Conclusions and Future Perspectives

# 26

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## Abstract

In view of the rapidly increasing global population and frequently changing environmental conditions, it becomes imperative to produce more food to secure the food security which created tremendous pressure on agriculture sector to ensure more food production. To meet this demand of food production, the agriculture sector is adopting every possible measures like the use of chemical compounds (agrochemicals) to enhance the food productivity and to protect the crops from the serious threat of pests. Excessive and unwarranted use of agrochemicals resulted in significant contamination of agricultural soil and water which posed a serious threat to the environment and human health risk; therefore, measures should be adopted to reduce the use of agrochemicals as well

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as microbe-assisted remediation of contaminated soil which should be a priority to negate the residual impact. Earthworms can also be employed for remediation. Soil-biochar and nanoformulations and development of high-yielding as well as pest-resistant varieties can serve the purpose.

**Keywords**

Agrochemicals · Bioremediation · Earthworm · Nanoformulations · Plant-microbe partnership · Soil-biochar

The Food and Agriculture Organization of the United Nations (FAO 2021) FAOSTAT ANALYTICAL BRIEF 29, ‘pesticides use, pesticides trade and pesticides indicators 1990–2019 describes that the pesticides are any substance or mixture of substances of chemical or biological ingredients intended for repelling, destroying or controlling any pest or for regulating plant growth. The term pesticide applies to insecticides, herbicides, fungicides, rodenticides, molluscicides, wood preservatives and various other substances used to control pests. Pesticides also include plant growth regulators, defoliants and desiccants (https://www.fao.org/news/story/en/item/1398779/icode/). In the EXPLANATORY NOTES of FAO (2021), FAOSTAT further expanded the domain of pesticides and provided the details of major pesticide groups. The 2020 update with new additions of pesticides revealed the gap-filled pesticides subcategories for the ten categories listed below are now being disseminated along with the pesticides (total) category globally by FAO (2021) and FAOSTAT ANALYTICAL BRIEF 29 (2021).

Insecticides (chlorinated hydrocarbons, organophosphates, carbamates-insecticides pyrethroids, botanical and biological products and others not elsewhere classified)

1. Mineral oils
2. Herbicides (phenoxy hormone products, triazines, amides, carbamates-herbicides, dinitroanilines, urea derivatives, sulfonyl urea, bipiridils, uracil, others not elsewhere classified)
3. Fungicides and bactericides (inorganic, dithiocarbamates, benzimidazoles, triazoles diazoles, diazines morpholines, others not elsewhere classified)
4. Seed treatment-fungicides (dithiocarbamates, benzimidazoles, triazoles diazoles, diazines morpholines, botanical products and biological, others not elsewhere classified)
5. Seed treatment-insecticides (organophosphates, carbamates-insecticides, pyrethroids, others not elsewhere classified)
6. Plant growth regulators
7. Rodenticides (anti-coagulants, cyanide generators, hypercalcaemics, narcotics, others not elsewhere classified)
8. Other pesticides NES (not elsewhere specified)
9. Disinfectants

In the era of frequently changing environmental conditions and ever-increasing global population, it becomes imperative to produce more food which puts excessive pressure on agriculture sector to feed the population. Therefore, every possible measure is being adopted by the agriculture sector which also includes the usage of chemical compounds to protect the crops from the serious threat of pests (Kumar and Sachan 2021). The above-listed agrochemicals (FAOSTAT ANALYTICAL BRIEF 29 2021) are being frequently used globally to protect and stimulate the growth and development of the crop plants by protecting the crops from diseases and abiotic stress factors but unrestricted and continuous application of pesticides resulted in significant contamination of agricultural soil and water which posed a serious threat to the environment and human health risk (Sharma et al. 2020). Furthermore, the pesticide residues in the agricultural soil can also cause severe phytotoxicity to rotation-sensitive crops (Huang et al. 2017). Therefore, agricultural pesticide usage and its negative impact on the quality of agricultural soil and water are visible globally and widespread throughout the world (Gunstone et al. 2021).

Therefore, it is imperative to remediate the contaminated agricultural soil and water by adopting sustainable measures like plant-microbe partnership for bioremediation of pesticides (Kumar and Sachan 2021), earthworm-assisted bioremediation of pesticides (Singh et al. 2020), soil-biochar formulations for improved absorption and reabsorption of pesticide (Ogura et al. 2021), nanoparticles and nanoformulations for remediation of pesticide-contaminated agricultural soil (Marcon et al. 2021). Further, development of pest-resistant genetically modified crops can also reduce the burden of synthetic pesticides on the agricultural soil.

Microbial secondary metabolites often possess novel chemical templates which may be developed into bio-rational eco-friendly counterparts of the conventional agrochemicals. Microbial natural products can be produced via fermentation processes and put to use on large scale. Nanotechnology promises a bright future in agricultural sector, as it is compact, efficient and eco-friendly. New agro-formulations with marketing proficiency will enhance their use in the near future. Educating the community of farmers especially in low resource rural areas regarding ecological and intergenerational conceptualization of organic farming implementation would improve soil health and crop productivity. If the government commits to organic farming in their country, they must follow the spoken commitment with financial assistance to farmers which would help in developing demand and providing opportunity for the farmers to sell their produce. The combined efforts will improve the health of the environment and people, climate issues and ultimately, food security. The evaluators also coordinate with authorized analytical facilities for pesticide monitoring in human body fluids and tissues to examine the likely impacts of pesticide exposure upon farmer's health. Judicious use of the suggested checklist will help the farming community recognize the potential risks associated with the toxicity of pesticides and quantitatively evaluate the prevailing situation in a farming zone.

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