Pratibha Singh
Sunita Kumari Singh
Sheo Mohan Prasad *Editors*

# Plant Responses to Soil Pollution

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*Dedicated to Our Parents*

# Foreword

I am pleased to write the foreword for this book edited by Dr. Pratibha Singh, Dr. Sunita Kumari Singh, and Dr. Sheo Mohan Prasad. They have focused this book on an extremely important area of active research—the effects of soil pollutants on plants. Anything entering the environment in any form will reach the soil ultimately and the water table in turn and thus entering the food chain. Plants play a major role in the functioning of terrestrial and aquatic ecosystems and are important in order to achieve the goal of food security to feed the ever-increasing population. Unfortunately, the fast pace of development is leading to the addition of contaminants in soil, air, and water in the form of inorganic contaminants, metals, radionuclides, pesticides, and even chemical fertilizers, which proved to be a boon to farmers during the Green Revolution. With time, the pollutants accumulate and show biomagnification when they enter the food chain and become harmful for the health of plants, animals, and human beings. The effect of these soil pollutants on plants may include the accumulation of contaminants into the plant, including the edible portion of food crops, growth, morphology, physiological, and biochemical processes of plants, and productivity. It then also affects the health of other living beings on earth as plants are a source of food to them. This book highlights the side effects of modern agricultural management practices on the health of soil in terms of fertility and also increase in greenhouse gases from agricultural land leading to climate change. Nowadays, there is a need to remediate the soil and various ways of eco-friendly remediation techniques as given in this book, which further adds to the value of this book. I believe this book makes an important contribution to our understanding of the impact of soil contaminants on plants, and its focus on mechanistic studies and risk assessment will be of interest to researchers as well as policy makers.

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Ademir S. F. Araujo

# Preface

Soil pollution is one of the major aspects of pollution emerging from urban advancements including the fast pace of industrialization and uncontrolled exploitation of natural resources. Anything beyond the threshold limit becomes pollutants. Soil pollution minimizes the yield and quality of the crops and also alters soil biodiversity, soil organic matter as well as groundwater which in turn disturb the equilibrium of soil nutrients and its uptake by plants. The book discusses the grade of soil contamination, its origin, and its aftereffects on plants and their productivity status. Soil pertains to the multiphasic, heterogeneous environments, and successful remediation is dependent on an interdisciplinary approach involving disciplines such as microbiology, engineering, ecology, geology, and chemistry. In this volume, different kinds of soil contaminants and how the soil biota and plants which are the keystone of this ecosystem get affected at various levels are discussed in detail. How the soil pollutants enter the food chain, accumulate in the environment, and the techniques on remediation of problem soils are explained in the following chapters of the book.

Chapter 1. *Soil Acidification and Its Impact on Plants*: Soil is a living entity. The chapter well manifests the structure, function of soil, and the significance of pH based on which the acidity and alkalinity of soil is determined. pH plays an important role behind various soil functions like soil aggregate stability, nutrient availability, metal toxicity, and biological activities. The chapter explains the causes behind soil acidification which nowadays relate to various anthropogenic practices and natural biogeochemical cycles. The effects of acidity on the nutrient availability for plant in soil, metal toxicity, soil biological functions, and physiology of plants are discussed. The pathways of how soil acidity affect the plant community structure are described. It also tells about the strategies to be adopted to combat soil acidification.

Chapter 2. *Challenges to Organic Farming in Restoration of Degraded Land in India*: Degraded land is the indication of declined levels of productivity and economy of a country. In India, soil degradation has created very critical image in both rainfed and irrigated areas; it becomes more significant as it supports 18% of world’s human population and 15% of world’s livestock population with only 2.4% of global land area in which 29% land is degraded. This chapter discusses some possible opportunities and challenges of organic agriculture in degraded lands as a reformative measure.

Chapter 3. *Biochemical and Molecular Responses of Plants Exposed to Radioactive Pollutants*: Radioactive substances are unstable natural substances that decay and emit ionic radiation continuously in their surroundings. These are widely used in medicine, electricity, agriculture, industry, and research practices, which accumulate in the surroundings. Plants uptake these radionuclide wastes from soil and absorb from air. These radionuclides with high energy interact with metabolic pathways and alter the molecular nature of plants eventually altering the biochemical products. This chapter discusses the accumulation of radioactive substances in the environment, their interaction with plants, and their rational aspects.

Chapter 4. *Cadmium*: *A Threatening Agent for Plants*: Amid all heavy metals, cadmium is one of the most serious pollutants as it can potentially accrue in plants and reaches to the next trophic level. A wide range of anthropogenic activities like phosphate fertilizers, green wastes, and sewage bio-solids to the soil leads to the addition of cadmium to soil. This chapter discusses its transport, mechanism of action and regulatory network, and harmful aspects of cadmium exposure to plants and its effect on seed germination, growth, development, chlorophyll content, photosystem and photosynthesis, carbon assimilation, and reproduction. It also explains the mechanism adopted by plants for cadmium detoxification and the technique adopted to nullify the toxicity of cadmium in halophytes and other treated plants.

Chapter 5. *Effect of Soil Polluted by Heavy Metals: Effect on Plants, Bioremediation, and Adoptive Evolution in Plants*: Heavy metals pertain to the most threatening agent affecting the biotic components of ecosystem due to its toxicity. The sources of heavy metal pollution in soil and how it affects the plant growth are detailed in the chapter. It manifests the factors affecting the metals bioavailability. The toxic effect of a variety of heavy metals in soil and on plants is discussed. The chapter gives details on the different eco-friendly remediation strategies evolved in the form of bioremediation/phytoremediation and the mechanism of their action along adoptive evolution in plants.

Chapter 6. *Plant Responses to Sewage Pollution*: Sewage is an amalgamation of various liquid and solid substances comprising both pathogenic and nonpathogenic microorganisms. The use of sewage as organic manure may increase the risk of exposure of soil and ultimately flora to pollutants. Heavy metals on being introduced into the food chain show bioaccumulation. This chapter discusses the positive as well as negative responses of plants to sewage effluents. Vermi-composting may be a safe alteration for sewage sludge. The transformation of sewage sludge compost by vermi-composting may be one of the most efficient tools to diminish the threat of heavy metal contamination caused by direct use of sewage sludge.

Chapter 7. *Soil Pollution Caused by Agricultural Practices and Strategies to Manage Them*: Soil plays the role of a mother for all living beings on earth. It acts as a source of water and nutrients facilitating the plant growth. Modern agricultural practices have resulted in another source of soil pollution due to overuse of agrochemicals and irrigation. These resulted in global food security but invariably affect the structure and function of soil biotic components, thus affecting soil fertility in turn. Long-term applications of agrochemicals affecting the soil physical properties and the activity of living nexus are detailed in this chapter. Among agrochemicals, pesticides are the most influential as it is bioaccumulable and enters the food chain and the water table due to its persistency, affecting the environment and human health in turn. The chapter also briefs the strategies to be adopted for reduction of agrochemicals and promoting organic farming.

Chapter 8. *Inorganic Soil Contaminants and Their Biological Remediation*: Soil remediation is indispensable for the sustainable development and conservation of ecosystem. There are several physical, chemical, and biological methods to remediate the contaminated area, among which biological methods are inexpensive, effortlessly pertinent, environmentally safe strategies. This chapter discusses the type of inorganic contaminants, their sources and implications for soils, and biological remediation potential of organisms and also provides an overview of the recent developments in this area.

Chapter 9. *Phytoremediation of Pollutants from Soil*: Due to unbridled industrialization various organic pollutants which are highly toxic and carcinogenic are released into the environment. Phytoremediation is an emerging, eco-friendly and potentially very effective green technology that utilizes plants to extract, detoxify, and accrue the toxic pollutants from the environment. This chapter focuses on remediation strategies for contaminated soil by using a variety of plants in order to understand the cleanup of the environment in an effective way. On the basis of their properties, organic pollutants can be degraded in the rhizosphere of the plants followed by degradation, sequestration, or volatilization.

Chapter 10. *Impacts of Soil Contaminants on Human Health with Special Reference to Human Physiognomy and Physiology*: Soil serves as a habitat for a broad spectrum of macro- and microorganisms. Discharge of pharmaceutical, medical, industrial, sewage, and household wastes in soil results in the growth of various lethal microbes, ultimately leading to the outburst of human diseases. Nutrient inequities of soil collectively with the pathogenic biotic community result in detrimental impacts on the health of humans, plants, and animals. This chapter endeavors to deliver elaborate and comprehensive information on the interaction between urban soil pollution and human health issues.

Chapter 11. *Impact of Herbicide Use on Soil Microorganisms*: Economic viability and easy application make herbicide use indispensable in modern agriculture. The effect of herbicide use on soil microorganisms, especially mycorrhiza, bacteria, and actinomycetes, ranges from positive to negative to no effects. Several short-term studies have shown transient negative effects in the early period of application. The chapter briefs the national and international status of pesticides and their effects on soil microorganisms. Any change in biotic components will alter the soil function in terms of soil heterotrophic respiration, activity of OM decomposing and nutrient-cycling microbes, enzyme activity determining the soil health, and plant productivity. The studies referred to in the chapter encourage the study of the long-term effect of herbicides involving various herbicides in variable environment.

Chapter 12. *Biological Magnification of Soil Pollutants*: Increasing population and urbanization pose a serious threat to the environment due to the unscientific disposal of huge solid and liquid wastes to its precious water bodies and agricultural land. Wastes released from industries had been proved to cause toxicity as heavy metals accumulate at different trophic levels without their role in the biological system. This chapter summarizes the main sources of soil pollutants and their role in biological magnification along with their adverse role at different trophic levels.

Chapter 13. *Soil Pollution and Human Health*: Disproportionate fertilizers and pesticide usage spoil groundwater through runoff and leaching. Accumulation of contaminants in soil may lead to their subsequent translocation to the food chain. Contaminants even at low levels may cause harm to human health and the environment. This chapter discusses the sources and assessment of soil contaminants, green technologies, policies, and the impact of pollution on human health.

Chapter 14. *Emission of Greenhouse Gases from Soil: An Assessment of Agricultural Management Practices*: Increase in the levels of greenhouse gases is a serious threat in the present scenario to both living beings and their niches. The agriculture sector has now become a potent contributor to emissions of greenhouse gases from soil to atmosphere and thus contributing to climate change. The chapter describes greenhouse gases and their characteristics. The methodology adopted in this chapter to draw conclusions was wide literature review with emphasis on developing countries over a period of 12 years from 2005 to 2016. The chapter provides information on the sources of greenhouse gases, position of agriculture in greenhouse gas emissions, and the role played by different agricultural management practices in the evolution of greenhouse gases. The chapter further discusses how environmental factors affect greenhouse gas emissions from soil and their effect on agriculture in turn and suggests different mitigation strategies to be adopted depending on the crop type and the environment.

Overall, this book provides all valuable information related to different kinds of soil pollutants, biomagnifications, their effect on soil and plants in terms of soil fertility, productivity, morphology, growth, physiology, and metabolism of plants along with biochemical changes. It also provides information on the evolution of greenhouse gases from soil on account of various agricultural management practices further leading to climate change in turn. The book also becomes the source of various remediation techniques adopted nowadays. It will definitely be useful for scientists, academicians, researchers as well as graduate and postgraduate students of different universities across the globe.

Prayagraj, UP, India — Pratibha Singh
Chapra, Bihar, India — Sunita Kumari Singh
Prayagraj, UP, India — Sheo Mohan Prasad

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# Contents

# About the Editors

**Pratibha Singh** has been working as DST—Women Scientist b (WOS b) in the Department of Botany at the University of Allahabad, India. Her areas of expertise include sustainable agriculture and the side effects of abiotic stresses present in the environment on soil and plants. The research work aims towards a holistic approach to achieving sustained soil fertility and productivity along with maintenance of plant health in terms of physiology and biochemistry in tropical croplands. Dr. Singh obtained her PhD in Botany from Banaras Hindu University, Varanasi, India. She received several fellowships from UGC, CSIR, and DST during her doctoral and postdoctoral programs. She has authored several scientific publications and two textbooks with reputed international publishers. She has participated in many national and international conferences and has presented her work in the form of both oral and poster presentations. She bagged several prizes as young scientist and won the best oral presentation award in an international conference. She has also delivered an invited talk at Malaya University, Kuala Lumpur, Malaysia. Dr. Singh is also the life member of Blue Planet Society and the Society for Science and Nature.

**Sunita Kumari Singh** is Assistant Professor in the Department of Botany at Jai Prakash University, Bihar, India. She obtained her PhD degree in Botany from Banaras Hindu University, Varanasi, India. Her expertise in research covers the effect of UV radiation stress on cyanobacteria. Her research interest is on environmental stress on cyanobacteria. She has authored many research publications in reputed journals and four book chapters. She has received UGC fellowships and Jawaharlal Nehru Memorial Fund scholarship during her PhD.

**Sheo Mohan Prasad** is Professor in the Department of Botany at the University of Allahabad. He obtained his MSc and PhD degrees from Banaras Hindu University, Varanasi, India. Prof. Prasad has authored more than 200 scientific publications and edited 10 books with renowned international publishers. He has guided 26 PhD students and 3 postdoctoral fellows and is supervising 10 research students on varied aspects of physiology and biochemistry of plants and cyanobacteria exposed to abiotic stresses—heavy metal, pesticide, salinity, high light and UV-B with special reference to the role of ROS as signaling and antioxidants regulation. Prof. Prasad is also the editor and reviewer of several reputed international journals. Prof. Prasad is also a fellow of the National Academy of Sciences, India, and the Indian Botanical Society and is a member of the International Society for Silicon in Agriculture.

# Abbreviations

| | |
|---|---|
| AM | Arbuscular mycorrhizal fungi |
| ANC | Acid neutralizing capacity |
| APEDA | Agricultural and Processed Food Products Export Development Authority |
| APOD | Ascorbate peroxidase |
| APOX | Ascorbate peroxidase |
| APX | Ascorbate peroxidase |
| ATP | Adenosine triphosphate |
| BD | Soil bulk density |
| BAF | Bioaccumulation factor |
| BNC | Base neutralizing capacity |
| BOD | Biological oxygen demand |
| CAT | Catalase |
| CDF | Cation diffusion facilitator |
| CEC | Cation exchange capacity |
| CEU | Continuing education unit |
| CFCs | Chlorofluorocarbons |
| Chernobyl NPP | Chernobyl Nuclear Power Plant |
| CPI | Crop pollution index |
| CRIDA | Central Research Institute for Dryland Agriculture |
| DAA | Days after application |
| DCP | 2,4-dichlorophenols |
| DDT | Dichlorodiphenyltrichloroethane |
| DH | Dehydrogenase |
| DHAA | Dehydroascorbic acid |
| DNA | Deoxyribonucleic acid |
| DSBs | Double-stranded breaks |
| DTT | 1,1,1-trichloro-2,2-bis p-chlorophenyl ethane |
| ECe | Soil electrical conductivity |
| EDTA | Ethylene diamine tetraacetic acid |
| EFSA | European Food Safety Authority |
| EMS | Ethyl methane sulfonate |
| EPA | Environmental Protection Agency |

| | |
|---|---|
| ESP | Exchangeable sodium percentage |
| ESRL | Earth System Research Laboratory |
| ETs | Economic thresholds |
| FAO | Food and Agriculture Organization |
| fb | followed by |
| FGD | Flue gas desulfurization |
| FMD | Foot and mouth disease |
| G6PDH | Glucose-6-phosphate dehydrogenase |
| GDP | Gross domestic product |
| GHGs | Greenhouse gases |
| GR | Glutathione reductase |
| GSH | Glutathione |
| GST | Glutathione S-transferase |
| GWP | Global warming potential |
| HFCs | Hydro-fluorocarbons |
| HMs | Heavy metals |
| ICAR | Indian Council of Agriculture Research |
| IPM | Integrated pest management |
| IQ | Intelligence quotient |
| IR | Ionizing radiation |
| IRT | Iron-regulated transporter |
| ISRO | Indian Space Research Organisation |
| IUCN | International Union for Conservation of Nature |
| $K_{\mathrm{sat}}$ | Saturated hydraulic conductivity |
| MDA | Malondialdehyde |
| MDGs | Millennium development goals |
| MIF | Micro irrigation fund |
| MRLs | Maximum residue limits |
| MTs | Metallothioneins |
| NABARD | National Bank for Agriculture and Rural Development |
| NADPH | Nicotinamide adenine dinucleotide phosphate |
| NAM | National Agriculture Market |
| NAPCC | National Action Plan on Climate Change |
| NGOs | Non-governmental organizations |
| NIH | National Institutes of Health |
| NORM | Naturally occurring radioactive materials |
| NPK | Nitrogen phosphorus potassium |
| NRA | Nitrate reductase |
| NWDPRA | National watershed development project for rainfed areas |
| OC | Organic carbon |
| OEC | Oxygen evolving complex |
| OM | Organic matter |
| OsHMA | *Oryza sativa* heavy metal ATPase |
| OsNRAMP | *Oryza sativa* natural resistance-associated macrophage proteins |
| OPT | Oligopeptide transporter |

| | |
|---|---|
| PAGE | Polyacrylamide gel electrophoresis |
| PAHs | Polycyclic aromatic hydrocarbons |
| PCBs | Polychlorinated biphenyls |
| PCP | Pentachlorophenols |
| PCs | Phytochelatins |
| PFCs | Per-fluorocarbons |
| PMFBY | Pradhan Mantri Fasal Bima Yojana |
| PE | Pre-emergence |
| POD | Peroxidase |
| POE | Post emergence |
| POPs | Persistent organic pollutants |
| POX | Guaiacol peroxidase |
| PPCPs | Pharmaceuticals and personal care products |
| PSCs | Pollution safe cultivars |
| RADP | Rainfed Area Development Programme |
| RAPD | Random amplification of polymorphic DNA |
| RNA | Ribonucleic acid |
| ROS | Reactive oxygen species |
| SAR | Sodium absorption ratio |
| SOC | Soil organic carbon |
| SOD | Superoxide dismutase |
| SOM | Soil organic matter |
| SQ | Soil quality |
| SSA | Sub-Saharan Africa |
| TBARS | Thiobarbituric acid reactive substances |
| TCE | Trichloroethylene |
| TERI | The Energy and Resources Institute |
| TN | Total nitrogen |
| TPH | Total petroleum hydrocarbon |
| TWI | Tolerable weekly intake |
| UN | United Nations |
| UNCCD | United Nations Convention to Combat Desertification |
| UNEP | UN Environment Programme |
| USNRC | United States Nuclear Regulatory Commission |
| USSR | Union of Soviet Socialist Republics |
| WAA | Weeks after application |
| WDCGG | World Data Centre for Greenhouse Gases |
| WFPS | Water-filled pore space |
| WHO | World Health Organization |
| WSC | Water splitting complex |

# Soil Acidification and its Impact on Plants

# 1

Durgesh Singh Yadav, Bhavna Jaiswal, Meenu Gautam, and Madhoolika Agrawal

## Abstract

Acidic soils are widespread covering nearly 40% of the world's total arable land area. However, soils of certain regions are naturally acidic but an increase in soil acidification as a result of accelerating anthropogenic activities is becoming a global issue. High emissions of acid precursors (nitrogen, sulfur, and carbon dioxide) in the atmosphere are chiefly responsible for acid precipitation, which in turn is a pre-eminent factor for soil acidification. Long-term application of nitrogen fertilizers is a major contributor in acidification of agricultural soil. Soil acidification is an important edaphic stress, which leads to cation leaching, instability in the soil aggregate structure, increases metal toxicity, lowers the soil nutrient availability, and consequently affects the soil biological properties and plant performances. The present chapter aimed to assess the consequent effects of soil acidification on plants and the plant community structure. It includes causes, processes, plants' responses, and remedial measures to combat soil acidification due to increasing pollution. Different plants may show different sensitivity to acidity and have diverse an optimal pH range for nutrient uptake. Besides, depletion of basic cations (Na, Ca, Mg, and K) due to leaching and increased solubility of toxic metals (Al and Mn) in soil restrict the plant's access to water and nutrients, thereby causing severe injury to roots, a reduction in crop yield, and an increase in plant susceptibility to pathogens. Plant diversity, species richness, and occurrence of species are significantly influenced by acidification of soil. Alteration in the plant community structure, in turn, may affect the ecosystem structure and functions. Acidification of soil could plausibly be ameliorated by nutrient management practices and by addition of acid-neutralizing substances.

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**Keywords**

Soil acidification · Plants · Crops · pH · Atmospheric depositions · Biodiversity

## 1.1 Introduction

The term “soil” has been derived from the Latin word “solum”, which means part of the earth’s crust that has been changed as a result of soil-forming processes. Soil (also known as the pedosphere) is the material, which slowly develops as a thin layer on the earth’s surface over time. It is mainly composed of organic matter, weathered mineral particles, living organisms, liquids, and gases; hence is one of the most important earth’s natural resources essential for living beings (Bhattacharyya and Pal 2015). Soil is a zone of plants’ growth where plant nutrients are stored through the interaction of diverse factors such as water, air, sunlight, rocks, flora, and fauna**.**

Depending upon various biotic and abiotic factors in different regions across the globe, there are broadly 12 classes of soil, viz. alfisols, andisols, aridisols, entisols, gelisols, histosols, inceptisols, mollisols, oxisols, spodosols, ultisols, vertisols, and others (rocky lands, shifting sand, and ice/glacier) (Fig. 1.1, Table 1.1).

### 1.1.1 Properties and Functions of the Soil

General physicochemical properties of the soil include texture (percentage of silt, clay, and sand in soil), temperature, pH, salinity, bulk density, porosity, moisture

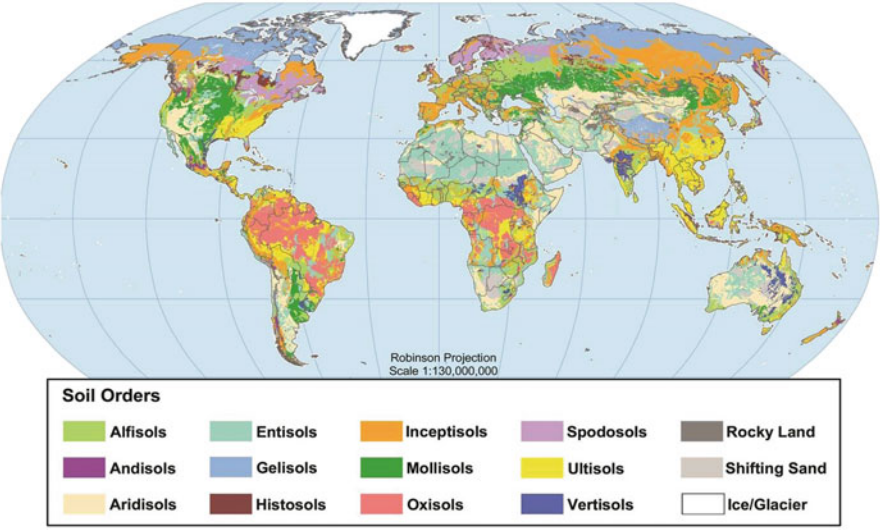


**Fig. 1.1** Types of the soil in various regions of the world (Source: Soil Survey Division 2005)

**Table 1.1** Key characteristics and occurrence of different classes of soil in various parts of the world

| No. | Class | Key characteristics | Regions |
|---|---|---|---|
| 1. | Alfisols | Commonly found in cool to hot humid areas, especially under forest and savannah grassland vegetation.<br>Fertile with moderate to high base saturation<br>Clay in subsoil horizons<br>Covers about 10% of the world's ice-free land area | Europe, Russia, southern part of the USA, Mississippi, and Ohio river valleys in the USA |
| 2. | Andisols | Form in volcanic ash and cinders<br>Not extensively weathered<br>High natural fertility and productivity<br>High organic matter, low bulk density and can easily be tilled.<br>Covers 1% of the world's ice-free land area | Limited geographic distribution |
| 3. | Aridisols | Generally light in color and extensively found in tropical latitudes, rain shadow areas, and arid climates.<br>Low organic matter with lime and salt accumulations<br>Water deficient with low productivity<br>High potential for land degradation due to overgrazing<br>Occupies 12% of the world's ice-free land area | South-western and northern part of the USA, Australia, and many middle east regions |
| 4. | Entisols | Little or no profile development in deep regolith<br>Found at the site of unstable environments (floodplains, sand dunes, or those found on steep slopes)<br>Vary in productivity potential | Geographically extensive and commonly found with aridisols |
| 5. | Gelisols | Soil associated with permafrost and have limited profile development<br>Soil organic matter on surface<br>Productivity limited by short growing season<br>Covers approximately 9% of the world's ice-free land area | Northern regions of Russia, Canada, and Alaska |
| 6. | Histosols | Organic peat lands or boggy soils<br>Consist of more than 20% organic materials by mass<br>Found in cool and marshy areas<br>Extent of the world's ice-free land area is 1% | Found mainly in geographically high latitude areas or other marshy wetlands |

(continued)

**Table 1.1** (continued)

| No. | Class | Key characteristics | Regions |
|---|---|---|---|
| 7. | Inceptisols | Found in the beginnings of soil profile development<br>Variable productivity potential<br>Covers 10% of the world's ice-free land area | Mainly in mountainous regions but occur almost everywhere |
| 8. | Mollisols | Mineral soils developed under grassland vegetation<br>Rich in organic matter<br>Very fertile due to high clay and organic matter contents<br>Extent of the world's ice-free land area is 7% | Eastern Europe, Russia, China, southern, and northern part of the USA |
| 9. | Oxisols | In hot and humid climates with high annual rainfall<br>Highly-weathered soils dominated by iron and aluminum oxides<br>Low in fertility and high in soil acidity<br>Physically stable soils with low shrink-swell properties<br>Covers 8% of the world's ice-free land area | Equatorial latitudes |
| 10. | Spodosols | Form in sandy materials under coniferous forest vegetation<br>Associated with a wet and cool climate<br>Coarse textured, high leaching potential, high organic matter, Fe and Al oxides contents. Acidic in nature and low soil fertility. Extent of the world's ice-free land area is 4% | Northern Europe, Russia, and north-eastern part of the USA |
| 11. | Ultisols | Intensely weathered soils of humid areas<br>Subsurface clay accumulations<br>Low in fertility and high in soil acidity<br>Covers 8% of the world's ice-free land area | Occur extensively in the south-eastern part of the USA, China, Indonesia, and equatorial regions of Africa |
| 12. | Vertisols | High content of clay minerals,<br>Dark colored with variable organic matter content (1–6%)<br>Typically form in limestone/basalt/ topographic depressions<br>Commonly formed in warm, subhumid, or semi-arid climates<br>Extent of the world's ice-free land area is 2% | North-Eastern Africa, India, and Australia with smaller areas scattered worldwide. |

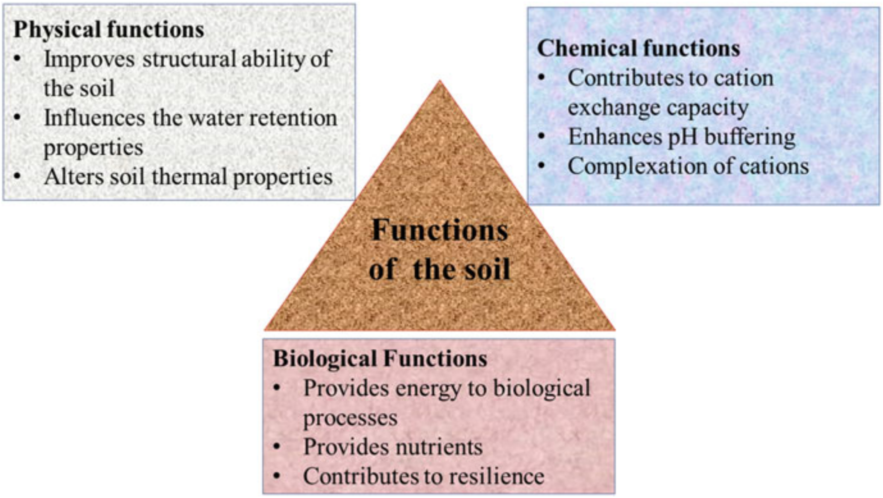


**Fig. 1.2** Physicochemical and biological functions of the soil

content, particle size, water-holding capacity, exchangeable cations ($Ca^{2+}$, $Na^+$, $Mg^{2+}$, $K^+$, $Al^{3+}$, and $Fe^{3+}$), cation exchange capacity, sodium exchangeable percentage, total nitrogen (N), available nitrogen (nitrate-N and ammonia-N), available phosphorous, total phosphorous, total organic carbon, organic and inorganic carbon, total and bioavailable metal(oid) contents (aluminum, Al; iron, Fe; zinc, Zn; nickel, Ni; selenium, Se; boron, B; copper, Cu; cobalt, Co; magnesium, Mg; manganese, Mn; cadmium, Cd; chromium, Cr; arsenic, As; and lead, Pb), humic acid, organic, and inorganic pesticides (Pandey et al. 2014; Gautam et al. 2017; Albers et al. 2019). Besides, microbial biomass, total enzymatic activities, activities of enzymes (dehydrogenase, peroxidase, alkaline phosphatase, polyphenol oxidase, urease, catalase, and nitrogenase), root exudates, soil basal respiration, and metabolic quotient are certain widely used biological parameters to assess the health of the soil (Choudhary et al. 2013; Pandey et al. 2014; Gautam et al. 2018).

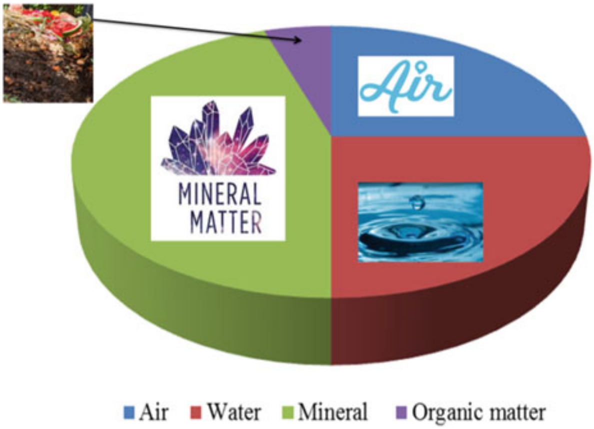
The soil functions within an ecosystem vary greatly from one place to another depending upon the parent material, position on the landscape, age of the soil, climatic variables, and animals' and plants' diversity (Fig. 1.2) (Schoonover and Crim 2015).

Soil functions are thus crucial for the biosphere and its main ecological roles include:

(a) **Support for structures**: The soils are widely used in making causeways and roads, as a foundation for buildings and bridges as well as for the establishment of agriculture crops and forestry.

(b) **Medium for plant growth**: The soil consists of four main components, viz. mineral matter (45%), organic matter (5%), water (25%), and air (25%) (Fig. 1.3). It is a source of physical support (root anchorage), air (ventilation),

**Fig. 1.3** Major components of the soil



water (holds rainwater, surface, and groundwater so that it can be utilized by plant roots), temperature moderation (acts as insulation for plants from extreme hot and cold conditions), protection from xenobiotics (removes toxic gases, decomposes, and absorbs organic/inorganic toxins), and supply nutrients (essential for their growth and development).

(c) **Regulate water supply**: The soil plays a pivotal role in cycling of freshwater. Water ending up into the water-body, i.e., lakes, rivers, estuaries, and aquifers, either traveled over the surface or through the soil. Soil filters and regulates water supply by restoration after precipitation. Management of the land area thus has a significant influence on the purity and amount of water that finds its way to aquatic systems.

(d) **Habitat for organisms**: Soil offers a shelter to billions of organisms (predators, prey, producers, consumers, and parasites). It provides a range of niche and habitat as well as types of habitats, which determine the specific organisms residing into it such as.

- Water-filled pores for swimming organisms like roundworms.
- Air-filled pores for insects and mites.
- Areas enriched in organic matter for various algae, fungi, parasites, lower, and higher plants.
- Areas with varied acidic, basic, and temperature regions for extreme dwellers.

(e) **Recycle wastes**: The soil system plays a significant role in nutrient cycling as soils have the ability to incorporate great quantities of organic waste, which then form humus. It converts the mineral nutrients of the wastes into utilizable constituents and has the ability to return carbon into the atmosphere in the form of $CO_2$. Plant residues and manures added to the soil increase nutrient concentrations, thereby enhancing the soil fertility.

### 1.1.2 Significance of pH

The pH is the measure of alkalinity and acidity of the soil (Fig. 1.4). Based on pH, the soil can be categorized into the following classes: extremely acid (≤4.4), very strongly acid (4.5–5.0), strongly acid (5.1–5.5), moderately acid (5.6–6.0), slightly acid (6.1–6.5), neutral (6.6–7.3), slightly alkaline (7.4–7.8), moderately alkaline (7.9–8.4), alkaline (8.5–9.0), and strongly alkaline (≥9.0). The pH scale (Fig. 1.4) shows various types of soils and their comparative relation with acidic and basic constituents based on their pH. Soil pH is one of the prime parameters that govern the soil aggregate stability, nutrient availability, metal toxicity, and biological activities (Goulding 2016).

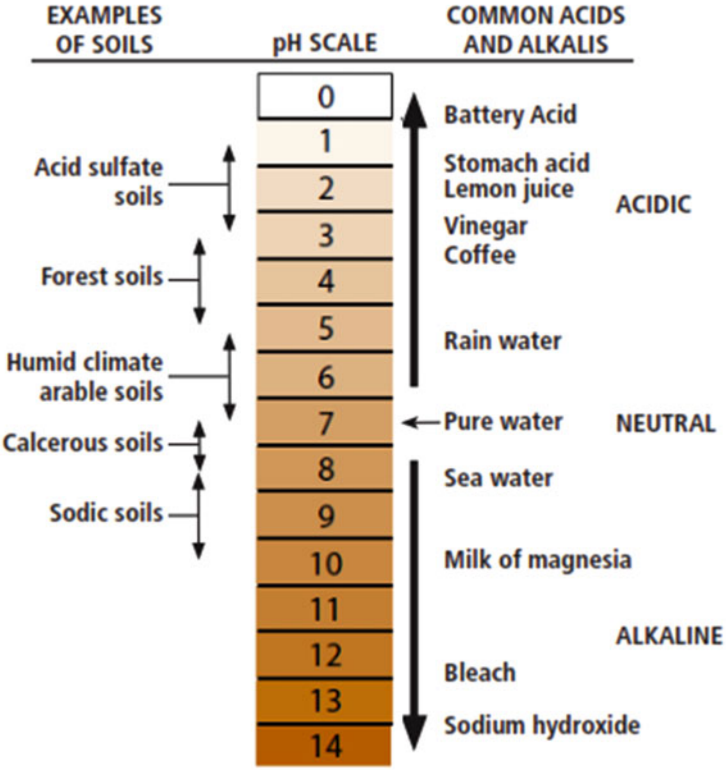


**Fig. 1.4** The pH scale (Source: McCauley et al. 2009)

## 1.2 Soil Acidification

The soil acidification is a process where pH of the soil decreases over time. It is defined as a decrease in acid-neutralizing capacity (ANC) or an increase in base-neutralizing capacity (BNC) resulting in an increase in acid strength as represented by a decrease in soil pH (Blake 2005):

$$\text{Soil acidity } (+\Delta \text{BNC}) = -(\text{soil alkalinity}) = \Delta \text{ANC}$$

Pedogenic acidification processes in aerated soils are (1) an addition of strong acid ($H_2SO_4$ and $HNO_3$) into soil through acid deposition, (2) release of many organic acids and $H^+$ ions into the soil by plants and soil microbes and (3) uptake of basic cations by biota.

Soil acidification under natural conditions mainly occurs due to weathering of parent materials having high silica (rhyolite and granite), and sand with low buffering capacities and in regions with high precipitation (McCauley et al. 2009). Precipitation leads to leaching of base-forming cations with a simultaneous lowering of soil pH. Naturally occurring acidic soils are commonly found in areas at higher elevation, mining sites containing pyritic (Fe and elemental S) minerals, forest soils, and in areas where soils are formed from the acid-forming parent material. The process of soil acidification nowadays has been accelerated by human-induced activities such as agricultural practices, mining, metallurgical processes, etc. For instance, almost 5,00,000 ha of agricultural and rural land have acidified in Queensland (Rolfe et al. 2002). Intensive agricultural practices in coastal areas with a high precipitation rate are most at the risk of soil acidification (Duan et al. 2016). Soil acidification is a consequence of a dramatic increase in anthropogenic acid deposition originating chiefly from atmospheric sulfur dioxide ($SO_2$) and nitrogen oxides ($NO_x$) during agricultural fertilization and fossil fuel combustion (Zhao et al. 2009; Yang et al. 2012).

Soil acidification may have a negative impact on the entire ecosystem because soil is a fundamental interface where the atmosphere, lithosphere, hydrosphere, and biosphere meet. Any undesirable change in the baseline properties of soil affects a range of natural resource functions, which include soil micro-flora and fauna, vegetation structure, terrestrial animals, aquatic biota, atmospheric constituents, weed control, infrastructure, and human health (Singh and Agrawal 2004; Yang et al. 2015; Chen et al. 2016; Stevens et al. 2018). Some of these have wide community impacts through soil degradation and include the loss of native biodiversity that may impact on recreation and tourism (Singh and Agrawal 2007; Tian and Niu 2015).

### 1.2.1 Causes of Soil Acidification

Acidification of soil is accomplished through protons ($H^+$), which release into the soil mainly by atmospheric acidic substances, cation assimilation by plants, mineralization of anions of organic matter, weak acid deprotonation, mineral weathering, oxidation-reactions, etc. Sources of soil acidification are given in the following subsections.

#### 1.2.1.1 Ammonium Fertilizers

Ammonium ions from the nitrogenous fertilizers form nitrate and hydrogen ions. Uptake of nitrate ions by the plants release hydroxide ($OH^-$) ions to maintain the ionic balance. Hydroxide ions combine with positively charged hydrogen ions to form water. On the other hand, when nitrate ions are not taken up by the plants, leaching of these ions occurs and hydrogen ions are left in the soil, thus causing acidification. Hydrogen ions are tightly bound to soil particles as compared to other ions, which causes leaching of other positive ions such as $Na^+$ and $Ca^{2+}$. (Blake 2005) thereby increasing the concentration of $H^+$ ions. Also, in the process of plant uptake of nitrate, one $H^+$ ion is left that cannot be neutralized by $OH^-$ ions, cumulatively contributing to soil acidification (Bolan et al. 1991). Excessive application of fertilizers thus leads to soil acidification. Use of N-fertilizers lowers the ANC of soil (Van Breemen et al. 1984). Bolan et al. (2005) reported that ammonium sulfate has the highest acidity equivalence (i.e., the required number of parts by weight of lime to neutralize the 100 parts of fertilizer.) of 110, followed by ammonium chloride, urea, diammonium phosphate, ammonium nitrate, etc.

Tian and Niu (2015) reported a reduction in soil pH on N addition. The effect was different on different ecosystems such as grassland, tropical, and temperate forests, which showed a significant difference while boreal forest soil pH was not much affected by N addition. Tian and Niu (2015) also reported that $NH_4^+$ and $NO_3^-$ forms of fertilizers are more contributing to soil acidification than the $NH_4^+$ form.

#### 1.2.1.2 Atmospheric Depositions

Atmospheric depositions of N and S contribute to soil acidification (Singh and Agrawal 2007). Emissions of $SO_2$ and $NO_x$ from combustion processes are chief sources of soil acidification in the region of temperate forest (Singh and Agrawal 2007). China has controlled its S emission since 2001, yet the Pearl river delta soil is acidified due to S deposition (Huang et al. 2019).

Acid rain has a remarkable contribution in acidification of soil (Singh and Agrawal 2007). $SO_2$ and $NO_x$ are the gases responsible for acid rain. Acid rain has pH generally less than 5.6 and $H^+$ ions more than 2.5 μ eq. $L^{-1}$ (Evans 1984). Various anthropogenic activities are responsible for emission of these gases such as fossil fuel combustion, industrial, mining processes, etc. Natural sources include volcanic eruption, oceans, lightening, and biological processes (Singh and Agrawal 2007). These gases react with water and other pollutants and cause acidification of rain. Wet depositions of acid directly add acid to the soil and when dry deposition occurs $SO_2$ mixes with soil water and produces acid ($H_2SO_4$). Similarly, $NH_4^+$ ions mix with water and produce nitric acid. Many reports showed that acid rain caused a significant decrease of soil pH (Singh and Agrawal 2007).

Increasing concentration of $CO_2$ in the atmosphere is also a source of soil acidification. Atmospheric $CO_2$ reacts with water to form carbonic acid whose deposition may lower soil pH. Oh and Richter Jr (2004) reported that the soil $CO_2$ concentration increases proportionally with the increase of atmospheric $CO_2$.

### 1.2.1.3 Leguminous Crops

Haynes (1983) reported that cropping of legumes either for short or long duration lowers the pH of soil. Legume cultivation induces soil acidification due to disturbance in the C and N cycles. Mineralization and nitrification processes cause $NO_3^-$ leaching and legume plants during $N_2$ fixation uptake more cations than anions, thereby releasing more $H^+$ ions from roots to the soil environment. When legume biomass is removed from the soil, pH of soil is reduced more, causing acidity (Yan et al. 1996). Different leguminous species have different acidifying capabilities. Legumes growing in the tropical region are less effective in acidifying soil than in the temperate region (Tang et al. 2013). Acidification of subsurface soil is more common as legumes have a deep root system. Surface-acidified soil can be easily reclaimed through liming or other methods; thus, subsurface soil acidification by leguminous plants is of more concern (Tang et al. 2013). Dinkelaker et al. (1989) reported that legumes induce more acidification in soil deficient with phosphorous (P). In young plant residue, organic N is higher and organic anions are low, which reduce the pH of soil and older plant residue tends to increase the pH (Yan et al. 1996). Thus, residue return is an important agricultural practice to prevent soil acidification.

Leaching of carbonates leads to soil acidification as carbonates in soil act as buffer. Wang et al. (2015) reported that up to a certain level ($<1\%$), carbonate in soil is required to reduce the drop level of carbonates to maintain the soil pH and to reduce the toxic effects of heavy metals.

### 1.2.1.4 Organic Acids

Formic acid, acetic acid, and oxalic acid are the major organic acids that are present in acid rain (Sun et al. 2016). There are two sources (direct and indirect) of organic acids in the atmosphere, contributing significantly to acid rain formation (Singh and Agrawal 2007). The direct sources of organic acids are fossil fuel and biomass burning, emission from vegetation and automobiles, volcanic eruptions, lightening, etc., whereas the indirect or secondary sources include secondary reactions involving the precursors such as terpenes, isoprenes, aldehydes, marine olefins, hydrocarbons, etc., and sunlight that occur in the atmosphere.

### 1.2.1.5 Industries

Mining and industrial processes such as coal and sulfide-containing ores' mining, manufacturing of electronic stuffs, textiles, tanneries, and food-processing activities, and drain acids in the environment are also some important contributors of soil acidification (Bolan et al. 2005). Many other industries discharge their acidic effluents that cause acidification of soil. Industries also emit $SO_x$ and $NO_x$ in the atmosphere that are deposited on soil, either in wet and dry forms and reduce soil pH.

## 1.2.2 Process of Acidification

Hydrogen ions in soil come from a wide range of sources including natural biogeochemical cycles:

### 1.2.2.1 Carbon Cycle

Carbon dioxide from the atmosphere enters the soil and forms carbonic acid, which further dissociates and adds $H^+$ ions to the soil. Similarly, organic acids also produce $H^+$ ions. The substrates for the reactions are available through various natural and anthropogenic processes and the processes generally occur in the forward direction (Robson 2012).

$$\mathrm{CO_2 from\ atmosphere} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \leftrightarrow \mathrm{H_2CO_3} \leftrightarrow \mathrm{HCO_3}^{-} \leftrightarrow \mathrm{CO_3}^{-2}\text{-Inorganic reaction}$$

$$C_6H_{12}O_6 \leftrightarrow RCOOH/ROH \leftrightarrow RCOO^{-}/RO^{-}\text{-Organic reaction}$$

### 1.2.2.2 Nitrogen Cycles

Several forms of N present in soil deposited through the atmosphere or through anthropogenic activities interchange forms and the dissociated $H^+$ ions are added to the $H^+$ ion pool of the soil. In the N cycle, plants share equal contribution in soil acidification, as the process of uptake and assimilation of $NH_4^+$ and $NO_3^-$ as well as N fixation directly or indirectly releases $H^+$ ions in soil. Similarly, processes of ammonification, nitrification, and volatilization of $NH_4^+$ cause acidification of the soil (Bolan et al. 1991). Nitrification of organic N reduces pH of the soil (Yan et al. 1996).

Nitrogen from the atmosphere, fertilizers, and other organic sources →

$$RNH_2 \leftrightarrow NH_3 \leftrightarrow NH_4^+ \leftrightarrow NO_3^-$$

$$Volatilization\ of\ NH_4^+ \rightarrow NH_4^+ \leftrightarrow NH_3 + H^+$$

### 1.2.2.3 Miscellaneous Processes

Sulfur and P cycles also contribute to addition of $H^+$ ions in soil that leads to acidification (Robson 2012).

Weak hydroxide-forming cations such as Al, Mn, and Fe either in their exchangeable forms or bound onto clay particles and/or organic matter react with water and release $H^+$ ions in the soil (Blake 2005).

$$\mathrm{Al^{3+}} + \mathrm{H_2O} \rightarrow \mathrm{AlOH^{2+}} + \mathrm{H^+}$$

$$\mathrm{Al^{3+} + 2\,H_2O \rightarrow Al(OH)_2{}^{+} + 2\,H^{+}}$$

Organic matter in soil after decomposition also releases $H^+$ ions (Bolan et al. 1991). Likewise, mineralization of organically bound N followed by nitrification of the product release $H^+$ ions in soil.

$$\mathrm{CO_2 + R\text{-}CH_2OH \rightarrow RCOO^{-} + H_2O + H^{+}}$$

$$R - C - \mathrm{NH_2 \rightarrow NH_3 + H^{+} \rightarrow NH_4{}^{+} + 2\,O_2 \rightarrow NO_3 + H_2O + 2\,H^{+}}$$

### 1.2.2.4 Acid Rain

For the formation of acid rain, oxides of S and N play lead roles. These oxides react with water in the presence of sunlight and form acid mists. These mists after condensation precipitate in the form of acid rain. Reactions involved in the formation of acid rain are given below.

$$SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow H^+ + HSO_3{}^-$$

$$HSO_3 + O_3 \rightarrow SO_4{}^{2-} + H^+ + O_2$$

$$2\,SO_2 + O_2 \rightarrow 2\,SO_3{}^-$$

$$SO_3{}^- + H_2O \rightarrow H_2SO_4$$

$$N_2 + O_2 \rightarrow 2\,NO$$

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

$$4NO_2 + O_2 + 2\,H_2O \rightarrow 4\,HNO_3$$

$$O_3 + NO_2 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \rightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2\,HNO_3$$

Ozone ($O_3$) molecules are also responsible for the formation of acid rain through generation of hydroxyl radicals, which help in breakdown of S and N oxides and other organic molecules to form organic acids (formic and acetic acids) (Singh and Agrawal 2007). Formic acid is produced by oxidation of formaldehyde. Hydrated formaldehyde is produced when formaldehyde combines with water, which in turn reacts with hydroxyl radicals to form formic acid. Reactions for organic acid formation are:

$$HCHO + H_2O \rightarrow CH_2(OH)_2$$

$$CH_2(OH)_2 + OH \rightarrow CH(OH)_2$$

$$CH(OH)_2 + O_2 \rightarrow HO_2 + HCOOH$$

## 1.3 Effects of Acidification on Soil Properties

Soil acidification poses influential impacts on soil fertility, biological activity, and plant productivity (Table 1.2). Acidification of soils either due to natural or anthropogenic interventions may cause the following problems:

### 1.3.1 Water Availability

Soil acidification alters the structural stability of soil, which ultimately affects its porosity and water-holding capacity. This, in turn, may limit the plant's ability to use soil moisture.

### 1.3.2 Soil Aggregate Instability

An increase in the availability of clay minerals such as oxides and hydroxides of Al and Fe plausibly results in a poor soil structure and irreversible damage to the clay content of soil. A lack of Ca in soil also causes soil structural problems (Pal et al. 2016).

**Table 1.2** Effects of pH on the availability of nutrients and metals in the soil

| pH range | Effects |
|---|---|
| <6.0 | Usually have a low availability of N, K, S, P, Ca, mg, and molybdenum (Mo), whereas solubility of heavy metals such as Al, Fe, Ni, co, cd, Cr, as, Pb, etc. is high under acidic conditions. |
| 6.0–7.0 | Favorable for plant growth because most plant nutrients are readily available in this pH range. However, some plants sustain at pH either above or below this range. |
| 6.6–7.3 | Favorable for microbial and enzymatic activities, thereby affecting availability of nutrients in soils. |
| >7.8 | Potassium, S, Ca, Mg, and Mo are abundant, while there is inadequate availability of N, Fe, Mn, Cu, Zn, and other toxic metals |
| >8.5 | Phosphorous and B are readily available |

### 1.3.3 Nutrient Cycling

Soil's ability to hold nutrients is significantly related to its cation and anion exchange capacities, which in turn are influenced by pH (McCauley et al. 2017). Soils with higher amounts of clay and/or organic matter have higher cation exchange capacity and so are able to bind more cations when compared to silty or sandy soils (McCauley et al. 2017). Maximum plant nutrients are optimally available in the pH range of 6.5 to 7.5 (Dinesh et al. 2014). This pH range is also suitable for plant root growth. Availabilities of Cu, Fe, Zn, Mn, and Al are increased in acidic soils because at low pH, fewer metal ions are adhered to the soil surface, readily found in soil solution, and thus are more available for plant uptake. At low pH, S and base-forming cations ($Ca^{2+}$, $Mg^{2+}$, $K^+$, and $Na^+$) are displaced by $H^+$ ions and may not be bioavailable because of their loss from the soil through leaching or uptake (McCauley et al. 2017). Nitrate is equally available across soil pH levels because it doesn't bond much to the soil. In general, N, P, K, Ca, Mg, and S are more available within soil pH is 6.5 to 8, while B, Cu, Fe, Mn, Ni, and Zn are more available within soil pH is 5 to 7. The soil pH below 6.0 may cause deficiencies of N, P, S, K, Ca, and Mg in the soil due to their reduced bioavailability under acidic conditions (Fig. 1.5). Maximum numbers of plant nutrients (especially micronutrients) tend to be unavailable at pH above 7.5 except Mo, which is abundant at moderately alkaline pH (Fig. 1.5). Plants showed poor root growth performance under acid soil conditions due to less availability of plant nutrients, which are essential for growth (Matsumoto et al. 2017). However, N, S, and K are the main plant nutrients, which are less affected by soil acidification to some extent.

Phosphorus is directly affected by soil conditions and becomes unavailable to plants at high and low soil pH. At pH greater than 7.5, phosphate ions react with Mg and Ca to form insoluble complexes. Similarly in acidic soil, phosphate ions react with Al and Fe to form least soluble compounds (Penn and Camberato 2019).

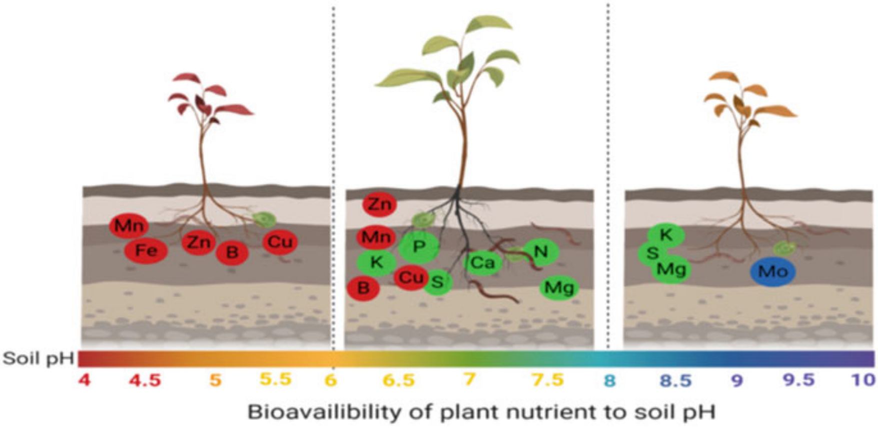


**Fig. 1.5** Plant nutrient availability in acidic, neutral, and basic soil pH ranges

$$\begin{array}{lll} Ca^{2+}(H_2PO_4)+2\,Ca^{2+} & \rightleftarrows & Ca_3(PO_4)_2+4H^+ \\ (\text{Soluble})\quad (\mathit{Adsorbed}) & & (\text{Insoluble}) \\ Al^3+(H_2PO_4)_2 & \rightleftarrows & 2H^+ + Al\,(\text{OH})_2H_2PO_4 \\ (\text{Soluble})(\text{Insoluble}) & & \end{array}$$

### 1.3.4 Metal Toxicity

Mobility of metals increases with a decrease in soil pH, which when crosses certain threshold levels may cause toxic effects on living organisms (Gautam and Agrawal 2019). Contents of metals such as Cd, Cr, As, and Pb are deleterious for soil biota, growth, and development of plants (Chibuike and Obiora 2014). At pH less than 5.5, high concentrations of Al and Mn in the soil solution can reach toxic levels and limit crop production (McCauley et al. 2009). Aluminum is toxic to plants and severely restricts root growth. Acidity of soil may increase the net loss of soil nutrients such as Mn, Cu, Fe, B, and Zn (Ahmadpour 2011). Low levels of Ca and Mg due to competitive behavior with metals may cause stock health problems such as milk fever and grass tetany (Boom 2002).

### 1.3.5 Soil Biological Properties

Soil microorganisms, primarily bacteria and fungi, have the ability to solubilize the nutrients, cause decomposition of organic matter, and regenerate secondary mineral nutrients. Acidification of soil reduces and even stops the activity and survival of useful soil organisms such as nitrogen fixers, decomposers, and nutrient recyclers (Jacoby et al. 2017). Soil acidity is thus becoming a major problem in modern agricultural systems, which are affecting the soil microbial community (Li et al. 2017). Moreover, the above-mentioned processes occur at desirable pH ranges and acidification of soil lowers the process and impede with soil ecological balance (Hayakawa et al. 2014). Rousk et al. (2010) and Lauber et al. (2009) reported that microbial diversity is often highest in near-neutral soils and significantly lowers in acidic soils.

Microbial activity is considerably reduced at pH 5 and below (Rashid et al. 2016). Certain “specialized” microorganisms, such as nitrifying and nitrogen-fixing bacteria associated with many legumes, generally perform poor when soil pH falls below 6 (McCauley et al. 2009). Nodulation in leguminous plant roots is regulated by soil pH. In acidic soil, more than 90% of nodule formation fails to persist in legumes such as cowpea, alfa-alfa, pea, and soybean in both determinate and indeterminate nodule formation (Ferguson et al. 2013). Furthermore, low soil pH limits both rhizobia survival, and root growth, and hence reduces the chances of root’s contact with enough bacteria, which help in nodule formation, resulting in nitrogen deficiency in soil (Ferguson et al. 2013). For instance, alfalfa (a leguminous plant) grows best in soils with pH levels greater than 6.2 when associated nitrogen-fixing bacteria also grow well (McCauley et al. 2009). Nutrient availability of plants gets reduced and causes poisoning mainly due to a decline in the rate of mineralization of nutrients by microorganisms under acidic soil (Zhalnina et al. 2015). In acidic soil, fungal dominance is greater than bacteria because of its growing ability over a broader range of soil pH (Herold et al. 2012). The fungi can best grow in the pH range of 4.5–7.5; however, high bacterial growth occurs within pH ranging from 5.5 to 7.0. Under acidic conditions, soil is majorly regulated by fungal dominance, whereas at high soil pH, bacterial denitrification occurs (Chen et al. 2015).

Organic mats often form on the soil surface as a result of reduced biological activity and organic matter is not being broken down. Helpful soil microorganisms may be prevented from recycling nutrients (e.g., nitrogen supply may be reduced). When soil pH is extremely acidic or basic, pH modifications may be needed to obtain optimal growing conditions for specific crops.

## 1.4 Effects of Soil Acidification on Plants

The s*oil*s are the prime receptor of *acid deposition* and function as sink. Soil acidification coupled with acid precipitation has been reported to have deleterious effects on plants (Bolan et al. 2005). The increasing rate of soil acidity is a worldwide problem and approximately 40% arable land is acidic (Ferguson et al. 2013).

Acid deposition has been very much discussed and now gained public attention since the 1970s in the European countries and the USA. It has now become an important problem in South Asia (Menz and Seip 2004). Acidic deposition can affect higher plants either through foliar surfaces or through roots. Under acidic deposition, a wide range of sensitivity has been shown by plants. Young rootlets, root hairs, leaves, and apical shoots are highly sensitive to acidic conditions (Lal 2016). Plant growth can be affected by both directly and indirectly due to acidic deposition. The direct effect of acid deposition includes foliar damage, which ultimately causes physiological and morphological alternations, necrotic spots, and discoloration (Singh and Agrawal 2007; Kohno 2017). Plant structures, specifically leaves, are highly sensitive to acidic deposition (Du et al. 2017). Some commonly observed changes in plants due to acidic deposition are loss of cuticular waxes due to alteration in its chemical composition (Elliott-Kingston et al. 2014), increase in membrane permeability (Jin et al. 2013), reduction in chlorophyll content (Du et al. 2017), altered dark respiration rate (Liang et al. 2013), and loss of cold tolerance habit (Menz and Seip 2004). Acidic soil can also prevent seed germination and the rate of seedling survival (Liu et al. 2011).

Indirect effects of acidic deposition encapsulate crown dieback, reduction of canopy cover, and increase in plants' mortality (Huang et al. 2015). Such deleterious effects of soil acidification caused by acid deposition ultimately lead to a decrease in plant growth and under extreme conditions dieback of entire forest occurs (Huang et al. 2015). Moreover, the pH 3.8 and 5.4 were found to be moderately inhibiting the germination rate of seeds of Norway spruce, Scots Pine, and Silver birch (Reid and Watmough 2014). It was also reported that 34% of trees population showed discoloration of needles as well as leave losses. Around half of Germany's woodland got infected by diseases by the end of 1984. After witnessing great losses in a forest ecosystem in Germany, United States, and Europe have started intensive research toward measuring the ecosystem losses due to acid precipitation, its precursors, and their possible effects on forests (United Nations/European Commission 2002).

### 1.4.1 Effects on Crop Plants

Sensitivity of plants to soil acidification may vary widely with different species of plants and according to their tolerance level to acidity. Therefore, plants have different optimal soil pH ranges (Matsumoto et al. 2017). The impact of soil acidity on plant growth is likely to be insidious and a major impact occurs in the root region. Table 1.3 enlists certain crop and forage species, which are sensitive toward acidification below a certain pH level. Critical soil pH differs with crop cultivar and soil texture; therefore, critical values mentioned in the literature vary. Certain horticultural crops, temperate legumes, and grasses are highly sensitive to acidic soil conditions (such as carrot, cabbage, tomato, alfalfa, white clover, macadamia nut, banana, avocado, litchi, perennial ryegrass, and red clover) (Goulding 2016; Tomic

**Table 1.3** Sensitivity of common crops and forage species and soil pH values below which growth may be restricted (adapted from Goulding 2016)

| Sr. No. | Critical soil pH | Crop & Forage |
|---|---|---|
| 1. | 6.0 | Field bean (*Vicia faba*) |
| 2. | 6.2 | Lucerne (*Medicago sativa*) |
| 3. | 5.9 | Barley (*Hordeum vulgare*)<br>Sugar beet (*Beta vulgaris*)<br>Pea (*Pisum sativum*)<br>Vetch (*Vicia sativa*)<br>Red clover (*Trifolium spp.*) |
| 4. | 5.6 | Oilseed rape (*Brassica napus*)<br>White clover (*Trifolium spp.*) |
| 5. | 5.5 | Maize (*Zea mays*)<br>Wheat (*Triticum aestivum*) |
| 6. | 5.4 | Kale (*Brassica oleracea var. acephala*)<br>Swede (*Brassica napus var. napobrassica*)<br>Linseed (*Linum usitatissimum*)<br>Turnips (*Brassica rapa*) |
| 7. | 5.3 | Oat (*Avena spp.*)<br>Timothy (*Phleum pratense*)<br>Cocksfoot (*Dactylis glomerata*) |
| 8. | 4.9 | Potato (*Solanum tuberosum*)<br>Rye (*Secale cereale*) |
| 9. | 4.7 | Fescue (*Festuca spp.*) |

et al. 2018). Furthermore, crops such as cowpea, oat, finger grass, sweet potato, kikuyu grass, catalina love grass, and sugarcane are highly tolerant (Haling et al. 2011). Nevertheless, severe soil acidity has been known to limit the growth of all plant species, including the highly tolerant ones (Goulding 2016).

The soil pH is the chief indicator of the soil situation, which affects the yield and quality of crops by increasing unavailability of essential elements (Morgenstern et al. 2010). Schroder et al. (2011) reported that wheat yield losses in Oklahoma between 1995 and 2002 were accorded with a higher change in soil pH during the same period of time. Under low soil pH conditions, the plant root system gets damaged, resulting in poor growth performance with no typical leaf symptoms as are often seen under N or K deficiencies.

Specific damaging effects on plants due to high dissolution of harmful elements in acidic soil include:

1. Poor and abnormal root development of plants due to the release of high amounts of $Al^{3+}$ in acidic soil. Morphologically, roots become stubby, short, and thick. Fine roots are poorly developed. Thus, insufficient water and nutrient uptake are facilitated by poor and inefficient root system (Rout et al. 2001; Bojorquez-Quintal et al. 2017).
2. The soils that have been acidified due to rigorous agricultural practices are prone to Mn toxicity. The legume crops such as dry beans growing in the temperate region showed sensitivity toward soluble forms of Mn at higher concentrations in soil. Recently, it has been observed that Southern Africa is facing a widespread problem due to increasing manganese toxicity (Reichman 2002).

### 1.4.2 Effects on Plant Community Structure

Plant community structure supports the ecosystem structure and functions such as productivity, resilience, and stability (Dovciak and Halpern 2010; Cardinale et al. 2012). Atmospheric deposition due to various anthropogenic activities leads to a significant increase in soil acidity due to fossil fuel combustion, agricultural emissions, waste discharges, etc. (Gheorghe and Ion 2011). The pathway to soil acidification-induced changes in plant community structure and productivity is illustrated in Fig. 1.6. Several studies have evidenced the decline in the plant community structure and productivity of aboveground plant accredited to an increase in soil acidification (Blake et al. 1994; Stevens et al. 2010; Van den Berg et al. 2011). Chen et al. (2013) reported higher reductions in plant species richness and productivity of *Stipa grandis*, *Agropyron cristatum*, *Achnatherum sibiricum, Cleistogenes squarrosa*, *Carex korshinskyi*, *Chenopodium aristatum*, *Salsola collina,* and *Chenopodium glaucum* in the second sampling year than in the first sampling year under seven different levels of acid additions (0, 2.76, 5.52, 8.28, 11.04, 13.80, and 16.56 mol $H^+$ $m^{-2}$ in the form of sulfuric acid solution) in the semiarid Inner Mongolian grassland region.

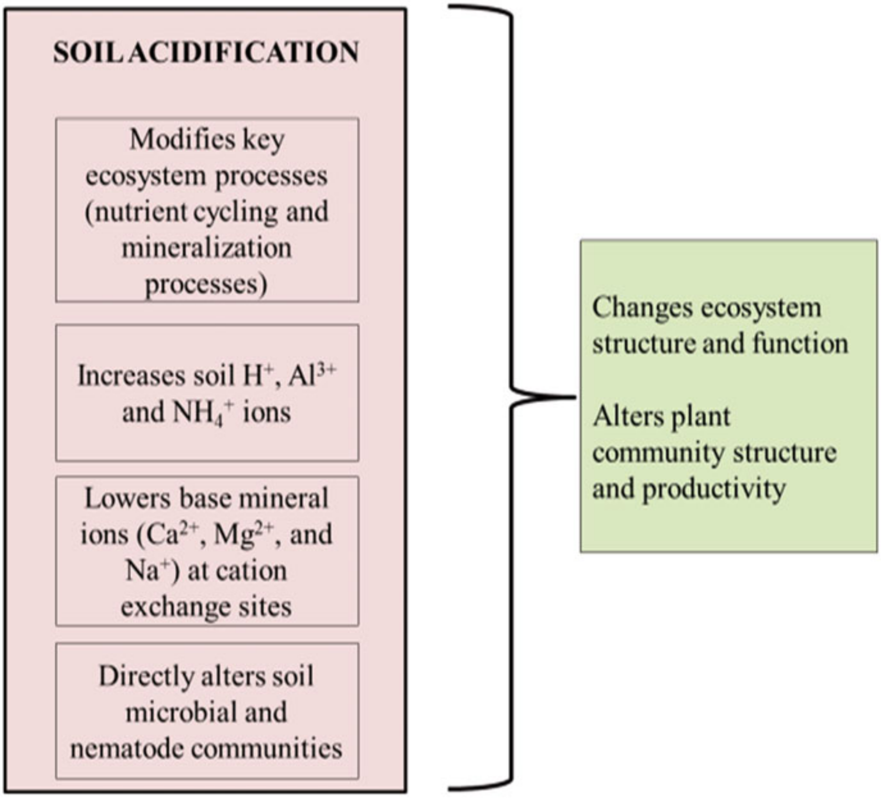


**Fig. 1.6** Effects of soil acidification on plant community structure through various pathways

Zarfos et al. (2019) surveyed soil and understory vegetation at 20 different watersheds in hardwood forests of Adirondack Park, New York. This northern temperate forest is typified with acidic soil (pH ranged from 2.96 to 4.56), mainly due to glacial scouring of granitic gneisses/metasedimentary rock and atmospheric depositions. The study showed a significant reduction in understory plant diversity and richness at places where soil pH is very low ($pH < 3$). Also, soil acidification alters the composition of plant communities.

## 1.5 Adaptive Strategies to Combat Soil Acidification

Soil acidification is becoming an issue in areas where soils are unable to buffer their decreasing pH levels (Kunhikrishnan et al. 2016). With the dawn of the industrial era, various S- and N-rich emissions from different sources led to acidic precipitations, which have caused the soil acidification. Other activities such as mining and metallurgical extractions also increase the input of acid produced by

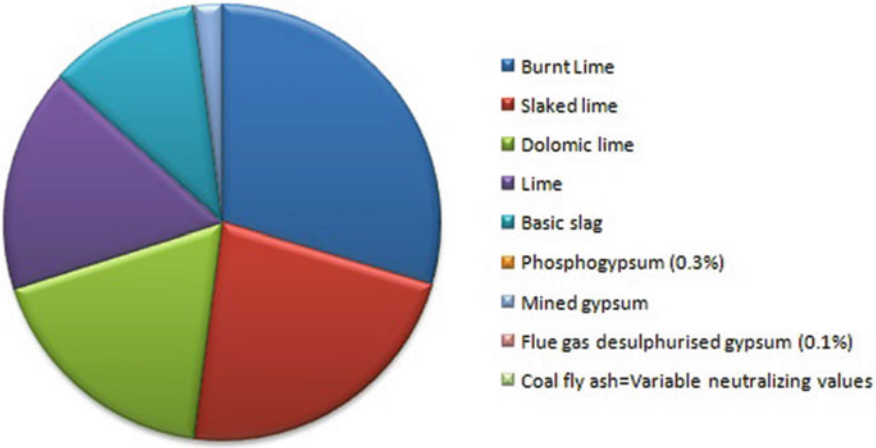


**Fig. 1.7** Various liming materials and their neutralizing value expressed as weight percentage of pure lime (Modified from Bolan et al. 2003)

pyrite oxidation (Pal 2017). Such practices resulted into massive destruction and decline to flora and fauna of the affected regions. In the view of above, mitigation and management of acidic soil come into focus. To deal with the issue of soil acidification three major strategies could be adapted:

1. Decease the extent of $H^+$ ion generation,
2. Reducing the extent of the processes involved in $H^+$ and $OH^-$ ions formation, and.
3. Countervail the produced acidity (Bolan et al. 2003).

These strategies could be implemented by the addition of some neutralizing materials into the soil.

Traditionally, addition of different forms of lime (Fig. 1.7) has been the most commonly used method to alleviate the acidification of the soil (Goulding 2016). However, the quantity of liming substances required for the acidity regulation depends on the buffering capacity of soil and the neutralizing value of liming substances (Fig. 1.7).

Apart from general liming materials, substances having Ca-containing liming potential such as phosphate rock, gypsum, fluidized bed boiler ash, and fly ash are also used for rectifying soil acidity (Dalefield 2017). Phosphate rocks are composed of two substances, viz. free calcium carbonate ($CaCO_3$) and apatite as phosphate minerals (Goulding 2016). Phosphate rocks have liming potential due to available free $CaCO_3$ and the $H^+$ ion-consuming capacity of apatite reduces the soil acidity. The $CaCO_3$ part of phosphate rocks dissolves rapidly and provides immediate response for soil acidity; while, apatite is a slowly dissolving substance, which makes the phosphate rocks last for a longer time (Zapata and Sikora 2002). Flue gas desulfurization (FGD) and gypsum ($CaSO_4.2H_2O$) are also used as soil amendments against soil acidity. The moderate solubility of FGD gypsum in water (solubility 2.5 g $L^{-1}$) makes it a good source of $Ca^{2+}$ and $SO_4^{2-}$ in the soil. Furthermore, it is also used to rectify the subsoil acidity and alkalinity of the soil (Walia and Dick 2016; Zhang et al. 2016).

The second widely used soil acidity neutralizing substance is alkaline stabilized biosolids, i.e., rice husks, animal manures, wood ashes, litter, and peat (Bolan et al. 2003; Behak 2017). These are widely used in the agricultural area as a substitute for inorganic amendments such as lime, limestone, coal ashes, cement, and lime kiln dust (Okagbue and Yakubu 2000). Alkaline-stabilized liming substances are recommended to increase the soil pH to 6.5 and more by the United States Environmental Protection Agency (Bolan et al. 2003).

Apart from conventional soil acidity neutralizers, biochars are also used in decreasing soil acidification. Biochars are produced from the pyrolyzed feed stocks ranging from lignocelluloses to manure at varying temperatures between 200 and 700 °C. The general properties of biochars include (i) soil acidity regulation by carbonates, silicate, alkaline oxides, and functional oxygen groups and (ii) soil nutrient pool maintenance by supplementation of macronutrients (N, P, K, and Ca) and micronutrients (Cu and Zn). Moreover, the high cation exchange capacity of biochar helps in nutrient retention in the soil (Dai et al. 2017). The properties of biochar vary with variability under the conditions of the product. For instance, Lehmann and Joseph (2015) reported that the pH of the biochar produced at 300–399 °C was 5.0, while its production at 600–699 °C showed a pH of 9.0.

Biochars can be used in waste disposal, energy production, climate change mitigation, and they also show positive responses on soil pH because of their alkaline nature and high pH-buffering capacity. It is also known to decrease the bioavailability of Al and alleviate its toxicity in acidic soil (Dai et al. 2017). However, the major drawback of using biochars on a large scale is its production cost and loss of huge portion of feedstock. Above all, moderation of soil acidification could only be achieved by minimizing the anthropogenically induced emissions and afforestation (Hong et al. 2018).

## 1.6 Conclusions

Soil is an interface that adjoins the atmosphere, lithosphere, hydrosphere, and biosphere. Acidification of soil thus has potentiality to alter the entire ecosystem structure and functions. Atmospheric depositions of nitrogen, sulfur, carbon dioxide, and other constituents, discharge of effluents and solid wastes, weathering of parent materials having acidic constituents, intense agricultural practices, and high precipitation are the major drivers of soil acidification. Lowering of the pH causes deterioration of soil fertility, loss of soil aggregate stability, and reduced soil biological activities due to metal toxicity. Terrestrial and aquatic habitats are negatively affected by constantly leaching of important basic cations ($Na^+$, $Ca^{2+}$, $Mg^{2+}$, and $K^+$) and increased solubilization of toxic metals ($Al^{3+}$, $Cr^{2+}$, $Cd^{2+}$, and $Pb^{2+}$). Soil flora and fauna are the organisms, which undergo a direct influence of soil acidification. Alteration in the soil properties due to soil acidification affects the growth, development, and productivity of crop plants, which invariably affects the countries' economy. The plant community structure pattern is an essential parameter to assess the change due to soil acidification. Atmospheric depositions (N and S) cause cuticle dissolution and inadequate availability of essential nutrients affect the plant species richness and their productivity. For the amelioration of acidified soil, different soil amendments are used such as lime, phosphate, and bio-wastes. However, advanced modification of flue stack, proper pretreatment of wastes, and afforestation are the most environmentally viable methods to combat the soil acidification.

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# Challenges to Organic Farming in Restoration of Degraded Land in India

# 2

Ashima Singh, Rana Pratap Singh, and Nandkishor More

## Abstract

Degraded land is not only a subject of soil quality but also an indication of declined levels of productivity and economy of a country. India had 29.3% (96.4 million hectare) degraded land area in 2013. It included 1.87 million hectare (0.57%) increment of degraded land as well as 1.95 million hectare reclaimed land. Annual economic loss due to changes in land use or degraded land in India was ($46.90 billion) in 2014–2015, i.e. 2.5% of the country's gross domestic product (GDP) in 2014–2015. On the other hand, India supports 60–70% workforce in 60.45% agricultural land with a landmark position in most production crops like wheat, rice, milk, etc. However, in the case of yield, its position is not the same when compared to other most production countries, and its agricultural growth also declined from 8.6 (in 2010–2011) to 0.8 (in 2015–2016). The most interesting is the decrease of Gross Domestic Product (GDP), which declined from 54% to 15.4% from 1950–1951 to 2015–2016 against in service sector, which grew from 30 to 53% for the same duration. Therefore, land reform is a demanding and challenging area in Indian economy. To focus on this framework, our agricultural management practices play a vital role in which organic farming as eco-friendly, soil-sustaining agricultural technique, sharing highest organic producers of 2.7 million (30%) of total organic producers with 1.49 million hectare organic agricultural land, can play a significant role in land reformation. The chapter discusses some possible opportunities and challenges of organic agriculture in degraded land as reformative measure.

## Keywords

Land Degradation · Economy · Organic farming

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## 2.1 Concept of Organic Farming in Indian Agriculture

Organic farming is now a holistic approach against the contaminated food production, health security, falls in bio-diversity, disturbed soil nutrient cycles, soil pollution and degraded agricultural land (Lal 2015; Elpiniki et al. 2016). Use of natural inputs, neither mining nor lead to degradation of soil nutrients, promotion of soil microbial growth, maintenance of soil from texture to soil ecosystem are today's ethics of organic farming.

Promotion of organic farming in India is mainly based on the requirement of huge quantity as well as quality of food for fast-growing population, increased agricultural-based economy, reduced GDP rate due to farming sector, overcoming degraded agricultural land area, requirement of soil sustainability and also saying "NO" to the use of chemicals for crop production.

## 2.2 Importance of Organic Farming in Sustainable Agriculture

Sustainable agriculture is the maintenance of regenerative capacity of natural resources like soil, biological diversity, particularly pollinators, micronutrients, pesticide resistance capacity, higher soil carbon level and ground water level along with quality and quantity of food production.

Microorganisms in soil play a leading role in rapid availability of micronutrients in soil as they promote the secretion of exo-polysaccharides, proteins, organic acids and other metabolites, which glue the soil particles and promote soil aggregation. This process enhances the availability of soil nutrients to plant uptake (Aislabie and Deslippe 2013; Rashid et al. 2016; Jacoby et al. 2017; Costa OYA et al. 2018). Organic supplements are easily colonized by microbes and increase other soil properties maintaining fertility stability. A balanced ratio of microbial biomass and activity is needed to consistently release nutrients for plant and microbial growth. Nutrient management through organic farming helps stabilizing soil fertility via improving nitrogen fixation and reducing nutrient leaching (Pandey and Singh 2012). Soil organic matter is a significant factor in soil sustainability, which depends upon the amount and type of organic matter applied. According to Bai et al. 2018, addition of compost, farmyard manure and slurry application enhanced soil organic matter (SOM) by 37%, 23% and 21%, respectively, in upper 10-cm soil cover (Spiegel et al. 2015).

Sustainable agriculture leads not only bio-ecological environment but also promotes economic and social sustainability in the form of cost to benefit ratio, mental and economic satisfaction of small farmers holders, rise in their living standard, their participation in country growth, etc. The cost of production of organic ragi and maize per acre was reported Rs. 24,817 and Rs. 30,299 versus conventional farming, which is Rs. 17,128 and Rs. 21,655, respectively, as reported by Kumar et al. (2017). It also indicates 9.2% reduced crop productivity with 22% net profit to farmers due to 20–40% available premium price for certified organic produce and 11.7% cost cultivation reduction.

## 2.3 Status of Degraded Agricultural Land in India

The modern lifestyle of human beings is the foremost basis of deforestation, degraded agricultural land worldwide using overloaded fertilizer application, short irrigation practice, use of harmful chemicals as fertilizer and pesticides, industrialization without using proper norms. Approximately, 40% of the world's agricultural soil is critically degraded and 24% area of productive soil requires attention (Rashid et al. 2016; Bai et al. 2018). On the basis of the report of ISRO 2016, in India, 29.3% of the total land was degraded till 2011–2013 with an increment of 0.57% (1.87 million hectare) compared to 2003–2005. TERI estimated the loss of 2.54% of India's GDP (US$ 46.9 billion) in 2014–2015. Therefore, serious attention is required to overcome the degraded agricultural land in India not only for sustainable agriculture but rather to sustain ecological and economic systems.

## 2.4 Challenges of Land Degradation in Productivity

Due to reduced reforming agricultural land, direct effect on productivity, food insecurity, economic depletion and land degradation remains an important subject of the twenty-first century. Actually, there are so many imperceptible aspects, which may lead to retention of degraded land ratio and need some attention.

According to the UN Department of Economic and Social affairs, "In roughly seven years, or around 2024, the population of India is expected to surpass that of China (United Nations [UN] et al. 2017)." This uncontrolled population and continuously increasing pressure on food demand leads to the use of high amount of chemical fertilizers, change in soil health status and loss of actual potential of soil.

Global warming is also an effective constraint of land degradation productivity mainly in tropical regions as it accelerates the rate of evaporation and indirectly promotes desertification (Karmakar et al. 2016). Availability of water resources is also based on climate change. High latitude contains 10–40%, while mid-latitude or dry tropics comprises 10–30% river runoff. On the other hand, the decomposition rate of soil organic matter is also high in high temperature and lost as carbon dioxide in the atmosphere as greenhouse gases (Kumar and Das 2014; Zhu et al. 2019). The amount of rainfall is also positively correlated with nutrient leaching and land acidification. Therefore, degraded land indirectly takes part in climate change in place of food productivity (International Union for Conservation of Nature [IUCN] 2017).

Above and beyond these reasons, loss of productivity is also affected by overuse and rough use of land, inequality of land capacity and application technology, adoption of mechanized and intensive agriculture (Eriksson et al. 1974; Eswaran et al. 2001), soil erosion (Dregne and Chou 1992), etc. Due to its distinguished effect on food productivity and its security, the degraded land issue is a global concern and demands global attention via some projects and policies for the conservation of soil resources.

## 2.5 Types of Land Degradation

Nkonya et al. (2016) state that 30% land of the world with about 3 billion population accounts for 300 billion USD annual global cost of land degradation. Sub-Saharan Africa (SSA) accounts for the largest share (22%) of the total global cost of land degradation. In the case of India, with only 2.4% of the world land area, it holds up to 18% of human and 15% of livestock population. However, the declining rate in the size of land holdings in agriculture from 2.30 to 1.16 ha during 1970–2010 was noticed. Therefore, to take any action or to make any policy against these issues, a detailed knowledge of land degradation type is very important (Fig. 2.1).

The world celebrates every fifth December as world soil day and the theme of 2018 was "Stop soil pollution." A Global Symposium on Soil Erosion 2019 with theme "Stop soil erosion save our future" was also organized by the UN Food and Agriculture Organization, Rome. So these are some events that were organized every year to make aware people of soil erosion, but over the last decade 20–30 Gt yr.$^{-1}$ and 5 Gt yr.$^{-1}$ loss of soil by water and wind erosion is estimated (FAO and ITPS 2015). The same data for India are 36.10 and 18.23 mha land in 2011–2013 (Indian Space Research Organization [ISRO] 2016), respectively.

Atmospheric depositions of heavy metals, excessive use of nutrient and pesticide applications in agriculture, and flood events are some influential anthropogenic activities responsible for land degradation. Asia is an important supplier of heavy metals such as cadmium (Cd), mercury (Hg), arsenic (As), etc. in which Cd is most hazardous due to its high mobility in the food chain to affect human health. According to the report of Huang (2011), about 12 million tons of grains were contaminated by heavy metals annually causing economic loss of 20 billion RMB (3.3 billion US Dollars). In India, approx 29.33 Mha land is represented by vegetative degradation (Indian Space Research Organization [ISRO] 2016), which is concerned with the above anthropogenic activities. Thus, various types of land degradation affect our land simultaneously, which need quick and serious attention.

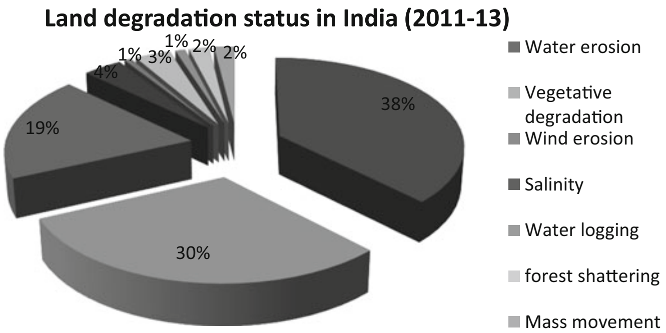

**Fig. 2.1** Types and status of organic farming in India

## 2.6 Need and General Process of Reforming Land

According to FAO terminology, the total agricultural area has been estimated to be 4.889 billion hectares consisting of arable land (28%), permanent crops (3%) and meadows and pastures (69%) (Rangel et al. 2019). Over the last century, the rate of degradation is continuously lagging behind the rate of land-reforming process. Soil erosion process in exhaustive arable of grazing land is found to be 100–1000 times higher than natural soil erosion rate. Due to this, loss of fertile soil affects the soil productivity and is a burden to farmers for fertilizer applications. Water erosion promotes the annual loss of 23–42 Mt. (megaton) N and 14.6–26.4 Mt. P from agricultural land, which requires annual fertilizer application rates of 112 Tg for N and 18 Tg of P; this demand may have a change in significant economic cost (FAO and ITPS 2015). On the other hand, the need of an increase in agricultural production by about 70% from 2005–2050 to feed the population of 7.3 billion to 9.5 billion from 2015 to 2050 (Lal 2015), to maintain the sustainability of soil productivity as well as soil health, is putting an unavoidable pressure on human body and the remaining productive land to innovate strategies in the direction of land reforming.

The land reformation process is not affected in one day or one year; it takes years and years. It needs attention on all the levels of agriculture, such as maintenance of soil structure, microbial biodiversity, level of soil organic carbon, balanced availability of nutrients with their cycles, positive effect of pesticides on soil quality, etc. These are some blank spaces, which are required to be filled to compile the process of land-reforming system (Fig. 2.2).

The phenomenon of coalescing should be avoided by keeping the soil's moisture level high, which maintains the soil structure and increases the porosity of the soil.

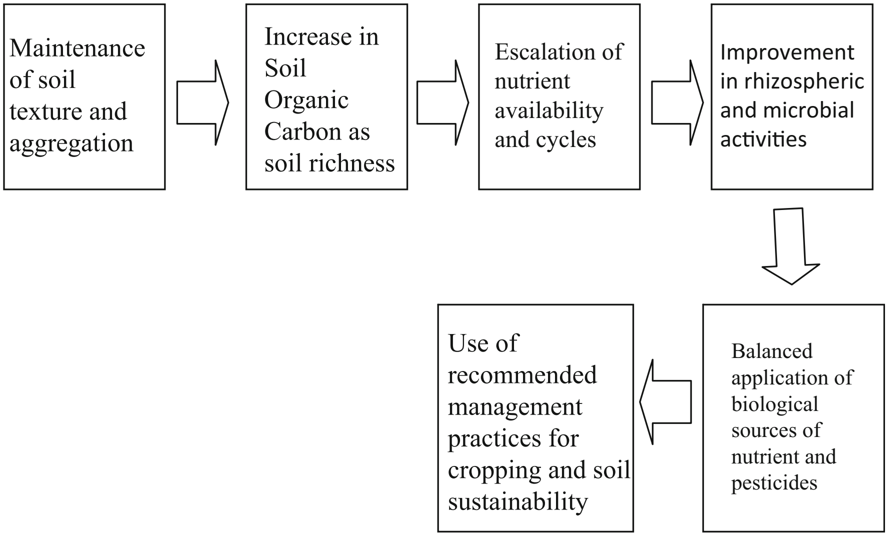

**Fig. 2.2** Lining framework of soil degradation form soil to ecosystem

Therefore, proper irrigation technology should be taken into priority. Incorporation of high-quality organic matter in soil requires increasing soil porosity, soil biological activities, microbial diversity, etc. Organic supplements or vermin compost, farmyard manures can be used here to enrich soil organic carbon, close nutrient cycles, and slow release of fertilizers for full-time availability of nutrients in the soil. The rate of mineralization also determines the availability of nutrients to plants (Bi et al. 2010). Therefore, the process of reclamation mainly depends upon the used recommended management practice for farming besides other factors. It also depends upon the type of soil and its specific recommended practice.

## 2.7 Role of Organic Supplements in Soil Restoration

The use of organic supplements in organic farming is not a recent technique to exploit; it had its scope from a very ancient time when agriculture had started and no compost or any type of fertilizer were in use – only cow dung was in use. That's why it doesn't lose its capacity to maintain the fertility level/health of the soil. Organic supplements are usually the derivative of animals and plant residues (Gaskell and Smith 2007; Bi et al. 2010) such as poultry manure, farmyard manure, vermi compost, hair and wool waste, cow dung with rice, wheat straw, sorghum stalks, pigeon pea, chickpea, sugarcane trash, etc.

On the basis of the quantity of nutrients available to the crops, manures are categorized into two parts: bulky organic manure and concentrated organic nutrients. As its name indicates, bulky organic manure has less quantity of nutrients, so a large quantity is needed to apply. However, they increase the nutrient availability of soil, recover the structural factors of soil, increase carbon content in soil, and maintain the balance of microbial quantity in soil. Farmyard manure, compost, and green manure are its best examples. In comparison to bulky, concentrated organic manure has a high quantity of nutrients, is rich in nitrogen fertilizers, and converted into ammonium nitrogen and nitrate nitrogen through mineralization. Oil cakes, fish manure, blood meals are some of the best types of concentrate organic manure (Reddy 2005). Organic manures are not immediately available to the soil, but they retain always in some amount. They release slowly as its requirement through mineralization by microbes; thus, its surplus requirement is not needed. Organic manure also maintains microbial diversity. Thus, they led to developing a nutrient and microbial-rich, structurally maintained, pollution-free soil covered land as the high demand for land reclamation.

## 2.8 Status of Organic Supplements in India

The nature of the soil is a key factor of sustainable agriculture (Tscharntke et al. 2012; Paustian et al. 2016). The role of organic supplements totally depends upon its high organic matter development in soil, minimizing food chain–associated health hazards and attaining closed nutrient cycles.

India has a large potential to produce various organic supplements due to its different agro-climatic regions, agriculture, and livestock-based economy. In livestock population, India achieved a remarkable position in the world with the largest cattle population in 2018 (63%) followed by Brazil & China (Livestock census 2012). On the other hand, it is estimated that about 300 million tons per annum of municipal solid waste will be generated by 1823 million urban populations until 2051. It contains 40–60% compostable waste having approximately 0.64% Nitrogen, 0.67% Phosphorus, 0.68% Potassium and 26% C/N ratio. The largest vermincompost plant was founded in Bengaluru (100 million tons per day capacity), besides Hyderabad, Mumbai and Faridabad (Joshi and Ahmad 2016).

Livestock itself is a major source of farmyard manure, cow dung, poultry manure, meat meal, bone meal, etc. (Table 2.1), which has a significant fertility-promoting supplement on sterile soil. In addition, its trampling process and removal and addition of nutrients through grazing and dung with the urine process are very important to maintain the soil health (Qu et al. 2016).

Municipal solid waste is also a rich source of various types of compost. Thus, the fast-booming population of humans and livestock can also play a positive role in the direction of land reformation indirectly, besides its hazardous effects on reducing the natural resources process. Besides animal refuse, plant refuse also indicates its rich availability for land reformation process as 60% of India's population relies upon agriculture for its livelihood.

Thus, India has a strong potential for the availability of organic supplements not only in the farming sector but also in the land reformation sector. However, it needs some steps and policies and its proper implementation through the Indian government.

## 2.9 Subsidies and Support of Indian Economy to Encourage Organic Farmers

As of 31st March 2018, the total area under organic certification process (registered under National Programme for Organic Production) is 3.56 million Hectare (2017–2018). This includes 1.78 million ha (50%) cultivable area and another 1.78 million Hectare (50%) for wild harvest collection (Sruthy and Vibini 2019). Among all the states, Madhya Pradesh has covered the largest area under organic certification followed by Rajasthan, Maharashtra, and Uttar Pradesh. During 2016, Sikkim had achieved a remarkable distinction of converting its entire cultivable land (more than 76,000 ha) under organic certification.

In the 14th Conference of Parties (COP-14) to the United Nations Convention to Combat Desertification (UNCCD), organized in Greater Noida, Prime Minister had launched a central scheme of Rs. 13,500 crore to control the livestock diseases, especially foot and mouth disease (FMD) and brucellosis, from the Mathura district in Uttar Pradesh. To improve soil health and fertility, soil status such as nutrients value should be known. For this purpose, Soil Health Card has been issued, which provides the nutrient status of their soil along with recommendations on

**Table 2.1** Average nutrient composition of NPK in various organic supplements

| Organic Supplements | Nutrient concentrations, % | | |
|---|---|---|---|
| Plant refuse | | | |
| | N | $P_20_5$ | $K_2O$ |
| Rice straw | 0.58 | 0.23 | 1.66 |
| Wheat straw | 0.49 | 0.25 | 1.28 |
| Sorghum stalks | 0.40 | 0.23 | 2.17 |
| Pearl millet stalks | 0.65 | 0.75 | 2.50 |
| Maize stalks | 0.59 | 0.31 | 1.31 |
| Average pulses | 1.60 | 0.15 | 2.00 |
| Pigeon pea | 1.10 | 0.58 | 1.28 |
| Chick pea | 1.19 | | 1.25 |
| Sugar cane trash | 0.35 | 0.04 | 0.50 |
| Edible/nonedible oil seed | | | |
| Ground nut | 7.29 | 1.65 | 1.33 |
| Mustard | 4.52 | 1.78 | 1.40 |
| Rapeseed | 5.21 | 1.84 | 1.19 |
| Linseed | 5.56 | 1.44 | 1.28 |
| Sesame | 6.22 | 2.09 | 1.26 |
| Cotton seed (decorticated) | 6.41 | 2.89 | 1.72 |
| Cotton seed (undecorticated) | 3.99 | 1.89 | 1.62 |
| Neem (Azadirachta indica) | 5.22 | 1.08 | 1.48 |
| Castor | 4.37 | 1.85 | 1.39 |
| Mahua (Madhuca indica) | 3.11 | 0.89 | 1.85 |
| Kusum (Schleichera oleosa) | 5.23 | 2.56 | 1.37 |
| Animal refuse | | | |
| Cattle dung | 0.3 | 0.10 | 0.15 |
| Sheep/goat dung | 0.65 | 0.5 | 0.03 |
| Human excreta | 1.2–1.5 | 0.8 | 0.5 |
| Hair and wool waste | 12.3 | 0.1 | 0.2 |
| Farmyard manure | 0.5 | 0.15 | 0.5 |
| Poultry manure | 2.87 | 2.90 | 2.35 |
| Town urban compost | 1.5 | 1.0 | 1.5 |
| Rural compost | 0.5 | 0.2 | 0.5 |
| Vermicompost | 0.6 | 1.5 | 0.4 |
| Meat meal | 10.5 | 2.5 | 0.5 |
| Bonemeal (raw) | 3–4 | 20–25 | – |
| Bonemeal (steamed) | 2–5 | 26–28 | – |
| Fishmeal | 4–10 | 3–9 | 1.8 |

the appropriate dosage of nutrients to be applied for improving soil health and its fertility. To promote sustainable agriculture, through climate change adaptation measures, enhancing agriculture productivity, especially in rainfed areas focusing on integrated farming, soil health management, and synergizing resource conservation, National Mission for Sustainable Agriculture was launched under National

Action Plan for Climate Change (NAPCC). To focus on the irrigation systems in agriculture, micro-irrigation was promoted under Pradhanmantri Krishi Sinchai Yojana from July 2015 implemented by the Ministry of Water Resources and Department of Land resources. For this purpose, micro-irrigation fund (MIF) created with NABARD (National Bank for Agriculture and Rural Development) has been approved with an initial corpus of Rs. 5000 crores (Rs. 2000 crores for 2018–2019 & Rs. 3000 crores for 2019–2020) for encouraging public and private investments in Microirrigation. In the field of organic farming, to improve soil health and organic matter content and increase the net income of the farmer so as to realize premium prices, an area of 5 lakh acre is targeted to be covered through 10,000 clusters of 50 acres each, from the year 2015–2016 to 2017–2018 (The Economic Times 2019).

To bring in transparency and competition to enable farmers to get improved remuneration for their produce moving toward ‘One Nation One Market’, National Agriculture Market (e-NAM) program was launched, which provides an e-marketing platform at the national level and support creation of infrastructure to enable e-marketing. To tackle aberrant monsoon situations leading to drought and floods, extreme events (heat waves, cold waves, frost, hailstorms, cyclone) adversely affecting crops, livestock and fisheries (including horticulture), Central Research Institute for Dryland Agriculture (CRIDA) and Indian Council of Agriculture Research (ICAR) have prepared a district-level agriculture contingency plan in collaboration with state agricultural universities using a standard template. For the development of rainfed-area farmers, Rainfed Area Development Programme (RADP) and National Watershed Development Project for Rainfed Areas (NWDPRA) have launched under Rashtriya Krishi Vikas Yojna.

To protect our harvested crop before marketing, Pradhan Mantri Fasal Bima Yojana (PMFBY) is started, which is an actuarial premium-based scheme under which farmers have to pay the maximum premium of 2% for Kharif, 1.5% for Rabi food & oilseed crops and 5% for annual commercial/horticultural crops and the remaining part of the actuarial/bidded premium is shared equally by the Centre and State Government. To protect the Livestock from diseases, The livestock insurance scheme was started to provide a protection mechanisms to the farmers and cattle rearers against any eventual loss of animals due to death. Therefore, there are so many schemes and insurances, which benefit the Indian farmers if they implement properly.

## 2.10 Recommendations/Suggestions and Follow-Up

In India, soil/land degradation has reached roots in great depth and created a very critical image in both rainfed and irrigated areas of India. It creates very dangerous conditions because it is attached to major issues such as economic losses, food security, degraded soil health, insufficient food production, etc. In the case of India, it becomes more significant as it supports 18% of the world’s human population, 15% of the world’s livestock population with only 2.4% of global land area in which 29% of land is degraded.

The land reformation process is not only possible with a single effort but also requires a mixed action of government policies, farmers' hard work, and support of local communities. All the policies announced by the government should be consumed until the lowest level of farmers, their importance should be in their knowledge, and workshops and conferences, play, and discussions should be organized at the panchayat/village level to create awareness in each category of people about its importance. Besides all these efforts, some major steps can be started:

- Focus on proper irrigation technology, promotion of afforesting process, to maintain the soil moisture, to maintain the vegetative cover as well as prevent soil, water, and other land degradation.
- If land becomes adequately moist, land should be prepared and allowed for grazing, which promotes the nutrient cycle efficiently.
- Recommended management practices should be used to prepare the land for farming using the organic supplement, no-tillage practice but after properly investigating the basic need of that particular land.
- Government organized seed banks should use to start farming because, initially the main focus should be on land regeneration, not food production.
- When the land physico chemical and biological properties can be maintained, the land takes under proper farming.

These steps are not possible without the financial support of the government and their implementation schemes and local bodies. Some NGOs should also come in front of this demanding issue. Organic farming is the earliest government-authorized and government-supported farming technology. The higher profitability of organic farming was due to minor labour requirement and to a greater market appreciation for organic products that granted a premium price respect to conventional prices (Sgroi et al. 2015; Akshu and Hooda 2017). The demand for Indian organic food products is on the constant increase worldwide as India exported organic products worth $ 515 million in the financial year 2017–2018, from $ 370 million in 2016–2017, by officials from Agricultural and Processed Food Products Export Development Authority (APEDA). Registering an increase of 39%, the total volume of export during 2017–18 was 4.58 lakh tones, they added. So this established agriculture technology plays a vital role not only in improving and maintaining the soil fertility stability, sustainable agriculture, food demand, and security but also in increasing the value of organic export, certified organic farms, use of livestock population, the human population as workers and reforming land as well as the country economy.

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# Biochemical and Molecular Responses of Plants Exposed to Radioactive Pollutants

# 3

Kaushal Kishore Choudhary

## Abstract

Radioactive substances are naturally existing rare elements that emit radiation of high energy (ionizing and non-ionizing) capable of transforming the physiological and biochemical attributes of living organisms. However, the extent of natural release is slow and also not sufficient enough to affect the biosystems. The exploitation of these radionuclides for electricity, medicine, agriculture, nuclear weapons, and geological and scientific research for human well-being has led to enhanced release and accumulation of radiation in natural environment, ultimately affecting the metabolic functioning. The most prominent effect is caused by ionizing radiation (high energy) when compared with non-ionizing radiation (low energy). Ionizing radiation causes water radiolysis and produces hydroxyl radicals (reactive oxygen species [ROS]), which in turn cause oxidative stress in living cells. The interaction of radiation-induced ROS with biological organic compounds causes chromosomal aberrations (inversions/deletions), DNA damage, reduction in growth, and developmental abnormalities. Responding to ionizing radiation, plants trigger the antioxidant defense system and produce antioxidative molecules such as glutathione and ascorbate as well as antioxidative enzymes such as catalase (CAT), glutathione reductase (GR), superoxide dismutase (SOD), and ascorbate peroxidase (APOD). Antioxidative biomolecules support plants in scavenging the free radicals generated in their cells and protect them from the harmful effects of radiation. Radionuclides, particularly neutrons-alpha-beta particles and gamma rays, have been used in artificial mutation breeding. Artificial mutation using physical mutagens is a powerful tool in developing new and unique plant varieties. In this chapter, radioactive substances, their accumulation in the environment, interaction with plants, and their sensible aspects are discussed.

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**Keywords**

Antioxidant · β-Radiation · γ-Radiation · DNA · Mutation breeding · Plants · Radioactive substances · Reactive oxygen species

## 3.1 Introduction

Radioactive substances and their associated radiation are present in the earth's atmosphere since its origin. It is assumed that life originated in a radioactive environment that had ionizing radiation (Zakariya and Kahn 2014). Radioactive substances are unstable natural substances that decay and emit ionic radiation continuously into their surroundings. Naturally occurring radioactive materials (NORMs) are present in the earth's crust, walls of buildings, food we eat, water we drink, and the air we breathe (Zakariya and Kahn 2014). It is noteworthy to mention that houses made up of bricks and stones have high radiation levels compared to wooden homes. The impact of radiation on living systems depends on the dose and duration of exposure to radiation. Doses and sources of ionizing radiation differ from time to time and place to place. However, naturally existing radionuclides and radiation released from them into their surroundings are not enough to affect the biological system.

Nowadays, radioactive substances are widely being used in several areas such as medicine, electricity, agriculture, industry, and research (Zakariya and Kahn 2014), thus contributing significantly to the society. Extensive and unplanned exploitation of these radioactive substances is resulting in the accumulation of radiation in surroundings at a higher rate. Natural environment is receiving radiation particularly from nuclear testing, radiation used to diagnose diseases, and cancer therapy. Small quantities of radiation are also released from coal and nuclear power plants. Accidental release, nuclear testing, uncontrolled use of radionuclides for medicinal purpose and research, and lack of proper strategy for the disposal of radionuclide waste are resulting in the deposition of the wastes in air, soil, and water; currently, the proper harvesting and safe disposal of radionuclide waste is worldwide concern. Continuous efforts to use these radioactive substances and their radiations for various purposes of human development have witnessed an associated health risk not only to humans but also to plants. Plants respond variously to ionizing and non-ionizing radiations depending on the dose and duration of radiation exposure. Animals, particularly humans, can escape the radiation exposure by leaving the place or by protecting themselves; however, plants cannot escape the radiation exposure because they are static and cannot change their position.

Plants uptake these radionuclide wastes from the soil along with water and leaves also absorb them from air. Radionuclides with high energy interact with metabolic pathways and alter the molecular nature of plants, ultimately altering the biochemical products. Plants counteract the reactive oxygen species (ROS and oxidative stress) generated by radiation exposure by producing antioxidative biomolecules. Radiations have varied impacts on the physiological and biochemical attributes of plants, and are positively correlated to the type, dose, and duration of radiation exposure. It has been reported that low doses of radiation have stimulatory effects, intermediate doses have harmful effects, whereas high doses can bring about a significant decrease in the growth, development, and productivity of plants (Kovalchuk et al. 2000). Furthermore, Holst and Nagel (1997) proposed that different plants respond variously to radiation depending on their age, morphology, species, physiology, and genomic organization. Radiation is always not harmful; rather, it is sometimes very fruitful. Radiation is widely used in plant breeding programs and has been proved to be very fruitful in producing new hybrid vigor varieties. In this chapter, the types and sources of radiation, the interaction with plants, and the biochemical responses of plants to radioactive pollutants will be discussed.

## 3.2 Radioactivity and Radioactive Substances

Radioactivity is defined in terms of the disintegration of atoms. In other words, radioactivity is the property of an element to emit particles or/and radiations spontaneously into its surroundings that cannot be altered using heat, electricity, temperature, pressure, or any other external force (Hazra 2018). Elements exhibiting radioactivity are called radioactive substances. The atom consists of a centrally placed positively charged proton and a neutral neutron (nuclei), and negatively charged electron in its outer orbit. The nuclei of elements having protons disintegrate and release energy in the form of radiation. The unit of radioactive decay is Becquerel, and one Becquerel is equal to one disintegration per second. The decay of radioactive substances continues till a stable element is formed. The time taken to decay half of the radionuclides is termed as 'half-life' of that element and it differs for different radionuclides. Half-life varies from seconds to billions of years. For example, the half-life of $^{131}$I is eight days, $^{238}$U is 4.5 billion years, and $^{40}$K is 1.25 billion years.

Radioactive substances emit three kinds of radiations: alpha (α), beta (β), and gamma (γ) particles or radiation (Fig. 3.1). Ionizing radiations are the electromagnetic waves that have the capability to pass through matter, thereby inducing the matter electrically charged or ionized. Alpha particles (alpha radiation or alpha decay) are high-energy positively charged particles (+2) consisting of two protons

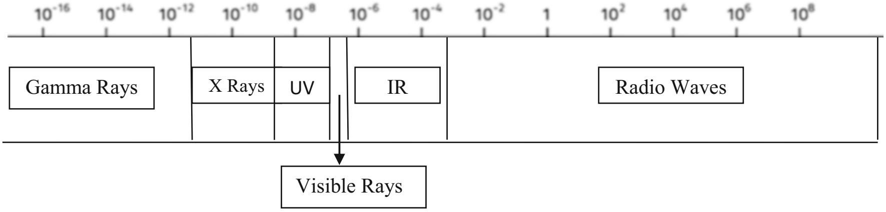


**Fig. 3.1** Wavelength (in m) of different rays

and two neutrons with a molecular mass of four units (He atom). Examples of alpha particles releasing radioactive substances are Uranium (U) and Radium (Ra). Beta particles (beta radiation or beta decay) are high-energy, high-speed negatively charged electrons, i.e., negatrons ($\beta^-$) or positrons ($\beta^+$) with a molecular mass of that of H. Beta particles have more penetrating power in comparison to alpha particles. Gamma rays are neutral and have very strong power of penetration and can penetrate the human body.

## 3.3 Types of Radiation

Radiation is a charged or neutral energy wave or particle that transports in the form of either electromagnetic waves or energetic particles (United Nations Scientific Committee on the Effects of Atomic Radiation [UNSCEAR] 2010; Smičiklas and Šljivić-Ivanović 2016). There are basically two types of radiations, ionizing radiation and non-ionizing radiation (Table 3.1).

### 3.3.1 Ionizing Radiation

Ionizing radiations are electromagnetic radiations with high energy and shorter wavelength. They are capable of ionizing the atoms or molecules of the medium or substances through which they pass. Charged molecules in the medium generated by the ionizing radiation break the chemical bonds of proteins, DNA, and other

**Table 3.1** Comparison of alpha, beta, and gamma rays

| Properties | Alpha ray (α) | Beta ray (β) | Gamma ray (γ) |
|---|---|---|---|
| Nature | High-speed helium nucleus | High-speed electrons | High-speed electromagnetic radiation |
| Mass | $6.65 \times 10^{-27}$kg | $9.20 \times 10^{-31}$kg | Negligible |
| Charge | +2 | −1 | No charge |
| Velocity | Less than the velocity of light (ranges between $1.4 \times 10^7$ ms$^{-1}$ to $2.1 \times 10^7$ ms$^{-1}$) | Nearly equal to the velocity of light (about $1.8 \times 10^8$ ms$^{-1}$) | Equal to the velocity of light in free space (equal to $3 \times 10^8$) |
| Penetration power | Low | Moderate | High |
| Ionizing power | Greater than beta and gamma rays | Very low | Very low |
| Effect of electric and magnetic fields | Deflects toward negative plate | Deflects toward positive plate | No deflection |
| Luminescence | Produces fluorescence and phosphorescence | Produces phosphorescence | Produces phosphorescence |

biological organic molecules thereby causing alteration in the metabolism of living systems.

### 3.3.2 Non-ionizing Radiation

Non-ionizing radiations are comparatively higher wavelength particles with low energy. They are not capable of ionizing or converting the atoms or molecules of the medium. However, the energy present in the non-ionizing radiations is capable of exciting the atoms or molecules of the medium through which they pass, causing the molecules to vibrate faster.

## 3.4 Sources of Radioactive Radiation

There are basically two sources of radiation, natural and man-made.

### 3.4.1 Natural Radiation

There are three main sources of natural radiation (Table 3.2):

1. Cosmic radiation—The sun and stars continuously release charged particles (+ & -), which interact with the earth's atmosphere and magnetic field. This interaction results in the production of radiation to which living organisms including plants are exposed. Common examples of radionuclides produced after the interaction of cosmic rays with atmosphere are $^{3}H$, $^{7,10}Be$, $^{14}C$, $^{26}Al$, and $^{39}Ar$ (Agency for Toxic Substances and Disease Registry [ATSDR] 1999; Smičiklas and Šljivić-Ivanović 2016). Such natural radiation varies on earth's surface due to the variation in the elevation in different parts of the world. Altitude and to a lesser extent latitude are the major factors on which radiation exposure due to cosmic rays depend. Cosmic radiation generally includes beta and gamma radiations.

**Table 3.2** Sources of radiation and their contribution (%) in natural environment (United State Nuclear Regulatory commission [USNRC])

| Type of radiation | Source of radiation | Contribution (%) |
|---|---|---|
| Natural radiation | Radon | 55 |
| | Cosmic | 08 |
| | Terrestrial | 08 |
| | Internal | 11 |
| Man-made radiation | Medical diagnostics | 11 |
| | Nuclear medicine | 04 |
| | Consumer products | 03 |

2. Terrestrial radiation—Terrestrial radiation is present on the earth's surface, that is, soil, water, and vegetation as rocks, minerals, and soil contain NORMs. Radioactive materials such as $^{238}$U, $^{232}$Th, and $^{40}$K are present in the earth's crust, which release radiations continuously into their surroundings, exposing the living organisms. Terrestrial radiation also varies from place to place on the earth's surface due to the variation in the availability of radioactive substances around the world.
3. Internal radiation—Internal sources of radiation are present inside the living body. They result from the consumption of food, water, and air carrying radioactive substances. These radiations do not vary significantly among species or person to person. Such radiations generally include $^{40}$K, $^{14}$C, and $^{210}$Pb.

### 3.4.2 Man-Made Radiation

Man-made radiations are those radiations which are produced by radioactive substances used at a large scale for human benefits. The important sources of such radiations are medical diagnostic sources (X-rays, nuclear medicine, and radiation therapy) and consumer products such as tobacco (Thorium), building materials, sources of fuel, smoke detectors, luminous watches and dials, electron tubes, and fluorescent starters. Nuclear fuel cycling and residual wastes from the testing of nuclear weapons (Chernobyl) are also the major sources of radiation on earth's surface. During the above-described processes, radioactive substances release radiation of high energy to which living organisms including plants are exposed. The rate of release of radiation and its accumulation in the atmosphere is increasing rapidly due to over unplanned exploitation of radioactive substances for human development.

## 3.5 Radioactive Pollution in Soil

Radioactive pollution or contamination is defined as the undesired accumulation of radioactive substances on surfaces of materials or within solids, liquids, gases, or biota (International Atomic Energy Agency [IAEA] 2007). Soil is the major receiving pool of emitted radionuclides. Soil receives radionuclides as radioactive wastes released during exploitation of radioactive substances for nuclear energy, nuclear weapon testing, medicine, agriculture, research, etc. It has been reported that soils contaminated with radionuclides lose their natural property of soil fertility for good agricultural produce (Aleksakhin 2009). Soil is the major factor that influences the growth and development in plants, and may be degraded rapidly due to the disposal of radionuclides, mostly at or around the site of the institute or industry using radioactive substances for human developmental processes. The quality of soil in terms of fertility is characterized by its physical, chemical, and biological properties

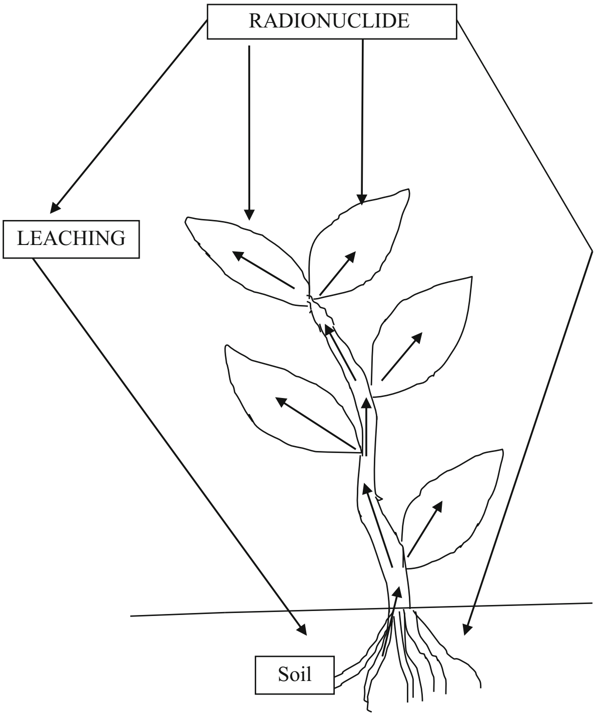
(Brady and Weil 2002; Osman 2013). The interaction between soil and radioactive pollutants is determined by the physical, chemical and biological properties of soil and nature of pollutants. The binding and retention of pollutants in soil is governed by the five basic components including water, minerals, gases, organic matter, and microorganisms. Soil captures the radioactive pollutants by physical (reversible) sorption carried out by the charges on soil surface and chemical (irreversible) sorption carried out by high-affinity, specific interactions and covalent bond formation (Sparks 2003; Sposito 2008). In this way, plants are exposed to radioactive pollutants and their products or radiations.

## 3.6 Absorption and Interaction of Radionuclides with Plants

The accumulation in the atmosphere depends on the availability of radiation sources. The higher the industrial and institutional practices, greater is the accumulation of radiation in that site (man-made radiation). When the availability of terrestrial sources of radiation is maximum, the availability and accumulation of radiation and exposure to living organisms is also maximum (terrestrial radiation). In this way, plants are exposed to radiations differently around the world.

The biosynthetic activity of plants is governed by at least 15–20 basic parameters of the plant physiology and environment. Minimum biosynthetic activity is essential for the absorption and accumulation of the radionuclides inside plants, which is possible only when the basic parameters are in the appropriate range. Plants interact with radionuclides either at their soil-root zones or the aerial-shoot zone (Fig. 3.2). Radioactive pollutants suspended in the air as particles or aerosols (and gases) are absorbed by the shoots of the plants (foliar absorption) and those present in the rhizosphere are absorbed by the roots (Koranda and Robison 1978). They showed that the uptake of $^{99}$Sr and $^{137}$Cs by the soil-root system is governed by the presence of organic matter, inorganic colloids (clay), and other competing elements of the soil. The activity of the plants for radionuclides depends on their retention in the atmosphere and the soil. It is evident that at the time of nuclear testing, radionuclides are released into the atmosphere and they remain suspended in the atmosphere for a certain period. During this period, plants accumulate the radionuclides in their body through foliar absorption (Koranda and Robison 1978). Radionuclides enter the plant body from the air either in the form of a solution or as gases. The solution reaches the leaf and finally the leaf tissue, whereas gases carrying radionuclides enter through the stomatal opening. After certain period of stay in the atmosphere, the radionuclides reach the soil from where they are absorbed by the plants through their root systems.

**Fig. 3.2** Diagrammatic representation of radionuclide uptake by plants



## 3.7 Impact of Radiation on the Physiological, Biochemical, and Molecular Attributes of Plants

Ionizing radiations have significant impact on the physiological, biochemical and molecular nature of plants (Table 3.3). The impact of ionizing radiations is controlled by the dose and duration. It has been discussed earlier that lower doses of an ionizing radiation might not negatively affect plant growth and development whereas higher doses have a negative or lethal effect on plants. The information on the effects of ionizing radiations is of wide interest because of their application in agriculture, horticulture, environmental protection, and space science (Caplin and Willey 2018).

### 3.7.1 Effects of Ionizing Radiation at the Molecular Level

It has been reported that radiation induces mutations, and, hence has been widely used in the development of hybrid plants since the concept of mutation was proposed by Hugo de Vries. The concept of the theory of mutation of Hugo de Vries was

**Table 3.3** Effects of radiations on the different aspects of plants

| Effect | |
|---|---|
| Denaturation of | Morphological, physiological, and biochemical response |
| • DNA | • Generation of defense against oxidative stress (DAOS) |
| • Protein | • Synthesis of antioxidant enzymes and molecules |
| • Organic molecules | • Stunted growth |
| • Chloroplasts | • Mutational breeding |
| • Cell membrane | • Chromosomal/DNA rearrangements |
| • Cell wall | • Activation of specific genes |
| • Biosynthetic pathway | |

published by Hubrecht (1904). Hugo de Vries proposed that mutations can be induced in plants using X-rays. More than 2500 cultivars currently used as food have been developed by mutagenesis induced by high doses of ionizing radiation (IR 10 s of Gy or more) (Cheng et al. 2014). Ionizing radiation is still playing a significant role in the development of improved varieties of crops such as rice and wheat (Caplin and Willey 2018; Cheng et al. 2014). Cheng et al. (2014) showed that 9.19% genome sequences of Red-1 varieties of rice (rich in beneficial ingredients), developed by gamma irradiation, was altered. They further showed that point mutation was the main factor responsible for alteration.

Experimental studies have suggested that irradiation of plants with gamma rays inhibits their growth and is associated with the synthesis of auxin and DNA. Further, it was postulated from experimental studies that (a) DNA is a prerequisite for auxin biogenesis, that is, DNA is required for auxin synthesis; (b) auxin is required for DNA formation; and (c) radiation affects other cellular entities essential for both DNA and auxin synthesis (Jan et al. 2012; Lage and Esquibel 1995; Momiyama et al. 1999). Ionization radiation brings about mutation in plants and is of wide interest for plant breeders (mutation breeding). Mutation breeding is one of the significant tools for the development of high yielding and qualitative plant varieties. Mutation breeding involves three types of mutagenesis generated either by treatment of ionizing radiation or chemical mutagen. The three kinds of mutagenesis are: (i) induced mutagenesis; (ii) site-directed mutagenesis (mutation at a specific site in the DNA molecule); and (iii) insertion mutagenesis (DNA insertion) (Forster and Shu 2012; Kharkwal and Shu 2009; Oladosu et al. 2016). Ionizing radiation has a high incidence of double-stranded breaks (DSBs) in DNA compared to other radiation or mutagens (Caplin and Willey 2018). Plants were exposed to a high degree of ionizing radiation during their early period of colonization of land surface as compared to today's level of ionizing radiation (Caplin and Willey 2018). Ionization radiation brings about DSBs that may result in the deletion of DNA segments (Kovalchuk et al. 2000, 2004; Sato et al. 2006). However, single-stranded breaks are also frequent due to the exposure to ionizing radiation (Cheng et al. 2014). Sato et al. (2006) conducted an experiment in which they treated rice with gamma rays and ethylmethanesulfonate (EMS) to obtain mutants. They showed that the point mutation rate was lower when treated with gamma radiation but higher when treated with EMS. Conversely, knockout mutation was higher when treated with gamma radiation compared that with EMS. It has been reported that acute doses of IR exposure (10–100 s Gy) produce a 'net' rate of mutation from $10^{-9}$ base pair mutation per Gy to $6.13 \times 10^{-6}$ bp mutation per 500 Gy (Sato et al. 2006). It has also been demonstrated that low doses of chronic ionizing exposure to plants have high rates of mutation compared to acute high doses. Kovalchuk et al. (2000) experimentally demonstrated that wheat, planted in Chernobyl NPP-affected soil and exposed to ionizing radiation of 0.3 Gy for a growing season of 100 days showed six-fold increase in its mutation rate.

Further studies to understand the effect of ionizing radiation (IR) on plants showed that IR induces changes in the gene expression of plants. It has been reported that acute high doses of IR exposure may change 100–1000 s of genes (Caplin and Willey 2018). The most notable information on changes in gene expression due to IR exposure involves the induction of DNA repair gene and antioxidant defense machinery of the plant system. Kim et al. (2014) reported that genes with changed expression have significant contribution in catalytic activity, endomembrane system, and are active in metabolism. They proposed that gamma irradiation brings about significant changes in gene transcripts and expression. They demonstrated that, in *Arabidopsis thaliana*, out of the 20,993 genes used as microarray probes, a total of 496 genes were up-regulated whereas 1042 were down-regulated by gamma irradiation. It has been reported that the exposure of the plant to 200 Gy of gamma irradiation showed alteration in gene expression responsible for sugar and starch metabolism (Hwang et al. 2014). Hwang et al. (2014) performed the experiment to study the effect of gamma rays, cosmic rays, and ion beams on rice. They proposed that the overall expression patterns were similar for gamma rays and ion beams but was different for cosmic rays. They further reported that changes in gene expression were related to sucrose–starch metabolism, finally resulting in an increased content of sugar and starch in all the three types of irradiation used in the experiment.

Further studies showed that exposure of plants to acute IR results in the up-regulation of genes responsible for DNA repair, oxidative stress response, and signal transduction pathways, whereas chronic exposure has no effect on the changes in gene expression (Caplin and Willey 2018). A similar observation of variation in physiological and gene expression of *Arabidopsis* plants was observed for acute and chronic exposure of plants with γ-irradiation (Goh et al. 2014). They demonstrated that exposure of *Arabidopsis* seedlings to 200 Gy γ-irradiation in an acute manner for 1 h or 24 h, or in a chronic manner for 1, 2 or 3 weeks resulted in a decrease in the plant height, silique number, and silique length. The up-regulation of gene expression in response to acute and chronic exposure to γ-irradiation involved gene encoding for zinc finger proteins, heat shock factors, NADPH oxidase, WRKyY DNA-binding proteins, and calcium-binding proteins (Goh et al. 2014). They further reported that out of the four antioxidant enzymes, catalase (CAT), peroxidase (POD), ascorbate peroxidase (APOD), and superoxide dismutase (SOD) studied for γ-irradiation, CAT and POD exhibited a decreased cellular activity for both acute and chronic exposure. Studies conducted by Kimura et al. (2008) on rice seedling leaves suggested that low-dose exposure to IR in the affected area in Chernobyl showed an up-regulation of gene expression related to defense mechanisms, cell wall synthesis, and secondary metabolite synthesis.

### 3.7.2 Effect of Ionizing Radiation on the Physiology and Biochemistry of Plants

Ionizing radiation plays a significant role in the radiolysis of water compared to the photolysis of water during photosynthesis. High doses of IR results in an increased rate of lysis of water, resulting in the generation of a high amount of free radicals, that is, ROS (Kovács and Keresztes 2002) such as superoxide radicals ($O^{2-}$), hydroxyl radicals ($OH^-$), and peroxide ($H_2O_2$) (Apel and Hirt 2004). Kovács and Keresztes (2002) demonstrated that gamma rays bring about softening of fruits and finally breaking of middle lamella of the cell. These radicals react simultaneously with the structural and functional organic molecules such as proteins, lipids, and nucleic acids and bring about an alteration in the cellular biosynthetic pathway (Salter and Hewitt 1992). Apel and Hirt (2004) describe that plants have developed mechanisms to synthesize antioxidant enzymes and molecules to combat stress and also generate ROS purposefully as a signal molecule to control pathogenic defense mechanism, programmed cell death, and stomatal behavior. Gamma irradiation has been reported to reduce the chlorophyll content in *Nicotiana tabacum* by 55.9% (Wada et al. 1998). Plants have developed mechanisms to encounter the oxidative stress created in the cellular compartments by producing a high amount of antioxidants (Willey 2016; Jan et al. 2012). These oxidative stresses are capable of degrading the protein and the metabolic activity in plants.

The impacts of IR-induced oxidative stress in plants include alteration in morphology, anatomy, biochemistry, and physiology of plants (Ashraf et al. 2003). Ashraf et al. (2003) demonstrated that basmati rice treated with gamma radiation showed a decline in seedling shoot and root lengths, panicle fertility, and grain yield. These morphological variations were negatively correlated to irradiation and were dose-dependent. Further observation suggested that changes in the cellular redox potential created due to oxidative stress brings about changes in the dilation of thylakoid membranes, alteration in photosynthesis, activation of antioxidant producing biosynthetic pathway, and accumulation of phenolic compounds (Kovacs and Keresztes 2002; Ashraf 2009; Wi et al. 2007). It has been reported that the induction of seeds with high doses of gamma irradiance resulted in decreased protein and carbohydrate contents due to the increased metabolic and hydrolyzing enzyme activities in the germinating seeds (Barros et al. 2002; Maity et al. 2004; Jan et al. 2012). The treatment of *Dacus carrota* L. with gamma irradiation resulted in an increased uptake of glucose, pyruvate, and a decreased uptake of acetate and succinate (Jan et al. 2012). Bourke et al. (1967) reported that gamma irradiation resulted in a decrease in all amino acids except serine and valine.

Plants have developed biosynthetic mechanisms to encounter the oxidative stress created in their cellular compartments by producing a high amount of antioxidants

(Willey 2016). They synthesize enzymes containing sulfur such as amino acids (cystine, cysteine) and SOD to disarm the free radicals and ultimately protect the plants from oxidative stress (Qin et al. 2000; Jan et al. 2012). Qin et al. (2000) reported that the change in the activity of SOD and POD in $^{60}$Coγ-ray and EMS-treated seeds of *Lathyrus sativus* was directly linked to the concentration of radiation. Zhang et al. (2016) showed that the treatment of *Arabidopsis* seeds resulted in a reduction in the root and shoot lengths due to the production of superoxide radicals and hydrogen peroxide. Simultaneously, the production of antioxidant enzymes was also up-regulated in *Arabidopsis* in response to the low-energy N(+) beam. They reported no effect of radiation or EMS on the CAT activity. Different types of antioxidant enzymes and molecules are synthesized and expressed in plants in response to ionizing radiation. Some of them have been discussed below:

## 3.8 Antioxidant Enzymes and Molecules

### 3.8.1 Superoxide Dismutase (SOD)

SOD plays a vital role in combating the oxidative stress generated by ionizing radiation in plants. It has been demonstrated that higher the content of SOD, CAT, and POD in the cellular pool, lower is the vulnerability of plants to the secondary effect of radiation. SOD probably acts as an electron donor in transition metal radiation-affected cells/tissues and protects the irradiated cells by sensitizing them against the effects of $H_2O_2$ (Jan et al. 2012). It has been observed that the treatment of *Vigna radiata* (L.) R. Wilczek with 20–200 Gy gamma irradiation showed sharp changes in both SOD and POD (Roy et al. 2006). It was seen that gamma irradiation of *V. radiata* resulted in a reduced height of seedling and germination frequency. Roy et al. (2006) also demonstrated that the RAPD analysis of gamma-irradiated plants (200 Gy) exhibited new bands, indicating DNA damage. Pramanik (1997) demonstrated the correlation between the morphological damage, such as the decrease in seedling height in *Plantago ovata,* and gamma irradiation. Also, dose-dependent gamma irradiation was related to changes in SOD activity. Changes in SOD isozyme pattern in response to oxidative stress is an indication of the development of radioprotection mechanism inside plants. The correlation between radiation doses and antioxidant enzyme activities has been demonstrated in vivo and in vitro by several workers (Singh 1974). Gupta et al. (1993) demonstrated the correlation between the expression of Cu/Zn SOD in tobacco leaves and stress. They further suggested that plants can withstand severe stress and can maintain their normal photosynthetic activity by producing the SOD isozyme. They showed that transgenic plants can retain their rate of photosynthesis 20% more than untransformed plants. They concluded that the SOD generated in the chloroplast plays a vital role in providing support to plants in tolerating stress.

Further study on irradiation suggest that the production of antioxidant molecules or enzymes are linked with the alteration in gene expression in response to stress created by radiation. Overexpression of SOD in irradiated cells is due to the induction of genes or alleles responsible for SOD enzyme synthesis (Inzé and Van Montagu 2002). Pramanik (1997) reported that the PAGE gel analysis of the SOD activity of irradiated calli showed an appearance of extra bands ($R_f$ value – 0.59). In some cases, disappearance of certain bands immediately after exposure to γ-irradiation has also been observed, which may be associated with the degradation of certain biomolecules (Sen Raychaudhuri and Deng 2000) or switching off of the metabolic pathway (Jan et al. 2012). Zaka et al. (2002) showed that the overexpression of antioxidant enzymes, particularly POD, CAT, GR, SOD, and G6PDH, or molecules is directly linked to gamma irradiation. They further showed that SOD and G6PDH in particular play a significant role in the protection of *Stipa capillata* from oxidative stress created by ROS. In this way, plants disarm the oxidative stress by producing SOD.

### 3.8.2 Peroxidase (APX; EC 111.1.11) and Catalase (CAT; EC 1.11.1.6)

The two other important antioxidant enzymes are POD and CAT, produced in response to ionizing radiation. The interaction of plants with the irradiated rays creates a stress in their cellular activity due to the production of oxidative radicals. Several studies suggest that ionizing radiation results in the production of hydrogen peroxide at a higher rate (Wi et al. 2006). Wi et al. (2006) reported an increased content of $H_2O_2$ in pumpkin (*Cucurbita ficifolia bouche*) with high doses of gamma irradiation. Hydrogen peroxide continued to be present in xylem vessels, plasma membrane, middle lamella, and also in parenchyma cells (Jan et al. 2012). The biochemical activity demonstration of irradiated cells showed an increased level of POD enzyme in the irradiated cells. A similar observation of the expression of POD enzymes associated with gamma irradiation has been reported by different workers in different plants such in garlic bulbs (Croci et al. 1994) and the root disks of sweet potato (Ogawa and Uritani 1970). Croci et al. (1994) reported that gamma irradiation of garlic cloves resulted in a decrease in the total DNA content of inner sprouts immediately and after 100 days of irradiation, whereas the total RNA, protein, and carbohydrate contents of the inner sprouts were not changed. They proposed that DNA is the most sensitive component of the cell to radiation exposure.

POD enzyme protects plants by disarming the effect of $H_2O_2$ by eliminating them (particularly lipid hydrogen peroxide) from the cellular pool. The overall equation of peroxyl radical removal by POD enzyme is as follows:

$$H_2O_2 + DH_2 \rightarrow 2H_2O + \mathrm{D}$$

There are several reports in the literature on the overproduction of POD enzyme in the irradiated cells of plants and their role in scavenging the oxidative radicals (Khanna and Maherchandani 1981). Khanna and Maherchandani (1981) proposed that lower doses of gamma radiation stimulated the POD activity in chickpea whereas a decrease in the POD activity was observed for higher doses of gamma irradiation. CAT is another enzyme which plays a significant role in the elimination or scavenging of free peroxyl radicals in plants. Aly and El-Beltagi (2010) showed that antioxidants can prevent plants from oxidative radical damage generated due to IR exposure. They observed the stimulation of POD, APOX, CAT, SOD, and GST under the influence of gamma irradiation and it was positively correlated dose-dependent. They also reported an increase in the malondialdehyde (MDA) content associated with gamma irradiation. The up-regulation of genes for CAT, POD, Cu/Zn SOD, GST, and the down-regulation of cytosolic and stromal APX have been reported in *Nicotiana tabacum* L. (Cho et al. 2000). Cho et al. (2000) reported that the gamma irradiation of tobacco showed varied responses. According to them, certain group of genes (glutathione-*S*-transferase, POD, SOD, and CAT) showed stimulating response, whereas other groups (cytosolic APOD, stromal APOD, and TMK-1 receptor like-kinase) showed reduction. There were also certain groups of genes that exhibited either no response or irregular response. These included pathogenesis-related proteins, tobacco $Ca^{2+}$-dependent protein kinase, the β-subunit of translational initiation factor 2B, and a chitinase-related receptor-like kinase (Cho et al. 2000). The overall reaction mechanism involving CAT and radicals is mentioned below:

$$ROOH \overset{catalase}{\rightarrow} H_2O + ROH + A(Jan\, et\, al.\, 2012)$$

$$2H_2O_2 \overset{catalse}{\rightarrow} 2H_20 + O_2$$

The investigation of the effect of irradiation on biochemical properties showed enhanced rate of production of POD and CAT with a consequential decline in growth (except at 5 krad which showed growth) of wheat irradiated with high doses of ionizing radiation (Chaomei and Yanlin 1993). They showed that irradiation of wheat plants above 20 krad resulted in an increased activity of both POD and acid phosphatase activity. The CAT activity was higher at 5 krad and 20 krad. Several reports are now available on the production of antioxidant enzymes such as POD, SOD, CAT, and APX, associated with the exposure of plants with ionizing radiation (Singh et al. 1993; Foyer et al. 1997; Zaka et al. 2002). Singh et al. (1993) demonstrated that phenolic content, polyphenol oxidase, and POD were positively correlated with different doses of gamma irradiation in sugarcanes. Foyer et al. (1997) suggested that thiol/disulphide exchange reactions involving glutathione pool and $H_2O_2$ play a crucial role in modulating metabolism and changes in gene expression corresponding to environmental and biotic stresses. It has been reported that chronic exposure of gamma irradiation to *Arabidopsis thaliana* has no effect on the concentration of non-enzymatic antioxidants, ascorbate, and glutathione (Vandenhove et al. 2009). Štajner et al. (2009) reported that gamma irradiation resulted in a decrease in the total antioxidant activity (15.7%) and an increase in MDA and $OH^-$ by 21.6 and 79.33%, respectively, in soybean compared to non-irradiated soybean.

### 3.8.3 Glutathione Reductase Activity (GR; EC 1.6.4.2)

A similar response of increased content of GR activity in plants was observed with gamma irradiation. The increased content of GR activity was reported in roots and shoots of three *Trigonella* L. genus irradiated with gamma radiation (Jan et al. 2012). Foyer et al. (1991) reported that the GR activity of transgenic *Nicotiana tabacum* var. Samsun was two- to ten-folds higher than the non-transgenic control tobacco plant. Synthesis and production of GR in irradiated plants is governed by gene regulation. Studies suggest the correlation between enhanced content of GR activity with an increase in the transcription rate of encoding genes (Foyer et al. 1995). They proposed that overexpression of GR activity in chloroplast is responsible for the increased antioxidant activity, ultimately supporting the Poplar plant in disarming the oxidative stress.

### 3.8.4 Ascorbate and Glutathione

Plants synthesize ascorbate to achieve their optimal growth and metabolic activity. It has been demonstrated that irradiation of plants has variable response associated with ascorbate synthesis (Vitamin C). In some plants, exposure to gamma radiation showed either no response or decrease in ascorbic acid (ascorbate; AA) such as in potato and strawberries, papaya, mango, strawberry, and litchi (Graham and Stevenson 1997; Beyers et al. 1979). Graham and Stevenson (1997) reported increase in dehydroascorbic acid (DHAA) content immediately after irradiation in strawberry plant. It has been reported that exposure of plants to ionizing radiation results into conversion of ascorbic acid into dehydroascorbic acid (DHAA) (Diehl 1990; Kilcast 1994; Jan et al. 2012).

Glutathione is another antioxidant molecule which supports plants in disarming the effect of oxidative stress. Halliwell and Gutteridge (1989) reported that glutathione protects plants from oxidative stress by directly interfering with free radicals. The overall reaction of glutathione with DHAA has been shown below:

Correlation between glutathione levels and ionizing radiation has been variously studied.

$DHAA + 2GS \rightarrow Ascorbate + GSSG$ (Jan et al., 2012)

$$GSSG + NADPH \rightarrow 2GSH + NADP$$

## 3.9 Conclusions

From the above discussion, it may be concluded that the research on the effect of ionizing radiation on metabolic adaptation of plants will certainly prove to be fruitful in maintaining the environmental condition sustainable. It will also make a platform for the development of new varieties of essential plants. The exploitation of radionuclides for the generation of energy, medical diagnosis and treatment, nuclear weapons, etc., is the need for the present generation and it will certainly increase the level of ionizing radiation in our surrounding, making it difficult for survival. Hence, it is the urgent need of the present research to focus on the findings and develop radiation-resistant, radiation-tolerant plants, which can minimize the level of radiation, making the environment sustainable.

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# Cadmium: A Threatening Agent for Plants

# 4

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## Abstract

Heavy metal pollution is one of the serious environmental problems, damaging all living organisms globally. Cadmium (Cd) is a nonessential, deadly toxic metal that has a harmful effect on plants. Entry of Cd inside the plant body causes an abiotic stress and provokes the plant to generate anti-stress agents, such as sodium dismutase, catalase, guaiacol peroxidase, and glutathione. Cadmium accumulates in plants and hinders their normal productivity. The accumulation depends on Cd entry in plants via roots, translocation via xylem and phloem, and through different processes, channels, and metal transporter. Even a very small dose of Cd influences the physio-biochemical parameters of the plant. Cadmium stress reduces the efficiency of plants by modulating their morphology, physiology, and biochemistry. This chapter underlines transport, mechanism of action, and regulatory network of Cd, and harmful aspects of Cd exposure to plants. The chapter also discusses the Cd effect on seed germination, growth, development, chlorophyll content, photosystem and photosynthesis, carbon assimilation, and reproduction.

## Keywords

Antioxidants · Cadmium · Morphology · Photosynthesis · Physiology · Reactive oxygen species · Stress · Toxicity

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## 4.1 Introduction

Crops growing under natural environment frequently face the impact of abiotic stresses during their growth period. Different stresses may overlap and affect the productivity and growth of the crop critically. As the defense against these stresses, plants do a couple of changes, like morphological, physiological, biochemical, and molecular (Jongdee et al. 2002; Chinnusamy et al. 2007; Najeeb et al. 2011; Basu et al. 2016; Wang et al. 2016; Anjum et al. 2017). Heavy metals are very dangerous for almost all living organisms present in the environment. Contamination of heavy metals results either from water sources or through biomagnifications. Mining is also one of the sources causing heavy metal contamination (Santona et al. 2006).

Heavy metals that are bioactive are broadly classified into two main categories, one as redox active, e.g., iron (Fe), copper (Cu), manganese (Mn), and chromium (Cr) and other as nonredox active, e.g., Cd, mercury, (Hg), nickel (Ni), zinc (Zn), and aluminum (Al) (Valko et al. 2005). Metals such as Cu, Cr, and Fe can initiate oxidative injury with the help of Fenton and Haber-Weiss reactions that ultimately produced free radicals of oxygen and reactive oxygen species (ROS) in plants, which result in disruption of cell homeostasis, protein damage, DNA breakage, damage to photosynthetic pigment and cell membrane, which can stimulate cell death (Schützendübel and Polle 2002; Flora 2009). On the other side, nonredox active metals cause oxidative stress through many mechanisms, like glutathione (GSH) depletion, binding to protein through sulfhydryl group (Valko et al. 2005), hampering antioxidative enzymes, or increasing the enzymes that generate ROS like NADPH oxidases (Bielen et al. 2013). Among all heavy metals, Cd is one of the most serious pollutants because it can potentially accumulate in plants and may reach to the next trophic level. Apart from the origin of Cd, a wide range of anthropogenic activities, like usage of phosphate fertilizers, green wastes, and sewage biosolids to the soil, leads to more addition of Cd to the soil (Nicholson et al. 1994). The credit for the discovery of Cd goes to a German scientist Friedric Strohmeyer in the year 1817. He discovered it from zinc ore as one of the constituents of smithsonite ($ZnCO_3$). Cd has a half-life of around 10-30 years (Berglund et al. 2015). It is a soft, silvery white compound having an atomic number of 48 and configuration [Kr] $4d^{10}$ $5s^2$. The most common mineral of Cd on the earth's crust is greenockite (CdS). After the discovery, it was mainly used as polishing agents or in batteries. Further researches confirmed its toxicity to humans because it affects kidneys, lungs, and bones (Page and Bingham 1973; Matović et al. 2011). Cadmium toxicity in plants can be understood by some visual symptoms like necrosis and chlorosis of leaves, root browning, and the cell apoptosis (Zemanová et al. 2016). Cadmium hinders the normal morphological, physiological, and biochemical processes of the various plants (Lu et al. 2018). According to FAO/WHO, the permissible level of Cd in rice is 0.2 mg/kg. For the tolerance and detoxification of Cd, plants have evolved efficient and unique mechanisms like Cd chelation, Cd influx–efflux management, Cd compartmentalization and remobilization, and ROS scavenging (Hall 2002; Kim et al. 2006; DalCorso et al. 2008, 2010; Lin and Aarts 2012; Shi et al. 2015). Cadmium has the tendency to interfere with the essential elements like calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), Zn, Cu, Fe, Mn, molybdenum (Mo), selenium (Se), trivalent chromium (Cr), boron (B), cobalt (Co), and many others (Lazarus 2010; Matović et al. 2010; Moulis 2010). European Food Safety Authority (EFSA) reduced the Tolerable Weekly Intake (TWI) of Cd to 0.36 μg/kg body weight/day (2.5 μg/kg body weight/week) (EFSA 2012). Various anthropogenic activities, like intensive agriculture, rapid industrialization, which are a consequence of population growth and modernity, induce destruction of the natural resources and promote extensive contamination of environment (Wan et al. 2012). Heavy metal contamination negatively influences the crop production as well as biological systems that ultimately results in quality and quantity losses (Hashem et al. 2016). Cadmium is considered as one of the most significant pollutants because of its high-water solubility and great toxicity (Pinto et al. 2004).

## 4.2 Cadmium Uptake and Transport Inside the Plant

Cadmium, if available, can be taken up by higher plants from water and soil via root cells or directly from atmosphere (Clemens 2006). Certain factors such as soil pH and features, rhizosphere, and availability of organic acids can influence the Cd availability to plants (Benavides et al. 2005). Research done on rapeseed plant confirmed that Cd content depends on both pH and soil type, as more Cd content was found in plant growing at pH 4.0 than at pH 5.0, and plants growing in sandy soil promote greater Cd uptake than clay soil (Eriksson 1989). In acidic environment, Cd is present as $Cd^{2+}$ but when the pH level exceeds 6-7, it is found as $CdHCO_3$, $CdCO_3$, $CdCl_2$ (Tudoreanu and Phillips 2004), and other Cd complexes (Smolders and McLaughlin 1996).

Apart from these several other factors, like plant species and its genotype, availability of other nutrients and minerals and environmental conditions also control the Cd accumulation (Volpe et al. 2015). The amount of organic acids present in the rhizospheric region also affects Cd accumulation (Cieśliński et al. 1998). Root exudates alter the rhizosphere pH, activity of some rhizospheric microbes, chelating potential for Cd ions, and redox potential. Secretion of low-molecular weight organic acids by plant roots play a major role in availability and solubility of Cd ions that may hinder metal speciation, uptake and translocation, and ultimately phytotoxicity (Mench and Martin 1991).

Cadmium enters via plant roots, is stored within root vacuoles, and is translocated to xylem and phloem, and further it is diluted within the whole plant shoot region. The concentration of Cd within plant decreases from roots to shoots indicating that xylem restricts the Cd transport in some plants. Similarly, its minimum concentration in tubers, fruits, and seeds indicates restriction of Cd transport by phloem (Seregin and Kozhevnikova 2008). Cd ions uptake was done by the same transporters that involve in uptake of $Fe^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, and $Cu^{2+}$ (Clemens 2006); nevertheless, some of these elements decrease the Cd uptake and accumulation in plant roots and translocation to upper parts (Gallego et al. 2012). High mobility along with water solubility enables the Cd uptake by root via cortical tissue and then reach xylem through symplastic or/and apoplastic pathway (Lux et al. 2010) by forming complex with phytochelatins or organic acids (Salt et al. 1995).

Cadmium ion is divalent in nature and chemically it is analog to other divalent ions like Zn and Fe and one of the main reasons of Cd toxicity is its competition with the essential minerals, particularly Fe, which is taken from the soil to the cells of plant root by IRON-REGULATED TRANSPORTER 1 (IRT1), which is a member of ZIP transporter family (Vert et al. 2002). Its specificity for Fe uptake is low; hence, it becomes very easy for Cd ion to be transported through IRT1 (Lombi et al. 2002; Yoshihara et al. 2005). As Cd competes with Fe for the same site present on IRT1, this competition makes a deficiency of iron in the plant (Lešková et al. 2017). A new transporter protein, namely, OLIGOPEPTIDE TRANSPORTER 3 (OPT3) was found to involve in iron uptake and the mutation in gene-regulating OPT1 results in overaccumulation of Cd in roots and seeds at the cost of disruption in Fe homeostasis (Mendoza-Cózatl et al. 2014).

The major transporter of Cd in rice is *Oryza sativa* heavy metal ATPase2 (OsHMA2), which helps in its movement from root to shoot (Satoh-Nagasawa et al. 2011). *Oryza sativa* natural resistance-associated macrophage proteins 1 (OsNRAMP1) take part in uptake as well as in transport of Cd in rice at the cellular level and its overexpression in the root region may enhance the accumulation of Cd in the shoot region (Takahashi et al. 2011). OsHMA3 also plays a crucial role for Cd stress because mutation of this protein leads to the absence of Cd function into vacuoles present in root cells that ultimately results in high Cd translocation from the roots to shoots (Ueno et al. 2009; Miyadate et al. 2010; Takahashi et al. 2011). Gene *OsNRAMP5* encodes for a natural resistance-associated macrophage protein in *Oryza sativa*, and the functional analysis showed that defect in this protein reduces the Cd uptake by roots via the use of mutation method in plant *Arabidopsis thaliana* (Ishikawa et al. 2012).

## 4.3 Mechanism of Cadmium Action

Position of Cd in the ranking is the 7th in the priority list of pollutants dispatched by the Agency for Toxic Substances and Disease Registry (Wynne 2008). Some recent studies confirmed that being a nonessential element Cd may not be toxic at the low concentration but became very toxic at high concentration in the plants (Mombo et al. 2015; Manquián-Cerda et al. 2016). Cadmium itself cannot induce ROS directly, but it can induce nonradicals $H_2O_2$ that ultimately generate free radicals through Fenton reaction (Watanabe et al. 2003; Rani et al. 2013).

For the detoxification of heavy metals, e.g., Cd, plants produce some cysteine-rich peptides like phytochelatins (PCs), GSH, or metallothioneins (MTs). PCs are a member of small enzymatically synthesized peptides with general structure $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ where the value of $n$ varies from 2 to 11. It was also reported that it is synthesized very rapidly in the presence of heavy metal stress in all tested plants (Grill et al. 1985, 1989; Rauser 1990, 1999; Zenk 1996; Cobbett 2000a, b).

The role of PCs in the tolerance of heavy metal has been characterized by *Arabidopsis thaliana* mutants for Cd sensitivity, *cad1* and *cad2* (Howden and Cobbett 1992; Howden et al. 1995; Cobbett et al. 1998). Both the mutants lack the ability of PC production because of mutation in PC synthase in *cad1* mutants or in glutamylcysteine synthetase in *cad2* mutants. Heavy metal form complexes with PCs in the cytosolic region and are then transferred to the vacuole (Grill et al. 1985; Zenk 1996; Cobbett 2000a, b). For the synthesis of PCs, enzyme PC synthase (γ-glutamylcysteine dipeptidyl transpeptidase) transfer the γ-Glu-Cys moiety of GSH to other PCs or GSH (Grill et al. 1989; Zenk 1996). Several reports show that higher tolerance and accumulation of Cd in transgenic plants result due to manipulating the gene responsible for PC synthesis. It was reported in some transgenic plants that by overexpressing the genes encoding GSH synthetase (Zhu et al. 1999a), γ-glutamylcysteine synthetase (Zhu et al. 1999b), *O*-acetylserine (thiol) lyase (Domínguez-Solís et al. 2000) results in the hypersynthesis of GSH or PCs under Cd stress.

## 4.4 Cadmium Toxicity in Plants

Being a nonessential element, Cd can interact with other essential elements such as Cu, Mn, and Zn and influence their translocation and uptake (Lachman et al. 2015). Certain researches reveal that Cd can impair the development of plants of different species by restricting the absorption of nutrients and water that give rise to several symptoms of injury *in vitro* or *in vivo* (Li et al. 2008). Cadmium can interact with various photosynthetic complexes that result in less photosynthetic carbon assimilation (Maksymiec et al. 2007). By interacting with calcium channels, Cd disturbs the guard cell regulation, hence affecting the water status of the plant (Perfus-Barbeoch et al. 2002). However, by interacting with other metals (Fe, Cu, Mn, and Zn), Cd may deposit in the shoots and roots of *Zea mays* (Wang et al. 2007). Cadmium was found to cause a remarkable reduction in the leaves and roots of *Pisum sativum* by inhibiting the photosynthetic rate and chlorophyll content of the leaves along with alteration in nutrient status (Table 4.1) (Sandalio et al. 2001). RNA-Seq data of bentgrass showed that more concentrations of Cd influence nutritional status and water uptake that cause tissue morphological disorder (Yuan et al. 2018).

### 4.4.1 Seed Germination and Seedling Growth

Cadmium has been found to cause germination delay and membrane damage, and to affect reserve food mobilization by increased cotyledon/embryo ratios of total soluble sugars, fructose, glucose, and amino acids (Fig. 4.1) (Rahoui et al. 2010). In *Medicago sativa*, higher Cd concentrations were found to be inhibitory for germination of seeds along as well as for shoot and root elongation (Peralta et al. 2001). Singh and Thakur (2014) reported that Cd can diminish the seed germination rate, while Singh and Lal (2018) reported that in *Ocimum basilicum* an inverse

**Table 4.1** Effect of Cd stress on the plant physiology

| Species | Concentration | Mode of application | Studied parameters | Author |
|---|---|---|---|---|
| *Brassica juncea* | 0–6 mM | Soil | Growth; $P_n$; $CO_2$ content; carbonic anhydrase activity; antioxidant enzymes activity | Faraz et al. (2019) |
| *Festuca arundinacea* | 0–150 mg $L^{-1}$ | Hoagland solution | Biomass; chlorophyll, ROS, MDA content; in photosystem II the electron transport from OEC to $Y_z$ residue in D1 protein was inhibited | Huang et al. (2017) |
| *Miscanthus* spp. | 0–200 μM | Hoagland solution | Growth; $P_n$; chlorophyll content; chloroplast structure; antioxidant enzymes activity | Guo et al. (2007) |
| *Elsholtzia argyi* | 0–100 μM $L^{-1}$ | Hydroponic solution | Chlorophyll fluorescence; $P_n$; $G_s$, $C_i$, $T_r$ | Li et al. (2015) |
| *Fragaria* × *ananassa* | 0-60 mg $kg^{-1}$ | Peat mixture | Chlorophyll, MDA content; antioxidant enzymes activity; nutrient content | Muradoglu et al. (2015) |
| *Brassica juncea* cv. Varuna | 0-6 mg $kg^{-1}$ | Soil | Chlorophyll, proline content; $P_n$, $G_s$, $C_i$, $T_r$ | Hayat et al. (2014) |
| *Cicer arietinum* | 0-100 mg $kg^{-1}$ | Soil | Growth, nodules; carbohydrates, leg hemoglobin content; antioxidant enzyme activity | Hayat et al. (2013) |
| *Juncus effusus* | 0-100 μM | Murashige and Skoog medium | Growth; biomass; MDA content, cell/cellular organelles; morphometric parameters | Najeeb et al. (2011) |
| *Cucumis sativus* | 0-100 mM | Nutrient solution | $P_n$, $G_s$; chlorophyll, carotenes content; chloroplast ultrastructure; antioxidant enzymes activity | Feng et al. (2010) |
| *Zea mays* | 0-25 μM | Hoagland solution | $P_n$; enzyme assay stress marker activity; salicylic acid level | Krantev et al. (2008) |
| *Allium cepa* | 0-40 μM | Aqueous solution | Cytogenetics | Seth et al. (2008) |
| *Pisum sativum* | 0-250 μM | $CdCl_2$ salt solution | Mitotic activity and aberrations; nucleus ploidy | Fusconi et al. (2006) |
| *Pisum sativum* | 0-50 μM | Nutrient medium | Enzyme assays; nutrient, MDA content; $P_n$ | Sandalio et al. (2001) |
| *Oryza sativa* | 0-500 μM | Sand + Hoagland solution | Proline content; ribonuclease activity | Shah and Dubey (1997) |

$C_i$, internal $CO_2$ concentration; $G_s$, stomatal conductance; MDA, malondialdehyde; OEC, oxygen evolution complex; $P_n$, net photosynthetic rate; ROS, reactive oxygen species; $T_r$, transpiration rate; $Y_z$, D1-$Tyr^{161}$, tyrosine residue

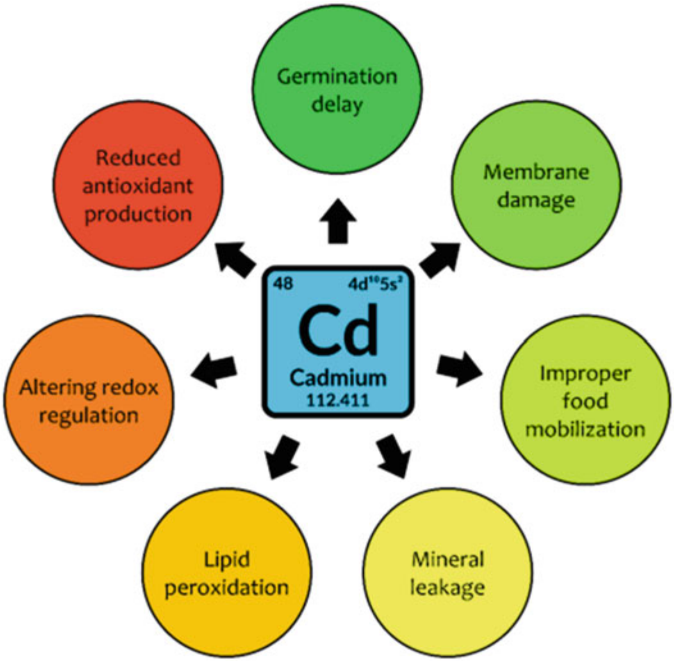

**Fig. 4.1** The toxic effect of cadmium on seeds

relation between percent seed germination and Cd concentration exists. Moreover, they found that the addition of jeevamrutha can increase the seed germination under Cd stress. Along with reduction in percent germination, Cd also reduces the growth of embryos and biomass distribution. It inhibits the activities of enzymes like alpha-amylase and invertase. Hence these soluble acids, cell wall-bound acids, and soluble neutrals disturb the integrity of membranes by a high content of malondialdehyde (MDA) and lipoxygenase activity (Sfaxi-Bousbih et al. 2010). High concentration of Cd results in inducing the expression of glutathione peroxidases (a thioredoxin-dependent enzyme present in plants) and severe reduction in the activity of enzyme glutathione reductase (GR) hence operate the thiol level during the germination process. Cd alters the redox regulation of mitochondria hence by altering the mitochondrial activity via the levels of glutaredoxin, GSH concentrations, and GR activities in the cotyledonary part of embryos (Smiri et al. 2011). In *Albizia lebbeck*, Cd in its increased level gradually reduced the seed germination rate (Fig. 4.1) along with the seedling vigor index (Farooqi et al. 2009). Cadmium stress to seeds can also lead to nutrient loss through mineral leakage (Fig. 4.1) (Sfaxi-Bousbih et al. 2010). Cadmium is accumulated in seeds (Ahsan et al. 2007), and over-accumulation of lipid peroxidation (Fig. 4.1) has also been reported (Smiri et al. 2011).

The Cd stress changes the concentration of hydrogen peroxide ($H_2O_2$), MDA, and proline content, and disturb the redox regulation (Fig. 4.1), whereas an inverse relationship occurs between Cd concentration and the total amount of soluble sugar, soluble proteins, and the total content of RNA and DNA. Further, studies confirmed that Cd stress enhances the activity of some enzymes (Fig. 4.1), such as guaiacol peroxidase (POX), catalase (CAT), polyphenol oxidase, and ascorbic acid oxidase, and subsequently diminished the activity of some other enzymes such as α-amylase, β-amylase, and protease enzymes. Exogenous application of nanoparticles, namely, titanium dioxide ($TiO_2$) and sodium nitroprusside enhance the drastic effect of Cd on *Triticum aestivum* and result in decreased seed germination and seedling growth (Faraji and Sepehri 2018). Recent research done on lettuce (variety *Moscow greenhouse*), grown in sod-podzolic soil, shows the toxic effect of Cd on its development. Results show the significant decrease in plant height, leaf number, and surface area as the exposure of Cd stress increases depending on Cd dose (Loi et al. 2018). Furthermore, research done on *Oryza sativa* by Ding et al. (2017) revealed that microRNA miR268 functions like a negative regulator for Cd stress tolerance and the expression of NRAMP3, which is a target gene of this microRNA, drastically decreased under the Cd stress. Overexpression of miR268 reduced the seedling growth. He et al. (2008) concluded that Cd stress influences the seed germination rate along with inhibition of the growth of radicle and plumule, particularly radicle growth. It was found in the *Vicia faba* that pretreatment of seeds with selenium can be useful to resist toxic effects caused by Cd (El-Sayed Selem 2018). Results clearly show that in roots of Barrel medic plant, Cd treatments reduce the level of endogenous nitric oxide after 48 h (Xu et al. 2010). Cd is distributed in soil and water as an unessential toxic element and its permissible limit in plant and soil is not higher than 0.005-0.02 mg $L^{-1}$ and 1 mg $L^{-1}$, respectively. The oxidation state of Cd is either 0 or 2+. Cd found in nature as $CdCO_3$, $CdSO_4$, and $Cd(OH)_2$ precipitate in the forms of phosphates, arsenates, sulfides, and chromates (Page and Bingham 1973; Benavides et al. 2005; Tchounwou et al. 2012; Chunhabundit 2016).

### 4.4.2 Plant Growth and Development

The growth of plant depends on reproductive and vegetative growth patterns as well as on source to sink relationship between two main plant organs, root and shoot system, maintaining the equilibrium (Anjum et al. 2011). Heavy metals caused adverse effects on plant growth compared with other environmental stresses. Cadmium toxicity can cause many abnormalities in different plant parts like root, shoot, leaves, and fruits, and it also increases dry to fresh mass (DM/FM) ratio in all organs (Greger and Lindberg 1986; Moya et al. 1993). Main symptoms of toxicity are root browning (Arduini et al. 1994), leaf chlorosis (Foy et al. 1978), leaf epinasty (Vázquez et al. 1989), and leaf red-brownish coloration (Malone et al. 1978). It was reported by Hayat et al. (2014) that exposure of Cd along with NaCl causes more significant damage. Heavy metals decrease plant growth rate by influencing root metabolism (Barceló and Poschenrieder 1990), causing oxidative stress in roots and leaves by disturbing redox environment of cells (Romero-Puertas et al. 2004; Ortega-Villasante et al. 2005), reducing chlorophyll content (Larsson et al. 1998) by disturbing enzyme activities (Tamás et al. 2006) altering membrane functioning

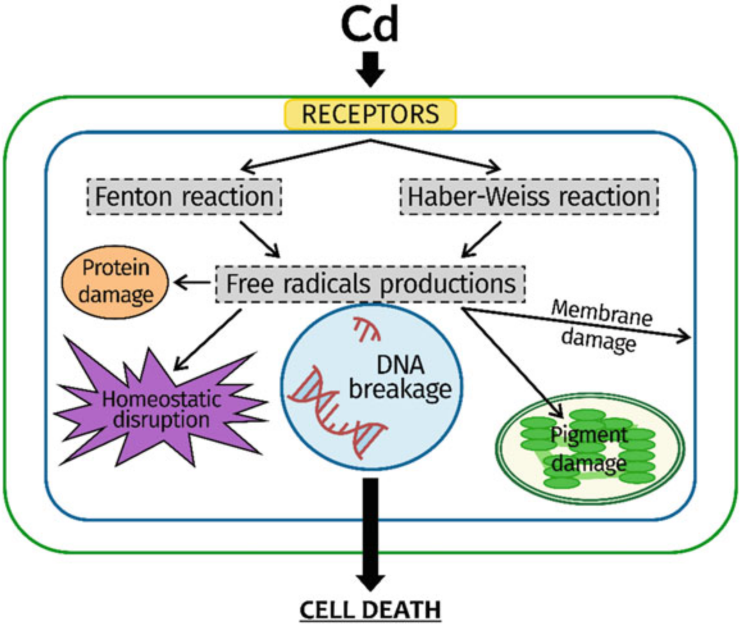

**Fig. 4.2** Cadmium impact after entering plant cell

(Hernandez et al. 1996), cross-linking, and oxidation of proteins (Ortega-Villasante et al. 2005), damaging DNA (Fig. 4.2) (Fojtova 2002; Gichner et al. 2004) hindering cell cycle (Table 4.1) (Fusconi et al. 2006) and ultimately resulting in cell death (Ortega-Villasante et al. 2005).

Beyond the threshold limit of Cd in the field, the quality and quantity of field product decreased (Hassan et al. 2005). Between two cultivars of *Brassica juncea* viz. Varuna and RH-30, Varuna shows better tolerance against Cd stress than RH-30 (Irfan et al. 2015). Physiological processes of plants get disturbed by high concentration of Cd inside the plant body (Van Assche and Clijsters 1990). Cadmium negatively influences biomass and plant growth. Under hydroponic conditions, Cd stress was found to reduce the root tips, surface area, and length in cultivars of pepper (Huang et al. 2015).

Even small concentrations of Cd (2 and 10 μM), applied to hydroponic setup, result in reduced fresh weight of two pepper cultivars (Xin et al. 2014). When 60 mg/kg of Cd was applied to the soil, it reduced the shoot-root length of potato seedlings (Hassan et al. 2016). Exposure of cabbage to Cd resulted in reduced total leaf area and dry weights of roots and shoots of cabbage (Jinadasa et al. 2016). Similar observations were also found in growth and biomass of lettuce (Monteiro et al. 2009), *Raphanus sativus* (Varalakshmi and Ganeshamurthy 2013), and soybean (Wang et al. 2016).

Cd toxicity was found to reduce root dry mass and root length while enhancing root diameter (Gratão et al. 2009). Root growth inhibition is taken as an exclusive symptom of the Cd toxicity that may be due to slow mitotic activities of meristem cells under Cd toxicity (Table 4.1) (Seth et al. 2008). Increment in cortical tissues and parenchyma cell size has a role in enhancing plant resistance to water as well as the flow of solutes. This may explain the reason for increasing root diameter under Cd stress (Maksimović et al. 2007). In addition, decrease in root length, number of root tips, and surface area are also entangled with Cd stress. Hence, these root morphological parameters are taken as an indicator for measuring Cd toxicity (Lu et al. 2013). In plant leaves, Cd stress causes various symptoms like stunting, desiccation, chlorosis, and necrosis. Plants can show all these symptoms when Cd concentration reaches 3–30 mg $kg^{-1}$ DW in plant tissue (Solis-Dominguez et al. 2007). Toxic symptoms of Cd are more significant in the younger leaves than the older ones (Ge et al. 2012). Leaf tissues with Cd concentration 0.05-0.2 mg $kg^{-1}$ DW show normal plant growth and no toxic symptoms (Solis-Dominguez et al. 2007). A measurable reduction in total leaf area along with dry weights of various parts of cabbage, such as leaves, stems, roots, and seeds, has also been observed due to Cd toxicity (Jinadasa et al. 2016; Rizwan et al. 2017). There are various reasons behind retarded plant growth caused by Cd toxicity because it negatively influences photosynthesis, nutrient and water uptake, nitrogen and carbon assimilation, and oxidative damage (Ismael et al. 2019).

### 4.4.3 Morphological and Structural Changes

Cd was found to cause toxic effects in the crop plants (Sethy and Ghosh 2013; Shanmugaraj et al. 2013). Cd uptake relies on its biological presence in the contaminated soil (Clemens 2006). It can be easily absorbed, translocated, and transported via root cortex to shoots symplastically (Tudoreanu and Phillips 2004). Cd shows many toxic symptoms in plants, which include growth retardation, altered stomatal movement, changes in photosynthetic activity, enzymatic activities, and membrane functioning and protein metabolism. Cd taken by plants is the main source of food contamination (Chunhabundit 2016). Even low concentration of Cd is toxic to most of the living organisms. Cd can be accumulated in plants with a concentration higher than 0.01% of shoot dry weight without causing the toxic symptoms (Reeves and Baker 2000; Verbruggen et al. 2009). Cd collects in the topsoil region in the proximity with organic fraction, which is highly accessible for those plants that are growing in the acidic soils (Tudoreanu and Phillips 2004; Kirkham 2006), hence increasing Cd solubility in root exudates (Luo et al. 2014). Plant cell wall recognized as the major site for heavy metal storage and its accumulation in cell wall is regarded as a heavy metal tolerance mechanism (Vázquez et al. 2006). The first plant part affected by heavy metals is the roots, as the metal ions are deposited more in roots than shoots (Singh et al. 2016). Observation of Cd localization under electron microscopy reveals that the cell wall of roots contains a majority of metals when compared with cytoplasm, because heavy metals bind to the cell wall due to their negative charge (Polle and Schützendübel 2003; DalCorso et al. 2010). Plant roots can easily absorb Cd and it is transported to shoots, which result in cellular, molecular, physiological, and biochemical changes that impair morphology and growth of plants (Shanmugaraj et al. 2013; Song et al. 2017).

Cd toxicity seemingly hinders plant root growth, disturbing root morphology (Daud et al. 2009a, b). Prolonged Cd exposure to plants may force roots to become brown, mucilaginous, and decomposed, with a decrease in shoots and root elongation, chlorosis, and rolling of leaves. Cd accumulation halts the formation of lateral root, while the main root becomes rigid, brown, and twisted (Table 4.1) (Krantev et al. 2008; Rascio et al. 2008; Yadav 2010). Cd exposure was found to reduce dry matter and root length and enhance the diameter of the root (Gratão et al. 2009). An increase in the root diameter may be due to an increase in the size of parenchymal cells and expansion of cortical tissue that has a key role in enhancing plant resistance to radial flow of water (Maksimović et al. 2007). In *Salix capra* F20, Cd treatment is found to decrease total root area (Vaculík et al. 2012). In differentiated roots, Cd stress can cause an abnormal number of nucleus populations (Table 4.1) (Fusconi et al. 2006) and it can inhibit the mitotic index, stimulate mitotic and chromosomal aberrations, and delay micronucleus formation. It can also cause DNA damage in the root-cap cells (Table 4.1). In onions, Cd was found to damage nucleoli in the root tip cells, induce mitotic and chromosomal aberrations (Liu et al. 1995; Seth et al. 2008). It also changes the RNA synthesis by inhibiting the activity of ribonuclease in rice (Table 4.1) (Shah and Dubey 1997).

Some plants are extremely sensitive to small Cd concentration taken through xylem from soil, which results in a decrease in photosynthetic rate along with root and shoot growth (Table 4.1) (Sandalio et al. 2001). It was reported in rice crop that Cd toxicity causes stunting growth, inhibition of seedling vigor, increased synthesis of some novel protein along with proline, and decrease in activities of many key hydrolytic enzymes (Shah and Dubey 1997; Shah et al. 2001).

Exogenous Cd application on alga *Sprirogyra setiformis* alters its morpho-biochemical structures. Small concentration of Cd can disturb the regular spiral chloroplasts and reduces the biomass, pigments, and protein production of the alga. It was also reported that anionic, amino, and amide groups may have a significant role in $Cd^{2+}$ uptake by the alga (Çelekli et al. 2015). Chloroplast structure of alga *Micrasterias* was also severely damaged under Cd stress (Molinari et al. 2007; Srivastava et al. 2009).

### 4.4.4 Chlorophyll Content and Photosystem

Chlorophyll is one of the necessary components of chloroplast for photosynthesis. It is linearly correlated with photosynthetic rate. Cd-treated plants show reduced chlorophyll content, which is mainly due to their disturbed biosynthesis (Stobart et al. 1985). *In vivo* Cd application reduces the plastid pigment concentrations. Observations revealed that concentration of chlorophyll *a* decreased more than that of chlorophyll *b* and carotenoids (Vassilev and Yordanov 1997). The effect of Cd on the plastid pigments depends on the plant development and leaf age. In strawberry, chlorophyll content decreased under Cd toxicity and the amount of chlorophyll *a* was found to be higher than chlorophyll *b* (Table 1) (Muradoglu et al. 2015). Cadmium responsive reduced chlorophyll and carotenoid content could be due to inhibition of enzymes responsible for pigment biosynthesis and this inhibition induced a kind of senescence (Qian et al. 2009). Chlorophyll content reduction under Cd stress was also reported in the leaf of mung bean (Doğanlar and Atmaca 2011). Inhibitory effect of Cd to chlorophyll synthesis and chlorophyll content were also reported in various plants (Shahabivand et al. 2012; Mangal et al. 2013; Liu et al. 2014). Fluorescence data revealed that transport of electron via photosystem II is retarded by Cd. Cd exposure to the plants reported to increase the chlorophyllase amount, which resulted in chlorophyll deterioration and reduces protochlorophyllide reductase complex and δ-aminolevulinic acid (Hayat et al. 2014). A research conducted by Hindarti and Larasati (2019) on species of phytoplankton *Nitzschia* sp. under Cd stress and studied various characters such as phytoplankton cultivation, cell density counting, and chlorophyll *a*, and carotenoid content and results revealed that increasing Cd concentration decreases the intracellular pigment content and cell density.

Previous studies reveal that heavy metals interact with components of cells, such as DNA and the nucleic proteins causing DNA damage. This DNA damage influences carcinogens in the cells and results in apoptosis. Cadmium affects signal transduction; it can induce the formation of inositol polyphosphate and switch the protein channels. Even low concentration of Cd (1-100 μM) binds with proteins and slows down the DNA repair ability, thus activating degradation of proteins and stimulating various genes encoding glutathione transferase, metallothionein, hemeoxygenase, and DNA polymerase (Tchounwou et al. 2012). *Festuca arundinacea*, known for rhizoremediation and high $Cd^{2+}$ tolerance, show reduced chlorophyll content under Cd stress. In the electron donor side of photosystem II, electron transport from water splitting complex (WSC) to tyrosine (Yz) residue of D1 protein was also retarded under high $Cd^{2+}$ concentration, the reason may be either ROS production or $Ca^{2+}$ replacement in the core of WSC. While in electron acceptor side, electron transport efficiency increased from quinine B to photosystem I acceptor under high $Cd^{2+}$ concentration (Table 4.1) (Huang et al. 2017).

Hydroponic experiment conducted by (Li et al. 2015) on seedlings of *Elsholtzia argyi* reveals that high concentration of Cd significantly influences the chlorophyll fluorescence and photosynthetic parameters (Table 4.1). The oxygen evolving complex (OEC) present at photosystem II is also influenced by $Cd^{2+}$ in Ca/Mn clusters that form the oxygen-evolving centers (Sigfridsson et al. 2004), and changing plastoquinone binding site (Geiken et al. 1998). In *Brassica napus*, Cd reduces the total chlorophyll and carotenoid content, and enhances nonphotochemical quenching (Larsson et al. 1998). Application of $Cd^{2+}$ and salicylic acid (SA) on *Brassica juncea* facing $Cd^{2+}$ exposure enhances the potential of plant for tolerating Cd stress by enhancing proline content and accumulation of chlorophyll in leaves (Table 4.1) (Hayat et al. 2014).

### 4.4.5 Photosynthesis, Carbon Assimilation, and Nutrient Status

Intake of Cd alters nutritional content, phytochemicals of plants, and hinders opening of stomata by interfering with water balance in plants (Table 4.1) (Feng et al. 2010). Cd uptake alters the Calvin cycle enzymes, metabolism of carbohydrate and photosynthesis (Mobin and Khan 2007; Shi et al. 2010), which further alter the antioxidant metabolism (Khan et al. 2009), influencing plant growth. Although plants have well-established defense system against metal stress (Shanmugaraj et al. 2013), but high Cd concentration damages the plant and can cause leaf roll, decrease chlorophyll content, and inhibits leaf photosynthesis by reducing the chlorophyll biosynthesis (He et al. 2008; Rascio et al. 2008; Lee et al. 2010; Liu et al. 2010; Miyadate et al. 2010). Cd exposure has been reported to inhibit photosynthesis in *Brassica napus*, *Helianthus annuus*, *Thlaspi caerulescens*, *Zea mays*, *Pisum sativum*, *Vigna radiata*, and *Triticum aestivum* (Bazzaz et al. 1974; Baryla et al. 2001; Di Cagno et al. 2001; Küpper et al. 2007; Popova et al. 2008; Wahid et al. 2008; Moussa and El-Gamal 2010). Cd toxicity influences the photosystem II (Baker 1991), and the alteration of chlorophyll in the fluorescence structures helps in identification of damaged photosystem II under stress (Maxwell and Johnson 2000). Two enzymes, namely, ribulose-1,5-bisphosphate carboxylase (rubisco) and phosphoenol pyruvate carboxylase, involved in $CO_2$ fixation are the main site for Cd damage. The rubisco activity is lowered by changing its structure, misplacing $Mg^{2+}$ that are vital cofactors of the carboxylation reactions, and swing toward the oxygenation reactions (Siedlecka et al. 1998).

Environmental stresses directly influence different photosynthetic reaction, like carbon reduction cycle $CO_2$ supply through stomatal aperture and increase carbohydrate accumulation. They also cause water balance and destruction of lipid via peroxidation (Allen and Ort 2001). Cd stress reduces the chlorophyll content and stomatal conductance that ultimately affect photosynthetic reaction (Ouzounidou et al. 2005). Excess Cd reduces photosynthetic rate via limiting the $CO_2$ availability (Bazzaz et al. 1974) and disturbs mineral nutrient uptake that finally causes reduction in photosynthetic rate (Gussarsson et al. 1996). It was reported in Cd-treated barley and wheat plants that an increase in leaf photosynthesis with a decrease in canopy photosynthesis occurs (Clijsters and Van Assche 1985; Landberg and Greger 1994; Krupa 1999; Vassilev and Manolov 1999; Küpper et al. 2007; Wahid et al. 2008; Li et al. 2015).

It is well known that Cd alters the photosynthesis rate. It induces the structural and functional changes in photosynthetic apparatus (Parmar et al. 2013). The first target of Cd is to damage photosynthetic apparatus, specifically the light-harvesting complex II and both photosystems I and II (Sanità di Toppi and Gabbrielli 1999; Küpper et al. 2007). This damage may lead to a decrease in carotenoid and chlorophyll contents. Destruction and retarded biosynthesis of chlorophyll in young as well as old leaves are the main factors responsible for Cd inducing chlorosis (Xue et al. 2013). Cd also disturbs the Calvin cycle by hindering the activity of different enzymes entangled in this process, hence leading to reduced photosynthesis rate (Ying et al. 2010). Apart from this, Cd impairs the ultrastructure of chloroplast and slows down the process of leaf transpiration and stomatal conductance (Table 4.1) (Najeeb et al. 2011; Souza et al. 2011). Cd stress results in stomatal closure independently regardless of the water status of plants. Entry of Cd into the guard cells resulted in stomatal closure and reduces the stomata number per unit area. $CO_2$ conductance also reduced that finally halts the overall photosynthesis process (Pietrini et al. 2010). At the level of atoms, Cd can promote various changes in the chlorophyll–protein complexes, such as Cd can displace Ca ions present in OEC and Mg ion of chlorophyll (Pagliano et al. 2006; Küpper et al. 2007). Cd halts photosynthesis by reducing transcription of photosynthesis-related genes, deactivate various enzymes participating in $CO_2$ fixation, enhance proteolysis, stimulate lipid peroxidation, and affect in the nitrogen and sulfur metabolism (Gallego et al. 2012). Cd influences the photosynthesis at various structural and functional levels such as thylokoid ultrastructure, pigments, and light capture, $CO_2$ access, stomatal conductance, photosynthetic electron transport, and activities of enzymes involved in Calvin cycle (Clijsters and Van Assche 1985; Krupa 1999; Cuypers et al. 2001). Effect of Cd on light-dependent photosynthetic processes is already studied in both *in vivo* and *in vitro* conditions (Van Assche and Clijsters 1990; Vassilev and Manolov 1999; Kalaji and Loboda 2008; Sagardoy et al. 2009).

Cd also shows an adverse effect on the content of sugars and amino acids in some plant species (Moya et al. 1993; Costa and Spitz 1997; Wu et al. 2004) by enhancing their concentration, indicating inhibition of starch hydrolysis (Bishnoi et al. 1993). Cd significantly lowers normal $H^+$-$K^+$ exchange, plasma membrane ATPase activity, and various other enzymes including glucose-6-phosphate dehydrogenase, glutamate dehydrogenase, malic enzymes, isocitrate dehydrogenase (Van Assche and Clijsters 1990; Mattioni et al. 1997), and carbonic anhydrase and rubisco (Siedlecka et al. 1997). It was reported in *Zea mays* seedlings exposed with 20 mM Cd, a significant increase in phosphoenolpyruvate carboxylase polypeptide without further synthesis of glutamate synthase and glutamate dehydrogenase were observed (Ju et al. 1997); whereas chromatin alteration was observed in pea plants (Hadwiger et al. 1973). Chemically, Cd ions are similar to Zn ions, and it can arrest the activity of Zn-finger transcription factors, replacing Zn ions, hence disturbing with transcription mechanisms (Sanità di Toppi and Gabbrielli 1999; Sanità di Toppi et al. 2007). Cd was found to replace $Ca^{2+}$ ions in calmodulin proteins, causing disturbance of the intracellular calcium levels and changing the calcium-dependent signaling pathways (Perfus-Barbeoch et al. 2002) via a mechanism resembling with the one observed with Zn transcription factors. Cd stress leads to a significant increase in $Ca^{2+}$ concentration (DalCorso et al. 2008, 2010), inducing calmodulin-like proteins for interacting with $Ca^{2+}$ ions by altering their conformation for regulating various mechanisms, such as stress tolerance, ion transport, metabolism, and gene regulation (Yang and Poovaiah 2003). Cd decreases the absorption of micro- and macronutrients, hence influencing transportation activities in the plants (Hernandez et al. 1996). Cd generates adverse effects by disturbing uptake, transport, and distribution of mineral elements, i.e., P, K, S, Ca, Mg, Fe, B, Cu, Mn, Zn, and Mo in some plant species including *Beta vulgaris* (Chang et al. 2003), peas (Metwally et al. 2005), and barley (Guo et al. 2007). It was observed in *Silene cucubalus* that Cd treatment affects uptake and transportation of nitrate from roots to the shoots by decreasing nitrate reductase activity (Mathys 1975). Cd induces changes in the fatty acid and lipid composition, changing the membrane functionality (Popova et al. 2009). High Cd concentration results in abnormal nutrient metabolism, including imbalances between sugars and proteins in plants (Costa and Spitz 1997).

Excessive Cd can influence the glycolytic pathway and the Cd-induced disturbance of photosynthetic apparatus and these alterations may have noticeable impact on the plants' ability to resist these kinds of stresses (Dahunsi et al. 2019). Glyceraldehyde-3-phosphate dehydrogenase, one of the key enzymes of glycolysis, was found to change its activity under Cd stress. Cd also damages the cell wall via increasing chitinase expression (van Keulen et al. 2008). Cd reduces the growth of plants belonging to various species via disturbing the processes of respiration, photosynthesis, and mineral uptake (Table 4.1) (Bazzaz et al. 1974; Clijsters and Van Assche 1985; Baker 1991; Moya et al. 1993; Krupa 1999; Wahid et al. 2008; Shi et al. 2010; Liu et al. 2014).

### 4.4.6 Reproductive Tissues

Reproductive tissues of many plant species are more prone to heavy metal toxicity than their vegetative tissues. Pollen fertility may be impaired by heavy metals. Pollen developed in the male reproductive organ, namely, anther travels from flower to flower via wind agency for pollination purpose. The effects of heavy metals on pollen grain are:

(a) reduced pollen viability and its germination rate by changing reproductive and biological functions;
(b) altering physicochemical properties of pollen surface;
(c) changing allergenic potential of pollen;
(d) adjuvant effect that increases health hazard potentially (Sénéchal et al. 2015).

Heavy metal toxicity increases the allergenicity of pollen. Pollen grains are considered as more sensitive to pollutants than vegetative parts (Sawidis and Reiss 1995; Behrendt et al. 1997; Sawidis 2008). Cadmium and lead can be accumulated by pollen grains. Heavy metal accumulation can reduce the pollen quality that affects its economic use. Loss of pollen viability due to pollutants reduces its fertility. Pollen germination and pollen tube growth are mostly affected by metal ions, such as $Cd^{2+}$, $Hg^{2+}$, and $Cu^{2+}$, whereas $Mn^{2+}$ mainly affects germination and growth rate (Zhang et al. 1999). Only $Cd^{2+}$ can influence the intracellular region and organelle distribution in the tip region and visibly disorganized (Strickland and Chaney 1979; Sawidis and Reiss 1995). Till now, most of the studies are done either *in vitro* or *in vivo* for evaluating the damaging effect of heavy metals on pollen grains. Cd stress potentially decreases pollen germination rate and pollen tube growth (Peralta et al. 2001; Xiong and Peng 2001; Tuna et al. 2002; He et al. 2008; Sawidis 2008; Farooqi et al. 2009; Sabrine et al. 2010; Ghosh and Sethy 2013; Sethy and Ghosh 2013). Pollen tubes growing in *in vitro* conditions under Cd toxicity show various strong morphological changes that are characterized by anomalous and irregular growth including swelling of tip of tube and highly contorted growth. Heavy metals in high concentrations reduce the enzyme activities and pollen germination, while low Cd concentrations show a stimulatory effect on the tube elongation and growth rate, which is ascribed to provoke enzyme activities at low concentration (Peralta et al. 2001; Tuna et al. 2002; He et al. 2008; Sawidis 2008; Farooqi et al. 2009; Sabrine et al. 2010; Ghosh and Sethy 2013; Sethy and Ghosh 2013). Cd at 0.001 μM was found to enhance the germination rate in pollen grains of *Nicotiana tabacum* and *Lilium longiflorum* (Sawidis 2008), around 10 μM Cd in *Plantago depressa* (Xiong and Peng 2001) and 1000 μM Cd in *Brassica napus* (Ismael et al. 2018).

## 4.4.7 Biochemical Responses

### 4.4.7.1 ROS/Electrolyte Leakage

Cd stress causes an increase in ROS that is harmful to cellular components (Schützendübel et al. 2001; Schützendübel and Polle 2002; Apel and Hirt 2004; Valko et al. 2005; Møller et al. 2007; Sanità di Toppi et al. 2007; Sharma and Dietz 2009; Ge et al. 2012). The content of MDA is a very common indicator of oxidative damage (Mittler 2002; Møller et al. 2007), which is also used as appropriate indicator for membrane lipid peroxidation. ROS causes a considerable decrease in lipid peroxidation in the membrane along with free radical reactions in tissues (Hassan et al. 2005; Shamsi et al. 2008). Oxidative stress triggered by Cd through convolute mechanism disturbs the electron transport chain (Schützendübel et al. 2001; Schützendübel and Polle 2002; Garnier et al. 2006). Interestingly, plants have already evolved a defensive mechanism to overcome Cd stress by mitigating and overcoming the damage caused by ROS (Overmyer et al. 2003; Edreva 2005).

### 4.4.7.2 Antioxidant Enzymes

Plant expels an injurious active oxygen out by enzyme-catalyzed cleanup system (Horváth et al. 2007). Thus, an imbalance between activities of antioxidative enzymes and ROS production indicates the possibility of oxidative signaling or damage (Møller et al. 2007). Plants have evolved a composite enzymatic and nonenzymatic antioxidant system to reduce the effects of oxidative stress, such as CAT, POX, ascorbate peroxidase (APX), low molecular mass antioxidants, i.e., GR, ascorbate, carotenoids, ROS scavenging enzymes, and SOD (Apel and Hirt 2004). The enzymatic system scavenges ROS either directly or indirectly via producing nonenzymatic antioxidant (Yang et al. 2009). The additive effects of nonenzymatic antioxidant help in maintaining the integrity of photosynthetic membranes (Mittler 2002). Furthermore, exogenous treatment of *Brassica* seedlings with citric acid and SA helps in mitigating Cd stress by enhancing the antioxidant activity of plant cells (Table 4.1) (Faraz et al. 2019). Heavy metal exposure influences the activity of leaf carbonic anhydrase and nitrate reductase in several plants including *Cicer arietinum* (Table 4.1). Shaw (1995) reported that in *Phaseolus vulgaris*, *Phaseolus aureus*, and

*Helianthus annuus*, the change in the antioxidant system with an increase in lipid peroxidation is straightforwardly related to Cd toxicity. Moreover, increase in ROS ($O_2^-$, $H_2O_2$) due to Cd toxicity results in a slight decrease of CAT activity in pine (Schützendübel et al. 2001) and pea roots (Dixit et al. 2001) and also in *Arabidopsis thaliana* (Cho and Seo 2005) and sunflower leaves (Laspina et al. 2005).

## 4.5 Mechanism of Cadmium Detoxification

Various defense mechanisms are used by plant cells to reduce the toxicity caused by heavy metals. Upregulation of some genes of plant genome related to sequestration, mobilization, and chelation enhance the metal detoxification process. Nicotianamine is a metal chelator that shows high affinity for some transition metals, like Ni, Fe, Zn, Mn, Cu, and Co, and reduces the toxicity through chelation. Cd stress tolerance can be enhanced by overexpressing this nicotianamine synthase gene by reducing Cd influx (Koen et al. 2013).

Vacuole is a well-regulated tank of the plant cell that works like a storage buffer for the mineral elements (Vögeli-Lange and Wagner 1990). Earlier studies have revealed that the tonoplast membrane of the plant vacuole mediates the metal ion transport through various transporters. Different tonoplast membrane proteins, such as metal tolerance protein, ABBCC-type transporter, and heavy metal ATPase accumulate and enhance the Cd tolerance by sequestration of Cd in *Arabidopsis* (Krämer 2005; Arrivault et al. 2006; Morel et al. 2008; Park et al. 2011). Moreover, NRAMP3 is also a tonoplast protein transporter associated with Fe and Cd mobilization. Overexpression of the NRAMP3 gives rise to Cd hypersensitivity in root growth of *Arabidopsis thaliana* (Thomine et al. 2000; Lanquar et al. 2005, 2010).

Apart from these, some cell membrane-localized ABC transporter pleiotropic drug resistance 8 and plant Cd resistance 1 increase the Cd resistance through exporting and pumping out Cd from the cell to decrease its concentration (Song et al. 2004; Kim et al. 2007). Yuan et al. (2018) reported four transcription families in creeping bentgrass that play a very important role against the Cd stress viz. WRKY, bZIP, ERF, and MYB. In future, with the help of transcriptomics, the severity level of Cd stress in the plants can be checked. In *Arabidopsis thaliana*, several MAPK factors including AtMAPKK1 have been found to be upregulated under Cd stress (Suzuki et al. 2001).

Production of ROS under the Cd stress was found to activate the MPK6 and MPK3 (Liu et al. 2010). Moreover, various types of MAPK have been discovered in different plant species suffering from Cd stress. Research conducted by Jian et al. (2018) in *Brassica napus* reveals seedling exposed to Cd stress differentially expressed 39 miRNAs, out of which 31 are novel. These Cd-responsive miRNAs may participate in tolerating Cd toxicity by regulating the transcription factors, which are important in secondary metabolism, ion transporters, and stress responses.

In a halophyte *Carpobrotus rossii*, NaCl addition to solution containing Cd not only did improve the plant growth, but also decreased Cd accumulation up to 70-87% by reducing root uptake and root-to-shoot translocation of Cd regardless of activity of $Cd^{2+}$ in solutions (Cheng et al. 2018). Furthermore, addition of the carbon dots to the $Cd^{2+}$ treated plants significantly decreased Cd concentration in leaves and roots of wheat (Xiao et al. 2019).

## 4.6 Conclusions

Cd is a threatening agent for the plants and causes serious damage. It enters the plant body through several transporters and interacts with different peptides, metals, etc. This interaction influences the plants in various aspects. Cd reduces the seed germination by inhibiting embryo growth and enzyme activities. Cd exposure not only heavily affects the plants by interfering with its normal metabolism, but also induces several changes in the structure and morphology of the plants. Cd stress negatively influences the photosynthesis, carbon assimilation, nutrient uptake, chlorophyll content, and photosystem. It reduces the reproductive potential and enhances generation of ROS. Plants exhibit various strategies for mitigating Cd toxicity, such as production of antioxidants and some cysteine-rich peptides, i.e., PCs, GSH, or MTs. These stress-mitigating strategies should be exploited using, e.g., exogenous application of growth regulators, genetic manipulation, or development of transgenic plants to increase tolerance against Cd stress.

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# Effect of Soil Polluted by Heavy Metals: Effect on Plants, Bioremediation and Adoptive Evolution in Plants

# 5

Pravin K. Singh

**Abstract**

Persistent heavy metal poses a major threat to living beings in the environment due to its toxic effects. Environmental pollution from heavy metals has adversely affected the natural ecosystem and is detrimental to all forms of life. Heavy metals are very reactive at low concentrations and could accumulate in agricultural soils and get into the food chain, thereby becoming a major threat to food security. Bioremediation of toxic metals has received considerable and growing interest because it is an environmentally benign and efficient method of reclaiming environments contaminated with heavy metals by using inherent biological mechanisms of microorganisms and plants to eradicate toxic heavy metals. Toxic effects of heavy metal in plants and mechanisms for bioremediation were discussed. It is also emphasized the importance of modern techniques or approaches in improving the ability of microorganisms to degrade or removal of heavy metals from the environment at a faster rate and highlighting the adaptive evolution in plants.

**Keywords**

ecosystem · toxic · food chain · bioremediation · adaptive evolution

## 5.1 Introduction

Heavy metals are naturally occurring elements. They are found in elemental form as well as in chemical compounds. Each form or compound has different properties. At first glance, it would be to define the "heavy metal" – it is a metal that is "heavy". Unfortunately, a more in-depth consideration reveals an enormous amount of

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problems with this simple definition. This definition is meant to suggest that heavy metals have high density, but this physical property is quite meaningless in the context of plants and other living organisms. The term heavy metals have been vaguely applied to a group of physically miscellaneous and chemically heterogeneous elements. From a chemistry point of view, the term heavy metal is strictly ascribed to transition metals having an atomic number more than 20 and specific gravity greater than 5. In biology point of view, “heavy metal” refers to a series of metals and metalloids that can be toxic to both plants and animals even at very low concentrations. Some authors define heavy metal as elements having atomic mass greater than that of sodium, whereas others define it inconsistently as a metal within a density range of 3.5–6 g $cm^{-3}$. Saxena and Misra (2010) deem approximately 65 elements as heavy metals. According to Srivastava and Majumder (2008), heavy metals are elements having atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0.

Some heavy metals are essential for animals and plants when present in low concentrations (micronutrients: Fe, Mn, Cu, Zn, Mo, Ni and Co); they become toxic or poisonous only when a concentration limit is exceeded (in which case the term ‘heavy metals’ rather than ‘micronutrients’ is used) and reduces plant growth due to reduced photosynthetic activities, plant mineral nutrition and reduced activity of essential enzymes (Kabata-Pendias 2010; Nematian and Kazemeini 2013). In humans, heavy metals are cytotoxic at low concentrations and could lead to cancer (Dixit et al. 2015a, b). These toxic metals could accumulate in the body when consumed in contaminated food and cause health risks to living organisms (Tak et al. 2013). These toxic metals also causes oxidative stress, an unevenness involving the production of free radicals and the capacity of cells to eradicate them or repair the damage (Chandra et al. 2015; Mani 2015).

Environmental pollution by heavy metals has become a serious problem in the world needing the highest priority. In last decades, rapid industrialization and technological advancement have put an increasing burden on the environment by releasing large quantities of hazardous waste, heavy metals (cadmium, chromium, and lead) and metalloids (elements with intermediate properties between those of typical metals and non-metals such as arsenic and antimony), and organic contaminants that have inflicted serious damage on the ecosystem (Ayansina and Olubukola 2017). The build-up of heavy metals and metalloids in soils and waters continues to create serious global health concerns, as these metals and metalloids cannot be degraded into non-toxic forms, but persist in the ecosystem. Contamination of the environment with heavy metals has increased beyond the recommended limit and is detrimental to all life forms (Tak et al. 2013; Gaur et al. 2014; Dixit et al. 2015a, b). Soil polluted by heavy metals is a critical global environmental problem.

## 5.2 Heavy Metal Polluted Soils

In the present age of rapid industrialization, it is not possible to avoid the toxic chemicals and metals in the environment, especially heavy metal pollution has become a serious threat to the environment and food security because of rapid growth in industries and agriculture and disturbance of natural ecosystem due to enormous increase in world population (Sarwar et al. 2017). Unlike organic pollutants, biodegradation of heavy metals is just out of the question and hence heavy metals are continuously accumulating in the environment (Sarwar et al. 2010). Accumulation of these heavy metals in agricultural soils and water resources poses a great threat to plant and human health due to the potential risk of their entry into the food chain.

Soil has been recognized as the major sink for anthropogenic heavy metal deposition through various pathways and accumulation of heavy metals in agricultural soils has been a wide concern of the public issue because of the food safety and potential health risks as well as its detrimental effects on soil ecosystems. The contamination of soil by heavy metals can cause problems at several levels because they do not degrade biologically and this always results in severe soil pollutions leading to concerns about the environmental quality. Metal-contaminated soil poses risks to animals and humans through absorption of plants that have bioaccumulated toxic heavy metals from contaminated soil (Ogunkunle and Fatoba 2014). Environmental pollution by heavy metals in agricultural soil has increased by human activities. At high concentrations, all heavy metals have strong toxic effects and are regarded as environmental pollutants. Excess concentrations of heavy metals in soils have caused the disruption of natural ecosystems. Heavy metals are elements that exhibit metallic properties such as conductivity, ductility, malleability, cation stability and ligand specificity. Heavy metals exist either as separate entities or in combination with some other soil components. The components of soil may include exchangeable ions absorbed on the surfaces of inorganic solids, non-exchangeable ions and insoluble inorganic metal compounds such as phosphates and carbonates, soluble metal compound or free metal ions in the soil solution, metal complex of organic materials and metals attached to silicate minerals (Marques et al. 2009). Heavy metal(s) affect the number, diversity, and activities of soil microorganisms.

## 5.3 Sources of Heavy Metal Contamination of Soils

There are many sources of heavy metals in the environment such as

(a) Natural sources.
(b) Agricultural sources.
(c) Industrial sources.
(d) Domestic effluent.
(e) Atmospheric sources.
(f) Miscellaneous sources.

**Table 5.1** Guideline for safe limits of heavy metals in agricultural soil ($\mu gg^{-1}$ or ppm)

| Heavy metals | Pb | Cu | Cd | Zn | Ni |
|---|---|---|---|---|---|
| Indian standard | 250–500 | 135–270 | 3–6 | 300–600 | 75–150 |

(a) **Natural sources:** Heavy metals naturally occur in soils usually at very low concentration, as a result of the weathering and other pedogenic processes acting on the rock fragments, which convert rock into soil parent materials. The initial sources of heavy metals in soils are the parent materials from which the soils were derived, but the influence of parent materials on the total concentrations and forms of metals in soils is modified to varying degrees by pedogenic processes. In areas affected lightly by human activities, heavy metals in the soils derived mainly from pedogenic parent materials and metals' accumulation status was affected by several factors such as soil moisture and management patterns (El-Gammal et al. 2014). During weathering processes, the primary crystalline structures of some rock minerals are completely broken and relevant chemical elements are thus either adsorbed in the topsoil or transported towards surface water or groundwater targets (Partha et al. 2011).

(b) **Agricultural sources (Fertilizers and agrochemicals):** The organic fertilizers and inorganic are the most important sources of heavy metals to agricultural soil. It includes liming, sewage sludge, irrigation waters and pesticides as sources of heavy metals in the agricultural soils. Others, particularly fungicides, inorganic fertilizers and phosphate fertilizers, have variable levels of Pb, Ni, Cd, Cr and Zn depending on their sources. Table 5.1 represents the safe limit of heavy metal pollution in agricultural soil. Cadmium is of particular concern in plants. It accumulates in leaves at very high levels, which may be consumed by animals and human beings. Cadmium (Cd) enrichment also occurs due to the application of sewage sludge, manure and limes. Although the levels of heavy metals in agricultural soil are very small, but repeated use of fertilizer and the long persistence time of metals, there may be dangerously high accumulation of heavy metals.

(c) **Waste water irrigation:** Continued irrigation of agricultural soil can lead to accumulation of heavy metals such as lead (Pb) and cadmium (Cd). After prolonged application of untreated wastewaters, significant amounts of heavy metals can accumulate in the soil at toxic levels. At present, heavy metals such as Pb, Cr, Zn, Cd, Ni, etc. are commonly found in soil irrigated with wastewater. Once the adsorption site of the soil for heavy metals is saturated, more heavy metals would be distributed in the aqueous phase and the bioavailability of heavy metals would subsequently be enhanced.

(d) **Mining:** Mining is one of the most important sources of heavy metals in the environment. Mining and milling operations together with grinding, concentrating ores and disposal of tailings, along with mine and mill waste water provide obvious sources of contamination. Therefore, large areas of agricultural land can be contaminated including paddy field. Mines can become an important point source of toxic elements including As, Cd, Cu, Pb and Zn in the surface (Lee et al. 2001). Heavy metals contained in residues coming from mining and metallurgical operations are often dispersed by wind, water (erosion), and by the atmosphere within a distance and transported up to several kilometres away from their sources, transferred to the soil and accumulated in plants, animals and can then be passed up the food chain to human beings as a final consumer and cause an adverse effect on the ecosystem around the metal mines (Alshaebi et al. 2009 and Ripin et al. 2014).

## 5.4 Effect of Heavy Metal-Polluted Soil on Plant Growth

Heavy metals exist in soil as a variety of chemical species in a dynamic equilibrium governed by various physical, chemical, and biological properties. In general, only a fraction of heavy metal in the soil is readily available (bioavailable) for plant uptake. Bioavailability is the fraction of total heavy metals that are available for intake into plant (bioaccumulation). It is not necessary that total metal concentrations correspond with metal bioavailability. Maximum amount of soil heavy metals are commonly found as insoluble compounds and unavailable transport into roots. But some of the metals (Zn and Cd) occur primarily as soluble or exchangeable, readily bioavailable form. Some other metals (Pb) occur as insoluble precipitates (carbonates, phosphates, and hydroxy-oxides), which are largely unavailable for plant uptake (Lasat 2002).

Innumerous factors are held responsible for affecting the mobility of heavy metals and phytoavailability in plants. They are solubility of heavy metals in soil solution, heavy metal-precipitates, heavy metal sorbed to clays, hydrous oxides, organic matter, and metals within the matrix of soil minerals. These different factors are all in dynamic equilibrium with each other. However, while the soluble metal in the soil solution is directly available for plant uptake, other soil metal pools are less available. Change in the concentration of heavy metal in the matrix of soil minerals is slow relative to exchange and desorption reactions between clays, hydrous oxides, organic matter, and the soil solution. Soil factors which have an effect on metal bioavailability (Reichman 2002; Singh et al. 2015a, b) are as follows:

Soil pH: Soil pH is a major factor affecting the availability of heavy metals in the soil for plant uptake. Under acidic conditions, $H^+$ ions displace metal cations from the cation exchange complex of soil components and cause metals to be released from variable-charged clays to which they have been absorbed. At low pH, retention of metals to soil organic matter is also weaker, resulting in more available heavy metal in the soil solution for root absorption. Many heavy metal cations (Cd, Cu, Hg, Ni, Pb, Zn, etc.) are more soluble and available in the soil solution at low pH (below 5.5). Increases in soil pH decreased with availability of heavy metals to the plant roots. At neutral or alkaline pH, most of the metals in soil are not available to plants; specifically, lead (Pb) and chromium (Cr) are inherently immobile. Decreasing pH in soils increases the competition between hydrogen ion and dissolved metals for ligands (carbonate, sulphate, sulphide, chloride, hydroxide, and phosphate ions). This increased competition decreases heavy metal adsorption capacity of soil particles leading to increased mobility of heavy metals, which ultimately boosts the bioavailability of the metals in the soil (Mkumbo et al. 2012).

### 5.4.1 Soil Organic Matter

Heavy metal ions can form complex with organic matter altering its availability to plants. The carboxylic groups in both solid and dissolved organic matter form stable complexes with heavy metals. Hence, the greater the amount of organic matter present in soil greater will be the formation of stable metal-organic matter complexes. In general, plants are unable to absorb the heavy metal-organic matter complexes (large size) and so the bioavailability of metals decreases (Reichman 2002). The organic matter is one of the most important factors that may reduce the ability of heavy metals to be phytotoxic in the soil due to the formation of heavy metal-organic complex. The presence of organic carbon increases the cation exchange capacity (CEC) of the soil, which retains nutrients assimilated by roots of plants. Increasing the amount of organic matter in the soil helps to minimize the absorption of heavy metals by plants. Land rich in organic matter actively retains heavy metals. Soils having low concentration of organic matter are more susceptible to contamination by trace elements. Compost amendments to contaminated soils containing labile elements (heavy metals) reduce the overall bioavailability of metals due to sorption processes (Laghlimi et al. 2015).

### 5.4.2 Redox Potential

The redox (oxidation/reduction) conditions of a soil can also play an important role in the availability of heavy metals. The redox status of the soil can be affected by many factors including water logging and compaction. Redox potential in soil is established by oxidation–reduction reactions (redox reaction) carried out by microbial activity. These redox reactions convert contaminants into non-hazardous or less toxic compounds that are more stable, less mobile or/and inert. However, in environments of soil, these reactions occur very slowly. Lack of oxygen in the soil causes start-up and increases the mobility of the large part of heavy metals.

## 5.5 Effect of Heavy Metal-Polluted Soil on Plant Growth

Although plants require some heavy metals for their growth and upkeep, but excess amounts of these heavy metals can become toxic to plants. Heavy metals cannot be broken down; when concentrations within the plant exceed optimal levels, they adversely affect the plant both directly and indirectly. Some of the direct toxic effects caused by high heavy metal concentration include inhibition of cytoplasmic enzymes and damage to cell structures due to oxidative stress (Jadia and Fulekar 2009). The indirect toxic effect of heavy metals in plants is replacement of essential nutrients at cation exchange sites of plants (Taiz and Zeiger 2002). Plant metabolism enzyme activities may also be hampered due to heavy metal interference with activities of soil microorganisms. These toxic effects (both direct and indirect) lead to a decline in plant growth, which sometimes results in the death of plants (Schaller and Diez 1991).

The toxic effect of heavy metal on the growth of plants varies according to the particular heavy metal involved in the process. Table 5.2 shows a summary of the toxic effects (Chibuike and Obiora 2014) of different heavy metals on biochemistry, physiology, and growth of various plants. Some heavy metals (Pb, Cd, Hg, and As) do not play any beneficial role in plant growth but adverse effects have been recorded at very low concentrations. Most of the reduction in growth parameters of plants growing on polluted soils can be attributed to reduced photosynthetic activities, plant mineral nutrition, and reduced activity of some enzymes (Kabata-Pendias 2001). Some other metals are beneficial to plants in small concentrations. These metals can actually improve plant growth and development. However, the higher concentrations of these metals reduce the plant growth. It is worth mentioning that in most real-life practices (such as disposal of sewage sludge and metal mining wastes) where soil may be polluted with more than one heavy metals, both synergistic and antagonistic relationships between heavy metals may affect plant metal toxicity. It is important to note that some plants are able to tolerate high concentration of heavy metals in their environment. Plants are tolerating heavy metals by following three mechanisms (Baker 1981): ***(i) Exclusion***: restriction of heavy metal transport and maintenance of a constant heavy metal concentration in the shoot over a wide range of soil concentrations. ***(ii) Inclusion***: Heavy metal concentrations in the shoot reflecting those in the soil solution through a linear relationship. ***(iii) Bioaccumulation*****:** accumulation of heavy metals in the shoot and roots of plants at both low and high soil concentrations.

## 5.6 Bioremediation of Heavy Metal-Polluted Soils

Bioremediation is the use of bios (microorganisms and/or plants) for the treatment of polluted soils. Since it is perceived to occur via natural processes, therefore is the widely accepted method of soil remediation. Bioremediation is usually a time-consuming and non-disruptive method of soil remediation and is also used for the treatment of heavy metal-polluted soils by the climatic and geological conditions. During bioremediation, heavy metals can neither degrade nor be destroyed, but can only be transformed from one oxidation state to another oxidation state or other organic complex. Due to change in their oxidation state, heavy metals may be transformed to less toxic, easily volatilized, less water soluble (which allows them to precipitate and become easily removed from the environment), more water soluble (and thus can be removed through leaching) or less bioavailable form (Garbisu and

**Table 5.2** Toxic effect of heavy metal on plants

| S.No. | Heavy Metal | Plant | Toxic effect |
|---|---|---|---|
| 1 | Lead (Pb) | Maize (*Zea mays*) | Reduction in germination percentage; suppressed growth; reduced plant biomass; decrease in plant protein content |
| | | Portia tree (*Thespesia populnea*) | Reduction in number of leaves and leaf area; reduced plant height; decrease in plant biomass |
| | | Inhibition of enzyme activity, which affected $CO_2$ fixation | Inhibition of enzyme activity, which affected $CO_2$ fixation |
| 2 | Mercury (hg) | Rice (*Oryza sativa*) | Decrease in plant height; reduced tiller and panicle formation; yield reduction; bioaccumulation in shoot and root of seedlings |
| | | Tomato (*Lycopersicon esculentum*) | Reduction in germination percentage; reduced plant height; reduction in flowering and fruit weight; chlorosis |
| 3. | Cadmium (cd) | Wheat (*Triticum* sp.) | Reduction in seed germination; decrease in plant nutrient content; reduced shoot and root length |
| | | Garlic (*Allium sativum*) | Reduced shoot growth; cd accumulation |
| | | Maize (*Zea mays*) | Reduced shoot growth; inhibition of root growth |
| 4 | Chromium (Cr) | Wheat (*Triticum* sp.) | Reduced shoot and root growth |
| | | Tomato (*Lycopersicon esculentum*) | Decrease in plant nutrient acquisition |
| | | Onion (*Allium cepa*) | Inhibition of germination process; reduction of plant biomass |
| 5 | Nickle (Ni) | Pigeon pea (*Cajanus cajan*) | Decrease in chlorophyll content and stomatal conductance; decreased enzyme activity, which affected Calvin cycle and $CO_2$ fixation |
| | | Rye grass (*Lolium perenne*) | Reduction in plant nutrient acquisition; decrease in shoot yield; chlorosis |
| | | Wheat (*Triticum* sp.) | Reduction in plant nutrient acquisition |
| | | Rice (*Oryza sativa*) | Inhibition of root growth |
| 6 | Zink (Zn) | Cluster bean (*Cyamopsis tetragonoloba*) | Reduction in germination percentage; reduced plant height and biomass; decrease in chlorophyll, carotenoid, sugar, starch and amino acid content |
| | | Pea (*Pisum sativum*) | Reduction in chlorophyll content; alteration in structure of chloroplast; reduction in photosystem II activity; reduced plant growth |
| | | Rye grass (*Lolium perenne*) | Accumulation of Zn in plant leaves; growth reduction; decrease in plant nutrient content; reduced efficiency of photosynthetic energy conversion |

(continued)

**Table 5.2** (continued)

| S.No. | Heavy Metal | Plant | Toxic effect |
|---|---|---|---|
| 7 | Manganese (Mn) | Broad bean (*Vicia faba*) | Mn accumulation in shoot and root; reduction in shoot and root length; chlorosis |
| | | Spearmint (*Mentha spicata*) | Decrease in chlorophyll *a* and carotenoid content; accumulation of Mn in plant roots |
| | | Pea (*Pisum sativum*) | Reduction in chlorophylls *a* and *b* content; reduction in relative growth rate; reduced photosynthetic $O_2$ evolution activity and photosystem II activity |
| | | Tomato (*Lycopersicon esculentum*) | Slower plant growth; decrease in chlorophyll concentration |
| 8 | Copper (cu) | Bean (*Phaseolus vulgaris*) | Accumulation of cu in plant roots; root malformation and reduction |
| | | Black bindweed (*Polygonum convolvulus*) | Plant mortality; reduced biomass and seed production |
| | | Rhodes grass (*Chloris gayana*) | Root growth reduction |
| 9 | Arsenic (as) | Rice (*Oryza sativa*) | Reduction in seed germination; decrease in seedling height; reduced leaf area and dry matter production |
| | | Tomato (*Lycopersicon esculentum*) | Reduced fruit yield; decrease in leaf fresh weight |
| | | Canola (*Brassica napus*) | Stunted growth; chlorosis; wilting |

Alkorta 1997; Garbisu and Alkorta 2003). Bioremediation of heavy metals can be achieved by the following methods:

### 5.6.1 Remediation of Heavy Metal-Polluted Soils by Using Microbes

Several microorganisms, especially bacteria (*Bacillus subtilis*, *Pseudomonas putida* and *Enterobacter cloacae*), have been successfully used for the conversion (Wang et al. 1989 and Garbisu et al. 1998) of a more toxic form of Chromium Cr(VI) to the less toxic Cr(III). Bioremediation can also occur indirectly by bioprecipitation. Sulphate-reducing bacteria (*Desulfovibrio desulfuricans*) converts sulphate ion to hydrogen sulphate ion, which subsequently reacts with heavy metals (Cd and Zn) to form insoluble forms of metal sulphides (CdS and ZnS) (White et al. 1998). Most of the above remediation is carried out ex situ. However, some in situ microbe assisted remediation of soluble mercuric ions Hg(II) to volatile metallic mercury and Hg (0) is carried out by mercury-resistant bacteria (Hobman and Brown 1997). The reduced Hg (0) can easily volatilize out of the environment and subsequently be diluted in the atmosphere (Lovley and Lloyd 2000).

Biochar is one organic material that is currently used for the management of heavy metal-polluted soils (Namgay et al. 2010). It is recorded that biochar reduces the availability of heavy metals in polluted soil; this, in turn, reduced plant absorption of the heavy metals. Unlike most of organic amendments, biochar increases soil pH (Novak et al. 2009). Further, more research is needed in order to understand the effect of biochar on soil microorganisms and how the interaction between biochar and soil microbes influences remediation of heavy metal-polluted soils because such studies are rare in literature.

### 5.6.2 Remediation of Heavy Metal-Polluted Soils by Using Plants (Phytoremediation)

Phytoremediation is a method of bioremediation in which plants are used for the treatment of polluted soils. This method is most suitable when the pollutants (heavy metals) cover a wide area and when they are within the root zone of the plant (Garbisu and Alkorta 2003). Phytoremediation of heavy metal-polluted soils may be achieved by the following mechanisms:

#### 5.6.2.1 Phytoextraction

This is the most common method of phytoremediation. It involves accumulation of heavy metals in the roots and shoots of phytoremediation plants. Later on, these plants will be harvested and incinerated. The plants used for phytoextraction must possess the following characteristics: extensive root system, rapid growth rate, high biomass, and the ability to tolerate high amounts of heavy metals. This ability to tolerate high concentration of heavy metals by these phytoremediation plants may lead to heavy metal accumulation in the harvestable parts of plants.

There are following two approaches for phytoextraction. The first approach involves the use of natural hyperaccumulators. In this approach, phytoremediation plants have very high metal-accumulating ability. However, in the second approach, phytoremediation plants have high biomass plants. In this approach, accumulation of metals in phytoremediation plants is induced by the use of chelates, i.e., soil amendments with metal mobilizing capacity (Salt et al. 1998).

Synthetic chelating agents are also used for extraction of heavy metals from polluted soils. These are EDTA (ethylenediaminetetracetic acid), EDDHA (ethylenediamine-di-*o*-hydroxyphenylacetic acid), DTPA (diethylenetriaminepentaacetic acid), EDDS (SS-ethylenediamine disuccinic acid), CDTA (*trans*-1,2-diaminocyclohexane-*N,N,N´,N´*-tetraacetic acid), and HEDTA (*N*-hydroxyethylenediaminetriacetic acid). EDTA is a widely used synthetic chelate that is not only because it is the least expensive compared with other synthetic chelates but also because it has a high ability to successfully improve plant metal uptake (Chibuike and Obiora 2014). Organic chelates such as malic acid and citric acid can also be used to improve phytoextraction of heavy metals from polluted soils

(Chiu et al. 2006). In general, availability/solubility of heavy metals for plant uptake and suitability of a site for phytoextraction are additional factors that should be considered (in addition to suitability of plants) before using phytoextraction for soil remediation (Blaylock and Huang 2000).

#### 5.6.2.2 Phytostabilization

Phytostabilization involves immobilization of heavy metals by using plants, thus reducing the bioavailability of heavy metals via leaching and erosion. This method is used when phytoextraction is not desirable (McGrath and Zhao 2003). Phytostabilization of heavy metals takes place as a result of sorption, precipitation, reduction of metal or complexation (Moral et al. 1995). The efficiency of phytostabilization depends on the soil and plant amendment. Plants used for phytostabilization should have the following characteristics: high ability to tolerate soil conditions, rapid growth to provide adequate ground coverage, dense rooting system, ease of establishment and maintenance under field conditions and longevity and ability to self-propagate. In general, phytostabilization is very useful when rapid immobilization of heavy metals is needed to prevent pollution of ground water.

#### 5.6.2.3 Phytovolatilization

In this method of phytoremediation, plants are used to take up pollutants from the soil and then these pollutants are transformed into volatile forms and subsequently transpired into the atmosphere (Chibuike and Obiora 2014). This method is mostly used for the remediation of soils polluted with mercury. The toxic form of mercury Hg(II) is transformed into the less-toxic form elemental mercury. The problem with this method is that the new product, elemental Hg, is formed, which may be redeposited into lakes and rivers after being recycled by precipitation; this, in turn, repeats the process of methyl-Hg production by anaerobic bacteria (Chibuike and Obiora 2014). Some transgenic plants, which have been used for phytovolatilization of mercury-polluted soils, are *Nicotiana tabacum*, *Arabidopsis thaliana* and *Liriodendron tulipifera* (Rugh et al. 1998; Meagher et al. 2000). These plants are usually genetically modified (Chibuike and Obiora 2014) to include gene for mercuric reductase, that is, merA. Organomercurial lyase (merB) is another bacterial gene used for the detoxification of methyl-Hg.

### 5.6.3 Remediation of Heavy Metal-Polluted Soil by Combining Plants and Microbes

The combined use of both plants and microorganisms for the remediation of polluted soils results in a faster and more efficient clean-up of the polluted site (Weyens et al. 2009). Mycorrhizal fungi have been used in several remediation studies involving heavy metals and the results obtained show that mycorrhizae employ different mechanisms for the remediation of heavy metal-polluted soils. For instance, while some studies have shown enhanced phytoextraction through the accumulation of heavy metals in plants (Chibuike and Obiora 2014).

## 5.7 Adoptive Evolution in Plants

### 5.7.1 Antioxidant Defence System

Plants develop a number of strategies to overcome the harmful effect imposed by heavy metals. Toxicity of heavy metals in plants may lead to overproduction of reactive oxygen species (ROS), resulting in peroxidation of many vital substances of the cell. Thus, plants have well-organized defence mechanism comprising a set of enzymatic and non-enzymatic antioxidants. A wide variety of enzymatic antioxidants consisting of superoxide dismutase, glutathione-s-transferase, catalase, peroxidase, which may convert the superoxide radicals into hydrogen peroxide and subsequently oxygen and water, while low-molecular weight non-enzymatic antioxidants consisting of proline, glutathione and ascorbic acid that may directly detoxify the reactive oxygen species (ROS) (Singh et al. 2015a, b).

### 5.7.2 Cellular Homeostasis

Proline may accumulate in the cytosol under various abiotic and biotic stress conditions (Chibuike and Obiora 2014). Exogenous application of proline may increase the endogenous proline level under heavy metal stress conditions. It helps to maintain intracellular redox homeostasis potential (Hoque et al. 2008) and the 3-D structure of proteins (Paleg et al. 1981), and protects enzymes and vital organelles including the cell membranes and also reducing the risk of peroxidation of lipids and proteins (Nagata et al. 2010). Proline enhances tolerance potential of plants by the formation of chelate with heavy metals in the cytoplasm, thereby maintaining osmotic adjustment through cellular homeostasis and reduce metal uptake regulating the water potential, which is often impaired by heavy metals (Singh et al. 2015a, b).

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# Plant Responses to Sewage Pollution

# 6

Priya and Gunjan Dubey

## Abstract

Sewage is the term used for waste water that often contains faeces, urine and laundry waste. The volume of sewage in the world is increasing in leaps and bounds together with the increasing population of the world. So, sewage pollution has become a major problem throughout the world. But the situation is particularly acute in developing countries due to exponential growth of population, urbanization and lack of technical development in these countries. It is important to highlight that although Antarctica has no native human population, yet, unprocessed sewage effluents from various research stations have been reported to cause negative effects on local wildlife of terrestrial and aquatic habitats. Sewage sludge contains excess of nutrients (nitrates, phosphates, organic matter) and heavy metals, which cause eutrophication in water bodies with subsequent increase in algal biomass, primary production and decrease in dissolved oxygen. The over-populating algae and bacteria use up most of the dissolved oxygen of water, making it difficult for other aquatic organisms to live. There are positive as well as negative responses of plants to the sewage effluents. Research shows that low and moderate concentration of sewage irrigation causes stimulated seed germination and seedling growth together with an increase in pigments synthesis, carbohydrates and nucleic acids synthesis. On the contrary, studies reveal that high dose of heavy metal concentration for plants via sewage irrigation/sewage sludge-amended soil caused inauspicious alterations in physiological and biochemical characteristics of plants like a decline in biomass and yield. Furthermore, continuous sewage irrigation in cropland leads to uninterrupted supply of minerals and nutrients resulting in adverse effects on yield quality and biomass due to oxidative damage and risks of plants to counteract stress factors. The plant either becomes toxic to its consumer or it dies from the mineral toxicity. Many

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plant species provide remedies to the sewage pollution by phytoremediation and this is a cost-effective method for sewage treatment.

**Keywords**

Sewage pollution · Sludge · Sewage effluents · Eutrophication · Heavy metal toxicity

## 6.1 Introduction

Water is one of the most vital substances on the earth. According to the United Nations, more than 80% of the world's waste water flows back into the environment without being treated. Sewage pollution is one of the biggest contributors to water pollution. It has become a major problem throughout the world. But the situation is particularly acute in developing countries, especially in slum areas due to exponential growth of population, urbanization and lack of technical development in these countries. At the same time, there are many countries which utilize sewage for farming purpose. Waste water is used by farmers in regions facing water scarcity even in developed countries of North America and Europe on a large scale. For example, according to the reports of CEU (1999), about 40% of the whole sewage sludge is utilized for agricultural and farming purposes in the European Union. Reports suggest that in the year 2010, countries like Belgium, Spain, Denmark, Ireland, France and the United Kingdom used more than 50% of sewage sludge for agriculture (Kacprzak et al. 2017). Numerous studies suggested a positive effect of sewage sludge application on crops like barley (Pasqualone et al. 2017), spinach (Bravo-Martín-Consuegra et al. 2016), bean (Zeid and Abou el Ghate 2007), etc. Studies suggest that sewage sludge is very useful not only for agricultural and farming purposes, but also for irrigating forest land including *Larix deciduas* (Bourioug et al. 2014). Thus, use of sewage sludge as a cheap and easily available means of irrigation for croplands and forests has continuously been increasing steadily over the years.

The term sewage in a layman's language is generally applied for urine and faecal waste from humans. But it is actually a wide-ranging term which encompasses animal wastes as well. Sewage is not made up of a single compound; instead, it is an amalgamation of various liquid and solid substances viz. liquids including by-products of waste water treatment and solids like a mixture of inorganic substances (grit, salt and metal) and organic substances (proteins, carbohydrates, fats and biological organisms like pathogenic, non-pathogenic bacteria and viruses). Sewage can be released in the form of treated and untreated sewage. There are many point sources (viz. municipal waste water treatment plants) and non-point sources (viz. pollutants released in a large area like City Street storm run-off) for the discharge of sewage.

Sewage sludge (also known as Biosolids) is rich in macronutrients like nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), sulphur (S) and magnesium (Mg), and few micronutrients. Sustainable utilization of these nutrients is used as soil improvement because biosolids are rich in important compounds and can thus be utilized for environmental potential enhancement (Londoño et al. 2017). The availability of nitrogen and phosphorus is limiting in terrestrial ecosystem (Batterman et al. 2013). Thus, sewage application to terrestrial agricultural lands may enhance the productivity of plants (Colón et al. 2017). Availability of nitrogen is more dependent on sludge treatment. Even untreated liquid sludge releases nitrogen, which gradually proves to be beneficial for the crop. Aerobically digested sludge has high contents of ammonia, which again is readily available to plants. Thus, sewage sludge is a nutrient-enriched fertilizer (Csattho 1994). Nitrogen present in sludge is likely to cause very less ground water pollution as compared with chemical fertilizers like urea (Long 2001). Therefore, sewage sludge may possibly be considered as a significant biological resource for agriculture and can be used as organic manure (Tsadilas et al. 1995; Tester 1990).

The greatest concern about the use of sewage as organic manure on terrestrial land is that its continued use may increase the risk of exposure to pollutants (e.g. heavy metals like Cd, Cu, Ni, Pb, Zn, Hg, Cr, etc.) and pathogens to plants and crops. Heavy metals on being introduced into the food chain show bioaccumulation. As discussed earlier, sewage sludge contains valuable components like organic matter, nitrogen (N), phosphorus (P), and rate of nutrient recycling is very slow. On the contrary, disposal of sewage sludge in aquatic ecosystems (oceans, lakes, ponds, etc.) causes various environmental threats (O'Sullivan 1971) like eutrophication and coral reef deterioration (Wear and Thurber 2015). For this, London Convention 96 Protocol was adopted, which prohibits sewage sludge discharge in oceans.

## 6.2 Composition of Sewage

As we have already discussed, sewage is an amalgamation of various abiotic and biotic compounds like:

### 6.2.1 Nutrients

Sewage water contains a very huge amount of inorganic nutrients, like nitrite, ammonium, nitrate, phosphate, etc. Nutrient enrichment enhances macro and micro algal growth causing algal bloom with the ultimate impact being extinction of native species (Wear and Thurber 2015).

### 6.2.2 Suspended Solids

Sewage consists of a high amount of suspended solids and most of the parts are made up of organic matter. Suspended solids enhance turbidity and hamper sunlight penetration (Rogers 1990; Tomascik and Sander 1985; Lewis 1997). Rate of sedimentation may also increase with sewage effluent discharge; simultaneously, storm events also occur (Reopanichkul et al. 2009), which cause physical stress. In addition, suspended solids also cause chemical stress because sewage effluents have a broad range of compounds with different chemical composition. Chemical inputs mainly from agricultural surface run-off (containing fertilizers, pesticides, herbicides, etc.) and natural soil erosion (containing organic matter and nutrients) (Pastorok and Bilyard 1985) in suspended solids may have toxic compounds and high levels of nutrients (Islam and Tanaka 2004; Johannes 1975). The organic compounds in sewage discharge enhance the biological oxygen demand (BOD) of polluted water via sewage. With an increase in BOD, there is a simultaneous increase in the population of microorganisms to utilize these organic compounds (Islam and Tanaka 2004; Johannes, 1975).

### 6.2.3 Pathogens

Sewage discharge has been recognized as the reservoir of the pathogen complex that can be responsible for various diseases (National Institutes of Health 2007). Sutherland et al. (2011) reported that sewage was the source of infection and disease, and that anthropogenic strain of the pathogen was the contributory driving force. This study was the first report for the transmission of an anthropogenic pathogen to the sea invertebrate sands; it gave strong confirmation for the connection between sewage discharge and disease in the sea atmosphere (Sutherland et al. 2011). This study presented that sewage is a big disease pool and that microorganisms such as bacteria and viruses present in the human gut are more common in sewage discharge. Sewage is the major cause of various health problems and most common diseases are like cholera, diarrhoea and typhoid fever (Griffin et al. 1999; Wetz et al. 2004 and Blinkova et al. 2009).

### 6.2.4 Heavy Metals

Heavy metals are usually found in sewage discharge (Grillo et al. 2001). Metals commonly present in sewage effluents consist of Zn, Pb, Cd, Hg, Cr, Co, Cu, Ni and Fe (Ščančar et al. 2000; Grillo et al. 2001). Normally, the enhancement of heavy metals leads to changes in metabolic activity as they are accumulated in the tissues of organisms. In addition to this, they also influence the bioactivity of enzymes and modify certain crucial physiological activities (Oves et al. 2016).

### 6.2.5 Toxic Compounds

An array of toxic compounds found in sewage discharge cause potential toxicity (Daughton and Ternes 1999). Toxin types occurring in sewage are dependent upon the local atmosphere; for example, the presence and kind of industries and agriculture. Chemicals like chlorine, polychlorinated biphenyls, petroleum hydrocarbons, pesticides, herbicides and products of pharmaceuticals, which are also commonly present in sewage (Pastorok and Bilyard 1985; Daughton and Ternes 1999; Islam and Tanaka 2004; Weigel et al. 2004; Fang et al. 2012).

## 6.3 Problems Associated with Sewage Pollution

### 6.3.1 Bioaccumulation of Heavy Metals

Sewage sludge application to soil has been vulnerable because of the heavy metal accumulation in soils and plants (Singh and Agrawal 2007).

### 6.3.2 Eutrophication

Nitrogen is not a limiting factor in aquatic ecosystems but this is somewhat true for fresh water and tropical water bodies. Nitrogen has been enhanced in sewage-polluted waters (oligotrophic water) in temperate regions leading to increased phytoplankton production (Khan and Ansari 2005). Various environmental factors like $CO_2$ concentration, temperature, pH, amount of dissolved oxygen, light intensity, etc. work as additives to the problem of eutrophication. The result of eutrophication is decrease in dissolved oxygen content and ultimately resulting in algal bloom formation. Other than this, the literature suggested that algal bloom also affected marshland plants and increased the rate of natural succession relatively more rapidly (Khan and Ansari 2005). There are many plant species which have been identified as best indicators of various stages of eutrophication; for example, phanerogam plants like *Potamogeton pectinatus* and *Myriophyllum spicatum* largely grow in eutrophic areas so that these plant species are regarded as tolerant for eutrophication (Wallentiuns 1979; Selig et al. 2007).

Many countries use sufficient managing strategies to control eutrophication and algal bloom. But these strategies are only partially useful in controlling the phosphorus unloading in water bodies (Khan and Ansari 2005).

### 6.3.3 Negative Impact on Local Wildlife

Sewage also influences local wildlife or change in their diversity or composition. It is important to emphasize that the entire world is facing the issue of sewage water problem. Antarctica, where there is no native human population, yet, unprocessed sewage effluents from various research stations have been reported to cause negative effects on local wildlife of terrestrial and aquatic habitats. Waste water of Antarctic research stations is a combination of human, domestic and industrial wastes released from laboratories. Waste water discharge has properties like municipal waste water although it is extra concentrated because of limited water supply. Treatment of waste water tries to decrease the amount of nutrients to avoid eutrophication of coastal water bodies. But in Antarctica due to limited water supply, treatment is a very difficult task that creates serious environmental threats like various metal and organic contaminants (Stark et al. 2015). Other than this, waste water in Antarctica has a huge number of pathogenic and non-pathogenic microorganisms, which are non-native to this region and survive in the coastal region of Antarctica (Smith and Riddle 2009). These non-native microbes may be causes of gene transfer, which lead to genetic pollution (Hernández et al. 2012). Various treatment processes are used in Antarctic stations; however, many of them are not competent enough for ameliorating the threat of waste water (Gröndahl et al. 2009; Stark et al. 2015).

In a study, 149 secondary sewage treatments were introduced at various locations of Virginia, Maryland and Pennsylvania. Presence of such a large number of sewage treatment plants led to accumulation of high amount of chlorine and turbidity, which caused reduction in diversity of fish species beneath the outfalls (Tsai 1973).

### 6.3.4 Coral Bleaching

Reports suggest that one of the major contributors to coastal pollution is sewage (Doty 1969; Banner 1974; Pastorok and Bilyard 1985; Islam and Tanaka 2004). Many coral reefs are situated by the side of the costal lines of developing countries, where sewage entering into oceans is completely unprocessed or inadequately treated. Tertiary sewage treatment in this zone is very uncommon (UNEP 1994; Islam and Tanaka 2004)**.** Most of the studies suggested that sewage effluents shave a destructive impact on coral reefs in the form of nutrient enrichment. Particularly, inorganic nutrient enrichment is the main cause of faster rate of algal growth and this is the main factor for coral diseases (Fabricius et al. 2005; Vega Thurber et al. 2014). For example, reports as early as 1996 by Marubini and Davies and later by Wooldridge (2009) clearly report that nutrient enrichment causes damage to the coral via acting on *Symbiodinium* (a symbiotic algal partner performing photosynthesis in corals). Nutrients can enhance the symbiont density that leads to parallel boost in reactive oxygen species, which possibly will result in damage to host cells that may lead to death and exclusion of the symbiont (Lesser 1996). Other than nutrients, various studies suggested that introduction of heavy metal with increasing concentration can cause coral bleaching, mortality and decreased fertilization success (Howard and Brown 1984; Reichelt-Brushett and Harrison 1999).

## 6.4 Sewage: A Double-Edged Sword

The demand for potable water is increasing continuously with an increase in population. This results in setting up of an increasing number of sewage treatment plants causing more and more water pollution. This can be explained as follows - to meet the Millennium Development Goals (MDGs), sustainable use of water and

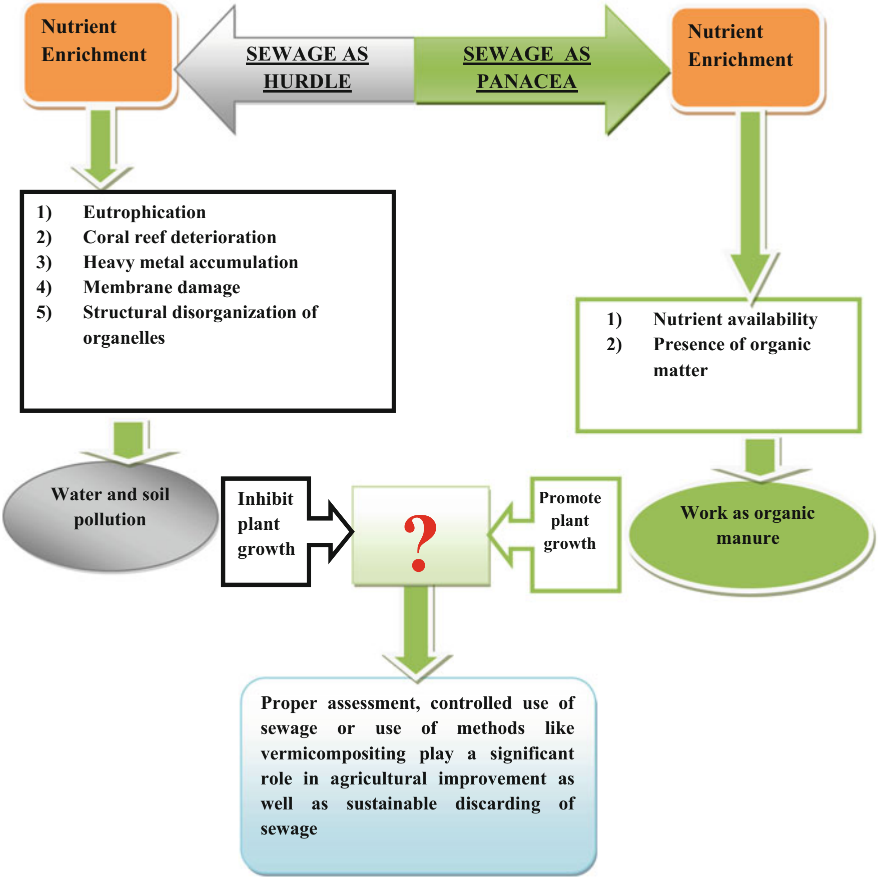

**Fig. 6.1** Distinct aspects of sewage

sanitation infrastructure and sewage treatment is required. Sewage treatment plants are a main source of pollution, contributing to various pollutants found in water bodies. Ground water also is at a risk of being polluted from immobile effluents leaking from these treatment plants. Other than pollution problems, sewage introduces a broad range of potentially infectious agents to water that may be consumed by the biotic communities, therefore, leading to increased outbreaks of waterborne diseases with significant future socio-economic implications (Fig. 6.1) (Craun 1991). Sewage is a major contributor to health issues like cholera, diarrhoea and typhoid fever (Griffin et al. 1999; Wetz et al. 2004 and Blinkova et al. 2009). Sewage effluent discharges were killing a large population of fish and destabilizing aquatic ecosystems (Mema 2010). Use of fertilizers for vegetation and agriculture proves to be an expensive method. On the contrary, the application of sewage sludge in agricultural land is the most economic, cost-effective and environmentally sustainable way (Kacprzak et al. 2017). Sewage waste water is normally used for irrigation in various developed countries viz. France, Denmark and Spain (Kacprzak et al. 2017) and also in developing countries like India (Sharma et al. 2007). Sewage is either released from treatment plants or from various point and non-point sources. Use of sewage sludge in agriculture is a global practice and is one of the most efficient and economic sludge disposal methods. Various studies suggested the positive effect of sewage sludge application on crops including spinach (Bravo-Martín-Consuegra et al. 2016) and barley (Pasqualone et al. 2017). Uninterrupted supply of sewage waste water for irrigation causes nutrient enrichment of soil through various macro and micronutrients, which is essential for plants (Das and Kau 1992; Kannan et al. 2005). Micronutrients promote the growth and metabolism of the plants but nutrients also turn out to be toxic if present in surplus than the necessity. Most of the micronutrients are heavy metals and well known to generate adverse effects on plants if they are present in surplus (Kocak et al. 2005). High amount of heavy metals causes stress-like conditions in the plant and interrupt metabolic and physiological functioning. Heavy metals cause membrane damage, structural disorganization of organelles and destruction in the physiological functioning, which finally hinders the growth of the plants (Kimbrough et al. 1999; Chien and Kao 2000; Zhang et al. 2002; Long 2001). Heavy metals enhance reactive oxygen species (ROS) generation, for example, hydrogen peroxide ($H_2O_2$), superoxide radicals and hydroxyl radicals. They transfer electrons involving metal cations or by inhibiting the metabolic reactions controlled by metals (Stohs and Bagchi 1995; Verma and Dubey 2001). In this sequence, plant endures stress condition, because they have antioxidants to remove ROS and free radicals (Gratão et al. 2005).

## 6.5 Responses of Plants to Sewage

The overall response of plants to sewage treatment is studied by analysing the following parameters:

- **Morphological responses** - growth and biomass studies like root length, shoot length,
  fresh weight, dry weight, leaf area, leaf size, etc.
- **Physiological responses** - include pigment content, alteration in metabolic activities of plants like photosynthesis, respiration, etc., and.
- **Ecological responses -** include alteration in antioxidant activity of plants, heavy metal accumulation in soil and various plant parts, etc.

Composting is suggested as an extremely suitable method to reprocess, recycle and reuse sewage sludge (Song and Lee 2010). Composting is a controlled biological method that is used to treat organic matter using microorganisms at temperatures less than 40–50 °C (Environmental Protection Agency 2006). Compost consisting sewage sludge is a proper solution for increasing the quality of soil. Thus, it is significant to study the impact of compost consisting sewage sludge on plants. In this context, various compost containing sewage sludge application studies on sawtooth oak (*Quercus acutissima*) and Japanese red pine (*Pinus densiflora*) have been performed. These studies illustrate that compost noticeably increases moisture and nitrogen content in the soil. With this observation, significant concomitant increase in plant height, biomass, nitrogen and chlorophyll content in leaves has also been reported as compared with control. As chlorophyll content increases, the rate of photosynthesis is automatically increased (Song and Lee 2010). Richard et al. (1998) found that after long-term field studies of sewage sludge application (20 years), accumulation of metals in soils were significantly increased as compared with control. Sewage sludge application also resulted in an increase in Zn, Cd, Cu and Ni concentration in grass-growing plot. As discussed earlier, sewage sludge improvement increases the concentration of heavy metal, organic matter and nutrients in soil. Organic matter reduces the pH of soil. A study suggests that sunflower (*Helianthus annuus*) has the capability to endure heavy metal toxicity (Elloumi et al. 2016). Sunflower roots accumulate a considerable amount of heavy metal and have the ability to translocate it into shoot. Thus, sunflower might be used in phytoremediation and accumulation of heavy metal was more in root tissues as compared with shoot tissues. (Elloumi et al. 2016) Sewage sludge application enhances morphological and physiological responses of sunflower like root-shoot length, number of leaves, antioxidant activity, glutathione, proline content, soluble sugar and biomass. This is due to induction of better defence mechanism induced in response to sewage sludge application and heavy metal stress (Elloumi et al. 2016). Labrecque et al. (1997) suggested that sludge possibly could be used as organic manure/fertilizer for improvement of quality of forest soils. To support this hypothesis, a study was conducted on small saplings (one-year-old) of *Eucalyptus camaldulensis* in which plants were treated with urban sludge together with soil. The amount of sludge content was gradually increased in pots. After 6 months of study, height, diameter at mid-height, base diameter and the number of leaves showed positive results to sludge application. A considerable variation was also reported in stem length and number of leaves in plants treated with sludge as compared with control. The growth enhancement was due to fast nutrient utilization (Labrecque et al. 1997). Bourioug et al. (2014) demonstrated good growth of larch (*Larix decidua*) on forest soil fertilized with municipal sludge, considered as a source of fertilizer due to its high content of organic matter and available nitrogen and phosphorus. In this study, he found limited absorption of the heavy metals via plants. Similar to the above studies, Table 6.1 shows responses of various plants to sewage or sludge application:

With sewage sludge application, a long-term study was conducted. Field studies extending over 2 years (Qiong et al. 2012) and 5 years (Li 2012) duration revealed little dissimilarity in heavy metal accumulation in soils. In a 2-year field study, the concentration of Cu, Cd and Zn were found to increase linearly in soil together with an increase in sewage sludge application. On the other hand, in a 5-year field study, Hg concentration was reported to increase in soil besides Cu, Cd and Zn. Similarly, accumulation along with translocation of such metal contaminants from sewage sludge in plant parts also shows variation (Yang et al. 2018). Thus, long-term studies are required to show the accumulation and bioavailability of heavy metals released

**Table 6.1** Various responses of plants to the sewage or sewage sludge application.

| Plant name | Effect | References |
|---|---|---|
| *Phaseolus vulgaris* (Bean) | 1. Increased germination percentage and shoot and root lengths, fresh and dry masses.<br>2. Increased yield criteria like number of pods/plant, length of pods, fresh and dry weights of pods. | Zeid & Abou el Ghate (2007) |
| *Eucalyptus camaldulensis* (One year old saplings) | 1. Increment in height and number of leaves.<br>2. Decrease in diameter of stem | Leila et al. (2017) |
| *Larix decidua* (Larch seedlings) | 1. Activity of Nitrate reductase decreases as increasing sludge application rates.<br>2. Sewage sludge did not influence larch seedling growth (after 6 week). | Bourioug et al. (2014) |
| *Beta vulgaris* (Palak) | 1. Positive effect on physiological, biochemical and growth characteristics.<br>2. Biomass and Yield did not change. | Singh and Agrawal (2010) |
| *Helianthus annuus* (sunflower) | 1. Increase in root and shoot length, leaves number, biomass, and antioxidant activities | Elloumi et al. (2016) |
| *Salix viminalis L.* (willow plants) | 1. Great increase of biomass and plant growth in small waste water treatment plant.<br>2. Efficient performance of the antioxidant system. | Wyrwicka and Urbaniak (2018) |
| *Solanum tuberosum* (Potato) | 1. Increased the concentrations of some potentially toxic trace elements in potato leaves and tubers (enhancement was normally elevated in leaves than in tubers) | Brar et al. (2000) |

by sewage sludge. In this sequence, a most recent long-term field study of 10 years with a wheat–maize crop alteration was done (Yang et al. 2018). The study was useful to consider the accumulation and bioavailability of heavy metals in soil containing adequate free calcium carbonate ($CaCO_3$). Sewage sludge was applied at various rates and accumulation of heavy metals in wheat was reported to be larger than that in maize. This study suggested that maize is more tolerant than wheat to heavy metals. This conclusion might be useful for the calcareous soil improvement via sewage sludge application (Yang et al. 2018).

In a study, palak (*Beta vulgaris* L. var. All green H1) is irrigated with waste water as compared with ground water. Uninterrupted supply of waste water via irrigation increases the nutrient concentration. According to this study, irrigation with waste water positively changes the physiological, biochemical and growth characteristics of plants, whereas biomass and yield did not differ considerably between waste water-irrigated site and ground water-irrigated site. Uptake and translocation ratio of heavy metals were higher in plants grown at waste water-irrigated site. The observed maximum uptake was of Mn followed by Zn, Cu, Pb, Ni, Cr and Cd. Plants produced more secondary metabolites and antioxidants to tolerate the negative impact of heavy metals at waste water-irrigated sites. Simultaneously, plants also produced more metabolites to compensate the toxicity of metals in the area and thus did not enhance the yield and biomass potential. So, reports suggest that plants growing in waste water-irrigated land have potentially developed the defence strategy to fight against heavy metal toxicity (Singh and Agrawal 2010). Greenhouse and field experiment studies also show variation in heavy metal content with sewage sludge application. Singh and Agrawal (2007, 2010) reported considerably increased amount of heavy metals like Cu, Zn, Cr, Cd, Pb and Ni in soil and plants. They also observed enhancement of Ni, Cd and Zn concentration in plants in greenhouse, whereas in field experiments, Cd, Ni and Pb concentration was increased in seeds.

Sewage disposal, without doubt, is a major environmental hazard if sludge effluent is incinerated or just deposited in the vicinity of waste water treatment plants. In this order, the effect of desiccated sewage sludge on few soil properties like pH of soil is very much influenced by sewage sludge application. Sewage sludge application to soil makes it more acidic and increases its electrical conductivity. In continuation with this study, sunflower (*Helianthus annuus* L.) plants exposed to sewage sludge in soil showed increased availability of nitrogen and phosphorus to plants. As a result, stem height, dry biomass of root and shoot was enhanced together with an increase in net $CO_2$ assimilation and a decrease in the rate of transpiration and stomatal conductance with an increase in sewage sludge concentration (Elloumi et al. 2016). Sewage sludge application results in a huge enhancement of biomass of willow (*Salix viminalis*) plant coupled with safeguard against oxidative damage and maintain the osmotic balance between the plant root and soil water (if the plant grows in low-grade soil). Catalase activity and proline content were also enhanced in this plant (Wyrwicka and Urbaniak 2018). Recent studies suggested that vermicomposting may be reducing the threat of contamination of heavy metal from sewage sludge (Zuo et al. 2019). It is well known that sewage sludge is a cost-effective and competent soil improvement method although the heavy metal contamination and accumulation is a major concern related to sewage sludge application. These days, sewage sludge alteration into vermicompost via earthworms might be the most successful method to reduce the heavy metal threat, which is very common in sewage sludge application vs direct application method. Vermicompost amendment enhances the quality of soil like decreasing soil bulk density, salinity and pH, increasing soil organic carbon, nitrogen and phosphorus contents in soil. As a result, biomass and yield of maize crop were considerably increased (Zuo et al. 2019). Although vermicompost amendment enhances accumulation of Cd, Cu, Mn, Ni, Pb and Zn in maize plant, particularly in roots. About the differences between sewage sludge application and vermicomposting application (under the situation of maintaining the same carbon input), heavy metals are permitted to accumulate in a more constant binding form in the top layer (approx. 20 cm) of mudflat soil. So, the danger of surface run-off and leaching of heavy metals and their bioavailability to plants is reduced in mudflat soil. So, vermicomposting application can decrease the accumulation of heavy metals in plants if compared with sewage sludge application (Zuo et al. 2019).

## 6.6 Conclusion

To feed the ever-increasing population, global agriculture is required to boost food production. To fulfil this demand, increasing use of chemical fertilizers causes various detrimental effects on human health; sewage amendment is a useful tool as organic manure. With increasing population, sewage sludge is escalating; thus, the significance of its harmless and sustainable discarding is also necessary. Sewage sludge application is the most effective, economic and efficient soil improvement method. Although sewage causes much pollution like soil and water pollution, proper and limited use of sewage water can take care of soil and improve quality. Transformation of sewage sludge compost mainly by vermicomposting via earthworms may be one of the most efficient tools to diminish the threat of heavy metal contamination caused by direct use of sewage sludge. Vermicomposting may be a safe alteration for sewage sludge.

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# Soil Pollution Caused by Agricultural Practices and Strategies to Manage It

# 7

Priti Upadhyay, Akhouri Vaishampayan, and Sanjay K. Jaiswal

**Abstract**

Soil has a role of 'mother' for all living beings present on Earth, including plants, animals, humans and microorganisms. It is source of water and nutrients that are required for suitable growth and development of plants. 'Soil pollution' is the contamination of soil with harmful contents or substances that have poisonous effects on growth and health of plants and all creatures. Since soil pollution cannot be directly assessed or visually perceived generally, it has become a hidden danger. Soil can be polluted in many ways, including precipitation deposits of acidic compounds, human developmental and mining activities, industrial activities, various agricultural activities such as use of pesticides and over-fertilization. All these affect soil pH, presence and activities of microorganisms in soil, occurrence of toxic metals in soil. The plants grown in such soil can uptake harmful components and pass these through various physiological pathways within the food chain. These soil contaminations ultimately affect the whole vegetation of an area and finally will pollute our future. The present chapter summarizes current knowledge on the effects of different soil contaminations on the development of crop plants and their channelization in food chain with effect on human health. This chapter suggests new perspectives and future challenges on the proposed topic.

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**Keywords**

Soil pollution · Pesticides · Fertilization · Food chain · Soil microorganisms

## 7.1 Introduction of Soil Pollution and Scenario Due to Agricultural Practices

Soil pollution primarily refers to the presence of a chemical or substance out of place and/or present at a higher-than-normal concentration that exerts adverse effects on its chemical, biological and physical properties. This cannot be directly assessed or visually perceived, and this makes it a hidden danger. Soil pollution has gradually become a major challenge for agriculture that we need to overcome for establishing a healthy environment assisting in growth of plants. The soil is the home for a large part of bacterial biodiversity and other microscopic and macroscopic living organisms that play a role in various pathways related to nutrient uptake by plants.

Agricultural pollution denotes addition of biotic or/and abiotic by-products of farming practices that result in contamination/degradation of the environment and surrounding ecosystems, and/or cause injury to humans and their economic interests. Such soil pollution may come from a variety of sources ranging from irrigation to management practices such as pesticides, herbicides, fertilizers and other chemicals. There is no doubt that these chemicals, used in agriculture, have made food security possible for increasing population by protecting crops and enhancing the production. Soil pollution by chemical uses during agriculture has become an increasing problem throughout the world as whole crop management practices mainly rely on the chemicals and change in the soil microflora (Fig. 7.1).

## 7.2 Effect of Fertilization on Soil Health and Crop Productivity

Healthy soil is the basic need for flourishing agriculture. From preparation of field to harvesting the produce, there are several activities that are practised in the field that creates harmful effect on soil health and ultimately cause soil pollution. These adversely affect the soil properties, both chemical and physical and micro-organisms residing in it. Chemical fertilizers can maintain or improve crop yields, but their application can directly or indirectly cause changes in soil chemical, physical and biological properties (Arévalo-Gardini et al. 2015). Long-term application of chemical fertilizer reduced the soil pH, which directed a modification in microbial biomass, activity and bacterial community structure. Long-term fertilization greatly increases soil microbial biomass C and dehydrogenase activity that eventually affect production of crop and health of soil. It has been observed that usage of chemical fertilizers for three decades worsened the soil health and produced similar effect as stated earlier on microorganisms residing in soil.

Many studies concluded that for better presence of soil microbe, a balanced augmentation with organic manure should be applied (Lori et al. 2017; Bargaz

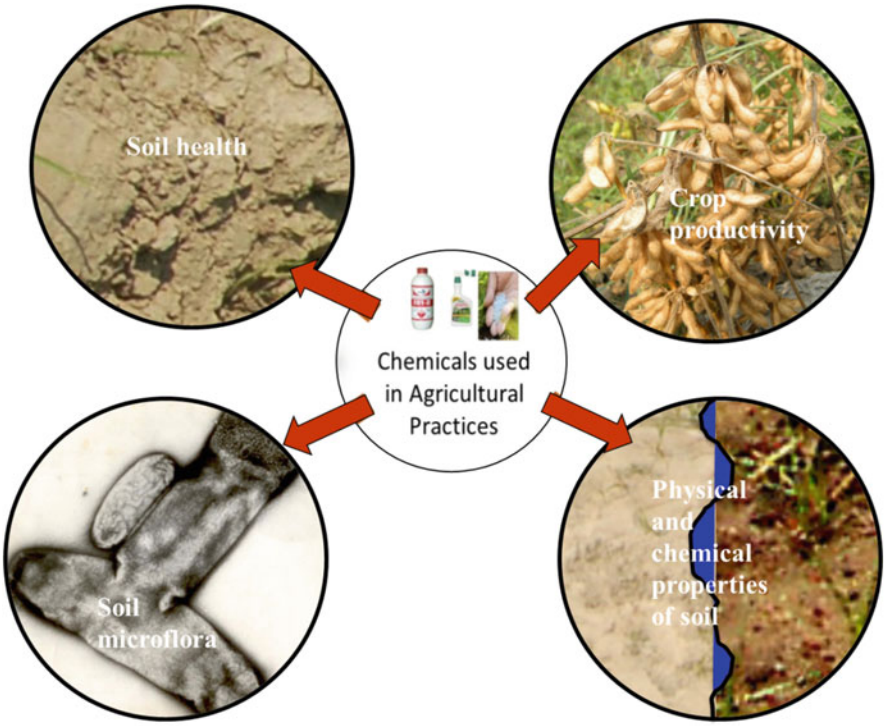

**Fig. 7.1** Chemicals used in agriculture and their effect

et al. 2018). In the early 1900s, organic manures (mainly animal manures) containing large amount of organic materials and legume crops were used as the major source of N for the crops. Introduction of chemical nitrogen fertilizers and use of fertilizer-sensitive crops boomed the production, but they created a reduction in use of organic manures that affected the volume of soil organic matter and ultimately its health. The use of N fertilizers, i.e., urea, exerts profound influence on the chemical, physical, and biological properties of the soil. Rate of decomposition of ‘low-quality’ or high C:N ratio organic inputs and SOM (soil organic matter) increases when fertilizers, particularly N, are applied to the soil (Recous et al. 1995). Fertilizer application increases microbial decomposer activity, which has been limited due to low nutrient concentrations in the organic materials. Thus, application of fertilizer N may lead to accelerated decomposition of SOM and adversely affect the soil health.

Presence of soil microbiomes constitutes an important soil health parameter that is adversely affected due to application of chemical fertilizers. While net primary production in agricultural ecosystems is generally nitrogen limited, activity of soil microorganisms may be carbon and/or nitrogen limited (Wardle 1992; Singh et al. 2011; Das et al. 2017). Use of fertilizer application produces harmful effect on the soil and is one of the notions that have been put forth many times to support the argument against fertilizers. Chemical sources of nitrogen may lead to increased acidity that adversely affects many soil functions. A very recent study by Poffenbarger et al. (2017) evaluated the impact of N fertilizer in Midwest U.S. maize fields and observed a site-to-site variability on soil health and crop yield. Similarly, a study by Wang et al. (2018) observed the influence of N and/or P inputs on below-ground microbial communities in subtropical forests using quantitative polymerase chain reaction and Illumina Miseq sequencing of the bacterial 16S rRNA gene to investigate bacterial abundance, diversity, and community composition in a Chinese fir plantation. The results depicted a decrease in bacterial richness and diversity with N addition (N and NP) input. *It also concluded that* addition of P fertilizers did not significantly affect soil bacterial communities.

Heavy metals are naturally present in the soil and needed by plant in a very small quantity, but at higher concentration in soils, they are harmful to both plants and animals. An experiment was designed to investigate the variability of chemical applications of cadmium, lead and arsenic concentrations on wheat-cultivated soils (Atafar et al. 2010). Soil sampling was done from 40 locations of a field and measured for heavy metal concentration, soil texture, pH, electrical conductivity, cationic exchange capacity, organic matter, and carbonate contents. It was indicated by this study that cadmium, lead and arsenic concentrations were increased in the cultivated soils due to fertilizer application. Soil scientists Lambert et al. (2007) investigated the solubility of cadmium and zinc in soils after the application of phosphate fertilizers containing those two metals and concluded that phosphate fertilizers increased the concentration of Cd in soil extracts compared to control in 87% and 80% of the treatments in field and laboratory experiments, respectively. Increase in heavy metal concentration may have manipulating effect on soil properties, including both physical and biological (Friedlová 2010). Heavy metals that get channelized in food chain will produce fatal effects in humans and animal too (Iheanacho et al. 2017). Various studies reflected that use of fertilizer positively affected the crop productivity, but over-application of fertilizers as well as the other agrochemicals that are used against insects, herbs, and rats had adversely affected soil and its properties.

## 7.3 Effect of Agrochemicals on Physico-Chemical Properties of Soil

Soil is a dynamic living system and considered as mother earth as lives of all living beings depend on it. It is habitat for variety of micro- and macro-flora and fauna, including bacteria, actinomycetes, fungi, nematodes, arthropods, crustaceans, and earthworms that play a crucial role in the degradation of plant and animal residues and other organic matter in the environment as well as in nitrogen fixation, nitrification and the release of nutrients from soil minerals. Any of our activity during agriculture with prolonged use of chemicals can adversely affect soil properties and activities of living nexus that will result in changed function of soils not only in crop production but also in the global C and N cycles and in the removal of a range of environmental pollutants. The consequences could thus be serious. Evaluation of long-term effects of pesticides and chemical fertilizer usage on soil properties and heavy metal accumulation depicted that soil physical characteristics such as bulk density were changed in long term and it was increased, compared to control soil (Yargholi and Azarneshan 2014). Besides heavy metal, inorganic fertilizers may have harmful effect on soil organic carbon (SOC), soil physical properties, and crop yields in a maize (*Zea mays*)–wheat (*Triticum aestivum*) rotation by prolonged use (Brar et al. 2015).

Prolonged fertilization badly impacts on soil physicochemical properties, microbial biomass carbon, microbial quotient, enzyme activities, and cypermethrin dissipation. By experimenting with five fertilization treatments, i.e., organic manure, NPK fertilizer, PK fertilizer, NK fertilizer, and no fertilizer (control), it was concluded that higher soil organic C, N, P contents and enzymatic activities occurred in soils with balanced fertilization as opposed to those with unbalanced fertilization, especially fertilization with organic manure (Xie and Zhou 2008). The studies also indicate that during agricultural practices, oversupplying N should be stopped as it is the major fertilizer that changes the pH, thus creating subsequent changes in physical and biological properties. Application of P fertilizer may be an efficient way to decrease N/P ratio and enhance cypermethrin dissipation in soil with high available N content. Application of chemical fertilizers alone or chemical fertilizers combined with organic amendments is commonly practiced to improve physicochemical properties and fertility of red soils (Wang and Zhang 2016). The microbes present in soil have specific requirements of pH and temperature for their enzymatic activities. Change in any of it can alter the activities and soil fertility in turn. Total N and total P content of soil significantly increased during the long-term fertilization. In contrast, total K contents in soil significantly decreased by the long-term fertilization.

Several other studies were done for enhancing the understanding of effect of fertilization on soil properties. A field experiment was conducted during 2010–2011 and 2011–2012 to investigate the effect of optimal (100% NPK) to super-optimal doses (200% NPK) of mineral fertilizers on soil enzymes such as dehydrogenase, acid phosphatase, alkaline phosphatase, fluorescien diacetate hydrolysis, urease, and nitrate reductase (NRA) at three physiological stages (CRI, anthesis and maturity) of wheat crop on an Inceptisol (Rakshit et al. 2016). The study illustrated a reduction in dehydrogenase activity by 28–37% with induction in urease and NRA positively by 43–44% and 213–231%, respectively. A significant positive interaction between fertilizer treatments and physiological stages of wheat growth was observed on soil enzyme activities (except urease and NRA), highest being at the anthesis stage of wheat. These studies produce evidence for avoiding over-application of fertilizers because they hinder the enzyme activities and vis-à-vis sustainable nutrient enrichment under rhizosphere that is prerequisite for growth and production.

The information for effects of long-term fertilization, use of pesticides and its persistence is limited. The discussed studies gave comprehensive information with consideration of soil fertility, crop yield, and environment. These observations suggest that a mixed application of organic manure and inorganic fertilizers is recommended to avoid reduction in soil fertility, change in chemical and biological properties of soil (Singh and Ghoshal 2010). Soil contamination and pollution by pesticides can be related to the concentration of chemical pesticides and chemical elements in the soil. This is the reason why state of the soil–managed application of pesticides and fertilizers is essential, and it requires planning to reduce or replace pesticide and fertilizer usage in order to keep the soil problem free.

## 7.4 Effect of Agrochemicals on the Soil Microflora

The quality of life is undistinguishably related to environmental health. The balance between livings and environment can be disturbed by biosphere contamination with fungicides and herbicides that are considered to be effective crop protection chemicals in modern agriculture. Such enhancement in crop production and crop protectants poses a serious problem for food safety and sustainable soil use. They can also employ toxic effects on non-target organisms, including soil-dwelling microbes. Therefore, there is need to monitor the environmental fate of fungicides or any chemical that changes microflora of soil as it affects the soil fertility in turn (Handa et al. 1999).

Microbes that reside in soil help plants to obtain nutrient from soil and degrade the organic matter. Fertilization and other chemicals that are used in various practices during agriculture can cause harm to these (Singh and Prasad 2019). Influence of the Falcon 460 EC fungicide on microbial diversity, enzyme activity and resistance, and plant growth was observed and found differences in the values of the colony development index and the eco-physiological index, which indicated that the mixture of spiroxamine, tebuconazole and triadimenol modified the biological diversity of the analysed groups of soil microorganisms (Baćmaga et al. 2016). The fungicides inhibit the activity of dehydrogenases, catalase, urease, acid phosphatase and alkaline phosphatase of microbes, thus reducing their ability to perform their function. Dehydrogenases, i.e. most resistant enzyme to soil contamination, were highly induced with the highest fungicide dose (300-fold higher than control). The phytotoxic test can reveal that the fungicide can inhibit seed germination capacity and root elongation by changing the nutrient availability in soil. It was also indicated by studies that excessive doses of the fungicide can induce changes in the biological activity of soil that help plants to grow and flourish. The analysed microbiological and biochemical parameters are reliable indicators of the fungicide's toxic effects on soil quality. Effect of multiple herbicides Alister Grande 190 OD, Fuego 500 SC and Lumax 537.5 SE on counts of actinomycetes as well as the activity of enzymes and their resistance to herbicides was investigated (Baćmaga et al. 2016) and found that soil contamination with herbicides contributed to elevated counts of actinomycetes. In case of enzymatic activities, urease was the most tolerant to soil contamination with the herbicides, while others got affected by herbicide contamination in soil. A study by Wyszkowska et al. (2016) analysed the effect of a mixture of pethoxamid (P) and terbuthylazine (T) contained in the herbicide Successor T 550 SE on organotrophic bacteria, total oligotrophic bacteria, *Azotobacter* and Actinomycetes, oligotrophic-sporulating bacteria, fungi and on the activities of dehydrogenases, catalase, urease, alkaline phosphatase, acid phosphatase, arylsulphatase and glucosidase in soil. The study also analysed phytotoxic effect of this pesticide on maize. The P + T mixture disturbed soil homeostasis and altered soil stability, resulting in a succession of K-strategy organotrophic bacteria. It also negatively affected bacteria of the genus *Azotobacter*, oligotrophic sporulating bacteria, actinomycetes and fungi, and a positive effect on oligotrophic bacteria. P + T in doses greater than 0.73 mg $kg^{-1}$ of soil resulted in a strong inhibition of dehydrogenases, catalase, urease, acid phosphatase, alkaline phosphatase, arylsulphatase and β-glucosidase and significantly inhibited the growth and development of maize.

Pesticides, the most cost-effective means of pest and weed control, allow the maintenance of current yields and so contribute to economic viability. But when it comes to concern about the environmental impact of repeated pesticide use and their fate in the environment, it emerges as a great problem, which can emigrate from treated fields to air, other land and water bodies. Pateiro-Moure (2007) reviewed many studies based on the influence of the physical and chemical characteristics of the soil system such as moisture content, organic matter and clay contents and pH on the sorption/desorption and degradation of pesticides and their access to groundwater and surface waters. There is evidence that chemicals applied to the soil surface may be transported rapidly to groundwater, bypassing the unsaturated soil zone (Johnson et al. 1995). The hypotheses proposed to explain this rapid transport include preferential flow (Elliott et al. 2000; Roulier and Jarvis 2003), co-transport with colloidal matter (Worrall et al. 1999; Hesketh et al. 2001) and a combination of both processes (Williams et al. 2000). Pesticides form large number of transformation products (TPs) (Barcelo and Hennion 1997) that are very harmful for both plant and environment. The parameters that provide information regarding its persistency, movement and their TPs are water solubility, soil-sorption constant ($K_{oc}$), the octanol/water partition coefficient ($K_{ow}$), and half-life in soil ($DT_{50}$). Pesticides and TPs could be grouped into: (a) Hydrophobic, persistent and bioaccumulable pesticides that are strongly bound to soil. Pesticides that exhibit such behaviour include the organochlorine DDT, endosulfan, endrin, heptachlor, lindane and their TPs. Most of them are now banned in agriculture, but their residues are still present. (b) Polar pesticides are represented mainly by herbicides in general, but they include also carbamates, fungicides and some organophosphorus insecticide TPs. They can be moved from soil by runoff and leaching, thereby constituting a problem for the supply of drinking water to the population. The most researched pesticide TPs in soil are undoubtedly those from herbicides. Several metabolic pathways have been suggested, involving transformation through hydrolysis, methylation and ring cleavage that produce several toxic phenolic compounds. The pesticides and their TPs are retained by soils to different degrees, depending on the interactions between soil and pesticide properties. The most influential soil characteristic is the organic matter content. The larger the organic matter content, the greater the adsorption of pesticides and TPs. The capacity of the soil to hold positively charged ions in an exchangeable form is important with paraquat and other pesticides that are positively charged. Strong mineral acid is required for extracting these chemicals without any analytical improvement or study reported in recent years.

Soil pH is also altered greatly by pesticide and herbicide application. Adsorption increases with decreasing soil pH for ionizable pesticides (e.g. 2,4-D, 2,4,5-T, picloram and atrazine) (Andreu and Picó 2004). Intensive treatment of soil with pesticides/herbicides can cause populations of beneficial soil microorganisms to decline that causes changes in physical properties of soil. Overuse of chemical fertilizers and pesticides has effects on the soil organisms that are similar to human overuse of antibiotics. A prolonged use of chemicals creates a non-significant change in the plants' response, organisms' reactions towards that chemical (Savonen 1997). Mycorrhizal fungi grow with the roots of many plants and aid in nutrient uptake. These fungi can also be damaged by herbicides in the soil. For example oryzalin, triclopyr and trifluralin inhibit the growth of certain species of mycorrhizal fungi (Kelley and South 1978; Chakravarty and Sidhu 1987). Oxadiazon reduces the number of mycorrhizal fungal spores (Moorman 1989). Abd-Alla et al. (2000) observed the effect of afugan, brominal, gramoxone, selecron and sumi oil herbicides on growth, nodulation and root colonization by arbuscular mycorrhizal (AM) fungi of the legumes. The results indicated that all five pesticides when used at field application not only changes the soil environment but also rates, reduced growth and related microbial activity in cowpea, common bean and lupin.

The experiments and ideas suggest that an understanding of the fate of pesticides/herbicides is essential for rational decision taking regarding their authorization. To reach an adequate understanding will require the concourse of soil science, clay mineralogy, physical chemistry, surface chemistry, environmental microbiology, plant physiology, and, no doubt, other disciplines also. By applying multidisciplinary approach to environmental research, it will be possible to plan, manage, pursue and integrate the results of the studies that will be necessary for the development of tools and techniques allowing effective environmental decision making.

## 7.5 Effect of Irrigation on Soil Properties

Irrigation is the application of water to the soil for the purpose of supplying moisture essential for plant growth. Throughout world, agriculture is dependent on the soil moisture as it is required for germination till grain filling. This demonstrates that irrigated agriculture is the backbone and plays an important role as a significant contributor to the world's food and fibre production. Irrigation has an important role in maintaining soil's physical and biological properties. To examine the effects of irrigation practices on some soil chemical properties, Adejumobi et al. (2014) took soil samples at variable depths from two operating lands of the study area. The samples were analysed for chemical parameters (pH, CEC, ESP, Mg2+, Ca2+, OM, and OC). The soil pH, which was in the neutral range (pH = 6.65–7.00) at inception of scheme, has become slightly acidic (pH = 6.53–6.60). Cation exchange capacity (CEC) levels have also increased from 10cmol.kg$^{-1}$ to 35cmol.kg$^{-1}$, while organic matter (OM) and organic carbon (OC) also have marked increase in their levels (baseline as 0.93 to 1.08; for year 2013 as 9.52 to 9.79). Generally, the analysis indicated a need for proper monitoring of the scheme soil to prevent further deterioration. In each and every field, it is suggested that proper irrigation scheduling is required since soil water content is critical to supply the water needs of the crop and to dissolve nutrients, which make them available to the plant. Excess water in the soil, however, depletes oxygen ($O_2$) and builds up carbon dioxide ($CO_2$) levels, so there is need for proper water exits in field. Field experiments for three growing seasons (2007–2009) at five different sites of soil types and salinity levels were conducted to monitor the effect of irrigation water quality on soil properties in Saudi Arabia (Al-Ghobari 2011). It was concluded that all irrigated fields have differed in salt concentration as indicated by soil electrical conductivity (ECe) values of the saturated paste extracts. The study indicated that salt accumulation in soil of fields was closely related to the salt concentration of irrigation water, and there was a progressive and significant increase in soil salinity values as the salinity of irrigation water increases. Also, the obtained results showed that the decrease or increase in soil salinity through the soil profiles for all fields occurred mainly at first season and slight increase in the following two seasons and not with the increase of the number of seasons, and the soil salinity values remains closely the same and does not get influenced by the prolonged use of low- or high-salinity waters for a number of years for all fields during the study. These observations directly linked soil pollution with quality of water used in irrigation.

To develop a sustainable agricultural system, limited information regarding the influence of long-term irrigation schedules on soil properties and crop performance is known. Sun et al. (2018) investigated the changes of soil bulk density (BD), saturated hydraulic conductivity ($K_{sat}$), water-stable aggregate, soil organic matter (SOM), and total nitrogen (TN) at the variable depths of soil with different irrigation amounts based on a 17-year-long experiment in a double-cropping system with crop residue removed and manual tillage in the North China Plain. The study summarized that BD increased as the irrigation amount increased. $K_{sat}$ reached a maximum level at a moderate irrigation level. It also indicated that irrigation timing also affected soil BD and $K_{sat}$. SOM and TN also got affected and decreasing trends with increased irrigation amount were observed. Soil quality and crop production may benefit from a reasonable irrigation strategy and the return of crop residue to the field. According to Razzaghi et al. (2016), wastewater irrigation can be beneficial or detrimental; it generally depends on the geographic region and the type of wastewater used. In Ghana, effects of four sources of irrigation water (river, canal, tap and well) were examined for chemical and physical properties of tomato-planted soil (Takase et al. 2011). The observations showed that continuous irrigation lowered values of the variables and values of soil nutrient. However, the water quality and soil chemical and physical data suggest that the sodification process and the increased soil erosion risk must be controlled in order to achieve a sustainable high production system. Soil irrigated with river water was most preferred for growing tomato by virtue of their optimum level of pH, EC, Na, Mg and $NH_4$-N. It is suggested that in case of waste water or water with any combination should not be used directly for irrigation as minerals released from such water create soil pollution. Treated wastewater for agricultural irrigation is common in arid and semi-arid regions as a solution to water scarcity (Keraita and Drechsel 2004; Uzen 2016).

## 7.6 Strategies to Use Alternatives to Agrochemicals

Fertilizers, Pesticides and herbicides are chemical compounds engaged with enhancing production, controlling pest and weed species in agricultural fields.

Heavy soil treatment with pesticides and herbicides can lead to depletion of populations of beneficial soil microorganisms, which are essential for maintaining soil fertility. Overuse of chemical fertilizers, herbicides and pesticides has effects on the soil organisms that are similar to effects of human overuse of antibiotics. Indiscriminate use of agrochemicals might give better productivity for initial years, but at later years, there aren't enough soil beneficial micro-organisms to hold onto the nutrients present in the soil. For example, to absorb nitrogen from soil, plants rely on a variety of nitrogen-fixing bacteria that are present in soil to convert atmospheric nitrogen into plant available nitrogen in the form of ammonia. Common herbicides disrupt nitrogen fixation: triclopyr inhibits bacteria that transform ammonia into nitrite; glyphosate reduces the growth and activity of free-living nitrogen-fixing bacteria in soil and 2, 4-D reduces nitrogen fixation by the bacteria that live on the roots of bean plants, reduces the growth and activity of nitrogen-fixing blue-green algae, and inhibits the transformation of ammonia into nitrates by soil bacteria (Bhat et al. 2019). Mycorrhizal fungi grow in symbiotic association with the roots of many plants and aid in nutrient uptake. These beneficial fungi can also be damaged by herbicide application. One study found that both oryzalin and trifluralin inhibited the growth of certain species of mycorrhizal fungi (Kelley and South 1978). Roundup has been shown to be toxic to mycorrhizal fungi, Triclopyr was also found to be toxic to several species of mycorrhizal fungi and oxadiazon reduced the number of mycorrhizal fungal spores.

There are a relatively few pesticide management tactics that have been proposed risk-free and have a reasonable chance of success under a variety of different circumstances. Prominent among these are monitoring of pest population in field before any pesticide application, alteration of pesticides with different modes of action, restricting number of applications over time and space, creating or exploiting refugia, avoiding unnecessary persistence, targeting pesticide applications against the most vulnerable stages of pest life cycle, using synergists that can enhance the toxicity of given pesticides by inhibiting the detoxification mechanisms in pest gut system.

Apart from reduction in pesticide use, biological control of pest is a more recent approach dealing with pest management in fields. Integrated pest management (IPM) is often intended to encompass the management of plant diseases and insect pests bringing the population of pest below the economic injury levels. IPM practices include monitoring pests and using economic thresholds (ETs), reducing pesticide rates, and diversifying cropping systems and control strategies to prevent pest problems. IPM approaches such as using genetic-crop-resistant varieties and maintaining populations of beneficial pest predator species aid in pest management.

Strategies for reduction in herbicide vary from organic culture practices where no herbicides are used to conventional agriculture systems in which endeavours are made to profit by herbicide use reduction. Organic farming is the most widely recognized form of reduced-pesticide agriculture. Its primary feature is that no synthetically or artificially produced herbicides, pesticides or fertilizers are used. Limited fertilizer application and reduction or elimination of pesticide or herbicide use may appear more feasible to many farmers than organic production in terms of productivity, but organic farming maintains the fertility of soil and gives products with higher monetary value in commercial market. Strategies for diminishing herbicide use can be set along a continuum of progressively devoted management practices: (1) herbicide substitution with other weed management methods, (2) efficiency in the use of herbicides and (3) redesigning the cropping system to prevent herbicides use. While most strategies can be utilized in any of the practices mentioned, the more prominent goal is to lessen herbicide use, the more vital it is to utilize strategies that seem further along the continuum. For instance, farmers who are determined to lessening herbicide utilization must decrease the requirement for herbicides by redesigning the cropping pattern in a way that diminishes interference capacity and size of the weed population. Organic farming must be firmly dedicated to their system since herbicide use is never a choice. Herbicide use can be improved by applying the learning of weed biology and ecology, for example, weed emergence and the critical weed control period. Improved application and comprehension of elements influencing herbicide performance can decrease the amount of herbicide utilized.

Weeds can be constrained by the utilization of living organisms (insects, fungi or bacteria), and this methodology is also referred as bio-herbicide. The utilization of sheep (*Ovisaries* L.) or flea beetles (*Aphthona* spp.) to constrain leafy spurge (*Euphorbia esula* L.) has been fruitful in Manitoba, Canada (Mico and Shay 2002). Building an effective delivery strategy for these bio-herbicides is the focal point of current research. There are a number of constraints to the applications of bio-herbicides, especially the generation of effective formulations. Currently, bioherbicides are frequently increasingly exorbitant, have lower adequacy, and require more thorough handling and capacity necessities than traditional herbicides.

Expulsion of weed seeds by seed pathogens and predators (for example, spineless creatures and rodents) is another type of biological control. However, there is little research with respect to how these biocontrol operators may effectively be controlled. In field crops, weed management is the management strategy of field-cropping systems to decrease weed densities and maintain their population at low levels, thus reducing herbicide necessity. The utilization of single non-synthetic weed management techniques is commonly not adequate for diminishing weed densities or keeping up weed densities at low levels. However, the mix of a few non-compound practices can be powerful.

## 7.7 Conclusion

Soil pollution is a hidden danger that affects the growth and health of living organisms. An overview of reports presented here in this chapter highlights the causes of soil pollution due to precipitation deposits of acidic compounds, human developmental and mining activities, industrial activities and various agricultural activities. Soil pollution has gradually become a major challenge for agriculture that we need to overcome for establishing a healthy environment assisting in growth of plants. All nations must invest regional survey to get national data of soil problem and take steps to prevent the migration of pollutants. Availability of global map of soil pollution will help to guide policymakers on soil pollution mitigation and soil management strategies.

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# Inorganic Soil Contaminants and Their Biological Remediation

# 8

Anil Kumar

## Abstract

Soil contamination is one of the biggest concerns of present time. It is caused by anthropogenic activities or alteration in the natural soil environment. The main reason for the soil contamination is industrialization, agricultural chemicals, and improper disposal of wastes. The most common chemicals involved are petroleum hydrocarbons, polynuclear aromatic hydrocarbons, solvents, pesticides and inorganic contaminants. Inorganic contaminants include toxic metals and different types of nutrients and salts. These contaminants generally occur in the form of dissolved anions and cations. Some inorganic contaminants persist in the soil for an indefinite time, whereas other compounds degrade or transform in very short duration. Inorganic contaminants adversely affect the soil quality parameters such as fertility levels, and physical and biological quality of the soil that subsequently results in loss of productivity. There are several methods to remediate such types of contaminated lands. The use of physical and chemical methods is often costly and it can even adversely affect the integrity of the soil ecosystem. Remediation of inorganic contaminated soils by biological processes has proven cost effective and is usually termed as clean technology. The biological remediation of inorganically contaminated soil includes mycoremediation, cyanoremediation, phytoremediation, biostimulation, bioaugmentation, biomineralization, genoremediation, bioleaching, biosorption, bioadsorption, biotransformation, bioventing, etc. This chapter discusses the type of inorganic contaminants, their sources and implications for soils, biological remediation potential of organisms and provides an overview of the recent development in this area.

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**Keywords**

Soil pollution · Inorganic contaminants · Mycoremediation · Cyanoremediation · Bioaugmentation · Biotransformation · Genoremediation · Phytoremediation

## 8.1 Introduction

Soil is a complex heterogeneous mixture of water, mineral nutrients, gases, organic matter, and diverse microorganisms. These components, when present in appropriate proportions, make the soil healthy. Soil health plays an important role in nutrient cycling and the availability of nutrients to sustain plant growth. Quality of soil ecosystems is a matter of significance because life on Earth would not be possible without two major contributions of plants, i.e. oxygen and food.

Soil ecosystems can be damaged by the force of nature or by poor management practices. Soil erosion, land clearing, unsustainable farming practices, ill-managed industrial activities, improper disposal of waste and mining activities are some of the anthropogenic factors that disturb the physicochemical properties of soil. Soil remediation is essential for the sustainable development and conservation of ecosystems along with their biodiversity. Remediation of contaminated lands depends upon the nature of contaminants, which include agrochemicals, chlorinated compounds, dyes, greenhouse gases, heavy metals (HMs), hydrocarbons, nuclear waste, plastics and sewage. There are several physical, chemical and biological methods to remediate the polluted site. Among these methods, biological methods are inexpensive, easily applicable, environmentally safe strategies to remediate contaminated sites because indigenous microorganisms present in polluted environments hold the key to solving most of the challenges associated with biodegradation and bioremediation of polluting substances (Verma and Jaiswal 2016). Bioremediation relies on biological mechanisms to reduce (degrade, detoxify, mineralize or transform) concentration of contaminants to an innocuous state.

### 8.1.1 Soil Pollution

Naturally, soil contains diverse types of chemical compounds. These may be metals, inorganic ions, and salts (e.g. phosphates, carbonates, sulphates, nitrates), and many organic compounds (e.g. lipids, proteins, DNA, fatty acids, hydrocarbons, polycyclic aromatic hydrocarbons, alcohols, etc.). Soil pollution can be defined as the addition of persistent toxic compounds, chemicals, salts, radioactive materials or disease-causing agents in the soil, which have adverse effects on plant and animal (Okrent 1999). Inorganic contaminants, especially HMs, are a global environmental menace because these pollutants persist in the form of ions and are non-degradable in nature. Soil pollution causes a serious threat to agricultural productivity, food safety and human health.

### 8.1.2 Inorganic Soil Contaminants

Inorganic compounds are the natural constituents of soil. The nutrients present in soils are usually chemically decomposing rocks and secondary minerals such as phyllo-silicates or clay minerals, oxides of Fe, Al, and Mn and sometimes carbonates (usually $CaCO_3$) (Berbecea et al. 2011). Among the inorganic contaminants, HMs have acquired paramount consideration and have affected the system most. HMs are natural constituents of the soil but due to human activity, these metals are concentrated in a particular site and considered as contaminants. Inorganic residues of industrial and mining waste cause serious problems to soil ecosystems. These residues contain HMs, which have a high potential for toxicity. Several HMs, including cadmium, chromium, copper, mercury, lead, nickel, zinc and arsenic, are widely used by industries, transportation, agriculture and released into the environment (Kumar and Aery 2016). Industrial activity emits large quantities of arsenic fluorides and sulphur dioxide (Richardson et al. 2006). Sulphur dioxide emitted by factories and thermal plants may cause soil acidification. The most common inorganic pollutants in the soil are nitrate, phosphate, cyanides, ammonium, sulphur, sodium, arsenic, cadmium, chromium, copper, zinc and mercury. Common inorganic contaminants and their sources are summarized in Table 8.1.

## 8.2 Impact of Inorganic Soil Contaminants on Ecosystem

Inorganic soil contaminants are known to adversely affect all components of an ecosystem. Elevated levels of soil contaminants negatively affect the plant, animal, microbe, and overall soil health. Contaminants such as HMs may change the plants' physiological processes, causing visible damage and reduce yields. Pollutants can alter physicochemical properties of soil and affect inhabitant organisms even at very low concentrations. The effects on plants, animals, microbes and soils depends on the properties of the soil, the levels of pollutants, the presence of specific pollutants and the sensitivity of a particular organism to existing pollution (Shayler et al. 2009). Inorganic soil pollution can increase salinity, reduce soil fertility, reduce nitrogen fixation, decrease nutrient bioavailability, affect soil fauna and flora adversely and reduce the crop yield subsequently. Further, the addition of inorganic soil contaminants to underground water pollutes the drinking water sources and creates serious problems for all living forms. The release of contaminant gases with unwholesome odour and release of radioactive rays affect the Earth's ecosystem and cause public health problems. Due to inorganic contaminants, the soil becomes less productive or sterile, eroded, less in number and diversity of soil microorganisms and subsequent disturbance in the whole ecosystem. A schematic representation of the pathway of inorganic soil contaminants and their entry route in the food chain is given in Fig. 8.1.

**Table 8.1** Inorganic soil contaminants and their source

| S. No. | Inorganic soil contaminants | Sources |
|---|---|---|
| 1. | Nitrate ($NO_3^{2-}$) | Agricultural runoff, nitrogen-based fertilizers, animal manure, sewage, seepage from wastewater |
| 2. | Phosphate ($PO_4^{2-}$) | Fertilizers, animal manure, detergents, human and animal faeces |
| 3. | Cyanides ($CN^-$) | Galvanic and metallurgical industry |
| 4. | Ammonia ($NH_3$) | Fertilizer applications, animal husbandry |
| 5. | Fluoride ($F^-$) | Rock weathering, phosphate fertilizers, coal combustion, emission of smelters |
| 6. | Sodium (Na) | Chlor-alkali, textiles, glass, rubber, soap production, animal hide processing and leather tanning, metal processing, pharmaceuticals, oil and gas drilling, pigment, ceramic manufacture |
| 7. | Aluminium (Al) | Manufacturing (kitchen utensils, wrappings and containers), medical and scientific equipment, food additives, cosmetics, water treatment |
| 8. | Nickel (Ni) | Smelting operations, thermal power plants, battery industry |
| 9. | Copper (cu) | Mining, electroplating, smelting operations, vanadium spent catalyst, sulphuric acid plant |
| 10. | Zinc (Zn) | Smelting, electroplating |
| 11. | Sulphur (S) | Fossil fuel combustion, wet deposition, acid rain |
| 12. | Chromium (Cr) | Mining, industrial effluents, chemical industries, leather and tanning industries |
| 13. | Arsenic (as) | Geogenic/natural processes, smelting operations, thermal power plants, fuel burning |
| 14. | Selenium (se) | Coal combustion, se-purifying industries, metal smelting, mining and milling operations, semiconductor manufacturing |
| 15. | Strontium (Sr) | Rock weathering, coal burning, use of phosphoric fertilizers and pyrotechnical devices |
| 16. | Cadmium (cd) | Zinc smelting, waste batteries, e-waste, paint sludge, incinerations and fuel combustion |
| 17. | Barium (Ba) | Getters in electronic tubes, rodenticide, colourant in paints, x-ray contrast medium and barite-mining activities. |
| 18. | Tungsten (W) | High-speed tools, knives, building materials, engine turbines, radiation shields, jewellery, lightning, electrodes and military munitions |
| 19. | Mercury (hg) | Lead-acid batteries, paints, e-waste, smelting industries, thermal power plants, ceramics |
| 20. | Lead (Pb) | Chlor-alkali plants, thermal power plants, fluorescent lamps, waste of medical equipment (thermometers, barometers, sphygmomanometers), electrical appliances |

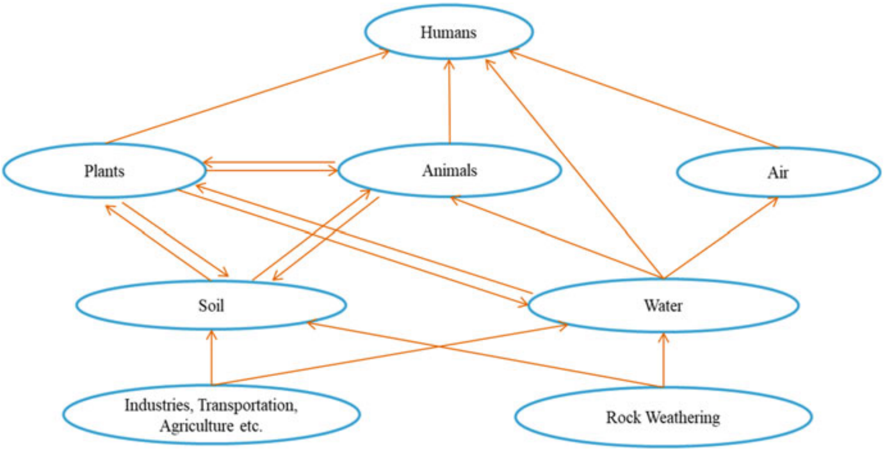

**Fig. 8.1** Schematic representation of the pathway of inorganic soil contaminants and their entry in the food chain

## 8.3 Biological Remediation of Soils Polluted with Inorganic Contaminants

Inorganic soil contaminants do not undergo chemically or biologically induced degradation that can reduce their toxicity (Knox et al. 2000). This makes these contaminants unique and more concerning as compared to other contaminants. Several microorganisms are known to play an essential role in the management of soil. *Flavobacterium, Pseudomonas, Bacillus, Arthrobacter, Corynebacterium, Methosinus, Rhodococcus, Mycobacterium, Stereum, Nocardia, Methanogens, Aspergillus, Pleurotus, Rhizopus, Azotobacter, Alcaligenes, Phormidium, Ganoderma* are some microorganisms that can act as bioremediator HMs (Verma and Kuila 2019). Microbes can accumulate, transform or detoxify these contaminants. In general, the presence of these microbes can have an enormous impact on soil and plant health. Metals cannot be destroyed but their transformation from one oxidation state or organic complex to another is biologically possible. As a consequence of the transformation, metal may become either: (i) more water soluble, (ii) less toxic, (iii) less water soluble so that it can precipitate and becomes less toxic, or (iv) volatile and thus can be removed from the polluted sites (Garbisu and Alkorta 1997). Mitigation of metals in soil largely depends upon the bioavailability that can further impair the process of remediation due to increased toxicity. Soil microorganisms confront these problems simultaneously by modulating growth of remediating organisms and by altering physicochemical properties of soil to improve metal bioavailability, which triggers rapid detoxification or removal of toxic metals from contaminated soil (Mishra et al. 2017; Seth and Kumar 2020). Following are several mechanisms that can be used to remediate contaminated soils.

### 8.3.1 Mycoremediation

In mycoremediation, fungi are employed as a tool to remove pollutants from contaminated sites. Properties such as large surface area and the rapid ramification of mycelium (Kulshreshtha et al. 2014) make them amenable for the remediation. Fungi are major decomposers along with bacteria that recycle nutrients that are locked within organic matter. The role of saprotrophic and biotrophic basidiomycetes has been widely recognized for remediation purposes (Baldrian 2008; Spina et al. 2018). Filamentous and macrofungi or mushrooms contain some enzymes such as laccase and glutathione transferase, which play an important role in the removal of pollutants (Bosco and Mollea 2019). Fungal enzymes can be employed to remove both organic and inorganic pollutants like HMs, radioactive waste, cyanide, carbonates, $CO_2$, etc.

Fungi show heavy metal tolerance by processes like extracellular and intracellular sequestration (Fawzy et al. 2017). The paucity of agricultural land can be solved by using potential fungi such as *Aspergillus flavus*, *Fusarium* sp., *Penicillium* sp., *Saccharomyces cerevisiae* to remove HMs in post-mining areas (Ahmad 2018). Similarly, Cu-tolerant fungi such as *Postia*, *Serpula*, *Fibroporia*, and *Wolfiporia* (De Groot and Woodward 1999; Clausen and Green 2003) reduce the toxicity of Cu-based wood preservatives by changing them into oxalate (Murphy and Levy 1983; Akgul and Akgul 2018). Remediation of Cu, Cd, Cr, Pb and Zn by using *Galerina vittiformis;* Bi, Ti by using *Marasmius oreades* and Ti, Sr, Mn by using *Hypholoma capnoides* has been reported (Singh and Gauba 2014).

Metabolic inhibitors such as cyanide can be treated by different strains of fungal species. By using simple hydrolytic detoxification pathway, a strain of fungus *Fusarium solani* could be utilized to treat industrial effluents containing free cyanide under alkaline conditions (Dumestre et al. 1997). The toxicity of HMs and radioactive cations to bioremediating organisms can be reduced by changes in oxidation states that convert them to forms of low solubility in the substrate (Singh et al. 2014). Fungi such as *Aspergillus niger* and *Paecilomyces javanicus* can precipitate uranium-containing phosphate biominerals, which can be applied for element recovery or bioremediation (Liang et al. 2015). MD1149 strain of *Rhodotorula taiwanensis*, a basidiomycetes fungus, can grow at low pH and under high level of gamma radiation. It is more significant in the treatment of acidic radioactive sites than radiation-resistant bacterium *Deinococcus radiodurans* due to its sensitivity to low pH (Tkavc et al. 2018).

It has also been reported that saline–alkali soil in Northern China is treated by haloalkaliphilic fungi such as strains of *Aspergillus glaucus*. In addition to that, a series of salt and/alkali resistance genes have been isolated and analysed, which can be employed in other organisms to cope with these conditions (Zhang et al. 2018). *Debaromyces hansenii*, a salt-loving fungus, can accumulate high concentrations of Na without showing any damage (Almagro et al. 2000). Globally, 20% of cultivated land and 33% of irrigated land are salt-affected (Machado and Serralheiro 2017). These organisms can play a vital role in the reclamation of such soils. Unlike other fungi, mycorrhizal fungi could be a potential candidate to sequester carbon in the soil as reported by Clemmensen et al. (2015) and Holden and Treseder (2013) in boreal forests.

### 8.3.2 Cyanoremediation

Cyanoremediation is the biological remediation of contaminated soil using cyanobacteria. Cyanobacteria can fix atmospheric nitrogen along with atmospheric carbon, thereby enhancing the fertility of the water and soils. These organisms have the capacity to degrade or detoxify many gaseous, solid and liquid recalcitrant contaminants, including both natural and xenobiotic originate, viz. carbon dioxide, nitrogen, HMs, phosphorous, phenolics, pesticides, antibiotics, melanoidin, lignin and detergents (Kertesz et al. 1994; Subramanian and Uma 1996; Mohamed 2001). They can grow in minimal nutritional conditions and use light as a sole energy source, hence can be utilized as cost-effective tool for bioremediation (Naghavi et al. 2012)

Cyanobacteria are able to tolerate a high concentration of toxic metals (De Filippis and Pallaghy 1994). These organisms can significantly remediate the contaminated sites incorporated with high concentrations of HMs like Fe, Mo, Se, Mn, Zn, Ni, Cu, V, Co, Cr, As, Hg, Cd and Pb, polycyclic aromatic hydrocarbons (PAHs) and dyes (Gupta et al. 2016). The main cyanobacterial strains are *Anabena, Nostoc, Phormidium, Aphanocapsa, Oscillatoria, Lyngbya, Spirulina, Aulosira, Anacystis* and appear to be promising bioremediators for the effluent-rich nitrates and phosphates (Gothalwal and Chillara 2012). De Philippis et al. (2003) studied the removal of Cu(II) using *Cyanospora capsulata* and *Nostoc* and reported the biosorption of Cu from the first minutes of contact with metals. *Synchococcus cedrorum* is tolerant to heavy metal and pesticides (Gothalwal and Bisen 1993). Raungsomboon et al. (2008) reported that *Gloeocapsa*. is capable of growing in concentration of Pb ranging 0–20 mg Pb $L^{-1}$ and able to remove Pb from the environment.

By using hydrogen cyanide as a substrate rather than the normal one (dinitrogen), nitrogenase enzyme of photosynthetic cyanobacteria can convert it into ammonia and methane (Gantzer and Maier 1999). *Chroococcus* sp., isolated from steel-manufacturing industrial wastewater, was utilized in cyanide bioremediation (Naghavi et al. 2012). The high concentration of salts adversely affects plant metabolism and growth (Deinlein et al. 2014) and destroys the microbial communities and carbon cycling in the soil (Rath and Rousk 2015). Nitrogen-fixing cyanobacteria could increase phosphate solubilization and mineral release, thus performing dual tasks of salt-affected soil remediation and nitrogen fixation (Singh 2015). Extreme radioresistance has also been reported from two species of nitrogen-fixing filamentous cyanobacteria *Anabaena*. Its high tolerance and photoautodiazotrophy make it a suitable alternative for remediation of radioactive waste (Singh et al. 2010).

### 8.3.3 Phytoremediation

Phytoremediation is a novel bioremediation technique in which plants are used to remove, transfer, stabilize and/or decompose pollutants in the soil and groundwater. It is an emerging technology that can be applied to organic as well as inorganic pollutants present in the soil, water or air (Salt et al. 1998; Aery 2016; Seth and Kumar 2020). This technique depends on the working of plants to mitigate the toxic effects of pollutants on contaminated sites. The main interactions are physical, biochemical, biological, chemical and microbiological. There are several mechanisms involved in the phytoremediation process, including accumulation, extraction, degradation, filtration, stabilization and volatilization. Plants have a wide range of primary as well as secondary compounds like phenols, proline, phytochelatins, metallothioneins, etc. with the capacity to mitigate heavy metal stress and high affinity for wide range of metals (Kumar and Aery 2011, 2012; Bhati and Kumar 2020). The mechanism of phytoremediation depends upon the type of contaminates – either it is an elemental or organic contaminant. Elemental pollutants (toxic HMs and radionuclides) are mostly removed by extraction, transformation and sequestration. On the other hand, organic pollutants (hydrocarbons and chlorinated compounds) are predominantly removed by degradation, rhizoremediation, stabilization and volatilization, with mineralization being possible with the help of plants such as willow and alfalfa (Meagher 2000; Kuiper et al. 2004). The plants suitable for remediation are either high biomass yielding like willow (Landberg and Greger 1996) or high metal-accumulating characteristics like *Thlaspi* and *Arabidopsis* (Lone et al. 2008). Phytoremediation of salt-affected soils can also improve nutrient availability to the plants (Bhuiyan et al. 2017). Salt-tolerant plants such as *Panicum repens, P. australis*, *Chenopodium album* and *Apocynum venetum* can be used in the restoration of saline soil (Hamidov et al. 2007). Au et al. (2018) investigated remediation of free cyanide and iron cyanide complexes by plants and the mechanisms involved in the process. Phytoremediation of inorganic contaminants, including HMs, is extensively reviewed by Tangahu et al. 2011; Adiloğlu 2017; Sumiahadi and Acar 2018 and Ashraf et al. 2019.

### 8.3.4 Bioremediation

Utilization of microbes in eradication of pollution from contaminated sites involves several modes of activity.

#### 8.3.4.1 Biostimulation

Biostimulation is the modification of the environment to support the growth of indigenous microbes. This can be done by addition of various forms of limiting nutrients and electron acceptors, such as P, $N_2$, $O_2$ or C, which are otherwise available in quantities low enough to restrain microbial processes (Elektorowicz 1994; Piehler et al. 1999; Rhykerd et al. 1999; Perfumo et al. 2007). The substrates containing N and P are the most popular stimulants because of their electron-accepting capabilities (Saxena and Misra 2010).

The microorganisms adapted at HMs-contaminated environment biostimulated in a minimal salt medium under aerobic conditions effectively remediate HMs (Cd, Cu, Fe) contaminated soil (Fulekar et al. 2012). The action of *Citrobacter* sp. promotes metal immobilization by reducing exchangeable Ni and increasing residual Ni, greatly reduces the metal toxicity (Ma et al. 2018) and improves the rate of bioremediation. In a study, Dong et al. (2013) used an electrokinetic-coupled biostimulation method for removal of Pb from Pb-oil co-contaminated soil. They reported that the addition of EDTA plays a role in reducing the heavy metal toxicity in soil and resulted in 81.7% removal of Pb from the soil.

#### 8.3.4.2 Bioaugmentation

Bioaugmentation is an alternate strategy for the bioremediation of contaminated environments. It can be defined as the addition of degradation-capable microorganisms to supplement the indigenous populations. The basis for this strategy is that native microbes may not be capable of degrading the wide range of potential pollutants present in complex mixtures (Leahy and Colwell 1990) or that they may be in a stressed state as a result of the exposure to pollution (Adams et al. 2015). It differs from biostimulation as it involves the addition of living cells to enhance the rate of remediation process rather than electron acceptors or liming factors, etc. Microorganisms are able to change the bioavailability of metals in the soil by processes like acidification, chelation, complexation, precipitation and redox reactions. Acidic pH conditions favour bioavailability and adsorption of metals in the rhizosphere (Merdy et al. 2009; Seth and Kumar 2020). Bacteria such as *Flavobacterium, Pseudomonas, Alcaligenes, Rhodococcus, Achromobacter, Bacillus,* and *Mycobacterium* have been extensively used for bioaugmentation purposes (Emenike et al. 2016, 2017; Singh et al. 2011). Bioaugmentation potential and heavy metal tolerance of fungi, namely, *Perenniporia subtephropora, Daldinia starbaeckii, Polyporales, Aspergillus niger, Aspergillus fumigatus, Penicillium cataractum*, have resulted into higher metal reduction in soil (Hassan et al. 2019). Soil bioaugmentation with fungi such as *Cyberlindnera* sp. and *Candida tropicalis* has been utilized in remediation of Cr-contaminated soil (Bahafid et al. 2013, 2017).

#### 8.3.4.3 Biomineralization

Biomineralization is the process of mineral formation by living organisms. The products of biomineralization are complex materials that contain both minerals and organic components (Li et al. 2014). The process creates heterogeneous accumulations, composites composed of organic and inorganic compounds, with nonhomogeneous distributions that reflect the environment in which they form (Skinner and Jahren 2007).

Li et al. (2013) studied biomineralization of Ni, Cu, Pb, Co, Zn and Cd using metal-resistant bacteria. These bacteria have high removal rates (88–99%) of HMs by producing the enzyme urease. Metals can also be precipitated on the surface of immobilized cells of bacteria like *Citrobacter* sp. as cell-bound metal phosphates.

Some HMs form metal phosphates, which result in efficient removal of HMs (Macaskie et al. 1994).

Li et al. (2014) studied biomineralization of metal carbonates using *Neurospora crassa* and reported that the $Cd^{2+}$ precipitated as pure otavite ($CdCO_3$). The precipitation of metal carbonates such as calcite and otavite suggests that urease-producing fungi may play a potential role in the production of novel biominerals and in metal bioremediation or bio-recovery (Li et al. 2014). The indigenous *Bacillus subtilis* immobilized the Cr, Cu and Zn within the industrially contaminated soil, significantly by microbial-induced mineral precipitation process (Maity et al. 2019). Biomineralization of radionuclide and metals into calcite occurs as a competitive co-precipitation reaction in which suitable divalent cations are integrated into the calcite lattice (Dhami et al. 2013).

#### 8.3.4.4 Genoremediation

Genoremediation is the engineering of bacterial genes to increase their bioremediation potential, with subsequent incorporation into plant genome (Mani and Kumar 2014). Genetic engineering can be used to improve the degradation of pollutants by creating genetically modified organisms. Recombinant organisms can be designed by recombinant DNA techniques or by the natural genetic exchange. The genes that are currently used to manipulate metal metabolism in plants are the genes of metal transporters and metal-binding ligands (chelators) (Koźmińska et al. 2018). There are several membrane transporters that have been implicated in the transport of HMs in different organisms and could serve such role in plants. These membrane transporters belong to heavy metal ATPases, the natural resistance-associated macrophage protein (Nramp) family, members of the cation diffusion facilitator (CDF) family, and the ZIP family (Kumar and Aery 2016). The effect of genetic transformation with ABC genes is linked with heavy metal mobility. Therefore, ABC genes could be overexpressed either to increase the translocation of mobile ions, like Cd and Cu, or to bind the non-mobile ones, like Pb in the roots (Koźmińska et al. 2018). Ruiz et al. (2011) reported a transgenic system that effectively expresses metallothionein and polyphosphate kinase genes in bacteria to provide high Hg resistance and accumulation.

#### 8.3.4.5 Bioleaching

Bioleaching is the extraction of metals from the contaminated soils by using living organisms. Some bacteria, such as *Thiobacillus ferrooxidans* and *T. thiooxidans*, and some fungi, such as *Aspergillus* and *Penicillium*, are the most common microbes with the potential of metal solubilization (Aung and Ting 2005). Chen and Lin (2010) reported metal solubilization with more than 80% efficiency. They also observed stability in soil and residual HMs was harmless to the environment after the bioleaching process. By using sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans*, isolated from sewage sludge, the bioleaching process of Cr, Cu, Pb and Zn has been optimized (Wen et al. 2012). Bioleaching remediation of Mn, Zn, Cd, etc. was performed by biosurfactant-producing Z-90 strain of *Burkholderia* sp. by adhesion of minerals to the strain and the formation of the metal complex with biosurfactant (Yang et al. 2016).

#### 8.3.4.6 Biosorption

Biosorption is the ability of biological originated materials to accumulate pollutants from contaminated sites. The process can be carried out by active or passive pathways of pollutant uptake or as a property of certain types of inactive, non-living microbial biomass, which bind and concentrate HMs from the environment even at very low concentration (Shamim 2018). Most biosorbent materials have good biosorption capabilities toward all types of metal ions, so many affordable and easily available biosorbents are derived from microbes (bacteria, fungi and algae), plants and polysaccharide materials (Oyewole et al. 2019). Biosorption may involve one or more than one method, including complexation, coordination, chelation, ion exchange, microprecipitation and entrapment (Pokethitiyook and Poolpak 2016).

Oyewole et al. (2019) studied the biosorption of Cu-, Cr-, Cd- and Ni-polluted soil using bacteria and fungi. They reported the ability of *Pseudomonas aeruginosa* to biosorb Cu and Cr and *Aspergillus niger* and *Penicillium notatum* to biosorb Cd and Ni from the environment and concluded that these organisms can be developed for the biosorption of soils polluted with Cu, Cr, Cd and Ni. The biosorption of metals such as Cd, Cr, Cu, Pb and Ni is successfully reported by the biomass of metal-tolerant *Bacillus thuringiensis* OSM29 from aqueous solution (Oves et al. 2013). Feng et al. (2018) observed that *Verticillium insectorum* absorbed Pb(II) and Zn(II) through cell surface binding and intracellular accumulation or precipitation. However, extracellular biosorption is the main process observed at higher concentrations (75–300 mg $L^{-1}$) of Pb and Zn. *Verticillium insectorum* alters the biosorption mechanism under lower or higher Pb(II) and Zn(II) concentrations and has proved to be a highly efficient biosorbent, especially for Pb(II). The biosorption capacity of the *Bacillus cereus* for the metallic ions recorded up to 98.9% for Mn at 600 mg $L^{-1}$ initial metal ion concentration (Zhenggang et al. 2018). Li et al. (2018) studied bioaccumulation and biosorption mechanisms of three cadmium-resistant PGPR, *Cupriavidus necator*, *Sphingomonas* sp., and *Curtobacterium* sp., under different initial Cd(II) concentrations. They reported that the dominant adsorption mechanism for *Cupriavidus necator* is bioaccumulation, while the dominant mechanisms for *Sphingomonas* sp. and *Curtobacterium* sp. are biosorption. *Macrophomina phaseolina* and *Rhizopus stolonifier* have significant roles as good biosorbent agents for Pb, Cd, Cu and Zn and show better uptake capacity for Pb, Zn and Cd compared to Cu (Fawzy et al. 2017).

#### 8.3.4.7 Bioadsorption

Bioadsorption is a physicochemical process in which the concentration of pollutants is adsorbed on the biologically originated non-living material. It is a metabolically passive, rapid and reversible process binding metal ions from aqueous solutions onto functional groups (González et al. 2017). The bioadsorption mechanism of metals includes electrostatic interaction, complexation, ion exchange or proton displacement ion exchange, coordination, chelation, and microprecipitation (Volesky 1990; Fourest and Roux 1992; Crist et al. 1999; Davis et al. 2003).

Mane et al. (2011) studied the effect of pre-treatment (heat, autoclaving, chemical treatments such as sodium hydroxide and acetic acid) of algal biomass on the Se biosorption capacity and reported that the pre-treated biomass adsorbed higher Se in comparison with live biomass. The bioadsorption capacity of methylene blue on the surface of the biomass of a brown alga *Durvillaea antarctica* is 702.9 mg $g^{-1}$ and proved as a material with great properties as a bioadsorbent (Guarín et al. 2018).

Pumpal et al. (1995) demonstrated the bioadsorptive potential of fungus *Aureobasidium pullulans* for the removal of Ni, Cr, Cd, Zn, Al, Si and Pb. Bioadsorption of Cr and Cd ranged from 6.20–9.5 and 2.3–8.21 mg $g^{-1}$, respectively, of dry mass at initial metal concentrations by *Aspergillus* and *Rhizopus* sp. Moreover, *Rhizopus* sp. bioadsorb higher concentration of Cr and Cd as compared to *Aspergillus* sp. (Ahmad et al. 2005). Vargas et al. (2012) successfully produced a local compost made from carnation flower waste having adsorbion potential of Cr(VI) from aqueous solutions in acid conditions.

#### 8.3.4.8 Biotransformation

Biotransformation is modification in the activity of contaminants or other compounds with the help of microbes, filamentous fungi, algae, yeast, animal, plants, actinomycetes, etc. (Smitha et al. 2017). Generally, these changes are of structural nature or resultant alteration in their relative polarity. These strategies are used to deal with chemicals produced in food, pharmaceuticals or agrochemical industries. Microbial metal–mineral transformations have applications in other areas of biotechnology and bioprocessing, such as biosensors, biocatalysis, electricity generation and nanotechnology (Gadd 2010). It can be significant due to the complexity and costliness associated with chemical methods. These processes are also involved in reducing solvent consumption, time and cost effectiveness, chemo-, regio- and stereo selectivity and energy efficiency as they generally occur at ambient or moderately elevated temperatures (Hüttel and Hoffmeister 2011). Microbial transformation is one such approach that is widely and successfully used due to the ubiquitous nature of microbes. For the microbial transformation cells (vegetative or resting), spores, enzymes, and immobilized cells or enzymes are generally used (Chibata and Wingard 2014).

Mercury is a well-known chemical that undergoes biotransformation by bacteria to methyl-mercury (Rai et al. 1981; Moore and Ramamoorthy 1984; Moore et al. 1990). Along with methylation, reduction and demethylation strategies of mercury resistance in bacteria were also investigated (Brown et al. 1989). Photosynthetic microorganisms (e.g. phytoplankton and cyanobacteria) can biotransform AsV into AsIII and methylarsenic (methylAs) species (Ye et al. 2012). *Halomonas* sp. (a halophilic-denitrifying bacterium) can biotransform toxic selenium into a non-toxic compound (de Souza et al. 2001) and insoluble uranium into soluble complexes (Francis et al. 2000). Bacterium *Klebsiella oxytoca* uses cyanide as sole nitrogen source in cyanide-containing industrial wastewater and can transform cyanide into end products like ammonia and methane (Kao et al. 2003).

Algae can transform metal ions to less toxic organic compounds (Moore et al. 1990). Some marine green and brown algae methylate arsenate to produce less toxic dimethyl arsenic derivatives (Stevenson et al. 1996). Bacteria and fungi are the significant Se-methylaters in soil (Karlson and Frankenberger 1988). Selenium methylation results in volatilization; it has been used to remove selenium from contaminated sites in California (Thompson-Eagle and Frankenberger Jr 1990).

Filamentous fungi can be utilized to produce compounds with improved biological properties or even new biological activities (Rico-Martinez et al. 2014). Along with Basidiomycota and Ascomycota division, Mucoromycotina subdivision of fungi includes some well-studied species that metabolize xenobiotics (Cha et al. 2001; Asha and Vidyavathi 2009). A yeast strain converts cysteine into hydrogen sulphide under aerobic conditions and elevates arsenic accumulation by the formation of PC–metal–sulphide complexes (Tsai et al. 2009). Apart from these strategies, in vitro plant cell, organ cultures and plant enzymes act as suitable biocatalysts to perform complex reactions (Giri et al. 2001).

#### 8.3.4.9 Bioreactor

A bioreactor is an artificial vessel in which raw materials are transformed to the product by the sequence of biological reactions. Batch, fed-batch, sequencing batch, continuous and multistage are different operating modes of bioreactor. Contaminated samples filled into a bioreactor are either as dry matter or slurry form. In both cases, the use of bioreactors in remediating contaminated soil has several advantages on other bioremediation techniques. Exceptional control of bioprocess parameters such as temperature, pH, agitation and aeration rates, substrate and inoculum concentrations is the major advantage of bioreactor-based bioremediation (Azubuike et al. 2016). A wide range of bioreactors are used to remove a variety of pollutants accordingly. Inorganic pollutants like a mixture of sulphonated amines and total nitrogen have been bioremediated with help of packed-bed reactors (Juárez-Ramírez et al. 2015) and Submerged attached growth bioreactors (Shannon et al. 2015), respectively.

#### 8.3.4.10 Land Farming

Land farming is the simplest bioremediation techniques due to its low cost and less equipment requirement. The depth at which pollutants present is the important aspect in the technique as land farming can be carried out either ex situ or in situ (Azubuike et al. 2016). In this technique, polluted soils are mixed with different amendments such as soil bulking agents and nutrients, and then they are tilled into the earth. Pollutants are degraded, transformed and immobilized by activities of microbes and oxidation. This technique of bioremediation is very simple to design and implement, cost effective and can be utilized to treat large volumes of contaminated soil with minimal environmental impact and energy requirement (Maila and Colete 2004).

### 8.3.4.11 Bioventing

Bioventing is the improvement of natural in situ biodegradation of aerobically degradable compounds by providing $O_2$ to the indigenous soil microbes. The process improves bioremediation by increasing activities of indigenous microbes by precise stimulation of airflow by delivering $O_2$ to the unsaturated zone. Further, some amendments can be made by adding nutrients and moisture to improve the rate of bioremediation by accomplishing the microbial transformation of pollutants to a harmless form (Philp and Atlas 2005).

It can also be used in anaerobic bioremediation especially in treating vadose zone polluted with chlorinated compounds, which are recalcitrant under aerobic environment (Azubuike et al. 2016). In the aforementioned situation instead of pure oxygen, a mixture of nitrogen with low concentrations of $CO_2$ and hydrogen can also be injected where hydrogen acts as the electron donor (Mihopoulos et al. 2000, 2002; Shah et al. 2001). The use of ozone might be useful for partial oxidation of recalcitrant compounds, which accelerate biodegradation (Philp and Atlas 2005).

### 8.3.4.12 Electrobioremediation

Electrobioremediation is a hybrid technology of two processes, i.e. bioremediation and electrokinetics. In this technology, bioremediation is used to degrade the contaminants and electrokinetics is used to induce the movement of pollutants from the matrix (Annamalai and Sundaram 2020). The acceleration of transport of pollutants or their intermediates is carried out by application of electrical fields (direct current) to remediating zones. This permits the volumetric rate of transport to increase about 50–60 times, and the constituents to collect at convenient removal sites (Chilingar et al. 1997). Electrobioremediation is aimed to activate microorganisms present by the use of nutrients to stimulate the growth, reproduction and metabolism of microorganisms capable of transforming contaminants in soil (Van Cauwenberghe 1997). In this method, removal of heavy metal contaminants from low permeability polluted soils is accomplished under the influence of direct current (Virkutyte et al. 2002). The success of electrochemical remediation depends on the specific conditions encountered in the field such as types and concentration of the contaminant, soil type, pH and organic content present in the polluted soil (Acar and Alshawabkeh 1993).

Ricart et al. (2005) reported that electrokinetic treatment is suitable to remove the Mn from polluted sludge (up to 68%). The same experiment also has shown the highest power consumption, shortest remediation time and highest amount of charge passed through the sludge sample. The use of *Pseudomonas putida* as an electrobioremediation agent has been proven to be an efficient organism and can remediate up to 89% Zn from the contaminated soil (Azhar et al. 2016). The electrobioremediation removal of nitrate with 100% efficiency (Choi et al. (2009)) and Ni with 58.5% efficiency (Ma et al. 2018) has been reported.

## 8.4 Conclusion

Healthy soil is necessary for a healthy ecosystem as it supports the growth and development of microbes, plants and all living forms. Soil ecosystems can be damaged by both natural and manmade activities. Poor management practices, land clearing, extensive use of fertilizers, industrial activity, improper disposal of waste and mining activities are the main anthropogenic factors that can disturb the physicochemical properties of soil. Inorganic contaminants, especially HMs, are causing a threat to soil ecosystems because these are non-degradable, so they persist in the environment. The remediation of contaminated soil is necessary for sustainable development and continual existence of life forms on the planet. Among all methods of soil remediation, including physical, chemical and biological methods, biological method of remediation or bioremediation is an inexpensive, easily applicable, environmentally safe strategy to remediate contaminated sites. However, the understanding of bioremediation is limited. Areas of poor understanding, where more research is needed, are:

- Microbial-induced soil processes and their effect on solubility and bioavailability of pollutants.
- Species change of pollutants in the soil and to understand how species changes altered the uptake and accumulation of pollutants by organisms.
- Interaction between different microorganisms and their interaction with more than one pollutant.
- Use of artificial chelators to improve the bioremediation.
- Use of genetically modified microorganisms to improve the bioremediation of pollutants.
- Efficacy of specific bioremediation techniques according to soil type, contaminant type, etc.

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# Phytoremediation of Pollutants from Soil

# 9

Awadhesh Kumar Shukla, Yogendra Kumar Singh,
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**Abstract**

Soil is continuously contaminated due to industrialization and enormous use of pollutants like aliphatic, aromatic compounds and pesticides. The huge inputs of pollutants in the environment have attracted the considerable attention of researchers continuously over the last two decades. Soil pollution is mainly caused by natural and anthropogenic sources through various organic, inorganic, persistent, and nonpersistent pollutants that directly alter the structural and functional aspects of the ecosystem and adversely affect human health hazards. Contamination of environmental components such as soil, air, and water is become a worldwide concern; hence, effective remediation strategies are warranted to decontaminate the environment. Various physicochemical methods have been utilized by earlier researchers for the removal of pollutants from soil, but unfortunately all methods have their own limitations. Recently, researchers are paying full attention towards phytoremediation, an eco-friendly technology with widely accepted and having potential for removal of contaminants from the environment. This chapter focuses on the remediation strategies of contaminated soil by using a variety of plants in order to understand the cleanup of environment in effective way.

**Keywords**

Industrialization · Persistent pollutants · Pesticides · Heavy metals · Phytoremediation

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## 9.1 Introduction

Phytoremediation is an emerging green technology that utilizes plants to extract, detoxify and hyperaccumulate the toxic pollutants (organic and inorganic) from the environmental components like air, soil and water (Alkorta and Garbisu 2001). It is an eco-friendly and potentially very effective alternative method compared to physicochemical remediation process such as capping or excavation and incineration at various sites contaminated with pollutants. The presence of organic pollutants in the environment is mostly anthropogenic and xenobiotic to various microorganisms (Nwoko 2010). It was reported by earlier researchers that most of the organic pollutants are highly toxic and carcinogenic in nature. Due to rampant industrialization, various organic pollutants are released into the environment via several routes such as oil spills, petrochemical, explosives, chemical weapons and agricultural pesticides, herbicides, etc. On the basis of their properties, organic pollutants can be degraded in the rhizosphere of the plants or there can be hyperaccumulation followed by degradation, sequestration, or volatilization (Nwoko 2010). Additionally, these toxic substances contribute to a variety of health effects on living being in the food chain (Jadia and Fulekar 2009) due to bio-accumulation and bio-magnification in living organisms (Manohar et al. 2006). It is reported that heavy metals like cadmium, copper, lead chromium, zinc, etc. are hazardous environmental pollutants, particularly in populated areas (United States Environmental Protection Agency [USEPA] 1997).

The removal of heavy metals such as arsenic, cadmium, lead, mercury, etc. using plants can be done either by hyperaccumulation of heavy metal in leaves, stems and woody tissue or converting them from an ion- or element-containing compound to a less toxic chemical compound. Phytoremediation and bioremediation cannot be discriminated separately (Reichenauer and Germida 2008). It is a fact that plants are continuously and constantly in interaction with microorganisms present in the vicinity of root or rhizosphere. These organisms may be mycorrhizal fungi that interact with higher plants in a symbiotic manner and help in removal of xenobiotic compounds (Shukla et al. 2019) or nitrogen-fixing rhizobacteria that form a symbiotic relation with legumes. It is reported that the microbial interactions with plants directly or indirectly enhanced the rate of phytoremediation (Reichenauer and Germida 2008). The problem of organic pollutants in the soil can be overcome by removal using plant uptake and their metabolism, or may be accomplished by microbial community residing in adjoining areas around the root of the plants through a process of rhizodegradation.

This chapter focuses on the removal of organic pollutants and heavy metals from the contaminated soil. Additionally, the factors influencing the phytoremediation process will also be discussed.

## 9.2 Removal of Heavy Metal

Phytoremediation is governed via various important steps for the removal of pollutants from the soil like phytoextraction, phytostabilization, phytovolatilization and phytodegradation (Alkorta et al. 2004; Ali et al. 2013). (1) In phytoextraction, pollutants are taken up by the plant roots from the soil or water and then translocated to the shoots (Rafati et al. 2011). (2) Phytostabilization is the exploitation of some plants for stabilization of pollutants in the soils (Singh 2012). This is used to reduce the mobility and bioavailability of pollutants in the environment and, hence, prevent the migration of pollutants to groundwater or into the food chain (Erakhrumen 2007; Ali et al. 2013). It is reported that the plant root exudates bind to the pollutants in the soil matrix and, hence, reduces their bioavailability through the process of phytostabilization (Tangahu et al. 2011). Certain plant species have been utilized in order to immobilize the pollutants in the soil matrix as well as in ground water via root zone through the process of absorption, adsorption and accumulation or precipitation within the root zone. This process is commonly used to decontaminate organics and metals contamination from the soils, sediments and sludges (Prasad and De Oliveira Freitas 2003). (3) Phytovolatilization is the process for the uptake of pollutants directly from soil using plants and converts into volatile form, then releases into the atmosphere. This is commonly used for the removal of organic pollutants and some heavy metals like Hg and Se (Ali et al. 2013). (4) Phytodegradation is a process under which the pollutants are degraded with the help of enzymes like dehalogenase and oxygenase. It is reported that phytodegradation is independent of rhizospheric microorganisms (Vishnoi and Srivastava 2008). Figure 9.1 explains the uptake of heavy metals via phytoextraction, phytostabilization, phytovolatilization and phytodegradation processes. Plants possess potential to accumulate pollutants from environment and detoxify them through their metabolic activities. Due to their activity, green plants are known as "green liver." This term was first coined by Sandermann (1992) to explain the metabolic processing of foreign chemicals (xenobiotics) by the plants. Doty et al. (2007) reported the use of genetically modified plant poplar for the removal of halogenated compounds through phytodegradation. Furthermore, due to fast cultivation and high-biomass production, plants like Jatropha, poplar and willow were potentially exploited for both phytoremediation and energy production (Abhilash et al. 2012). Recently, switchgrass (*Panicum virgatum*) is reported as a potential crop for phytoremediation of heavy metal from soil (Shrestha et al. 2019). They reported that Zn, Cd, Pb, Co and Ni were removed by the switchgrass during laboratory experiments (Shrestha et al. 2019). Table 9.1 suggests the potential of various plant species for accumulation of heavy metals from contaminated environment.

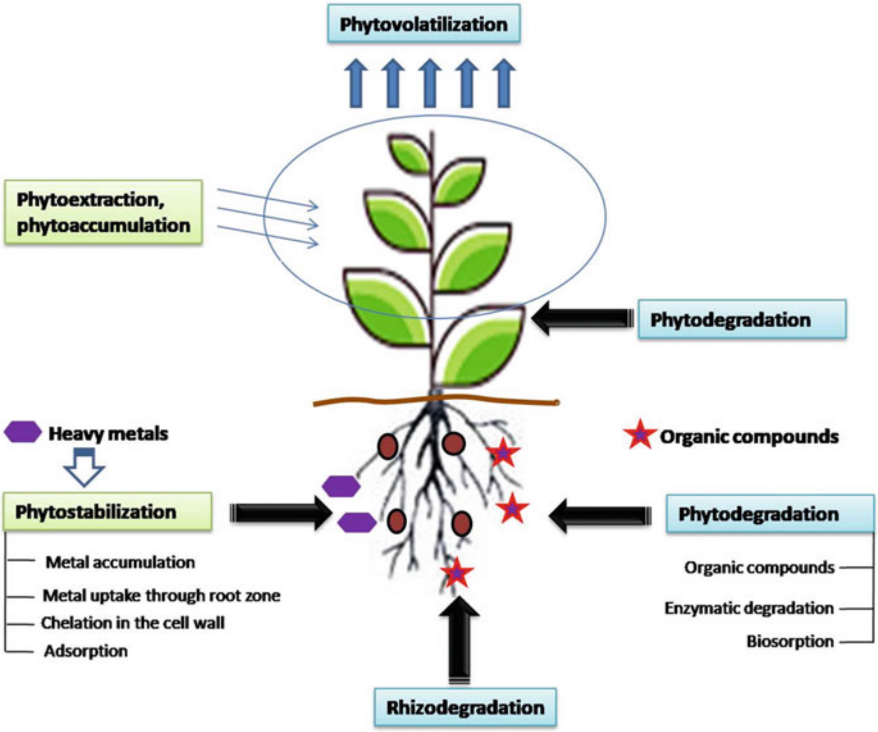

**Fig. 9.1** Mechanism of heavy metal uptake by the plants

**Table 9.1** List of some plants having potential accumulation of heavy metals

| Scientific name of Plants | Metals type | Concentration (mg $kg^{-1}$) | Reference |
|---|---|---|---|
| *Alyssum bertolonii* | Ni | 10,900 | Li et al. (2003) |
| *Alyssum heldreichii* | Ni | 11,800 | Bani et al. (2010) |
| *Azolla pinnata* | Cd | 740 | Rai (2008) |
| *Corrigiola telephiifolia* | As | 2110 | Garcia-Salgado et al. (2012) |
| *Eleocharis acicularis* | Cu | 20,200 | Sakakibara et al. (2011) |
| *Pteris vitatta* | As | 14,500 | Ma et al. (2001) |
| *Alyssum serpyllifolium* ssp. *Lusitanicum* | Cr<br>Cu<br>Pb<br>Zn | 263<br>264<br>1433<br>377 | Kidd and Monterroso (2005) |

## 9.3 Rhizospheric Phytoremediation

Rhizospheric remediation of the pollutants occurs around the root zone where the microbes reside and degrade it. It is reported that the extension of rhizosphere is found to be approximately 1 mm area around the root zone of the plant. Additionally, the plants release the root exudates in the vicinity of the rhizosphere and serve as a carbon source for microbes inhabiting the surrounding area (Bowen and Rovira 1991). The microbial biomass is more concentrated in the rhizospheric soil compared to bulk soils (Olson et al. 2003). Further, the microbes present in the rhizosphere could promote plant growth by stimulating root growth through production of variety of plant growth regulators and enhance the mineral and water uptake (Nwoko 2010). It is reported earlier that remediation of pollutants in the rhizosphere is a slow process. Pollutants (organic or inorganic) are passively adsorbed onto the plant surface through a process of lignification (Nwoko 2010). Pollutants are solubilized by releasing the bacterial biosurfactant such as rhamnolipid, while plants exudate contains lipophilic compounds that increase the solubility of the pollutants and also enhance the growth of bacterial populations (Volkering et al. 1998; Siciliano and Germids 1998).

It is well known that plants rhizosphere stimulate the bioremediation process through release of various metabolites and certain carbonic compounds in order to facilitate the growth of enormous microbial population around root zone. Secondly, plant root exudates may also induce the microbial genes involved in the degradation of the pollutants (Olson et al. 2003). Earlier researchers have reported that the nitrogen-fixing bacteria improve the C: N ratio of hydrocarbon-contaminated soils and consequently enhance the rate of rhizodegradation process (Nwoko 2010).

## 9.4 Factors Affecting the Metal Uptake

There are various factors that directly or indirectly affect the metal uptake. By knowing these factors, the performance of metal uptake by plant can be greatly improved. There are several factors such as plant species, property of medium, nature of roots, substrate concentration, chelation of metals, pH, and temperature that influence the metal removal in various ways. However, some of important factors are described.

1. Selection of plant species. Selection of the plants species (genotype) plays an important role in the remediation of metal; hence, screening of plants would become an essential approach for the removal of heavy metal from the contaminated sites (Burken and Schnoor 1996; Prasad and De Oliveira Freitas 2003; Tangahu et al. 2011).
2. Properties of Medium. Agricultural practices are developed in order to enhance the remediation process through adjustment of pH, addition of certain metal chelators and bio-fertilizers (Prasad and De Oliveira Freitas 2003; Tangahu et al. 2011).

3. Rhizosphere (root zone). The root zone is of special importance in phytoremediation of pollutants. It possesses inherent potential to adsorb, absorb or accumulate the pollutants and metabolize inside the plant tissue. Degradation of pollutants in the soil occurs through plants by releasing certain catabolic enzymes exuded from the rhizosphere, and this is an important mechanism of phytoremediation process.

## 9.5 Conclusions

The uptake of heavy metals by plants is an emerging technology in contaminated environment. Phytoremediation offers various advantages over other commonly used conventional technologies. The most important factor is selection of a suitable plant species, which can be used to accumulate the pollutants at larger extent. In order to fully elucidate the influence of heavy metals on plants, there is need to investigate the molecular characterization of microorganisms and plants in response to pollutants. Better understanding of plant–microbe interactions is still needed in order to engineer more efficient plant–microbe consortia for removal of the pollutants.

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# Impacts of Soil Pollution on Human Health with Special Reference to Human Physiognomy and Physiology

# 10

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## Abstract

Soil fulfills a wide range of ecological services such as a platform toward biomass generation, a filter/buffer for water, main store of carbon, important source of nutrients in our foodstuff as well as medicines like antibiotics and so on. However, currently, soil pollution has become one of the alarming issues in most of the developed/developing countries that is mainly contributed by anthropogenic activities like mining, smelting, manufacturing, pesticides, herbicides, etc. The rapid urbanization as well as industrialization led to enormous release of pollutants that adversely affects the characteristics of soil. Further, the nutrient inequities of soil together with the pathogenic biotic community result in undesirable impacts on human health, including plants, wildlife, and animals. In this context, concepts like soil security could offer a solution by involving multidisciplinary approaches. The amalgamation of diverse scientific and nonscientific approaches could contribute significantly towards addressing issues between soil pollution and its effect on human health, including other living organisms. Overall, this chapter is an attempt to deliver elaborate and comprehensive information on interaction between urban soil pollution and human health issues.

## Keywords

Human health · Industrialization · Soil pollution · Urbanization · Xenobiotic

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## 10.1 Introduction

The weathering process of earth surface over the centuries has resulted in the formation of soil. Soil supports a wide range of life, from flora, fauna, to microscopic organisms. In current scenario, this important support system has been polluted with herbicides, pesticides, heavy metals, etc. which have devastating impacts on a wide range of living organisms, including health conditions, together with welfare of humans (Summers et al. 2012). Human health has been affected by soil pollutants that mainly resulted through anthropogenic activities (Rhind 2009). For instance, the soil contamination resulting in agro-lands, urban lands, lands used for extraction of oils/gases, coal mines, etc. is caused due to anthropogenic activities (Li et al. 2017). The individuals that are in direct interaction with soil (like workers in construction sites or mines, or farmers, etc.) are at severe risk of health issues as soil not only provides various nutrients for good health, but also may deliver harmful elements through the foodstuff that we eat (Chibuike and Obiora 2014). Overall, the introduction of harmful compounds into the soil causes soil pollution, which is an alarming signal for human health (Brevik 2013). Usually, the staple crops cultivated in polluted soil absorb the contaminants through vascular tissues that eventually enter the human system either through direct consumption of such crops or via the food chain (Fig. 10.1). The animals feeding on contaminated crops grown in polluted soil also negatively suffer. Soil pollutant can also infiltrate the groundwater reservoir making the drinking water unfit for consumption. The soil factors that affect human health typically involve the nature of the contaminant (severity of their toxicity), amount of contaminant in the soil, and susceptibility of the population consuming the contaminant. Few of these contaminants like herbicides, pesticides, heavy metals, etc., can be carcinogenic, while others can lead to congenital diseases, kidney malfunction, liver failure and respiratory/neurological complications. The notable relationship between soil and human health has been described in the book by Moses in 1400 BC. Further, Columella in 60 BCE remarked about unseen infections from swamplands. In each case, the concept was to indicate the significance of soil on human health. However, in 1900, the awareness about the soil interaction with humans and its impact started gaining momentum that ultimately led to worldwide acceptance for conservation of soil. It was found that the soil fertility regulates the nutrient content of staple crops, thus regulating the human health. In 1957, the United States Department of Agriculture reported that soil contamination could lead to a source of toxicity to human diet. Since then, enormous amount of literature has been gathered and cited in this particular context. To name a few, extensive work to link soil effects on human health was reported by (Voisin 1959), which was one of the novel works of that time. (Gebremedhin et al. 1990) reported about the soil pollutants and their degradation affecting soil productivity. Likewise, (Brevik and Sauer 2015) reported the effects of soil pollution on human health. With the advent of technology and recent developments in soil sciences, it has been revealed that soil contamination significantly influences human health, making it imperative for further investigation. Considering these, the present chapter provides an overview on the links between soil and its potential effects on human health.

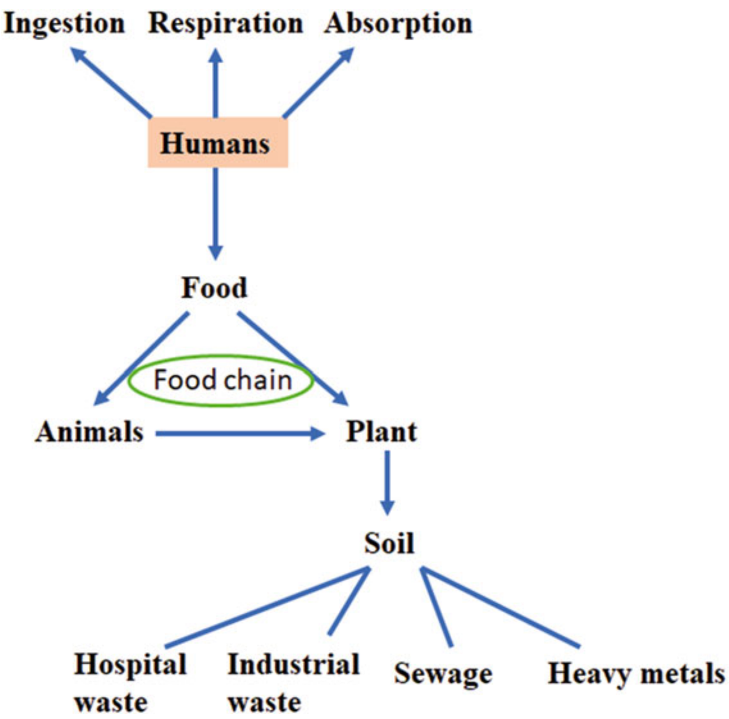

**Fig. 10.1** Schematic representation of soil pollution on humans

## 10.2 Route of Exposure of Human Beings to Soil

Human beings are exposed to the constituents of soil (Fig. 10.2) by means of three common ways.

### 10.2.1 Ingestion

It may be deliberate (geophagy), accidental (contaminated hand contact with mouth), or consumption of raw vegetable and fruits without proper cleansing and washing. However, a positive aspect of consuming soil may be a supply of nutrients (rare), but the negative aspects overcome this rare bliss. Generally, the consumption of soil tends to expose the human body to heavy metals, pathogenic bacteria, and harmful chemicals. This exposure eventually results in intestinal obstruction (Henry and Cring 2013).

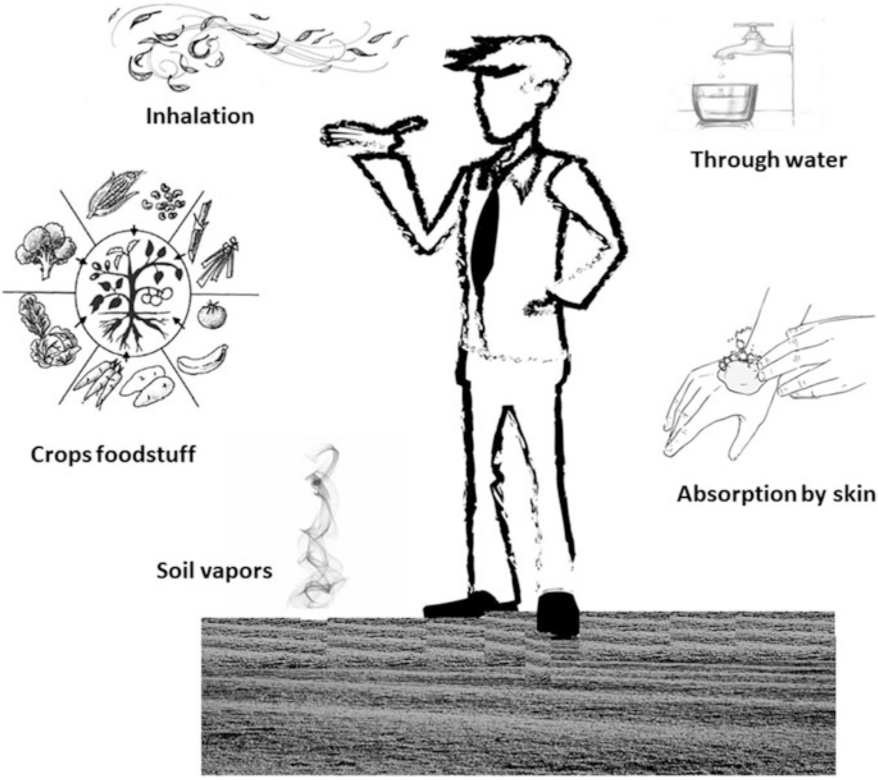

**Fig. 10.2** Route of soil pollution intake by humans

### 10.2.2 Respiration

As the name suggests, it occurs by inhaling contaminated soil. Over prolonged periods of inhalation of contaminated soil, symptoms of coccidioidomycosis (Bultman et al. 2013; Stockamp and Thompson 2016), mesothelioma (Buck et al. 2016), bronchitis, inflammation of bronchial passage, emphysema, etc., occur in humans.

### 10.2.3 Skin Absorption or Permeation

It exposes humans to pathogenic microbes and harmful chemicals (Brevik 2013). It can lead to podoconiosis (non-filarial elephantiasis common in farmers exposed to volcanic clay in the soil) (Deribe et al. 2013).

## 10.3 Modes of Soil Contamination

### 10.3.1 Soil Contamination by Heavy Metals

Growing population and their anthropogenic activities has led to several fold increase in soil pollution largely through heavy metal contamination. The contaminated soil with metals, when ingested or respired in non-optimal amounts, can be of great concern. Ingestion of higher concentrations of these metals by humans can result in toxicity. Moreover, the degree of exposure is another contributing factor in determining the level of toxicity by heavy metal contamination in soil. This could result in both morbidity and mortality. Heavy metals like mercury and lead are not required by humans as nutrients, but soil contaminated with these metals can pose serious health issues even if consumed in trace concentrations (Combs et al. 2005; Brevik and Burgess 2015). Few of the heavy metals and their probable effect on human health are listed.

#### 10.3.1.1 Lead

With the advent of industrial revolution in the eighteenth century, lead became the major contaminant worldwide through sources such as paints, Vinyl mini-blinds gasoline, mining, etc. Reports on mass lead poisoning in Senegal (Haefliger et al. 2009) by recycling of lead batteries and in Nigeria (Lo et al. 2012) by gold processing are few known examples. The ingestion or respiration of lead-contaminated soil caused severe lead poisoning, demonstrating the absolute need of awareness worldwide for soil pollution by heavy metals (Wu et al. 2015). Lead contributes to 0.6% of total world's disease. The adverse effect of lead is more pronounced on children and adolescents (Balabanova and Te 2017; Li et al. 2015). 15–20% children in USA suffer from lead toxicity because of lead-contaminated soil (Filippelli and Laidlaw 2010). Brain is most susceptible to lead contaminant. Lead can cause severe constipations, memory-based problems, headaches, sterility, tingling, behavioural issues and, in extreme case, coma and death.

#### 10.3.1.2 Arsenic

Similar to lead, arsenic is a major contaminant in developing world. It is majorly found in drinking water from deep tube wells (Ayotte et al. 2015) and in lumber imposing serious health hazard to adults and children (Gardner et al. 2013). Arsenic toxicity also occurs via irrigation of rice fields with arsenic-contaminated water. Rice being a major staple crop worldwide results in primary arsenic exposure (Zhao et al. 2010; Kidwai et al. 2018). It generally targets vital human organs like kidney, liver, lungs, and skin. Major health concerns due to arsenic include confusion, headaches, drowsiness, diarrhoea, convulsions, excess saliva, fingernail pigmentation, cramping muscles, limb sensation, digestion issues, nervous breakdown, blood while urination, etc. Excess exposure to arsenic can also cause shock, fits, coma, and even death.

#### 10.3.1.3 Mercury

Human activities such as gold mining, chlorine synthesis, coal burning, and dumping of compact fluorescent light bulbs contribute towards mercury contamination (Liang et al. 2015; Boerleider et al. 2017). Soil naturally contains mercury with a strong affinity for organic compounds. Microbes present in the soil methylate mercury eventually resulting in either uptake by plants or water contamination (Xu et al. 2015). Consuming sea food from methyl-mercury-contaminated water bodies and crops grown in methyl-mercury-contaminated soil are major routes for mercury hazard for human health. Hazardous effects of mercury on human health include anxiety, mood fluctuations, effects memory, depression, changes in mouth taste, vomiting, uncoordinated nervous system, respiration problems, difficulty in speaking or hearing, low IQ, delayed reflexes and in extreme exposure paralysis, stunted growth in infants, infertility, coronary heart disease, etc.

#### 10.3.1.4 Cadmium

Yet another destructive contaminant of soil is cadmium, largely contributed through industrialization, electroplating, and sewage wastes (Nordberg et al. 2015). Exceedingly high levels of cadmium in soil can concentrate in crops consumed by humans leading to toxic effects (Hunter 2008). Its availability in soil depends upon soil pH, soil aeration, and concentrations of other metals in the soil (Zhao et al. 2014). Cadmium toxicity in humans depends upon other nutrients such as Zinc and Iron (Brevik 2013; Morgan 2012). For example, a population in England was exposed to high levels of cadmium. However, due to large Zinc concentrations in the soil, the bioavailability of cadmium remained significantly low resulting in no health hazard (Chaney 2015). On the other hand, high cadmium levels with its corresponding high bioavailability in Japan led to the outbreak of itai-itai disease (Nordberg et al. 2015). Renal, cardiovascular, and respiratory disorders are generally associated with cadmium contamination.

### 10.3.2 Soil Contamination by Radioactive Substances

Radioactive elements pollute soil either by natural processes or by human activities. Radon is one such natural radioactive gas that accrues in underground basements (Appleton 2007). Since it is innate to the soil and causes lung cancer (Islami et al. 2015), adequate ventilation is necessary to decrease its accumulation (Khan and Gomes 2018). Apart from this, human activities discharge radionuclides in the soil, posing a great hazard to human health. This discharge can be accidental or deliberate. Radionuclides are secondary products from hospital wastes or nuclear activities resulting from testing, fallouts, power failures, and bombing (Hu et al. 2010). Fukushima Daiichi nuclear plant disaster in Japan and Chernobyl nuclear disaster in the Ukraine (former USSR) are two major accidental anthropogenic radioactive fallouts in environment, including soil, till date that have been a serious threat to human health and well-being (Chino et al. 2011; Brevik 2013). Direct exposure to radioactive substances results in onset of cancer and genetic mutations (Magill and

Galy 2004), while indirect exposure leads to nutrient imbalances in the soil (Brevik 2013).

### 10.3.3 Soil Contamination by Xenobiotic Chemicals

Artificially synthesized carbon-containing compounds are termed as xenobiotic chemicals. Since these are synthesized artificially, they are unnatural. They differ from their natural counterparts in terms of insertion of chlorine, fluorine, bromine, sulphur or nitrogen (Calabrese and Baldwin 1998; Kumar et al. 2015; Sharma et al. 2016; Singh et al. 2017; Salem et al. 2017; Singh et al. 2018; Singh et al. 2019). As xenobiotics are structurally different from their natural counterparts, microbes lack the presence of biotransformation pathways to metabolize these them (Sharma et al. 2016; Singh et al. 2020). This marks xenobiotic compounds resilient towards decomposition, and therefore they are highly toxic even in trace amounts. In rural areas, pesticides impose a severe threat and contribute towards soil pollution as they reach the soil. With green revolution, the application of pesticides increased worldwide, which eventually raised its percentage in soil as well. In urban areas, soil is polluted through discharges from hospitals, industries, waste incineration, mining, coal burning and other biowastes (Leake et al. 2009). Recently, pharmaceutical and cosmetic waste from hormonal treatment, antibiotics, and injections has increased several folds contributing towards soil pollution and imposing threat to human health (Albihn 2002; Aust et al. 2008; Crofts et al. 2017). Xenobiotics are often diluted forming mixtures in the uppermost layer of the soil. Some of the xenobiotics can also be referred to as persistent organic pollutants (POPs) because they have longer half-life periods. POPs are resistant to bio-decomposition and hence eventually accumulate in higher-order food chain. One classical example is DTT (1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane). DTT is known to adversely affect the hormonal balance in raptors making the eggshell fragile to sustain chicks (Vega et al. 2007). Other xenobiotics such as polycholorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and tricholoroethylene (TCE) also possess recalcitrant properties resulting in their bioaccumulation.

Major health hazards associated with xenobiotics include (i) physical - oedema, headache, drowsiness, multiple sclerosis, rheumatism, cardiac issues, and cancer (ii) psychological - autism, anxiety, laziness, difficulty in sleep, aggression, and mental disorders.

### 10.3.4 Elements in Soil as Basic Nutrients

There are 14 indispensable elements necessary for plant growth and development, which are often soil-derived. These nutrients are also crucial for human health (Combs et al. 2005). Humans obtain these nutrients (macronutrients and micronutrients) through plant or animal food consumption. To sustain human health, these macro- and micronutrients are indispensable (Combs et al. 2005). Therefore, plants grown in soil with adequate nutrients are important for human health as they are either directly consumed by humans or indirectly eaten by animals, which, in turn, are food for humans. Some of the important nutrients in view of human health are as follows.

#### 10.3.4.1 Iron

Iron is an important component of haemoglobin, which binds and releases oxygen in human body. Its deficiency is known to cause anaemia. A large population of the world is anaemic, especially women. Plants grown in soil with less iron concentrations will produce edibles with deficient iron content. In alkaline soils, plant roots are unable to absorb iron. When such plants are consumed by humans, they will consequently have lesser iron (Combs et al. 2005). Less iron will cause paleness, excessive fatigue, dizziness, shortness of breath, dry skin and hair, heart palpitations, soreness of tongue, brittle nails, etc.

#### 10.3.4.2 Iodine

Iodine deficiency, due to iodine-deficit-soil-cultivated plants consumed by humans, largely affects brain tissues. Paucities are prevalent in regions where soil is incapable to supply optimum iodine to crops. This is common in high-altitude regions of the world (Combs et al. 2005). It is more hazardous where a large population is vegetarian. Substantial efforts have been made through “Universal Salt Iodization” to combat iodine deficiency. Health hazards due to iodine scarcity include goitre, late physical growth, hypothyroidism, miscarriage, and stillbirth.

#### 10.3.4.3 Selenium

Selenium plays role in immunity and thyroid functioning (Fairweather-Tait et al. 2011). Its concentration varies from region to region depending upon geological, climatic and polluting factors. Thus, the bioavailability of selenium in staple crops also differs substantially (Haug et al. 2007). Humans consuming non-optimal selenium concentrations are at higher peril for cardiac diseases, tumour formation, compromised immune system, brittle nails, dull hair, nervous issues, kidney damage, lung failure, etc.

#### 10.3.4.4 Zinc

50% of the total world’s soil is deficit of zinc. Calcareous and highly acidic soils are reported to be in maximum deficit in adequate zinc content (Abrahams 2002; Combs et al. 2005). Zinc acts an imperative component in many enzymes and co-enzymes. Its deficiency due to polluted soil grown plants can be a serious threat to human populations. It affects differentiating tissues, immunity and gastrointestinal tract, prevents healing of wounds, stunted growth, bad mouth taste, etc.

#### 10.3.4.5 Magnesium

Similar to zinc, magnesium is also an integral part of enzymes and co-enzymes. Soil containing inadequate contents of magnesium due to contamination and/or pollution can be a potential hazard to human health and well-being. This is common in acidic, sandy and older soils of the tropical regions of the world. Its paucity leads to decrease in crop yield and quality, and makes the crops susceptible to microbial attack. Magnesium deficiency or hypomagnesemia leads to muscle twitches, osteoporosis, hypertension, asthma, cardiac problems, mental instability, etc.

#### 10.3.4.6 Calcium

Lower calcium levels are observed in soil, which are acidic, sandy or coarse. Deprived soil moisture due to pollution and excessive use of fertilizers also cause calcium scarcity in the soil. High levels of contaminants in polluted soil convert available calcium into insoluble forms, which is futile for the plant. Consumption of such nutrient-deprived plants by humans affects their health adversely, for example, calcium deficiency in humans is related to fatigue, fragile teeth, brittle bones, osteoporosis, anxiety, cramps, stiffness, etc.

### 10.3.5 Microbial Growth Due to Soil Pollution and its Impact on Human Health

Soil serves as habitat for a wide spectrum of macro- and microorganisms. Discharge of pharmaceutical, medical, industrial, sewage and household wastes in soil results in growth of various deadly microbes eventually leading to outbreak of human diseases. Most of these organisms are harmless for humans; however, few of them impose severe threat to humanity depending upon the climate, susceptibility of the population, soil condition and medical aid. One such disease is Coccidioidomycosis (Valley Fever) caused by the fungus *Coccidioides* spp. The microscopic spores of the fungus present in the soil generally enter the human body via inhalation (Stockamp and Thompson 2016). The fungus multiplies and develops in saline and highly alkaline soils. *Coccidioides* reproduce and grow inside and on the upper surface of the soil. Aerosolization (mixing of the spores in the air) of the fungal spores either naturally by storms, earthquake, strong winds or anthropogenically by construction, irrigation, etc., exposes humans to this fungus. Epidemic usually breaks after torrential downpours followed by a period of drought and dry winds.

The microbial community flourishing in the soil can impact human health directly or indirectly by facilitating antibiotic resistance or itself generating antibiotics. Resistance towards antibiotic occurs when the antibiotic fails to stop bacterial growth, thus making the bacteria impervious to that particular antibiotic. Antibiotic-resistant bacteria have gained a significant attention worldwide because of the threat they impose to mankind (Tanwir and Khiyani 2011; Khan and Khan 2016). Antibiotic resistance develops because, firstly, the antibiotics are over-prescribed/non-prescribed; secondly, the patient ceases the complete course of antibiotic before the infection is cured completely. Extensive literature is available on the relationship between soil and antibiotic resistance (Adegoke et al. 2017; Nesme and Simonet 2015). Soil provides an environmental niche for development and propagation of genes coding for antibiotic resistance (Vaz-Moreira et al. 2014). Soil often supports interchange of genetic material by which antibiotic resistance in bacteria develops (Forsberg et al. 2012; Woolhouse and Ward 2013). Diverse gene pools present in the soil confer antibiotic resistance (Nesme et al. 2014). Use of fertilizer, pesticides, insecticides considerably expands the pool of antibiotic-resistant genes and species with the soil (Popowska et al. 2012; Adegoke et al. 2016). It is still decisive that this gene pool possesses direct threat to human health (Forsberg et al. 2012; Pepper 2013; Udikovic-Kolic et al. 2014). However, sharp increase in antimicrobial tolerance is indicative of the fact that it does threaten human health to some extent. Nonetheless, this increase in bacterial tolerance has paved the way for discovery of new and more potent antibiotics. On the other hand, soil also provides a medium for natural antibiotics. Under extreme climatic conditions, soil also experiences stress and seldom produces antibiotic-like substances (Swiecilo and Zych-Wezyk 2013). The bacterial population naturally present in the soil produces compounds that hinder the survival of other bacteria and actinomycetes. Teixobactin is one such recently discovered antibiotic (Ling et al. 2015).

## 10.4 Probable Solutions to Prevent Soil Pollution

With the advancement in medical science, most of the stated health conditions arising from nutrient deficiency or toxin intake can be treated medically. However, taking into account “prevention is better than cure,” the key causes for these medical conditions should be focused and addressed. Soil pollution accounting from various natural and anthropogenic activities should be monitored and controlled to reduce its disastrous impact on human health. It is less expensive to prevent soil pollution than to manage it. Hence, new soil should be protected for soil pollution. The practice of “three R,” namely, “reduce, recycle and reuse” has recently gained momentum throughout the world to combat soil pollution. The reduction in usage of chemical-based pesticides, herbicides and fertilizers in agricultural practices can also be useful in combating soil pollution. Educating people and spreading awareness for the use of biodegradable products can also reduce soil pollution to several folds. To restore and maintain soil fertility the use of bio-fertilizers should be prompted by government agencies to the farmers. Providing bio-fertilizers for their chemical counterparts at a competitive price can encourage farmers to use them. The microbes present in these fertilizers will contribute towards soil fertility. Similarly, the usage of bio-pesticide and bio-herbicides on a large scale in rural areas can manage soil quality. These products definitely take a bit longer time to deliver the desired results, but to not impose a threat to the soil quality and fertility. Substituting chemical pesticides and fertilizers with manure can also help in maintaining soil integrity. Recycling wastes, especially household trash, can contribute to declining soil pollution due to landfills. Reusable materials should be made popular amongst masses to minimize the usage of plastic. Plastic disintegrates at a very slow rate or does not at all disintegrate, thus disturbing the soil harmony. In a similar vein, the use of paper should also be monitored strategically. Treating industrial waste to reduce or destroy its toxicity before disposal is necessary to eliminate soil pollution and, thus its devastating effects on human health. Responsible methods should be undertaken to dispose of the waste so that no soil contamination occurs. Consumption of organic food can help reduce the risk of deficiency of various vital elements, thus improving human health. Dumping grounds should be far from residential areas so that contaminated soil is not inhaled or ingested by humans. Moreover, several creatures thrive well underneath the soil. Disrupting their habitat could expose them to the danger to extension. Few of these organisms, microorganisms are pivotal to human health. For example, nitrogen-fixing bacteria maintain soil fertility, plant growth and yield, thus affecting human well-being. Sensible efforts should be made not to disturb this beneficial harmony. Further, to curb the disaster of soil pollution, rapid and efficient deforestation procedures have to be undertaken. The effect of soil erosion by strong winds and heavy rainfall multiplies when there no trees to impede the top layer of soil. Efforts should also be made religiously to circumvent over-cropping and grazing, since it leads to floods and soil erosion, thus relapsing the soil integrity.

## 10.5 Conclusion

Soil is a heterogeneous mixture that is strongly managed by natural and human activities. The anthropogenic activities accounting for heterogeneity of the soil discharge plethora of contaminants, which negatively impacts human health. Animals grazing on plants grown in polluted soil also accumulate these contaminants. As a part of food chain, humans feeding on these animals accrue toxins, which adversely affect their health. Combustion of petrol, usage of lead paints, industrialization, hospital and sewage wastes account for the major reasons of soil contamination and pollution. Although soil pollution has been controlled to some extent in developed countries, it still seems to be a life-threatening issue in developing world. Urbanization is yet another major factor contributing to soil pollution. The risk of soil-borne diseases increases proportionally with large populations shifting towards urbanization. With advancing compromise of human health due to soil pollution, enormous social, economic and political efforts are being made throughout the world by various organizations to improve soil quality. More interdisciplinary and transdisciplinary research and awareness in the coming years is necessary to fully comprehend the effect of polluted soil on human health. Political organizations should come forward to offer funding for carrying research to mitigate soil pollution. Moreover, general public should be educated and made aware of the health hazards they would face if they continue to pollute soil. People should also be made conscious towards the effort they should make to reduce soil pollution on a daily basis.

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# Impact of Herbicide Use on Soil Microorganisms

# 11

M. K. Singh, N. K. Singh, and S. P. Singh

## Abstract

Globally, weeds are a major threat for agriculture production from time immemorial. Discovery of 2,4-D herbicide in the 1940s revolutionized the modern-day agriculture. Since then, nearly 2000 herbicide molecules have been discovered and are used worldwide for the management of weeds in different arable crops. Economic viability coupled with easy application makes it one of the most widely preferred tools for weed management in modern-day agriculture. Herbicide contributes 16% of the global pesticide industry, and in recent years, consumption of herbicide increased many folds due to increased cost of agricultural labour. Researches showed that a number of herbicides have an impact on soil microorganisms. In this chapter, an attempt has been made to document the effect of widely used herbicides on soil microorganisms, especially on mycorrhiza, bacteria and actinomycetes. A number of herbicides showed reduced population of these soil microorganisms with transient inhibition up to 7–10 days. Contrary to that, some herbicides have no effect on microbial population and even increase their population. To overcome the limitation of studies and to generalize the effect of herbicides on soil microorganisms, these studies preferably involves long-term impact assessment having a number of herbicides and variable soil environment.

## Keywords

Pesticide status · Mycorrhiza · Bacteria · Actinomycetes · Limitations

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## 11.1 Introduction

Weeds are one of the major threats to the agriculture for ages. Globally, a number of chemicals are tested and used for weed management from time immemorial. However, the major shift in the use of agricultural chemicals was observed after World War II. Now the chemists and agronomists are overly optimistic about the use of agricultural chemicals in solving the pest problems (Trappe et al. 1984). The introduction of 2,4-Dichlorophenoxyacetic acid (2,4-D) in the 1940s totally revolutionized the agriculture and started the era of chemical weed control (Choudhury et al. 2016). Up till 2016, more than 2000 herbicides belonging to 15 different modes of action were introduced in the global market (Choudhury et al. 2016). Economic viability and easy application make it one of the most common tools for the weed management in modern-day agriculture. Intensity of utilization was further increased with adoption of conservation agriculture practices and herbicide-resistant genetically modified crops.

In fact, use of herbicide increases the profitability of the farm but at the expense of ecosystem functions. It is now apparent that use of these herbicides not only has unforeseen impact on the environment but also severely impacts our soil microflora (Trappe et al. 1984). Of late, Pimentel (1995) raises the concern that only small fractions of pesticide reach to the target organisms, leading to potential impact in soil and water and ultimately affecting the human, crop and animal health. Although it is true that use of pesticide increases the crop production but at the same time it acts as a double-edged weapon, because since the onset of Green Revolution, nearly 800,000 people in the developing countries have died due to pesticides (Devi et al. 2017). Furthermore, nearly, 20,000 people in the developing countries die every year due to pesticide consumption through food (Bhardwaj and Sharma 2013).

Nowadays, the impacts of herbicide use on soil microorganisms are being questioned and at the same time the comprehensive review on this topic is lacking. Keeping these facts, in the current chapter, we review the effect of commonly used herbicides on the soil microorganism.

## 11.2 Pesticide National and International Status

The use of chemical pesticides is an integral component of crop production in many regions of the world. It is important to note that herbicide constitutes nearly 60% of the total pesticide consumed worldwide (Sondhia et al. 2019). However, in India, the pesticide industry is dominated by insecticide (nearly 65%) followed by herbicide (16%), fungicide (15%) and other (4%) (Subash et al. 2017). In the last 10 years, herbicide consumption increased up to 25% of the total pesticide consumption (Sondhia 2019).

Presently, in India, 68 herbicides are registered for broad-spectrum weed management in various arable crops (Sondhia 2019). In India, the more common herbicide application is in wheat crop (44%), followed by rice (31%), plantation crops (10%), soybean (4%) and other crops (11%) (Sondhia 2019). Trends showed that from 2009 onwards there was a significant increase in the pesticide consumption, on both total and per hectare consumption. It is important to note the increase in pesticide consumption in recent years has been attributed to the increased consumption of herbicides because of labour scarcity in most regions and higher cost of crop production. In fact, amongst the pesticide production, the share of insecticide declines from 70% in 2003–2004 to 39% in 2016–2017 (Subash et al. 2017). Furthermore, the major herbicide products imported to India are glyphosate and atrazine, which was mainly imported from China (Subash et al. 2017). The top three importers of herbicides in India are China, Israel and Japan. Further, in the recent year, India exports the largest quantity of herbicides to Brazil (20,457.02 tonnes) and USA (6095.06 tonnes). It is noteworthy that India stands at the fourth position in the global supplier of agrochemicals, next only to the USA, Japan and China. India produces 68,490 tonnes of pesticide in 2011–2012 with the total value of Rs 8000 crore, of which worth Rs 6000 crore of pesticide consumed in domestic use. The pesticide market in India is expected to grow at the rate of 12–13% per annum (domestic growth 8–9% per annum and export 15–16% per annum) (Devi et al. 2017). Furthermore, it is important to note that in India although there was severe crop loss due to pest infestation, the intensity of pesticide consumption is lowest in the world (291.2 g/ha). Among the leading consumer of the pesticide in the world are China (14 kg/ha), Japan (11 kg/ha) and the USA (4.5 kg/ha), whereas the world average is 3.0 kg/ha.

## 11.3 Effect of Herbicides on Soil Microorganisms

In today’s world, microbial population in soil is the index of agricultural prosperity. Soil microorganisms are an important link between the soil–plant–herbicide–fauna–man relationships as they play a very vital role in the degradation of herbicides (Raj and Syriac 2017). In both the quantitative and qualitative terms, application of herbicides leads to significant change in soil microbial population (Saeki and Toyota 2004; Raj and Syriac 2017) (Table 11.1).

An ideal pesticide, including herbicide, must possess the ability to act on the target pest as well as detoxify into non-toxic substances as quickly as possible (Stanley et al. 2013). During the initial stage of herbicide application can lead to quantitative and qualitative changes in the soil microbial growth (either stimulating or depressive) and their enzymatic activities, depending on the phytotoxic nature of the herbicide (type and concentration), microbial species and environmental conditions (Latha and Gopal 2010; Zain et al. 2013a; Maheswari and Ramesh 2019). Further, these non-target effects on soil microorganisms may reduce the performance of critical soil functions include organic matter (OM) degradation, the nitrogen cycle and methane oxidation (Sebiomo et al. 2011). It is very important to note that many a time, application of herbicides, in general, reduces the microbial population, including bacteria, fungi, actinomycetes and protozoa, thereby upsetting the soil ecological balance between the plant pathogenic and beneficial organisms,

**Table 11.1** Effect of commonly used herbicides on the soil microorganisms

| Herbicide | Concentration | Effect on soil microbes | References |
|---|---|---|---|
| Atrazine | 3.4 kg/ha | Transient inhibition of bacterial growth during first WAA, repeated applications have no effect on viable bacteria or fungi population | Cole (1976) |
| Acetochlor | 1.25, 1.50, 2.50, 3.125 and 5.0 L/ha | Bacterial population adversely affected followed by (fb) fungi fb actinomycetes. At crop harvest, microbial population almost equal in all treatment or even more than original level in few treatments | Tyagi et al. (2018) |
| Oxyfluorfen | 850 mL/ha | Soil application cause transient reduction in microbial population | Adhikary et al. (2014) |
| Propaquizafop | 750 mL/ha | | |
| Pendimethalin | 3300 mL/ha | | |
| Atrazine | 100 μg/L | Application caused complete disappearance of cyanobacteria | Herman et al. (1986) |
| Paraquat | 4 μM | Inhibited the growth of *Nitrobacter agilis* (nitrite oxidizer), did not affect growth of *Nitrosomonas europaea* (ammonium oxidizer) | Tateo (1983) |
| Alachlor | 2.5 L/ha, kg/ha | Stimulated the fungal and azotobacter population | Bopaiah and Rai (1979) |
| Simazine | 4.0 L/ha | Stimulated the fungal and azotobacter population | |
| Propinol | 3.5 L/ha | Reduced bacterial population | |
| Nitrofen | 4.0 L/ha | Reduced bacterial population but stimulation in the azotobacter population | |
| 2,4-D-ethylester | 0.75 kg/ha | Reduced population of total heterotrophic bacteria | Latha and Gopal (2010) |
| Butachlor | 1.0 kg/ha | Reduced population of total heterotrophic bacteria | |
| Pretilachlor | 0.30 kg/ha | No differences in fungal population at different intervals | |
| Pyrazosulfuron ethyl | 25 g/ha | Reduced population of total heterotrophic bacteria but no differences in fungal population at different interval | |
| Imazethapyr | 90 g/ha | Stimulated growth of bacteria and actinomycetes; inhibited growth of fungi | Sawicka et al. (1996) |
| Linuron | 850 g/ha | Stimulated growth of bacteria and actinomycetes; inhibited growth of fungi | |
| Glufosinate-ammonium | 1, 10 and 100 ppm | Both stimulating and inhibitory effects on microbial populations depending on concentration of the herbicide and the period of incubation | Pampulha et al. (2007) |

(continued)

**Table 11.1** (continued)

| Herbicide | Concentration | Effect on soil microbes | References |
|---|---|---|---|
| Nicosulfuron | 0.3, 1.5, 3.0 and 15.0 mg/kg | Reduced population of actinomycetes in soil and in vitro at highest concentrations of herbicides (10× and 50×) | Šantrić et al. (2016) |
| Metribuzin | 12.0, 60.0, 120.0 and 600 mg/kg | | |
| Atrazine | 750 kg/ha | Long-term application altered soil community structure, particularly methanotrophic bacteria | Seghers et al. (2003) |
| Metolachlor | 2000 kg/ha | | |

thus the disease causing organisms to become a problem (Kalia and Gupta 2004). In fact, change in the soil microflora has been listed as one of the possible causes of the decline in productivity in rice cropping systems (Reichardt et al. 1998).

### 11.3.1 Effect on Mycorrhiza

Mycorrhiza is a mutualistic symbiotic relationship between plants and fungi, located in roots and root-like organs, which act as a bridge for the flow of energy between plant and soils (Traquair 2002; Naher et al. 2013). Of the seven types of mycorrhizae described (arbuscular, ecto, ectendo-, arbutoid, monotropoid, ericoid and orchidaceous mycorrhizae), arbuscular mycorrhizae and ectomycorrhizae are the most abundant and widespread (Siddiqui and Pichtel 2008). Globally, arbuscular mycorrhizal fungi (AMF) formed mutualistic association with more than 80% vascular plant species in the ecosystem (Huang et al. 2009). AMF form mutualistic relationship, where the plant supplying sugar to obligate biotrophic fungus and fungus supplies organic mineral nutrition to plants, particularly immobile nutrients such as phosphorus and zinc (Singh and Singh 2019). In general, forest species are completely dependent on the symbiotic association with ectomycorrhizae for the mobilization of minerals to the plant. These ectomycorrhizae have limited capability to degrade and utilize the complex carbohydrate from the organic detritus. Thus, they rely on the tree for the supply of nutrients (Siddiqui and Pichtel 2008).

To study the effect of herbicides on ectomycorrhizal formation in three conifer species (*Pinus ponderosa*, *Pseudosuga menziesii* and *Abies concolor*), three herbicides applied at recommended rates and double the recommended rates, i.e. sulfometuron and triclopyr at 4.5 and 9.0 kg a.i./ha and imazapyr 1.1 and 2.1 kg a.i./ha. Irrespective of all the herbicide treatments, ectomycorrhizae were observed on 91% of the root tips and hardly, 7 out of 69 treatment combination showed significant reduction in ectomycorrhizae. One of the reasons for the less effect of these herbicides on mycorrhizal growth might be due to acidic nature of experimental soil and weak acidic nature of herbicides; herbicide molecules are weakly adsorbed on clay micelle and remain active in the soil solution, until degraded or leached (Busse et al. 2004).

In forest nursery of *Pinus sylvestris* and *P. nigra*, application of simazine at recommended rates did not inhibit the growth of ectomycorrhizae and even under some conditions it will enhance the growth of the mycorrhizae (Smith and Ferry

1979). Similarly, application of simazine at the rate of 500–1250 mg/m$^2$ applied annually did not negatively impact mycorrhizal growth on coniferous seedlings (Uhlig 1966). Later on, it was hypothesized that simazine-induced release of sugar and amino acids from roots would lead to an increase in mycorrhizal growth (Schwab et al. 1982). Furthermore, application of bifenox (3.4 and 6.7 kg a.i./ha), DCPA (11.80 and 23.50 kg a.i./ha) and napropamide (3.4 and 6.7 kg a.i./ha) also showed no significant reduction in ectomycrorrhizal growth (Harvey et al. 1985).

A study was conducted to evaluate the effect of differential concentration of prometryn and acetochlor, i.e. 0.1, 1.0 and 10 mg/L, on dual monoxenic culture of *Glomus etunicatum* with Ri T-DNA carrot hairy roots. Both the herbicides negatively affect the AM fungi as well as symbiosis at the higher concentration; in fact, prometryn was apparently more toxic as compared to acetochlor. Furthermore, the spore formation was not affected with the application of irrespective concentrations of acetochlor; however, a significant decrease was noted with higher concentration of prometryn (Li et al. 2013). In pot culture experiment, atrazine added in soil at a concentration of 0.0, 0.5, 2.0 and 5.0 mg/kg soil; interestingly mycorrhizal root colonization decreased with a concentration from 0.0 to 2.0 mg/kg but was increased at a concentration of 5.0 mg/kg. It was hypothesized that enhanced mycorrhizal colonization at higher concentration might be due to the development of tolerance to the pollutant by the fungus (Huang et al. 2007). Moreover, mycorrhizal growth played a significant role in degradation of atrazine applied in maize (Huang et al. 2009).

Later on, application of fluazifop-*p*-butyl [187.5 g a.i./ha] and fomesafen [250 g a. i./ha] in *Phaseolus vulgaris* affected the mycorrhizal colonization under conventional-till system at 12 days after application (DAA), whereas no such effects observed in no-till system (Santos et al. 2006). Trappe et al. (1984) and Paula Jr and Zambolim (1994) were also in opinion that application of herbicide affects the mycorrhizal growth.

In pot culture experiment, repeated extreme exposure of nicosulfuron (×0, ×10, ×100, ×1000 the recommended dose) significantly reduced the mycorrhizal colonization and AMF richness. It was hypothesized that limiting establishment of AMF could be the result of either direct toxicity of herbicide on the AMF growth and colonization or indirect effect of maize plant to detoxify the herbicide (Karpouzas et al. 2014). However, Trappe et al. (1984) were in opinion that herbicide possibly alters the metabolism of plants, reduced the photosynthate production, thereby limiting the establishment of AM symbiosis. However, under the field condition, application of nicosulfuron even at the ×5 level did not significantly change the colonization ability or community structure of AMF (Karpouzas et al. 2014); contrary to this, application of paraquat at the recommended rates (Ramos-Zappata et al. 2012) or chlorsulfuron and glyphosate at higher than recommended rates (Mujica et al. 1999) significantly inhibited the mycorrhizal colonization. Sheng et al. (2012) observed almost similar AMF richness under glyphosate-treated and glyphosate-free plot. Furthermore, there was no significant effect on the rate of colonization in pea roots or wheat roots under both glyphosate-treated and glyphosate-free plots.

## 11.3.2 Effect on Bacteria

Bacteria are minute size (0.5–1.0 μm in diameter and 1.0–10.0 μm in length); unicellular organisms are the most abundant among the soil microflora. Most of the bacteria are adsorbed on the clay particles and humus component present in soil and their number varies with the type of soil, climatic condition and other environmental factors (Biswas and Mukherjee 1987). Reviews written in the early 1960s by Audus (1964), Bollen (1961), Fletcher (1960, 1961), and Smith and Fletcher (1964) were in opinion that most of the herbicides applied at recommended field rates did not bring significant change in soil microbial populations. However, repeated application of 2,4-D (4.48 kg/ha for five times/annum) and trifularin (1.12 kg/ha, once in a year) over a 5-year period resulted in significant reduction in bacterial population in the soil (Breazeale and Camper 1970). Similarly, in aqueous culture of nitrifying bacteria, low rate of application of paraquat (1 μg/mL) leads to complete inhibition of ammonium and nitrite oxidation up to 40 days. However, atrazine (1 and 2 μg/mL) leads to transient inhibition of ammonium oxidizing activity for short period, which can be resumed after 16–18 days, whereas the rate of nitrite oxidation was increased at 1 μg/mL (Gadkari 1988). However, in soil culture even at higher concentration, paraquat (100 μg/mL) showed no influence of nitrification; this might be due to the fact that paraquat is strongly adsorbed on the negatively charged clay particles; thus, it may not be accessible to micro-organisms for interaction (Mathur et al. 1976). However, later studies showed that application of paraquat and atrazine at recommended and half-the-recommended rate significantly reduced the bacterial population, diversity and distribution (Stanley et al. 2013). Sebiomo et al. (2011) also noticed that up to 20th day of soil application of atrazine, paraquat, glyphosate and ready-mix atrazine + metolachlor reduced the bacterial population. Even soil application of 2,4-D Ethyl Ester (EE), butachlor, pretilachlor and pyrazosulfuron ethyl at differential rates showed reduction in bacterial population and the highest reduction was observed with butachlor. Further, the decline in bacterial population was enhanced with an increased concentration of herbicide (Latha and Gopal 2010).

Contrary to these experiments, long-term application (9 years) of atrazine (3.4 kg/ha) in maize crop showed transient inhibition during the first week of application and thereafter showed no effect on viable bacteria, as well as relative abundance of bacteria producing hydrolytic enzyme and soil enzyme level (Cole 1976). Later on, Seghers et al. (2003) observed that long-term application of atrazine and metolachlor brought changes in soil community structure; however, these changes did not decrease community function; this might be due to total abundance of methanotrophs in soil was preserved. Similarly, application of pendimethalin, oxyfluorfen and propaquizafop at recommended rates in chilli crop inhibited the soil microbial populations up to 15 DAA; thereafter, treated plots exhibited a significant increase as compared to control. Maximum inhibition was noticed in oxyflourfen followed by pendimethalin and propaquizafop (Adhikary et al. 2014).

Furthermore, interestingly, it was observed that application of ioxynil, dalapon, mecoprop, MCPA + dichlorprop and amitrole at normal and tenfold rates increased the population of bacteria after the 2 and 4 weeks after application (WAA) as compared to the control; however, these stimulatory effects are not observed after 20 WAA. However, these herbicides at recommended rates specifically reduced the population of *Azotobacter chroococcum* at 2 and 4 WAA (van Schreven et al. 1970). A similar stimulatory effect was noted with repeated application of dalapon at much higher rates than recommended (Magee 1958). Imazethapyr and linuron applied in soil under legume crops increased the bacteria count by utilizing these herbicides as an additional source of food.

Glyphosate is one of the widely used non-selective herbicides. Earlier studies showed that its application would lead to a temporary increase in bacterial population and overall microbial activity (Wardle and Parkinson 1990a, b). However, later studies confirmed slight reduction in bacterial population (Araújo et al. 2003; Sebiomo et al. 2011).

Studies conducted by Ahmad and Malloch (1995) noticed that the application of phosphinotricin, an active ingredient of glufosinate-ammonium considered as a microbial toxin, significantly decreases the bacterial population. However, later studies conducted for three consecutive years found only 5% of the 300 species of bacteria are sensitive to this herbicide (Bartsch and Tebbe 1989). Moreover, up to 40 days, transient enhancement in bacterial population was noticed at different concentrations (1, 10 and 100 ppm), where the maximum increment noticed with an increase in concentration (Pampulha et al. 2007).

### 11.3.3 Effect on Actinomycetes

Actinomycetes were having the characteristics transitional between bacteria and fungi and are often referred to as fungi-like bacteria that constitute a major group of soil microorganism (Biswas and Mukherjee 1987). Repeated soil application of 2,4-D and trifluralin over the year showed that application of trifluralin increased the actinomycetes population by 89% over the control; however, no significant difference observed in actinomycetes population with the application of 2,4-D (Breazeale and Camper 1970), propinol, alachlor and simazine (Bopaiah and Rai 1979) as compared to the control plots.

Application of the most prominent herbicides in paddy, such as 2,4-D (EE), butachlor, pretilachlor and pyrazosulfuron ethyl revealed that butachlor recorded significantly lower population of actinomycetes as compared to pyrazasulfuron ethyl, pretilachlor and 2,4-D (EE). In fact, the transient inhibition was noticed for 7 days, whereas maximum population was observed at 30 days (Latha and Gopal 2010). Previous experiments also showed a significant reduction in actinomycetes population at variable concentrations (5.5–22.0 μg/g dried soil) of butachlor (Min et al. 2001) and no effect of 2,4-D(EE) on actinomycetes after 40 days (Deshmukh and Srikhande 1974).

Earlier studies revealed that repeated application of glyphosate over the year resulted in reduced population of actinomycetes (Araújo et al. 2003). However, later laboratory study on impact assessment of nicosulfuron, metribuzin and glyphosate applied at four rates, i.e. 1× (recommended), 5×, 10× and 50× revealed that application of herbicide caused transient inhibitory effect on actinomycetes in soil. Furthermore, the 10× and 50× of herbicides caused a significant inhibition of the number of actinomycetes in soil and growth of the isolates in vitro. Glyphosate caused highest inhibitory effect and the results were more pronounced at higher concentration (Šantrić et al. 2016). Similar transient inhibition of actinomycetes population was noticed for 7-DAA of metribuzin (Mohiuddin and Mohammed 2013; Lone et al. 2014) and 15-DAA of pendimethalin, oxyfluorfen and propaquizafop (Adhikary et al. 2014). Application of glyphosate also reduced the actinomycetes population on seventh day, whereas the highest population was noticed on 28th day of treatment (Baboo et al. 2013). Similar reduction in actinomycetes population in soil was recorded with the application of atrazine, atrazine + metolachlor, paraquat, glyphosate (Sebiomo et al. 2011), glufosinate-ammonium (Pampulha et al. 2007) and nitrofen (Bopaiah and Rai 1979).

It is important to note that the inhibitory effect of herbicides on actinomycetes was more under direct exposure (in vitro) than their growth in soil treatment (Zain et al. 2013b). Furthermore, the microbes using the herbicide as a source of carbon might be the reason for increased population after second to sixth WAA (Sebiomo et al. 2011).

## 11.4 Effect of Herbicide on Soil Functions

Application of herbicides affects not only the target organisms but also the soil microorganism. These non-target impacts on soil microorganisms many a time adversely affect the performance of important soil functions. One of the probable side effects of herbicides usage involves disturbance in soil biochemical process occurring in the soil. In fact, many a time, these herbicides hamper the rate of biochemical processes, interfering with the soil enzymatic activity and microbial growth (Maheswari and Ramesh 2019). Soil microbial population plays a significant role in the cycling of nitrogen, sulphur, and phosphorus, and the decomposition of organic residues (Nielsen and Winding 2002). Any alterations in the soil microorganism population or its activity disturb the biological equilibrium in the soil, which may adversely affect the soil fertility.

The soil application of herbicides is toxic to the microbial population, which in turn resulted in reduced microbial biomass, soil heterotrophic respiration and activity of OM decomposing and nutrient-cycling microbes (Rose et al. 2016). In contrast, many a time, it was noticed that the microbial populations and enzyme activities are recovered after initial transient inhibition; this might be due to the fact that the microbe gets adapted to these herbicides or due to their degradation. Simultaneously, where the plants die following herbicide application, the plant debris provides an increased supply of nutrients resource to support microbial growth and activity (Latha and Gopal 2010; Vandana et al. 2012; Sondhia et al. 2013; Maheswari and Ramesh 2019). The increment in soil dehydrogenase (DH) activity in herbicide applied soil after 7th day to 28th day could be attributed to an increase in microbial community having capabilities of utilizing the herbicides as carbon (C) source

(Vandana et al. 2012), whereas the activity of protease depends on the distribution of proteolytic bacteria (Subrahmanyam et al. 2011).

Application of glyphosate at recommended rate did not significantly affect the respiration (Rose et al. 2016), contrary to that; application of pretilachlor enhances the respiration activity as well as biomass (Kumar et al. 2012). The conventional rates of application of alachlor, metolachlor, and butachlor did not affect soil dehydrogenase activity (Dzantor and Felsot 1991; Subhani et al. 2002). Even the application of butachlor (from 5 to 100 mg/kg) significantly reduced the methane production in alluvial rich soil (Mohanty et al. 2004).

Furthermore, application of sulfonylurea herbicides at the recommended rates did not have a significant effect on respiration (Rose et al. 2016). Application of herbicidal mixture of nicosulfuron, atrazine, and dimethenamide did not significantly change the soil methane oxidation rate or the abundance of methane oxidizers (Seghers et al. 2005). Application of imazaquin (0.14 kg/ha) in field-grown soybean had no effect on soil microbial biomass, soil DH, or hydrolase activity (Seifert et al. 2001). However, application of imazethapyr (0.05 kg/ha) decreased the DH activity and increased hydrolyase, protease and catalase activity (Perucci and Scarponi 1994).

Application of atrazine at the rate greater than 100 mg/kg would lead to an increase in soil microbial activity such as respiration and dehydrogenase activity (Moreno et al. 2007). However, application of atrazine to five different soils at recommended rates (5 mg/kg) showed no significant effect on β-glucosidase activity (Mahía et al. 2011). Application of related herbicide terbuthylazine (4 kg/ha) to two different apple orchard soils showed no effect on soil respiration (Hartley et al. 1996); even higher rates of application (10 kg/ha) did not influence the soil respiration or straw decomposition (Hantschel et al. 1994).

Application of 2,4-D at low rates (0.5 mg/kg) produced minor effects on microbial respiration; however, application at higher rates (5 mg/kg) showed transient effects on inhibiting hydrolase activity and stimulating DH activity in the short term, i.e. $<$24 days (Rose et al. 2016). In another study, Niemi et al. (2009) applied linuron at the recommended rate (0.7 kg/ha) and also at 7 kg/ha, results showed negligible effect on the variety of soil enzyme activity. However, application of linuron and metoxuron at variable rates (5, 50, and 500 mg/kg) produced inhibitory effects on $CO_2$ evolution at 500 mg/kg, with some minor reduction also observed for linuron at 50 mg/kg. Furthermore, metoxuron 500 mg/kg greatly reduced nitrification, whereas linuron 500 mg/kg showed no effect on mineralization of nitrogen (N) (Grossbard and Marsh 1974).

Several studies revealed that application of prominent herbicides at the recommended rates, such as pendimethalin and difenzoquat (both 0.5–5 mg/kg), or thiobencarb (2.5–25 mg/kg) (Atlas et al. 1978); mesotrione (0.45 mg/kg) (Crouzet et al. 2010); propanil (5 mg/kg) (Kyaw and Toyota 2007); and dalapon at 2.6 or 26 mg/kg (Greaves et al. 1981) has a limited effect on the microbial activity. Moreover, Lewis et al. (1978) surveyed the impact of 25 herbicides, applied at recommended rates and observed no effect of these herbicides on soil microbial respiration and DH activity. In general, the herbicides at the recommended rate of application have non-inhibitory effects on the DH activity (Rao and Raman 1998).

Contrary to that, application of glufosinate-ammonium at variable rates (1, 10 or 100 mg/kg) drastically reduced the DH activity and that too it cannot be recovered even after 40 days of soil incubation (Pampulha et al. 2007).

In a nutshell, we can say that application of herbicides affects the number of soil biological functions, such as respiration, C and N mineralization, OM decomposition, enzymatic activity as well as nutrient cycling in the soil. The magnitude of impact and its direction depend on the number of factors, such as rate and time of application of herbicide and agro-climatic conditions (includes soil properties, temperature and moisture). In fact, a more number of researches on various herbicidal responses under variable conditions is required to estimate the precise impact of the herbicide on soil biological functions and underpinning its mechanisms.

## 11.5 Limitation and Future Research Needs

It is worth mentioning that in most of the herbicidal impact studies, the experiment was either conducted as auxinic culture, also called soil microcosm, a small-scale experiment containing soil microfauna of field communities offering higher resolution of ecotoxicological effects of chemicals in soil environments (Benton et al. 2007; Adhikary et al. 2014) or the herbicides are directly applied to the soil, and then their final impact was accessed. In diversity assessment study, the primary drawback of the soil microcosm is that the results are biased towards those species which are dominant and fast growing (Hill et al. 2000). However, under the field conditions, a number of other parameters are also acting and modify the herbicide behavior and their impact on the soil microflora, which are not normally taken into account during these experimentations, like the soil physico-chemical property which plays a vital role in fixation of herbicide molecules with the clay particles, temperature and moisture which help in dissipation and alterations in the microfloral population. Pampulha et al. (2007) opine that low clay and OM lead to minimal adsorption of herbicides as well as ensure maximal bioavailability of the herbicides to microbes. Furthermore, the time of application is also not taken into account in these studies; for example, it is true that soil-applied herbicide is applied as either pre-plant incorporated (PPI) or pre emergence (PE) herbicide, where there are more chances of herbicide interaction with the soil microflora but in the foliar applied herbicides, which is generally applied as post-emergence (POE), where the large proportion of herbicides are retained and subsequently absorbed by the foliage, if admixed with surfactants and thus very less quantity of the active toxicant reaches to the ground and interact with the soil microflora. Most importantly, most of the prominent herbicides used nowadays belong to the POE group, such as sulfosulfuron, clodinafop and fenoxaprop *p*-ethyl for monocot weed management and metsulfuron and halauxifen-methyl for dicot weed management in wheat; bispyribac-Na in paddy; imazethapyr in soybean; and mesotrione in maize. Thus, it is better to conduct a comparative study to assess the impact of PE with POE herbicides for quantification of the actual amount of toxicants that reach to the ground and interact with the soil microflora.

## 11.6 Conclusion

In modern-day agriculture, herbicides are the integral component of weed management. In recent years, the consumption of herbicide increased significantly. Herbicidal impact assessment studies involve two methodologies: viz. herbicide is applied in auxinic culture or applied directly in field. Application of herbicide leads to change in soil microbial population, in both the quantitative and qualitative terms. The most widely studied microorganisms affected by the herbicide are mycorrhiza, bacteria and actinomycetes. In general, most of the herbicides at the recommended rate of application either showed no negative effect or transient inhibition for the initial period, with slight contradiction with the few herbicides. Similarly, the herbicide also showed an impact on soil biological function, such as the soil microbial respiration, various enzymatic activities and nutrient recycling. Nevertheless to mention that, in general, the effects of herbicides on biological functions are more pronounced at higher rates of application as compared to the recommended rates. To generalize the effect as well as for precise understanding of the mechanism, more number of long-term studies, involving more number of herbicides and variable environment, are required.

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# Biological Magnification of Soil Pollutants

# 12

Amit Kumar Verma and Rahul Pandey

## Abstract

The mad rat races among the nations for development have jeopardized the human beings. The increasing population of the world is the major cause of anxiety for scientists as it leads to force human beings to change the natural environment, which is responsible for various types of pollution. These toxic pollutants are incorporated in the environment through soil, air, and water and in turn administered to the organisms at different trophic levels through food chains. Biomagnification is a condition where the chemical concentration of a compound in an organism exceeds the concentration of its food when the organism's diet is the major way of exposure for that compound. The toxic chemicals are exposed at different trophic levels and in turn are magnified through food chains and food webs. Soil is the most active site where the presence of various xenobiotics, chemicals pesticides, and heavy metals alters the natural soil environment as these chemicals are indispensable part of agriculture accounting for the main components of fertilizers. At successive trophic levels, these components are incorporated through producers to consumers and in turn amplified. Thus, soil pollutants play a pivotal role in biological magnification as they are the main source of contaminated products which are amplified in nature to affect adversely human beings. According to modern research, it has been concluded that human activities are mainly responsible for the majority of different types of soil pollutants. In this chapter, we will try to summarize the main sources of soil pollutants and their role in biological magnification along with their adverse role at different trophic levels.

## Keywords

Trophic levels · Biomagnifications · Xenobiotics · Pesticides · Slag · Solid waste

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## 12.1 Introduction to Soil Pollutants

Soil pollution can be defined as build-up in soils of persistent toxic chemicals, compounds, radioactive materials, salts, or disease-causing agents at enough concentration, which may cause a risk to human health, ecosystem, or both (Okrent 1999). Presently polluted soil is a burning challenge of current living organisms on earth. The soil contaminants are mainly caused by human activities including industrial processes, mining, household, business waste, human and animal pharmaceuticals. Apart from these chemicals, soil has also been reported to contain several types of biological contaminants such as parasites (hookworm) and pathogens (tetanus), which cause many well-documented impacts on human health (Brevik and Burgess 2013).

## 12.2 Sources of Soil Pollution

The increasing population and urbanization posed a serious threat to its environment for unscientific disposal of huge solid and liquid waste to its precious water bodies and agricultural land. Apart from this, in third world countries, modern economies include various types of activities such as industry, agriculture, and transportation, and produce a large amount of waste and pollutants. On considering major types of soil contaminations, the most common kinds of soil wastes can be classified into three groups: agricultural, industrial, and nuclear (Alloway 1995).

### 12.2.1 Agricultural Wastes and Their Magnification

The main agricultural source of soil pollutants includes a wide range of organic materials, pesticides, and animal wastes.

#### 12.2.1.1 Pesticides

The most common organic materials and pesticides belong to organochlorines, organophosphates, and carbamates. Organochlorine hydrocarbons include DDT and could be separated into dichlorophenyl ethane, cyclodienes, and other related compounds. The concentration of these hydrocarbons increase at successive trophic levels because DDT is metabolized and excreted much more slowly in comparison to other nutrients. Thus, the amount of these compounds tends to be accumulated especially in fat bodies of the organisms involved in food chain (Fig. 12.1).

Organophosphates are insecticides and were found to be toxic for insects. In other animals including birds, amphibians, and mammals, its toxicity was mainly due to phosphorylation of acetylcholinestrase enzyme (AChE). Some organophosphates such as diazinon, fenthion, and methyl parathion have been reported to be lipid soluble and had shown fat storage property and bioaccumulation (Roberts and Aaron 2007). Carbamates (carbaryl, carbofuran, and aldicarb) are the class of insecticide derived from carbamic acid, which is structurally and mechanistically similar to

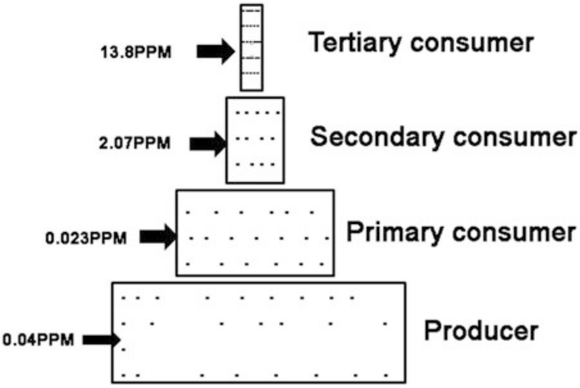

**Fig. 12.1** Biomagnification of dichlorodiphenyltrichloroethane (DDT) at different trophic levels from producer to consumer: The magnified amount of DDT has been denoted from producer to consumer in parts per million (ppm) at successive trophic level

organophosphate insecticides. The toxic exposure of these compounds has been reported to occur via dermal, inhalational, and gastrointestinal (GI) route. Further research has proved that carbamate compounds are also magnified in food chains and can create serious hazardous effects to human health (Vengayil et al. 2011).

### 12.2.1.2 Fertilizers

Fertilizers are used by farmers to maintain the soil deficiencies but excess use of fertilizer had also shown adverse consequences. The mostly used mixed fertilizers contain phosphorus as $P_2O_5$, potassium as $K_2O$, and nitrogen as $NH_4NO_3$. The raw materials used in the preparation of these fertilizers contain several types of heavy metals (As, Pb, and Cd) as well as other inorganic contaminants. Most of these metals had been reported to be nondegradable, causing indestructible poison for crops. The excess use of NPK (Nitrogen, Phosphate, and Potassium) fertilizers reduces the vegetable quality and crops grown for the years (Muhammad et al. 2014). Further researchers had been reported that the content of the carotene and vitamin C in a plant largely depends on the use of fertilizers (Ijdo 1936).

The heavy metals (Hg and Pb) and other inorganic substances used in the fertilizers had been reported to be biologically magnified at different trophic levels. The nondegradable nature of the ingested heavy metals is magnified in the food chains starting from the soil to tertiary consumers. On the other hand, heavy rain and draining water is responsible for leaching of these waste, which ultimately percolates to the water bodies and is taken by aquatic organisms such as fishes which in turn amplified at successive trophic levels through food chains and food webs.

### 12.2.2 Industrial Waste and Their Magnification

Industrial development of a country represents its growing GDP and plays a pivotal role in its economy. On the one hand, the growth of industries is important to make our life more convenient, easy, and opportunistic while on the other hand the waste releases from these industries had been proved to cause toxicity to our natural environment (water, air, and soil). The effluents discharged by the industrial units on to the land contain many toxic chemicals, which include mainly nonbiodegradable heavy metals, solid waste, and red mud deposition (Fig. 12.2).

#### 12.2.2.1 Heavy Metals

Heavy metal contamination had been reported mainly from the waste water stream of fertilizer, dyes, and the metal processing industries. The waste water streams of these industries are finally discharged in the rivers, which ultimately reach to our land ecosystem through leaching and irrigation management. Heavy metal contamination of the soil from industrial waste mainly includes Cu, Ni, Cd, Zn, Cr, and Pb (Hinojosa et al. 2004). These heavy metals had been reported to change the soil texture mainly in terms of clay content, organic matter, pH, etc. On one hand the contaminated heavy metals are reported to change the soil biochemical and biophysical properties while on other hand they also influence the soil microbial community by changing the enzymatic activities of soil (Belén et al. 2004; Vyas et al. 2017).

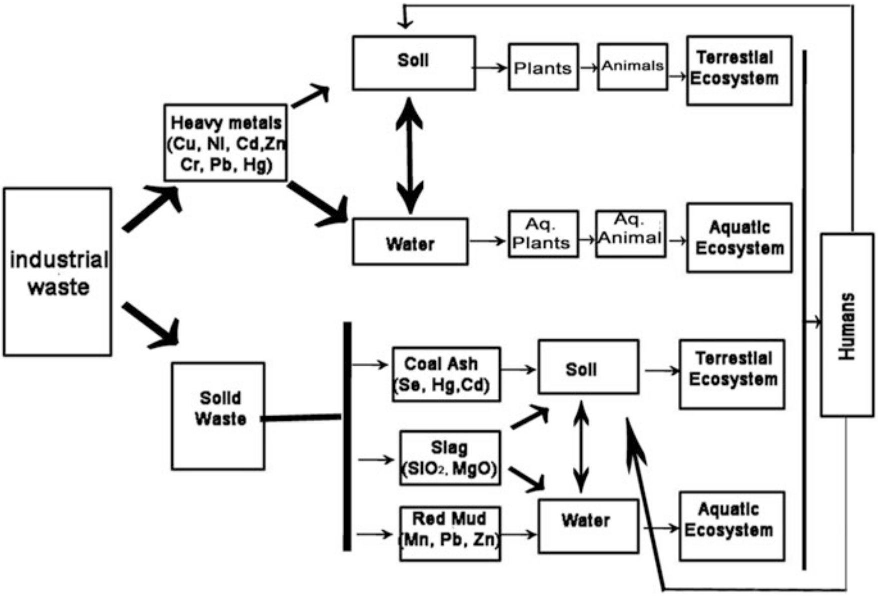

**Fig. 12.2** Biomagnification of industrial waste through soil: A schematic diagram representing different types of industrial waste released in the soil and their magnification up to humans

Excessive use of heavy metals is a global concern due to their potential toxic effects and their bioaccumulation properties, especially in the aquatic ecosystem (Batvari et al. 2015). Some heavy metals from industrial waste such as Cd, Hg, Cr, As, and Pb had been reported to accumulate at different trophic levels without their any role in a biological system (Canli and Atli 2003). On the other hand, metals such as Cu, Na, K, Ca, Mn, Se, Fe, and Zn are reported to be essential in fish metabolism but may also accumulate and reach to the toxic levels that can potentially destroy the ecological environment (Chakraborty 2019).

#### 12.2.2.2 Solid Waste

Solid waste is the major contaminated product of metallurgical, energy, and petrochemical industries. The disposal of solid wastes with violation of hygiene requirements concerning the placement and operation of landfills is the major cause of soil contamination and can become a threat to environmental safety of the population industrial centres (Grebeneva et al. 2014).

##### Important Industrial Solid Waste and Their Biomagnification

(a) *Coal ash*: Coal ash, also referred to as coal combustion residues are the major contaminants of the thermal power plants. The coal ash includes a number of by-products produced from burning coal, including fly-ash, bottom-ash, boiler slag, etc. According to a report (Gottlieb et al. 2010) coal ash typically contains heavy metals such as arsenic, lead, mercury, cadmium, chromium, and selenium as well as antimony, aluminum, barium, beryllium, boron, cobalt, etc. Most of these toxicants, if eaten, drunk, or inhaled, can cause cancer, and nervous system impacts such as developmental delays, behavioral problem, and cognitive deficits. According to an estimation of the Environmental Protection Agency (EPA), arsenic contamination of land, water, and soil from coal ash had increased the chance of cancer as 1 in 50.

Apart from the arsenic, other nonbiodegradable heavy metals from coal ash like selenium (Se) have also been reported for its bioaccumulation property. Further studies revealed that soil deposition of coal ash in wetlands can contaminate the rivers and agricultural lands which ultimately entered in different types of the food chain and in turn being magnified (Wu et al. 1995).

(b) *Integrated iron and Steel plant slag*: Slag in integrated steel and iron plants is dumped in surrounding areas of the steel plants making hillocks encroaching on the agricultural land. The slag from these steel plants mainly has the oxides of Si, Al, Ca, Mg, Mn, and Fe. Scientists have reported that heaps of steel-slag accumulated during more than 40 years in an agricultural land can change the soil texture by deposition of heavy metals such as Fe, Mg, Ca, and Si (Garcia-Guinea et al. 2010). These contaminants are also responsible for changing the soil pH and microbial strata of soil. Furthermore, most of the oxides of Al, Mg, and Mn deposited from slag industry in their surrounding area can reach to the agricultural lands through leaching and running water during heavy rain, which may become an integrated part of our food chain. Regarding the toxicity and bioaccumulation properties of these oxides, many experiments have been performed by preparing nanoparticles of these metals; the results showed that oxides of aluminum are accumulated in liver and kidney cells and in turn showed adverse effects to our immune system (Park et al. 2015). Similarly, the manganese oxide (MnO) is reported to be accumulated in the brain, lung, and bone cells of pigeons (Sierra et al. 1998). Thus, from the above discussion, we can draw a conclusion that the deposition of slag from various industries on agricultural lands can create a major problem through incorporation and magnification of its toxic components in the food chain.

(c) *Red mud*: Red mud is a solid waste, generated from nonferrous metal extraction industries like copper and aluminum. Presently, most of the red mud of these industries is disposed in tailing ponds for settling, which more often are reported to find its course into the rivers, especially during monsoon. The red mud toxicity includes various heavy metal contamination like Mn, Pb, and Zn (Liu et al. 2011) and can contaminate the soil and aquatic ecosystem. As previous studies had clearly indicated the bioaccumulation properties of these heavy metals (Canli and Atli 2003), disposal of the red mud is a burning challenge for the ecosystem and had adversely affected the human health.

### 12.2.3 Nuclear Energy and Soil Pollution

Exploitation of nuclear energy through fusion or fission of atoms can provide us an alternate way of large-scale carbon-free electricity source to fulfill the excessive demand for electricity. Presently, the urbanization and industrialization throughout the Globe has created a burning challenge for continuous supply of electricity. Regarding this, nuclear reactors or power plants have been designed, which can generate electricity through controlled nuclear reactions. On the one hand, these nuclear reactors have provided a better alternate opportunity for electrical energy while on the other hand the accidental release of radioactive pollutants from these reactors may adversely affect the ecosystem. Contamination of the soil with radioactive pollutants is an important origin of hazard for the environment and health safety as well as for economy.

The release of radionuclides mainly occurs at the time of processing of radioactive waste during segregation, transportation, treatments, characterization, and disposal. According to an estimation, soil contamination mainly occurs by fission product solidification, whereas leaching from the final disposal may result in the contamination of the soil with $^{90}$Sr, $^{137}$Cs, and actinides (Aleksakhin 2009). Furthermore, some corrosion products ($^{55}$Fe, $^{59}$Ni, $^{63}$Ni, $^{54}$Nb, $^{60}$Co, $^{39}$Ar, etc.) of these nuclear reactors may also significantly cause soil pollution. Apart from the nuclear reactors, regular nuclear weapon tests are the major cause of soil pollution through radioactive elements. The main concern is especially focused on to release of plutonium (Pu) isotopes due to its high biological toxicity and long half-lives of its isotopes (Mary et al. 2003; Gabrieli et al. 2011). Further studies have revealed that released radioisotopes of $^{137}$Cs, $^{241}$Am, $^{90}$Sr, and $^{131}$I are the major concern for its hazardous impact on the natural environment and human health issues (Prăvălie

2014). The mentioned isotopes had been reported in most of the nuclear sites worldwide, especially in western US soil (Turner et al. 2003; Cizdziel et al. 2008). In search of major radioactive pollutants of the ecosystem, scientists have found that the accidents held in Chernobyl (Ukrane-1986) and Fukushima (Japan-2011) were responsible for causing global contamination of the environment including air, water, soil, and living organism. In this event, a huge amount of radioactive elements, especially $^{131}$I, $^{137}$Cs, and $^{90}$Sr and the sum activity of $^{239}$Pu and $^{240}$Pu were found to be dispersed in the environment (Steinhauser et al. 2014). These radioactive elements can also be a major challenge for an aquatic ecosystem, which may reach from the contaminated soil to ground water or by flowing of these soils into rivers during heavy rain. Regarding this, scientists have reported that the Fukushima nuclear disaster delivered a massive amount of radioactivity into the sea and radioactive isotopes soon made their way into the marine food chain.

These radioactive elements which have been found to contaminate our land ecosystem have also been reported to accumulate in our body, which may enter through different food chains starting from soil. As radioactive materials are likely to be long-lived, mobile, and biologically active, once incorporated in our body they are responsible for causing several adverse consequences related to our health. In search of biomagnifications of radioactive elements, it has been found that $^{131}$I can be easily taken by fish through their thyroid tissue while $^{137}$Cs being mobile and long lived has been reported to be accumulated in organisms up to marine food chains and ultimately to human where we consume these marine creatures as food. Furthermore, $^{137}$Cs can be taken up by cells throughout the body and distributed in soft tissue, especially in muscle tissue, increasing cancer risk.

## 12.3 Conclusions

From this chapter, we can say that the increasing global population is a burning challenge for our ecosystem as the development of society demands to change the natural environment. The changing environment is the major cause of soil pollution that ultimately affects our life adversely. The soil pollutants adversely affect their texture and, in turn, fertility of the soil while on the other hand the components of contaminants (heavy metals, pesticides, radionuclide) can integrate into our food chain and, in turn, biologically magnified. The hazardous effect of these pollutants is the major concern for developing as well as developed countries. Finally, we may say that human activities and the unhygienic disposal of waste are the major area of concern to limit the toxic effect of different pollutants. To overcome these problems, the different summits had been organized by developing and developed countries from time to time and many resolutions and treaties had been signed by their representatives. The major problem is the unawareness and illiteracy of the people about their ecosystem so that the burning challenge is to wake up the people about the hazardous effect of these pollutants. The government of the countries should equip the proper waste management and should ensure its implementation to the agricultural and industrial waste to minimize the toxic effect of different pollutants.

Thus, waste management of pollutants can minimize the soil contaminants on the one hand, while on the other hand the recycling of these pollutants will be helpful for the economy.

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# Soil Pollution and Human Health

# 13

S. P. Singh and M. K. Singh

## Abstract

The soil is a natural entity acting as a buffer, and provides medium, anchorage, and nutrition to crop plants. Contaminants from agricultural soils entering into the human food chains have become a serious problem. Trace elements may enter into human food web via soil to water, plants, and animals. Soil once contaminated due to heavy metals (HM) or pesticide residues poses serious risks to human health and environmental safety. Anthropogenic sources lead to accumulation of trace metal elements in soil which persists for exceptionally longer period because of non-decay and their longer biological half-lives. Excessive fertilization and pesticide usage pollute ground water through runoff and leaching. Non-judicious application of agrochemicals is a threat to humans besides affecting nontarget plants and other macro and microorganisms in the agroecosystem. Necessary modifications in agricultural practices are needed on the use of fertilizers and pesticides. Highest safety against the use of agrochemicals may be ensured by imparting training, education, and policy considerations. Regulations are needed to abate cultivation on contaminated sites and disposal of harmful effluents on agricultural lands and avoid soil enrichment with potential pollutants. Remedial measures that can accelerate rejuvenation of contaminated sites, alternatives to intensive conventional agricultural practices, and safe strategies for plant protection are the need of the day. Information and data support on soil contaminants, their pathways, and mechanisms affecting human health are sparse. Further research with a multidisciplinary approach may handle the obstacles of the current techniques.

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**Keywords**

Soil contaminants · Heavy metals · Pesticides · Health risk · Policy considerations

## 13.1 Introduction

Soil pollution is the introduction of any material, biological organisms, or energy consequently leading to reduction in the soil quality which may influence day-to-day soil use or pose a threat to living environment and public health (Kumar et al. 2013). Complex structure of soil contains the major components viz. mineral matter, organic matter, water, air, and living organisms. The proportion of these components varies with location and thus soil plays a key role in sustaining the living being. Rapid industrialization has exerted ill effects on the environmental components threatening human health in long term. Occurrence of the heavy metals is natural and a few metals are essential in trace quantities, but their higher concentration is deleterious, indicating the extent of contamination in a particular area. Soil pollution has emerged as a widespread problem during the past few decades because of strenuous use of fertilizers and pesticides in agriculture, urban waste, industrial activities, and atmospheric discharges. The degree of occurrence depends on the extent of agrochemical use and industrialization. Soil pollution interferes in many ways by change in soil structure, reduction in soil fertility, disrupting the balance between soil flora and fauna, and contaminating crops and groundwater posing a serious threat to living organisms.

## 13.2 Sources of Soil Contaminants

The various soil pollutants include pesticides, heavy metals, petroleum hydrocarbons, dibenzo-*p*-dioxins/dibenzofurans, and polychlorobiphenyl. Heavy metals enter into the soil through anthropogenic sources (fertilizers, pesticides, organic and inorganic materials, wastes, and sludge residues). Contrary to injurious organic compounds, heavy metals do not break down or disappear and persist in the soil for many years (Lionetto et al. 2012). Disposal of industrial effluent and sewage (treated/untreated) to agricultural soil is one of the prime reasons for heavy metal contamination. An appropriate land management retaining quality of soil and precise information about heavy metals are required to equip us for suitable soil management (Chopra et al. 2009).

### 13.2.1 Impact of Agricultural Practices

#### 13.2.1.1 Inorganic Fertilizers

Inorganic fertilizers are the principal source to meet the demand for essential nutrients under intensive cropping systems. In order to ensure food security for ever-increasing population coupled with limited availability of the cultivable land puts a challenge to enhance the productivity per unit area per unit time. An increase in productivity demands a greater quantity of nutrients leading to excessive use of inorganic fertilizers in agricultural fields. Crop nutrition is one of the most important aspects that determine the productivity and quality of the produce. The inherent capacity of the soil to supply the nutrients essential for the crop growth varies with soils and the agricultural practices followed. The plant efficiency in utilizing the nutrients applied to soil also varies and largely depends on the characteristics of crop, soil, fertilizer, and its management practices. The trend of high fertilizer use may continue for the next three decades to achieve the required productivity. Excess fertilizer application causes eutrophication of surface water bodies and leaching of nitrate to ground water. Inorganic fertilizers mainly contain ammonium, nitrate, phosphate, and potassium salts. Leaching of highly mobile nitrate is considered a major pathway for N loss. The nitrate leaching depends upon rate and timing of N application and its synchronization with the demand and uptake by the crop. Besides the soil characteristics, source of N fertilizer, and availability of moisture/irrigation also play a crucial role in determining the quantum of leachable nitrate. Efficient management of N may substantially reduce the leaching potential. Ground water is one of the principal sources utilized for drinking water in India. Various inorganic and organic pollutants deteriorate the quality of ground water, making it unsafe for human consumption. Nitrate ($NO_3^-$) is one of the major inorganic pollutants dispensed by nitrogenous fertilizers, human and animal refuses, organic manures, and industrial effluents via biochemical activities of microbes. Apart from nitrate ($NO_3^-$) containing nitrogenous fertilizers, other forms viz. amide ($NH_2^-$) and ammonium ($NH_4^+$) are rapidly converted to nitrate in soil. High solubility and poor retention by soil particles lead to contamination of ground water with nitrate. Higher use of nitrogenous fertilizers is the principal cause for occurrence of more nitrates in ground water. Ground water with high nitrate concentration used as drinking water causes several health disorders viz. hypertension, methemoglobinemia, birth malformations, goiter, gastric cancer, etc. Increase in the use of nitrogenous fertilizers and the quantum of organic wastes generated may aggravate and pose an alarming situation in years to come. The maximum permissible limit for $NO_3^-N$ in drinking water is 10 mg $l^{-1}$ (Majumdar and Gupta 2000). Nitrate reaches water environment by way of leaching, drainage, and surface flow of water. Drinking water with high nitrate concentration ($>50$ mg $NO_3^-$ $l^{-1}$) causes inflammation, methemoglobinemia in infants (a blood disorder limiting oxygen supply to cells), and carcinogenic effects (Savci 2012). Fertilizers carrying heavy metals viz. arsenic (As), copper (Cu), cadmium (Cd), mercury (Hg), nickel (Ni), lead (Pb), and natural radionuclides deteriorate environment. Fertilizer application should be based on prior soil analysis, at right time, appropriate source and method to minimize the loss of energy, finance, and to environment (Savci 2012). Soils are integral to production of food and fiber in all terrestrial ecosystems. Reducing excessive nitrogen fertilizer use to economic optimal doses improves water quality but involves the risk of lowering the crop production. Improvement in timing and placement enhances the efficiency of the applied fertilizers with co-benefit of water quality particularly with the suboptimal nitrogen use (Paustian et al. 2016).

#### 13.2.1.2 Antibiotic Loaded Manures

Addition of antibiotics in animal feed supplements is common, aimed to enhance growth of food animals. However, excreted urine and feces contain substantial share of added antibiotics due to their incomplete absorption in the animal gut. Results of a greenhouse study revealed that the test crops i.e. cabbage (*Brassica oleracea* L. Capitata group), green onion (*Allium cepa* L.), and corn (*Zea mays* L.) grown on a mixture of pig manure and soil artificially spiked with antibiotics absorbed the antibiotic Chlortetracycline but Tylosin was not absorbed. The low concentrations of antibiotic Chlortetracycline found in plant tissues but it increased with increasing rate of antibiotics added to manure soil mixture. The study indicates the potential risks to human health associated upon consumption of crops grown on a soil altered with antibiotic loaded manures. Higher risks are involved for people allergic to antibiotics with chances of enhanced antimicrobial resistance due to consumption of such vegetables (Kumar et al. 2005).

#### 13.2.1.3 Industrial Effluent and Sewage Sludge

Addition of treated sewage sludge (biosolids) to agricultural land facilitates a way for waste management besides providing organic matter, essential nutrients, and considerably improving soil properties. However, it contains organic contaminants (dioxins) and pharmaceuticals in detectable concentrations (Clarke and Smith 2011; Wu et al. 2012). Accumulation of such contaminants in soil may lead their subsequent translocation to the food chain. Contaminants even at low levels may harm human health and environment. The possible human exposure pathways for soil-applied biosolids include entry of contaminants to food chain via consumption of edible plant parts and/or milk, meat, contaminated source (surface and ground water) of drinking water or by airborne inhalation. The utilization of biosolids to agricultural fields is often suggested to get benefit of recycling of nutrients, disposal of waste, sustainability, and economical aspect. However, potential risks involved due to the presence of emerging pollutants (PPCPs—pharmaceuticals and personal care products) and persistent organic pollutants (POPs) which may accumulate in the soil finally transferred to humans via contaminated produce (Clarke and Cummins 2015). Use of fertilizers, pesticides, and wastewater for irrigation has enhanced the heavy metal contamination in agricultural fields during past decades and showing an increasing trend. The assessment of heavy metal sources and their dispersal in agricultural land indicates that the pedogenic factors act as primary inputs of Ni, cobalt (Co), and chromium (Cr) and, anthropogenic sources for Cu, Zn, and Pb while Cd is linked with agricultural and industrial pollution. The heavy metals Cu, Cd, Ni, and zinc (Zn) evinced the high pollution risk because of agricultural practices and use of wastewater. Such results may be utilized for the formulation of remedial strategies in the affected area (Hani and Pazira 2011). Effect of heavy metal pollution (Zn, Cu, Cr, Co, Ni, and Pb) due to sewage and wastewater irrigation was assessed in soils on leafy and non-leafy vegetables, forage grass, and milk from cattle. Results have shown that high levels of Cu, Zn, and Cr were linked with labile fractions and thus were highly mobile and available to plants. The associated risk to human was assessed who were consuming these contaminated foods. Results revealed that the hazard quotient was high for Zn followed by Pb and Cr particularly with leafy vegetables viz. spinach and amaranthus (Chary et al. 2008). Vegetable crops viz. radish (*Raphanus sativus*), cabbage (*Brassica oleracea* var. *capitata*), tomato (*Lycopersicon esculentum*), okra (*Hibiscus esculentus*), brinjal (*Solanum melongena*), chili (*Capsicum annum*), spinach (*Spinacia oleracea* L), coriander (*Coriandrum sativum*), cress (*Lepidium sativum*), and dill (*Peucedanum graveolens*) showed variable patterns for accumulation and translocation of heavy metals. Regular irrigation with mixed industrial effluents results in higher concentration of metals [iron (Fe), manganese (Mn), Cd, Cr, Cu, Zn, Ni, As, and Pb] in soil and later in plants. Cultivation of spinach, radish, tomato, chili and cabbage was found to be unsafe in the areas receiving irrigation with mixed industrial effluent. High content of toxic metals (Cd, Cr, Ni, Pb, and As) found in the edible parts of such crops indicated their high accumulation and translocation potential. Results indicate enhanced risk and toxic impact on human health and ruminants via food chain. Hence, produce of polluted sites should be examined first for safe consumption of the human being or vice-versa discarded for cultivation. Vegetable crops that limit toxic metals in nonedible parts may be opted for cultivation at contaminated sites. Such studies suggest choice and planning of safe cropping system and helps in monitoring of agricultural fields for determination of toxic metals, management, and disposal of industrial effluents (Tiwari et al. 2011).

#### 13.2.1.4 Pesticides

The term pesticide includes a vast range of substances namely herbicides, insecticides, fungicides, nematicides, molluscicides, rodenticides, plant growth regulators, and others (Aktar Md et al. 2009). Pesticide is substance or their mixture used for prevention, destruction, to repel, or mitigate any pest or weed. Pesticides are used as an effective means for control of pests and weeds, protect yield losses, and for economic viability. More than 500 pesticide formulations are repeatedly being used. The major concern related to pesticide use includes their deleterious effects on nontarget organisms. Adverse effects have been identified on human beings, fishes, birds, and on the environment. In fact, $<0.1\%$ of the pesticide used reaches the target pest; the rest enters the environment polluting soil, water, and air harming nontarget organisms. Longer persistence of many pesticides may result its accumulation and progressive increase leading to higher concentrations in the tissues of living organisms (biomagnifications) after entering into the food chain. Pesticides use in agriculture will result in their existence in nonagricultural environments. Pesticides added directly to soil in the form of granules or sprayed on crop foliage reaches soil as wash-off. The residues of pesticides enter the surface or ground water through soil. The ultimate fate of pesticides within soil or their spread to air, water or food stuff varies with chemical properties of both product and soil. Several processes viz. uptake by plants, biological and chemical degradation, sorption, volatilization, leaching, and runoff also plays vital role. Physicochemical and biological properties of the soil environment like pH, proportion of clay particles, organic matter, moisture content, etc. governs the pesticide degradation and transfer of their carry over residues to air and water resources (Arias-Estévez et al. 2008).

Most of the organochlorine pesticides tend to accumulate in animal tissues. They are utmost stable and continue to exist in the environment and as a result can get into the food chain directly or indirectly. Pesticide residues volatilize from the warmer regions (tropical conditions), travel long distances with air and settle in other regions causing widespread contamination. Bioremediation strategy suggests that microorganisms such as several gram-negative bacteria have degrading potential. However, action-bacteria (gram-positive) particularly of Streptomyces genus have potential for biodegradation of inorganic and organic toxic compounds by dealkylation, partial dichlorination, and oxidation of dichlorodiphenyltrichloroethane (DDT), aldrin, and herbicides like atrazine and metolachlor. Streptomyces are befitted for soil inoculation because of their mycelial growth and rapid growth rate, ability of vegetative hyphal mass to differentiate into spores that help in spreading and persistence; longer survival period of spores and resistance against low water availability and nutrient concentrations. Microbial mixed cultures are considered more appropriate for bioremediation of recalcitrant compounds since, usually have elevated growth rates and substrate utilization than individual species. Results suggest that consortia of Streptomyces strains can effectively improve the biodegradation process and degrade xenobiotic from sediments, polluted soils, and wastewaters than the corresponding single strain (Fuentes et al. 2011). Application of herbicides at a wider scale to agricultural fields poses environmental problems. The Jews mallow growth in a saturated soil pretreated many times with cyanobacterial mats indicated the successful biodegradation of a popular herbicide Diuron. The Diuron degrades rapidly at low concentrations in soil (within 30 days) and the effect was more prominent when incubated with cyanobacteria in liquid medium (irrigation water). High concentrations of Diuron ($>0.22$ mg $kg^{-1}$ soil) may exert toxic effect on cyanobacterial mats. These promising findings suggest that cyanobacterial mats may be used as a remedial technique for water and/or soil pollution caused due to herbicides application (Safi et al. 2014).

With advancement in science and technology, the threats to environment have also increased because of disposal of contaminated wastes and depletion of natural resources. A huge number of chemically synthesized compounds (approximately $6 \times 10^6$) are available and about 1000 new chemicals being annually added to this list to restrain such waste materials carrying heavy metals and their unsound disposal creating ecological problems at the global level. Use of traditional methods involves high cost due to excavation and transportation processes. Bioremediation offers an eco-friendly and cost-effective way to replace conventional methods such as incineration which creates a new waste and do not get rid of the problem. The biological processes cause reduction, transform, or eliminate pollutants. The factors viz. type of pollutants, soil pH, moisture holding capacity, soil structure, fertility status, and microbial diversity are important for bioremediation. Bioremediation is the most effective technology to tackle environmental contamination increasing day by day due to anthropogenic activities since use of biological systems for pollution reduction. This novel approach involves multiple disciplines with key focus on microbiology. The technology includes revitalizing native microbial population (bio-stimulation), their artificial introduction (bioaugmentation), gradual buildup (bioaccumulation), as potential metal bio-sorbents (bio-sorption), by use of plants (phytoremediation) and by interaction of soil, microbes, and plant (rhizoremediation). Development of suitable methods and more scientific knowledge are required on natural processes for effective utilization of bioremediation technology to restore the contaminated environments. Interdisciplinary research may address to the present obstacles and issues in near future (Shukla et al. 2010). Assessment of risk and the measures to reduce them are crucial. It appears that there is enormous potential for development of potent, low environmental risk and dependable microbial-derived pesticides. Improved techniques with precise application may reduce pesticide rate. Improved formulations are required to enhance the retention, uptake, and translocation when used on target and reducing off target deposition. Such improvements may curtail transport and also avoid the upsurge of resistance in target organisms. The current environmental concerns related to agrochemical residues from soil, water, and foodstuffs will not disappear. However, to ensure minimal harm, pesticides should have low or no toxicity to the nontarget organisms. Surveys on pesticide sales and market to know pesticide use patterns should be promoted for policy considerations as global strategy (Arias-Estévez et al. 2008). The data on pesticide-associated risk assessment relevant to health and environment are scanty in developing countries which is much needed information for clear understanding of the problem. The strategic interventions to reduce the ill effects should be based on the periodic monitoring studies on high-risk groups. Imparting education and training to field-level workers may ensure safety against pesticides use. Scientific judgment should form prime basis for all pesticides-related exercises rather than the commercial considerations. Pesticides are recognized as an easy, low cost, and rapid solution for control of pests and weeds. Pesticide contamination can be reduced by adoption of nonchemical methods of pest control (including weed control). The prevention of harmful effects on health will lead to sustainable development. Although there is some ambiguity at present leading to lifelong exposure of people, but in spite of all reasons, knowledge-based health education packages are developed to minimize ill effects of pesticides to humans (Aktar Md et al. 2009).

## 13.3 Soil Contamination and Human Health

The soil is a porous medium containing organic matter, mineral matter, living organisms, water, and gas. The occurrence of heavy metals in soils is obvious though its extent may indicate the pollution load in a particular area. The accurate information about heavy metals is necessary for proper soil management because of their potential toxicity to the crop plants and human health. Usually heavy metals having density >4.5 g $cm^{-3}$ (Cu, Cd, Zn, Pb, Hg, Ni, Cr, etc.) are stable and thus they accumulate in soils and cannot be destroyed being nonthermodegradable or nonbiodegradable. Of several pathways for contamination of agricultural soils, the industrial discharges and sewage (treated/untreated) emerge as a prime source of heavy metal contamination. There is a need to find out potential microbial strains which can degrade heavy metals. Biotechnological approaches such as genetically engineered microorganisms with enhanced degradation efficiency may address the problem. Disposal of any type of effluents to agricultural lands should be stopped (Chopra et al. 2009). Analyses of eight metals of upper layer soils in rice fields revealed that Pb exhibited strong spatial dependency while other metals (Cu, Zn, Cd, Cr, Hg, As, and Co) showed moderate spatial dependency. The degrees of enrichment in rice soils varied with heavy metals since the anthropogenic activity had different influence on them. The results suggest that the anthropic factor controls Zn, Cu, and Cr, natural factors control Cd, Co, and As, while natural and anthropic both factors control Hg and Pb. The spatial map indicated that alterations are required in the present agricultural practices since >85% area under study evinced Zn, Cu, and Cr enrichment while some area shown high Hg (Wu et al. 2010). Heavy metals in low concentrations are found in phosphate rocks (as minor constituents), animal manures, and sewage sludge. The repeated fertilizer and/or large applications of manures may result in accumulation of heavy metals in soil. Among these, Cd may potentially harmful to human health. Other heavy metals are of less concern than Cd since they are not readily absorbed by the plants and relatively lesser harmful to human health. Few countries have imposed their regulations on concentrations of heavy metals in phosphate fertilizers, sewage biosolids and set the tolerance limit for addition of heavy metals to plough layer (upper 20–30 cm) soil. In fact, the rate of phosphorous application controls the input of Cd to soil (Mortvedt 1996).

### 13.3.1 Assessment of Contamination

Heavy metal contamination poses serious problems at the global level because of their abundant sources, accumulative nature, nonbiodegradable properties, and toxicity. A study assessed the soil HM contamination at a prominent site and measured the contents of Ni, Cr, Zn, Cd, As, Cu, Hg, and Pb in soil and crop samples (1822 pairs). The health risks evaluation as per the model of U.S. Environmental Protection Agency stated that single pollution index was found at unpolluted level while mean Nemerow composite pollution index at cautious level. The mean crop pollution index (CPI) exceeded the national standard value for Ni only. The standard exceeding rates of Cu, Cd, and Hg in soil and Ni, Cr, and As in crops were significantly greater than their corresponding values in crops and soil, respectively. The bio accumulation factor (BAF) indicated the translocation of heavy metals in the soil-crop system. The mean CPIs are noted in the order Ni > Cr > Zn > Cd > As > Cu > Hg > Pb and the BAF in the order of Cd > Zn > As > Cu > Ni > Hg > Cr > Pb. The crops exhibited variable capacities to absorb HMs and cadmium is most readily absorbed by crops than other HMs. The hazard quotient for HMs was at a safe level for various age groups indicating low potential noncarcinogenic risk to residents of the study area due to HMs. However, ingestion was found as the leading pathway to cause carcinogen risk to human health (Hu et al. 2017). Soils act as a (temporary) sink and source of several chemical pollutants and their accumulation in soils enhances the threat for direct (inhalation, ingestion of soil, and dermal contact) or indirect (drinking water or dietary intake) human exposure. Risks assessment to human health should essentially incorporate bioavailability adjustments beyond the routes of exposure at polluted areas. Variable concepts, uncertain methodologies, lack of data, and accurate methodology restrict proper soil risk evaluations and its validation including bioavailability measurements. Development of inexpensive and rapid tools needed to ascertain threshold concentrations of pollutants in soils and their potential risks because of human exposure. This would be useful to utilize the bioavailability data for assessment of risk and decision-making (Rodrigues and Römkens Paul 2018).

### 13.3.2 Pollution Safe Crop/Cultivar

Soils contaminations with heavy metals are important pathway for the entry of these toxic pollutants to the human food chain. Information on crops' responses to these contaminations either by single or multiple metals is scarce. Evaluation of asparagus bean (*Vigna unguiculata* subsp. *sesquipedalis* L.) for accumulation of Cd (low level: 0.8 mg $kg^{-1}$ and high level: 11.8 mg $kg^{-1}$) by cultivars and their exposure to multiple metals (Cd: 1.2, Pb: 486 and Zn: 1114 mg $kg^{-1}$) exhibited highly significant variations among the test cultivars regarding Cd accumulation by asparagus bean (stems, leaves, fruits, and roots). The harvested fruits (pods) of low and high Cd exposure (41.7% test cultivars) contained lower Cd concentrations ($<0.05$ mg $kg^{-1}$) found safe for consumption. Cultivars having black seed coats proved significantly superior since they showed low Cd concentrations (fruit) compared with red/spotted seed coats. Cadmium accumulations are governed by the genetic factors and asparagus bean is a low accumulator to Cd pollutant. Significant positive correlation noticed between Cd and Pb concentrations in fruits when kept under high-level Cd stress conditions. The study suggests that the Cd accumulation in fruits might be due to the presence of other heavy metals in the soil. Adoption of pollution safe cultivars (PSC) is a practicable strategy for asparagus bean. Further studies are required on various genetic aspects and a new breeding approach to understand the mechanism and develop PSC to minimize the threats of human exposure to heavy metals (Zhu et al. 2007). Agricultural production is continued on large acreage of polluted land in some countries to fulfill the growing demand for food. Growing of pollution safe cultivars (PSCs) which accumulate low level of specific pollutants in their edible parts may restrict the influx of pollutants. Such PSCs offer safe produce for consumption when grown in polluted soil. The feasibility of this concept was attempted in a pot experiment on 43 rice cultivars (23 hybrids and 20 normal cultivars) exposed to a low (1.75–1.85 mg $kg^{-1}$) and high (75.69–77.55 mg $kg^{-1}$) cadmium (Cd) level. Thirty test cultivars observed Cd-PSCs at low level of Cd exposure. Results emphasized that the Cd concentrations in grains found highly correlated ($p < 0.01$) among two experiments. Findings suggests that Cd accumulation in rice grains depends on genotype indicating future possibilities of screening PSCs with a definite level of soil contamination. However, at high-level exposure, none of the test cultivars fall under Cd-PSCs. Variations in yield responses of the cultivars at high soil Cd illustrate that reduction in yield is not an indicator of toxicity of the grains. Therefore, it is imperative to initiate breeding programs and screening for PSCs to effectively address the threat of human exposure to soil pollutants (Yu et al. 2006).

### 13.3.3 Green Technologies

Heavy metal contamination in soils is often irreversible and may suppress/sometime kill parts of the microbial community and lead to more tolerant microbial population. The extent of N-fixing cyanobacterial population and existence of heterocysts are affected in the soils having high chromium levels. The number of Cr (VI) tolerant heterotrophic bacteria significantly increased in the polluted soil than unpolluted one. Further research may help to delineate the chromium-contaminated environments by utilizing the tolerance of heterotrophic bacteria to Cr (VI) and occurrence of heterocysts in cyanobacteria and/or for supervising bioremediation process (Viti and Giovannetti 2001). Heavy metals pose long-term risks being highly reactive and toxic even at low concentrations. Their biotic effects vary as per specific metal and for adapted organisms. Some plants (metallophytes) have evolved mechanisms to contend with heavy metal stress. Hence, metallophytes may be used for cleaning of the metal-contaminated sites and to limit the spread of heavy metals outside the contaminated area. Proper exploitation of the green technologies will require vegetation surveys for possible discovery of hyper accumulating and metal-tolerant plants in more numbers from under studied habitats (Gall et al. 2015).

Phytoremediation is a promising technology that includes phytoextraction and phytostabilization to remediate polluted soils. The capacity of a soil to discharge its functions is termed as soil quality. The reversal process of any heavy metal-polluted soil includes removal of HM from soil with restoration of soil quality. Soil microbial properties are becoming popular as biological indicators of soil quality due to high sensitivity, rapid response, and facts that combine many environmental factors. Restoration of soil quality is judged during phytoremediation of HM via microbial monitoring, although soil microbial properties are highly dependent on circumstances and tough to interpret. Interpretation may be improved by classifying them into groups of higher ecological relevance viz. ecosystem health attributes, ecosystem services, and soil functions (Gómez-Sagasti et al. 2012).

Phytoremediation includes a number of technologies by which plants degrade, remove, reduce, or immobilize environmental toxic pollutants of anthropogenic origin to restore the contaminated sites to a reusable condition. Phytoremediation utilizes plants to hasten the degradation of organic contaminants with rhizosphere microorganisms, or to take out dangerous heavy metals from water or soils. Phytoremediation is eco-friendly technology and relatively inexpensive than alternate remediation strategies. Majority plants in nature are colonized by arbuscular mycorrhiza fungi and the bacteria helping mycorrhization may be exploited to improve it. To take advantage of microbes as bioprotectants against heavy metals and pathogens, their ecological complexity particularly in the mycorrhizosphere needs careful attention. Integration of such information on soil and root microbe activities and their distribution dynamics is required with physicochemical and spatial properties of soil. Such tasks may be accomplished by associative efforts of physicists, soil chemists, and biologists (Shirmohammadi et al. 2014).

### 13.3.4 Indicators of Soil Health

The sustenance of production depends on many factors that are interrelated and influence soil productivity. The soil health indicates the continued capacity of any soil to sustain productivity, maintain/improve the quality of environment within an ecosystem boundary, which supports human health and living. Increasing pressure on soils will require regular assessment and monitoring of soil health. Soil enzyme activities are one of the promising indicators of soil health among proposed biological indicators but require careful judgment and interpretation of the data. Soil enzyme activities are responsive to changes that occur in soil because of crop management practices (crop rotation, tillage, fertilization, residue management, etc.). Determinations of soil enzyme activities are comparatively easy, rapid, and low cost than physicochemical methods. Dependency on single measure (soil enzyme activities) may constitute certain limitations and thus an accurate diagnosis of soil health requires concomitance with physicochemical and other biological measures (Alkorta et al. 2003). Organisms that impart quantitative details about environmental quality are termed as biomonitors. Limitations in use of plants as biomonitors of soil pollution have been advocated by earlier workers. However, plant biomonitors are better indicators of soil quality and have key advantages than soil analyses particularly for large-scale exploration. Total metal concentration can be best measured by direct soil analyses. However, estimation of soil quality by plant biomonitors facilitates direct quantification of a biological effect to assess the influence of pollutants on ecosystem and humans. This approach manifests clearly the consequence on living organisms due to metal and not inferring only the values for total metal concentration in soil (Madejón et al. 2006). Plant biomonitors have certain experiential constraints over soil analyses. None of the single plant species can respond to a vast range of contaminants. The metal bioavailability and their uptake vary across the plant species and varieties therefore restricting the range to specific plant. Metal concentrations in leaves are resultant of time, plant developmental stage, and environmental factors; plant roots may ignore metal hotspots (Mertens et al. 2005). These constraints may be addressed by selection of most suitable plant species (more than one) as biomonitors that are important in the food cycle of an ecosystem (Madejón et al. 2006).

Earthworms improve soil fertility, decompose organic matter, and recycle nutrients. Earthworms can suitably be used as indicator organisms for biological impact assessment of the soil pollutants and soil ecotoxicological research.

Management and measurement of earthworms are easier to assess the biochemical responses, accumulation of pollutants, and its excretion, and facilitates the study on life span (growth and reproduction). Generally, low levels of contaminations turn out more rapidly in cells/tissues of an organism than higher levels such as ecological effects. Therefore, any change (cellular, physiological, and biochemical) in an organism due to pollutant exposure may be used as biomarkers to provide an early warning. Earthworm biomarkers use to monitor soil pollution and effect of contaminants on soil organisms is a recent approach. Identification and characterization of most suitable earthworm species is necessary on priority basis. Development of biomarkers of exposure should be able to address a wide range of soil contaminants since studies conducted so far largely are concerned with heavy metals only. Studies are scanty on earthworm biomarkers under real field conditions with use of native populations for assessment of soil pollution (Lionetto et al. 2012). A long-term screening revealed that microbial biomass, soil enzyme activity, and algal populations reduced in medium-to-high polluted soils with total petroleum hydrocarbon (TPH). The lower TPH pollution enhanced the algal populations but the microbial biomass and enzymes were found unaffected. Inhibitory effect on above parameters was more pronounced in high polluted soil than medium polluted soils. Medium-to-high polluted soils exhibited removal of sensitive algae species indicating a shift in composition. Results suggest such alterations in the soil algal composition may be utilized to find out environmental hazards at polluted sites and for making recommendations on soil quality. The soil algal tests hold extraordinary importance because of confined knowledge on toxicity to microorganisms due to exposure of pollutants' terrestrial environments (Megharaj et al. 2000).

## 13.4 Research Challenges and Policy Considerations

Assessment of soil quality (SQ) is a tough issue, since soils greatly vary in properties and functions. Development of methods to monitor and assess SQ is needed to ensure sustainable land use without any harm to human health. The holistic approach should adopt indicators of various types (physical, chemical, and biological) for judgment of SQ. Mostly single indicators are used and urban SQ not being properly assessed. Further efforts are needed to develop methodologies by incorporating exposure pathways or human health indicators for assessment of soil quality. Such methodologies should consider soil quality in terms of productivity, sustainability, ecosystem, and human health (Zornoza et al. 2015). Stockholm Convention to oversee identified POPs along with PPCPs on the basis of associated risk factors viz. persistence, bioaccumulation, and toxicity. Continuous addition of the emerging contaminants (PPCPs) is of great concern since it compensates their transformation/removal from the environment. More studies are needed on exposure pathways of contaminants and their long-term influence on human health with focus on PPCPs. Significant knowledge gap exists on long-term risk assessment because of exposure to PPCPs upon human consumption of water, food crops, and meat. Accurate risk assessment to human/environment by these contaminants will depend on execution of proper modeling approaches. Policy considerations are needed to mitigate the ill effects on environment by the use of readily degradable pharmaceuticals (greener pharmacology) and increase in the efficiency of biological treatments (wastewater treatment plants) (Clarke and Cummins 2015).

The importance of soil biodiversity is progressively admitted for offering advantages to human health due to suppression of soil organisms that induce diseases and facilitates clean water, air, and food. Environmental change and faulty land-management practices affect belowground communities globally, resulting in reduced benefits due to decrease in soil biodiversity. Current findings are indicative of the fact that sustainable management can partially restore and maintain soil biodiversity. Better management practices encourage soil biodiversity and ecological complexity and act with potential to improve human health through underused resource. Management options are available to conserve and enhance soil biodiversity for plant, animal, and humans. However, development and promotion of viable practices are urgently required. A new approach should consider usefulness of soil biota in land use and management to provide multiple benefits. Further, enhanced soil food web complexity amends resistance and flexibility to cope up the disruptions and shield the effects of extreme events. The appropriate practices and strategies that enhance soil biodiversity should be included in the land, water, and air use policies at regional and global levels for sustenance of human health. Initiatives have been started on global soil biodiversity to provide relevant information to policy makers and are preparing to publish the first Global Soil Biodiversity Atlas in collaboration with the European Union Joint Research Centre. The Global Soil Biodiversity Initiative is working to consider soil biodiversity at transnational platform on biodiversity and ecosystem services. Soil biodiversity provides a broad ecological foundation, linked to all forms of life and is certainly an underutilized resource. This is high time to save soils and soil biodiversity with effective management, sharing information among scientific community and policy makers, and framing new policies based on current knowledge. Development of implementation mechanism is crucial to get an easy update on related policies and best management practices. This will improve understanding of soil biodiversity management to boost human health (Wall et al. 2015). Public policies should prevent pollution by the factory farms. Strict provisions are required to reimburse the cleanup costs when any such industry pollutes area. Therefore, the products' prices must reflect their influence on the human health, environment, or the social and economic stability of rural communities (Horrigan et al. 2002). Conventional practices are posing threat to the agroecosystem health and the sustainability of the agricultural production system. Management practices opted should be able to address the root causes. Sustainability of the production system in future will depend on the site-specific technologies. Biodiversity of the below and above ground is of greater importance; proper exploitation of the benefits will largely depend on the future strategic research and perception of rhizospheric interactions under diverse conditions (Singh and Singh 2019).

## 13.5 Conclusion

Soil pollution has emerged as a widespread problem because of strenuous use of fertilizers and pesticides in agriculture, disposal of urban waste, and industrial activities. Contaminants like heavy metals or pesticide residues pose serious risks to human health and environmental safety. Soil pollution interferes in soil structure, reduces fertility, disrupts the balance between soil flora and fauna, contaminate crops and groundwater thus posing serious threat to living organisms. Heavy metals enter into soil through anthropogenic sources, do not break down, and persist exceptionally long in the soil. Disposal of industrial effluent and sewage to agricultural soil is the prime reason for heavy metal contamination. Precise information about heavy metals equip us for suitable soil management. Inorganic and organic pollutants deteriorate the quality of ground water making it unsafe for human consumption. Higher occurrence of nitrates in drinking water causes several health disorders. Fertilizers use efficiency may be enhanced by adoption of proper timing and placement with co-benefit of improvement in water quality. Produce of polluted sites should be examined first for safe consumption of the human being or vice-versa discarded for cultivation. Crops that limit toxic metals in nonedible parts may be opted for cultivation at contaminated sites. The data on pesticide-associated risk assessment relevant to health and environment are scanty in developing countries. The strategic interventions to reduce the ill effects should include periodic monitoring, education, and training to ensure safety. Phytoremediation is eco-friendly and relatively inexpensive technology though the successful use of microbes as bioprotectants will require more information on their activities and distribution dynamics with spatial properties of soil. Regulations are needed to abate cultivation on contaminated sites and disposal of harmful effluents on agricultural lands. Alternative safe agricultural practices and strategies are the need of the day. Information on soil contaminants, their pathways, and mechanisms is required with multidisciplinary research approach to tackle the current problems.

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# Emission of Greenhouse Gases from Soil: An Assessment of Agricultural Management Practices

## 14

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and Madhoolika Agrawal

## Abstract

Increasing concentrations of the atmospheric greenhouse gases (GHGs) are serious threats to the living beings and their niches. The rapid increase in GHGs is undoubtedly related to anthropogenic activities. Literature related to GHG emissions and mitigation approaches is widely available, but very few reviews concentrated on spatial-temporal trends of GHG emission from the agriculture sector. Agriculture is a potent contributor to GHG emissions, involving different agricultural practices followed by the farmers, which affect the rate of emission either positively or negatively. Agricultural soil management practices add excess nutrients, which disturb the natural mineral cycling leading to soil and water pollution and increase emission from soil to atmosphere, thus contributing to climate change. Research papers and reports related to GHG emission from different agricultural sectors in different parts of the world were reviewed to find the variations in emission pattern and intensities, and the factors influencing the emissions from the soil. The soil GHG emissions are directly or indirectly modified by natural as well as anthropogenic factors, like pH, soil texture, tilling, fertilizer application, mulching, irrigation, etc. The determinants taking part in the soil GHG emissions varied with region and different agricultural practices. Different mitigation approaches for GHGs from the agriculture sector were also compared for their efficacy in reducing emissions. A variety of advanced techniques developed to enhance the yield of crops were found to influence GHG emissions by direct influence on soil pH, temperature, and moisture. The conditions favorable for GHG emissions can be modified to reduce

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the emissions as the soil acts both as a reservoir and as an emitter of GHGs based on local natural and anthropogenic factors.

**Keywords**

Greenhouse gas · Agriculture · Soil · Impact on plants · Mitigation

## 14.1 Introduction

Climate change is a long-term alteration in weather conditions that include major changes in temperature, precipitation, wind patterns, etc., that occur over several decades or longer (IPCC 2014). The significant changes in weather variables may lead to large and potentially dangerous shifts in climate and weather. The Earth's average surface temperature has risen by 0.93 °C through 2016, since the start of global record in 1880 (Dahlman 2017). The ongoing rise in global mean temperature near the Earth surface is global warming. The major causes of global warming are the increasing concentrations of GHGs in the atmosphere. Water vapor ($H_2O$), carbon dioxide ($CO_2$), methane ($CH_4$), nitrous oxide ($N_2O$), ozone ($O_3$), etc. present in the atmosphere absorb the thermal infrared radiation that is emitted and reflected by the Earth surface and reradiate back to keep the Earth warmer. Thus, the GHGs are responsible for maintaining the optimum temperature of the Earth. If GHGs do not exist, the average temperature of the Earth would have been −18 °C. Due to the presence of GHGs, there is an increase in the temperature by 34 °C (NASA 2010). The greenhouse effect is the process of trapping and reradiating the thermal infrared radiation by GHGs into the atmosphere. The current increases in GHGs due to anthropogenic activities retain more thermal infrared radiation close to the Earth surface resulting in an increase in global mean temperature and thus to global warming. GHGs and their characteristics are given in Table 14.1.

The continuous increases in the concentrations of GHGs in the atmosphere are not only implicated the global warming, but also sea level rise and reductions in carbon sequestration in terrestrial and oceanic carbon pools (IPCC 2007). GHG emissions are rising every decade, but the anthropogenic emissions were highest during 2000–2010 (IPCC 2014). In 2010, from total anthropogenic emissions, $CO_2$ accounted for 76%, $CH_4$ for 16%, $N_2O$ for 6.2%, and 2% was contributed by fluorinated gases (IPCC 2014). Emissions from the agriculture sector also come under anthropogenic inputs. Major sources of agricultural soil pollution are applications of chemical fertilizers, pesticides, organic manure, and other inputs that are used vigorously to increase the productivity of plants. The nutrients from these inputs are not totally utilized by the plants and lost due to leaching, run off, and also emitted to the atmosphere, thus disturbing the nutrient cycle. These practices affect the emission of GHGs from soil. This review paper focuses on the current knowledge of GHG emissions from the agricultural sector, the local environmental and anthropogenic factors governing the emissions, and the effect on agriculture and the available strategies to reduce the concentrations of GHGs in the atmosphere.

**Table 14.1** Greenhouse gases and their characteristics

| Greenhouse gases | Concentration | Concentration (2005) (WDCGG) | Trend (per year, 2005–2016) (WDCGG) | Global warming potential (USEPA 2017) | Lifetime (years) (USEPA 2017) |
|---|---|---|---|---|---|
| Carbon dioxide ($CO_2$) | 403.3 ppm[a] | 379.2 ppm | 2.1 ppm | 1 | Variable |
| Methane ($CH_4$) | 1853 ppb[a] | 1785 ppb | 6.15 ppb | 25 | 8–12 |
| Nitrous oxide ($N_2O$) | 328.9 ppb[a] | 319.1 ppb | 0.9 ppb | 298 | >100–120 |
| Ozone ($O_3$) | 40.7 ppb[b] | – | – | 2000 | Short |
| Chlorofluorocarbons (CFCs) | 537 ppt[c] | – | – | 10,600 | >100 |
| Hydrofluorocarbons (HFCs) | 35 ppt[c] | – | – | Up to 14,800 | Up to 270 |
| Perfluorocarbons (PFCs) | 20 ppt[c] | – | – | 7390–12,200 | 2600–50,000 |
| Sulfur hexafluoride ($SF_6$) | 8.6 ppt[c] | – | – | 22,800 | 3200 |

[a] WDCGG (2016)
[b] ESRL GMD (2016)
[c] CDIAC (2016)

## 14.2 Methodology

A literature review was performed by using world wide web for related keywords such as greenhouse gas, agriculture, agricultural practices, soil emission, factors affecting GHG emission, effects of GHGs on agriculture, GHG emission mitigation etc., on Google Scholar and PubMed. Based on the related information, 250 eligible papers relevant to the topic were selected for further consideration. For analysis of the concentration and emission trend of GHGs, data from IPCC, NASA, ESRL (Earth System Research laboratory), and WDCGG (World Data Centre for Greenhouse Gases) were downloaded from respective websites. Relevant peer-reviewed papers were also extracted from the cited reference of most important papers in this field. Relevant information observed from those studies such as different agricultural practices influencing the emission of GHGs, soil conditions modifying GHG emissions, the contribution of agriculture in total GHGs emissions, and mitigation strategies in controlling GHG emissions were briefly explored. More emphasis was given to studies in developing countries. The data of WDCGG (2016) for the time period of 2005–2016 were used for the time series analysis of $CO_2$, $CH_4$, and $N_2O$ using the Theil-Sen approach in R-statistical software.

## 14.3 Greenhouse Gas Emissions

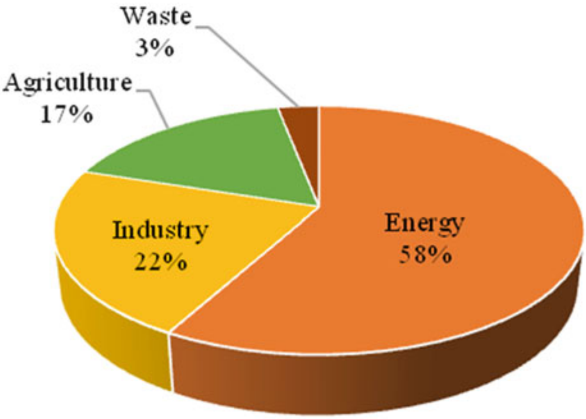
Natural sources of GHGs are decomposition, enteric fermentation in ruminants, anaerobic respiration in wetlands, denitrification, volcanic eruptions, etc. GHGs emitted from the natural sources are mainly $CO_2$, $CH_4$, and $N_2O$. Major anthropogenic sources of GHGs include energy production through fossil fuel burning like coal, petrol etc., biomass burning, waste decomposition, land-use change, industries, leakage during oil and gas exportation and transportation, leakage from air conditioners and refrigerators, cleaning of electronic components, production of plastic foams, propellants, and sprays, etc. (IPCC 2014). Anthropogenic sources contributing to global GHGs are given in Table 14.2.

Burning of fossil fuels is one of the major contributors in elevating the concentrations of GHGs and is involved in almost all the processes related to energy generation, electricity, industry, agriculture, transportation, etc. 9.4 and 9.6 billion metric tons of $CO_2$ were emitted globally from fossils fuel burnt during 2011 and 2012, respectively (ESRL GMD 2014). Emission with this rate is estimated to increase the $CO_2$ concentration by 11.5% over a period of 10 years. In 2012, Asia contributed to 46% in global GHG emissions and it has reached 14.5 Gt $CO_2$-e ($CO_2$-e is the concentration of $CO_2$ that would cause the same radiative forcing as a given mixture of $CO_2$ and other forcing components (IPCC 2014; US EIA 2016)). In Asia, GHG emissions are maximally contributed by energy production (48%) followed by agriculture (18%), industry (11%), residential (9%), transportation (9%), and waste (5%) (Marcotullio et al. 2012). According to a report of INCCA (2010), energy sector including electricity (37.8%) and transport (7.5%) produced higher $CO_2$-e whereas agriculture contributed to 17.6% of total emission in India

**Table 14.2** Global anthropogenic emission of GHGs (IPCC 2014)

| Sources | Emission (%) |
|---|---|
| Electricity and heat production (burning of fuels) | 25 |
| Industries (burning of fuels, chemical, metallurgical, and mineral transformation processes) | 21 |
| Agriculture, forestry, and other land use (cultivation of crops and livestock and deforestation) | 24 |
| Transportation (fossil fuel burning for all kinds of transport) | 14 |
| Buildings | 6 |
| Others | 10 |

**Fig. 14.1** Net $CO_2$ equivalent emission in India during 2007 (INCCA 2010)



(Fig. 14.1). CFCs (chlorofluorocarbons), HFCs (hydro-fluorocarbons) and PFCs (per-fluorocarbons) having very high global warming potential and lifespan are emitted only by human activities. CFCs are non-toxic, inert, and harmless gases in the lower atmosphere, but break down $O_3$ molecules in the stratosphere and thus contribute to $O_3$ depletion. The concentrations of CFCs decrease in response to the Montreal protocol.

## 14.4 Recent Temporal Trend of Major GHGs

Recent temporal variations in the $CO_2$ concentration showed a linear significant increase of 2.1 (CI, 2.01–2.2) ppm with distinct seasonal variations, whereas $CH_4$ and $N_2O$ showed linear increases of 6.1 (CI, 5.74–6.62) and 0.9 (CI, 0.89–0.9) ppb per year, respectively (Table 14.1 and Fig. 14.2). There are a clear and prominent pattern of variations in $CO_2$ and $CH_4$ concentrations during different months with least values in July, August, and September.

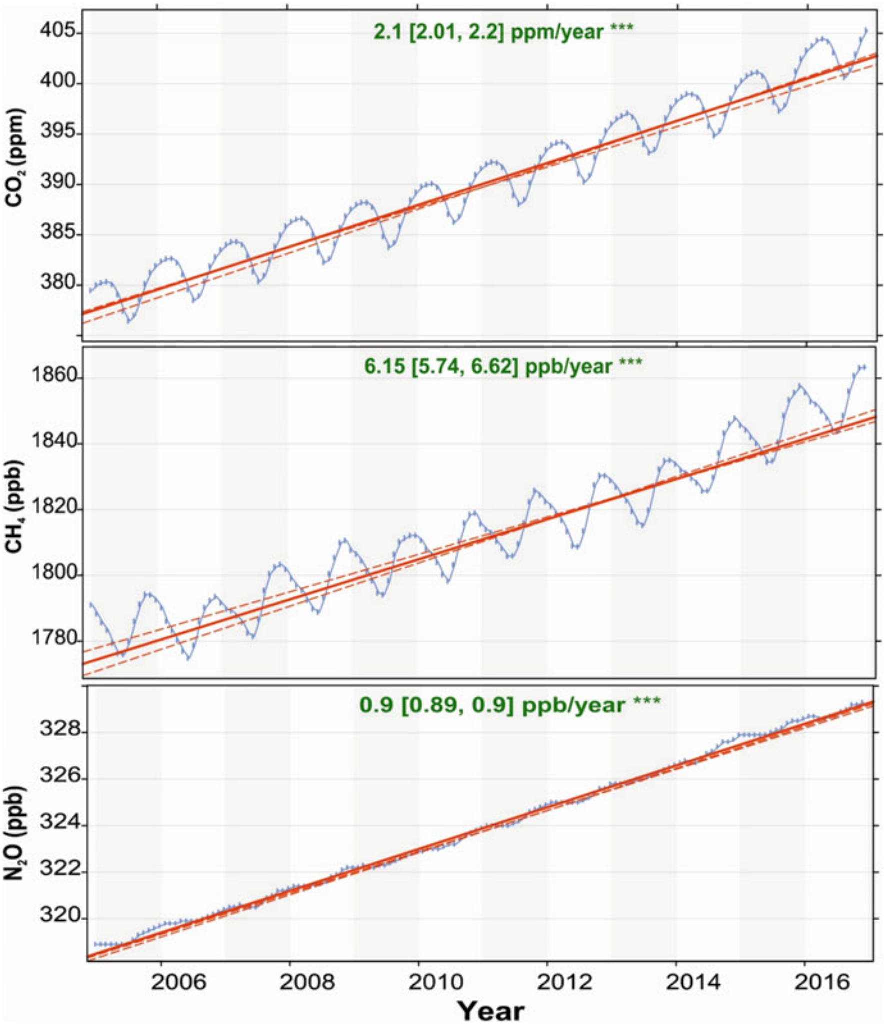


**Fig. 14.2** Temporal trends of increase in $CO_2$, $CH_4$, and $N_2O$ during 2005–2016

## 14.5 Greenhouse Gas Emission from Agriculture

Agriculture has occupied 179.7 M ha land in India and 1.5 billion ha globally (FAO 2003). Due to population pressure, the requirement for agricultural land continues to increase to fulfill the increasing demand for food. The contribution of agriculture in GHG emissions is increasing. Land-use, land cover change, and agricultural practices like tilling, fertilizer application, and mulching contributed about 24% (12 Gt $CO_2$-e) of total GHG emissions globally in 2010 (IPCC 2014). According to Scialabba and Müller-Lindenlauf (2010), global food production contributed almost one-third of total anthropogenic GHG emissions. In the United States, 9% contribution in GHGs was estimated from agriculture (USEPA 2016). In India, emission from agriculture is 334.41 million tons of $CO_2$ equivalent (INCCA 2010).

GHG emission from soil is due to microbial activity, root respiration, chemical decomposition processes, litter decomposition, heterotrophic respiration by soil fauna, oxidation of soil organic matter etc. The disintegration of carbon-based organic substrates emits $CO_2$. Root respiration utilizes intercellular and intracellular substrate molecules. The soil may act as a sink or source for GHGs depending upon the physicochemical properties of the soil and the local environment (Muñoz et al. 2010). The aerobic condition leads to the emission of $CO_2$, whereas anaerobic condition leads to $CH_4$ emission. The decomposition process also plays a major role in the carbon cycle and the process emits a significant amount of $CO_2$ and $CH_4$ (da Cunha-Santino et al. 2016). Decomposers break down organic materials in the plant and animal residues and the organic carbon present in organic materials gets converted into $CO_2$. In the tropical climate zone, $CO_2$ and $CH_4$ emissions are 14 tons of C $ha^{-1}$ $year^{-1}$ and 7.0 kg of C $ha^{-1}$ $year^{-1}$, respectively, from drained croplands (IPCC 2014). Rice cultivation is a potential anthropogenic source of GHG emissions. Developing countries are reported to contribute about 94% GHG emissions globally from rice cultivation during 2000–2010 and contribution of Asia was estimated to be about 90% (Tubiello et al. 2013).

$CO_2$ is although cycled in huge amounts but emitted in less amounts comparatively. It is emitted by deforestation, land-use change, fossil fuel burning, respiration, etc. Reay and Grace (2007) found that autotrophic respiration emits 60 Pg C $year^{-1}$ to the atmosphere and about the same amount is emitted by heterotrophic respiration. Water-filled pore space (WFPS) also emits a considerable amount of $CO_2$. In grassland soil, 20 to 40% WFPS emits high $CO_2$ (Schaufler et al. 2010).

Anaerobic respiration is an important source of $CH_4$ emission from soil. Wetlands are the major site of $CH_4$ emission, although they occupy a little global surface area. The rate of $CH_4$ emission has more than doubled over the last 25 years due to human activities (IPCC 2007). It is estimated that rice fields contribute about 11% of the total $CH_4$ emission globally (IPCC 2014). In 2007, 3327 thousand tons of $CH_4$ emission was reported from rice field, which contributed 24% of total emission from the agricultural sector in India (INCCA 2010). The live-stock management contributes maximally to total methane (73%) emission from agricultural sector (INCCA 2010) (Fig. 14.3).

In plants, methane is emitted through aerenchyma and micropores located in the leaves. As plants develop during their growing cycle, aerenchyma contribution is more than 90% in $CH_4$ diffusion to the atmosphere. While ebullition and diffusion through flooded water are less significant but ebullition provides major contribution during early stages (Le Mer and Roger 2001; Gupta et al. 2016). The diffusion rate is higher in the air than water so gas exchange through diffusion is very slow under waterlogged conditions. Bouwman (1990) reported that through aerenchyma, $CH_4$ diffusion varies on a daily basis due to the effects of environmental factors on the

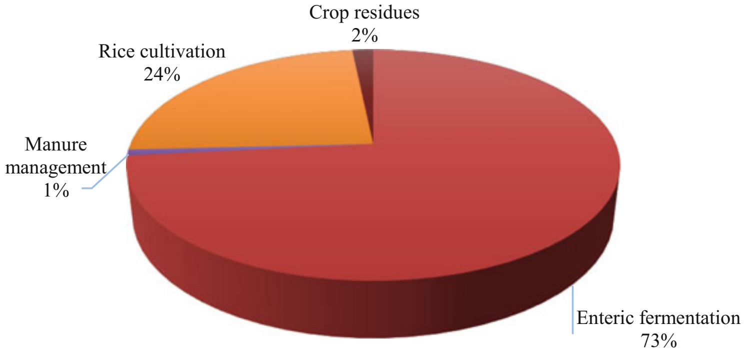


**Fig. 14.3** Methane emission from agriculture sector in India during 2007 (INCCA 2010)

rate of photosynthesis/respiration. Biochemical reactions involved in methanogenesis are following:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$CH_3COOH \rightarrow CH_4 + CO_2$$

This involves various substrates mainly acetic acid, $CO_2$, and other organic compounds, involving a number of coenzymes and cofactors.

Due to the highest global warming potential among the three major GHGs, $N_2O$ has a high impact on the environment despite being in very low concentration. The agriculture system potentially emits $N_2O$ due to fertilizer application and denitrification processes. The denitrification process is the conversion of $NO_3^-$ to $N_2$, which includes many intermediates as shown below. $N_2O$ is one of the intermediates that escape in the atmosphere. In some cases, $NO_3^-$ is converted to ammonia through the process of dissimilatory nitrate reduction to ammonium (DNRA) and $N_2O$ is released into the environment. Agricultural activities contribute about 77% of total $N_2O$ emission in U.S. (USEPA 2016). It is emitted under both aerobic and anaerobic conditions. Urea and ammonium sulfate are major fertilizers used in rice and other crop fields and are primary sources for $N_2O$ emission.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2.$$

DNRA: $$NO_3^- + 4H_2 + 2H^+ \overset{\overset{N_2O}{\uparrow}}{\rightarrow} NH_4^+ + 3H_2O.$$

## 14.6 Factors Affecting GHG Emissions from Soil

Different agricultural practices affect the pool of soil organic carbon and in turn, affect the emission of GHGs. Not only the management practices during agriculture but also the local environmental factors influence the emission of GHGs from the soil (Fig. 14.4). Effects of different factors on emissions of GHGs are described below.

### 14.6.1 Agricultural Practices Affecting GHG Emissions

Different agricultural practices that are utilized by the farmers to enhance the productivity like tilling, use of fertilizers, etc. may modify the GHG emissions significantly. Roles of agricultural practices in modifying GHG emissions are discussed below and the results are summarized in Table 14.3.

#### 14.6.1.1 Fertilizer Application

To increase the productivity of crops, the use of fertilizers has risen dramatically. Both organic and inorganic chemical fertilizers affect GHG emissions but organic fertilizers having carbon emit comparatively high $CH_4$. Mulching and organic manure application increase $CH_4$ emission (Ma et al. 2007). Emission of $N_2O$ from soil is largely dependent upon nitrogen availability in the soil (Pandey et al. 2012; Pathak et al. 2010). Application of nitrogen fertilizers greatly enhanced $N_2O$ flux from the rice-wheat system (Pandey et al. 2012) and fluxes of both $N_2O$ and $CO_2$ from sugarcane field (Pandey and Agrawal 2015). Nitrous oxide fluxes increased linearly with the nitrogenous fertilizer application rate (Gregorich et al. 2005), which may be due to increase in the substrate for microbes (Pandey et al. 2012). Organic manure amendment sites showed higher GHG fluxes (Thangarajan et al. 2013). Application of nitrogen fertilizer increases the plant growth and the carbon supply to methanogens, which leads to more production and transport of $CH_4$ to the atmosphere. According to a report of INCCA (2010), 0.115 million tons of $CH_4$ and 0.07 thousand tons of $N_2O$ were emitted in India due to manure addition mainly using dung cakes.

Chemical fertilizers like urea increase the emission of $CH_4$ by increasing the plant biomass and productivity thus providing more organic substrates to methanogens for biomass decomposition and root exudation (Jia et al. 2001). In contrast, nitrogen fertilizer application was reported to decrease $CH_4$ emission by 35–50% in paddy fields (Yao et al. 2012). This may be due to rhizospheric development, which may have improved oxygen transport and increment in methanotrophic activity (Bodelier et al. 2000). Chemical fertilizers affect the microbial community leading to low or high emission. Urea produces $CO_2$ after conversion into bicarbonate ($HCO_3^-$) in the presence of water. The mode of fertilizer application and the type of fertilizer have significant effects on $CH_4$ and $N_2O$ emission (Yao et al. 2017). When anhydrous ammonia is injected into the soil in the gaseous form, it produces a highly alkaline zone with a high ammonium concentration, which leads to high $N_2O$ emission

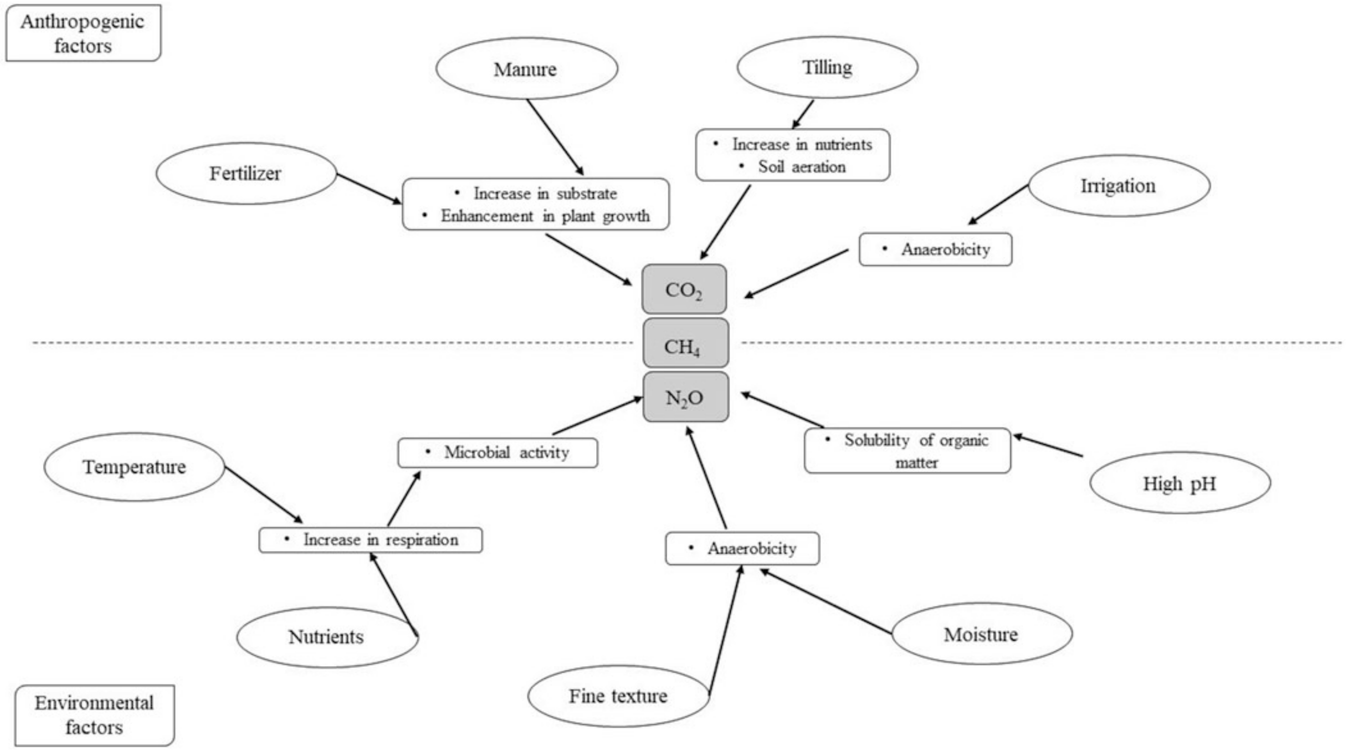


**Fig. 14.4** Factors influencing greenhouse gas emissions from agricultural land

**Table 14.3** GHG emissions under different agricultural practices

| S. no. | Agricultural practices | Location of sites | Study period | GHG emissions | | | | Inferences | References |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Practices | $CO_2$ | $CH_4$ | $N_2O$ | | |
| 1. | Crop rotation | Thailand | 2010–2011 | RF | 43,260 kg $ha^{-1}$ | 185.84 | 5.77 | Corn and sweet sorghum as alternative crops to rice for emission reduction | Cha-un et al. (2017) |
| | | | | RR | 89,810 | 893.49 | 1.54 | | |
| | | | | RC | 63,840 | 198.87 | 7.77 | | |
| | | | | RS | 82,120 | 165.72 | 8.93 | | |
| 2. | Fertilizer application | China | 2013–2014 | PNN | – | 83.6 kg $ha^{-1}$ | 0.14 | Deep placement of urea in underground cover production system reduced emission without affecting yield | Yao et al. (2017) |
| | | | | PBP | – | 79.9 | 1.91 | | |
| | | | | GNN | – | 21.8 | 0.14 | | |
| | | | | GBP | – | 13.0 | 5.09 | | |
| | | | | GDP | – | 13.7 | 2.71 | | |
| 3. | Fertilizer application | China | 2006 | C | – | 622 kg $ha^{-1}$ $year^{-1}$ | 1.15 | Inorganic fertilizer and long-term fertilizer application increase GHG emission | Shang et al. (2011) |
| | | | | NP | – | 685 | 2.46 | | |
| | | | | NK | – | 650 | 2.97 | | |
| | | | | NPK | – | 794 | 1.93 | | |
| | | | | FOM | – | 1174 | 4.11 | | |
| | | | | ROM | – | 1081 | 3.37 | | |

(continued)

**Table 14.3** (continued)

| S. no. | Agricultural practices | Location of sites | Study period | GHG emissions | | | | Inferences | References |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Practices | $CO_2$ | $CH_4$ | $N_2O$ | | |
| 4. | K fertilizer application | India | 2002 | C | – | 125.34 kg $ha^{-1}$ | – | K application significantly reduced $CH_4$ emission and enhance rain fed rice yield | Babu et al. (2006) |
| | | | | $K_{30}$ | – | 63.81 | – | | |
| | | | | $K_{60}$ | – | 82.03 | – | | |
| | | | | $K_{120}$ | – | 40.95 | – | | |
| 5. | N fertilizer, residue and tillage | India | 2013–2015 | CT-R + 100N | 321 kg $ha^{-1}$ | 380 g $ha^{-1}$ | – | GWP reduced significantly under no-tillage, surface residue application and real-time N management through Greenseeker | Nath et al. (2017) |
| | | | | CT + R + 100N | 318 | 360 | – | | |
| | | | | CT + R + 75N + GS | 301 | 330 | – | | |
| | | | | ZT-R + 100N | 289 | 440 | – | | |
| | | | | ZT + R + 100N | 280 | 420 | – | | |
| | | | | ZT + R + 75N + GS | 266 | 390 | – | | |
| 6. | Urea application | India | 2004–2005 | T1 | 1092 kg $ha^{-1}$ | 31.0 | 0.285 | Leaf color chart-based urea application reduced global warming potential of rice cultivation under rice-wheat system | Bhatia et al. (2012) |
| | | | | T2 | 1483 | 35.6 | 0.788 | | |
| | | | | T3 | 1348 | 32.1 | 0.665 | | |
| | | | | T4 | 1431 | 34.1 | 0.735 | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 7. | Irrigation | Denmark | 2014 | | GWP | | Islam et al. (2018) |
| | | | | CF<br>SM<br>LM<br>SE + SM<br>SE + LM<br>LE + SM<br>LE + LM | 11,598 mg g soil$^{-1}$<br>6385<br>6777<br>4546<br>3250<br>1638<br>1443 | Early season drainage in rice reduced emissions | |
| 8. | Irrigation | Italy | 2012–2013 | WFL<br>DFL<br>DIR | 9.65 $CO_2$ eq ha$^{-1}$ year$^{-1}$<br>4.26<br>1.62 | Dry seeding treatment and intermittent irrigation reduced emissions | Peyron et al. (2016) |

*RF* fallow-rice, *RR* rice–rice, *RC* corn-rice, and *RS* sweet sorghum-rice; *PNN* no N fertilization in the traditional paddy rice production system, *PBP* broadcast placement of urea at a common rate of 150 kg N ha$^{-1}$ in the traditional paddy rice production system, *GNN* no N fertilization in the ground cover rice production system, *GBP* broadcast placement of urea at a common rate of 150 kg N ha$^{-1}$ in the ground cover rice production system, *GDP* deep-point placement of urea at a common rate of 150 kg N ha$^{-1}$ in the ground cover rice production system; *NP* nitrogen and phosphorus fertilizer, *NK* nitrogen and potassium fertilizer, *NPK* balanced inorganic fertilizer, *FOM and ROM* combined inorganic/organic fertilizers at full and reduced rate respectively and *C* no fertilizer application; *C* control, *K* potassium application in kg ha$^{-1}$, values indicate the amount of potassium fertilizer; *CT* conventional tillage, *ZT* zero tillage; *R* residue application, *100N* 100% required N, *75N* 75% N, *GS* additional N based on need according to Greenseeker™, positive and negative signs showing presence and absence of particulars; *T1* unfertilized control, *T2* conventional urea application (120 kg N ha$^{-1}$), *T2* leaf chart color (LCC) based urea application (30 kg N ha$^{-1}$ at LCC $\leq$ 4, no basal N), *T4* LCC based urea application (30 kg N ha$^{-1}$ at LCC $\leq$ 5, no basal N); *CF* continuous flooding, *SM* short mid-season drainage, *LM* long mid-season drainage, *SE* short early-season drainage, *LE* long early-season drainage, *WFL* water seeding and continuous flooding, *DFL* dry seeding with flooding at tillering stage, and *DIR* dry seeding with intermittent irrigation

(Bouwman 1996). $KNO_3$ application in soil emits three to eight times higher $N_2O$ than ammoniacal fertilizer (Abbasi and Adams 2000). When the fertilizer is applied in dry weather, then the emission of $N_2O$ is small compared to humid conditions (Zhang and Han 2008). Ma et al. (2007) observed that $CH_4$ emission is enhanced when a low-nitrogen fertilizer is applied, but when high rates of fertilizer are applied, emission decreased. Deep placement of urea decreased $CH_4$ and $N_2O$ emission in the rice field and also increased the rice yield (Yao et al. 2017).

#### 14.6.1.2 Use of Pesticides

Excessive and improper use of pesticides can be a major environmental hazard and also a human health concern. Pesticide application usually decreases $CH_4$ emission. Mohanty et al. (2001) reported 20% decrease in $CH_4$ emission when herbicide Butachlor was applied in direct seeded flooded rice field. Glyphosate and Propanil inhibit $N_2O$ production in laboratory condition under organic amendment (Kyaw and Toyota 2007). Das et al. (2011) reported that when two herbicides Bensulfuron methyl and Pretilachlor were applied separately, $CH_4$ and $N_2O$ emissions decreased, but when applied in combination, the emissions increased. The population of methanogenic and methanotrophic bacteria is influenced significantly by herbicides (Das et al. 2011).

#### 14.6.1.3 Soil Cover

Plant residues are used as a soil cover to reduce erosion, maintain soil moisture, and increase soil quality, but they contribute to GHG emissions. Plant residues get colonized by decomposers that produce simpler, low molecular weight compounds from complex compounds such as cellulose, hemicellulose, lignin, proteins, etc. which may produce or consume GHGs. According to Muhammad et al. (2011) plant residues like sugarcane trash, maize and sorghum straw, cotton residues, and lucerne increased the cumulative $N_2O$ emission by about a factor of 3. In the crop rotation system, incorporation of maize and wheat straw increases $N_2O$ emission by increasing the temperature of soil due to its heat retention capacity (Liu et al. 2011). Baggs et al. (2000) observed increased $N_2O$ emission for about 2 weeks after the incorporation of crop residues. Biochemical composition of residue also affects the emission due to the availability of nutrients (Gomes et al. 2009). $N_2O$ emission is higher where soil receives residues with a low C/N ratio (Toma and Hatano 2007). Gupta et al. (2016) have also reported that a high C/N ratio in the rice residue reduces $N_2O$ emission by 12.8% and 11.1% in 2 consecutive years. Further high C/N ratio in residue increases the rate of immobilization, thus lowering the substrate availability for nitrification and denitrification. Kallenbach et al. (2010) reported that nonlegume cover crops like winter cereals reduced $N_2O$ emission possibly due to their deep roots taking up N more efficiently than legumes.

#### 14.6.1.4 Tillage

Tillage breaks down soil aggregates, help in mixing soil and organic particles, and improve infiltration and water-holding capacity of the soil. Tilling of the crop field influences the emission of GHGs due to disturbances in the soil, addition of residues in soil, and also decomposition of soil organic matter leading to changes in the properties of soil. According to Nath et al. (2017), higher emission of $CO_2$ occurs due to weak stabilization as tilling causes oxidation of carbon. Gaseous transport is affected under no tilling condition due to soil compactness and low mobility of gases along the soil profile. Almaraz et al. (2009) reported that soil with no tilling acts as a sink for $N_2O$ due to consumption in soil layer. In contrast, Liu et al. (2006) and Nath et al. (2017) reported greater $N_2O$ emission under no-tillage condition compared to conventional tilling. Gupta et al. (2016) found that $N_2O$ emission was 8–11% higher under zero tillage in wheat-cropped soil than conventional tillage. Tilling causes aeration of soil and denitrifiers are not able to produce $N_2O$ under aerobic conditions. $CH_4$ and $N_2O$ emissions are reduced, while $CO_2$ emission increased when tillage frequency is reduced in rice-wheat cropping system (Pandey et al. 2012). Conservation tillage and no-tillage lead to an increase in the carbon storage of soil. Minimum tillage resulted in highest $N_2O$ emission after surface application of the nitrogen fertilizer (Bouwman 1996).

#### 14.6.1.5 Water Management

Flooding or water-logging conditions lead to $CH_4$ emission. Rice is grown usually under submerged conditions. Nishiwaki et al. (2015) reported that highest emission of $CH_4$ occurs from the continuous-flooding treatment and small emission from low-water-level treatment. It was also reported that GHG fluxes were larger from rice growing fields than bare areas. Reduced timing for draining may decrease $CH_4$ emission. Rice field acted as a $CO_2$ sink and was not affected by variation in water treatments, while $N_2O$ fluxes did not show any specific pattern (Nishiwaki et al. 2015). Water management practices that limit $CH_4$ production, generally enhance $N_2O$ production (Zou et al. 2005). Intermittent irrigation in paddy fields emits less $CH_4$ compared to permanent flooding conditions (Pathak et al. 2010; Peyron et al. 2016). Under wetting and drying conditions of rice-wheat system, $CH_4$ emission was reduced under drying period as aerobic conditions prevailed at that time leading to higher methanotrophic compared to methanogenic activity but $CH_4$ flux was higher under wet conditions (Gupta et al. 2016).

#### 14.6.1.6 Crop Commodity

Vegetable cultivation is the major contributor to GHG emissions and the emission is largely dependent on use of fertilizers, mulching, etc. (Tongwane et al. 2016). Among the cereal crops, maize and wheat emit significantly higher GHGs in South Africa followed by sugarcane (Tongwane et al. 2016). Among the legumes and oilseeds, soybeans, sunflower, and ground nut are reported as the highest emitter of GHGs (Tongwane et al. 2016). Similarly, potato, cabbage, and tomato from the vegetable group contribute significantly to GHG emissions. Jain et al. (2016) observed no particular variations in $CO_2$ emission in different crops, but reported higher $CO_2$ emission from *rabi* crops due to temperature variations. The emission of $N_2O$ was more from wheat and maize than rice crop that might be due to a high rate of aerobic decomposition. On application of N fertilizer, $N_2O$ emission was found to be the highest in the case of pulses as compared to cereals and oilseeds (Jain et al.

2016). Metanalysis done by Linquist et al. (2012) also showed that wheat cropping emitted higher $N_2O$ than rice, and maize led to highest emission among them. $CH_4$ emission was higher from rice field and wheat and maize acted sinks for $CH_4$. Even the crop rotation helped in reducing the emission as lower fertilizer application was done (Gao et al. 2014). Pandey and Agrawal (2015) compared the emission between pigeon pea and sugarcane and found that pigeon pea emitted higher $CO_2$ than sugarcane, while a little difference was observed in $N_2O$ emission and both the crops acted as sinks for $CH_4$. Leguminous crops emit less $N_2O$ as no N fertilizer application is needed and also help in carbon sequestration (Jensen et al. 2012). Crop rotation with corn and soybean is reported to reduce $N_2O$ emission and increase in the yield compared to continuous corn or soybean cropping systems (Behnke et al. 2018).

### 14.6.2 Environmental Factors Affecting GHG Emissions from the Soil

The GHGs from the soil are produced as a result of microbial processes and hence largely depend on temperature, water availability, pH, nutrient availability, soil type, texture, etc.

#### 14.6.2.1 Soil Temperature

Microbial metabolism usually increases with increasing temperature and thus high respiration leads to high $CO_2$ emission and decreases in the $O_2$ concentration, which may produce anaerobic conditions leading to $N_2O$ and $CH_4$ production. Tang et al. (2003) reported that $N_2O$ and $CO_2$ emissions increase exponentially with temperature. The temperature response of gas emissions from soil is expressed as the temperature sensitivity factor ($Q_{10}$ value). It is the rate of change in a chemical or biological system with a temperature change of 10 °C (Berglund et al. 2010) and with soil depth this tends to increase (Tang et al. 2003). Dalal and Allen (2008) estimated a $Q_{10}$ value of approximately 4 for $CH_4$ emission. Wu et al. (2010) reported increase in $CO_2$ emission from 5 to 15 °C temperature but emission got reduced significantly when it is changed to −10 °C, suggesting that the $CH_4$ oxidation rate is greatly influenced by warmer temperature. $N_2O$ emission increased exponentially with increasing temperature from 0 to 50 °C (Liu et al. 2011). These reports show that temperature has a significant effect on the fluxes of GHGs and mostly they are positively correlated. Due to an increase in temperature, soil respiration and denitrification processes increase leading to the enhanced flux of GHGs.

#### 14.6.2.2 Soil Moisture

Moisture content of the soil is an important controlling factor of the microbial activity and thus influencing emission of GHGs. Moisture content is usually associated with the soil type. $CH_4$ emission increases with increasing soil humidity as strict anaerobic condition is required for the production of $CH_4$ (Gao et al. 2014). Emission is stimulated after wetting of a dry land and drying and wetting cycles of the soil leading to rapid emission of GHGs due to the mineralization of soil organic matter (Birch Effect) (Birch 1958) leading to increase in microbial metabolism due to availability of easily decomposing material (Ludwig et al. 2001). Sponseller (2007) reported that emission increases suddenly after rainfall and then declines after a few days to the background level.

Emission of $N_2O$ is also significantly affected by the moisture content of the soil. As the moisture content increases, $N_2O$ emission also increases (Baggs et al. 2000) and emission greatly enhances after rainfall and irrigation (Liu et al. 2006). Water-filled pore spaces (WFPS) play an important role in emission as they affect denitrification and respiration processes. Gao et al. (2014) observed that soil with 60% water-filled pore spaces showed optimum emission, while the least emission was reported at less than 30% WFPS. This may be due to the reason that high water-filled pore spaces provide less space for air inside the soil thus maintaining the anaerobic conditions favorable for denitrification.

#### 14.6.2.3 Soil Type

Fine-textured soil like clayey shows more $N_2O$ emission than coarse-textured like sandy soil (Stevens and Laughlin 1998). Similar findings were reported by Tan et al. (2009) that soil management practices in clay loam soil and rain-enhanced $N_2O$ emission by four times than in sandy loam. This is because fine-textured soil provides more anaerobic sites in micropores for denitrifiers than in sandy soil. $CO_2$ emission is also higher in fine-textured soil (Dilustro et al. 2005).

#### 14.6.2.4 pH

Soil pH affects microbial activity by affecting their enzymatic activities. Denitrification process is slowed down under low pH as the enzyme nitrous oxide reductase is inhibited by low pH and in presence of $O_2$ (Chapuis-Lardy et al. 2007). Similarly, $CO_2$ emission is decreased under low pH. Čuhel et al. (2010) reported that $N_2O$ emission is highest at neutral and alkaline soil pH. $CH_4$ production by methanogens is very sensitive to pH and their activities are optimum under near neutral or slightly alkaline pH (Wang et al. 1993; Garcia et al. 2000). A slight change in pH changes the rate of $CH_4$ emission (Wang et al. 1993). Some of the methanogenic species can grow even at a lower pH of 5.8 (Garcia et al. 2000). Ye et al. (2012) have reported that an increase in pH enhances the emission of $CO_2$ and $CH_4$. This may be due to an increase in the fermentation process and availability of methanogenic substrates. The solubility of organic matter also increases with an increase in pH in wetland soil and as a result, the microbes produce more $CO_2$ (Grybos et al. 2009).

#### 14.6.2.5 Nutrients

When the soil is carbon-rich, relatively higher $N_2O$ emission occurs (Brentrup et al. 2000). Higher carbon in the soil induces the microbial activity and the available oxygen in the soil is also consumed due to active growth of the microbes, thus providing an anaerobic condition to the microbes and organic carbon for the process of denitrification. The relation of organic matter availability and $N_2O$ emission depends upon the anaerobic conditions led by the microbes (Stevens and Laughlin

1998). C/N ratio is also an important factor in determining the process of nitrification and denitrification as it decides the balance between immobilization and mineralization. Baggs et al. (2000) reported that $N_2O$ emission is significantly less when the soil was provided with straw having a high C/N ratio due to the immobilization process and higher $N_2O$ emission occurred when no straw or straw with low C/N ratio was applied.

#### 14.6.2.6 Salinity

Salinity is emerging as a major problem for agriculture. Mainly the arid and semi-arid regions are affected by salinity due to low rainfall. According to the report of FAO (http://www.fao.org/soils-portal/soil-management/management-of-some-problem-soils/salt-affected-soils/more-information-on-salt-affected-soils/en/), about 397 and 434 M ha of the land area in the world are affected by salinity and sodicity, respectively. Salinity is an important factor that limits plant growth and yield due to the limitation of organic matter present, high salt concentration in the soil and low osmotic potential of the salt solution. High salt concentrations in the soil also alter the physico-chemical and biological properties of the soil. Saline soils are characterized by >4 $\mathrm{dSm}^{-1}$ electrical conductivity, >15 exchangeable sodium percentage (ESP) or more than 13 sodium absorption ratio (SAR). Areas affected by salinity are expected to increase due to natural and anthropogenic activities such as irregular irrigation practices, weathering of salt containing rocks and precipitation.

Emissions of GHG are also influenced by salinity. There are contradictory opinions about the salinity and microbial activity. Pathak and Rao (1998) observed reduced microbial activity when the electrical conductance of the soil was high enough to cause osmotic stress. In contrast, Nelson et al. (1996) reported high microbial activity at high SAR. Salinity negatively affects GHG emissions in paddy field (Tang et al. 2016). Emission of methane is higher from fresh water habitats than from saline wetlands (Poffenbarger et al. 2011). The salt marsh present near the sea receives a great amount of sulfate and sulfate-reducing microbes, which decompose organic matter anaerobically grow abundantly. Methanogenesis is reduced due to sulfate reduction (Wang et al. 1996). Salt marshes act as sinks for atmospheric $CO_2$ and $CH_4$ (Weston et al. 2014).

## 14.7 Impacts of Enhanced Greenhouse Gas Emissions on Agriculture

Agriculture is affected by an increase in temperature, changes in precipitation pattern, flooding of coastal areas, soil salinization (IPCC 2014), and many indirect effects on crops such as loss of pollinators, pest infestations, etc. (Bale et al. 2002). Agricultural crops are affected by heat stress by various ways like the rate of photosynthesis is reduced, pollen production and viability are decreased, the rate of seed abortion is increased and reductions in grain weight and number occurred (Prasad et al. 2006). Bale et al. (2002) have reported that higher temperature during winters increases the rate of herbivory and winter survival of pests. Different crops responded differently to varying temperature and have different optimum temperatures (Sánchez et al. 2014). Schlenker and Roberts (2009) reported a reduction in yield of rainfed crops at 30 °C air temperature in the United States. High temperature also causes evaporation from soil and water leading to loss of crop water. Due to evaporation of water from the soil, salinity also increases in the soil. Lobell et al. (2011) estimated the reduction in maize yield by 1% for each 1 °C increase above a base temperature of 30 °C in the sub-Saharan African region. Likewise, in India annual loss of wheat crop is estimated to be about six million tons for each 1 °C rise in mean temperature (Kang and Banga 2013). The high temperature is reported to damage the reproductive stages in cereals, millets, oilseeds, and pulses (Prasad et al. 2017).

Increasing temperature is reported to increase the biological invasion that competes for nutrients and space and thus negatively affects the diversity of native species and crop plants (Fuhrer 2003). An increase in the $CO_2$ concentration increases the growth of $C_4$ weeds that affect the growth of $C_3$ crops (Fuhrer 2003). Ziska (2000) reported that the presence of weeds neutralizes the positive effect of enhanced $CO_2$ on soybeans. Weed biomass is reported to increase under elevated $CO_2$ level by Ziska (2000).

The tropospheric ozone ($O_3$) concentration increases with an increase in the temperature especially when the temperature reaches above 32 °C. Tropospheric $O_3$ is known to adversely affect the rate of photosynthesis, plant growth, reproduction and yield throughout the world (Tiwari and Agrawal 2018).

Increases in $CO_2$ have significant effects on plant growth, leaf area, and yield (Mishra and Agrawal 2014). $CO_2$ enrichment also affects the nutritional quality of the crop plants. Myers et al. (2014) observed reductions of 7–15% in protein content in rice, wheat, barley, and potato tubers, but very little change in $C_3$ legumes and $C_4$ crops. Jena et al. (2018) found that $CO_2$ concentration at 490 ± 30 ppm reduced the grain yield by 10–13% in high yielding rice cultivar although the biomass increased by 27–29%. Grain quality and nutrient allocation were also negatively affected under elevated $CO_2$, whereas the low yielding cultivar of rice showed positive effects (Jena et al. 2018). Nutrient requirements of plants are increased under the elevated $CO_2$ level (Jena et al. 2018), so excess use of fertilizers will occur. Also, the higher $CO_2$ level increased the K uptake from soil but translocation of K toward storage was found to be reduced by Jena et al. (2018). Increasing the $CO_2$ concentration will increase the growth of both wanted and unwanted species. Meta-analysis study of Liu et al. (2018) observed that elevated $CO_2$ increases the flux of $CO_2$, $CH_4$, and $N_2O$ by increasing the C and N pools in soil. High atmospheric $CO_2$ increased the flux of $CO_2$ by 24%, $CH_4$ by 34% in rice fields, and 12% from wetlands, while $N_2O$ flux did not change significantly.

## 14.8 GHG Mitigation Strategies for Agriculture

As the temperature increases during summer, the equatorial regions get hotter resulting in damaging effects on the ecosystems. This necessitates the need to reduce the emission or trap the gases from the atmosphere to lessen the effects of GHGs.

Mitigation strategies involve two processes i.e. to reduce the emission and to increase the carbon sink in form of soil organic matter (SOM). Mitigation from agricultural soil involves the processes that enhance the soil carbon content, make use of applied nitrogen fertilizers efficiently by the plants, cause less soil disturbance, enhance photosynthesis, etc. The most effective mitigation measure is the amendment of organic matter to the soil. Following are the mitigation measures that are effective in reducing GHG emissions.

### 14.8.1 Reducing Tillage Frequency

It has been reported that no-till condition or reduced tilling leads to low flux of GHGs from soil as compared to conventional tillage (Gregorich et al. 2005; Nath et al. 2017; Pandey et al. 2012). Tilling of soil results in loosening and shattering of aggregates and thus soil organic matter decomposition and soil respiration are enhanced. The loss of soil water and disturbance in the microbial community lead to higher fluxes of GHGs under tilling, but no tilling also reduce the productivity of the soil (Soane et al. 2012). Under no tillage conditions, methanotrophic activity is more favored than conventional tillage leading to a reduction in $CH_4$ emission (Pandey et al. 2012).

### 14.8.2 Biochar Amendment

Application of biochar obtained from pyrolysis of straw and other crop residues is found to be an effective measure to enhance soil organic carbon (SOC) to improve the soil quality and to increase the plant productivity (Sohi et al. 2010). Zhang et al. (2010) reported 40–51% and 21–28% reductions in $N_2O$ emission with and without N fertilizer application, respectively, whereas the $CH_4$ flux was increased after wheat straw biochar amendment. Karhu et al. (2011) reported reduced fluxes of $CO_2$, $CH_4$, and $N_2O$ from an agricultural field after biochar application. Although biochar cannot be always used for the mitigation of GHGs, enhanced emission has also been reported on biochar amendment (Junna et al. 2014). The effects of biochar depend on many factors like biochar properties, application rates, soil texture, constituents of the soil, and their interactions (Cayuela et al. 2014).

### 14.8.3 Agronomic Practices

Improved crop varieties, deeply rooted plants, and better management of residues reduce GHG emissions (Smith et al. 2008). Different agronomic practices that enhance the plant productivity, high growth rate and higher biomass lead to increase in soil organic carbon (Abbas et al. 2017). The cover crops, catch crops, and crop rotation with leguminous crops are reported to provide carbon to the soil (Freibauer et al. 2004; Smith et al. 2008). Application of straw is reported to reduce $N_2O$

emission (Ma et al. 2007). Bare fallow land also causes more GHG fluxes (Freibauer et al. 2004). SOC in the soil is enhanced by high plant biodiversity, which also improves the soil structure. Organic polymers produced by soil biota help in formation and stabilization of aggregates (Lal 2004). Soil erosion decreases SOC. Nutrient cycling, biological nitrogen fixation, and other agro-ecological processes can be used to reduce GHG emissions (Thomson et al. 2012). Agroforestry results in a higher quantity of SOC in the deeper layer of soil as compared to crop cultivation. Soil microbial diversity enhanced due to tree plantation, which caused a positive effect on soil carbon sequestration (Abbas et al. 2017). In rice-wheat cropping system, application of neem oil coated urea, intermittent irrigation of rice crop, and no-tillage before wheat crop reduce the global warming potential (GWP) of the system (Gupta et al. 2016). Direct seeded rice reduced the GHG emissions effectively compared to transplanted rice (Gupta et al. 2016; Peyron et al. 2016). The ground cover rice production system is an effective measure to reduce GHG emissions as compared to the conventional rice production system (Yao et al. 2017).

### 14.8.4 Efficient Fertilizer Uses and Nutrient Management

Nutrient management is important to sequester carbon in the soil especially in the form of manure and compost than as an inorganic fertilizer. Fertilizers applied are not used by the plants effectively. Neem oil-coated urea has been reported to effectively reduce $N_2O$ and $CH_4$ emissions as neem oil inhibits the nitrification process and enhances the population of methanotrophs (Gupta et al. 2016). Real-time N management techniques like leaf color chart (Bhatia et al. 2012) and greenseeker (Nath et al. 2017) based N application are found to be effective in reducing the emission as well as to enhance the nitrogen use efficiency. Leaf color chart-based urea application not only reduced GWP of rice-wheat cropping system but also increased the yield (Bhatia et al. 2012). Leguminous crops and organic manure can be used to enhance the productivity in place of inorganic N fertilizers, which enhance the GHG flux (Mosier et al. 2002). Manure application for a longer time strengthened the SOC pool and improved aggregates for a longer period (Thomson et al. 2012). Fertilizer, when applied in depth of the soil profile, leads to low emission (Liu et al. 2006; Yao et al. 2017). By using nitrification inhibitor technology, avoiding unnecessary external inputs to the soil, increasing soil pH by using lime to reduce denitrification, the fluxes of $N_2O$ can be reduced (Thomson et al. 2012).

### 14.8.5 Irrigation Management

Irrigation management also influences GHG emission mainly in rice field. In drought-prone areas, proper water management practices enhance SOC by increasing the biomass (Lal 2004). Islam et al. (2018) observed about 90% reduction in $CH_4$ emission when practising early season drainage as compared to conventional flooding, while $N_2O$ emission was higher. Emission from soil is significantly reduced when there is drought-like condition and the soil acts as a sink for $N_2O$ (Goldberg and Gebauer 2009). Irrigation enhanced soil organic matter in the dry areas (Denef et al. 2008). The practices that increase SOC can decrease GHG emissions.

## 14.9 Conclusion

The agricultural sector directly or indirectly emits a significant proportion of GHGs and thus contributes to climate changes. Emissions of GHGs from soil mainly $CO_2$, $CH_4$, and $N_2O$ are influenced by many biological and abiological factors acting simultaneously in nature. Excessive use of chemicals, tilling of fields, improper irrigation, etc., enhance GHG emissions. Rice fields are a major contributor to $CH_4$ emission. Wetting and drying cycles of soil emit a significant proportion of $N_2O$. High temperature provides favorable conditions for GHG emissions likewise high moisture content in soil and fine-textured soil maintain anaerobic conditions and thus emit comparatively higher GHGs. GHG emissions are low at high pH as well as low salinity. Nutrient availability enhances $N_2O$ emission depending upon anaerobicity, C/N ratio, and active growth of microbes. Several factors influence the soil to act as a source or a sink for GHGs. Increased GHGs in the atmosphere affect the plant growth positively as well as negatively. A high $CO_2$ concentration increases the productivity of plant by increasing the photosynthetic rate and reducing transpiration, whereas the nutritional value is deteriorated. Different mitigation strategies can be adapted to reduce the GHG emissions from agricultural lands like reduced tilling, periodic irrigation, proper use of fertilizers, better crop varieties, and other agronomic practices depending upon the crop type and local environmental conditions.

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