Chapter 12
Pesticide Contamination: Environmental Problems and Remediation Strategies

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Abstract Pesticides are the chemicals used in the control of weeds and pests. The larger inputs of pesticides and fertilisers contaminate food commodities with trace amounts of chemical pesticides and its invasion in crops causes diseases, which is a growing source of concern for the universal population and environment in today's world. The extensive utilisation of pesticides possibly enhances their accumulation in the agricultural fields and environmental components, such as enlarged farms, field sizes, loss of landscape elements etc. Nevertheless, their low biodegradability has classified these chemical substances as a persistent toxic element. Furthermore, organo-chlorine pesticides have caused multiple problems of health hazards, such as acute and chronic effects including developmental effects and neurological disruptors in humans and animals. The biological stability of pesticides and the higher content of lipophilicity in food products create a significant effect on the physical condition of human beings and animals. As the bio-accumulation and bio-magnification of lethal pesticides are the main cause of the loss of plants, microbes and animal biodiversity, therefore, microbially based bioremediation of toxic pollutants from the polluted sites has been proposed to be a safe and sustainable means of decontaminating the environment. In this communication, we have tried to explain the source of environmental pollution by pesticides, its hazardous effects on living beings and remediation strategies.

Keywords Fertilisers · Pesticide · Bioremediation technologies · Composting

1 Introduction

Environmental exposure to toxic chemicals such as pesticides is a significant health risk to humans and other animals (Azmi et al. 2006; Kiefer and Firestone 2007; Rothlein et al. 2006; Singh et al. 2011). Use of organochlorine pesticides (OCPs) to

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control weeds creates resistance to agricultural pests and vector-borne diseases (Abhilash and Singh 2009). Degradation of dichlorodiphenyltrichloroethane (DDT) in soil is estimated to range from 4 to 30 years, whereas some other chlorinated OCPs may remain stable for many years after their use (Afful et al. 2010). Because of their inability to break down in the environment, their degradation is restricted in physical, chemical, biological and microbiological ways (Afful et al. 2010; Darko and Acquaah 2007; NCEH 2005; Swackhamer and Hites 1988; Kumar and Singh 2017). As they are fat-soluble components, they are able to bioaccumulate inside the lipid components of biota including fatty tissues, breast milk and blood within the food chain. As a result, humans and animals are exposed to the harmful effects of these micro-pollutants by eating foods in contact with contaminated soil or water (Belta et al. 2006; Raposo and Re-Poppi 2007; Mishra and Bharagava 2016). These pesticides are also highly toxic to most aquatic life and cause serious diseases in humans and animals. (Aiyesanmi and Idowu 2012) and soil microflora (Megharaj 2002). To tackle these environmental issues, different physico-chemical methods such as land-filling, incineration, composting or burning and chemical amendments have been used to remove pesticide contamination from the environment over the last few decades (Kempa 1997; Wehtje et al. 2000).

Using a broad range of chemicals to destroy pests is an essential aspect of agricultural practice in both developed and developing nations. This has increased crop production and decreased post-harvest losses. However, the extended use of several pesticides expectedly results in residues in foods and caused a worldwide issue over the potential adverse effects of these chemicals on the environment and human health. It is clear that the chance of exposure to pesticides is maximal amongst farm workers. Drinking water and food crops are also contaminated by pesticides, especially fruits and vegetables, which received the largest dosages of pesticides, and are therefore probably serious health hazards to consumers (Pimentel et al. 1992). The pesticides currently used, include a large mixture of chemical compounds, which show great differences in their mode of action, absorbance by the body, metabolism, removal from the body, and toxic effect on humans and other living organisms. Some pesticides show a high acute toxicity, but when they come in contact with the body they are freely metabolised and eliminated, but some others that show lower acute toxicity, and have strong inclination to assemble in the body.

Adverse effects may not only be caused by the critical ingredients and related impurities, but also by solvents, emulsifiers, carriers and other constituents of the formulated products. When lower costs, increased levels of environmental protection, and improved effectiveness are considered, then modern technologies such as bioremediation come into action, which can be more commercial and provide more effective clean-up than recognised treatment technologies (Rigas et al. 2005; Singh and Seneviratne 2017). Presently, the bioremediation tools, particularly microbial-based technologies have been proposed to be safe and sustainable means of decontaminating the toxic pollutants from the polluted sites and environment. Therefore, the present communication explains the various sources of pesticide pollution, its hazardous effects on living beings and how they can be removed from the contaminated sites.

2 Classification of Pesticides

The pesticides are those elements that are used globally as a fungicide, insecticides, herbicide molluscicides, nematicides, rodenticides and plant growth regulators, to control pests, weeds and diseases in crops and for the healthcare of human beings and animals. Millions of tons of pesticides are used every 12 months globally (Pimentel 2009), large amounts of which reach non-agricultural habitats by means of aerial drift, run-off, overspray or endangering organisms living in these regions (Giesy et al. 2000; Lehman and Williams 2010). Pesticides have an effect on behaviour, physiology, development, and ultimately on the survival and reproductive success of non-target organisms through direct toxicity, by means of disrupting endocrine functions and by exerting teratogenic and immune-toxic consequences (Hoffman 2003).

Pesticides are very handy and beneficial agents capable of preventing losses of crops and diseases in humans. Pesticides can be classified as destroying, repelling and mitigating agents. Insects and pests are getting immune to the commercial pesticides owing to over-usage. Recently, pesticides have been developed that target multiple species (Speck-Planche et al. 2012). Nowadays, chemical pesticides and insecticides are becoming a dominant agent for eliminating pests. When these chemical pesticides are used in a combination with an effective natural enemy, then that results in enhanced integrated pest management and acts as a comprehensive prophylactic and remedial treatment (Gentz et al. 2010). At the population level, the effects of pesticides depend on exposure and toxicity, and on different factors such as life history, characteristics, the timing of application, population structure and landscape structure (Schmolke et al. 2010). Nerve targets of insects that are known for the neuron-damaging insecticides include acetylcholinesterase for organophosphates and methyl carbamates, nicotinic acetylcholine receptors for neonicotinoids, gamma-aminobutyric acid receptor channel for polychlorocyclohexanes and fiproles and voltage-gated sodium channels for pyrethroids and DDT (Casida and Durkin 2013). It is an observation that the use of neonicotinoid pesticides is increasing. These pesticides are associated with different types of toxicities (Van Djik 2010).

Worldwide, pesticides are divided into different categories depending upon their target. Some of these categories include herbicides, insecticides, fungicides, rodenticides, molluscicides, nematicides and plant growth regulators. Non-regulated use of pesticides has had disastrous consequences for the environment. Serious concerns about human health and biodiversity are rising owing to the overuse of pesticides (Agrawal et al. 2010). Pesticides are considered to be more water soluble, heat-stable and polar, which makes it very difficult to reduce their lethal nature. Pesticides are not only toxic to people related to agriculture, but they also cause toxicity in industries and areas where pesticides are frequently used. Depending upon the target species, pesticides can cause toxicities in natural flora, natural fauna and aquatic life (Rashid et al. 2010).

3 Good Agricultural Practices and Management of Pesticide Residues

- Keep an inventory of all chemicals. Store all chemicals in their original containers. Never store herbicides with other pesticides.
- Always use only recommended pesticides at the specified doses and frequency and at specific times. Never use banned pesticides.
- Education and training should be provided for pesticide application. The improper use or misuse through lack of understanding creates residue problems.
- Unused pesticide solution and washings generated by cleaning spray pumps contain pesticide residue. Dispose of them properly to avoid pollution.
- An integrated pest management system should be used.
- Use safe pesticides that help in conserving predators/parasites.
- Strictly follow the prescribed waiting period before harvesting.
- Maintain healthy soil with compost and mulch to avoid pest problems.
- Vegetables and fruits should be thoroughly washed with clean water.
- Reduce spray drift in orchards by using lower pressures, larger nozzles and less volatile pesticides.
- Proper precautions must be taken for the control of household insects/stored grain pests.
- Use botanicals/microbial insecticides for the control of various crop pests.
- Get detailed information from the authorised people before mixing various pesticides and purchase pesticides only from authorised dealers.
- Always read the product description carefully.

4 Production and Usage of Pesticides in India

In 1952, pesticide production started in India. The first plant was established near Calcutta to produce benzene hexachloride. After establishment, pesticide production yield has been showing steady increment for example in 1958, a total of 5000 metric tons of technical-grade pesticide were produced which had become 102,240 metric tons by 1998. After China, India is the second largest producer of pesticides in Asia, whereas it is 12th in the global ranking (Mathur 1999). In India, 45% of pesticides are only used for cotton crops followed by paddy crops. Insecticides are mainly used in India rather than fungicides and herbicides. Andhra Pradesh is a major pesticide consumer state in India. India stands at the lowest rank in the world's per hectare pesticide consumption scale with 0.6 kg/ha, whereas Taiwan holds no. 1 position with 17 kg/ha.

5 Impact of Pesticide on Human Health, Environment and Biodiversity

5.1 Human Health

The past few decades have shown an increase in pesticide consumption, which is why their residues are found easily in different environment compartments and several cases have been reported in which pesticide residues cause problems in the environment, human, and all other living creatures. Figures 12.1 and 12.2 show the presence of residues of persistent organic pesticides in different states of India. In 1958, the first report regarding pesticide poisoning in Kerala (India) was reported, in which over 100 people died because of consumption of parathion-contaminated wheat flour (Karunakaran 1958).

Inhalation, ingestion and penetration through the skin are the common routes of pesticide entry into the human body (Spear 1991). Infants, children below the age of 10, pesticide applicators and farm workers are more susceptible to pesticide toxicity than others, Pesticide degradation or elimination is performed by the body, but some residues of are absorbed by blood (Jabbar and Mallick 1994). Hayo and Werf (1996) observed that when pesticide concentration is increased in the body and then its initial concentration in the environment, this causes toxicity. According to the WHO, every year, 220,000 fatalities and 3,000,000 pesticide poisoning cases are

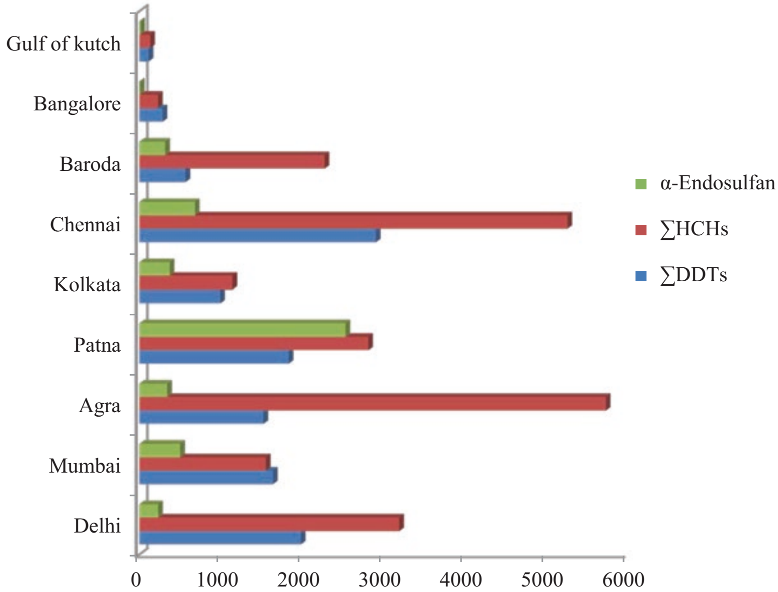

Fig. 12.1 Persistent organic pesticide residues (pg/m^3) in air from different regions of India. (Source: Chakraborty et al. (2010), Zhang et al. (2008), Pozo et al. (2011))

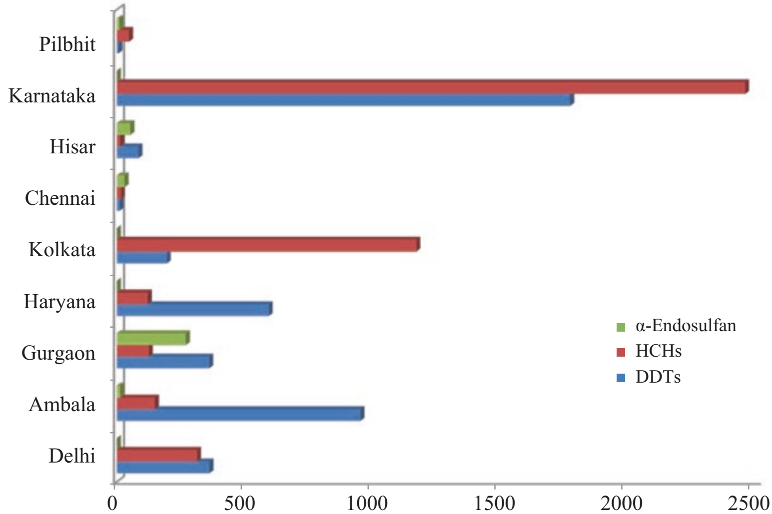

Fig 12.2 Persistent organic pesticide residues (ng/l) in water from different regions of India. (Source: Kaushik et al. (2008, 2010, 2012), Sundar et al. (2010), Ghose et al. (2009), Begum et al. (2009), Malik et al. (2009))

reported and approximately 2.2 million people are at a high risk of pesticide exposure in developing countries (Lah 2011; Hicks 2013).

5.1.1 Acute Effects of Pesticides

Acute effects are skin itching, irritation of the nose and throat, headache, appearance of a rash and blisters on the skin, nausea, vomiting, stinging of the eyes and skin, diarrhoea, dizziness, blindness, blurred vision and very rarely death, which may occur immediately after exposure to a pesticide (usually within 24 h). Most of the time, acute effects of pesticides are not severe enough to require medical attention every time.

5.1.2 Chronic Effects of Pesticides

Chronic effects take several years to appear, sometime years. These effects affect several parts of our body such as the liver, lungs and kidney. It can cause hypersensitivity, allergies, asthma and serious damage to the immune system (Culliney et al. 1992). The affected person can go through several neurological health conditions such as loss of memory and coordination, and their visual ability and motor signalling are reduced. Confusion, nervousness and hypersensitivity to light, sound and touch are symptoms that are also seen in OCP toxicity (Lah 2011). It can also cause oncogenic, mutagenic and carcinogenic effects. It affects the reproductive capabilities of the person by altering the male and female hormone levels. In other words, it causes infertility, spontaneous abortion, birth defects and stillbirth.

Richter (2002) observed that approximately 3 million tonnes of pesticides are used worldwide, which results in 26 million cases of non-fatal pesticide poisoning. Similarly, Hart and Pimentel (2002) reported that from all the cases of pesticide poisonings, 26 million patients are hospitalised and about 750,000 chronic diseases are caused every year. Symptoms of organophosphates and carbamates pesticide exposure are similar to those of another pesticide, which increases acetylcholine levels in the body. Convulsions, coma, improper breathing and death may occur in severe cases. Pyrethroid pesticide also causes reproductive and developmental effects and allergic skin responses.

Pyrethroids can cause an allergic skin response, aggressiveness, hyperexcitation, reproductive or developmental effects, in addition to tremors and seizures (Lah 2011). It is observed that there is a relationship between pesticides and Parkinson's disease/Alzheimer's disease (Casida and Durkin 2013).

5.2 Environment

Pesticide application is harmful in every prospectus. When applied it causes harm to soil; when water drifts from the applied area, it causes water contamination. In other words, pesticide affected not only target organisms, but also others such as birds who eat them, fishes and other aquatic animals in which pesticide residues accumulate, animals and the humans who eat the fishes and aquatic animals, other beneficial insects that died because of pesticide toxicity, and non-target plants. Among all classes of pesticides, insecticides cause most of the toxicity, although herbicides also pose a risk to non-target organisms. Water toxicity caused by pesticide is a major worldwide concern today because water is an essential part of our daily life (Kolpin et al. 1998).

5.2.1 Soil Contamination and Effect on Soil Fertility

Soil pollution has become a worldwide concern. Every day, a large number of contaminants such as pesticides, polycyclic aromatic hydrocarbons (PAHs), chlorophenols, petroleum and related products, and heavy metals, various pollutants enter the soil and pose a serious threat to the environment and human health (Gong et al. 2009; Kavamura and Esposito 2010; Udeigwe et al. 2011; Xu et al. 2012; Hu et al. 2013; Tang et al. 2014; Yadav et al. 2017). Soil contaminated mainly by agricultural and industrial activities has become an area of concern in recent years (Ha et al. 2014). Various transformation products from pesticides have been reported (Barcelo and Hennion 1997; Roberts 1998; Roberts and Hutson 1999). Soil pH also plays an important role in pesticide adsorption. When soil pH decreases, adsorption of ionisable pesticide (e.g. 2,4-D, 2,4,5-T, picloram atrazine) increases (Andreu and Pico 2004).

Overuse of pesticide can kill many beneficial microorganisms in the soil. According to Dr Elaine Ingham "soil will be degraded if we lose both fungi and bacteria". Overuse of pesticide and chemical fertiliser in the case of soil microbiota and overuse of antibiotics in the case of humans, both cases will end on an equal, drastic and damaging effect. Uncontrolled and random use of these chemicals may solve a problem now but because these soils will not able to hold as many beneficial microorganisms in future" (Savonen 1997). Plant needs many soil microorganisms to perform the nitrification process and because of pesticide discrimination, this process is disrupted (Singh 2015a, b, c, d, 2016). Pell et al. (1998) observed that triclopyr inhibits ammonia into nitrite transformation. Similarly, 2,4-D inhibits growth and activity of blue–green algae (Tozum-Çalgan and Sivaci-Guner 1993; Singh and Singh 1989), reduces the nitrogen fixation process (Fabra et al. 1997; Arias and Fabra 1993) and inhibits ammonia into nitrate transformation by soil microorganisms (Martens and Bremner 1993; Frankenberger et al. 1991). Santos and Flores (1995) observed that activity and growth of free-living N2-fixing bacteria are inhibited by glyphosate.

Mycorrhizal fungi show a symbiotic relationship with plant roots and help them to absorb nutrients. Pesticide overuse also causes damage to these fungi. Trifluralin and oryzalin can inhibit the growth of certain mycorrhizal fungal species (Kelley and South 1978). Similarly, oxadiazon triclopyr and Roundup® show damaging effects on mycorrhizal fungi species (Moorman 1989; Chakravarty and Sidhu 1987; Estok et al. 1989).

5.2.2 Water Contamination

Kole et al. (2001) collected fish and water samples from all streams of Calcutta and found that more than 90% of the sample contained one or more pesticides. Bortleson and Davis (1987–1995) observed all river streams of the USA that flow from urban and agricultural areas and reported that the water of the urban streams contains more pesticide than agricultural river streams. More than 58% of samples of drinking water were found to be contaminated with OCP under a survey conducted around the Bhopal city of Madhya Pradesh (Kole and Bagchi 1995). Clean-up of water is a very complex and costly procedure. Once water becomes polluted with pesticides or other toxic chemicals, its clean-up is difficult and takes years to achieve (US EPA 2001; Waskom 1994; O'Neil and Raucher 1998). Pesticide-contaminated water easily drifts into surface water, which is why the pesticide level is higher in surface water than in groundwater (Anon 1993). Owing to leakages, improper disposal and accidental spills, these pesticides can be transferred to groundwater (Pesticides in Groundwater 2014).

5.3 Biodiversity

5.3.1 Aquatic Biodiversity

The aquatic ecosystem is mainly affected by pesticide, which drifts from the land into rivers, lakes and other bodies of water. Rohr et al. (2008) observe that atrazine shows a toxic effect on some fish and amphibian species. They also found a link between atrazine exposure and variation in the abundance of larval trematodes in northern leopard frogs via an experimental mesocosm study. Relyea (2005) also found that carbaryl and the herbicide glyphosate (Roundup®) are toxic to amphibian species. Asian Amphibian Crisis (2009) state that amphibians species are not majorly affected by overexploitation and habitat loss, but by pesticide-contaminated surface waters. Endosulfan and chlorpyrifos are also toxic for amphibians (Sparling and Feller 2009) The presence of herbicides in aquatic ecosystems also reduces the reproductive abilities of some aquatic animals (Helfrich et al. 2009). Scholz et al. (2012) observed a significant reduction in the fish population when pesticides were overused. Pimentel and Greiner (1997), based on the United States Environmental Protection Agency (US EPA) (1990b), state that large numbers of fishes died every year because of pesticide toxicity in water. The total number of fishes that died of all causes was 141 million fish per year, of which 6–14 million died because of pesticide toxicity.

5.3.2 Terrestrial Biodiversity

Pesticide application affects not only target plants, but also non-target plants. Phenoxy herbicides are toxic for non-targeted trees and shrubs (Dreistadt et al. 1994). Herbicides, sulphonamides, sulfonylureas, and imidazolinones have a profound effect on the productivity of non-targeted crops, plants and associated wildlife (Fletcher et al. 1993). Application of herbicide glyphosate can increase the susceptibility of plants to disease and infection (Brammall and Higgins 1988).

Pesticides such as carbamates, pyrethroids and organophosphates can affect the population of beneficial insects such as beetles and bees. Pilling and Jepson (2006) observed that the synergistic effects of the fungicides pyrethroids and imidazole or triazole are harmful to honey bees. Similarly, neonicotinoid insecticides such as clothianidin and imidacloprid are found to be toxic to bees. A very low dose of imidacloprid can negatively affect the foraging behaviour of bees (Yang et al. 2008) and reduce their learning capability (Decourtye et al. 2003). In the early twenty-first century, neonicotinoids are majorly responsible for the sudden disappearance of honey bees. This has had a profound effect on the food industry, as one third of food production are heavily dependent upon pollination via bees. Several reports show the presence of a significant amount of neonicotinoids in commercial honey and wax. The honeybee population has dropped by 29–36% since 2006.

The bird population is also affected and as experienced a massive decline due to pesticide use. Pesticides enter a bird's body and start accumulating in their tissues, leading to their death. Liroff (2000) reported that DDT and its metabolite exposure are the major reason behind the declining population of the bald eagle in the USA. Fungicides, which are used for killing earthworms, indirectly reduced the birds and mammal population. Granular pesticides look similar to food grains, are swallowed by birds and cause toxicity. Pesticides in sublethal quantities can affect the nervous system and cause behaviour changes.

There are several methods of pesticide application such as spraying on the crop plants or on the soil, mixing in the soil, and can be applied in a granular form. After application, the pesticide can disappear from the target site via dispersion, degradation, leaching into water bodies, rivers or may be consumed by plants and soil microbes (Hayo and Werf 1996). Overuse of pesticide can affect the functioning of soil microbes and indirectly affect soil fertility. Lang and Cai (2009) reported that chlorothalonil and dinitrophenyl fungicides can disrupt nitrification and denitrification processes. Similarly, triclopyr (Pell et al. 1998) and 2,4-D (Frankenberger et al. 1991) affect ammonia-oxidising bacteria that are involved in ammonia into nitrite transformation, whereas glyphosate reduces activity and growth of nitrogen-fixing bacteria in soil (Santos and Flores 1995). In addition to bacteria, herbicides also cause damage to fungal species. The herbicides oryzalin, triclopyr and trifluralin inhibit the growth of mycorrhizal fungi (Kelly and South 1978; Chakravarty and Sidhu 1987,) whereas oxadiazon affects fungal spore production (Moorman 1989).

Earthworms are an inseparable part of the soil ecosystem. They make a major contribution to soil fertility. It is the model organism for testing soil toxicity and also acts as a bio-indicator for soil contamination. Reported that pesticides cause neurotoxic and physiological damage in earthworms. Glyphosate affects the abundance and the feeding activity of earthworms (Casabe et al. 2007). Goulson (2013) studied the harmful effect of neonicotinoids on the ecosystem and reported that it can kill *Eisenia foetida* species of earthworms.

6 Bioremediation Technologies

It is estimated that more than 100 million bacteria (5000–7000 different species) and more than 10,000 fungal colonies are present in only 1 g of soil (Dindal 1990; Melling 1993). Bioremediation approaches are safer and more economical than other commonly used physicochemical strategies (Vidali 2001). There are several compounds that contaminate the soil and require remediation, such as the inorganic compounds nitrates, phosphates and perchlorates (Nozawa-Inoue et al. 2005); explosives such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (Kitts et al. 1994); monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (known as BTEX) (Rooney-Varga et al. 1999); PAHs (Wang et al. 1990); a range of herbicides such as diuron, linuron and chlortoluron (Fantroussi et al. 1999); and heavy metals (Glick 2003). Bioremediation technologies are based on the principles of biostimulation and bioaugmentation for the successful application of bioremediation technology (Singh 2011; Singh and Pandey 2013; Bharagava et al. 2017). Sebate et al. (2004) proposed a protocol for the bio-treatability assays in two phases. Their metabolic activities and inhibitor presence are assessed under the first phase, whereas the second phase deals with the influences of nutrients, surfactants and the amount of inoculum administered at the polluted site. To achieve successful bioremediation, pollutants as substrates must be available and accessible either to microorganisms or to their extracellular enzymes so that metabolism occurs.

There are several microorganisms such as *Streptomyces* sp. strain M7, *Arthrobacter fluorescens* and *Arthrobacter giacomelloi*, *Chlorella vulgaris* and *Chlamydomonas reinhardtii, Clostridium sphenoides*, *S. Japonicum* UT26 that have been discovered by researchers that are capable of degrading the organochlorine insecticide lindane (Boudh et al. 2017). *Phanerochaete chrysosporium* and *P. sordida* also have the ability to degrade DDT in contaminated soil using a landfarming approach (Safferman et al. 1995). Different microbial mediated and other approaches such as composting, electro-bioremediation, microbially assisted phytoremediation and bio-augmentation are widely used to achieve successful bioremediation and sustainable environmental development (Singh and Strong 2016; Singh et al. 2016; Vimal et al. 2017).

6.1 Composting

Composting is a natural recycling process in which microorganisms rapidly consume organic matter and use these as an energy source, converting it into CO_2, water, microbial biomass, heat and compost. The feedstock used to fuel the composting process may be obtained from a variety of sources, including crop residues, manure, bio-solids and other agricultural residues. These materials may contain a number of synthetic organic compounds or xenobiotics, including pesticides. Composting provides an optimal environment for pesticide destruction. Compost is well-suited to pesticide degradation because elevated or thermophilic temperatures achieved during composting permit faster biochemical reactions than are possible under ambient temperatures and make pesticides more bioavailable, increasing the chance of microbial degradation. Microorganisms also co-metabolise pesticide during composting. By mixing remediated soil with contaminated soil, the effectiveness of composting can be increased because the remediated soil with acclimated microorganisms significantly influence pollutant degradation in the composting process (Hwang et al. 2001). In the composting matrices, microorganisms degrade pollutants into innocuous compounds, transform more pollutant substances into less toxic substances or help in locking up the chemical pollutants within the organic matrix, thereby reducing pollutant bioavailability. Even in the compost remediation strategy, the bioavailability and biodegradability of pollutants are the two most important factors that determine the degradation efficiency (Semple et al. 2001). The spent mushroom waste from *Pleurotus ostreatus* can degrade and mineralise DDT in soil (Purnomo et al. 2010). On the other hand, Alvey and Crowley (1995) observed that additions of compost can suppress soil mineralisation of atrazine. The critical parameters of composting depend on the type of contaminants and waste materials that may be used for composting. In addition, this composting efficiency essentially depends on the temperature and soil waste amendment ratio (Antizar-Ladislao et al. 2005).

Guerin (2000) recommended for the optimal removal of aged PAH during composting keeping the moisture and amendment ratio constant. Namkoong et al. (2002) studied that the soil amendment with sludge-only or compost-only in a ratio of 1:0.1, 1:0.3, 1:0.5, and 1:1 (soil/amendment, wet weight basis) increased the degradation rates of PAHs, but higher mix ratios did not increase the degradation rates of total PAHs correspondingly. Cai et al. (2007) observed the composting process for bioremediating sewage sludge, which is contaminated with PAHs, and found that intermittently aerated compost treatment showing a higher removal rate of high molecular weight PAHs compared with continuously aerated and manually aerated compost treatments. The nature of waste or soil organic matter, which consists of humic materials, plays an important role in the binding of contaminants such as PAHs and making them bioavailable for degradation. Plaza et al. (2009) reported that during composting, some humic material lost their aliphatic groups, their polarity had been increased and they also entered into aromatic polycondensation, which alters their structural and chemical properties, resulting in a decrease in PAH binding. Humic material acts like a surfactant in compost and plays a crucial role in releasing PAHs sorbed into the soil. It also increased the stability of soil. PAH degradation mostly occurs during the mesophilic stage of composting, whereas the thermophilic stage is inhibitory for biodegradation (Antizar-Ladislao et al. 2004; Haderlein et al. 2006; Sayara et al. 2009). Sayara et al. (2010) reported that stable composts that are present in municipal solid wastes enhanced the biodegradation of PAH, particularly during the initial phase of composting. Similar to any other technology used in bioremediation, composting has its own advantages and limitations. It is a sustainable and most cost-effective remediation method that may also improve the soil structure, nutrient status and microbial activity (Singh 2013a, b, 2014). During composting, the contaminant can degrade through different mechanisms such as mineralisation by microbial activity, transformation to products, volatilisation, and also the formation of non-extractable bound residues with organic matter. One of the critical knowledge gaps of composting is the lack of sufficient knowledge about the microorganisms involved in various stages of composting, especially in the thermophilic stage, which is almost like a black box. In fact, there are conflicting views of researchers about the role of the thermophilic stage of composting in bioremediation of contaminants. For better designing of composting as a bioremediation strategy for contaminated soils, knowledge of the nature and activity of the microorganisms involved in various stages of composting and on the degree of stability of compost and its humic matter content is essential.

6.2 Electro-Bioremediation

Electro-bioremediation is a hybrid technology that combines both technologies of bioremediation and electrokinetics, for the treatment of hydrophobic organic compounds. In this method, we use microbiological phenomena for pollutant degradation and electrokinetic phenomena for the acceleration and orientation of the transport of pollutants or their derivatives and the pollutant degrading microorganisms (Chilingar et al. 1997; Li et al. 2010). In this method, we use weak electric fields of about 0.2–2.0 V cm^{-1} to the soil (Saichek and Reddy 2005) and transport phenomena associated with electrokinetics are electro-osmotic flow, electromigration, and electrophoresis, which can be utilised to effectively deliver nutrients to indigenous bacteria in the soils and to enhance bioavailability. Luo et al. (2005) developed a non-uniform electrokinetic system in which the polarity of an electric field is reversed to accelerate the movement and facilitate higher and more uniform biodegradation of phenol in a sandy loam soil. According to Wick et al. (2007), the impact of the direct current on organism–soil interactions and the organism compound is often neglected. Fan et al. (2007) tested a two-dimensional (2-D) non-uniform electric field on a bench scale with a sandy loam soil and 2,4-dichlorophenol (2,4-DCP) at bidirectional and rotational modes, and observed that about 73.4% of 2,4-DCP was removed at the bidirectional mode and about 34.8% at the rotational mode.

Shi et al. (2008) observed that direct current ($X = 1$ V cm^{-1}; $J = 10.2$ mA cm^{-2}), which is typically applied for electro-bioremediation measures had no negative effect on the activity of a PAH-degrading soil bacterium (*Sphingomonas* sp. LB126), on the other hand, the DC-exposed cells exhibited up to 60% elevated intracellular ATP levels, but remained unaffected by all other levels of cellular integrity and functionality. Niqui-Arroyo and Ortega-Calvo (2007) used an integrated biodegradation and electro-osmosis approach for enhanced removal of PAHs from creosote-polluted soils.

Velasco-Alvarez et al. (2011) applied the low intensity electric current in an electrochemical cell packed with an inert support and observed degradation of hexadecane and higher biomass production by *Aspergillus niger*. Maillacheruvu and Chinchoud (2011) reported the synergistic removal of contaminants by using an electro-kinetically transported aerobic microbial consortium. There are some limitations of electro-bioremediation technologies such as pollutant solubility and its desorption from the soil matrix, availability of suitable microorganisms at the contamination site, the concentration ratio between target and non-target ions, the requirement of a conducting pore fluid to mobilise pollutants, heterogeneity or anomalies found at sites, and toxic electrode effects on microbial metabolism or breakdown of dielectric cell membrane or changes in the physicochemical surface properties of microbial cells (Sogorka et al. 1998; Velizarov 1999; Virkutyte et al. 2002).

6.3 Microbe-Assisted Bioremediation

Physical remediation, chemical remediation and bioaugmentation (the addition of biodegradative bacteria to contaminated soils) techniques are commonly used for the treatment of contaminated soils. These remediation methods are costly and introduced microorganisms often do not survive in the environment; thus, phytoremediation became a good choice for this purpose. It is a cost-effective technique in which plants and their associated microorganisms help to remove, transform, or assimilate toxic chemicals located in soils, sediments, groundwater, surface water, and even the atmosphere (Reichenauer 2008; Glick 2010). There are some beneficial plant–microbe relationships, particularly between plants and plant growth-promoting rhizobacteria, plant endophytic bacteria and mycorrhizal fungi, that exist in nature, which helps in the natural bioremediation process of contaminated soil in which microorganisms increase the availability of contaminants and help plants with the extraction and removal of inorganic and organic compounds by using appropriate degradation pathways and metabolic capabilities (Hare et al. 2017).

Several studies suggest that microbially assisted phytoremediation offers much potential for bioremediation compared with lone phytoremediation (McGuinness and Dowling 2009; Weyens et al. 2009; Glick 2010). Endophytic and rhizobacteria are involved in the degradation of toxic organic compounds in environmental soil. Endophytic bacteria are present naturally in the internal tissues of plants (called endophytes) and rhizobacteria are associated with the rhizosphere of plants. Endophytic bacteria promote plant growth and contribute to enhanced biodegradation of environmental soil pollutants (Weyens et al. 2009). Similarly, rhizobacteria synthesise compounds that protect plants by decreasing plant stress hormone levels, delivering key plant nutrients, protecting against plant pathogens and degrading contaminants (McGuinness and Dowling 2009; Glick 2010). Table 12.1 shows some examples of the successful microbially assisted phytoremediation of pollutants.

Yousaf et al. (2010) isolated hydrocarbon degraders *Pseudomonas*, *Arthrobacter*, *Enterobacter* and *Pantoea* spp. from the root and stem tissues of Italian ryegrass and birds foot trefoil vegetated in hydrocarbon contaminated soil. Similarly, Siciliano et al. (2001) found endophytic hydrocarbon degraders in tall fescue (*Festuca arundinacea*) and rose clover (*Trifolium fragiferum*) at an aged hydrocarbon-contaminated site.

Plants produce many secondary plant metabolites (SPMEs) such as phytohormones, phytoanticipins, allelopathic chemicals, root exudates and phytosiderophores (Hadacek 2002). Gilbert and Crowley (1998) and Kim et al. (2003) reported that SPMEs such as limonene, cymene, carvone and pinene enhanced degradation of polychlorinated biphenyls (PCBs). Kupier et al. (2002) observed that when *Pseudomonas putida* PCL1444 was grown in PAH-polluted soil, it degraded the PAHs. It is isolated from the rhizosphere of *Lolium multiflorum* cv. Narasimhan et al. (2003) applied the rhizosphere metabolomics-driven approach in the rhizosphere of *Arabidopsis* to degrade PCBs.

Table 12.1 Examples of some successful microbial assisted phytoremediation of pollutant

Pollutants	Plant species	Microorganisms	References
Tetrachlorophenol	Wheat (*Triticum* spp.)	*Herbaspirillum* sp *K1*	Mannisto et al. (2001)
Explosives	Popular tissues (*Populus deltoidesnigra*)	*Methylobacterium populi*	van Aken et al. (2004a) and van Aken et al. (2004b)
Hydrocarbons	Pea (*Pisum sativum*)	*Pseudomonas putida*	Germaine et al. 2009
Polycyclic aromatic hydrocarbons	Tall fescue grass (*Festuca arundinacea*)	*Azospirillum lipoferum* sp.	Huang et al. (2004)
		Enterobacter cloacae CAL2	
		Pseudomonas putida UW3	
2,4-dichlorophenoxyacetic acid	Barley (*Hordeum Sativum* L.)	*Burkholderia cepacia*	Jacobsen (1997) and Shaw and Burns (2004)
	Ryegrass (*Lolium perenne* L.)	*Indigenous degraders*	
Pentachlorophenol	Ryegrass (*Lolium perenne* L.)	*Indigenous degraders*	He et al. (2005)
Trichloroethylene	Wheat (*Triticum* spp.)	*Pseudomonas fluorescens*	Yee et al. (1998)

7 Pesticide Application

Irregular and uncontrolled use of pesticide leads to various problems in agriculture such as the development of pesticide resistance to the pest populations that are causing diseases. The timing of pesticide application is mainly linked with extreme and unusual weather events (Johnson et al. 1995; Otieno et al. 2013). For example, in autumn, soil moisture is highly decreased, which limits field work, while an increase in soil moisture in the rainy season also forbids field work (Rosenzweig et al. 2001; Miraglia et al. 2009). Earlier application of the pesticide in autumn can make winter weed control more difficult (Bailey 2003).

The total amount of herbicides and the rate of their application are higher than for insecticides or fungicides in the past (Probst et al. 2005). This may be because of favourable climatic conditions for the pest population (Goel et al. 2005). In general, the increased use of agricultural chemicals appears necessary (Rosenzweig et al. 2001; Hall et al. 2002). For example, infection symptoms that appear frequently after a short time interval lead to frequent pesticide applications so that infection can be prevented (Roos et al. 2011; Noyes et al. 2009). Similarly, the evolution of pesticide-resistance pests requires improvement in the current pest management strategies. Improved biological control tools may be a solution to this problem (Jackson et al. 2011). Poor organic farmers of developing countries needed cheap, easily available, biodegradable and low-risk pesticides (Ntonifor 2011). Thus, some countries increase or re-introduce banned or restricted pesticides in field applications (Macdonald et al. 2005).

8 Conclusion

Nowadays, people are more aware of environmental safety and protection. Organic farming, bio-fertilisers and biopesticides have become the public's favourite research, based on pesticide exposure in the environment. Therefore, more research works are focused on the removal of these pesticides from food chains and different trophic levels. As the pesticides are persistent pollutants and have bioaccumulation and biomagnifications properties at successive trophic levels in an ecosystem, ensuring their long-term presence, this removes organisms at higher trophic levels. Furthermore, as pesticide application affects the biodiversity, human health and the environment, we should learn to avoid their use and try to replace them with natural ones. Use of bio-pesticides and bio-fertilisers to enhance agricultural productivity will be helpful technology to save our biodiversity, agriculture and environmental pollution. Application of efficient microbes for plant growth promotion and bioremediation can add one more step to the development of sustainable agriculture and environment. There is an urgent need to explore and identify more efficient and microbial communities with the potential for the bioremediation of pesticides at contaminated sites, present all over the world.

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