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Contaminants in Agriculture and Environment Health Risks and Remediation

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Contaminants in Agriculture and Environment
Health Risks and Remediation | Volume 1

Contaminants in Agriculture and Environment Health Risks and Remediation

Volume 1

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Health Risks and Remediation

Volume 1

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Vinod Kumar
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Health Risks and Remediation

Volume 1

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Preface

Recent advances in chemical applications in the agricultural sector have been contributed to disruptive contamination of crop and environment. Besides the contribution in improving conventional farming, the development of new methods has also contributed to polluting agriculture as well as environments. The deposition of several contaminants in agricultural products, soil, water, air and even into the higher trophic levels of the food chain has disturbed the well-functioning of the earth ecosystem. This book is a forge guide to the students and researchers working in the field of agricultural pollution and seeking to get relevant material to understand the current trends of generation, impacts and remediation of pollutants affecting agricultural systems.

The contents of this book covers the aspects of agricultural contamination through different natural and man made practices. The methods of their mitigation are also included as well. The book specially focuses on heavy metal, pesticide, organic wastes, pest management, agricultural land use, and other contaminants. The harmful effects of such contaminants on birds, pests, fishes, human, plants and other living organisms has been taken as main part of this book. The book provides the collection of most pertinent material about themes to the readers. The book is helpful in understanding the basic concepts of agricultural pollution as well as the sources of pollutants in agriculture system.

In fact, the enhancement of agricultural productivity by various environmental friendly methods and their limitations is also implemented. Furthermore, the book comprises the information about impact of pollutants on growth and productivity of agricultural crops followed by various diseases and impacts of agricultural pollutants on human health as well as to other components of ecosystem. The case studies of some countries showing impacts on its population which is caused by such pollutants. The current status of generation of agricultural wastes and its best utilization by means of environmental friendly approaches is the emergence need in this book.

Lastly, the editors are thankful to the contributors who submitted their precious findings and views related to the book theme and to make it succeeded. We hope that this book will help the readers in its best to convenient the relevant information.

Editors

Chapter 1

An introduction to contaminants in agriculture and environment

Vinod Kumar, Pankaj Kumar* and Jogendra Singh

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Abstract

Recent advances in chemical applications in the agricultural sector have been contributed to disruptive contamination of crop and environment. Besides the contribution in improving conventional farming, the development of new methods has also contributed to polluting agriculture as well as environments. The deposition of several contaminants in agricultural products, soil, water, air and even into the higher trophic levels of the food chain has disturbed the well-functioning of the earth ecosystem. The present chapter focused on the primary information of the book regarding how the contaminants in agriculture are introduced with possible ways to mitigate their impacts.

Keywords: Agricultural pollution, Contaminants, Development, Sources, Twenty-first century, Urbanization

Agricultural contaminant definition: “An unwanted sediment or chemical present in the agriculture and their products which makes it unfit for consumption and survival of living beings”.

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Introduction

The production of foodstuffs related to meet the animal food requirements by growing and harvesting plants and their products is known as agriculture (Nagendran, 2011). Despite global agricultural and economic revolution during recent past 50 years, human beings have transformed the natural ecosystems according to their selfish necessities. This is due to increased demand of foodstuffs due to overexploitation of natural resources, uncontrolled increase in the global population, and use of chemical substances to promote the crop productivity and plant protection (Bergstrom and Randall, 2016). Besides the contribution in improving conventional farming, the development of new methods has also contributed to polluting agriculture as well as environments (Altieri, 2018).

The deposition of several contaminants in agricultural products, soil, water, air and even into the higher trophic levels of the food chain has disturbed the well-functioning of the earth ecosystem. Pollution has tended to cause anxiety among all living beings from small-sized microorganisms to big sized elephant (Pavlidis and Tsihrintzis, 2018). The recent advancements in the agriculture sector have been contributing to degrading the quality of the environment. Agricultural pollution is a complex combination of rehearses due to its wide range of contributing factors. For this, it has several negative consequences on biotic communities in terms of air, water, and soil pollution (Yang *et al.*, 2018). Moreover, the liquid runoffs from urbanized cities, industries, and agricultural fields contains highly noxious elements like long persisting heavy metals, polyaromatic hydrocarbons (PAH), plastics and polymers, pesticides, chemical and reagents, atmospheric depositions, bio-aerosols, pollen grains, microorganisms, biodegradable residues, which creates serious environmental and health issues in the living beings (Nilsen *et al.*, 2019). Recent reports have shown that the long term deposition of such elements caused serious health impacts on both animals as well as plants.

This exposure to a human being above the threshold may be fatal due to the destruction of body immunity and or organ failure (Liao *et al.*, 2018). Thus, the effective mitigation of such deposition is a challenging approach for the whole world. The effects of harmful toxicants on living cells may be brought either by alteration in the cellular enzyme activities or by chemical and physical modifications in the cell structure (Brunk *et al.*, 2018). These changes might be responsible for the serious health problems like cancer, kidney diseases, weak immunity, bacterial, viral, and fungal diseases, embryonic disorders, hormonal disturbances, organ failure, skin problems and much more (Deng *et al.*, 2018).

This book chapter emphasized an introduction to the contaminants in agriculture and environment and their possible consequences related to interacting biotic communities. The pollution which has been caused or being caused by various activities affecting the quality of agricultural products is well discussed. The necessity of this article was to spread the supplementary information among the global consumers to aware of them how the contaminants in agriculture arise and the possible ways to mitigate their impacts.

21st century and agricultural technology

It is obvious that the agricultural method today is quite different and advanced from the methods used in the year 1950. Today, the researchable association between agriculture and environment has received more attention due to the devastating impacts of contaminants on both biotic and abiotic components. These changes are brought by the recent revolutions in the agriculture sector in India. The modern agricultural practices involving the fertilizer, pesticide, machinery applications, raw foodstuff processing, transportation, preservation, and consumption are quite different from the traditional ways used by our ancestors (Tubiello *et al.*, 2015; Baker *et al.*, 2017). The advancements in the techniques of tillage, plowing, fertilizing, manure spreading, pesticide application, feedlots, and animal corrals utilization, irrigation, and clear-cutting has been revived the net profit and income of farmers (Nagendran, 2011). The integration of the industrial sector with agriculture is the most reason for this. Figure 1.1. It is well known that India has received many technological revolutions during the past 100 years (Figure 1.2). The major revolutions includes, green revolution for agricultural development, white revolution for milk production, blue revolution for fish and fisheries, grey revolutions for fertilizer developments, red revolution for meat production, sky revolution for the information and technological technologies, and finally the evergreen revolution which was meant for revolution of overall agriculture sector and production growth (Goldman and Smith, 1995; Breen, 2017).

Figure 1.1. Integrated framework of routes of contaminates in agriculture and environment.

Figure 1.2. Different revolutions in the history which acted as milestone for agriculture of India.

Contaminants in agriculture and environment

Whether the contaminants in agriculture arise from the farming and industrial practices or by natural pollutant deposition, they all are considered as agricultural contaminants as they all have negative impacts on the survivability of the living beings (Figure 1.3). Such renowned methods have contributed to contamination of both grounds as well as surface waters with several pathogens like bacteria, viruses, fungi and other microbes (Nagendran, 2011). The agricultural and industrial runoffs contribute to accumulating different salts into agricultural lands, water bodies, surface, and ground waters. The application of chemical fertilizers and pesticides has persisting and long term effects on the ecological contributors. Besides this, the high concentrations of trace heavy metal and radioactive elements released into the environment can cause serious health issues in animals and plants (Rawlins *et al.*, 1998; Harrison, 2015). Accumulation of different nutrients in water bodies from such runoffs are also. The various agricultural practices like tree cutting, shifting cultivation, forest clearing and overgrazing tend to accelerate the soil erosion rates in the respective regimes which often cause the siltation of the river bottoms and increased turbidity levels (Doula and Sarris, 2016). The altered water quality further affects the flora and fauna of both internal as well as external river system i.e. riparian zone (Petts, 2018). The intake of contaminated crops by household cattle, birds and rodents create severe disease which is sometimes fatal. The contaminated fodder when taken by cattle affects the quality of produced milk, and even the residues of heavy metals, pesticides, and other carcinogens have been reported by several researchers (Rawlins *et al.*, 1998). Besides this, among the other environmental impacts, soil erosion is also a major problem caused by agricultural and industrial runoffs.

However, forested areas show less soil erosion as compared to unprotected areas like fallow lands, which are directly affected by numerous natural as well as anthropogenic activities such as rainfall patterns, river streams, landslides, wind patterns, agricultural practices, overgrazing, deforestation and river bed mining are the major ones and therefore contribute to high soil loss (Jain *et al.*, 2001). Overgrazing is the process by which the fertile soil surfaces attached with

grasses are removed by means of the grazing and walking activities of livestock like sheep, goats, cattle, camels, horses, and others. Like other elements, overgrazing is also an important factor which contributes to the enhanced frequencies of agricultural contamination by means of incorporation of harmful pests, pathogens, and loosing soil strength and quality. The removal rate of soil nutrients is accelerated when the runoff process happened in such soils. Or the contaminants from other sites are transported to the agricultural soils via such liquid discharges.

Contaminant transmission pathways in the agriculture food chain

The transport mode of an agricultural contaminant in the food chains is strongly regulated by natural and anthropogenic factors. The pollutant retention in a particular trophic level depends on the metabolism and residual dispersion to higher ones (Fowler, 2018). The control of physical and chemical factors is also a determinant of contaminant mass transfer into living cells. Over-application of pesticides and fertilizers have contributed to accumulate their higher

Figure 1.3. Sources of contaminants in agriculture and their health consequences.

amounts in the soils and further their transportation the upper parts of the plants. On the other hand, higher trophic levels of the agricultural system are also affected by agricultural pollution (Liu *et al.*, 2015; Kumar *et al.*, 2018). The process of bio magnification of pesticides and heavy metals in a complex mechanism, where plant enzyme-proteins actively binds with such pollutants and transport them to the edible and non-edible parts of the plant. Later, the herbivores take the energy from those contaminated plants or plant products and help in transferring them to top consumers including human itself.

For example, in India, the case of house sparrow bird deaths was due to extensive pesticide accumulation in rice crop which declined its significant population in both rural and urban areas (Rawat and Agarwal, 2015). The accumulation of harmful pesticides in rice crop tends to increase the toxicity of early rice grains, which are taken by birds. On the other hand, the pesticide application on crop leaves kills the pests which are further fed to infants by mother sparrow. Consequentially, pesticides like Aldrin, DDT, Carbendazim, etc. act as toxic substances in the bird which further cause deaths. As not all insects are harmful to crops, many beneficial pests like a fly predator, lady beetle, moth egg parasite, honey bee, etc. are killed by such pesticide and fertilizer applications. This cause the disturbance in the natural food chain as many of them act as important keystone species to balance the agricultural ecosystems (Wojciechowska *et al.*, 2016). Livestock grazes large quantities of grasses, herbs, and shrubs present in the mountain areas. The walking and grazing activities create terracettes (steeper slopes) on the uppermost soil surfaces, where small contours, nearby 1.6 meters in depth. The formation of these slopes undergoes to make the soil detached from the mail surface layer and results in slow soil erosion (Pandey, 1996). If the process continues for a long time, it becomes a threat to the food chain and well as a risk to the concerning ecosystem caused by a decrease in the net gross productivity. The walking activity of livestock from one agricultural field to another spreads the pathogens easily. The probability of getting the non-disease crop increase when the number of livestock enters having such pests, or pathogen spores.

Conclusion

In conclusion, after surveying the past and current status of contaminants in agriculture and environment, we found that human revolution has significantly contributed to increasing the health problems by incorporating the harmful substances. Besides this, the development of advanced technologies for gaining more benefits has perceived more attention of farmers for using modern chemical fertilizers and pesticides.

Recent studies revealed that the agricultural and industrial runoffs contribute to accumulating different salts into agricultural lands, water bodies, surface, and ground waters. The high concentrations of trace heavy metal and radioactive elements released into the environment can cause serious health issues in animals and plants. Therefore, the responsive goals for mitigating these contaminants should be taken into account.

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Chapter 2

Role of some emerging agro-chemicals in groundwater contamination

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Abstract

The escalating food demand to feed the incessantly mounting world population has put a lot of pressure on our already over burdened agricultural system. The urge to cultivate more food has made us reliant on supplementary use of agrochemicals like pesticides and fertilizers. Unsystematic use of agrochemicals has amplified the production of crops but it has also posed rigorous hazards to environment because it has contaminated the natural resources, like groundwater. The groundwater resources are vulnerable to pollution, the occurrence of pesticide residues in the groundwater resources (water located beneath the soil's surface) constitutes a global problem worldwide, especially in the least developed countries where the use of plant protection products is very high. For the development of microbial originated pesticides, which

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are valuable, dependable and have a low environmental risk there seems to be a great potential. Also, novel application techniques, such as exactitude band spraying, can decrease the dose, which can be an extremely successful way to minimize transport and emanation and in addition can avoid a build-up of confrontation in target organisms. Enhanced formulations will besides be required to decrease off-target deposition, recover withholding on target, and augment uptake and translocation. The book chapter deals with the contributory approach of agrochemicals to contamination of ground water.

Keywords: Biomagnification, Degradation, Fertilizers, Groundwater, Pesticides

Introduction

Agrochemical, also referred to as agrichemical, a contracted form of agricultural chemical, is a phrase used for the different chemical products employed as a part of farming. Generally, agrichemical implies pesticides which include herbicides, fungicides, insecticides and nematocides (chemicals for killing round-worms). Agrochemicals also include synthetic fertilizers, hormones and other chemical growth drivers, and concentrated stores of raw animal manure (Pimentel *et al.*, 2004). The burgeoning population growth is continuously heightening the food demand which in turn has put a lot of pressure on our already over-burdened agrarian system. The prerequisite to produce more food has pressurized us to rely on extended use of agrochemicals. The agrochemicals have been playing a key role for fostering the agrarian productivity to meet the expanding population's needs since a long time. But now their use has caught an eye on account of their relentlessly irrational and non-judicious use. Nevertheless, there is no conflict of idea with regards to their utility in boosting the agricultural productivity and safeguarding the supply of agricultural produces meeting the food, health and other necessities of the animal and human population. Adsorption, degradation, and movement processes are key processes to know the persistence of a pesticide and its ability to contaminate groundwater bodies (Kumar *et al.*, 2018). The main factors affecting the fate of pesticides are their physicochemical properties (water solubility, vapour pressure, adsorption coefficient, etc.), soil characteristics (texture, organic matter content, etc.), site (hydrogeological conditions), and management practices (method of application and dosage).

Haphazard consumption of agrochemicals has instigated austere vulnerabilities to environment on a whole but in particular groundwater resource (Khanna and Gupta, 2018). Groundwater is the water that is present in porous soils and rocks below the surface of earth or the water present in aquifers beneath the land surface. So far groundwater source of water is deliberated as the most reliable source of unpolluted water, playing a pivotal role in upholding hydrological cycle owing to its direct link with the surface water. The prominence of groundwater for subsistence of humans can't be disregarded because it is the chief source of palatable water in both rural as well as urban India. Moreover, it is an eminent source of water for industrial and agricultural sector.

It is well-known that agriculture is the sole biggest consumer of freshwater sources, expending globally an average of 70% of all surface water supplies (Pimentel *et al.*, 2004). The water consumed for irrigation purpose is returned back to surface/ground water reserves except the water lost in the process of evapotranspiration. The exigency of water is incessantly intensifying in India owing to many reasons; greater amount of water is required to satiate the need of over-populated country, unpredictable precipitation patterns are compelling agriculture to rely on irrigation and swift industrialization is also incumbent upon greater consumption of water. The state of affairs of water emergency is further worsened due to contamination of the fresh water reserves present below and above ground. Faulty agrarian practices like over-use of agro-chemicals play a principal role in soiling and poisoning the ground water.

Agriculture is both source as well as victim of groundwater pollution. It becomes a causal agent triggering groundwater through the flux of chemical pollutants and sediments into groundwater system. Contrarily, when the same contaminated groundwater is tapped for irrigation purpose, it contaminates crops and transfers its negative effects in the ecosystem. Moreover, once groundwater gets soiled with noxious chemicals, it may take several years to detoxify or clear the contaminants. In this chapter, the negative impacts of these agrochemicals on the groundwater will be discussed. It has been found that the pollution of groundwater caused due to the use of agro-chemicals is mainly attributed to pesticides and fertilisers; hence the effect of these two agro-chemicals on environs will be reviewed.

Pesticides as groundwater contaminants

A pesticide also referred to as plant protection product is any “substance intended for preventing, destroying, repelling, or mitigating any pest in crops either before or after harvest to prevent deterioration during storage or transport” (Pérez-Lucas *et al.*, 2018). The pesticide term acts an umbrella for all the formulations including herbicides, fungicides, insecticides, rodenticides, insect growth regulators, defoliants, molluscicides, antimicrobials, and household disinfectants used to eradicate some pests (Ozkara *et al.*, 2016). Pesticide products consist of both active as well as inert ingredients. Active ingredients are employed to control diseases, pests, and weeds, whereas inert ingredients also referred to as adjuvants (dyes, stabilizers, etc.) are imperative for product usability and performance. Around 850 different pesticide formulations are in use (Cheremisinoff and Rosenfeld, 2010), although the restraint of public health vulnerabilities also lingers to be an important field of application. In last few decades, the use of pesticides has tremendously increased improving the quality and quantity of food on one hand, while as enhanced use has caused substantial pollution of terrestrial ecosystems and poisoning human foods (Carvalho, 2017).

Pesticides can be categorized according to their mode or period of action, their target or their chemical composition (Drum, 1980). The most widely known is the classification based on target. For instance, insecticides are the pesticides that aim killing insects, rodenticides target rodents,

and herbicides target plants. Likewise the others are fungicides, miticides, acaricides, bactericides, molluscicides, virucides and avicides. The other classification based on the way the pesticides interact with the plants categorises them into two classes: nonsystemic and systemic. Nonsystemic pesticides are those that don't substantially enter plant tissues and thus not transported within the plant vascular system. Contrarily, systemic pesticides are those that effectually penetrate plant tissues and get transported within the plant vascular system to cause the anticipated effect. The classification based on chemical nature and active ingredients is the most useful one while considering the effect of pesticides on environment because it helps in streamlining the application rates while taking into consideration the physical and chemical properties of individual pesticides. In accord with the chemical properties, pesticides can be divided broadly into seven types, comprising of organochlorines, organophosphorus, pyrethroids, carbamates, anilins, amides, and azotic heterocyclic compounds (Ozkara et al., 2016).

Table 2.1. Examples of different pesticides (Adopted from Jayaraj et al., 2016).

Pesticide type	Examples
Organochlorines	DDT (Dichlorodiphenyltrichloroethane), Eldrin, Dieldrin, Dicofol, Toxaphene, HCH (Hexachlorocyclohexane), DDD (Dichlorodiphenyldichloroethane), Lindane, Chlorobenzilate, Methoxychloro Aldrin, BHC, Chlordane, Endosufan, Heptaclor, Isodrin, Isobenzan, Chloro propylate
Organophosphates	Dimefox, Methyl Parathion, Mipafox, Bidrin, Ronnel, Enitrothion, Fenthion, Phorate, Abate, Dichlorovas, Caumphos, Phosphomidon, Diptrex, Oxydemeton-methyl, Dimethoate, Demetox, Malathion, Trichlorofan
Carbamates	Methyl: Dimetilan, Carbaryl, Isolan, Prupoxur, Carbanolate, Carbofuran, Dimethan, Pyrolan, Aldicarb, Aminocarb Thio: Diallate, Vernolate, Monilate, Pebulate, Trillate, Butylate, Thiourea, Cycloate Dithio: Thiram, Methan, Amoban, Ferban, Zineb, Maneb, Naban, Dithane
Pyrethroids	M- 45, Ziram Polyan Bonthrin, Allethrin, Tetramethrin, Dimethrin, Furethrin, Ptrethrin, Alphamethrin, Cyclethrin, Fenevelerate, Cypermethrin, Decamethrin
Amide pesticides	Butachlor, Acetochlor, Metolachlor
Anilins and dinitroaniline	Pendimethalin, Trifluralin
Nitrogen-containing heterocyclic pesticides	Triazole, Forimidazole

The examples of each group are presented in Table 2.1.

- **Organochlorine pesticides** are organic compounds having five or more chlorine atoms. They were the first artificial organic pesticides that were expended in agriculture and public health. These pesticides in general possess the stable chemical structure, eventually persist and get hoarded in the environment, hence belonging to the class of persistent organic pollutants (POPs). Most of them are broadly exploited as insecticides for the curbing wide-ranging insects.
- **Organophosphates** are another form of highly noxious pesticides that are esters of phosphoric acid. The synthetic organophosphates were recognised initially as warfare materials during the epoch of Second World War. Since then, they have been exploited in diverse fields like agriculture, cosmetics, industry, medicine, etc. They have the potential for inactivating the acetylcholine esterase (AChE) enzyme.
- **Carbamates** are organic pesticides derived from carbamic acid (NH_2COOH), which are akin to organophosphates in having the potential of incapacitating the enzyme acetylcholine esterase (AChE). However, the carbamates differ from organophosphates in their mode of action such that carbamates are species specific and their cholinesterase inhibition is reversible.
- **Pyrethroids** and pyrethrins are artificial analogues isolated from the flowers of pyrethrums (*Chrysanthemum Coccineum* and *Chrysanthemum cinerariaefolium*). They were spotted in the 1980s to impersonate the insecticidal venture of the natural pyrethrum. They are greatly recognized for their quick bowling down effect against insects, low mammalian toxicity and facile biodegradation.
- **Amide pesticides** are systemic pesticides which enter the food chain thereby affecting the nutrient cycling. Acetochlor, metolachlor, and butachlor are the amide pesticides which are widely used in recent years.
- **Anilins and dinitroaniline pesticides** are the widely used group of pesticides. For example, Trifluralin and pendimethalin.
- **Nitrogen-containing heterocyclic pesticides**, especially triazole and forimidazole heterocyclic chemicals, have turned into the hotspot for novel pesticide synthesis. Since the last decade, almost 70% of the newly developed pesticides belong to this class (Zheng et al., 2016).

Transportation of pesticides to groundwater

Every single pesticide present in groundwater, and majority residues there in surface water penetrate into the soil largely by overspills and recharge. There are mostly two major routes through which pesticides penetrate into the soil: discharge from granulates openly functional to the soil (López-Pérez et al., 2006) and spray drift to soil throughout floral management plus wash-off from treated flora (Rial Otero et al., 2003) (Figure 2.1). Nonpoint sources of pesticides originating from areas where they were applied- rather than point sources such as wastewater

Figure 2.1. Routes of a pesticide directed to a crop (Source: Arias-Estévez et al., 2008).

Figure 2.2. Movement of pesticides in environment (Source: Gilliom et al., 2006).

discharges- are the most widespread causes of pesticides occurrence in streams and groundwater. The movement of pesticides in an ecosystem is illustrated in Figure 2.2. The major primary approach of pesticides to reach groundwater is the water that permeates through the soil and exceeds all the way through the fundamental unsaturated region to the water table. As with watercourses, the majority of pesticide transfer to ground water is motivated by rainwater or irrigation when alone or both upshots in ground-water revitalization. Transport in ground-water is dissimilar from transportation in streams as only dissolved types of pesticides as well as degradates (novel compounds produced by the conversion of a pesticide by chemical or biological reactions) travel considerable distances with ground water. Soil and aquifer materials largely retain the particle bound compounds. Moreover, transportation of pesticide compounds

into and inside ground water to a large extent is less knowable in comparison to transport in streams since the surge of ground water is significantly slower and extra intricate than the surge of stream water. Pesticides as well as their degradates can travel voluntarily to ground water via portable zones, such as worm holes, or permeable sediments, cracks, however a fraction of pesticide compounds is reserved in stationary zones inside the subsurface where current is minimal. Pesticide compounds that are reserved in stationary zones can be unconstrained steadily to ground water by dissemination and consequent leaching, at times protracted following application.

Greatly as a soap-filled mop ought to be frequently washed and squeezed before all of the soap is separated, the soil operates as a basin from which pesticides and their degradates prolong to leach following submission. As a consequence, pesticides may perhaps be present in ground water much earlier than expected subsequent to application (for the reason of brisk movement through transportable zones), and also for comprehensive epoch afterward (because of regular discharge from immobile zones).

Pesticide in groundwater and allied hazards

Development of agriculture is strongly associated to exercise of pesticides. The utilization of pesticides has assisted in thwarting the damages originated by pest attacks and has enhanced the manufacturing prospective of crops, although these surplus amounts are escaping down to ground water thus creating its pollution. Pesticide contamination in ground water is exceedingly very much associated to perseverance of pesticides in soil. Perhaps, it has been approximated that less than 0.1% of the insect repellent applied to crops in reality contact the target pest; the rest go into the environment pointlessly, polluting the soil, water and air, where it can toxin or else negatively distress non target organisms (Pimentel and Levitan, 1986). In addition, a lot of pesticides can persevere for extended periods in an ecosystem, organochlorine insecticides, for example, were still evident in surface waters 20 years subsequent to their employment had been prohibited (Larson *et al.*, 1997); and formerly an unrelenting pesticide has penetrated the food chain, it can go through “biomagnification”, i.e., accretion in the body tissues of organisms, where it may attain absorption many times privileged than in the adjacent environment.

Capability of a pesticide to acquire absorption chooses whether it will trickle down to ground water or not. The pesticides having minimal adsorption or absorption capacity for surface of soil will percolate downwards to ground water and will direct to its contamination. Groundwater pollution on account of pesticides is a global glitch. As stated by the U.S. Geological Survey, at least 143 different pesticides and 21 transformation products have been discovered in ground water, including pesticides from every single major chemical class (Aktar *et al.*, 2009). Numeral reports are documented on the subject of the ground water contamination via remainders of pesticides. Pesticides source severe health risk to existing systems as they are hastily soluble in fat and they can mount up in objective organisms. The risks associated with consumption of ground-water contaminated due to pesticides can be grouped into two categories:

Hazards owing to highly noxious pesticides: Organochlorines, organophosphates, and carbamates are three cohorts of traditional highly toxic pesticides. Organochlorine insecticides operate as nervous system disruptors causing seizures and paralysis of the insect and its ultimate fatality. These pesticides can cause severe endocrine disarray in mammals, fish, and birds; therefore the majority of them have been prohibited in agriculture globally. The organophosphates pesticides reduce the acetylcholinesterase enzyme, responsible for hydrolyses acetylcholine in the nervous system of a lot of species, together with humans (Frasco *et al.*, 2006), hence impairing the nervous system. Even though they are simpler to be ruined than organochlorines, organophosphate pesticide remains is major threat to the ecosystem as well as food industry as their severe toxicities are permanent. Numerous populaces are exposed to pesticides professionally, and pesticide self-poisoning is a chief civic health crisis. Yearly, 3 million cases of severe poisoning have been accounted from pesticide contact, ensuing in the demises of 250 to 370000 people each year (Marrs, 1993). Hence, the practice of organophosphates has been constrained or prohibited globally.

Hazards occurred because of low toxic pesticides: The soon after developed anilines, amides, pyrethroids, and azotic heterocyclic complexes are normally less toxic. The pyrethroids are non-persistent sodium conduit modulators and are little noxious than carbamates and organophosphates to mammals. For that reason, the practice of pyrethroids has been augmented significantly in the last 30 years. Sadly, pyrethroids are extremely poisonous to marine organisms such as fish, mollusks, and arthropods (Koureas *et al.*, 2012). Butachlor can persevere in the surroundings for up to 10 weeks, and what's still inferior is that butachlor and metolachlor have been recognized as mutagens. The Trifluralin and pendimethalin pesticides demonstrate elevated toxicity to marine organisms and they can harm the thyroid gland and liver. Therefore, these two aniline herbicides have been prohibited in a lot of European countries.

Antagonistic effects of pesticide (herbicide) application on non-target plants

Herbicides are devised to eradicate the unwanted plants from the main crops. So, there is no surprise in realising that they have potential to damage or kill the desired crops if applied directly or indirectly while tapping contaminated groundwater. Additionally, the sub-lethal effects are caused due to pesticide exposure on plants. Phenoxy herbicides, including 2,4-D, have potential of injuring the shrubs and trees in vicinity if they coast on the leaves. Some herbicides like glyphosate are capable of sternly reducing seed quality, and increasing the disease vulnerability of particular plants. The pesticides can also affect the beneficial microbial count in soil and insects necessary for overall health of soil and plants. For instance, Glyphosate can reduce the development and activity of free-living nitrogen-fixing bacteria in the soil (Biswas *et al.*, 2014). Hence, it can be impressed upon that the plants not only can suffer directly at the hands of the pesticides, but can also encounter indirect repercussions of pesticide treatment when soil microorganisms and beneficial insects are maltreated.

Health-based guideline values for pesticide residues in potable water

Younes and Galal-Gorchev (2000) elucidated the existing WHO approach for assessing health-based recommendations (or guideline values, GVs) for pesticide residues in drinking water. GVs were computed from 1% of the tolerable daily intake (TDI) for the highly toxic pesticides like organochlorines and from 10% TDI for rest. The GV for potentially oncogenic pesticides is grounded on modelling approach and is related with an estimated upper-bound excess lifetime risk of 10⁻⁵. The guideline values arrived upon by Younes and Galal-Gorchev (2010) are shown in Table 2.2.

Fertilizers as groundwater contaminants

Disproportionate exploitation of nitrogenous fertilizers within agriculture has been one of the principal causes of soaring levels of nitrate in groundwater. Nitrogen is applied in two forms viz. ammonium (NH₄⁺) and amide (NH₂⁻), apart from nitrate, which produce nitrate in soil system through mineralization, which is comparatively swift in tropical and subtropical soils. Because of its elevated solubility in water and stumpy withholding by soil particles, nitrate is prone to discharge to the subsoil layers and eventually to the groundwater, if not engaged up by plants or denitrified to N₂O and N₂.

Table 2.2. Guideline values based on health developed by WHO for pesticide remainders in drinking water (Source: Younes and Galal-Gorchev, 2000).

Pesticides	Guideline value, µg/l	Pesticides	Guideline value, µg/l
Bentazone	300	Aldicarb	10
Metolachlor	10	Atrazine	2
Isoproturon	9	Carbofuran	7
Propanil	20	2,4-D	30
Pendimethalin	20	Cyanazine	0.6
Simazine	2	2,4-DB	90
Pyridate	100	Chlordane	0.2
Alachlor	20	Aldrin/dieldrin	0.03
Chlortoluron	30	DDT	2
1,2-Dibromo-3- chloropropane	1	Dichlorprop	20
1,3-Dichloropropene	20	Diquat	10
Methoxychlor	20	Fenoprop	9
EDB	0.4-15	Trifluralin	20
Heptachlor + epoxide	0.03	Hexachlorobenzene	1
Isoproturon	9	Mecoprop	10
MCPA	2	Lindane	2
Methoxychlor	20	Molinate	6
2,4,5-T	9	Terbuthylazine	7

Table 2.3. Tolerance limits of NO_3 in potable water recommended by different nations and organizations (Source: Majumdar and Gupta, 2000).

Country/Organization	Concentration as $\text{NO}_3\text{-N}$ (mg/l)	Concentration as NO_3 (mg/l)
*US Environmental Protection Agency	10	45
*WHO	10	45
*ICMR (India)	10	45
*Poland	10	45
*Canada	10	45
*EEC ^a	11.30	50
*Bulgaria	6.7	30
Denmark	11.3	50
Belgium	11.3	50
Hungary	9.0	40
Finland	6.8	30
USA	10	45
UK	11.3 ^b	50
	22.6 ^c	100

^a EEC countries are entitled to the above rules in special situation.

^b EEC directive.

^c Chief Medical Officer's recommendation.

The pace of discharge is directed by the characteristics of soil and quantity of water there in the soil system (Majumdar and Gupta, 2000). The influx of nitrate to groundwater can be improved by superficial groundwater table; undue submission of nitrogenous fertilizers, manures and irrigation; and profuse rainfall. The former imperative sources causative of high quantity of nitrate to groundwater are barnyards, livestock feeding, septic tanks, animal and human contamination. Within and around areas of towering urbanization and industrialization, public and industrial wilds may add soaring levels of nitrate to the groundwater. As soon as the nitrate loaded groundwater is propelled out and utilized for drinking, it sources lot of health muddles in humans. Diverse associations and countries have positioned valued standards for NO_3 in potable water (Table 2.3), to maintain public health from the dangers linked with high concentration of nitrate.

Health hazards related with nitrate in groundwater

Nitrate as such is not a problem but it becomes a problem only when it is transformed into nitrite in the human body and results in a disease like Methaemoglobinemia (also referred to as Blue Baby Disease or Blue Baby Syndrome), gastric cancer and some other health disorders in humans. Nitrite produced from nitrate in drinking water enters the bloodstream mainly through the upper gastrointestinal tract. The nitrite in bloodstream causes oxidation of haemoglobin to methaemoglobin, a Fe (III) compound with diminished oxygen carrying capacity owing to higher oxidation state of Fe making it incapable to bind with oxygen. Consequently, the oxygen carrying capacity of bloods gets depleted and oxygen shortage causes the cyanosis, i.e., skin colour turns

into blue. The babies are susceptible to this disease more as compared to adults owing to their high fluid intake, hence the name blue baby disease. Nitrate, can react with different organic compounds and result in the formation of carcinogenic compounds including nitrosamines and nitrosamides as a result of nitrosation reactions in the stomach. These carcinogenic nitroso compounds are considered to take part in the aetiology of some forms of cancers in humans. A carcinogen namely dimethylnitrosamine is produced in the stomach from dimethylamine present in gastric juice. Nonetheless the formation reaction of dimethylnitrosamine is slow in stomach and quantities produced may be low (Majumdar and Gupta, 2000), which can dormant the cancer for 20-30 years (Bockman and Granli, 1991). The high nitrate intake in drinking water has also reported to cause other health disorders namely hypertension (Malberg *et al.*, 1978), non-Hodgkin's lymphoma (Weisenburger, 1991) and enhanced infant mortality.

Conclusion

Ground water is one of the prized natural resources, but it is under continuous threat owing to the prolonged application of the agrochemicals. The application of the agrochemicals is the need of an hour so as to feed the burgeoning population, control the pest attack on plants and eradicate the weeds. However, their application is done at a significant cost, which warrants a threat to almost every sphere of ecosystem; groundwater being the delicate of all because it's cleansing needs years to return back it to its original clean state. In the light of the above cited facts, it is manifested that the agricultural activities serve as a potential pollutant of groundwater. Therefore, strategies need to be made to minimise the drift of excessive agrochemicals from agrarian fields to ground water. The agrochemicals should be applied and handled in accordance with the regulations and recommendations levied by different organisations which aim to minimise the negative impacts of these chemicals on the human health and environment. The agrochemical whose traces persist in the groundwater for years should be completely banned globally.

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Chapter 3

Organic wastes in agriculture: Risks and remedies for sustainable agriculture production

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Abstract

Agricultural and non-agricultural wastes are the valuable sources of plant nutrients which is useful to maintain soil health. The potential of their handling, storage and disposal have broad implications for the environment beyond the farm. Effective organic waste management and good agricultural practice can be done through valuing the organic waste nutrient content, reduce losses of organic wastes from storage and timely applications of organic wastes which significant influence on nutrient loss.

Keywords: Agricultural risks, Environmental pollution, Organic wastes, Sustainable agriculture, Waste minimization

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Introduction

Organic waste in agriculture is defined as "contaminants from the cultivation and processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy and crops." These comprise the non-product turn outs of agricultural production and processing that may include stuff beneficial to man but whose commercial worth is less than the expense of gathering, conveyance, and processing for favorable use. In this chapter, two different forms of organic waste that which are responsible for agricultural pollution have been discussed.

In the first place are those which are generated by agricultural activities. These primarily include excreta (urine and fecal matter) of farm animals but may also comprise additional substances such as silage effluent and unclean water from milk parlors. In the second place, are the residues like sewerage, slurry, paper-pulp and food processing residues. These wastes are generally produced off-farm (i.e. largely from households and industries) and are often brought onto agricultural lands and applied or recycled there. These agricultural and non-agricultural organic wastes include a variety of substances, such as carbohydrates, fats, proteins, nitrates, phosphates and ammonia, and possibly being subjected to contamination by pesticides, oils, veterinary products, trace metals and pathogens (Smith *et al.*, 2001). The present chapter will focus on:

- agricultural organic wastes and their production.
- the pollution risks associated with organic farm wastes and remedies to limit these risks.

Pollution from agricultural organic wastes

The utilization of organic wastes, particularly manure from cattle and other farm animals to agricultural land has conventionally been significant for preservation of soil fertility. Nutrient status as well as organic matter levels in the soil have been maintained by organic wastes since historical era. This scenario of utilization of agricultural wastes has changed significantly with an increase in specialization and upsurge of animal farming. Several significant trends have appeared in the production and use of these wastes. First and foremost, the quantity of manure and slurry produced is very high compared to the portion put to use. The unutilized wastes are generally disposed off without treatment. Secondly, upsurge inside the livestock sector has led to great number of animals being concentrated in comparatively limited areas, so in consequence the production of huge quantity of waste at an individual location.

Despite being a precious substitute to synthetic inorganic fertilizers, a number of farmers have somewhat limited notion of their nutritive value and as a result might manage them ineffectively and unproductively (MAFF, 2000). This results in inadequate utilization of their nutritive content. The farmers may continue extensive use of chemical fertilizers even after the application of animal manure. Application of organic farm wastes could have resulted in substantial saving in chemical fertilizer expenditures without compromising with the crop yield (Smith *et al.*, 2001). Another important consequence of underestimating the nutritive value of organic wastes is that a

huge quantity of these is applied in a small area of agricultural land. The excesses are washed due to rain and runoff causing nutrient leaching and environmental pollution.

A wide and extensive attitude needs to be adopted while controlling the pollution caused by the organic wastes. This is because the pollution caused by these wastes can take place in numerous ways. The waterways, particularly lakes, rivers, ponds and ditches, adjoining the areas producing, storing or using organic wastes are potentially susceptible to point-source pollution. Another risk associated with these wastes is the diffuse pollution caused by microbial break-down of manure which leads to nitrate leaching. Organic wastes not only pose a serious environmental threat but are problematic for crops as well as farm animals, various problems caused because of organic wastes to crops and farm animals are listed in Table 3.1.

Classification of farm wastes

Farm wastes can be grouped into four major classes:

Slurry

Slurry is defined as 'excreta produced by livestock in a yard or building or a mixture consisting entirely or primarily of such excreta, bedding, rainwater and washing from a building or yard used by livestock or any combination thereof ; a consistency that allows it to be pumped or discharged by gravity at any stage in the process of handling" (HMSO, 1991). Thus, a mixture of fecal matter, urine and water with dry matter not more than 10% is considered to be slurry (Shepherd and Gibbs, 2001).

Manure

Waste materials like straw from deep litter or conventionally covered yards having a high solid content such that it can be piled is called manure. The dry matter content is generally more than

Table 3.1. Problems caused through organic waste application for crops and livestock.

Problem	Reason
Winter kill	Application of organic wastes to crop during the winter may smother small seedlings, as well as promote growth during mild weather thereby increasing the risk of winter kill.
Scorch	Damage can be caused by direct contact slurry and the crop.
Fouling	Livestock may not feed on grassland tainted with organic waste
Disease	Diseases (parasites, bacteria etc.) may be passed onto livestock.
Staggers	Heavy application can cause nutrient in herbage and subsequently on grazing livestock (e.g. magnesium/potassium imbalance, known as hypomagnesaemia).
Flies	Excessive application can cause environmental nuisance.

10% and has a very low density when stacked afresh. Manure which has been piled for a long duration say a couple of months, tend to become darker in color, easily crumbled and of greater density than freshly stacked manure.

Dirty water

Water used for washing yards, milk-parlors, farmsteads, barns etc. contributes towards waste water from farms. Rainwater which has been contaminated by farm wastes, manure, crop residues is also included in waste water from farms (MAFF, 1993). This water has very low dry matter content of less than 3% and needs to be disposed off safely.

Silage effluent

This comprises the discharge from a variety of fodder crops, chiefly grass, when confined in a pit, silo or large bale during the course of making silage.

Pollution risks from farm wastes

Oxygen dissolved in water is continuously used up by the organisms living in water bodies. This oxygen is generally restored naturally due to processes like re-aeration and photosynthesis. Other processes also contribute in the replenishment of dissolved oxygen in water bodies. Temperature drop in water bodies reduce the microbial activities and cause a rise in the oxygen saturation potential of the water. Sometimes water rich in dissolved oxygen discharges in the water bodies increasing the concentration of dissolved oxygen (Nemerow, 1991). This equilibrium can be seriously disturbed organic pollutants enters a waterway. These serve as food material for the microbes as well as small invertebrates living in the water bodies. In case the concentration of organic wastes is high, this leads to rapid increase in the population of these organisms which deplete the dissolved oxygen at a rate much higher than the rate of replenishment (Mason, 1996). Thus, the levels of oxygen in the water bodies may fall to an extremely low level and cause serious damage to 'clean-water organisms.' The tolerance in fish to depleting oxygen levels is comparatively very low (Table 3.2).

Table 3.2. Relative tolerance to oxygen depletion by some river organisms.

Common name	Spices	Tolerance
Salmon	<i>Salmo solar</i>	Low
Brown trout	<i>Salmo trutta</i>	Low
Shrimp	<i>Gammarus pulex</i>	Medium
Water hog-louse	<i>Assellus aquaticus</i>	Medium
Chironomid midge	<i>Chironomus riparius</i>	High
Blood-worm	<i>Tubifex tubifex</i>	High

Thus, their population levels are affected drastically due to pollution from organic wastes. One of the most frequently applied measures for estimating the 'relative pollution potential' of an organic pollutant is in terms of oxygen required by microbes to break-down the material. It is referred to as the Biochemical Oxygen Demand (BOD). Higher values of BOD specify the presence of a potentially serious contaminant, as such its release into the waterway must be stopped. Each of the organic farm wastes belong to this category (Table 3.3). the poor management and disposal of slurries and silage effluents into water bodies can cause serious pollution hazards. Thus, even low quantities of these wastes should not be discharged into water bodies.

The contamination issues accompanying the silage wastewater are furthermore aggravated by two factors; firstly, the effluent is extremely corrosive (Table 3.4) and can leak through the floor of the silos, collection lines or storage reservoirs that may be damaged, rusty, fractured or permeable (Richardson *et al.*, 1999). Secondly, the water content in the silage determines its volume, which can be very large as the water content is high. Thus, the volume of effluent produced during silage making can be very large. The prediction of influence of an organic contaminant flowing into a waterway is somewhat complicated. This is due to the reason that these effects are governed by a number of factors; viz. temperature, dilution rates and the type of watercourse. The time or season of the year is also significant. Farm wastes produced in early summer is generally more problematic than winter produced materials (O'Donnell *et al.*, 1997). However, the process of self-purification enables the waterways to recuperate from organic over time, where the decomposition of organic material and replenishment of oxygen levels by natural processes takes place (Mason, 1996).

Table 3.3. The Biochemical Oxygen Demand (BOD, mg l^{-1}) of farm wastes in comparison with other organic materials (NRA, 1992).

Organic material	Typical BOD
Clean river water	<5
Untreated human sewage	350
Yard washings	2000
Animal slurry	30000
Silage effluent	60000

Table 3.4. Selected characteristics of silage effluent, collected from unwilld grass silage (O'Donnell *et al.*, 1995).

Characteristic	Value
pH	3.8
Titrateable acidity (mmd NaOH ⁻¹)	177
Lactic acid (g kg^{-1})	24
Acetic acid (g kg^{-1})	3.3
Volatile fatty acids (acetic, propionic and butyric acid) (g kg^{-1})	3.5

Ammonia toxicity in waterways

Ammonia naturally occurs in two different forms- ammonium ions (NH_4^+) and unionized ammonia, NH_3 , (Francis-Floyd 2009). Ammonia is formed naturally from the decomposition of organic matter as well as excreted by fish as a nitrogenous waste product. It is also a derivative of protein metabolism and is chiefly excreted through the gill membranes. A very little quantity is also excreted in the urine. Bacteria convert this ammonia into nitrite and nitrate (Figure 3.1). The quantities produced naturally are generally small and considered harmless for fish and other aquatic organisms (Francis-Floyd, 2009). The toxic nature of aquatic ammonia is primarily due to its unionized form, NH_3 (Arthur *et al.* 1987). With the increase in pH, the toxic nature of ammonia increases due to the increase in comparative quantity of unionized ammonia. This is shown in Figure 3.2 (Brinkman *et al.* 2009; Delos and Erickson, 1999).

Despite the fact that ammonia is an essential and life-sustaining nutrient, surplus amount of this compound may collect in the bodies of organisms and cause changes in metabolic system of aquatic biota or raise their body pH. Fish might experience a loss of equilibrium, hyper-excitability, increase in respiration and oxygen intake, and increase in heart-rate. The presence of significantly high levels of ammonia in organic farm wastes is an additional pollution hazard for fish and other freshwater invertebrates. The pollution caused by ammonia is not only limited to surface water bodies but affects groundwater also (DETR, 2001). A rise in the level of free ammonia in waterways can inhibit the process of nitrification in sediments, thus causing the potentially toxic accumulation of nitrite in the water body (Kim *et al.*, 2008).

Figure 3.1. Conversion of fish-generated ammonia in the environment.

Figure 3.2. Chemical speciation of ammonia over a range of pH values (EPA, 1999).

Furthermore, it was the production of manures and slurries, and washing of yards and milking parlors that was causing a measurable deterioration in the quality of watercourses (Epstein, 2011). Reductions in water quality during the study were also related to rainfall. Periods of heavy rainfall caused the increased run-off of slurry from yards as well as from fields that had recently received slurry applications (Tepe and Boyd, 2003).

Pathogens from farm wastes

Cattle and other farm animals are potential transporters of a number of disease-causing bacteria, viruses and parasites. These are carried to human beings if the application of these wastes to soil results in contamination of crops or water bodies. Increasing the awareness about various pathogenic microbes of animal origin (zoonoses) has been identified as a major community-health concern, particularly due to the outbreak of water-borne diseases, seemingly triggered by fecal contamination of organic wastes. Many pathogenic bacteria, viruses, and protozoa are present in even healthy animals, but can cause serious ailments or even death when transmitted to human beings. Some of the major pathways which transmit pathogens to humans are shown in Figure 3.3. The wastes from farm animals, like feces, respiratory secretions, urine, and sloughed feathers, fur or skin) usually comprise excessive concentrations of human and animal pathogens (Strauch and Ballarini, 1994). The concentration of certain pathogens in fecal matter of farm animals ranges from millions to billions per gram of wet weight or millions per milliliter of urine (Mustafa and Anjum, 2009). Moreover, the tendency of production establishments to raise a large number of animals in fairly modest spaces leads to the production of extremely large quantities of concentrated waste materials that needs to be efficiently taken care of in order to reduce environmental and community health hazards.

Figure 3.3. Sources and transmission pathways of pathogens to humans from animal agriculture (Sobsey et al., 2006).

Animal pathogens that pose potential risks to animal and possibly human health include a variety of viruses (Table 3.5), such as swine hepatitis E virus, bacteria (Table 3.6), *Salmonella species*, and parasites (Table 3.7) such as *Cryptosporidium parvum*. Several pathogenic organisms similar to those referred are prevalent in cattle and other farm animals and their eradication from livestock as well as their production centers is a challenging task. Since the pathogens are highly widespread in livestock, these are generally present in fresh animal manure and other animal wastes. Thus, these farm wastes need to be adequately treated and contained in order to prevent the health hazards they pose to animal as well as human health (Graczyk et al., 2000).

Sewage application to agricultural land

Sewage applied to agricultural lands is not only obtained from domestic sewage and waste-water, it may also collect impurities from industrial wastes and runoff from roads. Thus, it comprises various metal impurities including cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), lead (Pb) and zinc (Zn), as well as organic micro-pollutants such as Polynuclear Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) (Smith, 1995). However, due to implementation of different regulations, the contamination of sewage with metallic and other industrial products has significantly declined (Environment Agency, 2001). Despite various regulations, substantial quantity of chemicals may find their way to sewage sludge.

Table 3.5. Some important animal viruses potentially present in animal manure (Sobsey et al., 2006).

Virus or virus group	Taxonomic group	Animal hosts	Disease in animals	Human infection/disease	Transmission routes	Presence in manure
Enteroviruses	Picornaviridae	Bovine, porcine, avian	Yes, in some	No, but needs study	Fecal-oral and respiratory	Yes
Caliciviruses	Caliciviridae	Bovine, porcine, avian	Yes, in some	No, but needs study	Fecal-oral and respiratory	Yes
Reoviruses	Reoviridae	Wide host range for some	Yes, in some	Yes/No	Fecal-oral and respiratory	Yes
Rotaviruses	Reoviridae	Found in many animals	Yes, in some	No, but needs study	Fecal-oral and respiratory	Yes
Adenoviruses	Adenoviridae	In many animals	Yes, in some	No, but needs study	Fecal-oral and respiratory	Yes
Herpes viruses	Herpesviridae	In many animals	Yes, some	No, but needs study	Respiratory	Yes
Myxoviruses	Myxoviridae	In many animals	Yes, in some	Yes, some; no, others	Respiratory	Yes
Pestiviruses	Pestiviridae	In many animals	Yes, in some	No	Fecal-oral and respiratory	Maybe
Corona-viruses	Coronaviridae	In many animals	Yes, in some	No	Respiratory	Yes
Hepatitis E virus	Uncertain	Swine, rat, chicken, maybe others	Yes, but mild effects	Maybe	Respiratory and enteric	Yes
Vesicular stomatitis virus	Rhabdovirus	Cattle, horses, swine; others	Yes	Yes, occupationally	Contact with infected animals	Maybe

These include:

- dichlorobenzene from toilet cleaner and alkyl benzenes from detergents.
- Cu and Zn from domestic products such as shampoos, skin creams, toilet cleaners and mouthwash.
- Cu and Zn from plumbing fittings, water pipes and storage tanks;
- Hg from dental surgeries.

These metals are an essential component of the natural environment and are extremely important for the growth and development of both plants and animals, but at the same time their overdose is highly toxic. Many elements like Cd, Cu and Zn may also accumulate within the soil profile over the years and prove extremely detrimental to soil microbes, soil animals, crop plants and possibly enter the human food-chain (Renner, 2000). Another important concern associated with the application of sewage sludge to agricultural lands is the Nitrogen (N) and Phosphorous (P) pollution. Large scale applications of sewage and wastewater to agricultural lands might result in the leaching of these two nutrients into the waterways, thus contaminating them. Application of raw sewage slurries may also emit foul odor which is a serious environmental problem. Further-

Table 3.6. Some important bacteria potentially present in animals and their wastes (Sobsey et al., 2006).

Genus and species	Animal hosts	Disease in animal hosts	Human infection and disease	Transmission routes	Presence in manure?	Non-fecal sources?
<i>Aeromonas hydrophila</i>	Many	Usually no	Yes, but only virulent strains	Water, wounds, food	Yes	Yes
<i>Arcobacter butzleria</i>	Many	Yes, often	Yes	Direct contact, maybe food and water	Yes	No
<i>Bacillus anthracis</i>	Goats; others	Yes	Yes	Aerosols, skin (wounds), ingestion	Yes	Yes
<i>Brucella abortus</i>	Cattle	Yes	Yes	Direct contact, food, air, water	Yes, rare	No
<i>Campylobacter jejuni</i>	Poultry, other fowl	No	Yes	Food and water	Yes	Maybe
<i>Chlamydia psittaci</i>	Parrots; other fowl	-	Yes	Direct contact; airborne	Unlikely	No
<i>Clostridium perfringens</i>	Many	Sometimes	Yes	Food, wounds	Yes	Yes, soil and sediments
<i>Clostridium botulinum</i>	Many	Sometimes	Yes	Food	Maybe	Yes, soil and sediments
<i>Escherichia coli</i>	All mammals	No	Yes, pathogenic strains	Food and water	Yes	No, but natural occurrence in tropics
<i>Erysipelothrix rhusiopathiae</i>	Swine, other animals, fish and shellfish	Yes, sometimes	Yes, rare	Direct contact, skin abrasions	Yes	Yes, infected animals
<i>Francisella tularensis</i>	Ovines, other animals, ticks, deerflies	No	Yes	Direct contact, fomites	Yes	Animal tissue
<i>Leptospira interrogans</i> and other species	Many animals	No	Yes	Direct contact	Yes	Urine
<i>Listeria monocytogenes</i>	Many animals	No	Yes	Food, water, fomites	-	Soil, vegetation
<i>Mycobacterium tuberculosis</i>	Rare; some animals	-	Yes	Respiratory exposure	Yes	No
<i>Mycobacterium paratuberculosis</i>	Some animals	-	Yes	Respiratory	Yes	No
<i>Salmonella species</i>	Many animals	No	Yes	Food, water, fomites	Yes	No
<i>Yersinia pestis</i>	Rats, squirrels, other animals	No	Yes	Flea bite, direct contact	Yes	Animal tissue
<i>Yersinia enterocolitica</i>	Swine, other animals	No	Yes	Direct contact, food, water	Yes	Possibly environmental sources

Table 3.7. Some important parasites potentially present in animals and their wastes (Sobsey et al., 2006).

Parasite	Taxonomic group	Animal hosts	Disease in animals?	Human infection/ disease	Transmission routes	In manure?
<i>Ascaris suum</i>	Helminth, nematode	Swine	Yes	Yes	Ingestion of water, food, soil	Yes
<i>Balantidium coli</i>	Protozoan, ciliate	Swine, other animals	No	Yes	Contact, ingestion of water and soil	Yes
<i>Cryptosporidium parvum</i>	Protozoan, coccidian	Many animals	Yes	Yes	Ingestion of water	Yes
<i>Giardia lamblia</i>	Protozoan, flagellate	Many animals	Yes	Yes	Ingestion of water	Yes
<i>Microsporidia</i>	Protozoans, microsporidia	Many animals	No	Yes, immunocompromized	Ingestion, possibly water	Yes
<i>Pneumocystis carinii</i> *	Fungus; similar to protozoans	Environment and many animals	Yes	Yes, immunocompromized	Inhalation	Yes
<i>Toxoplasma gondii</i>	Protozoan, coccidian	Felines	Yes	Yes	Ingestion of feces, food, water	Yes, if an infected host

*Previously considered a protozoan parasite, but now known to be a mycotic agent.

Table 3.8. Required minimum separation distance between manure storage and watercourses, wetlands, and wells

Storage type	Distance to	
	Watercourse or wetland, m (ft)	Source of domestic water, m (ft)
On-farm storage facility	90 (300)	90 (300) *
Field storage	90 (300)	90 (300) *
Composting	90 (300)	90 (300) *

* Public water supply 300 m (984 ft).

Figure 3.4. In barn storage - manure pack.

Figure 3.5. Solid manure storage - curbed concrete slab with ramp.

Figure 3.6. Solid or semi-solid manure storage - concrete slab with sidewalls and drive-in ramp.

Figure 3.7. Liquid manure storage - circular concrete tank.

Figure 3.8. Biogas production (Source: Sobsey et al., 2006).

Figure 3.9. Reed bed treatment (Source: Sobsey et al., 2006).

more, the sewage sludges can also cause pathogen contamination similar to that of the livestock wastes. Some important pathogens present in the sewage include bacteria such as *Salmonella* (especially *Salmonella typhimurium* DT104), human viruses such as Hepatitis A, parasitic nematodes and worms, and parasitic protozoa such as *Cryptosporidium*.

Practical solutions

Poor management of organic wastes from farms is the primary cause of pollution resulting from the organic wastes. Poor management results in:

- spillages;
- run-off due to over-application in the field;
- run-off from yards;
- inadequate storage capacity, structure and management;
- leaking/unknown drainage systems;
- application of slurries when land is frozen or waterlogged.

Most pollution issues related to farm wastes can be evaded using good manure management practices, proper storage facilities, and adequate separation distances between non-compatible land uses. The management practices include collecting, storing, transporting and applying manure to land. The purpose of managing farm wastes must be to maximize the soil amending value of manure and to reduce the risk of environment pollution.

Handling and collection

The collection and storage of organic wastes depends on the moisture content of the waste. The storage facility is selected depending on whether the manure is solid, semi-solid or liquid. Solid wastes (<80% moisture content) can either be stacked and can be collected using equipment that

moves bulk materials. Semi-solid wastes have lower moisture content (80-95%) and does not flow. Thus, it can be collected and piled like solid wastes. Liquid wastes (>95% moisture content) flow under the influence of gravity and can be pumped for storage.

Storage

The storage facility for wastes should be sufficiently large to store wastes for a sufficiently long time and allow precipitation of solids and application to lands. Solid wastes can be stored in three different ways- in barns as solid manure packs (Figure 3.4); on curbed concrete pads which can contain runoff (Figure 3.5); and on curbed control slab with roof. Field storage of wastes should be avoided especially where the soil is highly permeable, is in proximity of a watercourse or has a shallow groundwater table. Semi-solid wastes can be stored on curbed concrete slabs with earthen beds. The floor should be sloping to allow access to tractors (Figure 3.6).

The earthen beds need to be designed and constructed carefully to prevent seepage. For soils having low clay content, semi-solid wastes may be stored in roofed structure with reinforced concrete walls. The storage structures should also be well-ventilated. Liquid wastes must be stored in impermeable enclosures such as concrete tanks, above ground glass-lined steel tanks and earthen ponds (Figure 3.7).

Setback considerations

Suitable distance between livestock facilities and neighbors is one means of recompensing for foul odor production and reduction in the potential for nuisance conflicts. Establishing farmyards in the vicinity of developing areas can assure for growth of the venture in future. Greater distance from settlements offers more time for odors to become diluted due to mixing with air.

The recommended Minimum Separation Distance (MSD) between a livestock operation and a single residence or residential and recreational areas varies with the following factors:

- size of the agricultural operation measured in animal units
- degree of expansion from existing operation
- type of manure storage
- type of housing
- type of livestock

With the increase in the size of livestock establishments, the distance from the residential areas should also increase. However, the criteria may change from area to area as well as recommendations of local municipalities. The municipality should be necessarily contacted before establishment of any new facility.

The location wells and watercourses the proximity of animal farms and manure storages should be planned in detail. This is more vital in earthen storage structures and areas with a shallow bedrock and water table. Required MSD between manure storage and watercourses, wetlands, and wells are given in Table 3.8.

Wells should be located uphill from storages and constructed in a manner that will reduce the risk of pollutants entering the well. Grouting the annular space outside the casing with cement or bentonite grout must be carried out.

Alternative technologies for farm waste treatment

Biogas production and reed bed treatment (RBT) have been identified as two of the most practical solutions to problems associated with organic agricultural wastes.

Biogas production

An alternative to applying slurry and manure to land is to anaerobically digest the organic materials with micro-organisms to produce biogas; a mixture of methane (55–65%) and carbon dioxide (35–45%). An anaerobic digester will partly convert manure to energy in the form of biogas which contains methane. Biogas is used as a renewable fuel and the byproducts of digestion can be used as a manure in the fields (Figure 3.8).

Reed bed treatment

An alternative way of treating dirty water, such as dairy washings and yard run-off, is to use an RBT system. This is an artificially constructed wetland usually planted with Common Reed (*Phragmites australis*) through which the dirty water slowly trickles (Figure 3.9). The reeds not only absorb nutrients such as nitrogen and phosphorus, but also have the ability to transfer oxygen down through their stems and out via their root system into the surrounding rhizosphere. This increases the capacity of the system for the aerobic bacterial decomposition of organic pollutants (e.g. milk, urine and faeces), as well as encouraging the proliferation of a wide range of aquatic organisms, some of which directly utilise additional pollutants (Shepherd and Gibbs, 2001). There are numerous designs of RBT system for treating sewage, industrial effluents and highways run-off, as well as agricultural wastes. Their main benefits, compared to the conventional treatment of dirty water in tanks and lagoons, are claimed to be low capital cost, very effective water treatment, minimal (if not enhanced) visual impact, and little smell.

Conclusion

It is clear from the above discussion that agricultural and non-agricultural wastes may be valuable sources of plant nutrients and soil conditioner/improver. Yet, potential problems associated with their handling, storage and disposal may have broad implications for the environment beyond the farm. Effective organic waste management and good agricultural practice may entail: knowing and valuing the organic waste nutrient content; using this information to balance nutrient inputs and removals, such as crop offtake; reduce losses of organic wastes from storage and animal housing; apply the wastes evenly and incorporate into

soil rapidly; timely applications of organic wastes have a significant influence on nutrient loss, i.e. avoid late summer or early autumn applications.

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Chapter 4

Heavy metals accumulation in crop plants: Sources, response mechanisms, stress tolerance and their effects

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Abstract

Heavy metals are one of the major substances concerned with agricultural pollution. The heavy

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metals are highly toxic to plants and living life. Heavy metals play a vital role in nature as they are essential for the plant's normal growth. These heavy metals are also involved in redox reactions, transferring electrons, basic functions in nucleic acid metabolisms, and being an integral part of several enzymes as a direct participant. The availability at a certain concentration of these essential metals in growing medium is very important, but their excess concentration results in several toxic effects. Therefore, the present book chapter comprised the information for better understanding of heavy metal toxicity and their accumulation mechanism by the plants.

Keywords: Heavy metals, Metallothioneins, Phytochelatins, Toxic effects, Stress tolerance mechanisms, Uptake mechanisms

Introduction

Environmental contamination by significant metals could be a worldwide issue as a result of rising in urbanization, increment, and mining activities, etc. and leads to varied short- and long-run effects on the environment (Kumar *et al.*, 2015; Khanna *et al.*, 2018). Heavy metals such as Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn, etc. are highly toxic to the environment (soil and water) (Kumar *et al.*, 2016; 2017). Heavy metals can be defined as any metallic element with a specific gravity greater than five (g/cm^3) (Khanna *et al.*, 2018). The plants grown on soils with contaminated effluent (heavy metals) show several physiological changes in the biochemical process like nutrient accumulation, respiration, gaseous exchanges, etc. The substantial metal has poisonous quality because of overwhelming the stress in plants which vary with a few variables like plant species, the convergence of the substantial metal and its concoction structure and soil creation (Nagajyoti *et al.*, 2010).

Role and sources of heavy metals in plants

Different heavy metals play a vital role in nature as they are essential for the plant's normal growth. Important heavy metals such as Cu, Zn, Fe, Mn, Mo, and Ni play important roles in plant biochemistry and physiology (Zhuang *et al.*, 2009). As essential micronutrients, Cu and Zn are very important for normal plant growth as they either serve as an enzyme reaction cofactor and activator or exert a catalytic property in metalloproteins such as a prosthetic group. These crucial heavy metals also involve redox reactions, transferring electrons, basic functions in nucleic acid metabolisms, and being an integral part of several enzymes as a direct participant. The availability at a certain concentration of these essential metals in growing medium is very important, but their excess concentration results in several toxic effects (Nagajyoti *et al.*, 2010). Since synthetic and industrialization are the expanding source, these toxic metal contaminations go in the farming soil and water bodies. The heavy metals sources are discussed in Table 4.1 (Khanna *et al.*, 2018).

Table 4.1. Different sources of heavy metals in the agriculture and environment.

Sources	Heavy metals	References
Mining activities/smeltering	Cr, Pb, Zn	Sumner (2000)
Geological and anthropic activities	Cr, Co and Ni, Cr, Pb, Zn	Facchinelli et al. (2001)
Sulfide mineral deposits	As	Nordstorm (2002)
Earth's crust	Cd, Hg, Pb, As	Järup (2003)
Phosphate fertilizers	Cd	Järup (2003)
Fossil fuels combustion, chemical industries, electroplating	Ni, As, Cr	Khodadoust et al. (2004)
Coal mining and steel processing industries	Zn	Greaney (2005)
Sewage, manures, sludge, limes	Cd	Yanqun et al. (2005)
Poultry waste, feed additives	As	Mukherjee et al. (2006)
Surface runoff from rain/snow	Hg	Kowalski et al. (2007)
Weathering of sedimentary rocks like sandstone and dolomite	Mn, Cr, As, Fe, Zn	Viers et al. (2007)
Industrial wastes	As	Tripathi et al. (2007)
Anthropogenic activities	Pb, Zn, Cu, Co, Ni, As	Jordanova et al. (2008)
Waste dumping	Cd, Pb, Cu	Zhuang et al. (2009)
Ores/mineral dissolution	Fe, Mn, Cr, Cd, Hg	Huffmeyer et al. (2009)
Pesticides	Hg, As, Cu, Zn	Arao et al. (2010)
Aerosols	As, Zn, Cd, Pb	Nagajyoti et al. (2010)
Atmospheric aerosols, windblown dust	Pb, Hg, Ni	Kang et al. (2011)
Industrial wastes and geological minerals	As	Murcott (2012)
Industrial waste pipes/additives	Cu	Mohod and Dhote (2013)
Volcanic emissions, forest fires, atmospheric deposition	Pb, Hg, Ni	Li et al. (2014)
Geological minerals	As, Cr, Pb, Mn	Kibria (2014)
Sewage irrigation	Cd, Pb, Cr, Hg	Su (2014)
Industrial pollution	As	Gillispie et al. (2015)
Geological processes and anthropogenic activities	Pb, As, Hg, Cd	Nkansah et al. (2016)
Metallic mining	Cd, Zn, Pb	Romero-Baena et al. (2017)
Chemical industries and geological minerals	Cd, Pb, Zn, As	Bech (2018)
Anthropogenic activities and industrialization	Cu, Cr, Zn, Ni	Adimalla (2019)
Smeltering activities and agricultural industry, industrialization and urbanization	Ni, Cu, Cr, Mn, Zn, Fe	Doabi et al. (2019)
Geological and anthropogenic activities	Al, Fe, Mn, Si, As Cr, Hg, Ni	Kambunga et al. (2019)

Figure 4.1. Summary of heavy metals induced toxicity mechanism in plants (Adopted from: Kumar et al., 2016).

These heavy metals are also known as trace elements (10mg/Kg or mg/L in soil/aquatic medium) or ultra-trace elements (1µg/Kg or µg/L in soil / aquatic medium) because of their presence in the soil environment. In addition to these essential trace elements, another category of heavy metals, Class B metals, considered to be non-essential trace elements such as Hg, Ag, Pb, and Ni, etc., are in nature very toxic. The mechanism of heavy metal-induced toxicity in plants is summarized in Figure 4.1. In a terrestrial system, plants are stationary and their roots are the main contact sites for trace metal ions, while the entire plant body is exposed in the aquatic system and metal ions are absorbed directly from the surfaces of the leaves due to particle deposition (Kibria, 2014). Plants are stationary, and plant roots for heavy metal ions are the main contact site. Because of this contact, due to the deposition of particles containing these metals, plants absorb heavy metals primarily through roots and also through the leaf surfaces. Those plants that are grown in aquatic systems face greater toxicity as the whole plant body is exposed to toxic ions in this type of plant. Some heavy metals are considered essential elements for plants (Fe, Cu, Mo, and Zn). Two key functions of essential heavy metals in cells are involvement in redox reactions and being an integral part of enzymes. Heavy metals such as Cu, Mo, Zn, etc.

Figure 4.2. Heavy metal toxicity symptoms in plants (Adopted from: Kumar and Aery, 2016).

serve as cofactor and activator of various enzyme reactions and play a vital role in the formation of enzymes / substrate metal complexes or as a catalytic property as a prothesis group in metalloenzymes participate in electron transport and structural functions in nucleic acid metabolism (Nagajyoti *et al.*, 2010). Figure 4.2 shows the toxic effects of some heavy metals. Metals pollution is a worldwide issue for soil and water environment. The adverse effect of heavy metals on the growth and activities of soil microbes may also indirectly affect plant growth (Kumar *et al.*, 2016).

Heavy metal interference with ionic homeostasis and enzyme activity affects single-organ physiological processes (such as root nutrient uptake) followed by multiple processes such as germination, photosynthesis, respiration, plant water balance, metabolism, and reproduction. Indeed, visible symptoms of toxicity to heavy metals include chlorosis, necrosis, senescence, and wilting, stunted growth, low production of biomass, limited seed numbers, and eventually death. The plants that grow under heavy metal stress must spend more energy on their survival, which would otherwise have been available for their other process. This deficiency in the amount of energy required may result in the overall decrease in the growth of the plant in such hostile metal-stressed environment (Kumar and Aery, 2016).

Mechanisms of heavy metal chelation in crop plants

Chelation is a kind of molecular chemical bonding of metal ions. Heavy metal chelation is the plant's main approach to detoxify and tolerate high heavy metal concentrations. The ligand binds through the donor atoms to a heavy metal ion, chelation happens. Ligands are components that relate to the central metal ion's electronic orbitals and form secondary valence bonds that result in a complex molecule. High production of various metal chelating molecules *viz.*; organic acids, phytochelatins, metallothioneins (MTs), phytosiderophores, and ferritin or overexpression of metal transporter proteins coding genes increases the tolerance and accumulation of heavy metals in plant tissue (Verkleij *et al.*, 2003; Kumar *et al.*, 2016). In the process of chelating heavy metals, heavy metals approach the rhizosphere. It takes place both outside the body of the plant and within the cell of the plant. Several organic acids present in roots exudate the extracellular chelation of heavy metals, whereas different organic acids, amino acids, and peptides are responsible for intracellular heavy metal chelation within the plant cell. Metal-binding proteins and peptides are preferably metal precisely so that only toxic metals (e.g., Cd, Hg, Pb, and Cr) are appropriated and important metals such as Zn, Cu, etc. are discounted (Ryu *et al.*, 2003; Yang *et al.*, 2005). Chelators can be classified as natural and synthetic chelating agents. The plants produce various types of ligands that contain such compounds as citric acid and malic acid, amino acids, and S-containing compounds that form metal complexes. Because these ligands play a major role as detoxifying influences and are used to inhibit heavy metal persistence in plants. Citrate is Ni's chief ligand in *Thlaspi vaingense* leaves (Krämer *et al.*, 2000), while citrate and acetate bind Cd in *Solanum nigrum* leaves (Sun *et al.*, 2006). In addition, a large proportion of Zn is complexed with malate in *Arabidopsis halleri* and Cd in *Thlaspi caerulescens* (Sarret *et al.*, 2002). In Se hyperaccumulator plants, the main detoxification strategy is to protect against selenoamino acids, primarily selenocysteine (Se-Cys), resulting from the assimilation of selenite in leaf chloroplasts. Al-induced release of organic anions such as malate, oxalate, or citrate that chelate Al^{3+} in the rhizosphere and present its entry into the root of a number of plant species (wheat, maize, buckwheat, rye, taro, snap bean) has been shown (Sors *et al.*, 2009).

Metallothioneins (MTs) are a family of small, extremely conserved, cysteine-rich metal-binding proteins that are important for zinc and copper homeostasis, oxidative stress protection, and toxic heavy metal buffering. Metallothioneins are classified into three types as (I) metallothioneins are mammal-related polypeptides consisting of 61 amino acids and lacking aromatic amino acids or histidines. (II) MTs are from *Candida albicans*, yeast or cyanobacteria (Winge *et al.*, 1985); similar chelators of this class are *Saccharomyces cerevisiae* metallothioneins, which contribute to high plant copper tolerance (Kagi, 1991). (III) MTs are distinct polypeptides consisting of units of π -glutamylcysteinyl. Metallothioneins (MTs) are cysteine-rich (more than 30% of all amino acids), metal-binding, low-molecular-mass (2–16 kDa) proteins that play a crucial role in metal detoxification and absorption. MTs have a unique property of binding d-block metal ions through the 20 cysteinyl groups that abound in their component structure. Phytochelatins are MTs of the Third

Type. Heavy metals such as Cd, Zn, Hg, Ag, and Pb, especially in animal and plant species, induce the production of metallothionein. Cd is the best metallothionein activator, followed by other metals such as Ag, Bi, Pb, Zn, Cu, Hg, and Au Kagi (1991). In tobacco plants with transgenic coding for the polyhistidine cluster combined with yeast metallothionein, Cd uptake increased significantly. The introduction of a tobacco metallothionein gene also enhances tolerance to certain heavy metals such as Cd, Zn, and Ni (Macek *et al.*, 2002; Pavlíková *et al.*, 2004). Phytochelatins are glutathione oligomers formed by the phytochelatin synthase enzyme. In plants, fungi, nematodes and all algae groups, including cyanobacteria, phytochelatins are found. Phytochelatins act as chelators and are important for detoxification of heavy metals. PC2 is abbreviated by PC11. Phytochelatins are the well-known plant heavy metal chelators, especially from the Cd tolerance perspective. Phytochelatin's common structure is $(\gamma\text{-Glu-Cys})_n\text{X}$, where X is Gly, $\gamma\text{-Ala}$, Ser, or Glu, and n is the number of peptides = 2–11. Most common PC forms have 2–4 peptides. Phytochelatins are synthesized in cytosol glutathione-derived peptides and are reported in a variety of plant species including monocots, dicots, gymnosperms, and algae (Cobbett and Goldsbrough, 2002). Plants exposed to Cd stress had 2.7–3 times more total phytochelatins than plants grown without Cd of the same lines. Phytochelatins form PC-metal (loid) complexes which are transported into vacuoles, thereby helping to reduce cytosol toxic metals (Guo *et al.*, 2012). Some synthetic chelators are also known beyond the aforementioned natural chelators. The practice of ethylenediaminetetraacetate (EDTA) among synthetic chelators has been more intensive (Grčman *et al.*, 2001). EDTA binds to and unloads heavy metal ions. High mobility and much easier to pass through the plasma membrane is an uncharged ion. EDTA application enhanced Pb accumulation in *Brassica juncea* (L.) Czern, 1000–10,000 times higher than control plants. In some cases, phytoremediation has recently used ethylenediamine disuccinate (EDDS) (a structural isomer of EDTA) to improve metal accumulation (Grčman *et al.*, 2003; Luo *et al.*, 2005).

Response of plants towards different heavy metals

The toxic heavy metals are also a serious fear of living organisms and plants as they are highly persistent and present in the soil ecosystem for a long time. The plant roots are the key contact sites for exposure to toxic heavy metals in terrestrial plants. For aquatic plants, the entire plant body is visible in the growing medium to the metal present. The growing medium includes crucial and non-essential metals that become toxic on excess, resulting in growth and development inhibition and even plant death (Figure 4.3). Plants have changed some effective and accurate mechanisms to deal with heavy metal stress in order to survive. The adaptive mechanism that plants have developed to cope with metal stress includes immobilization, exclusion of plasma membranes, restriction of absorption and transport, synthesis of specific heavy metal transporters, induction of stress proteins, chelation and sequestration by specific ligands, etc. (Clemens, 2001; Dalcorsio *et al.*, 2008; Adrees *et al.*, 2015). There are two simple ways to keep a low

Figure 4.3. Response of crop plants toward different kind of environmental pollutions.

concentration of metal ions in the cytoplasm by preventing toxic metal from being transported across the plasma membrane, the cellular mechanism for heavy metal tolerance. It can be achieved either by increasing metal ion binding to the cell wall or by pumping the metal out of the cell through active efflux pumps. Another process is to detoxify toxic metal ions by inactivating them through chelation or altering toxic metal ion to a lower toxic concentration (Tong *et al.*, 2004). Plants are highly capable of solubilizing and absorbing various types of soil nutrients by helping to generate chelating agents and change pH and redox reactions (oxidation

and reduction reaction). They also have extremely precise mechanisms for different nutrients or metals being translocated and accumulated. These processes also complete heavy metal uptake and translocation, the physical and chemical properties of which are similar to those of vital compounds (Tangahu *et al.*, 2011; Kumar *et al.*, 2017). A plant's accumulation of metals is significantly affected by a number of factors such as plant structure, plant life cycle, plant vigor, soil pH, root system depth, temperature, partial oxygen pressure, carbohydrate level, respiration rate, nutrient interface and microbial presence, etc. (Chen *et al.*, 2006). Plants can precipitate heavy metals strongly by changing the rhizosphere's pH or by excreting anions such as PO_3^{4-} . The root surface can bind many heavy metals during the adsorption process. These heavy metals (Cd, Ni, Pb, and Sr) concentrate rapidly in plant root tissues (Hossain *et al.*, 2012). The generally plants could be classified into three categories as excluders, accumulators and indicators based on the mechanism of action for survival under stress conditions as suggested by Baker (1981).

Hyperaccumulation of heavy metal is the process by which plants accumulate metals in excess of 0.1–1% of the dry weight. Baker and Brooks (1989) gave this term to define plants containing more than 1000 mg/g nickel in leaves. Baker *et al.* (2000) reported that plants that accumulate more than 100 mg Cd /Kg (0.01 %) or more than 500 mg Cr /Kg (0.05 %) in dry plant leaf tissue could be considered as hyperaccumulator species. A plant with hyperaccumulator can accumulate and tolerate enormous quantities of pollutants from metals. Some plant species have the capacity to grow in the soil, are contaminated with heavy metals and have the capacity to accumulate high quantities of metals in soil-containing metals as an ecological adaptation (Lombi *et al.*, 2002). The main methods involved in the hyperaccumulation of toxic metals in plants include bio-activation of heavy metals in the rhizosphere by means of root microbe interfaces, improved activity of metal conveyor proteins in the cell membranes, detoxification of metals by limiting them to apoplasts, chelation of heavy metals in the cytoplasm by several ligands and sequestration of metals into the vacuole by means of several ligands.

Silver (Ag)

Silver (Ag) concentration in the Earth's crust and soil averages approximately 0.06 and 0.13 mg/Kg. It is used primarily in photographic industries and is also useful in other areas such as batteries, coins, jewelry, silverware, catalysts, brazing, and soldering of electronics. Therefore, silver toxicity depends on the concentration of active free silver ions (Ag^+), found primarily in the aqueous stage. Several processes in medium and water characteristics reduce silver toxicity by preventing free Ag^+ formation or by avoiding binding Ag^+ to organisms' reactive surfaces. For a long time, the toxic effects of Ag on plants grown on the ground have not been reported (Khanna *et al.*, 2018). Ratte (1999) reported that about 5 mg/Kg Ag in shoots and about 1500 mg/Kg in bush bean roots significantly reduced yields without any symptoms of toxicity Wallace *et al.* (1977) reported that Ag in the nutrient medium at a very low concentration (10 $\mu\text{g/L}$) stimulated the growth of grass roots. He speculated that some cations (e.g., Ag, Co, and Cu) could indirectly change cell metabolism, leading to a higher cell growth rate. The Ag replaces K^+ sites in

membranes and prevents the roots from absorbing other cations. High Ag concentrations (up to 1 $\mu\text{M/L}$) significantly decrease growth and protein content, while sunflower enzyme urease activity is increased (Krizkova *et al.*, 2008).

Aluminum (Al)

Aluminum is the third richest element in the crust of the Earth, occurring at around 8%. It has some useful features that allow us to use it in various industries such as electrical, metallurgical, transportation, packaging, and chemical manufacturing. The various aluminum residences are often used in the manufacture of paper, sugar refining, water purification, wood preservation, leather tanning and textiles for water resistance (Kumar and Aery, 2016). As insoluble aluminosilicates and oxides, Al is present in the soil. In the initial phases of plant growth, it is easily accumulated by plant roots and translocated within the plant, but then drops sharply with advancing maturity. The concentration of other elements (P and Ca) in the rhizosphere affects the accumulation of Al.

Aluminum in the soil can inhibit the growth of plants at a level as low as 1 mg/Kg (Rana and Aery, 2000). The root tip, which turns brown, shows the earliest symptoms of Al toxicity. The damage is limited to the root tip's active growth of tissues. In particular, the distal part of the root apex transition zone is highly sensitive to Al toxicity (Kumar and Aery, 2016). This extensive damage to the root structure leads to the reduced and damaged root system and the absorption of limited water and mineral elements. This will result in the plant's deformed growth. Aluminum is known to affect other nutrients such as Ca, Mg, P, and K intake, transportation, and functions. The reduced absorption of nutrients leads to deficiencies in nutrients. The application of Al to plants can block the uptake of many cations such as Ca^{2+} , Mg^{2+} , K^{+} , and NH_4^{+} by interrelating directly with several different channel proteins (Pineros *et al.*, 2001).

Cadmium (Cd)

The usual Cd content is 0.1 and 0.41 mg/Kg, respectively, in the Earth's crust. Most cadmium is used in the production of batteries (Ni-Cd and Ag-Cd). It is also used in relatively large quantities as pigments (yellow), coatings and stabilizers. Cd is also used for alloys and is used as a stabilizer for various plastics due to certain distinctive physical and chemical characteristics (Kumar and Aery, 2016). Commonly, Cd is considered to be one of the most harmful metals that adversely affect all living organism biological processes including humans, animals, and plants. Although, plants are considered a non-essential heavy metal. Due to its high water solubility and high toxicity, cadmium was ranked 7th among the top 20 toxins (Prasad, 1995). Cadmium has been described among the class of heavy metal pollutants as a very important pollutant. The toxicity of cadmium can be easily identified in the form of stunt growth, chlorosis, root tip browning, and ultimately plant death (Kumar *et al.*, 2016). Excess Cd in growing soil may cause leaf chlorosis, but it may be due to iron deficiency and toxic metal interaction. Due to direct or indirect interaction with Fe in leaves, chlorosis may appear. It is also found that the presence of excess

cadmium in soils causes suppression in the uptake of iron by plants (Kumar *et al.*, 2016).

Cobalt (Co)

Cobalt has cobaltite, smaltite, and erythrite in the minerals. Like many other metals, Co-contaminated soil pollution is largely due to mining and smelting, sewage sludge dispersal, and fertilizer use, which can pose an environmental risk (Bakkaus *et al.*, 2005). It is, therefore, necessary to evaluate the possibility of adverse effects of Co on the terrestrial ecosystem. Some studies on Co toxicity to soil microbes and invertebrates have been conducted. But the literature on the toxicity and risk of Co to higher plants is limited. Some studies found that when given in high doses, Co is relatively toxic to plants. Cobalt uptake and distribution in plants is dependent on species and controlled by various mechanisms. Root absorption of Co^{2+} involves active transportation across cell membranes, even though the molecular mechanisms remain unknown. Although low mobility of Co^{2+} in plants restricts its transportation from roots to shoots, its distribution may involve organic complexes (Lock *et al.*, 2007).

Chromium (Cr)

Chromium (Cr) is Earth's 7th most abundant component and 21st in the crust, with an average concentration of 100 mg/Kg. It is used primarily for stainless steel, pigments, metal finishing, and preservatives of wood, chemicals, and chromate plating. For paints, varnishes, glazes, inks, and paper, chromium is usually used in the production of green tints. Significant amounts of Cr compounds are also used in leather tanning. Dyestuffs and leather tanning are the main source of Cr pollution in the environment when waste is discharged directly into aquatic bodies. (Aery and Kumar, 2016). Cr is considered a non-essential metal for the plant and plant growth and development has been well reported for its toxicity. Plants use inactive mechanisms to absorb chromium in its trivalent form, i.e. Cr(III), while Cr(VI) is inhibited by SO_4^{2-} and Ca^{2+} (Vikram *et al.*, 2011).

Due to their high oxidation power, hexavalent ions, i.e. Cr(VI), damage the root membranes. Cr enters plant roots through root exudates reduction and/or complexation, enhancing solubility and mobility through root xylem (Shanker *et al.*, 2005). However, Cr's accumulation and mobilization within the storage tissue depends on its ionic state, it accumulates mainly in roots and is poorly translocated to shoots. Like cadmium, Cr(VI) also reduces the uptake of many essential elements such as Fe, Mg, Mn, Ca, P, and K resulting in many negative plant growth effects (Peralta-Videa *et al.*, 2009).

Iron (Fe)

Iron plays an important role in animals, plants and as well as microbes. Plants mostly get Fe from the plant's rhizospheric zone. While iron is one of the largest abundant metals in the crust of the earth, it is very low to obtain plant roots. Iron through the Fenton reaction is very reactive and toxic. Thus, plants control Fe homeostasis tightly and react to both Fe deficiency and Fe excess.

Plant's ability to respond to the availability of Fe ultimately affects human nutrition in terms of both crop yield biomass and concentration of Fe in edible tissues. Thus, illuminating the mechanisms of Fe absorption and transportation is essential for the breeding of crops that are additional nutrient-rich and more tolerant of Fe-limited soils. Iron is primarily accumulated by plants, solubilizing Fe^{3+} and then reducing it to Fe^{2+} for absorption or transportation into the root (Kumar *et al.*, 2016). Iron plays an important role in many plant forms of physiology and biochemistry. It assists as a component of many vital enzymes such as the electron transport chain's cytochromes and is therefore essential for a wide range of biological activity. Iron is involved in chlorophyll synthesis in plants and is vital for maintaining the construction and function of chloroplast (Rout and Sahoo, 2015).

Fe is accumulated primarily by plants, solubilizing Fe^{3+} and then reducing it to Fe^{2+} for absorption or root transport. Fe is transferred as ferric citrate or iron(III) chelate form from roots to shoots and transported to active growing shooting regions. Iron is a crucial mineral for plants that is essential for the biological redox system, and it is also a vital component of numerous enzymes that play significant roles in plant physiology and biochemistry. It acts as a cofactor of key enzymes involved in plant hormone synthesis and is involved in many reactions to electron transfer (Jeong *et al.*, 2008). Because of their immovability, plants are exposed to varying changes in iron obtainability from the environment. Therefore, it is believed that either malnutrition or extra volumes of this component generate oxidative stress (Abdel-Kader, 2007), which leads to numerous nutritional disorders affecting plant physiology. The toxicity of reactive oxygen species depends on the presence of a Fenton catalyst, such as iron or copper ions, which leads to extremely reactive $\text{OH}^\cdot$ radicals in the presence of Fenton. The reactive toxic oxygen species cause damage to DNA proteins, lipids, chlorophyll, and nearly every other organic essential of living cells (Becker and Asch, 2005).

Mercury (Hg)

The average concentration of Hg in the Earth's crust is 0.07 mg/Kg; while it ranges from 0.58 to 1.8 mg/Kg in multi-group soils around the world, and the average global mean is estimated to be 1.1 mg/Kg. Mercury used primarily in gold mining, batteries, paints, pesticides, impregnation of wood, and electrical products. Because of its enormous use, this metal is accumulated at various sites and is reflected as a global pollutant (Kabata-Pendias, 2011). Plants take up mercury directly depends on its quantities in the soil. As the volume of Hg in the soil increased, there was an increase in plant concentration of Hg. While an extreme portion of Hg is found in roots, a significant fraction of Hg was also stored in leaves and grains. Not only is mercury accumulated from the soil by plants, but it is also immersed in progressively released Hg vapor from the soil (Israr *et al.*, 2006).

Stunted plant growth, reduced root development, and photosynthetic activity inhibition are the major common symptoms of Hg toxicity. It is also responsible for a various metabolic activity like a failure; photosynthesis, synthesis of chlorophyll, gas exchange, and respiration. The higher root

accumulation of Hg inhibits plant uptake of K^+ . It is also observed, however, that lower volume of Hg stimulates K^+ uptake. It is known that the toxicity of volatilized elemental Hg is the most serious for plants. By increasing the production of ethylene, Hg vapor induces processes related to senescence, and the most active toxicant is elemental Hg, not its ionic form. More than developed plants, young plants are more sensitive to Hg-saturated air. Mercury has a strong affinity with multiple proteins and enzyme amino acids. It appears that its binding nature to sulfhydryl groups is the key reaction to plant metabolism disruption (McNear *et al.*, 2012). The association of Hg with Se in soybean root molecules of high molecular weight. In addition, improved antioxidant enzyme activity is observed in some cases when mercury is applied to growth media (Zhou *et al.*, 2008).

Manganese (Mn)

Mn is a common metal in the crust of the earth and its occurrence in soils is primarily the result of the parent material. In recent times, however, the severe anthropogenic has focused on increasing manganese content and obtainability in many soils. Mine tailings and metal smelters, long-term and heavy use of sewage sludge (biosolids) or other organic changes in agricultural soils all result in an increase in manganese content or accessibility (Kumar *et al.*, 2016).). Mn is a vigorous plant component that interferes in several metabolic activities, mostly in photosynthesis and as an antioxidant-cofactor enzyme. Several studies on the toxicity of manganese and translocation of Mn from soil to plant tissue in the form of Mn^{2+} have confirmed their significance under low pH and redox soil conditions. Mechanisms that can tolerate this toxicity are also recorded when Mn metal is inside the plant cell, making it vital to compartmentalize this metal in different plant tissue (leaves, roots, shoots, and leaf plant cells) (Millaleo *et al.*, 2010). Also recorded as a defense mechanism was the important role of the antioxidant process in the plant in relation to the high concentration of manganese. Excessive concentrations of manganese in plant tissues can change numerous developments, such as the activity of enzymes, absorption, translocation and use of other mineral elements (Ca, Mg, Fe and P), which can cause oxidative stress. The Mn injury threshold, as well as the tolerance of an extra of this metal, is highly dependent on the species of plants and cultivars or genotypes within a species (Ma *et al.*, 2015). Nutrient translocation in epidermal root cells via an active transport system and transported to the plants as a divalent cation Mn^{2+} . The roots characterize Mn accumulates as a biphasic process. The early and rapid uptake phase is reversible and non-metabolic, with freely exchanged rhizosphere Mn^{2+} and Ca^{2+} or other cations. In this first phase, Mn^{2+} seems to be adsorbed by the root-cell apoplastic places 'negatively charged cell wall ingredients (Humphries *et al.*, 2007). The second phase is slow, with less easy exchange of Mn^{2+} .

It is dependent on plant metabolism to incorporate it into the symplast, although the precise mechanisms are not clear (Humphries *et al.*, 2007). The study has studied that Mn binds to this protein in transgenic tobacco converted with a tomato plant root protein at its N-terminus (LeGlpI) with a metal binding side. This strongly refers to LeGlpI's contribution to manganese soil

uptake (Takahashi and Sugiura, 2001).

Molybdenum (Mo)

Mo is present in the lithosphere at an average concentration of up to 23 mg/Kg but may increase concentration (300 mg/Kg) in shales containing important organic matter. Mo is present as numerous different complexes in agricultural soils depending on the soil section's chemical speciation (Kaiser *et al.*, 2005). The strong relationship between Mo and Fe metabolisms is presumed because (i) the absorption mechanisms for Mo and Fe affect each other, (ii) the majority of molybdoenzymes also require the-containing organic reductions or organic oxidation groups such as the-sulfur groups or heme, (iii) Mo metabolism has enrolled mechanisms typical of iron-sulfur cluster synthesis, and (iv) both Mo cofactor synthesis and extra synthesis. Tomatsu *et al.* (2007); Bittner *et al.* (2014) studied that Mo present in the soil are many forms in the soil such as molybdenite (MoS_2) or ferrimolybdate $[\text{Fe}_2(\text{MoO}_4)_3]$, and its dissolved and plant-available form molybdate (MoO_4^{2-}). Plants take up molybdate from the soil by Mo transporters, such as MOT1 in *A. thaliana*.

Nickel (Ni)

Ni is a key component of several metalloenzymes such as superoxide dismutase, NiFe hydrogenases, M-reductase methyl coenzyme, urease, Co-A acetyl synthase, dehydrogenase carbon monoxide, hydrogenases, and RNase A. In addition, Ni's high exposure in growing medium affects the activities of amylases, proteases, and ribonucleases that subsequently affect the digestion and metabolization of food reserves in seed germination. Ni is considered at a lower concentration (0.01 to 5 μg) as a vital component for plants. Ni uptake from growing medium occurs primarily through passive diffusion and active transport. Through the cation transport system, plants passively absorb soluble Ni compounds.

The chelated Ni compounds are taken and translocated using transportation proteins such as permeases through an active-transported-mediated system (Ahmad and Ashraf, 2011). The high concentration of Ni in growing medium causes physiological process alteration and various symptoms of toxicity such as chlorosis, necrosis, and wilting. Plants growing in excess of Ni medium have negative effects on photosynthesis, mineral nutrients, transport of sugar, and balance of water. Reduction in water intake is an indicator of increasing Ni toxicity in plants. High-level Ni exposure increases MDA concentration that could disturb membrane function and cytoplasmic ion balance, especially K^+ ; the highest mobile ion in the cell membrane (Gajewska *et al.*, 2006; Sethy and Ghosh, 2013).

Lead (Pb)

The average content of lead (Pb) in the crust of the Earth is estimated at 15 mg/Kg. Two types of Pb are known in the terrestrial environment, i.e. primary and secondary. At the time of their formation, primary Pb is of geogenic activates and incorporated into minerals, while secondary

Pb is of radiogenic origin from uranium and thorium decline. The greatest use of lead is in the production of batteries of lead acid. In solders, alloys, cables, and chemicals, it is also used.

Lead (Pb) is a non-essential toxic element that is one of the most omnipresent in the soil. The plant is mainly produced from soil and aerosol (Sharma and Dubey, 2005). Roots are more able to accumulate Pb in plants; however, their subsequent translocation to aerial parts is highly restricted. The availability of lead in soil depends heavily on soil conditions such as soil pH, particle size and capacity for cation exchange.

In addition, some other factors such as root surface area, root exudation, mycorrhization, and degree of transpiration also affect the availability and uptake of Pb. Plants' root absorbs the Pb through the apoplastic pathway or via Ca^{2+} permeable channels (Pourrut *et al.*, 2011). It accumulates after take-up primarily in root cells due to the blockage inside the endodermis by the Casparian strips. In addition, lead is also trapped on the roots cell wall by the negative charges (Seregin and Ivaniov, 2001). The accumulation of lead in plants has several deleterious effects, either directly or indirectly, on the morphological, physiological and biochemical functions of plants. When Pb enters the cells, toxicity is caused by altering the permeability of the cell membrane, by reacting with active metabolic enzyme groups, by replacing essential ions, and by complex formation with the ADP or ATP phosphate group. Lead toxicity causes inhibition of enzyme activity, disturbed mineral nutrition, water imbalance, hormonal disturbance, inhibition of ATP production, lipid peroxidation, changes in membrane permeability and damage to DNA by overproduction of reactive oxygen species (ROS) (Sharma and Dubey 2005; Pourrut *et al.*, 2011; Sethy and Ghosh, 2013).

Zinc (Zn)

Zinc is considered a vital plant micronutrient because it is crucial for normal cell metabolism and plant growth at an ideal concentration (Dhankhar *et al.*, 2012). In many physiological processes such as multiple biomolecules metabolism, gene expression and regulation, enzyme activation, protein synthesis, and reproductive development, it plays an essential role as a cofactor. However, higher concentration accumulation of zinc in the plant ($> 300\mu\text{g}^{-1}$ in dry weight) causes physiological alteration and inhibition of growth (Cakmak, 2000). High zinc exposure in growing medium inhibits several metabolic functions of plants, leads to stunted growth, and causes senescence. Zn toxicity limits root and shoot growth (Fontes and Cox, 1998). It also causes chlorosis in premature leaves at high concentration, which may extend on prolonged high exposure to older leaves.

The excess of Zn also causes a deficiency in shoots of other essential elements such as Mn and Cu, which hinders the transfer from root to shoot of these essential micronutrients. The possible reason for this translocation interference of these micronutrients is that the iron and manganese concentration in a plant grown in zinc-rich media is greater in root than the shoot (Ebbs and Kochian, 1997).

Conclusion

Anthropogenic activities have contributed to continuously increasing the levels of different contaminants in agricultural soils. The present book chapter revealed that the heavy metals impose several toxic effects on the plant and adversely affect the growth as well as the development of plants. The integrated response adopted by plants toward metal stress, particularly in the form of antioxidant ability is the most important mechanism by which the crop plants tolerate towards the toxic metals. Sometimes, due to the ionic affinity of the metals with plant root enzymes they were taken by the vegetative parts of crops which create the health issues in the respective consumer. The efficient mitigation of such heavy metals should be done to minimize the heavy metal risk for both the plant and living beings by adopting eco-friendly approaches.

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Chapter 5

Heavy metals in agro-ecosystems and their impacts on human health

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Abstract

Heavy metals are proved to be a major threat and their toxic effects have various effects on living organisms including health risks in humans. Even though the heavy metals do not have any biological role but they are present in some form which is harmful for humans and impairs with the proper functioning. Most of the times heavy metals interfere with the metabolic processes for example some heavy metals get accumulated in the food chain and do not undergo degradation exhibiting a chronic nature. Heavy metals toxicity is largely dependent upon the absorbed dose, the route of exposure and the time duration of exposure whether it is acute or chronic which can

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result in excessive damage due to oxidative stress induced by free radical formation. Several public health measures have been put forward to control, prevent and treat metal toxicity occurring in the environment.

Keywords: Heavy metals, Agro-ecosystems, Toxic elements, Health risks, Pollution

Introduction

Soil is an important compartment of the environment which plays many functions in supporting life on planet earth. Some of the important functions of soil includes: ecological functioning (provide habitat to the flora and fauna and plays an important role in contributing to the element cycling), bearing function (playgrounds and buildings), biomass production (vegetation and crop production), also serve as raw materials for mining and construction and for archaeological and paleontological research. The quality of soil directly influences the groundwater which may be used for drinking water or surface water recharge (De Haan and F.A.M, 1996; Blum, 1990; Harris *et al.*, 1996). Soil receives significant amount of pollutants from various sources every year, not only chemical pollutants are released into the soil; it also controls the natural transport of chemical substances in to the environment. With the advancement in techniques the standards of life have improved and it results in raising new challenges to the safety of environment as unrestricted industrialization have put the lives of living organisms at risk without proper emission control mechanisms (Kabata-Pendias and Pendias, 2001).

Agro-ecosystem includes the land where humans cultivate different kinds of plants which is used in food or in industry. In addition to the cultivated plants the agro-ecosystem possess different types of wild plants, animals, fungi and micro-organisms. Agro-ecosystem is largely contaminated with different types of toxicants by various sources which negatively affect the flora and fauna of soil and in addition to these higher trophic levels of food chain is also disturbed. The soil contamination can be distinguished in to two types: point source and non-point source contamination. Point source contamination is caused by single source for example pollution by accidental or deliberate human activities whereas non-point source is large scale contamination which is caused by a particular source or a combination of different sources for example sewage sludge in agriculture and fertilizer and heavy metal pollution of soil (Huang *et al.*, 2007). Thus the agro-ecosystem is largely contaminated with various different kinds of hazardous toxicants out of which heavy metals are most important as due to their increased concentrations in soil they get accumulated in plants and thus reaches to different trophic levels through food chain and produce a range of health problems (Zheng *et al.*, 2005).

The heavy metals usually bind with the protein sites which are not made for them by displacing the original metals from their natural binding sites which results in disrupting the normal functioning of cells causing oxidative damage which can lead to DNA damage at certain high levels (Flora *et al.*, 2008).

Heavy metals in agro-ecosystems

The exemplary definition of a metal refers to the physical properties of the elemental state, for example: ductility, electrical conductivity etc. The term heavy metal is often used to mean any metal with atomic number <20 (Davies, 1980). Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water (Fergusson, 1990). The heaviness and toxicity are presumed to be inter-related thus heavy metals including metalloids, such as arsenic induce toxicity even at low level of exposure. They are naturally occurring elements found throughout the earth's crust. Several reports have advocated that as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are essential nutrients that are necessary for various biochemical and physiological functions and their inadequate amount can cause variety of diseases or syndromes in humans. Heavy metals are potential environment toxicants posing risk to environment (Jaishankar *et al.*, 2013; Nagajyoti *et al.*, 2010). In addition to natural sources, the amount of metals entering the environment through anthropogenic sources has been increasing in recent years which are a major ecological and public health concern associated with environmental contamination by these metals (Bradl, 2002). Several studies reported the major sources of heavy metals are industrial, agricultural, domestic and technological applications (He Zl *et al.*, 2005), including soil erosion, natural weathering of rocks, mining, industrial effluents, urban run-off, sewage sludge discharge, pesticides applied to crops and many others (Morais *et al.*, 2012).

Source of heavy metals in agro-ecosystems

Heavy metals are comprised of heterogeneous group of elements which varies in their physico-chemical and biological properties. Heavy metals are found in a wide range of applications in our daily life and enter the environment mainly through anthropogenic activities such as mining, smelting, industrial and agricultural practices. Heavy metals are potential environmental pollutants because they are responsible for initiating a series of chain reactions that causes change in the quality of soil, water and atmosphere and are toxic to plants, animals and human beings. The entry of heavy metal in the environment and ultimately into the food chain at various trophic levels is an alarming concern to the human beings. Agro-ecosystem is contaminated with heavy metals through anthropogenic as well as natural activities. Natural sources of heavy metals include atmospheric emissions from volcanoes, continental dusts, weathering of rocks which are metal enriched (Ernst, 1998). Whereas, anthropogenic sources includes sewage sludge in agriculture fields, combustion, application of metal based pesticides or fertilizers, manufacture, use and disposal of electronics appliances i.e. mainly industrial, municipal and agricultural practices (Inogo *et al.*, 2013; Oves *et al.*, 2012). Heavy metals are highly toxic and they can build up in soil and get accumulated in the crops which ultimately

cause risk to human health (Huang *et al.*, 2007; Nguessan *et al.*, 2009). Soil contaminated with heavy metals from agricultural or industrial activities have raised serious concern nowadays regarding the risk to human health through the direct intake or bioaccumulation through food chain and ultimately their effect on ecological system.

Several studies have advocated that both essential heavy metals (copper, zinc and manganese) and non essential heavy metals (cadmium, chromium, manganese and lead) are highly toxic for human and aquatic life (Ouyang *et al.*, 2002).

Effect of heavy metals on human's health

Out of 35 metals 23 are heavy metals: arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc (Mosby *et al.*, 1996). All of these are commonly found in our environment and in small amounts they are essential for maintaining good health but in larger amount they can be toxic and cause damage. When the human is contacted with high doses of heavy metals for a longer duration this can result in lowering down the energy levels and for larger extent it is reported to damage the functioning of brain, lungs, kidney, liver and other important organs of body. The exposure to heavy metals is also known to cause several neurological disorder such as Parkinson's disease, Alzheimer's disease along with the physical impairments in human beings. Reports have been mentioned representing the fact that the repeated and long term exposure of heavy metals may even cause cancer (Jarup, 2003).

Effects of arsenic

The source of arsenic contamination includes both natural and anthropogenic processes. The human sources of arsenic pollution includes mining and ore processing, whereas the smelting process is also known to release arsenic in air as well as in soil (Matschullat, 2000). These sources usually affect the quality of surface water through groundwater run-off. Another source of arsenic pollution is through geological sources like arsenic minerals (Smedley and Kinniburgh, 2002). The inorganic forms of arsenic i.e. arsenite and arsenate are known to be more toxic to human health. Most of the times humans are exposed to these forms of arsenic by drinking water in more than 30 countries all over the world (Chowdhury *et al.*, 2000), water get contaminated by arsenic through disposal of chemicals, pesticides. These forms of arsenic are highly carcinogenic and are known to cause cancer of lungs, liver, bladder and skin. Several reports suggested that chronic toxicity in man mainly focuses on skin pigmentation (Martin and Griswold, 2009) and keratosis which is also known as "raindrops on a dusty road" (Smith *et al.*, 2000). The acute exposure of arsenic can cause nausea, vomiting, decrease in production of erythrocytes and leukocytes, abnormal heart beat etc, whereas chronic exposure results in irreversible changes in vital organs of the body of humans and the mortality rate is slightly higher (Mazumder, 2008; Shefali *et al.*, 2018).

Effects of lead

Anthropogenic activities like mining, burning of fossil fuels is the main reason for lead accumulation and other compounds in the environment mainly in air, water and soil. Lead is most commonly used in battery production, cosmetics etc. (Martin and Griswold, 2009). It is used in various products such as paints, gasoline and is highly toxic. One of the classic diseases caused by lead is its poisoning which is most common in children resulting in damaging the central nervous system and gastrointestinal tract (Markowitz, 2000). Most commonly lead poisoning occurs through drinking water, the pipes that carry the water may be made of lead and its compounds which contaminate the water (Brochin *et al.*, 2008). Lead is mainly considered as carcinogen according to the Environmental Protection Agency (EPA), and affects major organs of the human body. Acute exposure of lead mainly occurs in the place of work i.e. some manufacturing industries which uses lead and is known to cause loss of appetite, headache, hypertension, abdominal pain, renal dysfunction, fatigue, sleeplessness, arthritis, hallucinations and vertigo. When humans are exposed to lead for a longer duration of time it is known to cause mental retardation, allergies, psychosis, autism, dyslexia, hyperactivity, brain damage, kidney damage and at certain times may even known to cause death (Martin and Griswold, 2009).

Effects of mercury

Mercury poisoning is known as acrodynia or pink disease and it is considered as one of the most toxic heavy metal in the environment. Through anthropogenic sources mercury is released into the environment including the pharmaceuticals and agriculture industry (Morais *et al.*, 2012). Mercury usually combines with other elements and form organic and inorganic mercury. Chronic exposure to high levels of organic or inorganic mercury is known to damage the brain, kidneys and developing foetus (Alina *et al.*, 2012). Human nervous system is very sensitive of all types of mercury. Long time exposure to mercury is known to later the brain functions and leads to tremors, memory problems and in some cases change in vision or hearing. Symptoms of organic mercury poisoning include vomiting, nausea, increased heart rate or blood pressure, depression, memory problems, tremors, fatigue, headache, hair loss, etc (Martin and Griswold, 2009).

Effects of cadmium

Cadmium is basically a metal of the 20th century and is a byproduct of zinc pollution. Cadmium is mainly used in batteries, pigments, plastics and metal coatings for electroplating (Martin and Griswold, 2009) and it is also released in environment through natural activities like weathering of rocks, volcanic eruptions, and river transport. International Agency for Research on Cancer classified cadmium and its compounds as Group 1 carcinogens. Cadmium exposure to humans is highly toxic to kidneys as it accumulates in the proximal tubular cells when present in higher concentrations (Chakraborty *et al.*, 2013). Several studies advocated that cadmium causes disturbances in calcium metabolism leading to osteoporosis and is also known in formation of renal stones. If cadmium is inhaled in higher levels it can cause damage to lungs (Bernard, 2008).

Tobacco is the main source of cadmium intoxication as these plants accumulate cadmium from the soil at much higher pace thus; smokers are more susceptible to cadmium than non-smokers (Mudgal *et al.*, 2010).

Effects of chromium

Chromium is present everywhere even in rocks, soil, plants and animals. The chromium compounds can occur in various different states such as divalent, four-valent, five-valent and hexavalent state and can be present in solid, liquid or gas form. Cr(VI) and Cr(III) are the most stable forms and their relation to human exposure is highly studied (Zhitkovich, 2005). Cr(III) compounds are essential nutrient supplements for humans as well as for animals also and plays important role in glucose metabolism, whereas Cr(VI) compounds are highly toxic and carcinogenic in nature (Shefali *et al.*, 2019). Man-made sources of chromium includes metal coatings, metal alloys, magnetic tapes, paint pigments, rubber, cement, paper, wood preservatives, leather tanning and metal plating (Martin and Griswold, 2009). Exposure to chromium is known to cause ulcers, inhibition of erythrocyte glutathione reductase, which in turn lowers the capacity to reduce methemoglobin to hemoglobin (Koutras *et al.*, 1965; Schlatter and Kissling, 1973). Several studies have advocated that chromate compounds exposure can induce DNA damage (O'Brien *et al.*, 2001; Matsumoto *et al.*, 2006).

Effects of aluminum

Aluminum exists in only one oxidation state (3+) and it's the third most important element on the earth. Humans are exposed to aluminum through drinking water, food, beverages, and aluminum containing drugs. Aluminum exposure symptoms include: nausea, mouth ulcers, skin ulcers, skin rashes, vomiting and diarrhea. Aluminum mainly affects the nervous system of humans which results in loss of memory, problems with balance and loss of coordination (Krewski *et al.*, 2009).

Conclusion

The term metal toxicity or metal poisoning refers to the toxic effects of certain heavy metals in certain forms and doses on living organisms. In this chapter authors have briefed the toxic effects of certain heavy metals i.e. arsenic, lead, mercury, cadmium, chromium and aluminum on the living organisms, mainly human beings. Certain metals have no or little biological role and they are not even essential minerals but they are toxic to living organisms in a certain form. These heavy metals sometimes imitate the action of essential elements in the body thus, interfering with the metabolic process resulting in illness. Heavy metals do not undergo degradation as a result of this they get bio-accumulated in the body and in the food chain at certain trophic levels. Failure to control the level and dose of exposure leads to several adverse effects in humans. Thus, it is the need of the time to monitor the exposure and probable intervention for reducing the additional

exposure to heavy metals in the atmosphere and even in humans which can be a momentous step towards prevention.

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Chapter 6

Human health risk assessment and mitigation of heavy metal pollution in agriculture and environment

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Abstract

Heavy metals contamination in agricultural environment and its deleterious effects on the crops and human health is an issue of serious concern in the present time. Agricultural fields receive various heavy metals such as Zn, Ni, Mn, Cu, Cd, Cr, Pb, As and Hg etc. mainly from natural and anthropogenic sources. The greater concentration of heavy metals in the fields spoils the soil characteristics and has extreme consequences on both crops and human. Their persistence and non-degradable nature increases its accumulation in the agricultural field, crops and human body through various food chains. The present chapter highlights various sources of heavy metals in agricultural environment and its impacts on both crops and human health and gives various strategies to mitigate the heavy metal concentrations in agricultural environment.

Keywords: Agro-environment, Heavy metals, Human health, Risk assessment, Toxic effect

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Introduction

Heavy metals contamination in agricultural field is a serious concern in the present time due to their deleterious effects on both crop and human health. The establishment of industrial areas nears the villages and agricultural areas which releases tremendous amount of pollutants in the agricultural environment are alarming. Their abundance in agricultural environment is due to field irrigation with industrial and municipal waste water or heavily polluted river water, then subsequent soil erosion, weathering of rocks, use of various chemical fertilizers and pesticides which contaminates the agricultural fields with heavy metals such as Zn, Ni, Fe, Co, Cr, Cu, Cd, Pb, As and Hg etc (Morais *et al.*, 2012, Srivastava *et al.*, 2017a, Malik and Maurya, 2014; Kumar *et al.*, 2018). These metals are non-biodegradable and non-thermodegradable hence are persistent in the soil for longer duration and accumulated in the plant body (Wu *et al.*, 2010; Vodyanitskii, 2013; Yushu *et al.*, 2013; Kayastha, 2014).

Metals are essential and non-essential on the basis of their functions in the organisms. They act as co-factor in many enzymes and play important roles in various oxidation-reduction reactions (WHO, 1996). Essential heavy metals play important physiological and biochemical function in the organisms, however, their inadequate amounts causes a variety of deficiency diseases (WHO, 1996). The regulation and detoxification of heavy metals in organisms is done by metaloproteins such as metallothioneins, glutathione and phytochelatins. But metal concentration beyond the limit may alter the metal regulatory mechanism and initiate metal accumulation (Kumar *et al.*, 2017; Maurya and Malik, 2018). Heavy metals cause oxidative stress by the formation of free radicals and reactive oxygen species (ROS), resulting in cell and tissue damage (Dietz *et al.*, 1999; Leonard *et al.*, 2004).

During stress condition the level of ROS increases which causes cellular toxicity in the organisms while lower level is necessary for various physiological activity such as cell differentiation, cell proliferation, apoptosis and regulation of redox-sensitive signaling pathways (Shibanuma, 1988; Allen and Balon, 1989; Hockenbery *et al.*, 1993; Lo *et al.*, 1996). The ROS induced damage in organisms are cell death, chromosomal aberrations, mutations and carcinogenesis (Cerutti, 1985). ROS also affect various biomolecules such as carbohydrates, amino acid chain, proteins, membrane lipids, nucleic acids and pigments (Gratao *et al.*, 2005; Manikandan *et al.*, 2015; Venkatachalam *et al.*, 2017). Several researchers have reported that heavy metals affect the cellular components such as cell organelles and plasma membrane (Squibb, 1981). Metal ions interact with DNA and proteins causing DNA damage and protein conformational changes which may lead to cell cycle modulation and carcinogenesis or apoptosis (Berg, 1986; Leonard, 1986; Shahid *et al.*, 2014).

Organisms have several antioxidants which protect the cells or repair the cellular damages caused by reactive oxygen species (ROS). The antioxidant activity is maintained by both enzymatic and non-enzymatic components. The enzymatic components are superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APx), glutathione peroxidase (GPx), glutathione-S

transferase (GST) and the non-enzymatic components are reduced glutathione (GSH) and ascorbic acid (AA) (Gill and Tuteja, 2010; Miller *et al.*, 2010; Gill *et al.*, 2011). Both enzymatic and non-enzymatic antioxidant components are responsible for detoxification of ROS for cellular survival (Gill *et al.*, 2011; Das and Choudhury, 2014). High toxicity levels of heavy metals such as chromium (Cr), Lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) are posing health hazards impact on crops and human health. This encouraged the researcher to develop several strategies to remove the metals from agro-environment.

Sources of heavy metals in agro-environment

Agriculture field receives heavy metals from both natural and anthropogenic sources that percolates into the soil layers (Kabata-Pendias and Pendias, 2001; Dembitsky and Rezanka, 2003; Sidhu, 2016). Weathering of rocks, volcanic eruptions, windblown dust particles, sea spray and aerosols etc are the natural sources by which heavy metals come into the agricultural environment (Nagajyoti *et al.*, 2010; Srivastava *et al.*, 2017b). The anthropogenic sources such as inorganic and organic fertilizers, pesticides and fungicides that have variable level of Zn, Ni, Pb, Cd and Cr etc; along with these, field irrigation through municipal and industrial waste water, organic manure, atmospheric pollution from motor vehicles and the combustion of fossil fuels (Nicholson *et al.*, 2003; Zhang, 2006; Kelepertzis, 2014; Toth *et al.*, 2016; Malik *et al.*, 2017). The repeated use of fertilizers and pesticides continuously making the agricultural soils enriched with heavy metals. Several study have reported that the irrigation of cultivated vegetables in wastewater and use of chicken manure, chemical fertilizers and pesticides are the source of metals in food (Modaihsh *et al.*, 2004, Kumar *et al.*, 2017a, Kumar *et al.*, 2017b, Kumar *et al.*, 2018). The sources of various heavy metals in the environment are shown in Figure 6.1 and the sources of heavy metals in the agricultural environment and their effect on crops health are shown in Figure 6.2.

Arsenic (As)	• Pesticides, fungicides, metal smelters
Cadmium (Cd)	• Welding, electroplating, pesticides, fertilizer, batteries, nuclear fission plant
Chromium (Cr)	• Mining, electroplating, textile, tannery industries
Copper (Cu)	• Electroplating, pesticides, mining
Lead (Pb)	• Paint, pesticides, batteries, automobile emission, mining, burning of coal
Manganese (Mn)	• Welding, fuel addition, ferromanganese production
Mercury (Hg)	• Pesticides, batteries, paper industries
Nickel (Ni)	• Electroplating, zinc base casting, battery industries
Zinc (Zn)	• Refineries, brass manufacture, metal plating, immersion of painted idols

Figure 6.1. Sources of heavy metals in the environment (Adopted from Paul, 2017).

Figure 6.2. Sources of heavy metals in agro-environment and their effects on soil and crops (Adopted from Srivastava et al., 2017c).

Toxicity of heavy metals on human health

Heavy metal contamination in the agriculture environment and their bioaccumulation in human beings through the food chain and toxicity effect on crops and human health is one of the major problems in the present time.

Lead (Pb)

Lead is a non-essential metal for our body system; even its low concentration is harmful for human health. It enters in our body through contaminated food, water, air and also from beverages. EPA has reported that lead is a carcinogenic agent for human health. It has long biological half-life about 20-30 years and its accumulation takes place in teeth and bone from where it enters into bloodstream and binds with erythrocytes. It inhibits the function of enzymes that are necessary for hemoglobin synthesis thereby reduces the level of hemoglobin in the body and cause anemia (Landis et al., 2003; Bradl, 2005). Pregnant women and young children are more

susceptible to lead toxicity resulting in iron deficiency (Flora *et al.*, 2006).

Chromium (Cr)

Chromium is an essential trace element for lipid and carbohydrates metabolism and its deficiency causes cardiovascular diseases and diabetes (Mertz, 1998). The trivalent form of chromium (Cr III) is an essential micro nutrient while its hexavalent (Cr VI) form is more dangerous for human health. People who work in leather and textile industries are mostly affected by allergic reactions such as skin rashes, nose irritation and bleeding (Karadede *et al.*, 2004). A study has reported that the over concentration of chromium causes genetic defects in the body (Kherici *et al.*, 2009). It has also been reported that exposure of high dose of Cr compounds in human beings may lead to lung cancer (Jordao *et al.*, 2002).

Cadmium (Cd)

Cadmium enters into the human body through intake of contaminated foodstuffs such as mushrooms, liver and sea weeds (Jarup *et al.*, 2000). It gets transported into liver through blood circulation where it binds with metal binding protein metallothionein that sequesters it and transports to the kidney. In kidney, it accumulates and interferes with blood purification mechanisms. It causes kidney and liver damage and deformation of bones (Abbas *et al.*, 2008). Cadmium has been reported to be mutagenic, carcinogenic, teratogenic, embryo toxic, hyperglycemic agents and anemia inducing agents and has reduced immunopotency (Rehman and Sohail, 2010).

Copper (Cu)

Copper enters into the body through intake of foods, dietary supplements and drinking water. The tolerance limit of copper in the body recommended by Environmental protection Agency (EPA) is 1.3 mg/L while the WHO tolerance limits of copper in drinking water is 2.00 mg/L (World health organization, 2004). Long term exposure of Cu can cause irritation in mouth eyes and nose and also causes headaches, vomiting and diarrhoea. In India, Indian childhood cirrhosis is reported where large amount of copper are rapidly deposited in the liver (Tanner, 1998). Some visceral organs (liver, kidney) and some fruits and nuts have high copper contents (Pandit and Bhawe, 2002). Copper accumulation in the liver is being reported in a variety of pediatric hepatic diseases like idiopathic copper toxicosis (ICT), Wilson's disease, and Indian childhood cirrhosis (Muller, 1998).

Mercury (Hg)

Mercury is a highly neurotoxic pollutant to animals and human and especially affects the central nerve system (Lebel *et al.*, 1998). It enters in the body by food intake and in food it exists as inorganic and organic forms. The organic form is methylmercury (MeHg) which is more hazardous to health. The level of mercury in foods is inconsistent and reflects the level of pollution of the local environment (Dudka and Miller, 1999). It is the most toxic heavy metal in

the environment and its poisoning is referred to as acrodynia or pink disease. Mercury is released into the environment by the activities of various industries such as pharmaceuticals, paper and pulp preservatives, agriculture industry, and chlorine and caustic soda production industry (Morais *et al.*, 2012). Exposure to elevated levels of metallic, organic and inorganic mercury can damage the brain, kidneys and the developing fetus (Alina *et al.*, 2012).

Arsenic (As)

The exposure of arsenic causes organ and skin diseases but it may also affects the immune system (Duker *et al.*, 2005). It binds with sulfhydryl groups of enzymes and proteins and causes their denaturation within the cell (Gebel, 2004). It increases the formation of reactive oxygen species which damages cell and its components (Ahmad *et al.*, 2000). The agricultural pesticides, herbicides, veterinary and human medicine contain arsenic (Tchounwou, 1999). Its therapeutic action induces programmed cell death (apoptosis) in leukemia cells (Yedjou and Tchounwou, 2007).

Human health risk assessment

The high concentration of heavy metal reduces the soil fertility. Their transfer into the food chain and results in their accumulation in the food stuffs which causes potential health risks to the consumers (Khan *et al.*, 2008). Thus, it is important to determine their concentration in food stuffs and its amount transfer to the consumers during daily intake could be estimated by following formula (Wang *et al.*, 2005; Mitra *et al.*, 2012; Krishna *et al.*, 2014; Gupta *et al.*, 2017).

$$EDI = \frac{E_f \times E_d \times F_{ir} \times C_f \times C_m}{W_{ab} \times T_a} \times 10^{-3}$$

Where,

EDI: Estimated Daily Intake; Ef: Exposure frequency 365 days/year; Ed: Exposure duration, equivalent to average life time (65 years); Fir: Fresh food ingestion rate (g/person/day) which is considered to be India 55g/person/day; Cf: Conversion factor (= 0.208) (The content of fresh weight (fw) to dry weight (dw) considering 79% of moisture content); Cm: Concentration of heavy metal in food stuffs (mg/kg dw), Wab = Average body weight (60kg); Ta: Average exposure time for non-carcinogens (Ta = Ef×Ed).

Bioremediation as a tool to remove heavy metals from agro-environment

The approach of bioremediation is related to the use of biological strategies to overcome problems from environment using biological factors. Bioremediation is the most effective process for removal of heavy metal contamination from the agriculture environment. The term bioremediation has been used to describe the biological strategies to remove toxic waste from environment

by using biological agents. Phytoremediation involves various strategies for removal of heavy metals from agriculture field such as phytoextraction, phytovolatilization, phytostabilization, phytodegradation and rhizofiltration. Another method of biological remediation is the use of microbes for removal of heavy metals (Kumar *et al.*, 2015). The microbes change the pollutants' physical and chemical properties, affecting the mobility and transformation of heavy metals in the soil. To remedy the contaminated environment, microbes are very helpful. Bioremediation involves the number of microbes including aerobes, anaerobes and fungi.

Conclusion

From the literature report it is clear that heavy metal pollution poses serious threat on agriculture environment and human health. When the concentration level of heavy metals are elevated in agriculture field, it reduced the soil quality, productivity and yields. Heavy metal pollution also destroys cells and their component in plant and animals/human due to the production of reactive oxygen species (ROS) and causes various deficiency diseases and disorders. Phytoremediation and microbial remediation processes should be applied to clean up metals from polluted sites. Awareness should be created among the common people about metal toxicity and carefully monitoring and discharge treated effluent of industries. Furthermore, the use of various fertilizers, pesticides, herbicides that contain heavy metals should be avoided so that the heavy metal accumulation within the agriculture field can be stopped.

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Chapter 7

Pesticides in agriculture and environment: Impacts on human health

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Abstract

A sort of chemicals which are formed to get rid of a pest or halt its reproduction termed as pesticides. Pesticides are utilized generally to control weeds and insect invasion in farming fields and different pests and disease transporters (e.g., mosquitoes, rodents, ticks and mice) in houses, workplaces, shopping centers, and roads. As the methods of activity for pesticides are not species-specific, worries have been raised about environmental threat related with their exposure through different ways (e.g., residues in diet and drinking water). Various types of pesticides have been utilized for crop safety from hundreds of years. Pesticides advantage the harvests; though, they additionally leave a serious negative effect on nature. Over utilization of pesticides may prompt the damage of biodiversity. Numerous aquatic animals, birds are under the risk of destructive pesticides for their survival. Pesticides can move into the human body by oral, inhalation or dermal exposure, and well known to be the main reason of various diseases like

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respiratory disorders, cancer, skin problems, endocrine disruption, and reproduction failures. Pesticides acquired numerous advantages to humankind in the agricultural, industrial zone, yet their toxicities in both humans and animals have always been a reason to worry. Contamination therefore to overuse of pesticides and the long term effect of pesticides on nature are additionally discussed in the chapter. This article aims to discuss about pesticides, their types, environmental worries and human health complications related to them.

Keywords: Agriculture, Cancer, Disorder, Environmental pollutants, Respiratory disorders, Pesticide

Introduction

The most important commodity essential for survival is food. It conveys vitality and supplements for body development, upkeep, fix and generation. Generation of food adequate to satisfy the need of the worldwide population has never been a simple assignment. Farmers all through the world face a few biotic and abiotic worries over the generation procedure. Crop yield is significantly hampered by the harm from in excess of 10000 types of insects and 30000 types of weeds (Dhaliwal *et al.*, 2010). The proper supervision plan for crop harm emerging from pests is concentrated farming which incorporates the utilization of HYV seeds, improved irrigation facilities and utilization of composts and pesticides. Environmental protection and foodstuff security are the real concerns uncommonly increasing human population everywhere throughout the world. Pests cause a genuine harm in agricultural, regarding yield and high cost of synthetic chemicals that cost billions of dollars yearly and increment the agricultural generation spending plan (Chattopadhyay *et al.*, 2017). Nevertheless the surprising expenses, the far reaching utilization of chemical pesticides has been favored because of the advantages they give in cultivation, especially by defending crops from pest destruction.

According to the “The Food and Agriculture Organization” (FAO) the pesticide is any substance or blend of substances planned for avoiding, devastating, or controlling any irritation, including vectors of human or creature ailment, undesirable types of plants or creatures, causing destruction among or generally interfering with the generation, preparing, Storage, transport, or promoting of sustenance, horticultural items, wood and wood items or animal feedstuffs, or substances that might be directed to animals for the control of bugs or different pests in or on their bodies. US Environmental Protection Agency describes pesticides as the materials which are intended to control pests, as well as weeds are known as Pesticides (US-EPA, 2018). The term pesticide incorporates the majority of the accompanying: herbicide, insecticides (which may incorporate insect growth controllers, termiticides and so on.) nematicide, piscicide, avicide, rodenticide, molluscicide, bactericide, antimicrobial, bug repellent, creature repellent, fungicide and disinfectant (antimicrobial) (Carolyn *et al.*, 2013). The most well-known of these are herbicides which represent around 80% of all pesticide use (Food Print, 2018). Most pesticides are

proposed to fill in as plant security items (otherwise called harvest defense items), which all in all, guard plants from weeds, organisms, or insects. Target vermin can incorporate insects, weeds, plant pathogens, mollusks, winged creatures, fish, nematodes (roundworms), and microorganisms that wreck property, cause irritation, or spread malady, or are infection vectors.

The credits of pesticide use incorporate upgraded monetary potential as far as food generation and improvement of vector-borne illnesses.

Nevertheless, poor agricultural practices accepted by the farmers including the broad use of pesticides with the reasoning "if a little is great, more will be better" and appropriation of insufficient waiting periods before harvesting have brought about widespread ecological pollution. Abhilash and Singh (2009), gave the information that India was the biggest maker of pesticides in Asia and is twelfth world client of pesticides. Among the Indian states, Andhra Pradesh, Uttar Pradesh and Punjab are among the most elevated buyers of pesticides.

Aside from the high utilization insights, regular use of prohibited pesticides has also been informed in the country (Mandal and Singh, 2010). The utilization of pesticides was presented in India amid the mid-sixties as a piece of green revolution and malaria anticipation programs. (Tomer *et al.*, 2015). While pesticides turned valuable for bug control they were in the meantime responsible for human health injuries. Today these synthetic substances specifically those which amass in food chain, force a few human health threats. Intake of food containing pesticide deposits is archived to result in highest exposure, about 10^3 to 10^{10} times higher than that emerging from polluted drinking water or air (Tomer *et al.*, 2015). Pesticides have been accounted for to cause a few negative health impacts which rely upon the degree and span of exposure. Health impacts of pesticides range from mellow sensitivities, rashes, breathing challenges, neurotoxicity and reproductive complications to deadly chronic diseases like cancer. This test to food security might be tended to by preventive strategies which incorporate the utilization of alternative sustainable agricultural practices or relieving systems which depend on reducing pesticide exposure from diet and water by various preparing strategies (Tomer *et al.*, 2015).

Background and historical review of pesticide applications

Since before 2000 BC, people have used pesticides to secure their harvests. The primary realized pesticide was elemental sulfur dusting utilized in antiquated Sumer around 4500 years back in old Mesopotamia. The Rig Veda, which is around 4000 years of age, makes reference to the utilization of noxious plants for pest control (Rao *et al.*, 2007). In 15th century, poisonous chemicals, for example, mercury, arsenic and lead were being introduced to field crops to destroy bugs. In prehistoric Greece and Rome, inorganic chemicals, for instance, arsenic and sulfur were utilized to control insects. Arsenics were implemented as insect repellent by the Chinese, during the 16th century. In the 17th century, nicotine sulfate was pulled out from tobacco leaves to utilize as an insecticide. The spread of the Colorado beetle in the United States was controlled through an impure form of copper arsenite, in the late 19th century. In 19th century, two new pesticides

pyrethrum and rotenone were introduced which were more natural and derived from chrysanthemums and roots of tropical vegetables respectively. Chemical weed control was verified earlier in the 20th century in France though the first organomercury seed dressings were familiarized in Germany in 1913. Until the mid of 20th century, pesticides which had arsenic-based origin were leading (Ritter *et al.*, 2009). In 1939, the current chemical age of pesticides started with the disclosure of the insecticidal capability of dichlorodiphenyl trichloroethane (DDT) in Switzerland and the advancement of organophosphorous insect repellent sprays in Germany. The primary soil-acting carbamate herbicides were found in the UK in 1945 and, at the same time, the organochlorine bug spray chlordane was presented in the US and Germany. The commercial manufacturing of phenoxy acid herbicides started in the meantime in the United Kingdom. Paul Müller exposed that DDT was an extremely effective insecticide (Figure 7.1 and 7.2).

Figure 7.1. Applications of pesticides in various sectors.

Figure 7.2. Consumption of chemical pesticides in various states/Uts during 2010-11 to 2016-17 (Source: GOI, 2019).

Organochlorines, for example, DDT were prevailing, but they were substituted by organophosphates and carbamates in the United States by 1975.

From that point forward, pyrethrin mixes have turned into the predominant insecticide (Ritter *et al.*, 2009). Herbicides turned into common during the 1960s, driven by "triazine and other nitrogen-based combinations, carboxylic acids, for example, glyphosate and 2,4-dichlorophenoxyacetic acid (Ritter *et al.*, 2009). During the 1960s, a thoughtful risk to biodiversity was observed that DDT was inhibiting many fish-eating birds from reproducing. Numerous fungicides were introduced amid the 1970s, e.g., benomyl, and new foundational combinations, for example, metalaxyl and triadimefon. Amid the most recent 20 years, a superior comprehension of natural/biochemical systems has brought about the generation of pesticides that are powerful at lower doses. Another and vital age of insecticides, for instance, includes engineered light-stable pyrethroids created from normally happening pyrethrins.

New ways to deal with the structure and to strategies for application give a chance to lessen the danger of pesticide harming, and danger of malignancy. Rachel Carson composed the top selling book 'Silent Spring' about biological amplification. The farming utilization of DDT is currently restricted under the Stockholm Convention on Persistent Organic pollutants; however it is as yet utilized in some emerging countries for preventing malaria and other tropical infections by spraying on inside dividers for killing or repelling mosquitoes (Lobe, 2006).

Classification of pesticides

Pesticides can be categorized by target life form (e.g., herbicides, fungicides, bug sprays, pediculicides and rodenticides (Gilden *et al.*, 2010), chemical arrangement (e.g. natural, inorganic, engineered, or organic (biopesticide), and physical state (for example vaporous fumigant) (Amdur *et al.*, 1997). Biopesticides incorporate microbial pesticides and biochemical pesticides (US-EPA, 2017). Plant-determined pesticides, or "botanicals", have been growing rapidly. These consist of the pyrethroids, nicotinoids and rotenoids a fourth group that incorporates scilliroside and strychnine (Kamrin, 1997). The different classifications of pesticides are given in Table 7.1-7.3. According to the kind of pest they control, pesticides are frequently denoted. Pesticides can in like manner be considered as either biodegradable pesticides, which will be destroyed down by microorganisms and other living creatures into innocuous compounds and which may take months or years before they are broken down are tenacious pesticides: it was the persistence of DDT, for instance, which prompted its amassing in the food chain and food web and its killing of fowls at the uppermost level of the food chain.

Table 7.1. Classification of pesticides based on target pest (Aktar *et al.*, 2009).

Type	Target pest
Algicide	Algae
Avicide	Birds
Bactericide	Bacteria
Fungicide	Fungi
Herbicide	Weeds
Insecticide	Insects
Miticide	Mites
Molluscicide	Snails, slugs
Nematicide	Nematodes
Piscicide	Fish
Rodenticide	Rodents

Table 7.2. Classification of pesticides based on toxicity criteria (WHO, 2009).

Type	Toxicity level	LD ₅₀ for the rat (mg/kg body weight)*	
		Oral	Dermal
Ia	Extremely hazardous	<5	<50
Ib	Highly hazardous	5–50	50–200
II	Moderately hazardous	50–2000	200–2000
U	Unlikely to present acute hazard	5000 or higher	

*LD₅₀ is the amount of the substance required to kill 50% of the test population.

Table 7.3. Classification of pesticides based on the mode of formulation (Mascarelli, 2013).

Physical state	Pesticide characteristics
Emulsifiable concentrates	Do not need constant agitation to each application.
Wettable Powders	Require constant agitation prior to each application
Granules	Obtained by mixing the active ingredient with clay
Baits	Obtained by mixing the active ingredient with food
Dusts	Dusts cannot be mixed with water and they must be applied dry

Insecticides

Neuro-active insecticides chemically alike to nicotine constitutes a category termed as Neonicotinoids. The most broadly utilized bug spray worldwide is Imidacloprid which is from the neonicotanoïd family (Yamamoto, 1999). Neonicotinoids went under expanding investigation because of their ecological impact were connected to unfriendly environmental impacts in the late 1990s, as well as loss of birds because of a reduction in insect populations and honey-bee colony collapse disorder (CCD). The use of selected neonicotinoids were limited by the European Union and some non E.U countries in 2013 (Cressey, 2013). Organophosphate and carbamate bug sprays have a comparable method of activity. They influence the sensory system of target bugs (and non-target organisms) by disturbing acetylcholinesterase movement, the enzyme that controls acetylcholine, at nerve neural connections. This restraint is responsible for over-stimulation of the parasympathetic nervous system and an expansion in synaptic acetylcholine. (Colovic *et al.*, 2013) Several of these insecticides are very toxic, initially manufactured in the mid of twentieth 20th century. Although ordinarily utilized previously, numerous more established synthetic substances have been expelled from the market because of their health and ecological impacts (for example DDT, chlordane, and toxaphene). (ATSDR, 2002). Nevertheless, in the environment, several organophosphates are not persistent. Pyrethroid insecticides were created as an engineered variant of the naturally occurring pesticide pyrethrin, which is found in chrysanthemums. They have been changed to expand their stability in nature. Certain manufactured pyrethroids are harmful to the nervous system. (Soderlund, 2010).

Herbicides

Various sulfonylureas have been commercialized for weed control, including: flazasulfuron rimsulfuron, amidosulfuron, sulfometuron-methyl, metsulfuron-methyl terbacil, (Appleby *et al.*,

2002) nicosulfuron, and triflurosulfuron-methyl. These are expansive range herbicides that kill plants weeds or pests by hindering the enzyme acetolactate synthase. During the 1960s, more than 1 kg/ha (0.89 lb/ acre) crop assurance chemical was typically applied, while sulfonylureates permit as meager as 1% as much material to accomplish the equivalent effect (Lamberth *et al.*, 2013).

Biopesticides

Biopesticides are particular kinds of pesticides originated from such common materials as plants, animals, microbes, bacterias and certain minerals. For instance, canola oil and preparing soft drink have pesticidal applications and are considered biopesticides. Biopesticides fall into three noteworthy classes: Microbial pesticides which comprise of , entomopathogenic fungi or viruses (and sometimes incorporates the metabolites that microorganisms or fungi produce). Entomopathogenic nematodes are additionally regularly classed as microbial pesticides, despite the fact that they are multi-cellular. (Coombs, 2013; Borgio *et al.*, 2011). Naturally occurring materials that control (or monitor in the instance of pheromones) pests and microbial infections are herbal pesticides or biochemical pesticides (Pal *et al.*, 2013). Plant- incorporated protectants (PIPs) have hereditary material from different species joined into their genetic material (for example Genetically Modified crops). Their utilization is questionable, particularly in numerous European countries (US NPIC, 2017).

Environmental impacts of pesticides

Pesticides which are applied to land float to aquatic systems and there they are harmful to fishes and non-target creatures. These pesticides are poisonous themselves as well as interact with stressors which include injurious algal blooms. With the abuse of pesticides, a decrease in populations of various fish species is detected (Scholz *et al.*, 2012). There are three ways by which aquatic animals are exposed to harmful pesticides (Helfrich *et al.* 2009). *Dermally*: Absorption via skin directly; *Breathing*: During breathing, uptake through gills; *Orally*: Through drinking contaminated water. The dangers related with the utilization of uncontrolled utilization of these poisons can't be ignored. The pesticide impacts on populations of oceanic and terrestrial plants, creatures and birds, it is the need of great importance to consider. Accumulation of pesticides in the food chains is of most prominent worry as it straightforwardly influences the predators and raptors. However, incidentally, pesticides can likewise decrease the amount of weeds, bushes and insects on which higher orders feed. Spraying of bug sprays, herbicides and fungicide have additionally been connected to decreases in the number of inhabitants in rare species of animals and birds. Furthermore, their long term and regular utilization lead to bioaccumulation as discussed above (Pesticides lessen biodiversity, 2010). Around 80 % of the dissolved oxygen is given by the aquatic plants and it is essential for the sustenance of aquatic life. O₂ levels decreases drastically due to the killing of aquatic plants by the herbicides and eventually leads to lack of

oxygen to the fishes and decreases fish production (Helfrich *et al.* 2009). In any case, pesticides reach underground through drainage of degraded surface water, improper disposal and unplanned spills and spillages (Pesticides in Groundwater, 2014). Aquatic environments are encountering significant harm because of floating of pesticides into the lakes, lakes and streams. Atrazine likewise indirectly influences the immune system of certain amphibians and dangerous to some fish species (Forson and Storfer, 2006; Rohr *et al.*, 2008). Amphibians are mainly influenced by pesticides contaminated surface waters, notwithstanding overexploitation and habitat loss (The Asian Amphibian Crisis, 2009). Carbaryl has been discovered dangerous for a few land and water proficient species, while, herbicide glyphosate is known to cause high death rate of tadpoles and juvenile frogs (Relyea, 2005). Little centralizations of malathion have been appeared to change the abundance and composition of plankton and periphyton population that therefore influenced the development of frog tadpoles (Relyea and Hoverman, 2008). In addition, chlorpyrifos and endosulfan likewise cause severe harm to amphibians (Sparling and Feller, 2009). Meanwhile pre- agricultural times, 20– 25 % of the bird populations have deteriorated. One of the significant reasons for this enormous decay is the utilization of pesticides which was not known before 1962. Pesticide amassing in the tissues of bird species prompts their death. Bald eagle populations in the USA declined basically on account of exposure to DDT and its metabolites (Liroff, 2000). By killing earthworms on which birds and mammals feed, fungicides can circuitously reduce their populations. Granular types of pesticides are veiled as diet grains by birds. Organophosphate bug sprays are exceedingly dangerous to birds and they are known to have harmed raptors in the fields. Sub-lethal amounts of pesticides can influence the sensory system, causing communal changes (Pesticides lessen biodiversity, 2010). A few soil organisms are engaged with the obsession of atmospheric nitrogen to nitrates. Chlorothalonil and dinitrophenyl fungicides have been appeared to disrupt nitrification and de-nitrification bacteria subordinate procedures (Lang and Cai, 2009). By acting as bioindicators of soil pollution and as models for soil noxiousness testing earthworms play a significant role in the soil ecosystem. Earthworms likewise add to soil productivity. Pesticides have not saved Earthworms from their lethal impacts and the later is presented to the previous primarily by means of polluted soil pore water. Schreck *et al.* (2008) conveyed that bug sprays or potentially fungicides produce neurotoxic impacts in earthworms and after a long term contact they are physiologically harmed (Schreck *et al.*, 2008). Glyphosate and chlorpyrifos have injurious impacts on earthworms at the cellular level triggering DNA destruction. feeding activity and practicality of earthworms is influenced by Glyphosates (Casabé *et al.*, 2007). Goulson studied the damages of neonicotinoids on environment and animal life. He stated that as neonicotinoids tend to amass in the soil, thus, they can kill earthworms like *Eisenia foetida* species (Goulson, 2013).

Routes of pesticide exposure to human

There are four regular ways pesticides can move in the human body: dermal, oral, eye, and

respiratory pathways. The noxiousness of pesticides can differ contingent upon the sort of contact, for example, dermal, oral, or respiratory (inhalation). As would be commonly expected, the hazard of pesticide pollution typically rises on the dosage (concentration) and basic periods notwithstanding poisonous quality of chemical of interest (Meenakshi *et al.*, 2012). Exposure to pesticides can happen straightforwardly from occupational, household use and agricultural, while they can likewise be conveyed through eating regimen.

Besides, the overall public might be exposed to pesticides because of their application on golf courses, around major roads, and so forth. The fundamental courses of human introduction to pesticides are through the food chain, water, air, soil, fauna and flora (Anderson and Meade, 2014). Pesticides are dispersed all through the human body through the circulatory system however can be discharged through skin, urine, and exhaled air (Damalas and Eleftherohorinos, 2011).

Dermal exposure

Dermal exposure is a standout amongst the most widely recognized and compelling courses through which pesticide applicators are exposed to pesticides (Anderson and Meade, 2014). Dermal assimilation may happen because of a sprinkle, spill, or spray drift, when mixing, stacking, arranging, and additionally cleaning of pesticides (Salvatore *et al.*, 2008). Absorption may likewise result from exposure to large quantities of residue. Pesticide makings change comprehensively in physicochemical properties and in their ability to be assimilated through the skin (Beard *et al.*, 2014), which can be impacted by the sum and span of exposure, the presence of different materials on the skin, temperature and moistness, and the utilization of individual defensive stuff (Macfarlane *et al.*, 2013). On chlorpyrifos risk assessment, the Environmental Protection Agency assessed momentary dermal exposure for an aeronautical implement to be 50 $\text{lgkg}^{-1} \text{ day}^{-1}$ with a retained portion of 1.5 $\text{lgkg}^{-1} \text{ day}^{-1}$, accepting a 3 % dermal retention (US-EPA, 2007).

Oral ingestion

The consumption of the chemical through the mouth into the digestive tract is called as oral ingestion. This happens through occupational, intended or in-intentional pesticide use when very minor quantity of spray vapor enters the nose and mouth and is gulped during spraying (Thundiyil *et al.*, 2008). When a pesticide is introduced through oral contact, the most serious poisoning may result. Oral exposure of a pesticide typically rises by chance due to inattention or for intended reasons (Damalas and Eleftherohorinos, 2011). The most common instances of unintentional oral exposure were accounted for to happen when pesticides were exchanged from their unique marked container to an unlabeled bottle or food vessel (Gilden *et al.*, 2010). There are numerous cases in which individuals have been harmed by drinking pesticides kept in soda pop containers or subsequent to drinking water stored in pesticide-contaminated bottles (US-EPA, 2007). Labors handling pesticides or equipment for their application can likewise consume

pesticides on the off chance that they don't wash their hands before eating or smoking (US-EPA, 2007).

Respiratory exposure

Because of the presence of unstable constituents of pesticides, their potential for respiratory introduction is extraordinary (Amaral, 2014). Inward breath of adequate amounts of pesticides may make genuine harm to throat, nose and lung tissues (Damalas and Eleftherohorinos, 2011). Though, the danger of pesticide exposure is in overall comparatively small when pesticides are sprayed in huge drops with traditional application equipment. In any case, if low-volume equipment is utilized to apply a concentrated material, the potential for respiratory exposure is greater because of the creation of minor drops (Amaral, 2014).

Eye exposure

The potential for chemical damage is great for tissues of the eye. A few pesticides were accounted for to be captivated by the eyes in sufficient amounts to cause genuine or even lethal disorder (Gilden *et al.*, 2010). Granular pesticides represent a specific danger to the eyes relying upon the mass and weight of individual particles (Jaga and Dharmani, 2006). In the event that pesticides are applied through power equipment, the pellets may skip off vegetation or different surfaces at high speed to cause critical eye harm (Fareed *et al.*, 2012). Eye safety is additionally required when estimating or mixing concentrated or very poisonous pesticides. Defensive face shields or goggles ought to be worn at whatever spraying pesticides or to avoid eye contact with dirt.

Human health impacts of pesticide

Studies recommend that pesticides might be connected with different illnesses including leukemia, malignancies and asthma. The threat of health risks because of pesticide exposure depends on how poisonous the constituents are as well as on the dimension of exposure. Furthermore, certain individuals, for example, kids, pregnant ladies, or maturing populations might be more profound with the impacts of pesticides than others. Human exposure whether specifically or through eating routine may result in intense and postponed health impacts (Kaushik *et al.*, 2009). WHO estimations demonstrate that more than 500,000 individuals expired from self-poisoning in western Pacific and south east Asia in 2000 alone (WHO, 2001). In emerging countries, the assessed yearly frequency rate in agricultural laborers was observed to be 18.2 per 100 000 all day workers and 7.4 per million younger students (Bolognesi and Merlo, 2011).

In India, harming because of pesticides was first informed in 1958 in Kerala where over in excess of 100 individuals expired after feeding on parathion polluted wheat flour (Karunakaran, 1958). Long term impacts related with pesticides incorporate lymphomas, leukemia, soft tissue sarcomas, mind, bone and stomach malignant growths, harm to peripheral and central nervous

system, birth defects, reproductive complaints, disruption of the immune system and death (Michael *et al.*, 2013).

Cancer

Studies have uncovered the close relationship of pesticides and the development of malignant growths in the both children and adults. Individuals who are intently connected with pesticides exposure were observed to be at more serious risk to different malignancies, for example, Burkitt lymphoma, leukemia, neuroblastoma, Wilm's tumor Non-Hodgkin lymphoma, soft tissue sarcoma, ovarian disease, tumors of lung, rectum, stomach, colon and bladder (Bonner *et al.*, 2017; Polanco Rodriguez *et al.*, 2017; Schinasi and Leon, 2014).

Prostate cancer: Environmental endocrine disrupting chemicals (EDCs) for example, different pesticides and industrial chemicals are discharged into our environment and posture genuine medical issues. Increment rate of hormone subordinate diseases, for example, bosom, testis, prostate and of the male reproductive system have been related with the hormone disrupters (Skakkebaek, 2002). Chlorpyrifos (CPF) is an organophosphate pesticide and is broadly utilized in agricultural fields. Organophosphates are metabolically actuated and are irreversible inhibitor of cholinesterases and perform as neurotoxins (Amitai *et al.*, 1998). Chlorpyrifos when given to mouse with PTEN deletion makes the creature inclined to prostate malignancy. Chronic exposure for a time period of 32 weeks to chlorpyrifos did not encourage prostate malignancy in creatures but rather achieved appropriate stages to restrain acetylcholinesterase action in plasma (Svensson *et al.*, 2013), recommending more examinations are expected to conclude CPF as a cancer-causing agent. In a meta-examination, expanded danger of prostate cancer was studied in the farmers related with a polluted pesticide with exceedingly dangerous 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD). Five studies till 2006 were taken to explore 26706 individuals exposed to the pesticide which demonstrated a positive connection with pesticide exposure and death because of prostate malignancy (Kabir *et al.*, 2018).

Breast cancer: In an investigation, an unobtrusive increment in the threat of breast cancer was observed to be related with intense occasions in a subgroup of young females who were exposed in childhood and puberty (Niehoff *et al.*, 2016). A hazard study was directed in the life partners of pesticide applicators in an Agriculture Health Study. Among 30,003 women, 25.9% reported the utilization of organophosphate (OP) pesticides and 718 women exposed to OPs were determined to have malignant growth during the follow-up period. Organophosphate utilization was related with a raised threat of bosom malignancy (RR=1.20, 95% CI 1.01- 1.43), a standout amongst the most normally utilized OP, malathion was related with the raised danger of thyroid disease and utilization of diazinon was positively connected with expanded danger of ovarian malignant growth (RR=1.87, 95% CI 1.02- 3.43) (Lerro *et al.*, 2015).

Colorectal cancer: Colorectal malignancy (CRC) is the second important reason for cancer-associated deaths in the United States men and women mutually (Raina *et al.*, 2016). In an Agriculture Health Study (AHS), a study was done to demonstrate the connection among

pesticides and colorectal cancer. The vast majority of the pesticides were not found to have a relationship with colorectal cancer. For rectal malignancy, chlorpyrifos has appeared huge exposure-response pattern that was expanded by 2.7 fold. Aldicarb was observed to be fundamentally connected with colon cancer and most elevated exposure increased the hazard by 4.1 overlap (95% certainty interim: 1.3– 12.8). But, strong confirmations are missing to verify a close connection between these pesticides and colorectal cancers which requires further investigations with point by point process (Lee *et al.*, 2007).

Non-Hodgkin lymphoma (NHL)

Non-Hodgkin lymphoma is an assorted gathering of malignancies which influences lymph and immune system; it comprises of in excess of 20 unique malignancies. In the previous couple of decades, this specific sort of threat has been expanded around the world (Alavanja and Bonner, 2012). Rising proof demonstrate that exposure to organochlorine pesticides (OCPs) builds the danger of developing NHL. In a meta-analysis, the danger to pesticide exposure for NHL was considered, positive relationship for dichlorodiphenyldichloroethylene, hexachlorocyclohexane, chlordane, and hexachlorobenzene were informed (Luo *et al.*, 2016). It is informed that immune dysfunction is straightly associated with NHL. Malathion assaulted immune cells specifically while diazinon caused interruption of a neuro- immune system that includes a cholinergic arrangement of lymphocytes (Hu *et al.*, 2017).

Alzheimer's disease (chronic neurodegenerative disease)

Alzheimer's illness (AD) is a standout amongst the most widely recognized reasons for dementia in matured people. The characteristic highlights of the disorder incorporate the existence of extracellular amyloid- beta ($A\beta$) plaques, neuronal death and the loss of neurotransmitters. Environmental pollutants are observed to be emphatically connected with the pathogenesis of AD. Numerous investigations have discovered that chronically exposed people to pesticides have a high occurrence of psychological, behavioral and psychomotor dysfunction and Alzheimer's ailment dementia. Organophosphate pesticides are found to repress acetylcholinesterase likewise as the medications used to treat AD, have likewise appeared to cause deviations in microtubule preparations and tau hyper-phosphorylation (Zaganas *et al.*, 2013).

Reproductive disorders

Disclosure to pesticides in susceptible phases of life interferes with sexual growth, reproduction and fertility of a living being. It might prompt a few unwanted results like reduced fertility, infertility, premature births, undiagnosed miscarriages, birth defects, teratogenicity, transformations, mutations hereditary deformities and malignant growths (Sheiner *et al.*, 2003). Exposure to specific pesticides in adequate dosages may build the threat of sperm abnormalities, decreased fertility, aberrant abortions, defects in birth and fetal development impediment (Frazier, 2007). Carbosulfan, a carbamate pesticide has demonstrated an expansion in

chromosomal aberrations (CA), bone marrow micronucleus formation (MN), and sperm variation in mice. At all three intense amounts utilized in the investigation (5, 2.5 and 1.25 mg/kg) there was a increment in the CA which was concentration dependent, sperm head abnormalities and micronucleated polychromatic erythrocytes (PCEs) and, yet did not influence the all over sperm count. These discoveries demonstrate carbosulfan as a strong genotoxic agent and could likewise go about as a powerful germ cell mutagen (Giri *et al.*, 2002).

Respiratory disorders

During the 1700s, Bernardino Ramazzini was one of the primary scientists who informed the threats of respiratory disorders are more prominent in farmers (Hoppin *et al.*, 2006). Numerous clinical and epidemiological investigations have conveyed a relationship between pesticide exposure and indications of asthma and bronchial hyper-reactivity. Pesticide exposure may add to the intensification of asthma by inflammation, disturbance, immunosuppression, or endocrine interruption (Hernández *et al.*, 2011). The association between early life disclosure to organophosphates and respiratory results amongst 359 mothers and children in USA was additionally examined Raanan *et al.* (2014). They determined that such exposure could prompt respiratory signs consistent with childhood asthma. In a cross-sectional investigation in Africa covering female farm laborers (n=211), the predominance of ocular-nasal indications was decidedly connected with entering a pesticide-sprayed field (OR = 2.97; 95% CI: 0.93– 9.50) (Ndlovu *et al.*, 2014).

Liver and kidney disorders

Liver and kidneys are the primary body part for detoxification and excretion in human body. Every harmful compound in the body store here for conversion and excretion (Tomer *et al.*, 2015). Therefore, these have a tendency to accumulate high amounts of chemicals and poisons prompting structural and functional abnormalities. Conceivable mechanism for the activity of pesticides can be clarified with regards to tissue susceptibility to free radicals. Pesticides like chlorpyrifos which are Lipophilic pesticide, target lipoidal films and yield ROS and oxidation and corruption of lipid layer (Kumar *et al.*, 2011). Critical positive relationship between plasma levels of oxidative stress parameters (propelled oxidation protein items and malonaldehyde) And absolute pesticide level demonstrated amplification of oxidative stress with increased accumulation of pesticides in chronic kidney disease (CKD) patients (Fetouiet *et al.*, 2010) stress with amplified accumulation of pesticides in chronic kidney disease (CKD) patients (Fetouiet *et al.*, 2010).

Increased pesticide load pressurizes liver to effort extra for purification. This prompts expanded creation of digestive enzymes. Liver working tests amongst 86 pesticide sprayers from northwest Ethiopia indicated raised extents of alkaline phosphatase, glutamate oxaloacetate transaminase and glutamate pyruvate transaminase (Ejigu and Mekonnen, 2005).

Dermal Effects

Dermal abnormalities have generally been found in farm workers and pesticide applicators. Use of organochlorine pesticides prompts chloracne (Longnecker *et al.*, 2005), rashes and pain (Dasgupta *et al.*, 2007) and stimulating sensation when the pesticides are fell on skin (Fukuyama *et al.*, 2009). In an investigation directed in China, 106 (11.6 %) applicators out of 910 were found to have intense dermal poisoning indications like urticaria, hyperhidrosis, blisters, dermatitis, swelling and pruritus (Zhang *et al.*, 2011). Utmost pesticide related dermatoses are contact dermatitis, both irritant and allergic. Uncommon clinical structures likewise happen, including ashydermatosis, erythema multiforme, parakeratosis, chloracne, porphyria cutanea tarda skin hypopigmentation, hair and nail issue (Spiewak, 2001).

Conclusion

The above discussion plainly features the hazard anxieties of unpredictable utilization of pesticide, results in numerous negative impacts in the ecological parts and human wellbeing. Pesticides have turned out to be a gift for the agronomists as well as people all around the globe by expanding agricultural yield and by giving innumerable benefits to society in a roundabout way. In any case, the worry of hazards presented by pesticides to human wellbeing and the earth has raised worries about the safety of pesticides. Despite the fact that pesticides are created to counteract, expel, or control destructive bugs, worries of the dangers of pesticides towards the earth and human wellbeing have been raised by numerous investigations. Despite the fact that we can't totally take out the dangers related with pesticide use, however we can avoid them in one way or the other. Exposure to pesticides and thus the unkind results and unwanted impacts of this introduction can be limited by a few methods, for example, alternative cropping methods or by using well-maintained spraying equipments. Besides, there ought to be a focus on figuring out what kinds of synthetic compounds or formula are the most proper apparatuses for environmental and ecological management of pests. Uncertainly pesticides are utilized in suitable amounts and utilized just when required or vital, at that point pesticide dangers can be reduced. Likewise, if a less harmful formulation or low portion of a poisonous formulations is utilized, the destruction can be controlled. By way of " The right dose differentiates a poison from a remedy " said by Paracelsus once.

In addition, both general society and private divisions, for example, government offices, NGOs, and makers of pesticides should put a lot more noteworthy effort into research, item improvement, product testing and registration, and implementation of pesticide utilization strategies, while pushing state funded training concerning pesticides. This is the time that requires the best possible utilization of pesticides to ensure our environment and ultimately health threats related with it. To decrease the exhausted utilization of pesticides, it is a serious need to endorse the organic cultivating practices and search for the operative bio-pesticides or biological creatures to control agricultural pests to decrease the utilization of synthetic pesticides.

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Chapter 8

A systematic review on global environmental risks associated with pesticide application in agriculture

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Abstract

Pesticides are used to avoid, remove, or regulate damaging pests. The extensive use of these chemicals has resulted in the contamination of soil, terrestrial and aquatic ecosystems and has been shown to have toxic effects on humans and nonhuman biota. Pesticides include a number of chemical families, with hundreds of active ingredients, thousands of different formulations and many known or suspected adverse health outcomes. Pesticides have been found to be as a common contaminant of soil, air, water, turf, and other vegetation. In addition to affecting insects or weeds, they are also known to be toxic to other organisms including fish, birds, insects, and non-target plants. The present book chapter deals with the global fates associated with pesticide application and their possible mitigation measures.

Keywords: Agrochemicals, Global pesticide risks, Health impacts, Persistence compounds

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Introduction

Pesticides are chemicals mainly used in agriculture to protect plants from pests, weeds or diseases, and in public health protection programs to protect humans from vector-borne diseases, such as malaria, dengue, and schistosomiasis. Insecticides, herbicides, fungicides, and rodenticides are the typical examples. The chemical structure of pesticides varies significantly (Baker and Wilkinson, 1990). These include organochlorine (aldrin and DDT), organophosphorus (diazinon and chlorpyrifos), benzoic acids (dicamba), carbamates (carbaryl and aldicarb), dipyriddy derivatives (diquat and paraquat), pyrethrins and pyrethroids (cyfluthrin and cypermethrin), triazines (atrazine and simazine), glycine derivatives (glyphosate), dithiocarbamates (maneb and ziram), and phenoxyacetic derivatives (2, 4-D). Agrochemicals (pesticides and fertilizers) have enabled to duplicate food production in order to feed the rapid growing human population (Tanabe *et al.*, 1990). In addition to the active ingredients, pesticides also contain chemicals known as 'inerts' such as solvents, surfactants, preservatives, which may have toxic actions distinct from the active ingredients. Some contaminants come from the production process. Dioxin, for example, is a contaminant of production of some phenoxyacetic acid herbicides, and is classified as a human carcinogen (Gilden *et al.*, 2009). Depending on the formulation type, the controlled pest and, the application timing, different techniques are used for application of pesticides. It can be applied to the crop or to the soil. Liquid sprays are commonly used in crops, usually using tunnel sprayers, boom sprayers, or aerial application. On the other hand, pesticides can be injected as a fumigant, applied as granules, or sprayed onto the soil surface. Once application of pesticides has been done, it can be taken up by the targeted organisms, degraded, or transported to the groundwater; followed by entry into the surface water bodies, or volatilize to atmosphere, or get to non-target organisms by ingestion (US EPA, 2006).

Global scenario of pesticide pollution

Among the countries that still use OCs, India has been one in all the foremost producers and shoppers in recent years. As a consequence, wild birds in India area unit exposed to nice amounts of OC pesticides (Tanabe *et al.*, 1998). Use of OCs in tropical countries might not solely lead to exposure of resident birds however conjointly of migratory birds after they visit tropical regions in winter. The Indian sub-continent may be a host to a mess of birds from western Asia, Europe and Arctic Russia in winter (Woodcock, 1980). The Global pesticide consumption was mentioned in the Figure 8.1. Many species of water bird, as well as walk birds like plovers, terns and sandpipers, migrate every winter to India covering long distances (Grewal, 1990). Whereas concentrations of OC pesticides in whole body homogenates of birds are reportable elsewhere (Tanabe *et al.*, 1998), concentrations of OCs in prey things and in eggs of Indian birds haven't been reportable. A number of studies associated with the decline within the populations of barmy in numerous elements of the planet to OC exposure were conjointly being conducted (Altenbach *et*

Figure 8.1. Global pesticide consumption (Source: Pretty and Bharucha, 2015).

al., 1979; Clark, 1976; Clark, 1983; Thies and McBee, 1994). The planet population of barmy was calculable to be 87 million throughout 1936 and it declined to close to 2000 in 1973 (Geluso *et al.*, 1976) it's recovered slightly to Associate in Nursing calculable variety of 700,000 in 1991 (Geluso *et al.*, 1976; Thies and McBee, 1994). High tissue concentrations of p, p'-dichlorodiphenyldichloroethene (p, p'-DDE) are found in barmy in cavern in North American nation and in NM within the USA (Geluso *et al.*, 1976; Thies and McBee, 1994). Prevalence of stillbirths in very little brown barmy exposed to high concentrations of PCBs, p, p'-DDE, and/or oxychlordan was documented (Clark, 1976; Jefferies, 1972). These observations indicate that bats can accumulate high concentrations of OCs and will be plagued by their potential poisonous effects. The megabat or the new world megabat, short-nosed megabat and Indian pipistrel bat area unit resident species and area unit quite common in South India. Their surround is principally agricultural areas, rock caves, and abandoned homes in domesticated areas. Insects represent a crucial diet for several barmy, permitting the passage of OCs in their body (Mc Bee and Bickham, 1992). Many studies found OC pesticides and PCBs in livers and eggs of birds in developed countries (Bednarz *et al.*, 1990; Castillo *et al.*, 1994; Mora, 1996; Mora, 1997). Similarly, many studies reportable OCs in an exceedingly style of assemblage as well as humans and life from India (Senthilkumar *et al.*, 1999).

Risks of pesticides applications in agriculture

The ultimate fate of persistence and movement of the pesticide is defined by some of its properties, such as water solubility, half-life in soil and soil-sorption constant, the octanol/water partition coefficient and site conditions and management practices being used. Solubility of the

pesticide defines their fate of being surface run off or their leaching to groundwater. Higher solubility reflects higher carrying and leaching. Second important factor is the partition coefficient as many pesticides do not leach as they get adsorbed on the soil particles which further depend on soil type and chemical nature of pesticide. Pesticides with high vapour pressure enter the atmosphere as a gas. Environmental conditions such as temperature and humidity influence the volatility of pesticide from soil, plants, or water surface. This can further result in surface water pollution. In environment, pesticides can be degraded by various mechanisms like photodecomposition and a variety of chemical and physical reactions or can be degraded by microorganisms. Pesticides with low degradation properties remain in the environment for long time and are known as persistent pesticide. Organochlorine pesticides (DDT, endosulfan, endrin, heptachlor, lindane) are persistent in environment, whereas organophosphates, chloroacetanilides, phenoxyacid derivatives, carbamates, are non-persistent. Non-persistent chemicals are known to have much shorter environmental half-lives and thus do not have a tendency to bioaccumulate. Other important factor is the texture of the soil as coarse textured sands have high infiltration capacities, and water tends to percolate through the soil and reach groundwater. On the other hand, fine textured soil like clay have low infiltration so water tends to run off, reaching streams and lakes. The most significant soil characteristic affecting pesticide fate is the organic matter content. Soils with higher organic matter content can adsorb pesticides more as it retains water with dissolved chemicals. Soil with higher load of microorganisms has more possibility to degrade the pesticide. Adsorption property of soil increases with decreasing pH for ionizable pesticides (e.g. 2, 4-D, 2, 4, 5-T and atrazine) (Andreu and Pico', 2004). Site features like depth of ground water, topography and geological conditions. In the case of shallow groundwater, there is lesser adsorption by soil, so contamination is a major concern. Geological conditions also play an important role in defining the fate of pesticide. The presence of wells, or any highly permeable materials, such as gravel deposits, assists groundwater contamination. On the other hand, streams, ponds, and lakes increase the likelihood of contamination of surface water by rainfall or irrigation run off. In case of pesticides injected or incorporated into the soil, they are more prone to leaching into the groundwater, and those sprayed onto crops are more liable to volatilization and surface runoff, and finally entering into surface waters and the atmosphere.

Pesticides have been found to be as a common contaminant of soil, air, water, turf, and other vegetation. In addition to affecting insects or weeds, they are also known to be toxic to other organisms including fish, birds, insects, and non-target plants. Run off of pesticides from treated plants and soil results in contamination of surface water. More than 90 percent of samples from streams and major rivers were found to contain one, or more pesticides (Kole *et al.*, 2001; Bortleson and Davis, 1997). The USGS reported that concentrations of insecticides in urban streams commonly exceeded guidelines for protection of aquatic life (U.S. Geological Survey, 1999). The herbicides (2, 4-D, prometon and, diuron) and the insecticides (diazinon, and chlorpyrifos), which were commonly used by urban homeowners and school districts, were

detected in all surface and ground water (U.S. Geological Survey, 1998). Out of 20 river basins studied, 19 were found to contain trifluralin and 2, 4-D (Bevans *et al.*, 1998; Fenelon *et al.*, 1998; Levings *et al.*, 1998; Wall *et al.*, 1998). In most of cases, concentrations of insecticides in urban streams were commonly found to exceed as per the guidelines for protection of aquatic life (U.S. Geological Survey, 1999). Around 23 pesticides including 17 herbicides were detected in water bodies in the Puget Sound Basin. The most common pesticide detected in most of the streams was 2, 4-D. The weed-killers dichlobenil, triclopyr, diuron and glyphosate and insecticide diazinon, were also detected in Puget Sound basin streams (Bortleson and Davis, 1997). According to the USGS, more than 143 different pesticide belonging to all major chemical class and 21 transformation products have been detected in ground water. In India, 58% of drinking water samples from hand pumps and wells around Bhopal was found to be contaminated with organo chlorine pesticides exceeding the EPA standards (Kole *et al.*, 2001). Polar pesticides (carbamates, fungicides and some organophosphorus insecticide) move from soil by runoff and leaching, thereby posing a problem for the supply of drinking water to the population. Heavy use of soil with pesticides results in decline in the populations of beneficial soil microorganisms. Plants require microorganisms to transform atmospheric nitrogen into nitrates, usable form for plants.

Impact of pesticides on living beings

The reports of environmental impacts of pesticides and some human disease were reported in the Table 8.1 and 8.2. Despite importance of pesticides, they are known to adversely affect both humans and the environment. Many pesticides are known to be chemically persistent and remain there for years. This leads to their bioaccumulation and thus has toxic effects on environment. Impact of pesticides on the health of human is determined by the nature of the pesticide, the route and duration of exposure, and the health status of the individual. Skin contact, ingestion, or inhalation are the main routes of exposure to pesticides. In human or animal body, pesticides get metabolized, excreted, or stored. Health risks associated with pesticides include dermatological, carcinogenic, neurological, gastrointestinal, and other effects. General population gets exposed to pesticide residues either by occupational use or environmental contamination. The most effective route of the pesticide exposure to the pesticide applicator is via dermal exposure which might a result of a spill, splash or spray drift during loading, disposing, or cleaning of pesticides (Anderson and Meade, 2014; Salvatore *et al.*, 2008). The extent to which a pesticide gets absorbed through the skin is dependent on the physiochemical properties of pesticide, quantity and duration of the exposure, and temperature and humidity (Macfarlane *et al.*, 2013). Liquid formulations are more likely to get absorbed than solid forms of pesticides. Some parts of the body are more susceptible to pesticide absorption than others parts (Dennis *et al.*, 2010). The most severe route of exposure is oral exposure which usually occurs by accident. The most frequent cases were when pesticides were transferred to an unlabeled bottle or food container (Gilden *et al.*, 2010). Consumption of pesticide will also happen in the cases where workers handling

Table 8.1. Reports of environmental impacts of pesticides.

Pesticide	Effect	Reference
Chlorpyrifos	Highly toxic to fish, caused fish kills in waterways near treated fields or buildings	US EPA (2000)
Trifluralin	Highly toxic to both cold and warm water fish	US EPA (1996)
Trifluralin	Vertebral deformities in fish	Koyama (1996)
Ronstar and Roundup	Acute toxic to fish	Folmar <i>et al.</i> (1979); Shafiei and Costa (1990)
Glyphosate or glyphosate-containing product	Erratic swimming and labored breathing behaviour in fishes which make them more to predators	Koyama (1996)
2,4-D herbicides	Physiological stress responses in salmon	McBride <i>et al.</i> (1981)
2,4-D herbicides	Reduction in food-gathering ability of rainbow trout	Little (1990)
Pesticide	Poisoning of dolphins	Tanabe <i>et al.</i> (1988)
Pesticides	Endangerment of fish, other marine or freshwater animals	Mohan (1989)
DDT	Adverse effects on reproductive and immune-logical functions in captive and wild aquatic mammals	Ross <i>et al.</i> (1995); Martineau <i>et al.</i> (1987); Kannan <i>et al.</i> (1993); Colborn and Smolen (1996)
2,4-D or 2,4-D containing products	Toxic to shellfish and other aquatic species	Martineau <i>et al.</i> (1987)
Trifluralinis	Highly toxic to aquatic, estuarine and marine organisms	US EPA (1996)
Oxadiazon	Severely reduces algae growth	Ambrosi <i>et al.</i> (1978)
Atrazine and alachlor	Cell damage, blocked photosynthesis, and stunted growth of algae and diatoms	US Water News Online (2000)
Oxadiazon	Toxic to bees	Washington State Department of Transportation (1993)
2,4-D	Decline in spider and carabid beetle populations	Asteraki <i>et al.</i> (1992)
Brodifacoum	Highly toxic to birds	US EPA (2000)
Glyphosate	Decrease in bird population	MacKinnon <i>et al.</i> (1993)
Organochlorines pesticides (OCs)	Toxic to fish-eating water birds and marine mammals	Barron <i>et al.</i> (1995); Cooke (1979)
Triclopyr	Inhibition of soil bacteria that transform ammonia into nitrite Santos	Pell <i>et al.</i> (1998)
Glyphosate	Reduction in the growth and activity of free-living nitrogen-fixing bacteria in soil	Santos and Flores (1995)
2,4-D	Reduction in nitrogen fixation by the bacteria that live on the roots of bean plants	Arias and Fabra (1993); Fabra <i>et al.</i> (1997)
2,4-D	Reduction in the growth and activity of nitrogen-fixing blue-green algae	Singh and Singh (1989); Tözüm -Çalgan and Sivaci-Güner (1993)
2,4-D	Inhibits the transformation of ammonia into nitrates by soil bacteria	Frankenberger <i>et al.</i> (1991)
Oryzalin and trifluralin	Inhibition of the growth of certain species of mycorrhizal fungi	Kelley and South (1978)
Roundup	Toxic to mycorrhizal fungi	Chakravarty and Sidhu (1987); Estok <i>et al.</i> (1989)
Triclopyr	Toxic to mycorrhizal fungi	Chakravarty and Sidhu (1987)
Oxadiazon	Reduction in the number of mycorrhizal fungalspores	Moorman (1989)

Table 8.2. *Some examples of human disease reported.*

Pesticides	Effect	Reference
Imazethapyr and imazaquin	Bladder cancer	Koutros et al. (2015)
Pesticide	Bladder cancer	Amr et al. (2015)
Imazethapyr	Bladder cancer and colon cancer	Koutros et al. (2009)
Herbicide	Meningioma	Samanic et al. (2008)
Pesticides	Brain tumors and gliomas	Provost et al. (2007)
Chlorpyrifos (CPF)	Induction in redox imbalance	Ventura et al. (2015)
Organochlorine pesticides	Breast cancer	Arrebola et al. (2015)
Pesticide spray drift	Breast cancer	El-Zaemey et al. (2013)
Acetochlor herbicide	Lung cancer	Lerro et al. (2015)
Pesticide	Lung cancer	Luqman et al. (2014)
Pesticide	Exacerbation of asthma by irritation, inflammation, immunosuppression, or endocrine disruption	Hernández et al. (2011); Amaral (2014)
Pendimethalin and aldicarb	Asthma	Henneberger et al. (2014)
Pesticides	Damage in the bronchial mucosa	Hernández et al. (2011)
Pesticides	Atopic asthma	Hoppin et al. (2008)
Organochlorines	Associated with higher risk of developing type 2 diabetes	Sylvie Azandjeme et al. (2013); Jaacks and Staimez (2015)
Organochlorine	Increase in incidence risk of type 2 diabetes	Tang et al. (2014); Everett et al. (2007); Turyk et al. (2009)
Pesticide	PD	Moisan et al. (2015)
Pesticides	PD mortality	Brouwer et al. (2015)
Pesticide	PD at a younger age	Ratner et al. (2014)
Frequent use of pesticide	Increased risk of PD by 47%	Narayan et al. (2013)
Pesticide	Acute lymphoblastic leukemia	Bailey et al. (2015)
Pesticides	Acute leukemia	Maryam et al. (2015)
Pesticides	Children had lymphoma and leukemia when their mother was exposed during the prenatal period	Vinson et al. (2011)
Insecticides and herbicide	Children had leukemia when their mother were exposed to pesticides during pregnancy	Turner et al. (2011)
Pesticides	Prenatal exposure to OP resulted in lower IQ, poorer working memory and perceptual reasoning of children	Bouchard et al. (2011); Engel et al. (2011); Rauh et al. (2011)
Organophosphorous pesticides	Adverse effects on male reproductive system	Mehrpour et al. (2014); Michalakis et al. (2014)
Organophosphates pesticide	Induction of long-term neurobehavioral deficits and depression	Baker et al. (1990)
Organophosphate	Reduction in psychomotor speed, executive function, visuospatialability, and work and visual memory.	Ross et al. (2013)
Pesticides	High risk of Parkinson disease	Dardiotis et al. (2013) Barnhill et al. (2014)
Pesticides	hearing loss	Mehrpour et al. (2014)
Pesticides	Diabetes and obesity	Thayer et al. (2012)
Pesticides	non-malignant respiratory disease	Hoppin et al. (2014)
Pyrethroids at high levels	endocrine disruptors	Fortin et al. (2008)
Atrazine, a triazine herbicide	endocrine-disrupting effects on amphibians	Gupta et al. (2012)

pesticides or equipment for their application do not wash their hands prior to eating or smoking (US EPA, 2007). The other means of oral exposure to pesticides is through contaminated food. In 1996, apples, tomatoes, lettuce, strawberries and grapes were found to contain seven pesticides (acephate, chlorpyrifos, chlorpyrifos-methyl, methamidophos, iprodione, procymidone and chlorothalonil). Lettuce was found to be with the highest number of positive results, with residue levels exceeding the MRLs more frequently than in any of the other crops investigated.

Due to volatile property of the components of the pesticides, their potential for respiratory exposure is higher (Amaral, 2014). Inhalation of ample amounts of pesticides can cause serious effects to nose, throat, and lung tissues (Damalas and Eleftherohorinos, 2011). Application of concentrated pesticides in small droplets results in higher potential risks (Amaral, 2014). Pesticides should be applied at air temperatures below 30°C as higher temperature increase the vapour levels of pesticides (USEPA, 2007). In a study, elevated levels of DAPs were found in hair and urine samples of persons involved in spraying organophosphorus pesticides (OPPs) compared to control group (Koutroulakis *et al.*, 2014). Around 97.8% of 415 women's amniotic fluid (AF) was found to be were positive for at least one of the non-specific dialkyl-phosphate (DAPs) metabolites during the second gestational trimester (Koutroulakis *et al.*, 2014). Analysis of rabbit hair also showed higher levels for Cypermethrin (a synthetic pyrethroid used as an insecticide) metabolites (Koutroulakis *et al.*, 2014). Absorption of some pesticides by the eyes was reported causing serious illness (Gilden *et al.*, 2010). Eye protection (face shields or goggles) is recommended while measuring or mixing highly toxic pesticides.

Fish area unit sensitive to pyrethrin and pyrethroid merchandise, and contamination of lakes, streams, ponds, or any aquatic surround could be a concern. The US National Academy of Sciences expressed that the DDT matter DDE causes egg shell dilution which the eagle population within us declined primarily due to exposure to DDT and its metabolites (Liroff, 2000). Future Can we have a tendency to do better? The need for manufacturing a lot of food to feed the growing human population is probably going to extend (UN, 2015). To fulfil this goal, many choices area unit open. One choice could be to continue the trail of intensive use of agrochemicals, as well as pesticides, with subsidiary analysis to supply a lot of selective pesticides and improved application techniques. Alternative different choices are projected and embody the employment of genetically changed organisms for higher yield crops and crops proof against pests, organic farming, development of recent cultivars and convalescence of recent cultivars, enhanced use of bio-pesticides and secretion traps to manage pests, and alter of dietary habits of human populations. the present pathway of applying artificial crop protection chemicals has been walked through on a circular approach consisting of identification of a pesterer, development of a chemical, observation of collateral effects and rise of recent issues, development of recent chemicals, etc. we have a tendency to may take into account this as AN approach supported the trial and error technique. There has been results quickly achieved, certainly, however they continuously have go along with AN associated value.

Contamination of agricultural products with pesticides

Today, food and setting contamination with nephrotoxic chemicals contact on public health over many human generations is taken into account unaffordable. Probably, agriculture and intensive food production might not dispense the employment of current agrochemicals within the next few years. Many measures might be introduced to raised mitigate their collateral effects within the meanwhile. For instance, introduction of exactitude application of agrochemicals (as well as exactitude irrigation) may scale back the number of chemicals (and water) applied over the fields. another easy measures might be additionally forthwith applied everyplace, such as: a) recovery and treatment of contaminated agriculture runoff with installation of ground stripes appropriate to wash up runoff and water drainage) reinforce education of farmers and also the public normally regarding chemical hazards; and c) thorough toxicity testing and correct registration of chemicals and formulations. These measures might facilitate to achieve some beyond regular time. Meanwhile, we should always look on the far side this time for property solutions. There's agreement that intense analysis on higher food production and production of food with higher quality is required. what is more, it's recognized that productive soil could be a finite resource (as water) and, so as to make sure continued production of food, the agriculture should go facet by facet with soil and ecosystems preservation, restoration, and science analysis on higher yield cultivars. Therefore, it's pressing to realize a generalized agreement on chemical application and adoption of fine agriculture practices, considerately to integrated pesterer Management (IPM) techniques. Consumers and also the public normally have rejected already the environmental and health prices of unsafe chemicals, and awareness of chemical residues in foods created the demand for clean foods. A lot of food and safer food is, therefore, required, however the human population and natural ecosystems might not survive longer to poor designing and poor agriculture practices.

Susceptibility of Genetically Modified Organisms (GMOs) towards pesticides

A scientific application of the precaution principle within the introduction and application of all chemicals, as well as pesticides, is required (EEA, 2013). This needs thorough risk assessment of chemicals toxicity to setting and humans. Rising different ways in food production, like development of GMO varieties and unharneass national agriculture while not application of the precaution principle and satisfactory risk assessment, should be avoided. This issue deserves pressing international discussion. AN agreement ought to be reached supported science and on moral principles for making certain food security and food safety. Moreover, different ways for food production mustn't repeat the mistakes of chemical applications and should reach making certain food safety and food security. Current and future increase in food production should go together with production of food with higher quality and with less nephrotoxic contaminants.

Different ways to the intensive use of crop protection chemicals area unit open, like genetically built organisms, organic farming, amendment of dietary habits, and development of food technologies. Agro industries have to be compelled to any develop advanced practices to shield public health, which needs a lot of cautious use of agrochemicals through previous testing, careful risk assessment, and licensing, however additionally through education of farmers and users normally, measures for higher protection of ecosystems, and sensible practices for property development of agriculture, fisheries, and cultivation. Increased research for brand new developments in food production and food safety, likewise as for environmental protection, could be a necessary a part of this endeavour. What is more, worldwide agreement on sensible agriculture practices, as well as development of genetically changed organisms (GMOs) and unharness for international agriculture, could also be pressing to make sure the success of safe food production. Pesticides area unit agrochemicals employed in agricultural lands, public health programs, and concrete inexperienced areas so as to shield plants and humans from varied diseases. However, because of their celebrated ability to cause an oversized variety of negative health and environmental effects, their facet effects are often a vital environmental health risk issue. The pressing would like for a lot of property and ecological approach has created several innovative ideas, among them agriculture reforms and food production implementing property apply evolving to food sovereignty.

Conclusion

Although pesticides are developed to prevent, remove, or control harmful pests, concerns of the hazards of pesticides towards the environment and human health have been raised by many studies. There are indeed many inherent problems in conducting large-scale experiments to directly assess the causation of the human health problems associated with the use of pesticides. However, the statistical associations between exposure to certain pesticides and the incidence of some diseases are compelling and cannot be ignored. Moreover, some members of the population have an inherent genetic susceptibility to pesticide associated diseases and are thus likely to be more at risk than others. Evidence suggests that much of this exposure is presented as multiple mixtures of chemicals and that the toxic effect of such exposure is unknown, particularly over longer time scales. It is very important to develop the precision and accuracy in the quantitation of pesticides along with improved safety profiles to reduce possibly adverse effects on human health and the environment. Furthermore, there should be a focus on determining what types of chemicals or formula are the most appropriate tools for environmental and ecological management of pests. Hence, natural bio-control agents, such as beneficial bacteria, viruses, insects, and nematodes, should be used for agricultural purposes. Moreover, both the public and private sectors such as government agencies, NGOs, and manufacturers should put much greater effort into research, product development, product testing and registration, and implementation of pesticide use strategies, while advocating public education concerning pesticides.

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Chapter 9

Impacts of pesticide application on aquatic environments and fish diversity

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Abstract

In this chapter, we provide opinions of the latest clinical findings on health results and preference valuation of health dangers associated with insecticides and the position of benefit-value analysis in regulations associated with insecticides. Aquatic animals and aquatic sources are precious herbal belongings. Better productivity and protein yield as is offered by aquatic animals as compared to agriculture or animal husbandry and have much less power expenditure for food manufacturing. Besides protein, fish flesh consists of sufficient quantity of vitamins and minerals, which are vital for the boom. Agrochemicals publicity durations and levels, kinds of agrochemicals used (regarding toxicity and endurance), and diverse environmental circumstance of the areas are also factors for acute and chronic poisoning on the aquatic animal as well as human fitness and environment. This chapter provides information about the dangerous effect like

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cancer, neural issues, beginning defects, reproductive and developmental anomalies, mutagenicity and other fitness related problems and environmental dangers related to agrochemicals.

Keyword: Accumulation, Agriculture, Contamination, Fish, Pesticides, Toxicity

Introduction

Aquatic Toxicology is the study of the impacts of pollutants on the aquatic spectrum, such as pesticides, insecticides, etc. on the physical condition of fish species or other aquatic organisms (Pereira *et al.*, 2009). Pesticides are used for various agriculture purposes to control pests mainly insects, aquatic weeds, different types of plants diseases, and aquatic snails that carry the cause of schistosomiasis. Pesticides have been found to be vastly noxious not only to fish species but also for other aquatic organisms, which constitute the tropic food chain. Pesticides are wide-ranging, are used very widely in various agriculture practices, in different forestry and in veterinary practices (Fabra *et al.*, 1997; REBECA, 2007).

Pesticides are categorized into various types according to their objective use. Mainly pesticides are categorized into the three major types are herbicides (used for weed control), insecticides (used for insect control), and fungicides (use for mycotic control), but in comparison to all three types, insecticides are the more and acute toxic. Fishes species are the imperative wellsprings of proteins and lipids for humans and domestic animals, so the health of fish species is very essential for human beings. Insecticides are the synthetic compounds used to control various types of insects by killing or preventing them from engaging in undesirable behaviours or destructive.

Surface water contaminated by pesticides is notorious to impact on the aquatic and terrestrial ecosystem, the toxicant traveling from the lithosphere, hydrosphere and atmosphere shown in the Figure 9.1, To affect the survival and reproduction of the aquatic organism. Unfortunately, along with various advantages, of pesticides are threatening for the lasting survival of major ecosystems by interruption of ecological relationships between aquatic organisms and loss of biodiversity. Different types of pesticides used are organophosphate, carbamates, organochlorine, pyrethroids, and nicotinoids. The residues of the pesticides used for intensive agriculture practices can contaminate the water (surface runoff and surface drainage) generally within a few weeks after the appliance. Use of insecticides results in a decrease in the rate of growth and also causes many metabolic and reproductive disorders. Especially in fish species, it may cause histopathological changes in gills, liver, hematopoietic tissue such as the spleen, kidney, and renal tubules, in endocrine tissues as well as brain, neurological, behavioural disorder and also cause genetic defect on exposure to insecticides. Some fish species are very sensitive to the environmental contamination of water (Maurya and Malik, 2016a). Hence, insecticides pollution in water may drastically damage in certain physiology and biochemical processes can cause serious mutilation

Figure 9.1. Transportation of pesticides through atmospheric rotation.

to physiological and health status as well as the structure of fish species. Aquaculture is solitary fastest growing fish food-producing sectors, supplying on an approximately 40-45% of the world's fish food (Mullen *et al.*, 1997).

Besides all these benefits to society, the industry also faces various problems. Exposure of large quantities of pollutants might be an immediate effect as measured by mortality suddenly in large-scale aquaculture, for example, fish mortality caused by pollution of waterways with agricultural insecticides. A small quantity of pollution discharge may result in the accumulation of pollutants in fish species and also by aquatic organisms. This paper presents the further in order to the concerning effects (acute, sub chronic and chronic) of the different types and different concentrations of insecticides on some aspects of fish's biology, physiology, behaviour, the genetic and immune system of fish species. Also, when insecticides must choosing sensibly and are used in combination with various management tools, and also applied safely, in the result to avoid the surface water pollution and contamination of our aquatic life (Maurya *et al.*, 2018).

Aquatic and fisheries resources in the form of lake, reservoir, ponds, rivers, seas, and oceans are supplying human with long term reimbursement. Those benefits can be the form of financial support which can provide employment, profit, water requirement, etc. to the humans. For example, the aquaculture and seafood industries provide jobs for commercial fisheries, wholesalers, and retailers. More round about, but equally important, benefits of fish and aquatic ecosystems include recreational activities like boating, sport fishing, swimming and natural beauty (Little *et al.*, 1990; Malik and Maurya, 2015).

There are various occupational hazards and security concerns in the aquaculture industry. Some practices have caused environmental degradation. Community perception regarding the farmed

fish species is that they are "cleaner" comparable to the wild fish species. On the other hand, various farmed fish have a much higher body burden of natural as well as man-made toxic production, e.g., in the form of antibiotics, insecticides, and pushy organic pollutants, than wild fish species. These types of contaminants in fish species can cause various health issues to unsuspecting consumers, mainly in pregnant or nursing women. The rule and regulations, as well as international oversight for the aquaculture industries, are very complex, in which various agencies indulge in aquaculture practices follow these regulation i.e. selection of site, control over pollution, quality of water, feed and also the safety of food. Different types of agricultural practices used insecticides results estrogenic and anti-estrogenic contaminants in the ecosystem can cause endocrine disruption and also effect on fish reproduction rate. Application of insecticides used for control a wide variety of insectivorous which would otherwise diminish both the quantity and quality of food production. Desolately, in spite of various advantages, the synthesized chemical compounds have significant drawbacks also threaten the long-lasting survival of major environmental disorder in relations between the aquatic organisms and also the loss of biodiversity. There are various major categories of insecticides that are habitually applied chlorinated hydrocarbons, carbamate, organophosphate, pyrethroids, and nicotinoids. Surface water contamination by insecticides is generally due to different agriculture practices combined with surface runoff and surface drainage, usually within a few weeks after application. Fish species are chiefly sensitive to the environmental contamination of water. Hence, pollutants like insecticides may effect on various physiological and biochemical processes that types of insecticides can cause a serious threat to the health status of fishes (Maurya and Malik, 2016a).

In modern agriculture activity, various types of chemical in the form of Pesticides, insecticides are used due to increased demand for productivity. Increased in productivity significantly increased the concentration of a chemical in food as well as in the ecosystem, which causes negative effects on human and other living organism health. (Richter, 2002) described that annually there are above million cases of pesticide poisonings worldwide. Moreover, with the progression of time, it may now better implicit that different pesticides have significant chronic health effects on the organism, including various types of cancer, nerve effects, diabetes, respiratory diseases, infant including fatal diseases, and genetic disorders. This type of health effects are different varied on the degree of exposure as well as the type of exposure. Normally, these effects are frequently for farmers, who are unswervingly exposed to pesticides, compared to the farmers living in rural areas who are less exposed to the following activities. Pesticides not only affect the farmer health but can also affect on consumer's health through residues of pesticide present in the food (Maurya and Malik, 2016b).

Regulation and use of Pesticides have long been controversial (Carson, 1962) in his famous publication made a popular observation in relation to risks associated with DDT (dichlorodiphenyltrichloroethane) and was followed by the US authorities for cancelation of this pesticide in agricultural uses. Various other examples of pesticide cancelation include EDB (ethylene dibromide) in 1983 and methyl bromide in 2005. It is now clear that a significant

fraction of pesticides are carcinogenic; for instance, 18% of all insecticides and 90% of all fungicides were found to be carcinogenic (NAS, 1987), also it is well known that residues of the pesticide remain for long periods of time and that they are especially toxic to the young. Also, the uses of pesticides kill domestic animals, aquatic animals especially fishes and bees. Moreover, use of this type of chemical results in the development and evolution of pesticide resistance indifferent type insects, weeds and plant pathogens. All the same hundreds of different types of pesticides are used around the worldwide landscape, and some particular pesticides are used in some countries and not in other parts of countries. The main pesticide used for corn production in the various parts of US is atrazine, but this pesticide has been banned in the EU because of its heavy toxic effect since 2004 (Official Journal of the European Union 2004/248/CE). Public decisions concerning pesticides effects have long been suspected of regulatory capture. Main reasons for transferring pesticides in 1970 regulatory accountability from the US Department of Agriculture to the Environmental Protection Agency (EPA) was to lessen the influence of farmers and pesticide producers.

But this shift of liability naturally increased the persuade of consumers and environmentalists. Indeed, Cropper *et al.* (1992) showed that both grower and environmental groups' participation played a key role in explaining the EPA decisions to cancel a pesticide in the 1970s and 1980s. Risk assessment practices also play a role in pesticides regulation. The zero-risk or "de-minimise risk" target has long been the sophisticated objective of regulators. But this objective is overly ambitious and often not implemented as a result. Some of the evidence for instance that a significant fraction of food samples still exceeds the maximum residue limits set by regulators both in the US and in Europe. Finally, risk perceptions may also persuade pesticide regulation. Slovic (2000) reported the grass root of these challenges, there is the gigantic difficulty of producing more food with the minimum use of pesticide, and the vagueness about health sound effects of pesticides. Given the mounting health concerns over the population, some extreme actions to curb the employ of pesticides have been decided in some countries.

Denmark decided in 1986 to diminish the pesticide treatment rate of recurrence in agriculture. Recently, France also announced in 2008 a lessening by two of pesticide use by 2018 in its "Ecophyto 2018" plan (MAP, 2009). A key problem with such ruthless policy targets is that they need not replicate an appropriate balance of benefits and costs induced by pesticides used in our societies. Also, these policy targets may be difficult, if not impossible, to implement in practice, in part because of the opposition of farmers. However, only a few types of research are available in relation to benefit-cost analysis (BCA) concerning pesticides have been produced so far (Pimentel, 2005).

Aquatic toxicology

Aquatic toxicology is the study of the effects of environmental contaminants on aquatic organisms, such as the effect of pesticides on the health of fish or other aquatic organisms' Figure 9.2. A

Figure 9.2. Different route of exposure of pesticides in aquatic system (Adopted from Maurya and Malik 2016b).

pesticide's capacity to accelerate the harmful effect of fish and aquatic animals are large. Its toxicity always depends upon exposure time, dose rate, persistence time in the environment. Toxicity of the pesticide refers to how poisonous it is. Brief exposure to some chemicals may have little effect on fish, whereas longer exposure may cause harm (Arbuekal and Server, 1998; Barone *et al.*, 2000). Bio-concentration is the accumulation of pesticides in animal tissue at stages more than the ones in the water or soil to which they have been carried out. The poisonous substance enters into the aquatic animal body and affects the idea of attention of toxicant. The sediment and soil are ecologically important for aquatic habitat, which plays a significant role in nutrients holding capacity. Highly polluted sediments or accumulation of nutrients are adversely affecting the ecological functioning of rivers due to persistence in the environment and long-range transport. Repeated exposure to certain insecticides can result in decreased fish egg production and hatching, nest and brood abandonment, decrease resistance to disease, reduced body weight, hormonal modifications, and reduced avoidance of predators. The general effects of sub-lethal doses of insecticides can be decreased adult survival and reduced population abundance (Hoppin *et al.*, 2002; Kamel and Hoppin, 2004; Gupta, 2004).

Different aquatic animals exposed to a pesticide, its survival relies upon its biological availability (bioavailability), bioconcentration, biomagnification, and persistence inside the surroundings. Bioavailability refers to the amount of pesticide within the environment to be had to fish and flora and fauna. Some insecticides swiftly breakdown after utility. Some bind tightly to

soil debris suspended in the water column or to stream bottoms, thereby reducing their availability.

Challenges of the global pesticide market

Fast increase in globalization are affecting pest management practices on and off the farm. The decline in the trade barriers also increases the competitive pressures and provides extra incentives for farmers to reduce costs and increase crop yields. Former participation and input markets, often branded as successful marketplace reform, can lead to incompetent pesticide use and high external costs (FAO, 2009). Other types of forms of trade barriers create a disincentive for adopting new technology such as the unwillingness of the EU to accept (GMO) genetically modified organisms. It may be imperative to indicate that it is not only the big multinational that are an important group of parties in pesticide policy but also the many new based companies in the developing countries who manufacture generics. An increases trend in the agrichemical industries is the big movement of many chemical pesticides off patent. As a result of these chemicals become generic pesticides, manufacturers lose their monopolies on them. Overall, generic type companies make up about 30 % of total sales. Mounting sales of generic pesticides, especially in some countries not only in Africa and Latin America but also in some of the Asian countries, is often facilitated by weak authoritarian control and the lack of an IPM oriented national policy framework (FAO, 2009). Around 30 to 35% of pesticides marketed in the developing countries with an estimated market value of USD 900 million manually do not get together internationally accepted quality standards. They preteens a serious threat to human health and also on their associated environment. Such types of pesticides often put into the accumulation of outdated pesticide stocks in developing countries (FAO, 2009).

Crop losses to pests

Crop productivity may be greater than before in many regions in various parts by high-yielding varieties, enhanced water quality and soil supervision, fertilization and other cultivation modern techniques. As a result of increased in the yield potential of crops, still, it is often linked with high insusceptibility to pest attack leading to increasing absolute losses and loss rates (Oerke *et al.*, 1994). An average of about 35 to 35 % of potential crop yield is lost to pre-harvest pests worldwide (Oerke, 2005). In adding together to the pre-harvest losses transport, pre-processing, storage space, dispensation, packaging, promotion, and plate waste losses along with the whole food chain account for another 30 to 35 %. In adding together to lessen crop losses due to pests, avoiding squander along with the whole distance end to end of the foodstuff chain is also a key (Popp, 2011). Evolutionary communications between pests and farmers predate predictable pesticides by thousands of years. Various levels of loss may be differentiated, e.g. direct and indirect level of losses or in the ways of primary and secondary losses, indicating that pests not

only imperil crop yield and reduce the farmer's net income but may also affect the contribution of food and feed as well as the economy of different rural areas and even countries (Zadoks and Schein, 1979). Weeds affect crop efficiency particularly due to the antagonism for inorganic nutrients (Boote *et al.*, 1983). Crop fortification has been residential for the prevention and control of yield losses due to pests in the field (pre-harvest losses) and during storage space (post-harvest losses). This paper concentrates on pre-harvest losses, i.e. the effect of pests on crop production in the field and the effect of control measures applied by farmers in order to minimize losses to an acceptable level (Oerke, 2005).

Costs and benefits of pesticide use

The profitable analyses of pesticide remuneration are hindered by the lack of pesticide use data and fiscal models for minor and crops as well as non-agricultural pesticides. Cost-benefit analysis of pesticides use is increasingly used to measure resource supervision and environmental policies. This approach monetizes all costs as well as benefits so that they are deliberate in currencies and its full functioning might be constrained by data limitations factor and difficulties in monetizing human and environmental health risks. Further economic impacts are complicated by the various government programmes that support pesticide users, such as price and cost supports system and deficit payments.

The most usually economic incentives are based on the "polluter pays" principle, including the use of licensing fees, user fees or taxes. Denmark, Sweden, and Norway are some of the countries which experience the introduced taxes in such a way of reducing pesticide use. However, the price elasticity of this chemical is estimated very low and can suggest comparatively very little effect in terms of quantity reductions, unless they may set very high rates relative to price. Some suggestions in regard to pesticides are to revenue and recycling may have been more effectual, with revenues redirected to research and information. Using further research or to encourage various changes in farming activities would appear to make more sense (Pearce and Koundouri, 2003).

Pesticides may vary in their toxicity by design, by concentration and also according to the conditions in which they are receiving environment. The main theoretical solution is to articulate the tax as an absolute sum per unit of toxicity-weighted ingredient. The overall stipulate for pesticides and insecticides are not reduced drastically by a tax, a toxicity-differentiated tax may be more effective if the exchange between pesticides will occur in a way that the all over the toxic force of pesticides will be abridged. This means that the pesticide and its use, as well as toxicity, could be "decoupled" by a pesticide tax. The various problems with pesticide tax studies are few of them simulate the "cross-price effects" of such a policy, i.e. they do not look directly at the changeover between different types of pesticides (or between pesticides and other inputs such as fertilizers and land). Simulations of such type of toxicity-weighted taxes for the UK show that overall cost price elasticity is demand for pesticides was consistently low and may never greater

than -0.39 . Nevertheless, cross-price elasticities in between the “banded” pesticides (banded according to toxicity) were greater than the “own” price elasticity, telltale that farmers might be switch between various types of pesticide (Pearce and Koundouri, 2003). Nonetheless, the “polluter pays” principle (i.e. adding the environmental and public health costs to the price paid by consumers) can be an efficient loom toward internalizing the social costs of pesticide use. The fees, as well as taxes generated, can be used to enhance (sustainable) pest management system. In instruct to place the right level of levies and taxes, it may be obligatory to estimate the positive and negative impacts of pesticides. Various attempts have been made to establish the costs price related to public health (risks to farm workers and consumers and drift risk) and spoil to favourable species, and also to the ecosystem (Pimentel *et al.*, 1992; Pimentel and Greiner, 1997; Pimentel, 2005). However, the result of the use of the pesticides can in a range of benefits including wider public outcomes with benefits being manifested in increased income and reduced risk, plus the aptitude to hire manual labour and provide the employment opportunities and other services. Some other outcomes were also the evolution of more multipart hamlet facilities, such as educational institutes, schools, and shops in such a way to improved health structure (Bennett *et al.*, 2010). Some of the sub-lethal effects include:

- Loss of attention.
- Low diseases resistance.
- Low predator avoidance.
- Reduced egg production.
- Sterility.
- Weight loss.

Exposure of pesticides to aquatic animals

Both in fish species, as well as aquatic flora and fauna, are exposed to a variety of pesticides in three common ways as dermal, direct absorption all the way through integument by swimming in contaminated surface water with pesticide as well as subordinate surfaces of waters in form of lentic and lotic water bodies, direct or indirect uptake of pesticides through inhalation by the way of gills during respiration, and directly throughout, drinking pesticides contaminated water or feed pesticide contaminated prey as in Figure 9.3. The sources of pesticides in the aquatic system through the agricultural runoff and industrial effluents, the entire foreign toxic compound mixed in the aquatic ecosystem and disturbed all aquatic life.

There are also some minor causes that affect the attention of fish species and aquatic flora and fauna to pesticides and resulted in toxicity. By the utilization of pesticide contaminated animal and their by-products also transfer toxicity to consumer’s i.e. various carnivorous fish species feed upon the variety of aquatic insects already killed due to the toxicity of pesticide may transfer effect to next tropic level. Mainly surface water of the riverine ecosystem generally comes first with pesticides contact, and various organic substances like algae, mosses, vascular hydrophytes,

leaf litter, and branches, etc. may also behave as secondary causes of toxicity. The revelation of any fish species and other aquatic community to pesticide may be widespread problem realized by the people. Most of the case related to the pesticide toxicity in fish species goes unreported and also in some known cases, the quantity of fish species mortality is often underestimating.

The scientific knowledge regarding possible pesticides affect fish species and other aquatic living organism depend mainly upon seven factors i.e. category of pesticide and its by-product, concentration rates, climate conditions, type of aquatic species concerned, degree of the dilemma (number of fish mortality), place and dimension of water body affected. Acute effect of toxicity with different types of pesticides mainly depends upon the fish species and duration of exposure as in Tables 9.1-9.3.

Various steps to reduce the effect of pesticides: Before using any pesticide, think about the following:

- Only use the pesticide whenever necessary.
- Use another ways of treating the predicament. Landowners should think about the expenses and consequences of pesticide cure relative to the problem.
- Use pesticides having less toxicity.

Figure 9.3. Distribution toxicant by route of exposure in the animal body and representation of the toxic kinetic model (Source: Maurya and Malik, 2016a).

- To reduce the sound effects of pesticides on aquatic ecosystems, use only those least toxic pesticides to the aquatic organism. Some relative toxicity lists of pesticides used in various agricultural activities are presented in tables at the end of this booklet.
- Application methods must be safe and sensible
- The initial tenet of accountable in the use of pesticide is to understand and then go through the pesticide label and follow the guidelines precisely. Label information sometimes can be mystifying. Contact extension agent, supplier in a case if don't recognize the directions or the company of pesticide for more information.
- Give meticulous awareness to the word of warning about ecological hazards on the sticky label. Look the label to confirm that: "These manufactured goods are toxic to fish species." think about supplementary pesticide or any other alternative control technique.
- Certify that equipment is working in fine proviso. Check for any leakage, reinstate worn out parts, and vigilantly standardize your equipment.
- While preparing the pesticides for relevance, subsist that you are assimilation them accurately.
- Never rinse spray tools in lakes, ponds, or rivers. If you use water directly from the natural ponds, lakes, or streams, use an anti-siphon device to avoid backflow.
- In some case applying pesticides near surface water, ensure the sticky label to locate the suggested buffer zone. Buffer strip widths varied between the water and the treatment areas. Depart a broad buffer zone to shun contaminating fish species and aquatic flora and fauna.
- Store up and dispose of unused pesticides and their containers according to the label directions.
- Avoid the use of pesticide waft into no target areas, or applications for the period of wet, turbulent weather that may endorse runoff to non-target streams, ponds, or lakes. Mist on cool days or in the early hours or evening when it is less windy.
- Pesticide applicators are legally responsible for downstream fish mortality and pesticide contamination.

Table 9.1. *The toxicity of pesticides on the basis of concentration.*

Hazard rating	Dose (mg/L)
Toxicity	LC50
Minimal	>100
Slight	10-100
Moderate	1-10
High	0.01-0.1
Extreme	0.01-0.1
Super	<0.01

Table 9.2. The acute toxicity (LC50) of some pesticides against certain fish species.

Name of pesticide	Fish species	Duration of exposure
DDT	Rainbow trout	96 hrs-8.7 µg/l
Akton	Channel catfish	96 hrs-400 µg/l
Acephate	Feathed M.	96hrs>1000 µg/l
Alachlor	Rainbow trout	96hrs 2.4 µg/l
Endosulfan	Channel catfish	96hrs 1.5 µg/l
Malathion	Labeorohita	96hrs 15 µg/l
Malathion	Heteropneustesfossilis	96hrs 0.98 ppm
Methyl parathion	Catlacatla	96hrs 4.8 ppm
Roger	Pontius stigma	96hrs 7.1 and 7.8 ppm

Table 9.3. Acute toxicity of some insecticides against certain fish species (Source: Hanazato, 2011).

Insecticides	Fish species	96hLC50
Azodrin	Rainbow trout(RT), bluegill (BG), Channel catfish, Feathered minnows (FM)	4.9-50 ppm
Aldrin	FM, Chinook Salmon, RT, blue head, bluegill	2.5-53 ppm
Carbaryl	Coho salmon, Chinook salmon, RT, green sunfish, largemouth bass, yellow perch, and black crappie	0.9-39 ppm
Carbofuran	Walked catfish, Chubs	0.22-23 ppm
Chlordane	Coho salmon, cutthroat, RT, FM, Channel catfish	0.72-11.9 ppm
Chlorpyrifos	Nile tilapia (NT), Bluegill , FM, RT, Goldfish	0.72-11.9 ppm
DDT	Coho salmon, cutthroat, RT, FM, Channel catfish	1.5-21.5 ppb
Diazinon	Guppies, Channapunctatus	0.9-2.6 ppm
Dieldrin	Coho salmon, Chinook salmon, RT, green sunfish, largemouth bass, yellow perch and black crappie, Cutthroat	1.2-19 ppb
Diflubenzuron	FM, Brook trout, Yellow perch, RT and Cutthroat	25-240 ppm
Dinitrocresol	RT and bluegill	66-360 ppb
Dioxathion	Cutthroat, Largemouth bass	22-110 ppb
Disulfoton	Coho salmon, Chinook salmon, RT, green sunfish, largemouth bass, yellow perch, and black crappie, Cutthroat	60-4700 ppb
Fenthion	Coho salmon, Chinook salmon, RT, green sunfish, largemouth bass, yellow perch and black crappie, Cutthroat	1.1-3.4 ppm
Trichlorfon	Eel, RT, Cutthroat, Brown trout, bluegill, Largemouth bass	1.1-3.4 ppm

Modification in habitat

Increase in pesticides concentration can diminish the accessibility of aquatic plants and insects that in order to serve as food for fish species and another aquatic organism. Use of pesticides in various agricultural practices can affect the food chain of insect eating birds and also for fish species. An unexpected, insufficient availability of insect's food can force fish species to migrate in search of food, where they might found the availability of greater revelation to predation. Similar to pesticides, herbicides can also trim down the reproductive success of fish species and other aquatic flora and fauna (Malik *et al.*, 2015; Maurya *et al.*, 2016c; Maurya *et al.*, 2019).

The deep, weedy nursery areas for various fish species supply rich food and protection for fry and fingerlings. Spraying pesticides along weedy nurseries can diminish the quantity of cover and protection that fry and fingerlings need in order to hide from predators and to feed. Most fry and fingerlings depend on aquatic plants as a refuge in their nursery areas (Schreinemachers *et al.*, 1999). Aquatic flora contributed about 80% of the total dissolved oxygen essential for aquatic organism present in different ponds and lakes. Pesticides kill all aquatic organisms due to the low oxygen levels and the suffocation mainly in fish species. Future use of herbicides to utterly "clean up" a pond will drastically reduce fish habit and habitat, food supply, dissolved oxygen, and fish yield.

Control of pests

Chemical control

The remedial technique for pest control with noxious chemicals has been proved the major prevailing pest control approach about an average of 50 years. Security exertion and environmental disruptions go on to ensure (Wright, 1996) and renewed appeals for efficient, safe, and cost-effectively adequate alternatives (Benbrook, 1996).

Pesticides carry synthetic chemical are the most extensively used scheme of pest management. Mainly four problems are encountered with toxic pesticides are its residues, pest resistance, pests as secondary form, and pest resurrection (Lewis, 1997). Many pesticides, as well as organophosphates that are eco-friendly, must be preferred and synthetic form pesticides should only be preferred as the last option as to use only when required.

Biological control

From time to time, the word "biological control" has been used in a broad perspective to include a full scale of biological organisms and products based biologically including some i.e. phero-110 Weed and Pest Control - Conventional and New Challenges mones, resistant plant varieties, and autocidal techniques such as sterile insects. IPM is mostly intended at developing systems based on the use of various biological and non-chemical methods as much as possible.

Mechanical control

By the help of machinery and other modern tools as well as advanced technique are used now a day to control pests in any agricultural practices. It involves some farming practices like tillage, slash and burn, and also by manual hand weeding. The pruning of infected parts of various fruits, forest trees and defoliation in certain standing crops help to reduce the population of the pest. Chaffing of sorghum/maize part of stalks and blazing of stubbles to kills maize borer is also used.

Sanitary control

Sanitary control comprises cleaning field equipment (tillage equipment, haying equipment, etc.), certified seeds should be planting and quarantine of infected crops from farmlands. These are some methods which help to prevent the introduction of a pest into the agricultural field.

Natural control

Certain techniques which only involve the improvement of naturally occurring pest management methods to conflict with pests like using valuable insects. Here only insecticides are applied to efficiently realistic and it is obvious that natural predators will help to control the pests.

Resistance in the host plant

This method involves various breeding strategies with enviable financial traits, but a smaller amount of attractive for pests, egg laying and consequent progress of insect, disease as well as a nematode. It also involves the infestation/infection or the lessening of pests to some level that they are not in huge figures during the growth period of an aquatic plant (Sharma, 2007).

Cultural measures

The developments of cultural control are the oldest methods that have been used to manage pest populations. However, with the development of synthetic pesticides, these controls were rapidly de-emphasized and research on them was largely discontinued. The involves practices that suppress pest problems by minimizing the conditions that favour their existence of life (water, shelter, food). The selection of an appropriate site for the cultivation of field crops and fruit trees can reduce future infestation from insect pests. The culture should be selected in such a manner that it should be suitable for growing in the area and tolerant of important pests diseases of the area.

Integrated pest management (IPM)

IPM is a science based on scientific thought and decision-making process that identifies and reduces the risk of pest management related strategies. IPM coordinates the pest biology of the environmental information and available different technology to prevent unacceptable levels of pest damage by the most economical means while minimizing risk to people, property, resources, and the environment. The key to pest control strategies is to determine the extent of the problem. IPM

takes benefit of these natural controls and their programs come to mind in numerous places all over the country. They may be applying in several situations from small home gardens to trade water weed administration. IPM involves an array of methods, including pesticides in order to reduce the pest contaminated populations to adequate levels. Due to the overdependence on pesticides, IPM was developed. Many factors i.e. contamination in groundwater, the ever-increasing cost of agricultural pesticides, concerns of the customer regarding pesticide contaminated foods, and also concern about the environment persuade the use of IPM. IPM provides an effective improvement, all encompassing, low risk approach to protect resources and people from pests" (USDA NIFA, 2013). IPM integrates multiple management tactics mostly allow the production system to move away from traditional, chemical-based management in ways that usually allow production systems to move away from traditional management to ecologically sound strategies. IPM practices are typically crop and region-specific and are intended to result in effective, timely and affordable pest control while also reducing the use of pesticides to health and the environment (Biddinger and Rajotte, 2015). IPM can readily evolve to meet new challenges such as food safety. IPM protocols, or collections of practices for specific crops and regions, often include related practices such as irrigation and nutrient management, at least to the extent that they influence pest management. The carefully timing management for irrigation cycles so plant foliage will dry quickly limits the potential for plant disease growth and spread (Waage, 1997). On the other hand, bio-pesticides may be safer comparing to that of conventional pesticides, the manufacturing groups of these bio-pesticides composed mostly of small to average sized enterprises, and it is very difficult for such companies to fulfil and comprehensively subsidize investigate and expansion, marketing and promotion services of such companies required to make a successful way to aware the use and benefits of bio-pesticide. Yet it is a major challenge for anyone to initiate this process due to the lack of innovative bio-pesticide goods impending to the open market and also for their registration (Popp, 2011; Farm Chemical Internationals, 2010). Types of strategies under IPM include:

- Cultural control in the form of crop rotation and planting season to avoid pests.
- Host resistance plants are used and select livestock that is resistant to pests.
- Mechanical control by uprooting, weed harvesting, cultivation, and use of various types of traps to the captured insect)
- Biological control as stocking some carp fish species that feed on water weeds.
- Control of pesticides with chemical
- Proper sanitation

Efficient supervision practices for the protective quality of water

- Preferred only IPM practices in order to avoid the chemical controls methods or will be applied only whenever necessary. Preventive measures should be taken before using any

pesticide and can be applied safely and in an effective manner.

- Estimate the concentrations of chemical control in agricultural practices. Separate out the major option that is the slightest adverse impact on water quality. Select those products which reduce waste and applicator exposure.
- Proper care should while incorporation and loading pesticides. Check equipment working correctly and is properly calibrated in advance. Prepare only the required amount of pesticide needed for the urgent application.
- Apply pesticides in short and precise time period. Think about climate as well as the life cycle of pest before planning applications.
- Store pesticides products safely in a ventilated away from sunlight, and protected area free from flooding.
- Disposal of empty containers of pesticides should not rinse in water.
- Keep records about the concentration and timing of all pesticide used in the area. This will help in assessment of pest control efforts and also help to plan future treatments.

Conclusion

Exposure of aquatic as well as terrestrial organisms to pesticides for the long term means an incessant health risk for the inhabitants. So, directly and indirectly, human populace is at elevated risk by consuming the toxicities fish species. This clearly reveals that the individual should take the required preventative measure in the application of pesticides to guard the fish population and also to other aquatic fauna. Thus it is probable that many approaches using according to molecular biology techniques will modernize toxicological applications that are cheaper and do not entail the animals to identify ecological stressors. Different effect of pesticide toxicity in fish species has been premeditated by a number of researchers, who have revealed that at chronic level, may cause different effects i.e. oxidative damage, the reticence of AchE movement, changes in histopathological, embryonic and developmental changes, carcinogenicity and mutagenesis. Usage of pesticide and its undesirable effects on non-target aquatic organisms including fish species, it has befallen crucial to plan rigid rules and regulations against the arbitrary use of this pesticide.

Since pesticide in the environment have some other toxicant compound i.e. compounds of organophosphate, additive responses to organophosphate compounds may bring on poisonous or lethal effects in fish species. Therefore it is an issue of enormous public healthiness consequence to habitually supervise the concentration of pesticide residues in foods material and also supervise the humans in a way to measure the resident's exposure to the pesticide. More experimental effort should be performed to establish the concentration and exposure time of these pesticides and also induce significant lethal and sub-lethal effects on the organism.

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Chapter 10

Pesticide applications in agriculture and their effects on birds: An overview

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Abstract

Avifauna is one of the successful diverse and evolutionary groups and occurs in the tropics in large numbers as compared to temperate zone. Fluctuation in the diversity of birds provides early warning of environmental problems. The threats to their community structure due to various reasons. Agricultural pesticides have been shown to affect 87 percent of the bird species that are threatened globally. Over the past four decades, many farmland avian species have shown alarming declines in numbers and/or range. Approximately five million plenty of pesticides are used annually in the world, of which about seventieth is used for agriculture causing decline in avian population in the agro-agriculture ecosystem. In this review an attempt has been made to focus on the effects of pesticide applications on birds. The possible health effects of pesticide applications on avifauna has been discussed as well.

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Introduction

Agriculture has always been India's backbone and has helped advance the country. With population growth and diminishing agricultural land, this sector has been subjected to severe stress. Pesticides and fertilizers have come to rescue in the past by acting as a catalyst in stabilizing the higher yields gained by using hybrid seeds. According to the Directorate of Plant Protection, Quarantine and Storage, the use of pesticides have reduced in recent years because of practices of IPM (Integrated Pest Management), use of biopesticides (Neem) and few others (Yadav, 2010). There are several types of organisms which are useful for farming and therefore pesticides have to be very specific about their targets like insecticides, fungicides, rodenticides, herbicides and a few others. In the 1960s the circumstances were such that country needed Green Revolution and as early as possible since food security was need of the hour but today circumstances have changed perhaps that is why MS Swaminathan, father of green revolution feels that there is a need of evergreen revolution since "Green revolution has some repercussion like overuse of pesticide and now focus should be given on continuous improvement of productivity without harming ecology (Swaminathan, 2017). The rising cases of brain ailments and another acute chronic disease in recent years are also due to the adverse effect of pesticides (Abdollahi *et al.*, 2004). Avian species play an important role in the ecosystem. Avifauna is one of the diverse and evolutionary successful groups and occurs in large number in the tropics. The threats leading to their population decline are due to different reasons but agriculture pesticides alone affect 87% of the globally threatened bird species (BLI, 2008). Substantial information on them is available which is largely lacking for other groups. Fluctuation in the population of avian species in an ecosystem provides early warning of environmental problems and the healthy avian populations are indicators of ecological integrity. The decline in avian population shows a collapsing ecosystem (US FWS, 2002). This should be better to prevent birds from avicides with pesticide use directly or indirectly. Nowadays this should be better to resolve by using biodiversity ecofriendly pesticides. (Weldemariam and Getachew, 2016). Figure 10.1 shows a schematic diagram showing how pesticide application affects the survival of avifauna.

Many species of farmland birds have shown alarming declines in numbers and/or range over the past four decades (Baillie *et al.*, 1997, Fuller *et al.*, 1995, Marchant and Gregory, 1994, Siriwardena *et al.*, 1998), and these declines have been attributed to changes in farming practice (Chamberlain *et al.*, 2000). Agriculture has become increasingly intensive in the UK since the Second World War, and particularly since 1973 when the UK joined the EC (Donald *et al.*, 2002). This intensification has taken place as a suite of changes in farming practice, such as loss of mixed farming, the switch from hay to silage, the switch from spring to autumn sowing of cereals and associated loss of over-winter stubbles, increased agrochemical input and loss of unfarmed structures such as hedgerows and ponds (Evans *et al.*, 1995; O'Connor and Shrub, 1986).

Pesticide use in agriculture

In the Republic of India, Currently one hundred forty-five pesticides are registered to be used at this time. Pesticide production began in 1952 from a BHC plant close to the metropolis, West Bengal. India currently stands the second largest manufacturer of pesticides in Asia and twelfth globally. In India, seventy-six of the pesticides are used as pesticides, whereas globally the percent stand at forty-four (Mathur, 1999). Use of chemical was reduced in the Eighties because of the introduction of a recent chemical compound. During the DDT era regarding eighty-fifths of the farmers of used an organochlorine chemical at the speed of 0.39 kilogram/ha covering 282 million hectares of agricultural land. Now, the consumption of chemical pesticides is highest in Andhra Pradesh (33%), followed by Punjab, Karnataka, Tamilnadu, Maharastra, Haryana, Gujarat, Uttar Pradesh, and the remaining states account less than 9.5 percent of the total. Nearly seventieth of the chemicals consumed in India is reported to be utilized for cotton (45%) and rice (22%) and such quantity of pesticide use has remained virtually unchanged during the last five decades (Vyas, 1998). In India, chemical use has accrued dramatically and currently, it's turning into a worldwide drawback. Recent findings recommend that chemical utilization was negatively related to the scientific orientation. (Mukherjee *et al.*, 2006). Pesticides such as aldrin, aromatic hydrocarbon hexachloride, calcium cyanide, chlordane, copper acetoarsenite, bromochloro-propane, endrin, ethyl mercury chloride, heptachloride, menazone, nitrogen, paraquat dimethyl sulphate, pentachloronitrobenzene, pentachlorophenol, phenylmercury acetate, sodium methane arsenate, tetradfone, toxafen, DDT, dieldrin, diazinon, parathione, aldicarb, atrazine, paraquat,

Figure 10.1. A schematic diagram showing how pesticide application affect the survival of avifauna.

and glyphosate are some of the most important hard pesticides. About five million plenty of pesticides are applied annually within the world, of that seventieth is employed for agriculture and the remainder by public health and Government agencies for vector control and by some owners (Yadav, 2010).

Effects of organochlorines (OCs) or chlorinated hydrocarbons on birds

The OCs are divided into three groups, *viz.* the dichlorodiphenyltrichloroethane connected compounds, the cyclodiene pesticides (aldrin, dieldrin, endrin, heptachlor, and endosulfan) and isomers of hexachlorocyclohexane (HCH). The acute toxicity of p, p'-DDT affect action on nerve fiber voltage-dependent Na⁺ channels. Normally once Na⁺ current is generated throughout the passage of a nerve impulse, the signal is quickly concluded by the closure of the metal channel. In dichlorodiphenyltrichloroethane poisoned nerves, the closure of the channel is delayed inflicting disruption of impulse regulation which may result in repetitive discharges (Walker, 2008). Dichloro-diphenyl-dichloro-ethylene (DDE) is responsible for the severe egg cover thinning of Yankee kestrel, Falco peregrinus, sparrow hawks and gannets. Regarding bioaccumulation of organochlorines pesticide, Tanabe *et al.* (1998) studied the migratory birds of South India and concluded that resident birds had the highest residues of HCHs and moderate to high residues of DDTs.

Acute toxicity of chlorinated hydrocarbon

DDE residues found in eggs of birds were nearly 10 ppm (Peakall, 1993). DDT has moreover caused local mass death of birds. LD50 of DDT in birds is <500 mg/Kg (Edson *et al.*, 1966). Cyclodiene pesticides over stimulate the inside nervous system and clinical signs of their vigilant poisoning include salivation, hyperactivity, respiratory distress, diarrhea, tremors, hunching and convulsions (WHO, 1989). Cyclodienes have an increased potential effect than DDT to land vertebrates. The LD50 of dieldrin is 67 mg/Kg in the pigeon (WHO, 1989). Residues of dieldrin, heptachlor epoxide and other OCs in the tissues of British sparrow hawk and Kestrel from 1963 to the 1990s were recorded (Newton and Wyllie, 1992). The cyclodiene endosulfan is extremely toxic to birds (Kidd and James, 1991). It transported over long distances through the air and has been found within the Arctic aloof from any sources of use (Sang *et al.*, 1999). Endosulfan stays deposited within the upholstered tissue and in stressed conditions. Acute oral studies conducted in mallards treated with endosulfan resulted in birds exhibiting wings crossed high over their back, tremors, falling and alternative symptoms when 10 minutes of oral alimentation dose administration.

Sublethal toxicity of chlorinated hydrocarbon

Effect on behavior: Chronic low-level OC exposure affects the fruitful success of birds and changes their sexual union behavior. The affected birds ignore territorial barriers, exhibit less

attentiveness to young and reduce the extent of their home territory (Fry, 1995). Once fed with DDE for extended length, wooing behavior in ring doves (Haegele and Hudson, 1977) and nocturnal activity in *Zonotrichia albicollis* were disturbed. Sub fatal doses of dieldrin have an effect on the aggressive behavior of duck, social and breeding behavior of bobwhite and a spread of effects within the pheasant (Peakall, 1985).

Effect on development: The developing chicks showed deformed beaks and skeleton, fluid retention in their heart and issues in sex determination when chronic sub fatal OC exposure (Gilbertson and Fox, 1977).

Effect on the endocrine system: Most of the grainous birds are exposed to pesticides through contaminated seed consumption. Some small birds are significantly in danger because of their low weight. The birds face high risk due to the consumption of high quantities of seed. Insecticide affects bodily fluid internal secretion level that is very important in reproduction and metabolism. The reduced hormone levels resulted in decreased egg production (Herbst and van Esch, 1991).

Effect on the hematological and immune system: Anaemia and reduced Hb concentration is documented when birds were exposed to insecticide (Mandal *et al.*, 1986). Suppression of T-cell mediated immunity within the wild Caspian terns and herring gulls were found to be related to high perinatal exposure to OC compounds (Grasman *et al.*, 1996). After administration of two ppm endosulfan in chicks for eight weeks, there was a major decrease within the range of T and B lymphocytes and total leucocytes along with atrophy and reduction in size of the follicles and hemorrhages within the thymus (Garg *et al.*, 2004).

Effects of organophosphates (OPs) and carbamates (CMs) on birds

OPs and CMs are most typically used pesticides throughout the planet due to their low bio-accumulation properties as compared to OCs. These pesticides inhibit acetylcholinesterase (AChE) at the postsynaptic membrane of cholinergic synapses (Bishop *et al.*, 1998) within the central and peripheral nervous systems of all vertebrate species. Ops inhibit AChE by forming a phosphorylated catalyst derivative, making it a lot of resistant to chemical reaction than the normal acetylated by-product (Taylor, 1990). Birds seem to be a lot of sense to acute exposure to anticholinesterase pesticides because of a reduced level of anticholinesterase detoxifying enzymes (Parker and Goldstein, 2000). While recovery from CMs typically happens within 1-2 h, acute OP exposure causes avian mortality within twenty-four h (Hill, 1992). The metabolism of latent inhibitors in the brain, quantity, and frequency of exposure and the sensitivity of brain AChE to inhibition are 3 most significant causes of OP toxicity (Hill, 1992).

Acute toxicity of OPs and CMs

The U.S. Department of Interior's National wildlife medical institution reported that fifty of the documented cases of lethal poisoning of birds are caused by ops and CMs (Madison, 1993). The possible route of exposure of these pesticides is the consumption of seeds or insects contaminated

on their surface with lethal amounts of pesticide (Prosser and Hart, 2005). Organophosphates are involved in 335 separate mortality events inflicting the deaths of about birds in the USA between 1980 and 2000 (Fleischli *et al.*, 2004). Worldwide, over 100,000 bird deaths caused by monocrotophos, the worst organophosphate, are documented (Hooper, 2002). Application of diazinon, another widely used OP pesticide, to lawns, golf courses, and turf farms have killed thousands of birds in the U.S (Tattersall, 1991). Although many reports are available on the short-term changes of behavior in birds, after exposure to sub fatal doses (Grue *et al.*, 1997) reports on the long changes in the behavior of birds appear to be few (Grue *et al.*, 1991).

Sublethal toxicity of OPs and CMs

Effect on feeding behaviors: OP and CM intoxication are usually related to anorexia and symptoms of gastrointestinal stress (Grue *et al.*, 1991). Long-term effects of a very small amount of OP have an effect on the feeding behavior of breeding Red-winged Blackbirds (Nicolaus and Lee, 1999). Reduction in body weight following sublethal exposure with an average weight loss of 14% was also noted in previous studies (Grue and Shipley, 1984).

Effect on the endocrine system and reproductive behavior: Alteration in the reproductive behavior and gonadal development in birds (Kuenzel, 1994) have been noticed following acute sublethal exposure to OPs and CMs because of ventromedial neural structure lesions. Delayed development and degeneration of spermatogenic cells have occurred when domestic and semi-domestic birds were exposed to OPs. Alteration in the migratory behavior (Vyas *et al.*, 1995), sexual behavior (Grue and Shipley, 1981; Hart, 1993), litter and clutch size (Bennett *et al.*, 1991) and parental care (Grue, 1982), are because of reduced levels of reproductive hormones which results from chemical pesticide exposure. Reduction in singing and displaying in the European starling (Hart, 1993) and raised aggression in each sex (Grue *et al.*, 1991) are powerfully correlated with brain AChE inhibition. In OP exposed mallards, hatching success was reduced by forty-third as compared to controls because of abnormal incubation behavior including nest abandonment and extended time of nests (Bennett *et al.*, 1991). OP and CMs decreased egg laying capability. Reduction in food consumption alone is accounted for reductions in egg laying in Northern Bobwhites fed a diet contaminated with methamidophos for fifteen days (Stromborg, 1986). In female bobwhite quail, an important decrease in plasma titers of LH, progesterone, and corticosterone (Rattner *et al.*, 1982) were noted following the short term ingestion of parathion.

Effect on thermoregulation: OPs and CMs have an effect on thermoregulation also in birds. Acute sublethal exposure to OP results in pronounced, short-lived hypothermia (Grue *et al.*, 1991). OP and CM-induced reductions in body temperatures in birds are often related to decreases in AChE activity of more than five hundredths (Clement, 1991). The interaction between low temperatures and pesticide toxicity appears to be the result of the impairment of thermoregulation, inflicting inability of birds to withstand the cold (Martin and Solomon, 1991).

Effect on the hematological system and immune system response: Exposure to high doses of OPs will cause direct injury to cells and organs of the immune system and reduce the immune

function (Voccia et al., 1999; Ambali et al., 2010). Different effects include direct injury to proteins and deoxyribonucleic acid. OPs interfere with immune system response in animals through anticholinergic and non-cholinergic pathway (Barnett and Rodgers, 1994). Sublethal exposure to chlorpyrifos and methidathion to young chickens results in a reduction in WBC and neutrophils (Obaineh and Matthew, 2009).

Conclusion

In the light of the above information it can be concluded that the chemical pesticides cause serious sub-lethal effects during the reproductive stages of birds. Sub lethal exposure could contribute to other causes of mortality like trauma. Some bird species are highly susceptible to the pesticide in which breeding season coincide with the most important application of pesticides. Exposure to pesticides during reproductive stages affects hatching success and fledgling survival, as well as increase the possibility of reproductive failure. The preying birds like the peregrine falcon, whooping Crain, and bald eagle are subjected to secondary poisoning when they consumed prey. Pesticides and their residues have an effect on birds and their young directly or indirectly by contaminating food sources. Alteration of feeding behavior compromised the immune system, and increased predation further reduces the ability of these birds to maintain healthy populations.

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Chapter 11

Impact of insect pests and pesticides on fruit productivity in Kumaun Himalaya, Uttarakhand, India

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Abstract

Assessment of major insect pests, pesticides and their impact on the productivity of apple fruit crops were conducted in the fruit orchard of Khabrar village of district Nainital, Uttarakhand, during cropping season 2017-18. From the study area, an area of one acre was purposively selected to analyze the diversity of insect pests at regular time interval. Insect pests such as beetles, bugs, aphids and moths were the most dominant pests observed during the study period.

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Eight varieties of apple fruit trees are present in the Khabrar fruit orchards such as [*Malus domestica* (Borkh)]: Red Delicious; Golden Delicious; Prima; Ambri Kashmiri; Chaubatia Anupam; Red Spur; Oregon Spur and Red Delicious Buhra. Data was analyzed by using descriptive statistics by employing PAST software version 3.

Maximum diversity of insect pests was observed during the rainy season followed by spring season, autumn and winter season, respectively. The incidence of infestation rate was also calculated that depicts the maximum emergence of insect pests on the apple crops during the months of June, July and August. The observations made during the field work revealed the use of pesticides leads to the loss of important insect groups such as pollinators and predators. Therefore, this study recommended that there is an urgent need from concerned offices to improve apple organic farming system in the study area.

Keywords: Apple, Diversity, Insects, Orchard, Pesticides, Pests, Species.

Introduction

Temperate fruits are the most important tree fruits (apple, peach, plum, pear, apricot, walnut, cherry and kiwi) known in the world that are grown in temperate regions having a distant cold climates (Thind, 2001; Fetana and Lemma, 2014). Apples are major temperate fruit crops and grown over several years in the same habitat which serves as a permanent abode for the multiplication of various insect pests. Thousands of insect pests have been recorded from temperate fruit trees all over the world, of which, more than 600 pests are found on apples alone (Gupta and Pathania, 2017). Apple is one of the most widely cultivated temperate fruit tree in all the hilly areas of the world and India is ranked as the sixth largest world's apple producing country and second largest country in area.

Apple is considered as one of the most important and widely grown fruit crops in temperate zones of the world with regard to its acreage, production, economic returns, high nutritive value and popularity (Mir *et al.*, 2018). Apple is a highly remunerative crop and is grown in all temperate regions of the world. In India, apple is grown in Uttarakhand, Jammu and Kashmir, Himachal Pradesh and some parts of Arunachal Pradesh. However, the production and quality of apple is poor as compared to that of the developed countries because of several factors including insect and diseases. Although a large number of insect pests attacks to apple crops but some of them are very serious and need attention for their control (Sherwani *et al.*, 2016). Apple trees are prone to several insect pests and diseases depending on different local field conditions. It is a melancholy fact that the apple is attacked by a wide range of insect pests and diseases which at worst can reduce the crop to zero, and damage or even kill the tree.

Therefore, in the current study, occurrence and characterization of insect pests, pesticides and their impacts on the productivity of apple fruit tree crops were studied in Khabrar village of Nainital district, Uttarakhand.

Materials and methods

Study area

The present survey was conducted in the temperate fruit orchards of Khabrar village (29°25.942' N and 79°35.535' E) located in Nainital district of Uttarakhand state during the study period 2017-18. It is located in Ramgarh fruit block, 47 km away from the Nainital city, at an altitude of 2310 meters above sea level, within sight of the western peaks of the Himalayas. This fruit block is situated in open habitat at the top and receives low level of disturbances. Two types of fruit trees are present in this block such as Apple [*Malus domestica* (Borkh)] with eight varieties: Red Delicious; Golden Delicious; Prima; Ambri Kashmiri; Chaubatia Anupam; Red Spur; Oregon Spur and Red Delicious Buhra) and Pear [*Pyrus communis* (Linnaeus)] with only two varieties: Yog and Starkrimson Red. During the study period, the temperature varied from 7.5°C to 22°C and the relative humidity ranged from 34% to 95%, respectively. The selected study site is rich in scenic beauty, with magnificent views of the Indian Himalayas including India's second highest peak, Nanda Devi. Because of the hilly topography, agriculture in the area consists chiefly of potato fields and is bounded by fruit orchards on terraces cut into hilly sides surrounded by oak and coniferous forests (Figure 11.1).

Sampling and data analysis methodology

Calculation of infestation rate: The study was carried out in an apple orchards located at Khabrar village of Ramgarh temperate fruit block region Nainital district. To assess the environmental influence especially temperature and humidity on the incidence of insect pests observed in the months of May, June, July and August and the productivity of the same orchard was also assessed during 2017-18. The data regarding incidence of insect pests and productivity

Figure 11.1. A view of Khabrar village of district Nainital selected as study area.

was recorded and presented in the form of Figures. The infestation rate was calculated by using the formula adopted by Bandey *et al.* (2012) as under:

$$\text{Infestation rate} = \frac{\text{Total number of plants infested}}{\text{Total number of plants}} \times 100$$

Species composition and characterization of status of insect pests: To determine the composition and distribution of identified insect pests, species were arranged according to their families and an inventory was prepared. The status of insect pests were characterized into two main groups such as major and minor pests based on the nature of damage caused to apple trees during the study period. The insect pests that leads to heavy damage to the apple crops which lowers the economy of the fruits and weakens the health of fruit tree is categorized under major pests. The pests that do not cause much harm to the plant parts and economy of the fruit growers are characterized as minor.

Diversity analysis

Shannon- Wiener diversity Index: The species diversity will be calculated based on Shannon Wiener Index (H),

$$H'(S) = - \sum_{i=1}^S p_i \log p_i$$

Where, p_i = fraction of entire population made up of species i , S = total number of species encountered and i = proportion of species

Evenness index:

It was calculated as per Hill, i.e. $E = H / \ln S$. Where, S = total number of species and H = Index of species.

Margalef's Index: This index was used as a simple measure of species richness Margalef,

Margalef's Index = $(S-1) / \ln N$, Where, S = total number of species, N = total number of individuals in sample and $\ln$ = natural logarithm.

Results

Species composition and abundance

The study revealed the total of 623 individuals and 15 species of insect pests belonging to 10 families and three orders distributed over three orders listed in Table 11.1. Scarabaeidae was found to be the most dominant family during the study period represented by four species that constituted 26.66 percent, followed by Chrysomelidae and Pentatomidae (two species and 13.33% each), Elateridae, Aphididae, Diaspididae, Erebidae, Lasiocampidae, Saturniidae and Tortricidae each represented by single species that constituted 6.66 percent each, respectively (Figure 11.2).

Figure 11.2. Percent contribution of different families of insect pests of apple crops recorded during the study period.

Across the entire study period, *Eriosoma lanigerum* Hausmann was the most dominant species constituting 12.68 percent of the total number of individuals recorded, followed by *Malacosoma indica* (Walker) (10.91%), *Erthesina fullo* (Thunberg) constituting 8.98 percent, *Brahmina coriacea* (Hope) (8.45%) and *Anomala lineatopennis* Blanchard (8.09%). On the other hand, *Adelocera* species constituting 3.69 percent, *Actias luna* (Linnaeus) (3.85%), *Dalpa dajugatoria* Lethierry (4.01%), *Lymantria concolor* Walker (4.17%) and *Quadraspidiotus perniciosus* Comstock constituting 4.49 percent to the total individuals were observed less abundant species during the entire study period.

Seasonal diversity of insect pests

A total 15 species of insect pests of apple crops recorded across the different seasons of the year, depicts that 14 species with 324 individuals constituted 52.06 percent were aggregated in the rainy season, followed by 12 species and 181 species (29.05%) in the spring season, eight species and 72 individuals (11.55%) in the autumn season and five species with 46 individuals that constituted 7.38 percent were encountered during the winter season. The Shannon diversity index indicated the maximum value of insect pests was calculated in rainy season (2.60) followed by spring season (2.36), autumn season (2.01) and winter season (1.49). The calculated value of evenness across different seasons of the selected fruit orchard was recorded high during the rainy season (0.965), followed by autumn season (0.934), winter season (0.889) and winter season (0.887). Species richness of insect pests was analyzed by using Margalef's index where the maximum value was examined in the rainy season (2.24), followed by spring season (2.11), autumn season (1.63) and winter season (1.04), respectively shown in Table 11.2.

Table 11.1. Species composition, relative abundance and status of different species of insect pests recorded from Khabrar village, Nainital.

S. No.	Species composition	Relative abundance (%)	Status
ORDER: COLEOPTERA			
	Family: Scarabaeidae		
1.	<i>Anomala lineatopennis</i> Blanchard	8.09	Major
2.	<i>Brahmina coriacea</i> (Hope)	8.45	Major
3.	<i>Cotinis nitida</i> Linnaeus	6.58	Minor
4.	<i>Eupatorus</i> sp.	4.81	Minor
	Family: Chrysomelidae		
5.	<i>Dicladispa</i> sp.	5.13	Minor
6.	<i>Galerucida cyanura</i> Hope	7.68	Minor
	Family: Elateridae		
7.	<i>Adeloceras</i> p.	3.69	Major
ORDER: HEMIPTERA			
	Family: Pentatomidae		
8.	<i>Dalpada jugatoria</i> Lethriery	4.01	Minor
9.	<i>Erthesina fullo</i> (Thunberg)	8.98	Major
	Family: Aphididae		
10.	<i>Eriosoma lanigerum</i> (Hausmann)	12.68	Major
	Family: Diaspididae		
11.	<i>Quadraspidiotus perniciosus</i> Comstock	4.49	Major
ORDER: LEPIDOPTERA			
	Family: Erebiidae		
12.	<i>Lymantria concolor</i> Walker	4.17	Major
	Family: Lasiocampidae		
13.	<i>Malacosoma indica</i> (Walker)	10.91	Major
	Family: Saturniidae		
14.	<i>Actias luna</i> (Linnaeus)	3.85	Minor
	Family: Tortricidae		
15.	<i>Cydia pomonella</i> (Linnaeus)	5.61	Major

Characterization of status of insect pests

Based on the nature of damage caused by insect pests to apple crops, the total collected 15 species of insect pests were listed in two main categories viz. major and minor pests, respectively. Nine species were found to cause much harm to the apple fruit trees and thus lowers the economy of the fruits were categorized under the major pests that constituted 60 percent. On the other hand, six species were observed that do not cause much harm to different parts of the apple tree and economy of fruit growers were categorized as minor pests, constituted 40 percent of the total species recorded.

Table 11.2. Various diversity indices calculated for insect pests across different seasons during the study period.

Diversity indices	Rainy	Autumn	Winter	Spring	Total
Taxa_S	14	8	5	12	15
Individuals	324	72	46	181	623
Dominance_D	0.07668	0.1416	0.2514	0.1061	0.08056
Simpson_1-D	0.9233	0.8584	0.7486	0.8939	0.9194
Shannon_H	2.604	2.011	1.492	2.366	2.613
Evenness_e^H/S	0.9656	0.9342	0.8893	0.8879	0.9093
Margalef	2.249	1.637	1.045	2.116	2.176
Equitability_J	0.9867	0.9673	0.9271	0.9521	0.9649
Fisher_alpha	2.98	2.303	1.427	2.889	2.767

Figure 11.3. Incidence of insect pests on the apple crops during the study period.

Figure 11.4. Productivity status from one acre apple orchard with and without infestation during the study period.

Analyzing infestation rate

The data pertaining to population buildup of different insect pests found infesting apple crops depicts that they remain dormant during the winter season. The emergence of insect pests of apple crops recorded started emerging during the onset of spring season and their population buildup was examined very high during the months of May, June, July and August because of favorable climatic conditions. The results of the rate of incidence of different insect pests exerted that during the month of May it was 23.65 percent under 17°C temperature and 89 percent humidity, whereas the rate of incidence of insect found during June was 32.25 percent under temperature 17°C and humidity 89 percent. The rate of incidence was 40.86 percent under 21.2°C temperate and humidity 89 percent for the month of July. The maximum rate of incidence of insect pests of apple fruit crops were examined in the month of August (91%) at 20.5°C temperature and 91 percent humidity, respectively (Figure 11.3). The data regarding the productivity in one acre of apple fruit orchard showed that with infestation the productivity was 1900 Kilograms (Kg), whereas the productivity was 2900 Kg where no infestation was occur shown in Figure 11.4.

Major pesticides used in study area

The pest problem has become a global concern among all the fruit growers of the world that affected the soundness and appearance of the fruits. During the present field observations, it was noticed that the fruit growers were seen more addictive to pesticides rather than the bio-control practices to control insect pests. The pesticides used by the farmers to get rid of insect pests were Chlorpyrifos 20 EC and Dimethonate 30 EC with dosage of 10 ml/100 liters of water during summer; Methyl-O-demeton 25 EC @ 80 ml/100 liters of water during the spring season that prevent infestation in summer; Carbofuran 3 CG@ 70 to 100g/ tree under the canopy area followed by hoeing of the soil in order prevent the infestation in root parts and Dicofol 18.5 EC@ 1.08 ml/ liter of water used as the summer spray. In spite of the pesticide use to control insect pests, other important insect groups such as pollinators and bio-control agents (predators) gets targeted leads to greater loss of the economically important insects and thus the loss of biodiversity. The population of such insect pests could be controlled by different practices such as proper planting management via pruning of fruit trees from time to time and removal of weeds that serve as alternate hosts of insect pests during off season, use of high yielding varieties, providing fertilizers supplement, efficient irrigation systems and integrated disease and pest management and use of clonal rootstocks.

Discussion

In comparison, Joshi and Joshi (1980) conducted the survey on different pests of fruit trees in Kumaun hills, where they reported numerous insect pests caused considerable damage to the these fruit trees hence reducing their productivity. The insect pest surveyed that infest apple fruit

crops of Kumaun hills include *Dorysthenes hugelii* Redtenbacher, *Cantharsius molossus* (Linnaeus), *Lucanus lunifer* Hope, *Melolontha* species, *Brahmina* species, *Eriosoma lanigerum* Hausmann, *Quadraspidiotus perniciosus* Comstock, *Lymantria obfusca* Walker and *Malacosoma indica* Walker. Brown (2003) studied the characterization of Stink bug (Pentatomidae) that caused depression on the surface of apple fruits.

Fetena and Lemma (2014) assessed the major apple pests in different apple varieties, of which green apple aphids, scale insects and green plant bugs were observed to feed on the leaves of the fruit plant. Sherwani *et al.* (2016) reported the incidence of major insect pests of apple trees in different orchards of Kashmir. The reported insect pests examined during the study period were San Jose Scale, Woolly Apple Aphid, Tent Caterpillar, European Red Mite, Codling Moth, Apple Root Borer, Apple Stem Borers, Gypsy Moth and Bark Beetle, respectively. The codling moth, *Cydia pomonella* (Linnaeus) is one of the key pests of apple fruit trees that directly affect the economy and cause severe damage to the apple trees (Pajac *et al.*, 2011; Shah Nawaz *et al.*, 2014; Mahzoum *et al.*, 2017). Gupta and Pathania (2017) investigated the diversity of hemipteran pests that feeds on apple crops in different districts of Jammu and Kashmir State of India. They reported the total of 12 species infesting apple crops from different apple growing areas of Jammu division, among which *Eriosoma lanigerum* Hausmann, *Quadraspidiotus perniciosus* Comstock and *Dalpada* sp. were found to be the most dominant insect pests during the study. Bandey *et al.* (2012) studied the diversity of apple pests and analyzed the infestation rate of insect pests that target the productivity in Jammu region of Jammu & Kashmir State. They selected three kanal gardens and analyzed the data that showed the productivity of apple fruits was reduced to 800 Kg (with infestation) from 1500 Kg (without infestation) during the study period.

Conclusion

The findings of the present study revealed the presence of 15 species of insect pests represented by 10 families and distributed over three orders. Coleoptera was found to be the most dominant order represented by seven species followed by Hemiptera and Lepidoptera with four species each. *Eriosoma lanigerum* Hausmann was the most dominant species constituting 12.68 percent of the total number of individuals recorded followed by *Malacosoma indica* (Walker) (10.91%), whereas *Adelocera* sp. constituting 3.69 percent and *Actias luna* (Linnaeus) (3.85%) were observed less abundant species during the entire study period. Across the different seasons, maximum Shannon diversity index value was found to be during the rainy season followed by spring, autumn and winter season, respectively. Nine species were noticed to inflict considerable damage to the plant parts hence were characterized as major pests, where remaining six species do not caused too much harm were regarded as minor pests.

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Chapter 12

Groundwater pollution, causes, assessment methods and remedies for mitigation: A special attention to Indian Punjab

Mahesh Chand Singh

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Abstract

In parallel to over-exploitation of groundwater resources of Indian Punjab, water pollution has turned out to be another serious challenge chiefly due to increased use of Agrochemicals (fertilizers, pesticides, insecticides, fungicides, herbicides, etc.). The Malwa region of the state consumes about 75% of the total pesticides used in Punjab. Nitrogen and phosphorus use of the state is nearly twice of that at national level. About 80% groundwater of Malwa region has

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become unfit for drinking containing high levels of pesticides, nitrate, magnesium, fluoride and heavy metals or trace elements. Under such a situation, the precision agricultural tools such as Leaf Colour Chart (LCC) and N-sensors for need based fertilizers application require their promotion in the state. Use of pesticides can be replaced through adoption of Integrated Pest Management (IPM), bio-pesticides, organic manures and crop diversification. There is a need to review and fortify the community programs for safe use of the chemicals through improved pesticide policies. The soilless cultivation of vegetable crops can also be adopted to have reduced water and soil pollution through controlled use of fertilizers. There arises a need for timely understanding and identification of sources of pollution and detection of contaminants associated with groundwater through appropriate measures such as complete blood analysis, physical and chemical analysis of water separately for pre- and post-monsoon seasons.

Keywords: Groundwater pollution, Heavy metals, Pesticides, Nitrate, Management

Introduction

Punjab occupies only 1.57% (50,362 km²) of geographical area of the country having 83% of its land in agriculture compared to national average which is only 40.4% (Gupta, 2009). At present, the total sown area of the state is about 2.5 times of that during late sixties and the cropping intensity more than 190%. Out of the total cropped area of the state, 72.5% area is irrigated through tube wells, 26.2% through canals and the rest 1.3% by others (GoI, 2009). The agriculture in the state has become intensive in terms of land, capital, energy, nutrients, agricultural water and other agricultural inputs.. The population of the state has also increased from 27,704,234 (approx. 27.7 million) in 2011 to 30,452,879 (approx. 30.5 million) in 2018 (Anon, 2019a). Previously, during the retro of Green Revolution (supported jointly by institutional and technological factors), Punjab witnessed an incredible increase in the agricultural production and named as “Food Basket of the Country” and “Granary of India” due to its significant contribution for rice and wheat production to central pool.

However, the groundwater pollution in the state has become an uninviting challenge as a result of direct factors (extreme use of fertilizers, pesticides, over-pumping, injudicious dumping of wastes, mining activities industrial effluents, pharmaceuticals, sewage wastes and others) and indirect factors (prolonged urban development, local climatic conditions, water basins, river network interruption etc.). A fast variation in groundwater quality with respect to time and space is consistently being recorded in alluvial aquifers of the state. The use of insecticides in Indian agriculture has already crossed 76% compared to the world which is 44% (Mathur *et al.*, 2005). India has become the second largest manufacturer of pesticides in Asia after China with 12th rank in the world (Mathur, 1999; Yadav, 2010). The main use of pesticides in India is for cotton crops (45%) followed by paddy and wheat. The states of Punjab, Haryana and Uttar Pradesh consume

more than 5000 MT pesticide annually and come under category-I.

The dissolution of minerals and ion exchange processes during pre-monsoon affect the groundwater quality (Stagnitti *et al.*, 1994). However, during post-monsoon season, the rainwater loaded with salts from the unsaturated zone contributes to the groundwater pollution. Thus, monitoring of alluvial aquifers has become imperative due to their vulnerability to anthropogenic pollution (Kumar *et al.*, 2009; Sidhu *et al.*, 2013) and to assess the suitability of the groundwater for irrigation and drinking. The route of pesticide contamination of surface and ground water resources has been indicated through Figure 12.1 (Stagnitti *et al.*, 1994). The parameters viz. electrical conductivity (EC), Kelly's ratio (KR), magnesium adsorption ratio (MAR), soluble sodium percentage (SSP), permeability index (PI), sodium adsorption ratio (SAR), soluble sodium percentage (SSP) and residual sodium carbonate (RSC) can be used to assess the quality or suitability of water (or groundwater) for irrigation (Table 12.6).

Figure 12.1. Route for groundwater contamination through pesticide application.

Likewise, the suitability of groundwater for drinking can also be assessed through computation of parameters such as pH, total dissolved solids (TDS), total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-), fluoride (F^-), alkalinity (as CaCO_3), water quality index (WQI) and others (Table 12.7). The heavy metals viz. lead (Pb), chromium (Cr), arsenic (As), cadmium (Cd), mercury (Hg), zinc (Zn), copper (Cu), cobalt (Co) and nickel (Ni) are responsible for inorganic chemical hazard in water (Jarup, 2003) as a result of their concentrations beyond the limit in the shallow and deeper aquifers. Among these, Pb, Cr, As, Cd and Hg are reported to be the key pollutants in Malwa region of Indian Punjab. A heavy metal like As which comes under first 20 most hazardous metals can cause acute and chronic health effects in human (Gray *et al.*, 1989; Saha, 2003) as reported worldwide (Smedley *et al.*, 2002; Bhattacharya *et al.*, 2002; Bhattacharya *et al.*, 2011). However, the establishment or socioeconomic development of a stable community is highly dependent on the availability of safe and reliable

fresh water resources such as groundwater. Thus, assessment of groundwater quality (chemical, physical and biological parameters) and timely detection of pollutants has become essential for its suitability for drinking, irrigation and taking effective remedial measures for its improvement (Raju *et al.*, 2009). This chapter demonstrates the current scenario of water pollution in Indian Punjab, possible causes, sources, long-term effect of water pollution on mankind and remedial measures for its control.

Routes of water pollution through point and non-point sources

The contaminants can enter water bodies through (i) direct discharge of domestic and industrial waste water, (ii) surface runoff and seepage, (iii) river flow transport, (iv) reaction and transport through the water-sediment interface and (v) reaction and transport across the air-water interface (Anon, 2019b). The transport of pollutants through unsaturated zone is encouraged by hydraulic and mass transport factors such as hydraulic conductivity and gradient, soil moisture content, degree of homogeneity of soil, relative portion of active pore spaces, boundary conditions of the unsaturated zone and climatic conditions of the region. The active pore space traps the pollutants through restricting the movements of water by conveying water to dead end space. The boundary conditions of the unsaturated zone influence the amount of moisture available for percolation and evapotranspiration. However, the transport of contaminants through saturated zone is carried by convection and dispersion processes. Convection (advection) refers to contaminant transport by moving water with same velocity and direction.

Figure 12.2. Water pollution (surface and groundwater) through point and non-point sources.

While, dispersion refers to spreading of contaminants dissolved in the water by local variations in velocity of water. There are several sources of surface and groundwater pollution which can be categorized as point and non-point (diffuse) sources of pollution. Figure 12.2 demonstrates the routes through which the different point and non-point sources of pollution contribute to the water pollution (surface and groundwater). The groundwater pollution is directly related with surface water pollution as indicated in Figure 12.2 (Stefanakis *et al.*, 2015). In structured soils, the macro pore flow often causes rapid non uniform leaching via preferential flow paths, where a fraction of the contaminant percolates into ground water before it can degrade or be adsorbed by the soil (Sharma *et al.*, 2016). Water undergoes changes in its chemical composition through different chemical processes and reactions after percolation in soil, vadose zone and movement in saturated zone (Anon, 2019b). Those processes and reactions include, acid and base reaction, biochemical reactions, heavy metal reactions, ion exchange and adsorption, oxidation and reduction, solubility and precipitation, and volatility. However, some processes such as biological degradation, buffering of pH, dilution, mechanical filtration, membrane filtration, precipitation, oxidation-reduction reaction and volatilization may help in controlling the groundwater contamination.

The present study was planned with the following objectives:

- To identify the contaminants and routes of water pollution through human interventions
- To discuss the extent of water pollution through different contaminants and their major causes

Table 12.1. Abbreviations used in this study.

Abbreviation	
MT	Million tonne
DDT	Dichlorodiphenyltrichloroethane
BHC	Benzenehexa Chloride
HCH	Hexachlorocyclohexane
BIS	Bureau of Indian Standards
CGWA	Central Ground Water Authority
CGWB	Central Ground Water Board
EPA	Environment protection Act, 1986
GoI	Government of India
GoP	Government of Punjab
MoEF	Ministry of Environment and Forests
MoWR	Ministry of Water Resources
PAU	Punjab Agricultural University
PSFC	Punjab State Farmers' Commission
PWRED	Punjab Water Resources and Environment Directorate
TERI	The Energy Resource Institute
WHO	World Health Organization

- To identify the health hazards due to water pollution
- To understand how to identify the sources of contaminants and problems associated
- To review and demonstrate the different techniques for computation of water quality indices for irrigation and drinking water suitability.
- Remedies for management or control of water pollution.

General description

Indian Punjab is situated between 29°30′ N to 32°32′ N latitude and 73°55′ E to 76°50′ E longitude with an altitude in the range of 230-700 m from the mean sea level. Agro-climatologically and hydrologically Punjab has been divided into three zones viz. North-East, Central and South-West comprising of 19, 40 and 41% respectively of the geographical area of the state. North-East zone of the state is facing a problem of soil erosion mainly due to water (80 t/ha/year). Central and South-West zones of Punjab are facing acute depletion of fresh groundwater resources and water logging with poor quality water respectively. Punjab has three perennial rivers viz. Beas, Satluj and Ravi and a seasonal river Ghaggar. It has a canal network of about 14,500 km for supplying water from these rivers. Average annual rainfall of the state ranges from 1250 mm in the North to 350 mm in the South-West. More than 70% of the annual rainfall occurs during the monsoon season (July to September). However, a decline in rainfall in the range of 40-50% has been recorded during last two decades between 1994 and 2014 (PWRED, 2014). The fresh groundwater resources of the state has gone under threat from last few couple of decades in terms of over-exploitation leading to depleted water resources.

Extent of groundwater pollution in Punjab

Apart from the critical groundwater depletion, pollution of water (surface and groundwater) has become another serious issue at present in the state. The sources of groundwater pollution include heavy metals (Cd, Cr, Cu, Pb, Hg & others), inorganic compounds (NO_2^- , NO_3^- , PO_4^{3-} and others), toxic compounds (Se, CN^- etc.), radioactive substances (radon caused by uranium and thorium series decay), synthetic organic compounds (chlorinated hydrocarbons, detergents, paint colors, petroleum products, pesticides, phenols etc.) and pathogenic micro-organisms (bacteria and viruses) which can origin diseases such as diarrhoea and dysentery. The fresh groundwater water resources have been now badly contaminated, particularly the Malwa region of the state through entry of toxic chemicals (e.g. pesticides, etc.) and heavy metals (e.g. arsenic, fluoride, etc.) moved down into groundwater from soil or rock layers as well as through direct contamination from poorly designed hazardous waste sites and industrial sites (Table 12.2). There exists an interaction of poor quality surface water with the good quality fresh groundwater through leaching or percolation (preferential flow) as indicated in Figure 12.1. For an example, the water being pumped through hand pumps from shallow aquifers particularly near Buddha Nallah in Rural Ludhiana (Bhamian Kalan, Khasi Kalan and Wallipur) is now degraded both physically

and chemically as a result of direct discharge of untreated industrial effluents including dyes, tanning, nickel and chrome plating units (Kaur *et al.*, 2014); which in turn polluting the surface water resources (Satluj river) and thereby the groundwater resources. A deliberated industrial discharge of about 50000 m³day⁻¹ of most toxic industrial effluents into the Buddha Nallah in Ludhiana district has been reported, which is further responsible for recharge of the groundwater aquifers in the city (CGWB, 1998). According to CGWB, the concentrations of heavy metals viz. Cd, CN, Pb and Cr was beyond the limit in the shallow aquifers with a small amounts of these heavy metals in the deeper aquifers too.

Causes of water pollution (point and non-point sources) prevalence of deadly diseases

- Prompt increase in population and urbanization
- Agricultural practices
 - * Introduction of high yielding crop varieties.
 - * Excessive use of pesticides (fungicides, insecticides and weedicides or herbicides etc.).
 - * Exposure interval and levels to agrochemicals, toxicity and persistence of agrochemical used, and several environmental conditions are also responsible factors for acute and chronic poisoning on human health and the environment.
 - * Lack of awareness, training and adequate knowledge for using the agrochemicals.
 - * Deliberately extensive use of fertilizers for the sake of improving crop productivity.
 - * Leaching of salts in the unsaturated zone, contribution of water soluble fertilizers and livestock excrement play a substantial role in groundwater contamination (shallow aquifers).
 - * Over irrigation in crops like rice, creates a scope for nitrate contamination in the groundwater through leaching due to its high solubility in water and less retention by soil particles.
 - * In addition to nitrate, DDT is another major hazardous chemical responsible for groundwater pollution.
 - * Untreated wastewater (containing industrial chemicals) being used for irrigation contains heavy metals (e.g. As, Cr, Cd, Co, Pb, etc.).
- Industrialization
 - * Injudicious disposal (or dumping) of untreated industrial chemical waste contaminates the shallow aquifers, rivers and streams leading to groundwater pollution. Example: direct discharges of wastewaters containing chemicals to Buddha Nallah of district Ludhiana in Punjab and Yamuna River in Delhi.
 - * Disposal of untreated mercury contaminated effluent from caustic manufacturing into groundwater aquifers.

- * Lack of proper drainage systems for treated effluents in industries which again leach down to meet groundwater.
- Inappropriate approaches for artificial groundwater recharge (in-situ RWH) through abandon bore wells. Example: directing untreated wastewater or runoff water containing several hazardous contaminants such as agricultural chemicals, and heavy metals directly into the bore wells.
- Surface water contamination through direct disposal of untreated sewage waste (human and animal) into rivers. Example: Satluj River between Ludhiana and Jalandhar in Punjab and Yamuna River in Delhi.
- Fluoride and arsenic contamination due to over-exploitation of groundwater.
- Disposal of liquid and solid wastes into open water bodies
- By-products and waste from of mining activities
- Dumping of wastes (e.g. lubricants) from the service centres of motor vehicles.
- Disposal of wastes from hospitals in open environment (water) and dumping into soils.
- Disposal of nuclear energy wastes
- River network interruption
- Mineral processing of radioactive substances
- Cemeteries

Table 12.2 Districts affected with groundwater pollution through heavy metals, salinity and trace elements.

Heavy metal	Location
Arsenic (>0.05 mg/L)	Amritsar, Gurdaspur, Hoshiarpur, Kapurthala, Ropar According to recent study: Bathinda, Faridkot, Ferozpur, Mansa, moga and Muktsar (Sharma and Dutta, 2017)
Flouride (>1.5 mg/L)	Amritsar, Barnala, Bathinda, Faridkot (Sharma <i>et al.</i> , 2016), Fatehgarh Sahib, Ferozpur, Gurdaspur, Jalandhar, Ludhiana, Mansa, Moga, Muktsar, Patiala, Ropar, Sangrur, Tarn-Taran According to recent study: Barnala, Bathinda, Faridkot, Mansa and Muktsar (Kaur <i>et al.</i> , 2017)
Iron (>1.0 mg/L)	Bathinda, Faridkot, Fatehgarh Sahib, Ferozpur (Sharma and Dutta, 2017), Gurdaspur, Hosiarpur, Mansa, Moga (Sharma and Dutta, 2017), Ropar, Sangrur
Nitrate (>45 mg/L)	Amritsar, Barnala, Bathinda(Sharma <i>et al.</i> , 2016), Faridkot (Sharma <i>et al.</i> , 2016), Fatehgarh Sahib, Ferozpur (Sharma <i>et al.</i> , 2016), Gurdaspur, Hoshiarpur, Jalandhar, Kapurthala, Ludhiana, Mansa, Moga, Muktsar, Nawan Shahr, Patiala, Ropar, Sangrur, Tarn-Taran
Salinity	Bathinda, Faridkot, Ferozpur, Gurdaspur, Mansa, Moga, Muktsar, Patiala, Sangrur (Chopra and Krishan, 2014)
Trace elements	Se Nawan Shahr, Hoshiarpur and Tarn-Taran (Dhillon and Dhillon, 1991) Rn Bathinda, Gurdaspur (Virk <i>et al.</i> , 2001) U Barnala, Bathinda, Fazilka, Ferozpur, Ludhiana, Moga, Sangrur

Further, similar to fresh water pollution through seawater intrusion process, the depleting groundwater level in Central Indian Punjab and rising water table in South-Western Punjab may further create a potential gradient for bad quality water to flow and enter into fresh groundwater resources of the state. Thus, a regular assessment of quality of groundwater for different purposes (agricultural and domestic) is of great importance (Raju *et al.*, 2009).

Quality of irrigation water in Punjab

At present, the assessment of groundwater to check its suitability for irrigation and drinking has become imperative through computation of different quality parameters (reported above). Considering EC and RSC values of groundwater as criteria for checking its suitability for irrigation, about 95.6% water was found unfit in Muktsar district followed by Mansa (73.0%) and Bathinda (66.9%) (Table 12.3) (Chopra and Krishan, 2014). The EC and RSC values of groundwater of the districts viz. Bathinda, Faridkot, Mansa and Muktsar were recorded to be more than 4000.0 $\mu\text{mho}/\text{cm}$ and 5.0 meq/L respectively. Out of the total area of Punjab, the groundwater in 24.8% area was not found suitable for irrigation, 21.9% as marginally fit and 53.3% as fit for irrigation. However, the groundwater in Hoshiarpur district was 100.0% groundwater fit for irrigation followed by Gurdaspur (99.6%), Nawan Shahr (98.0%) and Ropar (92.1%). For Amritsar,

Table 12.3. District-wise categorization of groundwater quality for irrigation (45-60 m depth).

District	Area (km ²)	Fit (%)	Marginal (%)	Unfit (%)
Amritsar	2647	78.8	21.2	0.0
Barnala	1410	27.7	51.1	21.3
Bathinda	3385	2.5	30.6	66.9
Faridkot	1469	2.9	37.7	59.4
Fatehgarh Sahib	1180	73.9	26.1	0.0
Ferozepur	5303	27.2	24.4	48.3
Gurdaspur	3564	99.6	0.4	0.0
Hosiapur	3365	100.0	0.0	0.0
Jalandhar	2632	88.6	10.5	0.9
Kapurthala	1632	83.1	12.3	4.6
Ludhiana	3767	88.7	10.6	0.7
Mansa	2171	4.1	23.0	73.0
Moga	2216	30.0	46.3	23.7
Muktsar	2615	0.0	4.4	95.6
Nawan Shahr	1267	98.0	2.0	0.0
Patiala	3218	64.1	27.3	8.5
Ropar	1369	92.8	7.2	0.0
Sangrur	3610	33.1	40.3	26.6
SAS Nagar Mohali	1093	76.2	23.8	0.0
Tarn Taran	2449	25.8	53.8	20.4
Total area (km²)	50362	26847	11041	12474
EC ($\mu\text{mho}/\text{cm}$)	-	<2000	2000-4000	>4000
RSC (meq/L)	-	<2.5	2.5-5.0	>5.0

Table 12.4. Concentration of heavy metals in drinking water in Malwa region of Indian Punjab.

District	Mean concentration of heavy metal and essential element in drinking water (mg/L)						
	As	Cd	Cr	Fe	Hg	Pb	Zn
Barnala	0.03	0.005	0.00	0.32	0.002	0.02	0.84
Bathinda	1.28	0.013	0.00	0.40	0.200	15.11	0.99
Faridkot	1.35	0.006	1.55	0.15	0.186	14.62	0.52
Ferozpur	1.16	0.005	2.10	1.52	0.170	14.73	0.92
Mansa	2.13	0.005	1.03	0.45	0.003	15.22	1.03
Moga	0.99	0.004	0.52	1.03	0.210	1.07	2.73
Muktsar	1.25	0.004	2.66	0.14	0.200	1.55	5.64
Sangrur	0.03	0.005	0.00	0.31	0.002	0.01	1.17
Average	1.03	0.006	0.98	0.54	0.122	7.79	1.73

Fatehgarh Sahib, Jalandhar, Kapurthala, Ludhiana and SAS Nagar, the groundwater was recorded to be suitable for irrigation (73.9-88.7%). Districts, Tarn Taran and Barnala were found more than 50.0% in marginally fit category. Keeping EC and RSC as quality criteria, groundwater was found fit in 53% and marginal to fit in 47% (Chopra and Krishan, 2014).

Water pollution through heavy metals and trace elements

There are several heavy metals or trace elements responsible for inorganic chemical hazard in water (Jarup, 2003). Among those, Pb, Cr, As, Cd and Hg are reported to be the key pollutants. Furthermore, the trace elements such as Se (Dhillon and Dhillon, 1991) and radioactive elements such as Rd are also being reported in the groundwater (Virk *et al.*, 2001). The above mentioned heavy metals have been categorised as strong pollutants by the International Agency for Research on Cancer and their presence in water can create many health issues such as intellectual and developmental disabilities (Sarkar, 2002). As per the news by “The Tribune” on 6th February 2018, Indian Punjab accounts for about 88% of the total habitations in the country adversely affected through presence of heavy metals in groundwater (Anon, 2019c). All the samples collected for analysis for Pb concentration in drinking water from districts viz. Muktsar, Faridkot, Ferozpur, Mansa and Moga were found 100% unsafe (Table 12.4) (Sharma and Dutta, 2017). The mean concentration of Pb was recorded to be beyond the permissible limit (≤ 0.01 mg/L) as per BIS standards for all districts in the following order, Mansa > Bathinda > Ferozpur > Faridkot > Muktsar > Barnala > Sangrur. The sample taken for analysis of As in drinking water from districts viz. Bathinda, Muktsar, Faridkot, Ferozpur and Moga were found unsafe beyond 50%. The mean concentration of As was beyond the permissible limit (≤ 0.05 mg/L) as per BIS standards for all districts except Barnala and Sangrur with the following order, Mansa > Faridkot > Bathinda > Muktsar > Ferozpur > Moga > Barnala = Sangrur (Table 12.4).

The samples taken for analysis of Fe in drinking water from Ferozpur district were 100% unsafe followed by Barnala and Sangrur with unsafe concentration of 60% each. The mean concentration of Fe was beyond the permissible limit (≤ 1.0 mg/L) as per BIS standards for Ferozpur and Moga

districts and the concentration of Fe in drinking water was in the following order, Ferozepur > Moga > Mansa > Bathinda > Barnala > Sangrur > Faridkot > Muktsar. The Cd concentration in drinking water for all the districts was also beyond the safe limit (≤ 0.003 mg/L). The drinking water from the districts viz. Bathinda, Barnala and Sangrur were found safe for chromium concentration (Table 12.4). However, the concentration of Cr in drinking water for the districts viz. Muktsar, Faridkot, Ferozepur, Moga and Mansa was reported to be beyond permissible limit (≤ 0.05 mg/L). The concentration of Cr in drinking water samples from different districts was in the following order, Muktsar > Ferozepur > Faridkot > Mansa > Moga > Bathinda > Barnala > Sangrur. The concentration of Hg in drinking water samples from all the districts was recorded to be beyond the permissible limit (≤ 0.001 mg/L) with the following order, Moga > Bathinda > Muktsar > Faridkot > Ferozepur > Mansa > Barnala > Sangrur. The mean concentration of Zn in drinking water samples from all the districts was found within safe limit except for Muktsar and the order was, Muktsar > Moga > Sangrur > Mansa > Bathinda > Ferozepur > Barnala > Faridkot. Groundwater contamination through high levels of uranium (trace element) in south-western Punjab has also been reported in past. The drinking water quality characteristics have been demonstrated in Table 12.7. Contamination of groundwater through presence of arsenic (As) has been reported in Amritsar, Kapurthala and Ropar districts of Indian Punjab. As concentration of more than 10 $\mu\text{g/L}$ has been reported at several locations in Muktsar-Malout belt in south west region of the state (Singh *et al.*, 2015). The mean concentrations of arsenic of 9.37 and 11.01 $\mu\text{g/L}$ were recorded in groundwater during summer and winter season respectively (Kaur *et al.*, 2017).

Groundwater pollution through fluoride and iron

Groundwater (drinking water) pollution through excessive concentrations of fluoride, nitrate and iron has also become a serious challenge in Malwa region particularly in Bathinda, Faridkot and Ferozepur districts. In a study (Sharma *et al.*, 2016), about 95 and 59% samples of groundwater were reported to have nitrate and fluoride content. The maximum concentration of fluoride has been recorded to be 10.6 mg/L at Faridkot. The mean value of fluoride was obtained to be 3.03 mg/L with standard deviation of 10.32. Most recently, 75% groundwater samples in Malwa region (Barnala, Bathinda, Faridkot, Mansa and Muktsar) were found to have fluoride concentration beyond permissible limit (Kaur *et al.*, 2017). The fluoride concentration was found in the range of 1.29-3.74 mg/L and 0.81-2.98 mg/L during summer and winter season respectively with mean values of 2.31 and 1.97 mg/L. Fluoride in groundwater which was beyond the permissible limit (> 1.5 mg/L) (BIS, 1991) causes health hazards of Fluorosis. Likewise, the iron (Fe) concentration in groundwater was recorded to be in the range of 0.009-5.41 mg/L and 0.074 to 7.7 mg/L during summer and winter respectively with mean values of 0.05 and 1.08 mg/L.

Groundwater contamination through use of pesticides and fertilizers

Malwa region is the cotton belt of the state and has the highest pesticide consumption density in

Table 12.5. Cancer cases in Indian Punjab due to pesticide contamination.

District	Number of cancer patients per million population					Cancer deaths in last 5 years (2013)
	2001	2002	2005	2009	2013	
Bathinda	359	353	592	750	1258	2058
Faridkot	261	257	280	446	1346	1112
Mansa	-	-	574	498	1348	1212
Muktsar	246	242	547	751	1363	1791
Patiala	349	336	-	235	868	1498

the country consuming nearly 75% of the total pesticides used in Punjab. This region has been described as India's "cancer capital" due to abnormally high number of cancer cases (Table 12.5) (Mittal *et al.*, 2014), which have increased three folds in the last 10 years (Mittal *et al.*, 2014). Nearly 80% water of Malwa region has been reported as unfit for drinking containing high levels of pesticides, fertilizers (nitrate), magnesium, fluorine, phosphates along with the chemicals such as magnesium and fluoride which were naturally found in groundwater (Anon, 2019d). Two types of bad effects (chronic and acute) are possible on human health due to pesticide exposure (Kumar *et al.*, 2013). Chronic effects of pesticide exposure include reduced attention span, memory disorders, abridged co-ordination, and reproductive problems including miscarriages, birth defects, reduced infant development, depression and cancer. While the acute effects of pesticide exposure include headaches, blurred vision, salivation, diarrhea, vomiting, nausea, wheezing, eye problems, coma, seizure and even death.

The prevalence and symptoms of cancer as well as deaths due to cancer have been reported highest in Malwa (followed by Doaba region) region of Punjab compared to Doaba and Majha regions (Figure 12.3). The key reason for spread of cancer in Indian Punjab is excessive use of pesticides and fertilizers. In India, the largest consumer of pesticides is cotton crop (45%) followed by paddy and wheat. Alachor, Aldicarb, Carbofuran, Chlorpyrifos, Lindane, Malathion and Methoxychlor are the different pesticides used in Punjab. In Indian Punjab, the traces of the banned pesticides viz. BHC, Endosulfan, DDT and HCH have been found in the most safe and sacred mother's milk in many cases. The use of Endosulfan has resulted in increased birth rate of mentally retarded children. Above 20% of Indian food products contain pesticides residues above the tolerance level compared to only 2% globally. Punjab has just 2.5% of total agricultural land in India and consumes nearly 18% of the total pesticides used in the nation (Dutt, 2008). Consumption of pesticides and insecticides (Technical Grade) has augmented from 3200.0 MT in 1980-81 to 6150.0 MT in 2011-12. Industrial waste and sewage waste from urban area are other major factors responsible for cancer in Malwa region of Punjab. The fertilizer consumption particularly nitrogen (N) and P_2O_5 has significantly increased in Punjab compared to the country. Punjab alone uses nearly twice of the fertilizers (N and P_2O_5) used at national level. The total consumption of chemical fertilizers (NPK) has increased from 213 thousand tons (37.5 kg/ha) in 1970-71 to 1936 thousand tons (246.0 kg/ha) in 2011-12. As per GoI (2014), the national fertilizer consumption was 84.54, 33.44 and 10.36 kg respectively for N, P_2O_5 and K_2O in 2012-13.

Whereas, it was 188.47, 58.67 and 3.05 kg respectively for N, P₂O₅ and K₂O in Punjab. In Punjab, N and P₂O₅ applications were nearly 2.3 and 1.8 times of that of India in 2012-13. However, the application of potash was nearly one third of that at national level. Groundwater (drinking water) pollution through excessive concentrations of nitrate has also become a serious challenge in Malwa region particularly in Bathinda, Faridkot and Ferozepur districts. From the water samples taken from wells before monsoon, 32%, 48%, 16%, and 4% presented NO₃-N concentrations of <10, 10-15, 15-20 and >20 mg/L respectively and after monsoon, 16%, 49%, 29%, and 6% respectively (ICAR, 1998). In a study (Sharma *et al.*, 2016), about 95% samples of groundwater were reported to have nitrate content. The maximum concentration of nitrate was recorded to be 90 mg/L at Bathinda. The mean values of nitrate was obtained to be 25.14 with standard deviation 1.317. The extent of prevalence, symptoms and spread of cancer in Punjab due to the above discussed reasons is demonstrated in Figure 12.3 (GoP, 2013).

Problem identification and precautions

- A complete blood analysis can be an appropriate practice for examining the exposure of a spray man to environmental pollutants mainly pesticides and the analysis can be carried out using a Gas Chromatograph Mass Spectrometer (GC-MS) multi residue analytical technique (Hayat *et al.*, 2010).
- Analysis for physical and chemical properties of groundwater samples for pre and post-monsoon seasons can help to assess the suitability of groundwater for drinking and irrigation.

Figure 12.3. Spread of cancer in Indian Punjab.

Following precautions are required to be taken while application of toxic agricultural chemicals:

- Using a proper protecting kit during application of agrochemicals to a crop.
- Regular monitoring of groundwater is essential to avoid environmental threats.

Water treatment and computation of water quality parameters (physio-chemical)

There are three methods of water treatment viz. primary, secondary and complete treatment. The primary treatment includes chlorination, membrane filtration, ozone treatment and ultraviolet treatment. Secondary treatment includes sedimentation and filtration followed by chlorination. There are four types of filtration systems viz. cartridge filtration, multimedia sand filtration, up-flow filtration and rapid sand filtration. The complete treatment comprises of flocculation, coagulation, sedimentation and filtration followed by disinfection. Flocculation and coagulation can help in removing contaminants through addition of lime to make the water slightly alkaline, followed by addition of coagulants like aluminium sulphate (Alum), ferric chloride or ferric sulphate. The precipitate hence formed can be removed through sedimentation and filtration. Further, to reduce the extreme levels of manganese, iron and organic matter, chemical treatment may be required followed by clarification.

The EC value of water can be determined using digital water proof testers or EC meters. SAR, MAR, RSC, SSP, PI and KR can be computed using the formulae listed in Table 12.6 for examining the suitability of groundwater for irrigation (Table 12.6). The pH of drinking water can be measured using digital waterproof pH meters. Similarly, TDS, TH and WQI can be computed using the methods (formulae) listed in Table 12.6. The suitability ranges for all these parameters (EC, MAR, RSC, SSP, PI, KR, TDS, TH and WQI) have been also reported in Table 12.6. The computation methods for other parameters for testing drinking water suitability include Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- , F^- and as CaCO_3 and others including heavy metals or trace elements (Pb, Cr, As, Cd, Hg, Zn, Cu, Co, Ni etc.) have been listed in Table 12.7. Quality characteristics for drinking water (desirable and permissible limits standardised by BIS, WHO and EPA have been presented in Table 12.8. Biological test can be performed by Most Probable Number (MPN) method. The maximum permissible COD level for industrial effluents is 250 mg/L (Singh, 2001). The methods for removal of several contaminants from drinking water are suggested in Table 12.9.

Remedies for controlling water pollution through use of pesticides, fertilizers, industrial wastes and other sources

- Adoption of precision agricultural practices or resource conservation techniques for optimal use of input resources such as fertilizers.
 - * Use of LCC (rice, wheat and maize) recommended by PAU Ludhiana for supplying

Table 12.6. Formulae for computation of different quality indicators of water and their range.

Parameter	Abbreviation	Formula/gadget	Unit of measurement	Suitability of groundwater for drinking/irrigation
Electrical conductivity	EC	Digital waterproof testers of Hanna Instruments	$\mu\text{S}/\text{cm}$	<250 (excellent), 250-750 (good), 750-2000 (permissible), 2000-3000 (doubtful) and >3000 (not suitable) (Sharma <i>et al.</i> , 2016; WHO, 2008)
Sodium absorption ratio	SAR	$\frac{\text{Na}^+}{\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}}$ (Richards, 1954)	-	<10 (excellent for irrigation), 10-18 (good), 18-26 (doubtful) and >26 (not safe) (Richards, 1954; Das and Nag, 2015)
Magnesium ratio	MR	$\frac{\text{Mg}^{2+} \times 100}{(\text{Ca}^{2+} + \text{Mg}^{2+})}$ (Paliwal, 1972)	-	<50 (suitable for irrigation) >50 (not suitable for irrigation)
Residual sodium carbonate	RSC	$(\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+})$ (Eaton, 1950; Raghunath, 1987)	mg/L	<1.25 (suitable), 1.25-2.5 (marginally suitable) and >2.5 (not suitable for irrigation) (Lloyd and Heathcote, 1985)
Soluble sodium percentage	SSP	$\frac{(\text{Na}^+ + \text{K}^+) \times 100}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+}$ (Raghunath, 1987; Wilcox, 1948)	-	<20 (excellent for irrigation), 20-40 (good), 40-60 (permissible), 60-80 (doubtful) and >80 (not safe)
Permeability index	PI	$\left(\frac{\text{Na}^+ + \sqrt{\text{ECO}_3}}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+} \right) \times 100$ (Doneen, 1964)	-	<80 (good), 80-100 (moderate) and 100-120 (poor) (Das and Nag, 2015)
Kelly's Ratio	KR	$\frac{\text{Na}^{2+}}{\text{Ca}^{2+} + \text{Mg}^{2+}}$ (Kelly, 1963)	-	<1 (suitable) and >1 (not suitable) (Das and Nag, 2015)
Total dissolved solids	TDS	Constant factor (CF) $\times$ EC ($\mu\text{S}/\text{cm}$) Where, CF=0.65 (Shakha, 2016) or 0.67 (Sharma <i>et al.</i> , 2016)	mg/L	<500 (desirable), 500-1000 (permissible), 1000-3000 (useful for irrigation) and >3000 (unfit for drinking and irrigation) (Sharma <i>et al.</i> , 2016)
Total hardness	TH	$2.497 \times \text{Ca}^{2+} + 4.115 \times \text{Mg}^{2+}$ (Todd, 1980)	mg/L of CaCO_3	<75 (soft), 75-150 (moderately hard), 150-300 (hard) and >300 (very hard) (Sawyer and McCarty, 1967) OR <60 (soft), 60-120 (moderately hard), 121-180 (hard) and >180 (very hard) (Sharma <i>et al.</i> , 2016)
Water quality index	WQI	$\text{WQI}_i = \sum_{j=1}^n w_j q_j / \sum_{j=1}^n w_j$ $q_j = 100 \times (V_i - V_{id}) / (S_i - V_{id})$ Where, n is number of variables, w_i is the relative weight of i^{th} parameter, q_i is the water quality rating of the i^{th} parameter, V_i , S_i and V_{id} are the observed, standard permissible and ideal value of i^{th} parameter (Horton, 1965; Brown <i>et al.</i> , 1972)	-	0-25 (excellent), 26-50 (good), 51-75 (poor), 76-100 (very poor) and >100 (not fit for drinking) (Brown <i>et al.</i> , 1972; Chatterjee and Raziuddin, 2002)

Table 12.7. *Methods of determination of water quality parameters for drinking water.*

Parameter	Abbrevia- tion	Method (s) for determination	Unit of measure- ment
Aluminium	Al	Graphite Furnace Atomic Absorption Spectrometry	mg/L
Anionic deter- gents	MBAS	Spectrophotometric Method or Crystal Violet Method	mg/L
Arsenic	As	Graphite Furnace Atomic Absorption Spectrometry	mg/L
Boron	B	Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Spectrophotometric Method	mg/L
Cadmium	Cd	Graphite Furnace Atomic Absorption Spectrometry	mg/L
Calcium	Ca	Titrimetry (EDTA as titrant and murexide as indicator)	mg/L
Chlorides	Cl ⁻	Titrimetry (AgNO ₃ with Potassium Chromate as indicator)	mg/L
Chromium	Cr ⁶⁺	Gas Chromatography, Polarography and Spectrophotometry	mg/L
Copper	Cu	Atomic absorption spectroscopy or spectrophotometry	mg/L
Cyanide	CN	Ion Chromatography Method with Pulsed Amperometric De- tection , GC/MS Headspace Analysis	mg/L
Fluoride	F	Spectrophotometer (SPADNS reagent)	mg/L
Iron	Fe	Spectrophotometric Method or Atomic Absorption Spectrome- try	mg/L
Lead	Pb	Graphite Furnace Atomic Absorption Spectrometry	mg/L
Magnesium	Mg	Titrimetry (EDTA as titrant and erichrome black T as indica- tor)	mg/L
Manganese	Mn	Extraction-photometric methods	mg/L
Mercury	Hg	Cold Vapor Atomic Absorption Spectrometry,	mg/L
Mineral Oil		Gas-chromatographic analysis	mg/L
Nitrate	NO ₃ ⁻	Spectrophotometer (Phenol disulphonic acid)	mg/L
Pesticides		Solid Phase Extraction and Capillary Column GAS Chroma- tography/Mass Spectrometry	mg/L
Phenolic Compounds	C ₆ H ₅ OH	Alternating-Current Oscillopolarographic Titration, Solid Phase Extraction and Capillary Column GAS Chromatog- raphy/Mass Spectrometry	mg/L
Potassium	K	Flame Photometer	mg/L
Residual, free chlorine		Iodometric Back Titrations, Amperometric Direct and Back Titrations, DPD Titration, DPD Colorimetric Method and Ori- on 97-70 Chlorine Specific Ion Electrode Method	mg/L
Selenium	Se	Atomic Absorption Spectrometry with Hydride Generation	mg/L
Sodium	Na	Flame Photometer	mg/L
Sulfate	SO ₄ ⁻	Turbidimetric Method	mg/L
Turbidity	Turb	Nephelometer	NTU
Zinc	Zn	Atomic Absorption Spectrometry	mg/L

Table 12.8. Drinking water quality criteria (desirable and permissible limits) by different international standards.

Substance or Characteristic	BIS (1991)		EPA (2018)		WHO (1971)	
	Desirable (mg/L)	Permissible (mg/L)	Desirable (mg/L)	Permissible (mg/L)	Desirable (mg/L)	Permissible (mg/L)
Alkalinity	200	600	xxx	xxx	xxx	xxx
Aluminium (Al)	0.03	0.2	0.05	0.2	xxx	xxx
Anionic detergents (MBAS)	0.2	1	xxx	xxx	0.2	1
Arsenic (As)	0.01	xx	0.01	xx	0.05	xx
Boron (B)	1	5	3	6	xxx	xxx
Cadmium (Cd)	0.01	xx	0.005	xx	0.01	xx
Calcium (Ca)	75	200	xxx	xxx	75	200
Chlorides (Cl)	250	1000	250	xxx	200	600
Chromium (Cr ⁶⁺)	0.05	xx	0.1	xx	xxx	xxx
Copper (Cu)	0.05	1.5	1	xxx	0.05	1.5
Cyanide (CN)	0.05	xx	0.2	xx	0.05	xx
Dissolved solids	500	2000	500	2000	500	1500
Fluoride (F)	1	1.5	2		0.6	1.7
Iron (Fe)	0.3	1	0.3	xxx	0.1	1
Lead (Pb)	0.05	xx	0.015	xx	0.1	xx
Magnesium (Mg)	30	100	xxx	xxx	30	150
Manganese (Mn)	0.1	0.3	0.05	xxx	0.05	0.5
Mercury (Hg)	0.001	xx	0.002	xx	0.001	xx
Mineral Oil	0.01	0.03	xxx	xxx	0.01	0.3
Nitrate (NO ₃)	45	xx	10	xx	xxx	xxx
Pesticides	x	0.001	xxx	xxx	xxx	xxx
pH	6.5-8.5	xx	6.5-8.5	xx	7.0-8.5	6.5-9.2
Phenolic Compounds (C ₆ H ₅ OH)	0.001	0.002	0.001	0.002	0.001	0.002
Residual free chlorine	0.2	xxx	3	3.5	0.1	xxx
Selenium (Se)	0.01	xx	0.05	xx	0.01	xx
Sulfate (SO ₄)	200	400	250	xxx	200	400
Total Hardness (CaCO ₃)	300	600	-	xxx	100	500
Turbidity (NTU)	5	10	5	10	5	25
Zinc (Zn)	5	15	5	15	5	15

required quantity of nitrogen to be applied in crops at right time to get the maximum productivity (Kumar *et al.*, 2018).

- * Use of sensors to determine fertilizer requirement by observing and recording various indices for different crops and taking soil samples.
- * Example: Using a tractor mounted N-sensor (Yara International make) to predict nitrogen (N) requirement for wheat.
- Efficient use of agro-chemicals such as pesticides (insecticides, nematicides and fungicides etc.)

Table 12.9. Methods (or remedial measures) for removal of contaminants from drinking water.

Parameter	Source	Method/technique for removal of contaminant
Aluminum (Al^{+3}) Low water solubility 0.1-9.0 ppm (natural water) Desirable: 0.05-0.2 mg/L (US EPA)	Earth's surface Use of aluminum sulfate (alum) as a coagulant in water treatment plants	Reverse Osmosis (removal by more than 98%) Distillation (removal more than 99%) Electro-dialysis
Arsenic (As) Difficult to dissolve in water Classified as a carcinogen (US EPA) Desirable: ≤ 0.05 mg/L	Mining or metallurgical operations Runoff from agricultural	Reverse osmosis (removal rate up to 90%) Activated alumina Ion/anion exchange (removal rate of 90-100%) Activated carbon (removal rate of 40 - 70%) Distillation (removal rate of 98%)
Barium (Ba^{+2}) Desirable: ≤ 2.0 mg/L	Surface and ground waters Oil and gas drilling muds, waste from coal-fired power plants, automotive paints and jet fuels	Sodium form cation exchange units (softeners) Reverse Osmosis Electro-dialysis
Bromine or bromide (Br) Widely used in pharmaceutical industry. Used to disinfect swimming pools and cooling towers Desirable: ≤ 0.05 mg/L	Found in seawater and exists as the bromide ion (65 mg/l) Occurs normally in blood (1.5 to 50 mg/l)	Reverse Osmosis (removal rate of 93-96%) Activated Carbon Ultrafiltration or Electro-dialysis
Cadmium (Cd) Desirable: ≤ 0.005 mg/L (US EPA)	Found in zinc as an impurity Found in by-products from mining, electroplating, pigment, smelting and plasticizer production	Sodium form cation exchange units (softeners) Reverse Osmosis (removal rate of 95-98%) Electro-dialysis
Calcium (Ca^{+2}) It is the major component of hardness in water (5-500 mg/L as $CaCO_3$)	Derived from rocks, but mainly found in limestone and gypsum	Sodium form cation exchange (softener) Reverse Osmosis (removal rate of 95-98%) Electro-dialysis Ultrafiltration Using hydrogen form cation exchanger
Chloride (Cl^-) Chloride content in water ranges from 10 to 100 mg/L Desirable: ≤ 250 mg/l (US EPA)	Major anions found in water (combined with calcium, magnesium and sodium)	Reverse Osmosis (removal rate of 90 - 95%) Electro-dialysis Distillation Strong base anion exchanger
Chromium (trivalent: Cr^{+3} / hexavalent: Cr^{+6}) Cr^{+3} (slightly soluble in water) is essential for efficient lipid, glucose and protein metabolism in living beings Cr^{+6} is considered toxic Desirable: ≤ 0.005 mg/L (US EPA)	Found in drinking water entered from industrial waste contaminants	Cr^{+3} : strong acid cation resin regenerated with hydrochloric acid Cr^{+6} : strong base anion exchanger regenerated with caustic soda (sodium hydroxide) NaOH Reverse osmosis (removal rate 90-97%) Distillation

Table 9. Continued...

Copper ($\text{Cu}^+/\text{Cu}^{+2}$) Its range for drinking water is 2-5 mg/l Desirable: ≤ 1.3 mg/L (US EPA)	Derived from rock weathering Corrosion of copper and brass piping and addition of copper salts for algal control	Sodium form strong acid cation resin (softener) Reverse osmosis (removal rate of 97-98%) Activated carbon filtration
Cyanide (CN^-)	Normally found in waste water from metal finishing operations	Chlorine feed, retention and filtration
Fluoride (F^-) Desirable: ≤ 4 mg/L (US EPA)	Waste water from the manufacture of glass and steel Foundry operations	Reverse osmosis (removal rate of 90-95%) By anion exchange Activated carbon Reverse osmosis (removal rate of 93-95%)
Iron ($\text{Fe}^{+2}/\text{Fe}^{+3}$)	Occurs naturally in ground waters as: Ferrous Iron i.e. clear water iron Ferric Iron i.e. red water iron Heme Iron i.e. organic iron	Ferrous Iron : using a softener (provided it is <0.5 ppm and the pH of the water >6.8) If the ferrous iron >5.0 ppm, it must be converted to ferric iron before its removal by mechanical filtration Heme iron: using an organic scavenger anion resin or by oxidation with chlorine followed by mechanical filtration
Lead (Pb^{+2}) Desirable: ≤ 0.05 mg/L	Metallurgical wastes or from lead-containing industrial poisons Primarily from the corrosion of the lead solder used to put the copper piping together	Water softener Activated carbon filtration Reverse osmosis (removal rate of 94-98%) Distillation
Magnesium (Mg^{+2})	Found in minerals including dolomite, magnesite and clay In sea water (five times the amount of calcium)	Using a softener or purification exchanger in hydrogen form (to <1 mg/l) Ion exchange (sodium form cation-softener) Chemical oxidation-retention-filtration
Manganese ($\text{Mg}^{+2}/\text{Mn}^{+3}$) Found in groundwater (2-3 mg/L) Desirable: ≤ 0.05 mg/L	Found in soils Sediments Rocks	
Mercury (Hg^{+2}) Desirable: ≤ 0.002 mg/L	Occurs as an inorganic salt or an organic compound (methyl mercury)	Activated carbon filtration Reverse osmosis (removal rate of 95-97%)
Nickel ($\text{Ni}^{+2}/\text{Ni}^{+3}$)	Exists in almost 85% of the water supplies (about 1 ppb)	By a strong acid cation exchanger Activated-carbon filtration Reverse osmosis (removal rate of 97-98%)
Nitrate (NO_3^-) Desirable: ≤ 10 mg/L (US EPA)	Comes into water supplies through the nitrogen cycle It is one of the major ions in natural waters Septic systems, feed lots and agricultural fertilizers	Reverse osmosis (92-95%) Anion exchange resin Distillation
Pesticides Pesticides are common synthetic organic chemicals (SOCs)	Water supplies (surface and groundwater) from the runoff in agricultural areas	Activated carbon filtration Ultrafiltration Reverse osmosis (removal rate 97-99%)

Table 9. Continued...

Potassium (K ⁺)	-	A cation exchange resin (softener)
Radium (Rn)	Pitchblende and other uranium minerals	Reverse osmosis (removal rate of 94-97%)
Used in the treatment of cancer and some skin diseases	Naturally or man-made processes	By sodium for cation exchange resin (softener)
Desirable: ≤5 pCi/L (US EPA)		Reverse osmosis (removal rate of 95-98%)
Radon (Rn)	Formed through atomic disintegration of radium	By aeration
Desirable: ≤15 pCi/L (US EPA)	Radionuclide (e.g. Radon 222) is of most concern	Carbon filtration
Selenium (Se ⁻)	Found in drinking water and comes from natural minerals	Anion exchange (removal rate of 60-95%)
Desirable: ≤0.05 mg/L	Copper mining or smelting	Reverse osmosis
Silica (SiO ₂)	It is an oxide of silicon present in almost all minerals	Anion exchange portion of the demineralization process
Found in surface and groundwater (1-100 mg/L)		Reverse osmosis (removal rate of 85-90%)
Silver (Ag ⁺)	Found in natural and finished water supplies	Distillation (removal rate of 98%)
Desirable: ≤0.1 mg/L (US EPA)		Activated carbon filtration (removal rate of 60%)
		Cation/anion exchange (removal rate of 90%)
		Reverse osmosis (removal rate of up to 90%)
Sodium (Na ⁺)	All water supplies contain some sodium depending on local soil conditions	Hydrogen form cation exchanger
Desirable: ≤20 mg/L (US EPA)	Corrosive nature of water increases with sodium content	Reverse osmosis (removal rate of 94-98%)
Sulfate (SO ₄ ²⁻)	Occurs in almost all natural water	Distillation
Desirable: ≤250 mg/L (US EPA)	Mostly originate from the oxidation of sulfite ores, the presence of shales and existence of industrial wastes	Reverse osmosis (removal rate of 97-98%)
Total Dissolved Solids (TDS)	Total Dissolved Solids (TDS) consist mainly of carbonates, bicarbonates, iron, chlorides, sulfates, nitrates, phosphates, calcium, magnesium, potassium, sodium, manganese, etc.	Using a strong base anion exchanger
Desirable: ≤500 mg/L (US EPA)	Naturally occurring radionuclide	Reverse osmosis
Uranium (U)		Electro-dialysis
Desirable: ≤15 pCi/L (US EPA)		Reverse osmosis (removal rate of 95-98%)
pCi/L stands for picoCuries per liter		Ultrafiltration
		Activated alumina

Significant information has been taken from <https://www.aquapurefilters.com/contaminants/150/>

Figure 12.4. Acts and rules for monitoring use of pesticides in India.

- Promotion of organic manures with a significant reduction on use of artificial chemical fertilizers.
- Promotion of soilless cultivation practices (substrate culture cultivation, hydroponics and aeroponics etc.) particularly in vegetable crops (e.g. tomato, capsicum, cucumber, etc.) and fruit crops (e.g. strawberry). This technology can help to reduce the water pollution through controlled (re-circulation of nutrient solution) and reduced use of fertilizers (no wastage) along with saving in water use and improved crop yields (Singh *et al.*, 2018a, Singh *et al.*, 2018b; Singh *et al.*, 2019a; Singh *et al.*, 2019b).
- The chemical pesticides can be replaced with the following practices to control pollution:
 - * IPM: Mechanical and biological control with greater emphasis on use of crop rotation, bio-pesticides and pesticides for plant origin like neem formulation.
 - * Bio pesticides: The pesticides derived naturally from the waste materials from animals, plants, bacteria and minerals. It includes neem and the plant based formulations alike Indene, Repline, Neemmark and Guava family.
 - * Organic farming: It is dependent upon crop rotation, animal manures, crop residues, off-farm organic wastes, mineral grade rock additives and biological system of nutrients mobilization and plant protection.
 - * Crop diversification: Shifting from one particular cropping system to a diverse and multi cropping system to stabilize farm income in order to protect the natural resources.
- Use of class-I pesticides (as classified by WHO and other agencies) which are found highly

dangerous to human health should be banned with immediate effect.

- Active participation of the ministries through different mediating agencies or Acts (e.g. MoWR, MoEF, CGWA, CGWB, EPA Act 1986 and PPSW Act, 2009) is highly needed at present to protect the water resources (surface and groundwater) both in terms of quality and quantity through developing operational policy guidelines not as usual. The various acts and rules for regulating the use of pesticides in India are listed in Figure 12.4. The full names of above abbreviations are given in Table 12.1.
 - * On 10th December 1996, Supreme Court of India directed the Union MoEF to authorize the CGWB under the EPA Act, 1986, against overexploitation of ground-water resources of the country through formation of the CGWA. However, not much success was achieved in managing the further over-exploitation of ground-water resources and quality.
 - * Recently in February 2018, in order to stop the continued pesticide pollution in drinking water and food, the department of Agriculture, Punjab Government has banned the sale of 20 pesticides (insecticides) including Endosulfan based on the recommendations of Registration Committee, PAU and PSFC. The banned insecticides included Benfuracarb, Bifenthrin, Chlorfenapyr, Carbosulfan, Dicofof, Endosulfan, Ethofenprox, Trichlorofon, Methomyl, Phosphamidon, Thiophanate Methyl, Phorate, Triazophos, Dazomet, Diflubenzuron, Fenitrothion, Metaldehyde, Kasugamycin, Alachor and Monocrotophos (Anon, 2019e). Among these pesticides, Methomyl, Monocrotophos, Phosphamidion, Phorate, Triazophos are considered in class I by World Health Organization (WHO).
- Every individual should be encouraged to save water and retain its quality through proper waste (domestic, agricultural and industrial) management for sustainable quality food production and mankind. The community participation can play a great role in making the public aware of the current situation of depleting and polluting water resources of the state and their bad outcomes which may make the future darker.

Conclusion

The establishment or socioeconomic development of a stable community is highly dependent on the availability of safe and reliable fresh water resources such as groundwater. However, the quality of groundwater is extremely dependent on several anthropogenic factors (direct and indirect) that origin the pollution. The urban runoff, agricultural fertilizers including agro-chemicals (e.g. pesticides) and leaching from polluted industrial discharge and sewage disposal (containing heavy metals) sites have been identified to be the main causes of groundwater pollution in the state. The deadly illness to people of Malwa region due to pesticide contamination through direct contact with pesticide or drinking groundwater (80% contamination) has become a serious challenge for the modern and future Indian Punjab. The

drinking water of this particular region contains high levels of pesticides, nitrate, magnesium, fluoride, iron, phosphates. The long-term excessive use of pesticides seems to be a main origin for prevalence of different deadly diseases in Malwa region of Punjab (cotton belt). Thus, to prevent the further health hazards to the people of the region through chemical contamination, there is a need to review and fortify the community programs for safe use of the chemicals through improved pesticide policies. Due to ineffectiveness of pollution control authorities in dealing with the groundwater crisis; it has become very important to involve the local people and society to evaluate the pollution status of groundwater. Thus, for improved and safe water supply, effective public policies, plans and technologies should be implemented in addition to political, socio-economic and other factors. Furthermore, the diminishing groundwater level in central zone and increasing water table in south-western zone may lead to gradient of flow from south-western to central zone thereby polluting the precious fresh water resource of central Indian Punjab in near future. It is obvious that there is a lack of proper monitoring of water quality and utilization of groundwater resources of the state. Thus, there arises a need for timely understanding and identification of sources of pollution and detection of contaminants associated with water (surface and groundwater) through appropriate measures such as complete blood analysis, physical and chemical analysis of water separately for pre and post-monsoon seasonal basis.

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Chapter 13

Toxicity induced alterations as biomarker of environmental pollution

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Abstract

Over the past few decades dye contamination of aquatic systems has attracted the attention of several investigators both in the developed and developing countries of the world. A large quantity of these dyes enters aquatic bodies from time to time because a substantial amount of a dye (10-15% unbound dyes) is lost in the effluent during dyeing processes. In return the aquatic bodies end up being the final destination of a large quantity of wastes from these sectors. Waste waters from dye manufacturing, paper, leather and textile industries bring tons of dyes into the aquifers, most of which are highly toxic to the flora and fauna of the receiving water bodies. Scanning electron microscopic observations were made for the changes in the surface ultra morphology of gills of *Cirrhinus mrigala* on exposure to lethal (0.1, 0.2, 0.4, 0.6 and 0.8 mg/L dye) doses of Basic Violet-1 (an important textile and hair colorant; CI: 42535, Trade name- Methyl Violet-2B). Present study was taken up as insufficient data exist regarding safety of this dye. The dye was observed to be cytotoxic in nature during the acute (96h) exposure to lethal doses. The dye caused reduction or complete loss of microridges, increase in mucous openings and

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degeneration of gill lamellae and rakers. Therefore, time to time monitoring of ultra morphology of tissues will provide us early indicators for the stress of very low levels of pollutants which may later cause mortality of the fish. The study holds importance because fishes are an important link in the food chain of man, respond to toxicants in a manner similar to higher vertebrates causing serious diseases.

Keywords: Acute exposure, *Cirrhinus mrigala*, Gills, Scanning electron microscopy, Ultra morphology

Introduction

Aquatic ecosystems are of extreme importance for the world population, as these are used for domestic, agricultural, industrial as well as recreational activities. In return the aquatic bodies end up being the final destination of a large quantity of wastes from these sectors. Waste waters from dye manufacturing, paper, leather and textile industries bring tons of dyes into the aquifers, most of which are highly toxic to the flora and fauna of the receiving water bodies (McCarthy, 1997). Uncontrolled discharge of dyes in water bodies causes serious problems due to change in colour of the water and production of even more toxic by-products after reduction in light (Chung, 1983). As a result, various dyes are banned and maximum residue levels exist in Europe and USA, however, in several other countries of the world, these dyes are openly sold in the market without any information regarding their chemical nature, purity, toxicity and possible mutagenicity (Mathur *et al.*, 2005). Unregulated use of dyes will therefore have grave consequences for human health and aquatic ecosystems in these countries. The aquatic environment is of primary concern because many a times these various toxic chemicals not only have significant implications for long-term survival of natural populations of the organisms living therein but cause heritable mutations that may lead to loss of the total genetic diversity of an ecosystem.

Many industries releasing industrial wastes and effluents contain various levels of organic and inorganic pollutants including acids, alkalis, inorganic ions, heavy metals etc. are one of the major sources of environmental pollutants in India. They discharge their effluents directly or indirectly into rivers and agricultural land used to irrigate agricultural fields, make the water and soil polluted, which is not good for agricultural purposes (Samanta *et al.*, 2018). The industries utilize many poisonous substances, which are very harmful to the plants and soil microorganism. The river water polluted with industrial effluent contains various toxic chemicals, dyes and heavy metals such as mercury (Hg), Cadmium (Cd), Chromium (Cr) and Zinc (Zn). When the effluent is used for irrigation, these metals are strongly bound to polypeptide and proteins of aquatic plants and animals. Of all the aquatic organisms fish have become vulnerable indicators for evaluation of the effects of such noxious compounds (Khidr and Mekkawy, 2008; Kaur and Dua, 2015) as these are the ultimate sufferers of pollution and form an important link in the food chain of humans.

By virtue of their high reactivity, dyes and other genotoxins contribute to structural modifications in the DNA of fish which then become the underlying cause of metabolic dysfunction and death. These disturbances being irreversible are transmitted to the future generations, have long lasting effects and appear even at those levels of toxins which are otherwise safe for survival.

Although light microscopic studies provide good information about stress induced alterations in the cell morphology under stress but for obtaining finer and early details of the underlying causes of the death, electron microscopic technique-Scanning electron microscopic (SEM) studies for detailed information about the surface morphological variations in gills is preferred. Use of electron microscopy in relation to pollution and environmental conditions is a recent approach and is considered a very useful tool as it adds a valuable third dimension for understanding the structural deformations as well as for obtaining information much before fish exhibit many other visible symptoms of toxicity (Hidayati *et al.*, 2013). Therefore, in the present study electron microscopy (SEM) has been used collectively for evaluating toxicity of Basic Violet-1 (a triphenylmethane dye) because toxicity data for this dye is not available (Diamante *et al.*, 2009). Dyes with triphenylmethane pharmacophore (Basic Violet-1, Gentian Violet, Crystal Violet) have a long history of human use (Souza Pietra *et al.*, 2013) but these interact with lipid bilayers of the cellular membrane and perturb membrane structure as well as ionic balance of the cell (Dell Antoneet *et al.*, 1972; Aljofan *et al.*, 2009). In living systems these are biotransformed to demethylated derivatives which react with DNA and lead to tumour development (Culp *et al.*, 2006). Present work envisages evaluation of toxic potential of Basic Violet-1 (BV-1, CI:42535: Trade name- Methyl Violet-2B) which is commonly used as a direct synthetic (non oxidative dye) fibre/textile dye and a hair colorant (Diamante *et al.*, 2009). *Cirrhinus mrigala*, an Indian Major Carp, abundantly present in fresh waters of India has been selected as a test model for this study to detect most prominent changes in the epithelial cells and morphology of the gills that can act as a biomarker for the stress of very low doses of such dyes. Predominantly, the gills constitute a multifunctional organ (respiration, acid base regulation, ion regulation, nitrogenous waste excretion) accounting for well over fifty per cent of the total surface area of the animal. They are the major site of uptake for most water borne toxicants and site of toxic impact for many of them. (Ale *et al.*, 2018).

The main aim was to assess the suitability of ultramorphological changes in the pavement cells, chloride cells, and mucous openings in the gill as early indicators of the dose dependent stress of Basic Violet-1. This research work has been envisaged as insufficient data exist to support the safety for this dye (Diamante *et al.* 2009).

Materials and methods

Experimental model

For the present study *C. mrigala* was selected as a model for evaluating acute toxicity of a dye, BV-1.

Procurement and acclimation of fish: Fish weighing 22 ± 1.25 g and measuring 10.50 ± 1.22 cm were procured from the Government Fish Farm, Rajasansi, Amritsar, Punjab, India. The fish were given a bath in 0.1% KMnO_4 for 2-3 minutes for disinfection, diseased fish were sorted and not subjected to experimentation. Fish were acclimated for 21 days under laboratory conditions and fed with a pelleted commercial Toya feed on alternate days @ 2% of the biomass.

Toxicant used: BV-1 (CI: 42535), purchased from the local market, Amritsar, India was used for the present study. The commercial grade preparation was a green coloured powder soluble in water.

Test containers: Toxicity tests were conducted in plastic pools of 200 L capacity.

Dilution water and control: Dechlorinated tap water was used as control and for making various concentrations of the dye.

Exposure period and observations

Acute exposure: Ten fish were exposed in triplicate to 0, 0.10, 0.20, 0.40, 0.60, 0.80 and 1.0 mg/L dye. Semi static daily renewal 96h bioassay was conducted according to OECD guidelines (1992) and APHA (1998). No food was given 24h prior to the exposure during the bioassay. Mortality was recorded at 24h intervals and dead fish were removed immediately to avoid asphyxiation of other fish. A fish was considered dead when no opercula movement was there and it did not move on prodding with a glass rod.

Observations: Observations were recorded at the beginning and at the end of the acute exposure for ultra morphological changes (scanning electron microscopic studies on gill) in the fish during the study.

Gill: Second and third gill arch from the right side were immediately excised and fixed in the Karnovsky's fixative for 6-12h. Post fixation was done in 1% Osmium tetroxide for 2h at 4°C . Three washings were given in 0.1M phosphate buffer (pH 7.4), and dehydration of the sample was carried for 15 min each in 30, 50, 70, 90 and 100% anhydrous alcohol. The dehydrated tissue was critical-point dried and placed over the silver tape attached to the aluminium stub.

Coating and viewing: Gold coating of the samples was done with a sputter coater [Model: Q150RES (QUORUM)] for viewing under Carl Zeiss EVO | LS 10, Scanning electron microscope at The Central Instrumentation Facility, Guru Nanak Dev University, Amritsar and Carl Zeiss EVO | MA 10 at The Indian Agricultural Research Institute, New Delhi at low acceleration voltage of 10-20 kV. Till the time of viewing, the stubs were kept in a desiccator.

Results and discussion

For evaluating toxicity of Basic Violet-1, fingerlings of *C. mrigala* were given acute (96h) exposures to BV-1. Data were recorded for ultra structural changes in the gills of fish during the exposure period. *C. mrigala* has four pairs of lateral gills which are reddish in colour and protected by an operculum. Each gill arch bears two rows of primary filaments upon which are situated two rows

of secondary lamellae. Gill filaments, lamellae and rakers were found to be lined by pavement cells (simple squamous epithelial cells) which were polygonal or hexagonal in shape. A single or double ridged border (Micro border) was seen between pavement cells or pavement cell and chloride cell junction. The dye induced changes in the morphology of filaments, lamellae as well as rakers of the gill. Two rows of stiff denticular gill rakers are present on the other side of gill arch. The microvilli or micro ridges overlying the pavement cells of the gill arch, primary filament and secondary lamella showed considerable disorganization with respect to their size and shape in the dye exposed fish.

On exposure to different concentrations of the dye, there was no change in gill morphology of control (after 96h) and 0.10 mg/L dye exposed fish (after the acute exposure) in the present study (Figure 13.1a-b). No change was observed in the gillrakers of control and 0.10 mg/L dye exposed fish as they were spaced equally (Figure 13.1c) while a dose dependent increase was observed during the acute exposure. Microridges of pavement cells of primary and secondary gill lamellae of control and 0.10 mg/L dye exposed fish were observed to be shorter, interwoven and random-

Figure 13.1. Gills of control *C. mrigala* after 96h exposure (a-e); Pf – Primary gill filament, Sl- Secondary lamellae, GR- Gill rakers, Es- Equally spaced, PVC- Pavement cells, Mr- Microridges, Mb- Microborder, CC- Chloride cells, MV- Microvilli.

ly oriented at the beginning as well as at the end of exposure as well as microvilli of chloride cells were observed to be normal (Figure 13.1d-e).

There was a dose dependent loss of secondary lamellae and collapse of structural integrity of the epithelial cells after 96h exposure. On exposure to 0.20 and 0.40 mg/L dye, fusion of secondary lamellae (Figure 13.2a) initiated while in 0.60 mg/L dye, mucous cell openings and sloughing of the epithelium of primary gill filaments at tips was also observed at some places (Figure 13.2b-c). In 0.80 mg/L dye, mucous cell openings, necrosis and degeneration of epithelium on the secondary gill lamellae were noticed all over the gill surface (Figure 13.2d).

Alteration in the shape of the microridges started appearing in 0.20 and 0.40 mg/L dye and became more pronounced with the increase in dose (Figure 13.3a). Mucous cell openings and gall like structures were noticed in some of the pavement cells on exposure to 0.60 mg/L dye which increased further in 0.80 mg/L dye and were accompanied with degeneration of microridges of the whole surface of gill (Figure 13.3a-b). Slight changes were observed in the morphology of gill rakers of fish exposed to 0.20-0.40 mg/L dye but there was a marked change in structural conformity like swelling, erosion and necrosis of the surface of rakers on exposure to 0.60 and 0.80 mg/L dye (Figure 13.3c). There was no change in the pavement cells of the rakers of 0.20 and 0.40 mg/L dye exposed fish. Fusion of pavement cells, loss of micro ridges was also noticed in 0.60 mg/L dye along with these changes, degeneration of pavement cells, microridges and microvilli of the rakers was common in 0.80 mg/L dye (Figure 13.3d).

Figure 13.2. Gills of dye exposed (0.20-0.80 mg/L dye) *C. mrigala* (a-d); Pf- Primary gill filament, Sl- Secondary lamellae, Lf- Lamellar fusion, Slg- Sloughing, Mo- Mucous opening, Ne- Necrosis.

Figure 13.3. Gills of dye exposed (0.60-0.80 mg/L dye) *C. mrigala* showing degeneration of microridges (Pavement cells) and microvilli (Chloride cells) of lamellae and gill rakers (a-d); Alt. Mr- Alternating microridges, Ga- Gall like appearances, MO- Mucous opening, Disapp. Mr- Disappearance of microridges, Er- Erosion, Ne- Necrosis, Dr- Gill rakers, Red MV- Reduction in Microvilli, De PVC- Degenerating Pavement Cells, Deg. Mr- Degenerating microridges, De. CC- Degenerating Chloride Cells.

In the present study, ultra structural changes were observed in *C. mrigala* after acute (96h) exposure to BV-1. Toxic effects of the present dye on the gill of fish can be divided into two categories: lesions and reactions. Lesions, the direct and deleterious effects including necrosis and rupture of respiratory epithelium (Temminck *et al.*, 1983) were observed to be dose dependent during acute exposure. Lesions due to the present dye may have developed either due to the stress induced autolysis by the cell's own enzymes or due to the direct cytotoxic action of the dye (Mallatt, 1985). Perturbation of membrane structure due to direct binding of the cationic dyes to lipid bilayers has been reported by Zachowski and Durand (1988). The reactions like epithelial lifting, fusion, hypertrophy, hyperplasia, increase in mucous secretion, vascular stasis, mucous cell proliferation, loss of microvilli and chloride cell proliferation (Morgan and Tovell, 1973; Mallatt, 1985; Dutta *et al.*, 1996) are generally considered to be defensive mechanisms for reducing the surface area in contact with the toxins (Dutta *et al.*, 1997) but in the present study these were replaced with lesions with the dose of the dye.

During the acute exposure, reactions were prominent in 0.20 and 0.40 mg/L dye but the incidence of lesions and reactions was equal in 0.60 and 0.80 mg/L dye. As a result, lesions appeared even due to very low doses of the dye with the increasing dose of exposure. Drastic changes like loss of

structural integrity and necrosis hint towards carcinogenic or mutagenic nature of this dye. Several dyes have been reported to be carcinogenic, mutagenic and teratogenic with a potential to cause chromosomal fracture (Khanna and Das, 1991). Being water soluble, the present dye might have been degraded by anaerobic intestinal microorganisms (Chung and Stevens, 1993) and this could have activated a procarcinogen to a mutagen (McCoy *et al.*, 1977). On the other hand, dose dependent increase in extrusion of mucous, epithelial lifting, lamellar fusion and reduction of micro ridges in lower doses of acute (0.20 and 0.40 mg/L dye) exposure can be considered to be defensive reactions of the dye stressed fish. Loss of microridges in fish gills under the stress of toxicants has been observed by many workers (Hart and Oglesby, 1979; Jacobs *et al.*, 1981; Jagoe and Haines, 1983; Roy *et al.*, 1986; Roy and Munshi, 1991). Lamellar swelling, epithelial lifting and reduction of micro ridges in the present fish may have been to reduce the surface area of the gills in contact with the dye so as to sustain the progressive loss of the basic function of the gill (Temmink *et al.*, 1983). This may also have been to increase the barrier distance for diffusion from outside to blood capillaries (Dutta *et al.*, 1992).

Present dye seems to be abrasive in nature as it promoted necrosis, mucous cell openings and copious mucous secretion in a dose dependent manner (Kaur and Jindal, 2016). The dose dependent increase in extrusion of mucus may have been to facilitate respiration in the dye exposed fish as mucous decreases the co-efficient of drag for water flow across the gills, reduces the resistance of gill and plays a role in ion exchange and water balance under stress (Shephard, 1994; Macirella and Brunelli, 2017). However, loss of microridge pattern and copious mucous seems to have reduced the effectiveness of exchange processes, especially gaseous exchange and further stressed the fish and caused mortality. Enormous damage to the epidermis and destruction of cell processes and nerve supply of melanophores due to absorption of Chrome Black T has been reported by Singh (2007) in *Colisa chuna*. Misreplication of dye induced DNA lesions after its N-hydroxylation (Culp *et al.*, 2006) may have resulted in mutations that resulted in appearance of gall like structures in 0.60 mg/L dye after acute exposure to BV-1.

The present dye seems to affect the ionic balance of the fish as it caused erosion of rakers in some doses. Dose dependent increase in the appearance of chloride cells but reduction in their microvilli (the short and stubby microridges) during the acute exposure could also be an effort of the stressed fish for maintaining ionic balance under the influence of this cationic dye as the chloride cells or ionocytes are associated with electrolyte balance of the body. An increase in intracellular concentration of calcium and a large decrease in sodium ion concentration due to loss of cellular membrane integrity under the stress of cationic dyes have been reported by Aljofan *et al.* (2009). Similar changes in chloride cells have been reported by Ghanbousi *et al.* (2012) in *Aphanius dispar* exposed to deltamethrin. However, Wong and Wong (2000) reported augmentation of micro ridges in pavement cells and an increase in the density and apical membrane area of chloride cells of *O. mossambicus* after a short term exposure to cadmium. This highlights the significance of ultrastructural changes in gills over mortality as early indicators of the stress of cationic dyes like BV-1.

Conclusion

The electron microscopic studies in gills will provide us early indicators of the stress of very minute doses of cationic dyes like BV-1. Therefore, time to time monitoring of ultramorphology of tissues will provide us early indicators for the stress of very low levels of pollutants which may later cause mortality of the fish. The results clearly show that BV-1 is mutagenic, carcinogenic as well as cytotoxic in nature and this effect becomes more prominent at 0.80 mg/L dye showing deleterious effects. The toxicants present in the industrial dyes or effluents when come in contact with biological environment may create serious long-term toxicity effect to the living organisms. However, the extent of toxicity depends upon their concentration and duration of exposure to the vulnerable site.

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Author contributions

The study was designed by A Kaur and provided overall supervision and management of the work. K. Kaur performed the experiment and wrote the first draft. Both the authors were involved in interpretation of results, critical evaluation, and approval of the final manuscript.

Conflict of interest

The authors declare that there are no conflicts of interest.

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Chapter 14

Microbial degradation of plastics: Biofilms and degradation pathways

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Abstract

Plastics are recalcitrant polymers released in the environment through unpredicted use leading to accumulation and increased water and soil pollution. Transportation of these recalcitrant polymers in agricultural soil, sediment, and water has been causing concerns for environmentalists. Biofilm community adhered on plastic polymers have a significant contribution in their degradation as they warrant bioavailability of substrates, sharing of metabolites and increased cell viability thereby accelerating biodegradation. Metabolic enzymes of the microbes can be exploited as a potent tool for polymer degradation. However very little or

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no reports are available about the influence of biofilm and plastic degradation and vice versa. The present chapter reports the impact of biofilm microbes in the degradation of commonly used plastics. Furthermore, potent microorganisms and their interactions with the plastic surface has been deciphered, which would serve as a better understanding of the utilization of biofilm-based methods in the development of plastic waste management.

Keywords: Plastics, Biofilm, Degradation, Pathways, Microbes

Introduction

Plastics are being contemplated as one of the most recalcitrant pollutants in the environment (Bonhomme *et al.*, 2004). It comprises around 80% litter in agricultural lands, landfills and water bodies resulting in its accumulation (Rummel *et al.*, 2017; Pathak and Navneet, 2017). About 110,000 and 730,000 tonnes of plastics are transported to agricultural landscapes accounting to a more considerable amount than ocean waters. Plastics produced through household activities get runoff and accumulated in the sludge of WTPs (waste treatment plants). It is then carried to agricultural soils leading to accumulation (Nizetto *et al.*, 2016). Accumulation and adsorption of these recalcitrant polymers lead to the transportation of invasive and harmful species. Furthermore, the hazardous after-effects involve swallowing by animals due to mistaken as food resulting in entanglement (Rios *et al.*, 2007; Yoshida *et al.*, 2016). Therefore, many attempts have been made to reduce plastic wastes. Several physical and chemical degradation methods such as UV treatment, physical stress, oxidants, methanolysis, ammonolysis, hydrolysis, etc. have been developed (Kamini *et al.*, 2001; Gewert *et al.*, 2015). But, these processes usually require elevated temperatures and generally produces toxic substances (Hauenstein *et al.*, 2016).

However, biocatalytic degradation is an eco-friendly process which eliminates the accumulation of harmful metabolic byproducts (Florez *et al.*, 2015). However, the extent of plastic biodegradability confides on their physical and chemical properties (Das and Kumar, 2013). Microbes can degrade ester bonds in the plastics via enzymatic hydrolysis by attaching and colonizing onto the surface (Uchida *et al.*, 2000; Arutchelvi *et al.*, 2008). Consequently, the degradation mechanism must be understood and their products should be identified to ascertain probable environmental hazards.

Moreover, the effect of persistent organic pollutants and additives that adsorb to the plastic surface were also considered (Gewert *et al.*, 2015). However, the chemicals produced by biodegradation of the plastic polymers themselves are not adequately investigated from an environmental aspect. Microorganisms adhered on the plastic surface forms a biofilm which degrades both natural and synthetic polymers (Gu, 2003). Biofilms are functionally, and phylogenetically diverse communities of bacteria, fungi, and algae, conjointly termed as a microbial conglomeration, attached to a surface (Ghosh *et al.*, 2017b). They are mostly embedded in extracellular polymeric substance (EPS) (Ghosh *et al.*, 2016; Ghosh *et al.*, 2019). Biofilm provides

a plethora of benefits for survival and competition strategies, which includes bioavailability of nutrients, horizontal gene transfer, cell viability and prevents toxic shock (Qureshi *et al.*, 2015; Ghosh *et al.*, 2017a). They accelerate plastic surface utilization either as a substrate or support. However, microbes adhered depends on the organism source as well as film conditioning. Any kind of plastic in contact with water is being accessible to sunlight, physical stress, oxidants. They are colonized by microorganisms, may over time influence degradation and weathering (Mincer *et al.*, 2016). However, floating plastic debris undergoes fouling, which diminishes the buoyancy and renders the polymer to sink (Eich *et al.*, 2015). Hence, the biofilm community composition and its activity concerning plastic degradation required to be thoroughly investigated. Although little or no reports are available about the significance of microbial biofilm in plastic degradation. In the present chapter, the available information of the natural and engineered degradation pathways and metabolic products formed during degradation of microplastics which are usually found in agricultural soil and water are reviewed. Degradation products turn out to be low molecular weight oligomers and monomers where new end group formation takes place, i.e., carboxylic acids. We further summarize the influence of the adhered biofilm community in plastic degradation and their interactions, which serves a better understanding of the development of biofilm-based remediation methods in curbing plastic pollution.

Plastic degradation pathways in bacteria

Synthetic polymers serve as nutrient (energy and carbon) source for heterotrophs such as fungi and bacteria in many ways (Dey *et al.*, 2012). Synthetic polymers such as homo or heteropolymer, which may contains same or different kinds of monomers. It includes PET (polyethylene terephthalate), PUR (polyurethane), PS(polystyrene), LDPE/HDPE(Low-density polyethylene, High density polyethylene) are commonly found in agricultural soils as microplastics (Nizetto *et al.*, 2016). When microbes do not get into contact with the plastic, oxygen, and UV-radiation are the most crucial determinants that initiate chain scission in a carbon-carbon backbone. Shorter polymer fragments or oligomers generated during this process are susceptible to get attacked by microbes. Therefore abiotic degradation is preceded over biodegradation (Gewert *et al.*, 2015). The degradation process is achieved by microbes having different bond cleavage and enzymatic activities. Two kinds of enzymes, namely extracellular and intracellular depolymerases are involved. Exo-enzymes produces monomers or short chains which are short enough to penetrate through the cells. It undergoes subsequent chain cleavage to be further metabolized. (Dey *et al.*, 2012). The microbial attack on the polymer surface can be direct or indirect (Shalini and Sasikumar, 2015). In the direct mechanism microbe attacks and degrade the polymer for its nutrition and growth. On the contrary, in the indirect mechanism, the metabolic products produced by microbes degrade or deteriorate the polymer. It occurs in a consecutive manner, where physical and chemical traits of the polymer are altered (biodegradation) followed by enzymatic cleavage (fragmentation), assimilation and mineralization (Singh and Sharma, 2008).

Both aerobic and anaerobic degradation could occur during an indirect mechanism. During aerobic degradation, CO₂ and H₂O are formed, whereas CO₂, CH₄, and H₂O are produced under anaerobic mode (Singh and Sharma, 2008).

Both bacteria and fungi synergistically play an important role in polymer degradation in the natural environment. TCA cycle is employed as the main central metabolic pathway for energy generation from most of the plastic polymers (Upreti and Srivastava, 2003; Ghosh *et al.*, 2017a).

Natural metabolic pathways

Depolymerases are mainly employed in plastic degradation. (Gu, 2003). Extracellular enzymes are secreted by microorganisms which cleaves complex polymers to their corresponding monomers and dimers. They generally undergo hydrolytic cleavage in the periplasmic space or the cell membrane (Koutny *et al.*, 2006). Consequently, short sized oligomers can be transported across the cytoplasmic membrane (Shah *et al.*, 2008). These are further exploited as carbon and energy sources by the intracellular enzymes (Koutny *et al.*, 2006). Oligomers can be directly internalized, presumably with the aid of biosurfactants produced by microbes. Thus, entering beta-oxidation (Kawai *et al.*, 2004; Kawai *et al.*, 2002) or can be further cleaved by abiotic processes before internalization (Albertsson and Banhidi, 1980). Biosurfactants are produced during biofilm formation. Alternatively, these monomers can also undergo sequential degradation into a common metabolite of the TCA cycle and enters into central carbon metabolism (Figure 14.1). Also, Mooney *et al.* (2006) reported the appearance of acetaldehyde, pyruvate, 2-vinylmuconate, and 2-phenyl ethanol, during biodegradation of styrene. These compounds are further metabolized to phenyl-acetyl-CoA and enter into the central carbon metabolism or tricarboxylic acid (TCA) cycle. However, the degree of degradability of PCL is dependent on its degree of crystallinity and molecular weight. The amorphous region was rapidly degraded than the crystalline region by two fungal strains. Also, the participation of several proteases towards plastics biodegradation cannot be ignored, where Williams, 1981 tested the degradation of Poly (L-lactide) PLA using three proteases such as bromelain, pronase and proteinase K. Among these, proteinase K from *Tritirachium album* was proved to be most efficient for cleavage of polymer chains. Proteinase K favored the hydrolysis of an amorphous section of L-PLA and thereby accelerated the degradation rate. But it was decreased in the crystalline region (Chaignon *et al.*, 2007; Gilan and Sivan, 2013). However, some strains possess specific enzymes for a particular polymer. In the case of PET degradation, *Ideonella sakaiensis* secretes PETase. It has a Ser-His-Asp catalytic triad at its active site which could hydrolyze PET to monohydroxyethyl terephthalate (MHET), terephthalate and ethylene glycol which further metabolizes to protocatechuate and beta-oxidation pathway (Joo *et al.*, 2018).

Engineered pathways

During the degradation of homopolymeric plastic materials, one kind of monomer is being produced, which either undergoes beta-oxidation or TCA cycle (Shah *et al.*, 2008; Koutny *et al.*,

2006). When the polymer is comprised of two or more monomer, the degradation becomes difficult. In those cases, a single species could carry out some stages of degradation, but not all. Generally, the complete degradation pathways genes are complemented by engineering different bacterial species.

Additionally, a European website has reported during PET degradation, *E.coli* BL-21 synthesizes LC-cutinase which hydrolyzes the polymer to yield terephthalate and ethylene glycol as two principal monomers, this is the first step in the degradation pathway (iGEM, 2016). Polymers harboring hydrocarbon chains are degraded by polyurethanase alkane monooxygenase cutinase and amylase commonly termed as depolymerases (Seneviratne et al., 2006). A strain derived from *Commamonas testosteroni* degrades terephthalate and terminates in a toxic molecule, protocatechuate. Consequently, *P. putida* utilizes protocatechuate and undergoes central metabolism route by recruiting various dioxygenases to utilize it as a nutrient source (Jimenez et al., 2002).

Figure 14.1. Metabolic pathways for plastic degradation by biofilm forming microbes.

The ethylene glycol is further degraded and mineralized by *E.coli* BL-21 to CO₂ and H₂O. However, in some cases, bacterial strains are genetically modified and complemented with other genes of the pathway to carry out degradation (iGEM, 2016). The polymer can be cleaved outside the cell into its corresponding monomers, or the engineered strain may possess transporters which are coupled with the degradation pathway genes to transport as well as degrade the molecule inside the cell (iGEM, 2016). As in the case of polyurethane (PUR) degradation, polyurethane esterase cleaves PUR polymer into ethylene glycol, which can diffuse across the membrane of the bacterium (Kang *et al.*, 2011). However, *osmY*, encodes osmotic inducible protein Y, that fuses with PUR esterase and exports the fused enzyme outside the cell (Bokinsky *et al.*, 2011; Kang *et al.*, 2011). The engineered strain also contains an operon in a second plasmid composed of glycoaldehyde dehydrogenase (*aldA*) and glycolaldehyde reductase that allows the bacterium to use ethylene glycol as its central metabolite.

Hence complete degradation enzymes are present in a single species (Boronat *et al.*, 1983). It allows the species to be self-sufficient in utilizing PUR as a nutrient source to convert the plastics into bacterial biomass which would, in turn, degrade more PUR. (iGEM, 2012). iGEM teams have designed a bioreactor where they have used *E. coli* engineered construct to degrade PUR. The construct is equipped with PUR esterase transport apparatus and secretion tags. With this apparatus, PUR esterase will be released from the cell. It then attacks the polymer and cleaves the ester bond to release ethylene glycol and sugars. Ethylene glycol will be utilized by a different organism and sugars are subsequently consumed to produce biomass.

Biofilm forming microbes involved in degradation

Microbial communities accumulate on the solid surface thereby forming a biofilm (Zettler *et al.*, 2013). Abiotic degradation allows chain scission to generate oligomers and monomers and their radicals followed by their biodegradation. (Gewert *et al.*, 2015). Although, chemical and physical properties of the polymer, determine the degree of degradation. At the same, the floating plastic gets fouled due to the settling of biomass (Van Sebille *et al.*, 2015). Biofouling involves adsorption, biomass immobilization followed by micro and macrofouling. Bacteria serve as primary colonizers which entraps other organisms such as fungi, diatoms, etc (Selim *et al.*, 2017). Metabolic activity of the attached biomass leads to desorption, adsorption, and fragmentation of polymer chain or degradation of the debris (Harrison *et al.*, 2011). Other factors such as molecular weight, hydrophobicity, temperature chemical structure, elasticity, transition state, etc affect the degradation process (Balasubramanian *et al.*, 2010).

Bacteria

Around 90 microbial genera were reported to degrade plastics (Chee *et al.*, 2010). Microbial community composition varies in regions. Reports on PCL degradation suggests the involvement of *Pseudomonas* and *Rhodococcus* sp along with two fungal strains. Together they have degraded

PCL films up to 53% (w/w) in 30 days of incubation (Urbanek et al., 2017). Hence, *Pseudomonas* and *Rhodococcus* sp are salient bacterial candidate involved in biodegradation. Temperature plays a crucial role in degradation. During the degradation of biodegradable plastics such as PBS, PBSA, PLA and polyhydroxybutyrate (PHB), the microbial activity proceeded at 4°C but no degradation was observed at normal temperatures (Sekiguchi et al., 2011). Microbial genera responsible are *Pseudomonas*, *Tenacibaculum* and *Alcanivorax* sp where *Pseudomonas* spp. strains were active at low temperature (Sekiguchi et al., 2011).

Pseudomonas sp.

Biodegradation depends on the organism type in addition to the nature of pretreatment and polymer characteristics (Shah et al., 2008). In polyethylene degradation, *Pseudomonas* sp formed most viscous and flocculent biofilms on the surface among the other species in three week period. It was assumed that bacteria selectively utilized basal nutrients when they got depleted in the medium polyethylene then acted as the readily available nutrient source. As the medium was unperturbed without incorporation or elimination of nutrients. (Nanda and Sahu, 2010). *Pseudomonas* sp along with *Actinomycetes* sp degraded treated (UV and HNO₃) polypropylene and formed crystals (Sepperumal and Markandan, 2014). The presence of flocculent microcolonies of *Pseudomonas* sp. and *Actinomycetes* sp on the PP surface is also well supported by Arkatkar et al. (2010) during polypropylene (PP) degradation. *Pseudomonas* sp undoubtedly gets attached to biodegradable PE films. In this study, biofilm formed on various plastic films from flask experiments were subjected to CFU counts. Results point out that *Pseudomonas* sp. was significantly found and have maximum CFU among the two bacteria of 1.9×10^{10} /plastic strip on UK BD PE selected native microorganisms, in three months (Poonam et al., 2013). Some strains of *Pseudomonas* sp, i.e., *Pseudomonas azotoformans* and *P. stutzeri* secrete biosurfactant rendering PP films relatively more hydrophilic. It allows the subsequent degradation of the polymer (Sepperumal and Markandan, 2014). The degradation ability of *Pseudomonas* is dissimilar among the strains. *Pseudomonas* sp. strain accounted to 20% weight loss in the tested PE in 120 days (Yang et al., 2014), while another strain of *Pseudomonas* sp. AKS2 could degrade PE films up to 5 % in 45 days without initial oxidation. Available reports articulate that PE biodegradation by *Pseudomonas* sp. could be attuned by modulating the hydrophobic interaction between the PE film and the microbe. Certain agents such as mineral oil stimulated hydrophobic interactions, resulting in increased bacterial attachment and biofilm formation. This enhanced attachment accelerated polymer degradation. Unlikely, Tween 80 reduced biofilm formation by lowering hydrophobic interactions and thereby reduces bacterial attachment and PE degradation. (Tribedi et al., 2013).

Rhodococcus sp.

Apart from *Pseudomonas* sp, other bacterial species were also found to be potent in the plastic degradation process. Gilan et al. (2004) reported that *Rhodococcus ruber* (C208), used PE as a sole

carbon source and formed a dense biofilm on its surface in flask culture experiment. Weight loss analysis revealed polymer degradation up to 8% within 30 days of incubation. It is also reported to degrade polyolefins. Initially adhered cells in the biofilm transforms into cellular aggregate forming microcolonies. Further differentiation of the biofilm generates "mushroom-like" three-dimensional structures (Sivan et al., 2006). EPS of *Rhodococcus* sp is mainly comprised of proteins. As the addition of proteases hampers biofilm formation followed by plastic biodegradation (Gilan and Sivan, 2013).

Rhodococcus sp possess distinct polymer degrading characteristics. However, degradation also depends on isolation sites. *Rhodococcus* sp 36 isolated from soil sediments could degrade PP efficiently than *Bacillus* sp. Both strains could utilize PP (polypropylene) microplastic for growth. *Rhodococcus* sp. strain 36 degraded PP up to 6.4% while *Bacillus* sp up to 4.0% in 40 days incubation time (Auta et al., 2018). On the contrary, in a report, *Rhodococcus* sp showed the lowest degradation of PE compared to *Pseudomonas* and *Brevibacillus* sp respectively (Nanda and Sahu, 2010).

Other bacteria

It has been known that microbes of varying genera are responsible for polymer degradation in addition to *Pseudomonas* and *Rhodococcus* sp. It was observed in a report that the maximum amount of polyethylene degradation was observed in *Staphylococcus* sp (52%) and 11% by *Pseudomonas* sp (Vatsaldutt and Anbuselvi, 2014). However, Yang et al. (2014) provided strong evidence for the involvement of *Enterobacter asburiae* YT1 and *Bacillus* sp. YP1 isolated from the guts of plastic-ingesting waxworms, in PEA degradation. (Yang et al., 2014). However, they have mentioned earlier that microbial colonization and degradation depends on the material type. The characterization of PET degrading communities showed an abundance of *Tenacibaculum* and different members of *Flavobacteriaceae* and *Bacterioidetes*.

The genera *Owenweeksia* and *Crocinitomix* belonging to *Cryomorphaceae* and *Bacterioidetes* were also strongly represented on PET. Furthermore, available reports also suggested the abundance of *Saprospiraceae*, *Cryomorphaceae*, *Flavobacteriaceae*, in PET degradation (Oberbeckmann et al., 2016). Moreover, many strains of *Bacillus* sp were indicated in several reports as Wasserbauer et al. (1990) pointed out that PE foils, when exposed to *Bacillus brevis* showed carbonyl-like groups and signs of oxidation in FTIR spectra (Wasserbauer et al., 1990). Other bacterial species important to biodegradation process include *Ideonella*, *Actinomycetes*, *Klebsiella*, *Streptomyces*, *Thermoactinomycetes*, *Nocardia*, *Mycobacterium*, *Micromonospora*, *Flavobacterium*, *Rhodococcus*, *Escherichia*, *Comamonas*, *Alcaligenes*, and *Azotobacter*. Some of them were reported to sequester the polymer up to 90% of the dry weight and reported to degrade plastic films (Leja et al., 2010; Joo et al., 2018).

Raghul et al., 2014 observed the involvement of consortium containing *Vibrio alginolyticus* and *V. parahaemolyticus* towards degradation of polyvinyl alcohol-low linear density polyethylene (PVA-LLDPE) blend film while LLDPE film did not have *Vibrio* sp. (Raghul et al., 2014).

Fungus

Both bacteria and fungi are reported to be involved in the biodegradation process. (Bonhomme *et al.*, 2003; Yamada-Onodera *et al.*, 2001; El-Shafei *et al.*, 1998). During the fouling process on the plastic surface, bacteria are the pioneer invaders. After colonizing onto the plastic surface. They allow entrapment of fungi and succession of other species (Mathur *et al.*, 2011). It allows sharing of metabolic intermediates and accelerates degradation (Gilan *et al.*, 2004). Fungus from agricultural soils was reported in degradation, the plastic pieces buried in agricultural soil mixed with sewage sludge.

Community analysis revealed bacterial and fungal attachment on the plastic surface, indicating probable usage of LDPE as a nutrient source. The isolated fungi are species of *Penicillium*, *Aspergillus*, and *Fusarium* (Shah, 2007). Consequently, in most of the degradation studies *Aspergillus*, *Penicillium* sp are indicated. Unlike bacteria, the capability of biofilm formation by fungal species on polyethylene was associated with a progressive decline in hydrophobicity of the surface (Gilan *et al.*, 2004). Reports point out that *Fusarium* sp and other fungal species eroded the surface after their attachment (Shah, 2007; Bonhomme *et al.* 2003). However, some strains of *Mucor* sp. along with other fungal species such as *Aspergillus* are associated in fouling and degradation of polyethylene blended with 6% starch (Premraj and Mukesh, 2005).

Aspergillus sp.

Many species of *Aspergillus* have the potency to degrade polyethylene. A study conducted on the isolation of fungi from polyethylene polluted sites revealed mostly identified organisms as *Aspergillus niger* and *A. japonicus*. However, the degrading ability varies among the species where *A. niger* degraded LDPE up to 5.8%, and *A. japonicas* were more potent in degrading up to 11.11% in one month in vitro (Raaman *et al.*, 2012). However, the degradation ability of *A. niger* was highest and degraded up to 38% in 60 days than 31% by *A. flavus* respectively. Mostly, fungi were utilized for the degradation of highly resistant plastics such as low-density polyethylene (LDPE) due to their capability to secrete hydrophobic proteins for attachment with the other organism for colonization (Mohan & Suresh, 2015). Some strains of *A. niger* (ITCC 6052) could also degrade modified polyethylene. Approximately 3.44% weight reduction and 61% decline in tensile strength was detected after 30 days of incubation in thermally oxidized polyethylene SEM analysis indicated to fissures and dense network of biofilm on the polymer surface.

Penicillium sp.

Aspergillus sp are mainly involved in the LDPE degradation, while species of *Penicillium* could degrade both LDPE and HDPE. As available reports suggest the involvement of *P. chrysogenum* and *P. oxalicum* towards LDPE and HDPE degradation. It degraded HDPE and LDPE to 55.598% and 34.35% in 90 days of incubation (Ojha *et al.*, 2017). The degradation is followed by pH reduction which indicated that the culture is producing metabolic products by utilizing the

polymer LDPE or HDPE for its growth as compared its positive control (media with sucrose). Since isolates could carry out the degradation without initial treatment or oxidation, it is probable that these species possess enzyme(s) with alkene bonds oxidizing ability to generate carboxylic acids and carbonyl compounds. Thus, eliminating the need for initial oxidation (Yoon *et al.*, 2012). Some species of *Penicillium* possess initial degrading enzymes which are responsible for the generation short chain oligomers which get degraded further. Strains of *P. simplicissimum* produces laccase and manganese peroxidase (Ojha *et al.*, 2017). During PHB degradation, both fungi and bacteria secrete PHB depolymerase which hydrolyzes PHB into mono (3-hydroxybutyrate) and short chain oligomers. The enzyme of 35 kDa, binds to the polymer surface with its substrate binding domain and carry out the catalysis (Ojha *et al.*, 2017), which are further degraded and assimilated to carbon dioxide and water. PHB-decarboxylase is produced by two *Penicillium* sp., namely, *P. pinophilum* and *Penicillium* sp. (Panagiotidou *et al.*, 2014). *Penicillium* sp., when present in a consortium of *Bacillus megaterium*, *Pseudomonas mediterranea*, *Aspergillus* sp., *Pseudomonas putida*, and *Phanerochaete* sp., increased the degradation of PE films within 45 days of incubation compared to individual cultures under 90 days incubation period (Mahalakshmi and Siddiq, 2015). Also, EDAX results indicated the use of PE film as a carbon source. FTIR and GC-MS analysis confirmed the presence of aromatic compounds such as 1-methyl-4-[1-methylethenyl]-acetate Cyclohexanol, Benzene,1,2-[methylene dioxy]-4-propenyl-,[E] and Cyclohexene,1-methyl-3-[1-methylethenyl]-[n] suggesting that the degradation followed central catabolic pathway (Mahalakshmi and Siddiq, 2015).

***Mucor* sp.**

Mucor sp. are generally found associated with other microbes and carry out PE biodegradation synergistically. *Aspergillus flavus* and *Mucor circinilloides* isolated from municipal landfill area showed promising LDPE degradation with a maximum weight loss of 18.1 and 6% when mixed with cow dung and poultry dropping after nine months (Pramila and VijayaRamesh, 2011). The degradation potential varies depending upon the type of consortia used. In some cases, consortia may decrease the degrading ability of the fungi as in a study carried out by Singh and Gupta (2014) where fungal consortia comprised of *A. flavus* F1 (30%) *Fusarium* sp F6 (32%), *A. japonicas* F3 (36%), showed significant biodegradation results in four weeks as compared to 24,20,16% by *Penicillium* sp F5, *A. niger* F2, *Mucor* sp. F4 in terms of LDPE weight loss measurements. (Singh and Gupta, 2014).

Influence of biofilm on plastic degradation

Biofouling plays a crucial role in governing the buoyancy of plastic debris (Moore *et al.*, 2001; Ye and Andrady, 1991). Biofilm formation on plastic surface is a preferred mode of growth by plastic degraders. They are in charge of significant physicochemical changes in the properties of plastic. As Morét-Ferguson *et al.* (2010) concluded that attached biomass degraded the polymer chains

and rapid defouling hindered degradation and density loss (Ye and Andradý, 1991; Yokota et al., 2017). Hydrophobicity is an important factor in bacterial attachment and degradation. As the plastic polymers are hydrophobic, bacteria have to initiate hydrophobic interactions with the plastic surface (Sivan, 2011). The current report stated that the hydrophobicity could be increased by starving the bacterial culture. It was shown that with carbon starved *R. corallinus* became more hydrophobic and adhered strongly than the non-starved cells thereby aggravated degradation (Sanin et al., 2003). These findings also support the increased affinity of *R. ruber* cells for attachment with the PE surface and raise the possibility that low carbon availability promotes hydrophobic interactions and biofilm establishment (Sivan et al., 2006). Biofilms from other bacterial species from soil and marine microflora also represent a similar scenario. Adhered microbes were reported to be hydrocarbon degraders, as the synthetic polymers are mainly comprised of hydrocarbons so their enzymes may be employed in the degradation (Harrison et al., 2014). Non-specific chemical bonds and several functional groups are introduced into the polymer by the adhered microbial flora which increase degradation and hydrophilicity (Fotopoulou et al., 2015). After attachment, the plethora of process occurs in different types of plastics facilitating abiotic biodegradation. Abiotic degradation by UV light allows the plastic surface to get weathered by introducing polar hydrophilic groups into the polymer resulting in a modification of its topography, increased roughness. (Fotopoulou et al., 2015; Cooper and Concoran, 2010). Increased roughness favors the microbial attachment which further modifies the polymer structure and composition and vice versa. Taken together, these processes allow polymer fragmentation with a high surface-to-volume ratio, which is also an essential aspect of the degradation process (Rummel et al., 2017).

Biofilm-plastic interactions

Attached microbes initiate hydrophobic interactions upon its contact with the polymer surface (Gilan et al., 2004; Sivan et al., 2006). It inevitably changes particle properties. Plastic was adsorbed by inorganic ions and molecules which promotes microbial attachment. Film conditioning customizes community colonization by governing material-specific surface attributes resulting in leaching of carbon compounds. Michels et al. (2018) and Rogers et al. (1990) observed elevated bacterial numbers on PVC and PE than stainless steel, which they speculated to leaching of additives, served as a possible nutrient source. Polysaccharides and nucleic acids of the EPS secreted by initiator organisms adhered to the film are known to be relatively sticky, which also conditions the film. It facilitates colonization for other organisms. (Flemming, 1998; Ghosh et al., 2016; Ghosh et al., 2017b; Michels et al., 2018). Furthermore, biofilm interacts with the synthetic polymer in several ways. Microbes get adhered to the surface, thereby masking surface properties and contaminates the surrounding fluid by organisms which failed to adhere. The enzymatic attack leads breakage of polymer chains and loss of mechanical stability. However, microbial filaments delve deep inside the polymer synthesizes biosurfactants and accumulate water for

further hydrolysis, which also leads to increased conductivity. Finally, lipophilic pigments are released assisting to discoloration of the plastic (Zettler *et al.*, 2013).

Conclusion

Plastics are thermo-elastic, water-insoluble, polymers are posing a great environmental challenge. Microbial degradation is better than physical and chemical methods as the degradation pathway leads to complete degradation and mineralization of polymer. However, biodegradability depends upon the microbial biofilm community adhered in it. Biofilm community plays a significant role in modifying the physicochemical properties and degradation of plastics. As biofilm offers bioavailability of nutrients, sharing of metabolites without accumulation of metabolic products resulting in increased cell viability and degradation efficiency. However, fewer reports are available about the interconnection of biofilm with plastic degradation and vice versa. In the present chapter, we review the influence of biofilm microbes in the degradation of commonly used plastics. Both natural and engineered biodegradation pathways employed by the adhered microbes to execute degradation are deciphered. Furthermore, potent microbes and their interactions with the plastic surface has also been summarized. Hence, this would serve as a better understanding of the development of plastic remediation.

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Chapter 15

Strategic framework and phenomenon of zero waste for sustainable future

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Abstract

The idealistic concept of zero waste promotes a systematic procedure of waste planning and recovery of resources from waste. The Zero waste concept is to minimize waste production so as to reduce waste in the landfill. A strategic zero waste framework (ZWF) is essential for the development and achievement of systematic waste management activities in order to achieve general objectives. The developing phenomenon of zero waste includes the theory, practice and learning of characters, families, businesses, communities and government organizations, responding to the perceptions of crisis and failures around conventional waste management. Furthermore, a constant assessment of progress towards zero waste targets is essential. It is expected that, taking into account local circumstances, the proposed strategic guidelines would be beneficial for local authorities and stakeholders, while developing their zero-rejection strategy. Waste management from the beginning of waste disposal, waste sorting, producer responsibility and waste collection based on the quantity of waste, community waste management and the provision of incentives and disincentives is the zero waste implementation parameter. This concept should be assimilated into local policy so it becomes an obligation for the government

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and the community to implement it. A number of cities around the world have implemented zero waste policies and set a goal to reduce waste disposal to tonnes per annum (TPA) as small as possible.

Keywords: Landfills, Recycling, Resource conservation, Waste, Waste management, Zero waste

Introduction

Waste is one of the main world ecociders. Indeed, the waste meets all the standards of an ecocide; it causes the destruction of the environment, damages ecosystems, impedes any kind of life and pays no attention to the rights of future generations. Waste is the living proof of the degree of self-centeredness and stupidity of the most intellectual generation of human beings this planet has seen. Nature creates no waste; it is a genuine human creation. In nature nothing and nobody goes to waste because the definition of an ecosystem is a system of cooperative and symbiotic relationships; the discards of a process are the input for another one. Everything is up-cycled into the system so that the system is sustainable and resilient. In an ecosystem all energy used is renewable and non-polluting and all resources are obtained in the vicinity using non-extractive, low-energy-intensive techniques. Processes take place at normal local temperatures and pressures and combustion is not an option. The current linear passing society is the opposite of sustainability; resources are extracted, transported, manufactured, sold, used and discarded, committing ecocide at almost each and every stage of the process.

Zero waste (ZW) is one of the most studied topics, but the most discussed disadvantage of waste management research in recent years (Greyson, 2007; Seltenrich, 2013; Zaman 2015; LaBrecque, 2015). Zero Waste is defined as "systematically designing and managing products and processes to eradicate waste and materials, conserve and recover all resources and not burn or bury them" (ZWIA, 2004). Thus, Zero Waste is about waste deterrence through sustainable design and consumption practices, optimum resource recovery from waste and not about managing waste by incineration or landfills (Zaman and Lehmann, 2011). It is comprehensible that Zero Waste strongly supports waste prevention and deterrence approaches rather than waste treatment and disposal. However, it may not be possible to accomplish zero landfill and zero incineration objectives under the current system of resource consumption and waste management practices.

Waste has been treated as a burden and social problem and thus largely managed by "end-of-pipe" solutions such as landfill (Zaman, 2015). With few exceptions in the developed countries in Europe, North America and Asia-Pacific, the traditional waste management system, which primarily relies on landfill, significantly pollutes our environment, and thus an enhanced and effective waste management system is required. This study starts from the position that waste is not an "end-of-life" problem alone, but rather waste is an intermediate stage in the conversion of resources that occurs in the consumption process. The resources that are transformed into "waste" thus need to be readdressed in the production process through holistic Zero Waste

management systems. In addition, waste is a social problem and it entails social technologies to solve it. Hence the goal of zero waste is to consume and utilize resources within a circular economic model, with least environmental deficiency using industrialized symbiosis, recycling or “up cycling”, centered on nature’s “no-waste” belief (Zaman, 2015).

Strategic waste management policies are commonly used by local governments and business organizations for managing waste problems (USEPA, 2013). A strategic framework for waste management is essential for the successful execution of a waste management plan as it forms the basis of an effective planning procedure (King, 2004). A number of studies have been conducted on the development of waste management frameworks (Gillwald *et al.*, 2013; Lu and Yuan, 2011), including decision frameworks (Ramesh and Kodali, 2012), legislative frameworks (Sentime, 2014) and hierarchical frameworks (Liao and Chiu, 2011). A facility helps decision makers comprehend, improve, evaluate and guide waste management systems. This study aims to ascertain the key guiding principles that help to develop a strategic zero waste framework. The purpose of the zero waste strategic framework is to guide waste management policy and decision makers while developing and proposing waste management strategies and policies.

The key features for the development of zero waste strategy

Many local councils set their zero waste goals to “alteration of waste from landfill”; however, alteration of waste alone may not be sufficient as it requires inventive design and sustainable consumption to accomplish the long-term goals. The 3R principles (reduction, re-use and recycling) are among the top three in the waste hierarchy and they are considered as the establishing principles of sustainable waste management system (Hansen, 2002). The “3R” principles in the European Union Waste Framework Directive 2008, have been extended to five steps of the waste hierarchy: prevention, re-use, recycling, recovery (including energy retrieval), and disposal (European Commission, 2012).

A number of approaches have been acknowledged in various studies such as eco-design, responsible shopping behavior, etc., in relation to waste prevention and anticipation (Braungart *et al.*, 2007; Schmidt, 2012). Waste prevention is one of the most important concerns in zero waste and it requires collective social awareness and knowledge on waste and ingenious manufacturing and business models (Cox *et al.*, 2010). Attentiveness awareness and transformative knowledge are often understood to motivate behavior change in relation to pro-environmental lifestyle choice (Jackson, 2005).

Responsible and sustainable consumer behavior is another significant issue in waste prevention. Collaborative consumption increases efficacy in resource consumption and improves social collaboration (Rogers and Botsman, 2010). The collaborative ownership or collaborative consumption model encourages service-based business and waste prevention (D-Waste, 2013). Therefore, re-circulation (circulate the materials in the supply chain for a repetitive use) of post-consumer products through re-use and re-sell is essential and it boosts the circular economy

and enhances social capital.

Waste management and treatment technologies are used in resolving waste problems for more than centuries (UNEP/GRID, 2006). Zero waste takes the position that technology alone cannot solve the waste evils sustainably, as it requires community participation, service infrastructure, regulatory policy and eco-friendly treatment technology. A number of studies have acknowledged that effective collection systems, decentralized waste recycling centers, social technology such as recycling, composting, regulatory policies such as pay-as-you-throw (PAYT) and eco-friendly advanced waste treatment technologies are the vital issues performance evaluation is an integral part of a strategic framework to govern the impending direction of waste management systems. Moreover, accurate and reliable data on waste management systems is absolutely important to assess and monitor the overall performance of the waste management systems is entirely important to assess and observe the overall performance of the waste management strategies and programmers. Zero waste research in relation to data analysis, foretelling waste strategies and programmers. Zero waste research in relation to data analysis, forecasting waste generation and management developments and continuous expansion in waste prevention and avoidance and techniques (DE, 2013).

Global waste issues and cities: why zero waste?

Resources from all over the biosphere are described as being, “funneled” into the world’s cities to meet the expanding consumption, driven by hastening globalization, urbanization, and affluence (Girardet, 2000; Krzeminska *et al.*, 2017). A commonly cited metric illustrating the associated imbalance and exploitation is that cities occupy just two per cent of the earth’s land surface, yet use over 75 per cent of its resources and discharge corresponding proportions of waste (Girardet, 2000). Similarly, urban societies currently account for over 70 per cent of global energy-related CO₂ emissions (Edenhofer *et al.*, 2014). The cities that extrapolate this more interconnected exploitation-discharge seem to be the upper part of the “anthroposphere”, which Manahan enunciates as centrally implanted in a rubric of material, energy and waste altercation within the dynamic interaction of atmosphere, biosphere hydrosphere, and geosphere (Manahan, 1999). Such reporting draws a unambiguous distinction between the extractive, carbon intensive, lineal, disposal orientated human systems, and the “biological analogy” (Ayres and Ayres, 2002) and “ecosystem” design metaphor (Korhonen, 2004; Isenmann, 2008) offered in, what are popularly inferred as the infinitely sustainable, solar powered, zero emissions, circular metabolism of natural systems (Lehmann, 2010; Lehmann, 2011). The functionality of urban systems is said to govern whether the waste outputs of cities, discharge to atmosphere, or gets deposited in dumps/landfills, or unintentionally/deliberately litters the landscape, before accumulating in rivers and the ocean (Zaman and Lehmann, 2011; Hoornweg *et al.*, 2015). In respect of a lot of sustainably managing the universally significant urban resource/waste stocks, flows, and sinks, the development of sustainable future cities is cited as demanding a regenerative design mind-set

and fostering new technical and organizational solutions, which bio-mimic nature's inherently successful—circular design (Benyus, 1997; Garcia-Serna *et al* 2007; McDonough and Braungart, 2010). Striving for zero-carbon transport, energy and building systems (i.e., “nZEB”) (Riffat *et al.*, 2016), resource preservation and efficiency, and the beneficial recycling and reabsorbing non-toxic non-polluting water (Verstraete and Vlaeminck, 2011) and waste flows, as a resource (hence improving quality of life and the long-term environmental sustainability of the whole system) are identified as critical challenges within future city discourse (Verstraete and Vlaeminck, 2011; Mezher, 2011; Porse, 2013). Zero waste (inclusive of future zero waste city models) has been described as a pathway being “forged” towards a desirable long-term goal (Bartl, 2011) and in some sectors almost achieved (Mezher, 2011). However, zero waste is also regarded negatively by some, as a potentially harmful myth (Premalatha *et al.*, 2013). Notwithstanding this spectrum of reporting, a range of integrated green urban design principles, such as sustainable design and circular urban metabolisms, have been discussed as being central to realising the concept of a zero waste city (Lehmann, 2010; Lehmann, 2011). Given the conflicting assertions that the phenomenon of zero waste affords a critical opportunity to address waste issues (Zaman and Swapn, 2016), a starting point in exploring these claims, is to scrutinize current global “progress to date” in managing waste. A cluster of international reports describe the issues that are associated with waste, as of becoming a globalised public and environmental health emergency, necessitating an urgent, internationally coordinated, comprehensive, and effective response (Mavropoulos and Newman, 2015; Mavropoulos *et al.*, 2017). The environmental and social consequence of humanities failure to effectively manage waste, has resulted in some of the most polluted and poverty stricken places on Earth (Mavropoulos *et al.*, 2017). Whilst this syndrome is often localised and most concentrated around (mega) cities (UN-Habitat, 2010; Mavropoulos, 2010; Guerrero *et al.*, 2012), the interrelated aquatic and atmospheric dimensions of impacts of terrestrially generated waste is now being registered across the entire global biosphere (Ryan *et al.*, 2009; Moore, 2008; Hodzic *et al.*, 2012; Wiedinmyer *et al.*, 2014; Thompson, 2014). The World Bank reported that, the 2012 baseline of 1.3 billion tons of municipal solid waste (MSW) generated by cities globally, is projected to double by 2025 to 2.2 billion tones pa (Hoornweg and Bhada-Tata, 2012). The current trajectory of growing population, urbanization and consumer demand, underwrite such projections (Troschinetz and Mihelcic, 2009; Mavropoulos, 2010; Mavropoulos, 2011). Given this, it appears unlikely that the vital challenge of reducing waste generation (i.e., located as the highest priority of the “5R” waste hierarchy (i.e. firstly: reduce, reuse, recycle, recover energy and then lastly residual disposal)) is, under “business as usual” conditions, immediately achievable. Concerning, it has been reported that, unless aggressive sustainability scenarios are successfully implemented, “global peak waste” might not occur until 2100 (Hoornweg *et al.*, 2015; Serpe *et al.*, 2015). Increasingly, the interconnected dimensions of the waste issue, (i.e., ocean plastics, disaster waste management, chemical toxicity and dissipation, food-waste, organized crime, nuclear waste, and emerging “NBRIC” (i.e. nanotechnologies, biotechnologies, information and communication technologies (i.e. WEEE), robotics and cognitive

sciences (Graedel and Allenby, 2010) is attracting media reporting and a correlated escalation in public awareness and alarm. This extent and assortment of waste issues, is overlain by systemic causalities, such as history, geography, infrastructure and technology, entrusted interests and ideology i.e., privatisation (Iskandar and Tjell, 2009), and individual and collective cultural and socio-economic imperatives, which adds to associations of “super wicked” complexity and inflexibility.

In terms of the global provision of “residual disposal” (i.e., the supposed least priority, at the bottom of the 5R waste hierarchy) the efficacy and outcome to date of the conventional waste management paradigm and practice, also raises questions. The International Solid Waste Association’s (ISWA) – “Global Waste Management Outlook” (GWMO) bring into line with other similar reporting, in estimating that, between 2 and 3 billion people live below the most basic waste management system benchmarks of collection and controlled disposal (Zero Waste South Australia, 2013; Wilson *et al.*, 2015). Aggravating apprehensions around the pollution and climate change impacts of systemic failings in global waste management, reporting indicates that the default disposal “treatment” for approximately 41% of global waste is uncontrolled burning (Wiedinmyer *et al.*, 2014; Thompson, 2014). The critically important global ISWA program seeking to rectify this syndrome (Mavropoulos *et al.*, 2017) has set challenging goals (i.e. “As an preliminary step, aim to: accomplish 100% collection coverage in all cities with a population more than 1 million, eliminate open burning of municipal solid wastes, similar wastes and turn them into controlled launching” (Wilson, 2015). Achieving these goals characterizes a key initial benchmark in modern “integrated solid waste management” (UNEP, 2009; ISWA, 2003; Zeng *et al.*, 2010). However, it is important to recognize that achieving those baselines, is just the starting point for the intended transition to holistic, sustainable resource conservation, and material circularity, which advocated in, for example, “circular integrated waste management systems” (CIWMS), zero waste and a circular economy discourse (Zaman and Lehmann, 2011). Whilst it can be accepted that “the world can’t recycle its way out of waste” (Mace and Szaky, 2016). Equally, the common scientific oratory offered by the USEPA (USEPA, 2013) underwrites the growing ubiquity and popularity of recycling today. Keynote environmental commentators correspondingly link the benefit of recycling to the challenge of addressing climate change. Stern argues that, because recycling makes such foremost and under-appreciated contributions to reducing GHG emissions it is one of the “best kept secrets in energy and climate change” policy (Stern, 2009). Such glowing assessments has been more recently “reality checked” by China’s successive “Green Fence”, “National Sword”, and “Blue Sky” import policies applying to recycled materials, which has sent repercussions through global recycling markets (WasteMINZ, 2018). Overall, the importance and positive opportunity of “recycling citizenship” confirmed by the informal sector and communities across the global spectrum of socio-economic development, is now well recognized (Seyfang, 2005; Silva *et al.*, 2017).

However, in spite of the significant environmental and social opportunities that are ascribed to recycling, it is estimated that globally, currently only one-quarter to a third of the total 3.4–4

billion tons of MSW and industrial waste produced annually, is recycled (D-Waste, 2013). So in summary, international waste data designates that, after over four decades of significantly investing in the widely established principles of the “waste hierarchy”, there are still significant barriers in realizing the stated: top (reduce), middle (recycle), or even lowest (residual disposal) priorities. Whilst conventional waste management theory, concentrated into the near universal rubric of the waste hierarchy, clarifies our priorities and can be seen as having catalyzed a measure of development, overall we are yet to globally actualise this principle and appear to be “entangled/trapped” in limitations of this paradigm (Bartl, 2014; Van and Stegemann, 2016; Pollans, 2017). The net result is that, most of these sources which flow through the global economy still shipment via the destructive and polluting linear model, variously described as –“take-make-waste”(Jessen, 2003)/“dispose” (Ellen, 2013). Evidencing this, socio-metabolic research, which assessed the degree of circularity of resources flowing through the global economy, describes this as currently, only in the early phases (Haas *et al.*, 2015; Ghisellini *et al.*, 2016). Currently, the progress of a more “circular economy” is limited by a rapid growth in “socio economic stocks”, a focus on recycling rather than reuse/reduction and an estimated 44% of processed materials that are incinerated to “provide energy”(Haas *et al.*, 2015), and hence, exit rather realize economic circularity. The zero waste movement (Anderson, 2011) can be regarded as one of a cluster of sustainability actors, which both highlight and respond to the link of failure, inertia, and growing sense of crisis, which is associated with the conventional waste management paradigm (Hannon, 2015). The zero waste movement comprehends a range of perspectives and approaches and can be regarded as a neologism, residing in a busy “eco-ideas marketplace”, alongside interrelated and complementary theses on how sustainable development can be engineered (Glavic and Lukman, 2007). For instance, whilst disciplines, such as industrial ecology (IE), urban metabolism (UM), and bio economy (BE), and the activities for a “circular economy” (CE) and zero waste each arise out of differing: perspectives, personalities, and intellectual traditions, the appearance of shared cognitive DNA seems clear (Veleva *et al.*, 2017). These movements are conceptually aligned and complimentary in seeking to confront and re-design and replace the existing “exploitative”, lineal economic model with progressively more cyclical and sustainable resource management, where anthropogenic systems “bio-mimic” the modelling of natural systems (Hawken *et al.*, 1999). However, in this sphere, zero waste also has a unique identity and assumes a distinctive role, expressed in the broadly accepted, peer-reviewed definition offered by the Zero Waste International Alliance (ZWIA, 2004; ZWIA, 2009). In the adoption of confrontational terminology, a campaign posture and in advocating for a hyper-aspirational continuum of innovation, zero waste seeks to confront the perceptions of normalcy and intractability around waste. The embrace of dissent and involvement in the framing of zero waste, together with the embrace of community/NGO involvement and the economically redistributive aspects, is why the movement is simultaneously controversial, and arguably indispensable (Lombardi and Bailey, 2015).

Encompassed in the prickly opposition to incineration and landfill, zero waste pursues to refute

and disrupt the predominant normalization of waste and our “throw-away society, as a relatively recent socio-economic construction, which can and must, be redesigned (Herbert, 1998; Waste Watch UK, 2004). Zero waste directly challenges the waste management industry’s twin bury and burn profit centers, on the basis that disseminating our “flame, flush or fling” (Seadon, 2010) disposal mentality, ultimately binds human society to linear material flows, rather than enables the growth of a more circular economy. Rather than admiring the supposed technical progress of reforming disposal systems (such as sanitizing, or optimizing landfill or extracting energy from incineration) zero waste regards these “developments” as confirmation of societal capture to a failing and unsustainable socio-economic model (Seadon, 2010; Connett, 2013; Lombardi and Bailey, 2015). The dissatisfied global progress toward genuinely sustainable material resource management is the central provocation catalyzing the global search for alternative modes for generating innovation and development. Within this spectrum of activity, a growing regiment of organizations and practitioners choose to self-identify, under the heterogeneous brand of zero waste.

The development of zero waste concept

Eliminating waste from production process to costumer usage is a waste minimization strategy (Zero Waste SA Strategy, 2010). Waste is more often observed as useless goods by society and even industry. This is actually a deceitful view if humans understand and comprehend how waste has a price and can also harm environment. A global understanding has appeared, widely accepting the effects of climate change, including loss of biodiversity, increased air pollution, soil and water, deforestation and reduced resources and materials, as a consequence of disproportionate consumption of unsustainable production processes. About 20% of the waste can be recycled or recovered annually where the world's waste engenders four billion metric (Chalmin and Gaillochot, 2009). Increased waste generation is produced by linear material flow rate system where the waste ends in the landfill. In present time the world is more run a linear economic system where the product will end up just like that in the landfill. While the concept of zero waste (ZW) is the contrary of linear circular system is the flow rate of material is a circular system where the end of the product becomes the beginning of another product as well (nothing is wasted). Figure 15.1 shows the comparison of the material flow rate between linear and circular systems.

(Palmer, 2004) was the first to use the term Zero Waste in 1973 as a term to recover resources from chemical waste. A number of cities in the world in 1995 implemented No Waste legislation to achieve the 2010 targets and Canberra became the first city in the world to successively and effectively achieve Zero Waste targets (Snow and Dickinson, 2003; Connett, 2013). The advent of Zero Waste regulations in New Zealand in 1997 supported the initiative to minimize waste through the Zero Waste movement in the country. This movement voiced thorough "closed loop material economy system in which a product is made for reuse, repair and recycling, an economic

Figure 15.1. Flow rate of material through circular (zero waste) and linear systems (Song et al., 2015).

Table 15.1. Achievements and events related to zero waste.

Year	Country	Milestone/event
1970s	USA	The term 'Zero Waste' was introduced by Paul Palmer
1986	USA	The National Coalition against Mass Burn Incineration was formed
1988	USA	Seattle presented the Pay-As-You-Throw (PAYT)
1989	USA	The California Integrated Waste Management Act was passed to accomplish the 25% target of waste diversification from landfills in 1995 and 50% in 2000
1990	Sweden	Thomas Lindhqvist presented 'Extended Producer Responsibility.
1995	Australia	Canberra passes Act No Waste by 2010
1997	New Zealand	The Zero Waste New Zealand Trust was established
1997	USA	The California Resource Recovery Association (CRRRA) held a Zero Waste conference
1998	USA	Zero Waste is encompassed as a key principle of waste management in North Carolina, Seattle, Washington, & Washington DC
1999	USA	CRAA conducted a Zero Waste conference in San Francisco
2000	USA	The Global Alliance for Incinerator Alternatives was formed
2001	USA	Grass Roots Recycling Network published 'A Citizen's Agenda for Zero Waste.'
2002	New Zealand	The Cradle-to-Cradle book was published
2002	USA	Zero Waste International Alliance (ZWIA) was formed The first Zero Waste Summit was held in New Zealand
2004	USA	ZWIA defines Zero Waste GRRN adopts Zero Waste business principles
2004	Australia	Zero Waste SA was established in South Australia
2008	USA	The Sierra Club adopted the Zero Waste producer responsibility policy
2012	USA	The documentary Trashed premiered at the Cannes film festival The Zero Waste Business Council was founded in the United States.

system that reduces and ultimately closed circle of the economy; one in which products are made for reuse, repair and recycling, economies that minimize and ultimately eliminate waste” (Tennant, 2003). In 2000, Del Norte County, California became the first state in the USA to implement a inclusive Zero Waste plan and in 2001, the California Integrated Waste Management Board adopted the Zero Waste goal as a strategic waste management plan (Connett, 2013). Achievements, accomplishments and events related to Zero Waste development can be seen in Table 15.1. Applying zero waste means eradicating all disposals in soil, water or air which is a threat to the planet, human health, animals or plants (ZWIA, 2004).

Figure 15.2. Steps to implement the zero waste action plan (Source: Zaman, 2017).

Eradicating incinerators, landfills, throwaway societies and creating communities that manage sustainable waste are ideals of zero waste. Zero waste implementation cannot be predictable to run in short time or for example within a year, but we can plan a situation that is very close to zero waste in the next five or ten years (Connett, 2007). Disproportionate exploitation causes the natural resources to become increasingly limited in number, creating ambiguous future development. This should be prevented, therefore humans should involve in sustainable consumption and waste management strategies based on (1) waste avoidance, (2) material efficacy and (3) restoration of resources (Lehmann, 2011). The zero waste concept continues to grow, not stopping just as recycled but also restructuring the product design to avert the issue of waste in the early stages (Tennant, 2003). Figure 15.2 shows the steps that can be done if the city implements zero waste well then the city can be bowed into a city of zero waste.

Zero waste initiative in the world

Canberra became the first city in the world to endorse zero waste laws in 1996. In 2004, the city of Canberra has grasped 70% of waste diversification. One of Canberra's programs is to establish a place called "Resource Recovery Park" to help industry creates products from separate materials and they can market reusable materials. Adelaide, a city in South Australia has established and implemented a zero waste strategy. The waste composting program is increasing expressively and they are targeting by 2015, the compost capacity must be higher than the waste sent to the landfills. The city has a high percentage of waste diversification, reaching 82%. Stockholm is one of Europe's leading cities and environmental standards are very high and have ambitions to improve the quality of the environment. Stockholm has already instigated its goal of being a fossil-free city in 2050 (Stockholm City, 2009). One of the key goals of this 2030 vision is to alter Stockholm city into a resource-efficient area (RUFSS, 2010). The city of Halifax-Nova Scotia, Canada reaches 60% of the rate of waste diversification. The Zero Waste program creates 1000 jobs in garbage collection and processing. In addition 2000 jobs were created in the sector of used goods collection industry. Almost all separately-used goods are reused by industry in Nova Scotia (Dahlen and Lagerkvist, 2010). The most progressive city is San Francisco, with a population of 850,000, has reached 77% of waste diversification, the highest in the United States, with a three-pronged approach: implementing strict waste reduction laws, partnering with waste management companies to innovate new programs, and work to create a culture of recycling and composting through enticements and working with communities. San Francisco endeavors to adopt the Zero Waste goal to be achieved by 2020 (Zaman and Lehman, 2013).

Conclusion

A strategic zero waste framework is indispensable for initiating major activities to achieve zero waste goals. This study tried to ascertain the key guiding principles for the development of a

strategic zero waste framework based on a unanimity analysis of waste experts. The key elements of the zero waste framework are acknowledged by the literature focusing on waste prevention and circumvention, waste management and treatment, and monitoring and assessment. The expert survey identified eighteen strategic elements as important guiding principles for the development of a holistic zero waste framework. The study acknowledged that all the strategic elements may not be possible in all countries, especially in the developing countries where appropriate infrastructure and governing policies are not available and for developed countries where secondary waste management costs are very high. A further study can be conducted to identify and explain the elements that are appropriate for different economic frameworks (developed and developing). It is expected that by considering the local circumstances such as local waste management priorities, waste market and economic condition, the proposed elements would work as directorial principles for achieving the zero waste goals. The fundamental transformation of existing systems is prerequisite and the study concluded that the zero waste goals may not be accomplished without a closed-loop production system in place, wide application of liable consumption practices, conservative waste management systems and continuous development through monitoring and assessment of waste management performance. The conclusions of this study are important and can underwrite to the knowledge of zero waste management. Therefore, it would be beneficial for local establishments to consider the proposed strategic elements while developing local and national zero waste strategies. Zero Waste can be an alternative concept in waste management because zero waste is a concept that starts from, prevents waste in "upstream" to "downstream", not just control waste by dumping it to landfill. Require the association of all parties in implementing the concept of zero waste, ranging from private parties, governments and communities in the execution of this concept. Policy support from the national government in the form of a stable regulation is required for zero waste to be implemented properly.

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Chapter 16

Zinc oxide nanostructure and its application as agricultural and industrial material

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Abstract

Nano sized particles of semiconductor materials have achieved great interest in recent years due to their desirable properties and applications in different areas such as agricultural, rubber industries, pharmaceutical and cosmetic, textile industries, electronic industries, sensors, photoelectronic devices and photocatalysts. These nanomaterials have unusual thermal, structural and electronic properties, which are of important scientific interests in the fundamental and applied research fields. Zinc oxide (ZnO) is a promising material which gained increasing interest in recent years owing to its distinctive properties. In this review paper an attempt has been made to elaborate the promising applications of ZnO nanoparticles in various fields.

Keywords: Antibacterial, Biosensors, Photocatalyst, UV- blockers, ZnO nanoparticles

Introduction

Nano sized particles of semiconductor materials have achieved great interest in recent years due to their desirable properties and applications in different areas such as rubber industries, pharmaceutical and cosmetic, textile industries, electronic industries, sensors, photoelectronic

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devices and photocatalysts. These nanomaterial's have unusual thermal, structural and electronic properties, which are of important scientific interests in the fundamental and applied research fields (Gancheva *et al.*, 2016, Thirumavalavan *et al.*, 2013). ZnO is a promising, and versatile inorganic material with a broad range of applications. Zinc oxide (ZnO) is usually a semiconductor having wide band gap with an energy gap of 3.37 eV at normal room temperature. Zinc oxide (ZnO), which can exhibit a wide variety of nanostructures, possesses unique semi-conducting, optical, and piezoelectric properties (Wang, 2008, Yang *et al.*, 2010). ZnO is characterized by photo catalytic ability and photo-oxidizing capacity against chemical and biological species. It is a wide band gap semiconductor and this has significant effect on its properties, such as the electrical conductivity and optical absorption. The excitonic emission can persevere higher at room temperature and the conductivity increases when ZnO doped with other metals (Wang, 2004). ZnO-NPs possess unique antibacterial, antifungal properties, high catalytic and high photochemical activities. ZnO possesses high optical absorption in the UV region which is beneficial in antibacterial response and used as a UV protector in cosmetics. ZnO nanoparticles have recently fascinated consideration owing to its unique features. There are potentially numerous promising applications of ZnO nanoparticles in various industries which are summarized below in flow Figure 16.1.

Zinc oxide – properties and agricultural/industrial applications

In rubber industry as fillers and activators for rubber compounds

Between 50% and 60% of ZnO use is in the rubber industry (Moezzi *et al.*, 2012). Zinc oxide along with stearic acid is used in the vulcanization of rubber (Porter, 1991). Zinc oxide is used as additive, it promotes the process of vulcanization in rubber that is used for tire manufacturing. In addition, its good conductivity improves the removal of heat that is generated during the

Figure 16.1. Industrial applications of zinc oxide.

churning motion of the tires also protect rubber from fungi and UV light.

In pharmaceutical and cosmetic industry as a component of sunscreen, lotions, powders, dental pastes, etc., absorber of UV radiation

Nanoparticulate zinc oxide is the broadest spectrum UVA and UVB absorber that is approved for use as a sunscreen by the U.S. Food and Drug Administration (FDA), and is completely photostable (Mitchnick *et al.*, 1999). ZnO is basically included in some cosmetic lotions as it is also known to maintain UV blocking and absorbing capabilities. In sunscreen applications, because of the ingredient of bulk ZnO, it leaves a whitish tint when applied to the skin, but when ZnO nanoparticle is used in sunscreen application due to its transparent nature, it doesn't leave any tint on the skin while applying. Compared to titanium dioxide (TiO₂), ZnO is considered to be a good ingredient in sunscreen applications because of its wide band gap due to which they can block UVA rays which are at the wavelength range of 320-400 nm. Compared to titanium dioxide zinc oxide is considered to be non-irritating, non-allergenic, and non-comedogenic. Zinc oxide also imparts the optical and biochemical properties and therefore it is used by the pharmaceutical industry for manufacturing zinc ointments, zinc pastes, adhesive tapes, and bandages for skin and wound treatment. When mixed with eugenol, a ligand, zinc oxide eugenol is formed, which is used as a restorative and prosthodontic in dentistry. Zinc oxide is widely used to treat a variety of skin conditions, including dermatitis and acne. It is used in products such as baby powder, calamine lotion, and barrier creams to treat diaper rashes, anti-shampoos and antiseptic ointments. ZnO can also be used as the astringent for wounds healing, anti-hemorrhoids, itching due to eczema and excoriation in the human medicine. Zinc oxide tape used by athletes as a bandage to prevent soft tissue damage during workouts (Hughes and McLean, 1988). Researches have shown that nano ZnO which has the average size between 20 nm and 45 nm can enhance the antibacterial activity of ciprofloxacin against *Staphylococcus aureus* and *Escherichia coli* in vitro (Banoee *et al.*, 2010).

In textile industry as antibacterial and UV blocker

The incorporation of nanoparticles like ZnO, TiO₂ or clay nanoparticles into textiles are becoming more demanding, as they provide protection from harmful UV radiation. Fine particles of the zinc oxide have deodorizing and antibacterial properties and for this reason they are added into materials including cotton fabric. In comparison to conventional UV absorbers (organic and inorganic), nanoparticles are more efficient at absorbing and scattering UV radiation, because they have a larger surface area per unit mass and volume than the conventional materials. Textiles coated with nanoparticles keep the UV blocking property more time than conventional materials. Hence, these nanoparticles increase the effectiveness of blocking UV radiation. Zinc oxide provides an excellent UV-protection when cotton fabrics are treated with zinc oxide nanorods of 10 to 50 nm in length. ZnO nanoparticles inlaid in polymer matrices (e.g., soluble starch) have a good potential for applications such as UV protection ability in textiles. In fact,

ZnO is said to have the broadest spectrum absorption range among many inorganic UV absorbers. However, ZnO suffers from poor chemical stability. It can dissolve under both high and low pH conditions. TiO₂ has excellent chemical stability, but the UV-absorption range is narrower than ZnO so that it often relies on light scattering effects in addition to light absorption effects to block UV light. Due to these reasons, zinc oxide seems to be ideal for the preparation of highly UV-absorbing, nanosol-based coatings.

Textile and clothing are carriers of microorganisms such as bacteria and fungi because of the adhesion of these organisms on the fabric surface. Antibacterial finishes are applied in sport clothing, inner wears and medical textiles as a safe and effective means against various bacteria, fungi and chlamydia. These textiles are generally treated with silver ions, but also with zinc oxide (ZnO) nanoparticles, copper oxide (CuO) nanoparticles, aluminum oxide (Al₂O₃) and magnesium oxide (MgO) nanoparticles. The influence of ZnO nanoparticulate fillers on antibacterial effects of various polymer nanocomposites against both grampositive and gram-negative bacteria, represented mostly by *Staphylococcus aureus* and *Escherichia coli*, respectively, have been proven by many authors. ZnO NPs are added to polymers such as polyurethanes (Ma and Zhang, 2009, Li *et al.*, 2009) polypropylene (Altan and Yildirim, 2012), high density polyethylene (Li and Wang, 2010) or poly(vinyl chloride) (Geilich and Webster, 2013), where all authors observed reduction of bacterial species as compared to the initial untreated polymer samples. The use of 0.6% nano-ZnO for coating can be sufficient to provide antimicrobial property to wearable cotton textiles, whereas 1% of nano-ZnO is recommended for medical textiles due to its high antimicrobial activity. ZnO nanoparticles scores over nano-silver in terms of cost-effectiveness, whiteness and UV-blocking property.

In agriculture and electronic industry in the manufacture of LEDS and solar cells, field emitters, photo diodes, sensors, etc.

There are different electronic components, for example piezo-electric converters, transparent conducting oxides, sensors, luminous diodes, and optoelectronic or spintronic components, that at present are barely conceivable without zinc oxide. Zinc oxide-based semiconductors are used as transparent conductive layers in blue light-emitting diodes, liquid-crystal screens, and thin-film solar cells.

Light emitting diodes and solar cells: Since ZnO semiconducting NPs possess a wide band gap of about 3.37 eV and a large exciton binding energy at of 60 meV at room temperature, their electronic and luminescent properties have been extensively studied in connection with the potential applications in light emitting devices (LEDs). Within this field, most of the attention has been devoted to low dimensional structures such as ZnO quantum dots, nanorods or nanowires. ZnO can be combined with GaN for LED-applications since ZnO overlap with that of GaN, which has a similar bandgap (~3.4 eV at room temperature). Compared to GaN, ZnO has a larger exciton binding energy (~60 meV, 2.4 times of the room-temperature thermal energy), which results in bright room-temperature emission from ZnO. Moreover, organic light emitting diodes

(OLEDs) utilize a nanocomposite layer composed of a semiconductive polymer and luminescent ZnO nanoparticles (Willander *et al.*, 2010).

Dye sensitized solar cells (DSCs): DSSCs are the devices which convert visible light into electricity based on sensitization of wide band gap semiconductor. ZnO has been considered as a promising candidate for DSSCs due to its carrier mobility and direct band gap, and position of conduction band but in spite of these advantages, the efficiencies of zinc oxide based DSSCs are usually low. Continuous improvement of dye sensitized solar cells (DSCs) represents one option for harvesting energy from the light. For this purpose, DSCs based on ZnO hierarchical nanostructures manifested maximum conversion efficiency up to 5.4 % (Zhang *et al.*, 2009).

Field effect transistor: The zinc oxide (ZnO) nanostructures nanowire-based field-effect transistors (FETs) are the basic element for nano-electronics applications (Makhniy and Melnik, 2003). Also, the ZnO nanowires FETs are the fundamental building blocks for many nanoscale electronic devices. Early studies of zinc oxide (ZnO) nanowire FETs have focused only on their device performance, and photo detection (Jain *et al.*, 2016; Al-Sabahi *et al.*, 2016; Shan *et al.*, 2016). The interface roughness plays a prominent role in the electronic transport for transistors. The zinc oxide (ZnO) nanowires FET shows excellent properties, such as good transparency to visible light, excellent uniformity, and high mobility compared with traditional amorphous/polycrystalline silicon devices.

Photo diodes: The zinc oxide (ZnO) nanostructures are synthesized and fabricated as photo diodes also. There are increasingly plenty of scientific and industrial applications of photo diodes at nanoscale (Marie *et al.*, 2015; Kim *et al.*, 2014). The experimental analysis of zinc oxide (ZnO) reported that the nanostructures of ZnO heterojunction photodiodes consisting of p-Si and n-ZnO nanowire core and shell structures. The conformal coating made by an n-type ZnO layer that encircled a p-type silicon (Si) nanowire is applied in many photo diode applications. These photodiodes present enhanced ultra violet (UV) and visible responsivities compared to other planar thin film photodiodes (Singh *et al.*, 1984).

Biosensors: Biosensors (e.g. photometric, calorimetric, electrochemical, piezoelectric, among others when categorized based on the detection principles) are widely used in healthcare, chemical/ biological analysis, environmental monitoring, agriculture and food industry. Nanomaterials, alone or in combination with biologically active substances, are attracting ever-increasing attention since they can provide a suitable platform for the development of high performance biosensors due to their unique properties (Yakimova *et al.*, 2012). For example, the high surface area of nanomaterials can be employed to immobilize various biomolecules such as enzymes, antibodies, and other proteins. In addition, they can allow for direct electron transfer between active sites of the biomolecules and the electrode. Besides semiconducting properties, ZnO nanomaterials also exhibit various desirable traits for biosensing such as high catalytic efficiency, strong adsorption capability, and high isoelectric point (IEP; ~ 9.5) which are suitable for adsorption of certain proteins (e.g. enzymes and antibodies with low IEPs) by electrostatic interaction (Wang *et al.*, 2006). Furthermore, high surface area, good biocompatibility/stability,

low toxicity, and high electron transfer capability also make them promising nanomaterials for biosensors (Kumar and Chen, 2008). The majority of reported ZnO-based biosensors are for the detection of various small molecule analytes such as glucose, phenol, H_2O_2 , cholesterol, urea, etc.

Humidity sensors: ZnO nanocomposites also find applications as humidity sensors (Zainelabdin *et al.*, 2012). Humidity sensors are inserted into the textile along the weft direction as a replacement for weft yarn. Warp threads are replaced by conductive yarns to contact the sensors inside the textile. Humidity sensors have a detection range from 25 to 85% with 10% sensitivity. Several approaches of humidity sensor development via smart textile technology for healthcare applications as ulcer prevention, monitoring of sweat rate and moisture in wounds are put into use.

Gas sensors: Many researches have focused on the preparation of metal oxide semiconductor gas sensors in the form of thin films. These operate upon the change of the resistance of metal oxide nanoparticles due to the adsorption of reducing gases (Lee, 2009). Selectivity to hydrogen gas was achieved by sputtering Pd clusters on the nanorod surface. The addition of Pd is effective in the catalytic dissociation of hydrogen molecules into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 parts per million at room temperature, whereas there is no response to oxygen in a similar way, ZnO based sensors designed for nitrogen dioxide (Chen *et al.*, 2011), ammonia and ethanol (Zhang *et al.*, 2011) were successfully fabricated.

In food industry as an antibacterial agent and food packaging

ZnO shows photocatalytic properties and therefore it acts as an excellent antibacterial agent. This material can be activated by UV and visible light to form the electron-hole pairs. The holes thus formed can split the H_2O molecule (from suspension from ZnO) to OH^- and H^+ . Dissolved oxygen molecules on could be converted to superoxide radical anions ($\bullet\text{O}_2^-$) which react with H^+ to produce ($\text{HO}_2\bullet$) radicals. The collisions of ($\text{HO}_2\bullet$) with electrons produce the hydrogen peroxide anion (HO_2^-). These species react with hydrogen ions to produce H_2O_2 molecules that can penetrate the cell membranes and kill the bacteria (Padmavathy and Vijayaraghavan, 2008).

One of these essential applications is in food industry; as an antibacterial agent in food packaging and towards foodborne pathogen. Some of the main benefits of using NPs in food nanotechnology are the addition of NPs onto food surfaces to inhibit bacterial growth, also using of NPs as intelligent packaging materials and for nano-sensing (Chaudhry and Castle, 2011). Among these NPs, ZnO-NPs developed as a successful candidate in the food industry. The antibacterial influence of ZnO-NPs against foodborne pathogens stimulates proficient applications in food packaging, and can be introduced in food nanotechnology. Researches have showed that ZnO-NPs can inhibit and kill common as well as major foodborne pathogens. The bactericidal activity of ZnO-NPs (8–10 nm size) against *E. coli DH5a* and *S. aureus* was examined and found to be effective at 80 and 100 $\mu\text{g mL}^{-1}$. These concentrations disrupted the cell membrane causing cytoplasmic leakage (Kaur *et al.*, 2011). Narayanan *et al.*, 2012 tested the antibacterial activity of

ZnO-NPs against some human pathogens such as *P. aeruginosa*, *E. coli*, *S. aureus*, and *E. faecalis*. They emerged with the result that ZnO-NPs have strong antibacterial activity toward these human pathogens. Likewise, the antimicrobial activity of ZnO-NPs was studied (Chitra and Annadurai, 2013) toward *P. aeruginosa* and *E. coli* which were isolated from mint leaf extract and frozen ice cream, and ZnO was prepared using wet chemical method, yielding spherical morphology with smooth surface, of concentrations 20, 50, and 100 L. Both bacteria showed decreased growth rate at the highest concentration 100 L, and they explained the growth inhibition as a result of cell membrane damage through penetration of ZnO-NPs. Protection of food from microbial pollution is one of the main purposes in food packaging. The emergence of nanotechnology assisted to present novel food packaging materials with antimicrobial properties and with novel nano-sensors to trace and monitor the food. Several studies have addressed the antibacterial properties and potential applications of ZnO-NPs in food processing. For example, ZnO has been included into a number of food linings in packaging to avoid spoilage plus it maintains colors. ZnO-NPs provide antimicrobial activity for food packaging. Once they are introduced in a polymeric matrix, it permits interaction of food with the packaging possessing functional part in the conservation. The use of polymer nanotechnology in packaging was introduced by Silvestre *et al.* (2011) to achieve novel way of packaging that mainly meet the requirements of protection against bacteria. These materials with improved antimicrobial properties permit also tracking of food during storage and transfer.

Photocatalysis for waste water treatment

Nanostructured metal-oxide semiconductors are promising candidates for photocatalytic environmental remediation (Lines, 2008; Arivalagan *et al.*, 2011). Many kinds of semi-conductor oxides such as TiO₂, ZnO, Fe₂O₃, ZrO₂, have been widely used as photocatalysts in waste water decontamination (Padmavath *et al.*, 2008). Among those metal-oxide semiconductors, zinc oxide has attracted much attention for its high photosensitivity, environmental friendliness, low cost, and strong oxidizing power (Li and Li, 2010; Vijayakumar *et al.*, 2010; Qamar, *et al.*, 2015). In the field of photocatalysis, titanium dioxide (TiO₂) is undoubtedly the material most extensively studied (Asahi *et al.*, 2001; Maeda *et al.*, 2006). However, ZnO has been reported to exhibit photocatalytic activity comparable or sometimes even better to TiO₂ and is considered as a very promising alternative. Moreover, ZnO is cheap, low-toxic material that can be prepared by a large variety of methods (Rolison, 2003; Kim *et al.*, 2005). As the photocatalytic activity of semiconductors generally depends on crystal size, surface area, morphology and native defects, the abundances in morphologies makes ZnO representative material in the research field of photocatalysis (Arai *et al.*, 2007; Ang *et al.*, 2013). However, there are some non-ignorable faults in the wide band gap semiconductors (such as TiO₂ and ZnO) as photocatalysts because they can only be excited for photocatalysis under UV light irradiation (Linsebigler *et al.*, 1995; Han, 2005). It is noted that visible light with spectral wavelength between 400 and 700 nm accounts for about

45% of the total energy of the solar radiation, while UV light occupies less than 10%. Thus, it is of great interest to improve the photocatalytic activity for practical photocatalytic applications under visible light. Besides, the fast recombination rate of the photogenerated electron-hole pairs in the monocomponent semiconductors restricts their photocatalytic efficiency (Hoffmann *et al.*, 1995). Semiconductor/semiconductor heterostructure photocatalysts may increase the photocatalytic activity by extending the photo-responding range and increasing the charge separation rate (Serpone *et al.*, 1995). ZnO hollow spheroids were successfully used for the complete photocatalytic degradation of aqueous solution of rhodamine B (as the model organic dye used for textiles colouring) under UV light within minutes. Neither in the presence of ZnO spheroids and absence of UV light nor with UV illumination and without the ZnO, did any photocatalytic degradation of rhodamine B took place (Sinha *et al.*, 2010). Similarly, another group of authors synthesized nanorods assembled flowers which demonstrated 91 % and 80 % degradation of methylene blue and rhodamine B dye, respectively, within 140 minutes (Rahman *et al.*, 2013). In addition, the effect of morphology of ZnO particles prepared by microwave assisted solvothermal synthesis on photodegradation of methyl orange was evaluated among six different samples. The best result represented by 98% degradation of methyl orange within 40 min was manifested by hierarchically structured spheres; the authors' explanation was related to the highest specific surface area (Zhang and Zhu, 2009).

Conclusion

The properties of ZnO at nanoscale, applications in industries can be applied to many industrial applications. ZnO nanostructure material has gained much interest owing to its wide applications for various devices such as solar cells, transistors, transducers, transparent conducting electrodes, sensors and catalysts. ZnO nanoparticles are one of the most abundantly used nanomaterials in consumer products and biomedical applications due to their specific properties, e.g. transparency, high isoelectric point, biocompatibility and photocatalytic efficiency. ZnO nanoparticles used as antimicrobial agents in food packaging materials show good antimicrobial activity. ZnO nanoparticles are known for their anti-bacterial activity and hence it finds application in various commercial products such as cosmetics and sunscreens. The ZnO-based textile exhibit excellent photocatalytic and antibacterial activities, and it shows a promising sensing response. The combination of sensing, photocatalysis, and antibacterial properties provided by ZnO NRs is used in the concept of smart textiles for wearable sensing without a deodorant and antibacterial control. Advanced technologies included incorporation of moisture, temperature, pressure sensors, drug release, and fiber optics powered by textile-based batteries.

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Chapter 17

Application of husk charcoal for waste risk minimization by growing *Acacia mangium* (Willd.) on gold mining media

Basuki Wasis* and Kevin Assamsi

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Abstract

Husk charcoal is a crop waste that can be used to improve tailings media. Tailings have several characters including, low organic matter content, low microorganism activity, low essential nutrient content, low cation exchange capacity and high heavy metals. The design used in this experiment was a complete randomized design factorial with 2 factors. The first factor was the husk charcoal and the second factor was the application of compost fertilizer. The treatment of husk charcoal and compost did not significantly affect the growth of total dry weight and root

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shoot ratio. The interaction between husk charcoal and compost has a significant effect on total dry weight and root shoot ratio. The treatment of A4B1 (1000 g of tailing + 100 g of husk charcoal + 20 g of compost) gave the most significant effect on the total dry weight of *Acacia mangium* seedlings with an average of 9,630 g and with an increase in control of 57,53%. Husk charcoal, which is waste from rice plants and compost from urban waste, can be used for bioremediation of ex-gold mine land.

Keywords: *Acacia mangium* (Willd.), Environmental impacts, Gold mining media, Husk charcoal

Introduction

Excessive exploitation of natural resources and not paying attention to environmental aspects will have an impact on natural damage and a decrease in the quality of land. Activities of exploitation of natural resources which have an impact on decreasing the quality of land, namely mining activities of minerals such as gold mining, where the mining method is deep mining (Fauzi, 2006; Setiadi, 2006). The results of the processing of gold are produced by waste in the form of rock-dump and tailings. Tailings are one form of waste produced in large quantities in gold mining activities. Tailings have several characters including, low organic matter content, low microorganism activity, low essential nutrient content, low cation exchange capacity (CEC) and high heavy metal content (Winata *et al.*, 2016; Komboj *et al.*, 2017; Wasis and Andika, 2017; Wasis *et al.*, 2018). The tailings waste generated from the treatment process will be accommodated in special storage areas at the expense of the surrounding land which has an impact on decreasing the quality of the land. The clearing of forest land designated as a storage area for tailings waste needs revegetation as an effort to restore and restore land function. (Wasis and Andika, 2017, Wasis *et al.*, 2018). The success rate of revegetation activities is influenced by soil conditions (edafis), climate (climatic), type selection, and handling. The choice of type is prioritized using pioneer, catalytic, and fast growing species. The type of plant according to these characteristics is acacia (*Acacia mangium*).

One type of fast-growing plant commonly used for revegetation is *Acacia mangium*. Willd. (Herianto and Siregar, 2004; Siregar, 2004; Zulkifli, 2013). *A. mangium* does not require high growth requirements, *A. mangium* is able to grow on poor and infertile land such as land with low pH, eroded soil, and former logging and is easy to adapt to the local environment (Retnowati, 1998; Setiadi and Cakyayanti, 2014). Husk charcoal is a result of rice crop waste which is expected to be used to improve gold taling media. Compost is a municipal waste treatment product that is often used to improve soil fertility (Shalsabila *et al.*, 2017; Wasis *et al.*, 2018. Wasis *et al.*, 2019). The treatment of husk charcoal and municipal waste is new and needs to be tried to improve ex-gold mine land and increase the growth of *A. mangium*.

Materials and methods

Time and place of research

The research was conducted from September to November 2015, housed in a permanent nursery greenhouse dramaga, Faculty of Forestry IPB, and soil analysis in the Laboratory of the Department of Soil Sciences and Land Resources, Faculty of Agriculture, Bogor Agricultural University (IPB), Indonesia.

Experimental design and data analysis

Experimental design used was factorial completely randomized design with two factors. Factor A was husk charcoal with 5 doses (0, 25, 50, 75, 100 g) and factor B (0, 20, 40, 60 g) was compost with 4 doses. Each treatments were conducted with four repetitions. Obtained data based on measurement of height, diameter, total wet weight, total dry weight and Root-shoot ratio was analyzed by using linear model (Mattjik and Sumertajaya, 2013; Stell and Torries, 1991; Wibisono, 2009). Only if there is significant effect, Duncan's Multiple Range Test will be measured for getting further statistic data.

Research tools and materials

The tools used in this study are hoes, watering tools, small shovels, scales (analytical balance), digital scales, rulers, calipers, Tallysheet, calculators (stationery), stationery, digital cameras, Microsoft Excel 2007 software, and SAS 9.1.3 software. The materials used in this study were used as tailings gold media, polybags with a size of 20 cm x 20 cm compost, husk charcoal, and *A. mangium* aged ± 3 months.

Research procedures

The initial step taken in this study was the retrieval of tailings media in Pongkor District, Bogor Regency. This research was carried out through several stages, namely preparation of planting media, seed weaning, seedling maintenance, observation and data collection, as well as experimental design and data analysis.

Media preparation

The preparation stage includes media preparation and preparation of *A. mangium* seedlings. The prepared media consisted of the composition of tailings, compost, and husk charcoal. All of these ingredients are dry air. Measuring the composition of the media using scales (analytic balance) with the composition of the material for the media according to the dose, after obtaining a dose combination of each ingredient and then put into polybags. The dosage composition for control is tailings at a rate of 1 kg. The composition of the husk charcoal ingredients, each is 0 g/polybag (as a control), 25 g/polybag, 50 g/polybag, 75 g/polybag and 100 g/polybag. The dosage composition of compost fertilizer is 0 g/polybag (as a control), 20 g/polybag, 40 g/poly bag, 60

g/poly bag. Preparation of *A. mangium* seedlings was carried out including selection of healthy seedlings, which were uniform and fresh, fresh and free of pests and diseases.

Seed weaning and maintenance

Weaning is the stage of transferring *A. mangium* with its root ball (root ball) to the media prepared in the previous stage. Weaning is done in the afternoon. The steps taken in weaning *A. mangium* seeds are pressing polybags to compact the soil media. Then remove the poly bag and make a planting hole. The seedlings are planted into polybags along with the soil media to maintain the condition of the seeds so that the roots do not experience stress when weaning into the tailings media. All *A. mangium* was weaned, then placed in a greenhouse for 3 months. Watering is done in the morning and evening and weeding is needed as needed by observing the condition of the planting media in a polybag.

Data collection and analysis

Data collection was conducted every week in the period of September – November 2015. The variables observed were height and diameter. In the last week *A. mangium* seedlings were harvested. After that, those were weighed to know the wet weight. Then, seedlings were dried off in the oven at 80°C as long as 24 hours (Wasis and Fathia, 2011; Wasis and Angga, 2017). After that, *A. mangium* seedlings were weighed again to know the dry weight. In other hand, two samples of soil / tailing (planting medium) were analyzed to know the soil characteristics. The two samples of these medium were soil / medium with control treatment and the best treatment which gave the best growth preformance of *A. mangium*.

Results and discussion

Growth of *A. mangium* seedling in the tailing

The results of variance showed that the treatment of single husk charcoal, single compost fertilizer and the interaction of the combination of husk charcoal and compost did not significantly affect the height, diameter and total wet weight. The combination of husk charcoal and compost was significantly affected for total dry weight and root shoot ratio (Table 17.1). The Duncan test results of the interaction between the combination treatment of husk charcoal and compost showed that the treatment of husk charcoal of 100 g with compost 10 g with (A4B1) was the best combination treatment that could increase the total dry weight of *A. mangium* seedlings with an increase of 57.53%, while the lowest total dry weight in the combination of giving husk charcoal was 75 g with compost 60 g with an increase of control of -36.69% (Table 17.2). The combination of husk charcoal of 25 g and compost fertilizer of 40 g (A1B2) showed the highest yield and different from other treatments, with an average root shoot ratio value of 6.957 and an increase in percentage of control of 104.80%. Root shoot ratio was obtained based on a comparison between the dry weight of shoot tops divided by the dry weight of plant roots.

Table 17.1. The recapitulation of the variance of the effect of various treatments on the parameters of *A. mangium* seedling growth.

Parameter	Treatment		
	Husk charcoal	Compost	Husk charcoal x Compost
Height	0.0648 ^{tn}	0.1396 ^{tn}	0.0756 ^{tn}
Diameter	0.1510 ^{tn}	0.8830 ^{tn}	0.2904 ^{tn}
Total wet weight	0.7056 ^{tn}	0.6670 ^{tn}	0.8659 ^{tn}
Total dry weight	0.1615 ^{tn}	0.6560 ^{tn}	0.0233 *
Root shoot ratio	0.9918 ^{tn}	0.8293 ^{tn}	0.0485 *

* Factual treatment with trust range 95%, significant value ($Pr < F$) 0.05 (a) ^{tn} factual treatment with trust range 95% ($Pr > F$) 0.05 (a).

Table 17.2. Duncan's further test results interaction of husk charcoal and compost fertilizer on the total dry weight of *A. mangium* seedlings.

Treatment	Average of total dry weight (g)	Increasing toward control (%)
A0B0	6.113 bc	0.00
A0B1	5527 bc	-9.59
A0B2	6.737 abc	10.21
A0B3	5.917 bc	-3.21
A1B0	8.103 ab	32.55
A1B1	5.097 bc	-16.62
A1B2	5.230 bc	-14.44
A1B3	7.580 ab	24.00
A2B0	5.560 bc	-9.05
A2B1	6.747 abc	10.37
A2B2	7.023 abc	14.89
A2B3	7.927 ab	29.67
A3B0	5.870 bc	-3.98
A3B1	6.610 abc	8.13
A3B2	5.033 bc	-17.67
A3B3	3.870 c	-36.69
A4B0	6.417 bc	4.97
A4B1	9.630 a	57.53
A4B2	6.417 bc	4.97
A4B3	4.967 bc	-18.75

The number followed by the same letter shows that the treatment is not significantly different from the 95% confidence interval.

This value has an important role because with a balanced ratio between shoots and roots, the plants will grow well. The best root shoot ratio range from 1-3. (Wasis and Andika, 2017; Wasis *et al.*, 2018). Research shows that *A. mangium* seedling root shoot ratio > 3 shows that plants do not grow well on tailings media (Figure 17.1).

Effects on soil nutrient properties

Nutrient analysis was carried out at the end of the study, which was taken from several treatments as supporting data. Soil analysis was carried out on the control treatment (A0B0) and

Table 17.3. Duncan's further test results on the interaction of husk charcoal and compost fertilizer on *A. mangium* seedling root shoot ratio.

Treatment	Average of root shoot ratio	Increasing toward control (%)
A0B0	3.397 bc	0.00
A0B1	5.357 abc	57.70
A0B2	5.120 abc	50.72
A0B3	4.183 abc	23.14
A1B0	3.460 abc	1.85
A1B1	4.370 abc	28.64
A1B2	6.957 a	104.80
A1B3	3.470 abc	2.15
A2B0	6.920 ab	103.71
A2B1	3.167 c	-6.77
A2B2	3.690 abc	8.63
A2B3	3.257 c	-4.12
A3B0	4.060 abc	19.52
A3B1	4.250 abc	25.11
A3B2	3.953 abc	16.37
A3B3	6.070 abc	78.69
A4B0	4.993 abc	46.98
A4B1	3.417 abc	0.59
A4B2	3.710 abc	9.21
A4B3	5.630 abc	65.73

The number followed by the same letter shows that the treatment is not significantly different from the 95% confidence interval.

Figure 17.1. Growth of shoots and roots of *A. mangium* seedlings on media a) A0B0 (control); b) A1B2 (root shoot ratio Value 6,957); c) A2B1 (root shoot ratio value 3,167).

Table 17.4. Characteristic of planting medium (tailing) of *A. mangium*.

Parameter	A0B0	A4B1	Change
pH (H ₂ O)	7.4 N	7.45 N	+0.05
organic C (%)	0.07 VL	0.69 VL	+0.62
Nitrogen (N) (%)	0.03 VL	0.07 VL	+0.04
Phosphorus (ppm)	3.22 VL	22.8 M	+19.58
Calcium (Ca) (me/100g)	22.05 VH	4.05 L	-18.00
Magnesium (Mg) (me/100g)	0.83 L	3.69 H	+2.86
Potassium (K) (me/100g)	0.24 L	1.45 VH	+1.21
Cation exchange capacity (CEC) (me/100g)	2.39 VL	22.49 M	+20.10

Criteria for soil chemistry according to Hardjowigeno (2003), N = neutral VL = very low, L = Low, M = Medium, H = High, VH = very high

the best treatment was a combination of husk charcoal of 100 g with compost fertilizer of 10 g (A4B1) (Table 17.3 and 17.4). Based on the results of soil analysis shows that the most basic problem of tailings is the very low CEC value of 2.39 me/100 grams. At CEC very low, the water and nutrients given will be washed away.

Soils with high CEC are able to absorb and provide nutrients better than those with low CEC (Tan, 1994; Hardjowigeno, 2003; Kusuma *et al.*, 2013). In the treatment A4B1 has a CEC of 22.49 me/100 g so that the media can store water and nutrients higher than A0B0 (control). This study shows that the treatment of the interaction of husk charcoal and compost can increase soil CEC due to organic colloidal formation. The interaction of charcoal and compost can improve the physical, chemical and biological properties of the soil. Generally, soil with high texture such as tailings will have a low CEC due to low clay content (Hardjowigeno, 2003; Munawar, 2011, Phillip *et al.*, 2015).

The results of soil analysis on tailings media through the interaction treatment of 100 g of husk charcoal and 20 g of compost have also improved soil fertility. Increased soil fertility can be seen by increasing soil pH, organic C, soil N, available P, Mg, and K. Increased soil fertility has improved the growth of *A. mangium* plants. Fertilization aims to add nutrients to the soil with the aim of improving soil fertility (Tan, 1994; Hardjowigeno, 2003; Wasis *et al.*, 2018; Wasis *et al.*, 2019). But the treatment of husk and compost charcoal has not significantly increased the levels of N and P in the media, this is the main reason why the administration of husk and compost does not significantly influence the main parameters such as height, diameter and total wet weight. This research shows that husk charcoal which is an agricultural waste can be reused for bioremediation of ex-gold mine land. Likewise, organic waste from households that are processed into compost can also be reused to repair former gold mining land. The use of husk charcoal and compost can reduce agricultural land waste and can increase the growth of *A. mangium*.

Conclusion

The treatment of husk charcoal and compost fertilizer did not significantly affect the growth of total dry weight and root shoot ratio. The interaction between husk charcoal and compost has a significant effect on total dry weight and root shoot ratio. The treatment of A4B1 (1000 g of tailing + 100 g of husk charcoal + 20 g of compost) gave the most significant effect on the total dry weight of *A. mangium* seedlings with an average of 9.630 g and with an increase in control of 57.53%. The treatment of A2B1 (1000 g of tailing + 50 g of husk charcoal + 20 g of compost) gave the most significant influence on the root shoot ratio of *A. mangium* seedlings with an average of root shoot ratio 3.167. Husk charcoal, which is waste from rice plants and compost from urban waste, can be used for bioremediation of ex-gold mine land.

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Chapter 18

A case study on changing pattern of agriculture and related factors at Najibabad region of Bijnor, India

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Abstract

The study was conducted to assess the changing pattern of agriculture and related factors at Najibabad in Bijnor district of Uttar Pradesh. Survey was conducted in the study area for data

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collection. Data were collected from the villagers and farmers following simple random sampling technique, compiled and interpreted as per objectives of the study. Most of the farmers were middle aged and they had primary level of education with small and large farm size. Education level was increased among the farming families but the famers do not want to involve their educated children in farming therefore it was very difficult to increase the awareness among the farming families. A very less number of young aged children were found in the farming profession. About 70% of the farmers had medium knowledge on use of agro-chemicals in the crops. Land consolidation was also observed in the study area. During the last eight years minimum and maximum temperature was found nearly constant in the study area. During the last eight years rainfall was decreased from 170mm to 90mm. Therefore arrangement of need based training with more extension contact for the farmers and awareness campaign will be helpful to improve the behaviour of using agro-chemicals.

Keywords: Agro-chemicals, Crop production, Contaminants, Hand to mouth, Land consolidation, Land fragmentation

Introduction

Agriculture is the science and art or practice of cultivating the soil for the growing of crops, and raising livestock and the rearing of animals to provide food, wool, and other products and marketing of the resulting products. After hunting agriculture is the second oldest profession that mankind has learnt. Agriculture accounts for about one seventh of the GDP, provides sustenance to nearly two-third of our population. Besides, it provides crucial backward and forward linkages to the rest of the economy (MOCF, 2018). Agriculture has progressed from the primitive nomadic hand to mouth exercise to the present commercially profitable practice with the advancement of agricultural research and development efforts over several centuries. During last few decades it is observed that Indian agriculture has continuously switched over from traditional to scientific manner (Kuba and Jha, 2008). It is well known that agriculture is one of the backbones of the Indian economy and sustainability in the agricultural sector must address the issues of food security and stable generation of income for a fastly growing population (Lee, 2005; Bhutto and Bazmi, 2007). To achieve maximum production and to earn maximum profit Well-judged application of fertilizers by the farmers in crops is very much essential. Most of the farmers are using continuously larger quantities of chemical fertilizers to increase production without knowing the fertility status of the soils of their fields (Srivastava and Pandey, 1999; Yadav *et al.*, 2006). Declined soil fertility can be combat by traditional practices. The traditional practices include a wise use of livestock in cropping systems, where livestock provides traction power for tillage, manure for organic matter and cash income for the purchase of mineral fertilizers. The manure is obtained through symbiotic arrangements between farmers and herdsman where animals are corralled on farmers' fields in exchange for food (Enyong *et al.*, 1999).

Adoption of new agricultural technology is influenced by physical, mental and socio-economic factors including, agro-ecological conditions, age, family size, education, source of information, and farmer's attitudes towards the technology (Feder *et al.*, 1985; Rogers, 2003; Neupane *et al.*, 2002). Farmers of high rainfall regions are more likely to be found to adopt improved maize varieties and chemical fertilizers (Kaliba *et al.*, 2000; Hintze *et al.*, 2003). In comparison to old farmers, young farmers easily adopt a new technology because they have had more schooling and are more susceptible to attitude change (CIMMYT, 1993; Byerlee, 1994). Education level also affects the decision making and the adoption of agricultural technologies. Family size plays a role on labour provision. Adoption of new varieties requires more labour inputs (Feder *et al.*, 1985). Knowledge influences adoption. Farmers who have sufficient knowledge of technology use are likely to adopt it easily (Abebaw and Belay, 2001; Rogers, 2003). Farmers' attitudes determine adoption of improved technology. Attitudes are evaluative responses towards the technology, and are formed as farmers gain information about it. Adopters tend to hold positive attitudes towards the technology (Chilonda and Van Huylenbroeck, 2001).

Presently the world shows considerable worries on the destructive effects of advanced agricultural technologies on the environment, natural resources and long-term sustainability of agronomy systems (Sadati *et al.*, 2010). Soil erosion, water pollution, excessive use of chemicals, waste of water, destruction of natural habitats for wildlife and insects and pests resistance against insecticide and pesticide are only a few of the concerns expressed by environmentalists, public, agricultural professionals, policy makers and farmers (Leeuwis, 2004; Al-Subaiee *et al.*, 2005). Despite these environmental effects at many places, the modern agriculture has been involved in many economic and social changes both in the industrial and developing countries. Among this involvement one may name: loss of job, transfer of economic opportunities from men to women, increasing specialization in livelihood, the rural institutions becoming governmental and many other cases (Pretty, 1995; Atte, 1989; Minakshi and Pirabu, 2015). Large number of small and marginal farmers (82%) pose momentous challenge to Indian agriculture (Bhalla *et al.*, 2012) because it rises the problems like land fragmentation, poverty (Chand *et al.*, 2011), low bargaining power to farmers, low risk bearing ability, low productivity, low extension contact etc. (Hegde, 2010; Nikam *et al.*, 2015). The problem of productivity dissimilarity (risk) among farms is more noticeable in areas with uncertain water supply (Abel, 1975). The presence of risk in agriculture has long been viewed as having a serious impact on farmers' production decisions (Bond and Wonder, 1980; Sekar and Ramasamy, 2001).

Due to uncertain and low rainfall, harsh weather, degraded soil fertility, lack of knowledge and lack of irrigation facility the agriculture in the area under study is going to become restrict to only some people. A large number of the people handover their agricultural land to other people on share basis. As the census indicates that population in the city become approximately four times during the last twenty years. Increasing population put a pressure on the natural resources as well as on the agriculture. Large population demands more food but area available for agriculture is decreasing continuously.

- To study the increase or decrease in the number of farmers in the selected villages.
- To study the changing pattern of crops and agricultural land in the area.
- To study the changing pattern of fertilizer used by the farmers.
- To study the type of pesticides, insecticides and herbicides used by the farmers.

Study area

Figure 18.1. Map Showing the city Najibabad and the village around the city.

The summer season is characterized by heat with maximum temperature of 44°C, while in winter season cold waves are frequent which bring down the temperature to a minimum of 2°C. The soils in this area are originated from Siwalik Belt of Himalaya. Generally sandy, clay-loam and light loam soils are found. The city of Bijnor under study is Najibabad (29.63°N 78.33°E). It has an elevation of about 295.5 metres (1014 feet). In 1901, Najibabad had a population of 19568 while in 2011 it was 88535.

Study design and data collection

The study was conducted in the selected villages of city Najibabad in Bijnor district of Uttar Pradesh. The Area was selected for time and resources availability, well communication facilities to carry out the research study in this area. The total numbers of farmers of the research villages were the population of the study. Data were collected through direct interview using questionnaire of questionnaire. The interview schedule was prepared in Hindi for easy understanding and for the easy collection of data (Iqbal *et al.*, 2014). Some data was collected from the official website of Krishi Vigyan Kendra, Bijnor. The Methodology was adopted from Nikam *et al.* (2015) and Zaidi and Munir (2014). Simple random sampling technique was used for the data collection among the total population. The population for the study of the objective 2, 3 and 4 were the farmers, private shopkeepers and Shahkari samities (Govt. Shop of fertilizers and pesticides). For the first objective the population was the villagers and farmers.

Results and discussion

A survey was carried out in the study area to know the status of agriculture and related factors. Survey was carried out with help of personal interview using questionnaire and with the help of meetings with the elder persons of the villages.

Change in the rainfall

The amount of rainfall in mm and the number of rainy days was presented in the Figure 18.2. From the figure it was observed that amount of rainfall was decreasing continuously from 2010 to 2018. More than 150 mm rainfall was observed in 2010 but it reduced to 110 mm in 2011. During 2012 and 2013 the rainfall was same and it was approximately 140 mm. During 2014 the rain fall was found below 50 mm (approximately 40 mm) while in the year 2015 the rain fall was found above 50 mm (approximately 60 mm). During 2016, 2017 and 2018 the rainfall was about 75 mm to 90 mm. During last 18 year the rainfall was decreased approximately 50 mm. During all the years the rainfall was uncertain. Although in the some villages of study area irrigation facilities are available but not in all the villages. In most of the villages the sources of irrigation are surface water bodies such as pond and rivers and in some cases tube well driven by the tractors or other engines due to lack of power supply.

Decreased amount of rainfall increased the cost of the crops as well as type of crops grown in the

study area. There is a shift in the type of crops grown by the farmers towards the crops which can bear the shortage of water such as sugarcane. A large damage of crops was also observed in the study area sometimes due to shortage of water (in summer season) and sometimes due to lodging of water (in monsoon season) and also due to soil erosion by the river water (in some villages Malin was responsible and in some villages Rāmgangā was responsible).

Change in temperature

The minimum, maximum and average temperature was presented in the Figure 18.3. During the last eight years a very small change in temperature was observed. Maximum temperature during summer season was ranged from 38°C to 42°C while during winter season was ranged from 19°C to 22°C. During summer season minimum temperature was ranged from 26°C to 28°C while

Figure 18.2. Rainfall amount (mm) and Rainy days of Najibabad city from 2010-2018 (Source: Website of KVK Bijnor).

Figure 18.3. Maximum and minimum temperature of Najibabad city from 2010-2018 (Source: Website of KVK Bijnor).

during winter season minimum temperature was ranged from 6°C to 10°C. Pattern of temperature change was found similar to the pattern of rainfall in the study area. Temperature has direct effect on the produce of some crops such as wheat and paddy. In the study area a sharp increase was observed in the temperature during late winter which affects the yield of wheat crop in the area. Crops sown earlier give a better yield than the crops sown later. Similar findings were observed by Zhao *et al.* (2017) and Asseng *et al.* (2015).

Change in the percentage of farmers

An extensive survey was carried out to know the change in the number of farmers in the study area and data was presented in the Table 18.1. A drastic decrease was found in the number of farmers in the study area. People do not want their children to adopt this profession because of

Table 18.1. Villages, population and percentage of farmers in the villages of study area.

Name of the site	Present population	Percentage of farmers	
		Before 2000	After 2000
Akbarpur Chauganna	2950	65	20
Akbrabad	6238	60	25
Alipura	4767	65	30
Barampur	2,390	65	30
Basera	1024	65	28
Bhaguwala	13036	60	18
Budgara	3422	70	28
Budgari	2325	70	30
Chandouk	2900	65	30
Dhansini	2649	75	25
Dhanora	2549	70	25
Fajalpur Habib	3413	80	30
Harsuwara Ahatmali	4028	50	15
Humayun Puriddu	1429	75	30
Issepur	2897	70	25
Jaswantpur	5064	80	30
Jatpura Bhonda	2483	80	30
Jawalilala	2698	85	35
Kalhedi Bila Ahatmali	1078	60	15
Kalyanpur	514	85	30
Kamrajpur	3244	80	25
Kishorpur Ahatmali	2134	85	32
Mauzampur Sadat	1752	85	30
Meman	5527	70	25
Mohamadalipur Hirdey	3527	60	12
Mubarakpur	3244	50	10
Najimpur	636	70	20
Nangal	6576	80	28
Nangla Ubhan	1181	85	30
Narayanpur Inchha	402	90	40
Puranpur Garhi	3216	80	30
Purshotampur	2251	70	30
Rahatpur Khurd	3789	70	25
Sabalgah	4187	75	22
Samipur	4533	60	18
Shyami Wala	3945	70	20
Tisotra	3921	65	20

uncertainty in the yield of crops due to different factors. In some villages we found that some families completely turned towards other profession. In most of the villages we found that land owner were performing agriculture on the sharing basis by other peoples while they himself was involves in other business. An alarming situation of agriculture was observed in the study area. A very less young generation was found involved in the profession of agriculture. During the survey we found that in all the villages percentage of people involved in the agriculture was decreasing. Before 2000 in all the villages percentage of farmers was ranged from 50% to 90% while after 2000 percentage of farmers was ranged from 10% to 40%. Maximum percentage of farmers before and after 2000 was observed in the same village named Narayanpur Inchha due to low education level and more number of financially backward families.

Change in cropping pattern

Earlier the farmers of the study area used to grow maize, barley, jowar or bajra, wheat, rice, pulses vegetables and sugarcane. But now the farmers grow only wheat, rice, vegetables and sugarcane. Only few farmers grow maize, barley and Jowar or bajra and they grow these crops only for animal feeds and not for the human consumption while in olden day's people grow these crops for both the purposes. Zaid crops such as watermelon, muskmelon and cucumber are grown by only a few farmers. In the study area Cucumber dominates among all the zaid crops. The whole study area is observed dominated by sugarcane due to its high resistance to water scarcity and because of its regeneration power.

During the survey we observed that pulses and vegetables are completely vanished from some villages along with zaid crop. Before 2000, approximately 50% farmers in the study area used to grow ground nut but now only few farmers in few villages grow ground nut and in most of the villages people do not grow this crop. Cropping pattern of study area along with whole state is dependent on the monsoon rainfall and water availability (Singh *et al.*, 2011). The major cropping pattern of study area observed during the survey is Rice-wheat and sugarcane. Similar findings were observed by Singh *et al.* (2011) and Goyal and Kumar (2013).

Change in the fertilizers use patterns by the farmers

During the survey we found that the average farmer doesn't know as much about fertilizer as some think he does. They do not want to go in the detail of the fertilizer. There are only few farmers who know about the different type of chemical and biological fertilizers. We found that farmers did not have any idea about the dosing of fertilizer and they also did not know about the soil testing facility available in the area and most of them are unaware of the term "soil testing" due to lack of education. Before 2000 farmers prefer to put manure in their fields but after 2000 there is an era of chemical fertilizers. But now we observed reducing trends of chemical fertilizers among the farmers of the study area. Farmers now preferring organic fertilizer instead of chemical fertilizers due to the bad consequences of chemical fertilizers.

One thing was also observed during the survey that before the farmer buys fertilizer, he often

turns to others around him for advice. Nearly 60% covered in the study report one or more talks with people close to the situation. Most often the farmers consult with dealers of local market due to lack of knowledge (Zaidi and Munir, 2014).

Change in the land possession pattern

In the study area from the survey it was revealed that in olden days most of the people hold small piece of land but now the land consolidation was observed (number of land owner was decreased and size of land holding was increased). Size of farms was increased in comparison to olden days. Most of the people were found leaving farming profession due to damage of crops by natural as well as anthropogenic factors. Uncertain rainfall, damage due to animals and a very increment in the price of fertilizers

(urea from Rs. 210 to Rs. 270, DAP from Rs. 500 to Rs. 1250) pesticides and a very low increase in the price of crops. From the last of 5 years price of sugarcane increased from Rs. 240 to Rs. 310. This may be the reason that peoples are leaving farming. Due to this land fragmentation decreased and land consolidation increased.

Change in the education pattern

Illiteracy is a serious problem of India. In rural India, literacy rate is too painful. The role of education in the development of agriculture hardly needs any emphasis. Education creates a favourable mental attitude among the farmers for the acceptance of new practices, especially information-intensive and management-intensive practices (Waller, 1998 and Caswell, 2001). During the survey we observed an increasing trend of education among the villager. However dominant education level was found senior secondary. Figure 18.4 gives the

Figure 18.4. Percentage of different education groups.

graphical representation of this data.

Willingness and ability to adopt new farming techniques

Farmers, who are motivated and have the required skills, are likely to be the most successful technology adopters. As shown in Figure 18.5, program designers can more cost effectively target interventions if information about both farmer ability and farmer willingness is available. Education also plays an important role in the adoption of new technology. The farmers which have intermediate level of education easily adopt the new technology. The age group also have an impact of on the adoption of new technology (Gaffney *et al.*, 2013).

Change in the pesticides use patterns

India is the second largest manufacturer of pesticides in Asia after China and ranks 12th globally (Mathur, 1999). Herbs compete with the crops for nutrient and sunlight such as *Phalaris minor* (Locally known as Bandri grass) compete with the winter crops mostly with the wheat crop. It is essential to remove these weeds and insects from the crops for healthy crops and good crop yields. The use of bio-pesticide has increased 66 times in India in 10 years—from 123 tonnes in 1994-95 to 8110 tonnes in 2011-12 resulting a declined in chemical pesticide by one-third from 75033 tonnes in terms of technical grade in 1990-91 to 50583 tonnes in 2011-12. Consumption of pesticides in India is less than 1 kg/ha as against 4.5 kg/ha in USA and 11 kg/ha in Japan.

Figure 18.5. Willingness and ability to adopt new technology (Source: Gaffney *et al.*, 2013)

Figure 18.6. Origin, transport and fate of pesticides (Source: WHO, 2002)

Figure 18.7. Consumption pattern of pesticides (Source: Mathur, 1995)

Presently there are only 230 registered pesticides in India, while it's more than 1000 in the US and for the EU, it is around 700.

Out of these, 66 pesticides are banned in India but are exported (MOCF, 2013). This is because use of pesticides tends to be more intense and unsafe, and regulatory, health and education systems are weaker in developing countries (UNEP, UNICEF, WHO, 2002). In the study area similar trend in the use of pesticides was also observed. Now the farmers preferred bio-pesticides (onion and Neem leaves) instead of chemical pesticides. The distribution route and how these pesticides affect receptor organism were shown in Figure 18.6. Pesticide usage pattern in India is different from that for of the world. From the Figure 18.7, it can be seen that in India 76% of the pesticide used is insecticide, as against 44% globally (Mathur, 1999). If the credit of enhanced economic potential in terms of increased production of food and fibre and reduction of vector-borne diseases goes to pesticides then their impacts have resulted in serious health implications to man and his environment (Aktar *et al.*, 2009).

Conclusion

On the basis of present study it was concluded that the percentage of famers was continuously decreasing in the study area. Number of young people involved in the farming was also found decreasing in the study area. Due to industrialization job opportunities was increased resulting in the less involvement of young people in the farming and related activities. Land consolidation was also observed in the area. This study has confirmed that extension should strengthen farmers' knowledge and skills in fertilizer application through literacy programs. A very less number of awareness campaign was observed in the study area resulting in the lack of knowledge of modern tools and techniques, about fertilizers and pesticides. So there is an urgent need of such awareness programme in the study area.

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Chapter 19

Riverbed mining as a threat to in-stream agricultural floodplain and biodiversity of Ganges River, India

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Abstract

Growth of urbanization, infrastructural and economic development activities in the last few decades all over the world have increased the demand of riverbed material for construction purposes. This high demand of materials has resulted in unsystematic and unscientific mining in in-stream and floodplain and agricultural area of the river basin and has caused severe damage in

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the form of changes in channel morphology, degradation of water quality, loss of biodiversity (aquatic and terrestrial), soil erosion and loss of agricultural fields. The present study makes an attempt to know the effect of riverbed mining in in-stream and floodplain area of River Ganga. Also, suggestions have been made thereafter for the improvement of the overall River Ganga basin.

Keywords: Environmental impacts, Floodplain mining, Haridwar, In-stream mining, River Ganga, Riverbed mining

Introduction

Rivers are the main source of riverbed materials (boulder, stone and sand) and also provide habitat for many aquatic and terrestrial animals and plants (Lu *et al.*, 2007; Padmalal and Maya, 2014). Riverbed mining is an extraction activity, unrelated to the process of navigating degrading (Kondolf, 1997; Padmalal and Maya, 2014; Kamboj *et al.*, 2017). The mining process involves the displacement of bottom sediments and underlying materials and is adopted by using some mechanical or physical dredge style operation (Erskine, 2008; Erskine *et al.*, 1985). The riverbed materials like sand, gravel and boulder are mechanically removed from river channels for a variety of reasons i.e. to improve navigation, flood control, agricultural drainage, and stability of river channel and production of construction aggregate (Kondolf, 2000; Erskine, 2008). The extraction of riverbed materials: sand, gravel and boulders for construction purpose is the largest mining industry all over the world. Nowadays, the population increase has increased the demands on the riverbed materials increase to develop the urban and industrial sector (Sreebha and Padmalal, 2011). The excess amount of riverbed mining causes many problems like channel erosion, degrading of water quality, groundwater depletion, loss of aquatic habitat, loss of riparian vegetation and flood-like conditions (Kamboj *et al.*, 2012; Kamboj *et al.*, 2017). The aquatic habitat like stone and boulder, are the habitat of many fishes and other aquatic animals. Fishes are spawning into the stone and boulders where the fish eggs are protected from the predators and other factors. But due to mining these stones and boulders are removed from the riverbed which affects the population of the fishes (Kondolf, 1994; Erskine, 2008). Due to these developments, the removal of riverbed materials in in-stream and floodplain area of the rivers shows the up hazard and unscientific mining activity (Sreebha and Padmalal, 2011). The up hazard and unscientific mining create severe environmental impact in that area where an excess amount of mining occur i.e. in-stream and floodplain area. In-stream mining involves the mechanical removal of riverbed materials (sand, stone and gravel) directly from the active channel of rivers and streams. Active channel deposits are desirable as construction aggregates because they are typically strong, well-sorted, and frequently located near markets or on transportation routes. In-stream mining commonly causes morphology of the river and channel erosion, which can spread the river in upstream and downstream for kilometers (Kondolf, 1994). Floodplain mining involves the

mechanical removal of riverbed materials (sand, stone and gravel) directly from the non-active channel of rivers, river bank and agriculture field. These types of mining mainly occur in nearby areas of rivers. Floodplain mining, commonly causes nearby vegetation, agriculture area and land use of the area. Because of the high demand for raw materials, this type of mining increase in an illegal way (Langer, 2003).

River Ganga also faces these types of problems in the Haridwar district of Uttarakhand state. So the present study is carried out to know the effect of riverbed mining activity in in-stream and floodplain area of River Ganga. The altered water quality due to incorporation of different kinds of soil contaminants from the river-bed mining practices has been discussed as well.

Materials and methods

Study area

The present study was carried out from June 2017 to May 2018 in the River Ganga, near Bhogpur village in district Haridwar (Figure 19.1). Haridwar district covers an area about 2360 sq. Km in of the western part of the Uttarakhand state of India. The geo-coordinates of the district Haridwar are as follows: Latitude: 29° 56' 52.48" N Longitude: 78° 09' 36.90" E. In Haridwar district, Bhogpur

Figure 19.1. Satellite map of study area of River Ganga (Source: Google Earth).

village is famous for providing the raw material (sand, gravel and boulders) for construction purpose. The Geo-coordinates of the Bhogpur village are as follows: Latitude: 29° 51' 43.79" N and Longitude: 78° 08' 34.17" E. In Bhogpur village (Haridwar) the mining activity takes place in two ways: 1. In-stream mining 2. Floodplain mining.

Methodology for in-stream mining area

Channel morphology: The changing in channel morphology of River Ganga in two decades was analysed through satellite image (Google earth pro) and drainage map made by using QGIS (free trial version). The data was collected from the official site of USGS (Landsat 4-5 TM C1, Landsat 7 ETM+C1) to find out the changes in land use/land cover and ground survey was conducted.

Physico-chemical analysis of surface water

The Sampling of Physiographical parameters, water quality parameters (physico-chemical) and Fish fauna were performed from June 2017 to May 2018. The physiographical parameters were analysed through visualization and studied as per standard methods (Wentworth, 1922). Water samples were collected from 2 different stream orders of River Ganga in Bhogpur village by grab sampling. The water samples were collected from 8 a.m. to 10 a.m. when mining is active. A total of 15 physico-chemical parameters, water velocity, river depth, water temperature, Conductivity, pH, TDS, Analytical parameters like alkalinity, total Hardness, calcium, magnesium, dissolve oxygen (DO), BOD, sodium and potassium were analysed in the laboratory, following the standard methods (APHA *et al.*, 2012; Trivedy and Goal, 1998). Experimental fishing was carried out in the River Ganga with the help of locally hired professional fisherman. Fish species were collected with gill nets (mesh size 2.5 × 2.5 cm; 3 × 3 cm; 7 × 7 cm; length × breadth = 75 × 1.3 m; 50 × 1 m), cast nets (mesh size 0.6 × 0.6 cm), drag nets or locally called Mahajal (mesh 0.7 × 0.7 mm, L×B = 80 × 2.5 m with varying mesh size) and fry collecting nets (indigenous nets using nylon mosquito nets tied with the bamboo in both ends. All the gears except cast nets were used at least ten times during sampling. The cast nets (5.5 m²) were operated 20 times in sampling area covering about 100² meter of river segment allowing 3-5 minutes settled times in each cast. Fish species identified by Day (1875); Badola and Pant (1973).

Methodology for floodplain mining area

The Sampling of Riparian Vegetation was performed from June 2017 to May 2018. Riparian vegetation sampling was done by Quadrature method. For vegetation samples, a total of 5 sampling plots were selected on 2-3 Km stretch of River Ganga. The size of quadrates was decided by number of species-area curve and mostly 5 m × 5m for shrubs, and 1 m × 1 m for herbaceous species. Identification of the Phyto-diversity was done with the help of standard identification (Gangwar and Gangwar, 2011; Gangwar and Joshi, 2006). Data was collected by ground survey and secondary data was collected from the forest department. The data of mining activity in the agricultural field of Bhogpur village was taken with the help of photographs.

Statistical analysis of the data

The data presented in this study is mean followed by standard deviation of three replicates.

Results and discussion

Channel morphology

The change in flow energy of water and sediments has evolved the river channel in different bed forms. The flow of the river built up and maintains the river channel by deposition of sediments and erosion of nearby area (Whiting, 1998; Heede, 1986; Padmalal and Maya, 2014). Riverbed mining is one of the most devastating anthropogenic activities which affects and obstructs the natural riverbed forms. Extraction of riverbed materials targets the morphology of river and disturbs the balance of river channels by interception of the material load. The changes in channel pattern are due to the reduced supply of bed load sediments. Due to the riverbed mining activity, the main channel got divided into the various small stream orders which led to the different riverbed forms. The changes in the channel morphology of River Ganga near Bhogpur village are shown in Figure 19.2 through satellite images of 1991, 2001, 2011, and 2017. Figure 19.3 shows the drainage map of River Ganga during 1991, 2001, 2011, 2017 and demonstrates the large measurable changes in channel pattern of River Ganga over two decades.

Figure 19.2. Changing pattern of channel morphology of River Ganga in Bhogpur Village during 1991, 2001, 2011 and 2017.

Figure 19.3. Drainage map of River Ganga shows changes in channel morphology in Bhogpur Village during 1991, 2001, 2011 and 2017.

In the past two decades, both manual and mechanical mining has changed the channel pattern in way of channel instability, changes in channel width, division of the main channel in various small stream orders and bank erosion. In the upstream mining, the head cutting of channel increase the slope of the river. Gravel bar skimming found out during the study period and it creates the instability of channel and changes the width of the river. Kondolf (1997); Kondolf and Swanson (1993) show the change in channel pattern due to the dams and gravel mining. Rinaldi (2005); Padmalal and Maya (2014); Kamboj *et al.* (2017) also described the effect of sand mining on channel morphology like changes in width, an increase of slope due to the upstream mining, instability of channel due to the downstream mining, changes in cross-sectional area of the river.

Physiographical parameters

The physiographical parameters are an important part of the river bed; it is the mixture of boulder, stone, gravel, cobbles, sand, silt and clay. The physiographical parameters of River Ganga are shown in Table 19.1. During the study period, the bottom substrate covered with 2% boulders, 16% cobbles, 22% pebbles, 15% gravel and 45% sand. The physiographical parameters important for the aquatic organisms for their reproduction process, and habitat of many aquatic organisms like benthos, fishes (Figure 19.4).

Figure 19.4. Physiographical parameters of river Ganga at Bhogpur village.

Water quality parameters

The physico-chemical parameters provide a fair idea of water quality of a water body. A total of 15 water quality parameters were selected to know the quality of River Ganga in a stretch of Bhogpur village shown in Table 19.2. Mean of water velocity 2.3 ± 1.9 m/s, average depth of river 5.6 ± 1.4 ft, average water temperature of river water $20.9 \pm 4.6^\circ\text{C}$, mean pH value of river water 7.6 ± 0.6 ; conductivity value 171.8 ± 44.7 $\mu\text{S/cm}$; TDS value of river water 115.1 ± 29.9 mg/L; turbidity value of river water 177.5 ± 204.1 NTU; dissolved oxygen of river water 7.8 ± 0.5 mg/L; biochemical oxygen demand (BOD) of river water 1.7 ± 0.6 mg/L; alkalinity of river water 87.9 ± 11.6 mg/L as CaCO_3 ; total hardness of river water 129.8 ± 16.6 mg/L, average value of calcium and magnesium 63.5 ± 9.1 mg/L and 18.2 ± 2.15 mg/L respectively, average value of sodium and potassium 3.6 ± 0.7 mg/L and 2.2 ± 0.4 mg/L respectively were recorded during the study period. All the parameters were within the permissible limit given by BIS standards 2012, except turbidity. During the study period, turbidity was higher because of the mining activity but the turbidity of water persists temporarily because of the high velocity of water (Figure 19.5).

Table 19.1. Physiographical parameters of River Ganga at Bhogpur village (Haridwar).

Physiographical variables	%
Boulders (>256mm)	2
Cobbles (64-256mm)	16
Pebbles(16-64mm)	22
Gravels(2-16mm)	15
Sand(<2mm)	45

Table 19.2. Average value of water quality of River Ganga at Bhogpur village (Haridwar).

Parameters	Mean $\pm$ S.D.	BIS Standards (2012)
Water velocity (m/s)	2.3 $\pm$ 1.9	----
Depth (ft)	5.6 $\pm$ 1.4	---
pH	7.6 $\pm$ 0.6	6.5-8.5
Conductivity (μ S/cm)	171.8 $\pm$ 44.7	300
Water temperature ($^{\circ}$ C)	20.9 $\pm$ 4.6	--
Turbidity (NTU)	177.5 $\pm$ 204.1	5-10
TDS (mg/L)	115.1 $\pm$ 29.9	500
Dissolve oxygen (mg/L)	7.8 $\pm$ 0.5	5
BOD (mg/L)	1.7 $\pm$ 0.6	5
Sodium (mg/L)	3.6 $\pm$ 0.7	---
Potassium (mg/L)	2.2 $\pm$ 0.4	---
Total hardness (mg/L)	129.8 $\pm$ 16.6	300
Alkalinity (mg/L)	87.9 $\pm$ 11.6	120
Ca (mg/L)	63.5 $\pm$ 9.1	75
Mg (mg/L)	18.2 $\pm$ 2.15	30

Figure 19.5. Water quality of River Ganga at Bhogpur Village.

Fish fauna

In Haridwar region, a total of 20 fish species belonging to 5 families were found in River Ganga (Table 19.3 and Figure 19.6), in which Cyprinidae family were the dominant (>60 % of total fish catch) in the riverine segment of the river Ganga, while the fish diversity diminished in Bhogpur village because of the mining activities (mining impacted area). The reason for the decline in the fish diversity in this region was found to be unscientific mining. Due to the mining activity, River Ganga got divided into the small stream orders. In the summer and winter season these stream orders are dry and all the aquatic animal's phytoplankton, zooplankton, benthos and fish were disturbed during these seasons. Stream orders are shown in Figure 19.2 and Figure 19.3. In Past decades, some researchers like Khanna *et al.* (2013); Vass *et al.* (2010); Sarkar *et al.* (2012) studied the diversity of fish in the Ganga River in lower Shivalik Himalaya and show the present status of fish in River Ganga. In the Bhogpur Patch of Ganga river, some fish species were showing the abundance, and some fish species rarely found due to the anthropogenic activities like river bed mining.

Table 19.3. Status of fish diversity in the Bhogpur village stretch of river Ganga.

Scientific Name	Common Name	Present status	Past decades fish fauna status of Ganga River	References
Family- Cyprinidae				
<i>Tor tor</i>	Mahseer	-	P	Khanna <i>et al.</i> (2013) Nautiyal <i>et al.</i> (2013) Vass <i>et al.</i> (2010) Sarkar <i>et al.</i> (2012)
<i>Cyprinus carpio</i>	China carp	+	P	Sarkar <i>et al.</i> (2012) Nautiyal <i>et al.</i> (2013)
<i>Rainas bola</i>	Indian trout	*	P	Khanna <i>et al.</i> (2013) Sarkar <i>et al.</i> (2012)
<i>Barilius bendelisis</i>	Fulra	+	P	Khanna <i>et al.</i> (2013) Sarkar <i>et al.</i> (2012)
<i>Barilius barna</i>	Gunthala	*	P	Khanna <i>et al.</i> (2013) Sarkar <i>et al.</i> (2012)
<i>Garra gotyla gotyla</i>	Gunthala	-	P	Khanna <i>et al.</i> (2013) Nautiyal <i>et al.</i> (2013)
<i>Puntius ticto</i>	Ticto barb	*	P	Khanna <i>et al.</i> (2013) Sarkar <i>et al.</i> (2012)
<i>Puntius sophore</i>	Dark mahseer	*	P	Khanna <i>et al.</i> (2013)
<i>Labeo rohita</i>	Rohu	+	P	Khanna <i>et al.</i> (2013) Sarkar <i>et al.</i> (2012)
<i>Crossocheilus latius latius</i>	Gangatic latia	*	P	Sarkar <i>et al.</i> (2012)
Family - Cobitidae				
<i>Noemacheliopus rupicola</i>	Gadiyal	+	P	Khanna <i>et al.</i> (2013) Nautiyal <i>et al.</i> (2013)
<i>Noemacheliopus beavani</i>	Gadiyal	+	P	Khanna <i>et al.</i> (2013)
<i>Noemacheliopus montanus</i>	Gadiyal	-	P	Khanna <i>et al.</i> (2013)
<i>Noemacheliopus Savone</i>	Gadiyal	-	P	Khanna <i>et al.</i> (2013) Nautiyal <i>et al.</i> (2013)
<i>Noemacheliopus multifasciatus</i>	Gadiyal	-	P	Khanna <i>et al.</i> (2013)
<i>Botia dario</i>	Bengal loach	*	P	Khanna <i>et al.</i> (2013) Nautiyal <i>et al.</i> (2013)
Family- Belonidae				
<i>Xenentodon cancila</i>	Needal Fish	+	P	Khanna <i>et al.</i> (2013) Sarkar <i>et al.</i> (2012) Kamboj and Kamboj (2019)
Family- Siluridae				
<i>Wallago attu</i>	Singhara	+	P	Vass <i>et al.</i> , (2010) Sarkar <i>et al.</i> (2012)
Family - Sisrodade				
<i>Bagarius bagarius</i>	Goonch	*	P	Vass <i>et al.</i> , (2010) Sarkar <i>et al.</i> (2012)
<i>Glyptothorax cavia</i>	Nayid	*	P	Khanna <i>et al.</i> (2013) Nautiyal <i>et al.</i> (2013)

+ = Abundance/ Common, * = Rare, - = Nil, P= present, A= absent

Figure 19.6. Fish species found in Ganga River near Bhogpur village.

Table 19.4. Status of floral diversity in the Bhogpur village stretch of river Ganga.

Name of Species	Common/ Local name	Present Status	Past decade status	References
Shrubs				
<i>Cannabis sativa</i>	Bhang	*	P	UFDC (2015)
<i>Cassia opaca</i>	Karonda	*	P	UFDC (2015)
<i>Cassia tora</i>	Panwar	-	P	UFDC (2015)
<i>Lantana camara</i>	Kurrii	+	P	Gangwar and Gangwar (2011); UFDC (2015)
<i>Murraya koeingli</i>	Karipatta	*	P	Gangwar and Gangwar (2011); UFDC (2015)
<i>Rubus elliptica</i>	Hisalu	*	P	UFDC (2015)
<i>Rouwolfia Serpentia</i>	Dhuala	+	P	UFDC (2015); Krishnamurti (1991)
Herbs				
<i>Cynodon dactylon</i>	Doovghas	+	P	UFDC (2015)
<i>Sida cordifolia</i>		*	P	UFDC (2015); Gangwar and Gangwar (2011); Krishnamurti (1991)
<i>Sida rhombiolia</i>	Sahadeva	*	P	UFDC (2015); Gangwar and Gangwar (2011); Krishnamurti (1991)
<i>Sida acuta</i>	Wire weed	+	P	UFDC (2015); Gangwar and Gangwar (2011); Krishnamurti (1991)
<i>Ischaemum rugosum</i>	Ribbed	*	P	Gangwar and Gangwar (2011)
<i>Parthenium hysterophorus</i>	Congress grass	+	P	UFDC (2015); Gangwar and Gangwar (2011); Krishnamurti (1991)
<i>Saccharum spontaneum</i>	Muni	-	*	Gangwar and Gangwar (2011)
<i>Tinospora cordifora</i>	Amrita	-	P	Gangwar and Gangwar (2011); Krishnamurti (1991)

+ = Abundance/ Common, * = Rare, - = Nil, P= present, A= absent

Riparian vegetation

The riparian vegetation is a link between aquatic and terrestrial ecosystem of a river. The riparian vegetation pertains to the vegetation which is found on the banks of any river. A good riparian zone was recorded on both the banks of river Ganga. The vegetation was recorded in the form of many types of shrubs and herbs shown in Table 19.4. The main factors for degradation of the riparian vegetation were the transport process of the raw material and illegal mining near the bank of the river shown in Figure 19.7.

Agriculture

Bhogpur village has a good agriculture field. The common agricultural crops are wheat, rice, popular, sugar cane. But due to the high demand of the raw materials, the agriculture area was destroyed by the illegal mining. They removed the upper layer of the agricultural field by using mechanical sources like JCB, after the removal of the fertile soil layer; they extract the stone, boulder from the lowest layer of the agricultural field shown in Figure 19.8.

Conclusion and recommendations

Unscientific and up hazard mining of riverbed materials over the years has forced irreparable damages to River Ganga ecosystem in Haridwar region. Lack of sufficient information regarding the extent of environmental impacts caused by riverbed mining is a noteworthy lacuna challenging regulatory efforts and minimizing the adverse effects of riverbed mining. The present study discloses the facts that unscientific and up hazard riverbed mining has degraded the Ganga basin in Haridwar region over the past few decades. The main degradation of riverbed mining in in-stream mining area is the changing pattern of channel morphology in last two decades and it divides the River Ganga in the various small stream orders. The changing pattern of channels has caused the degradation of water quality and aquatic biodiversity of the River Ganga. In Flood-plain mining area, the riparian vegetation has also degraded due to the transportation of the riverbed materials and due to the illegal mining, the nearby agricultural field was destroyed.

For the present study, a set of recommendations are drawn for recovering and improving the overall environmental quality of River Ganga basin in the study area.

- The Riverbed mining activity should be done in a scientific way and according to the guidelines of the Ministry of Environment Forest and Climate Change (MoEFCC) for Sand mining.
- Construction of Roads for transportation of raw materials from the river.
- River bed mining should be done manually without the use of any machinery like JCB.
- Awareness programmes to be conducted among people of that area about the various impacts of riverbed mining and immediate need for control measures.
- Training cum awareness programme should be mandatory for the people who are engaged in mining activity.

Figure 19.7. Riparian vegetation disturbed due to the transportation of Riverbed material.

Figure 19.8. Unscientific mining in the agricultural fields at Bhogpur village.

- Ban the illegal mining in agricultural fields and reclaim that area by landfilling.
- Extraction of riverbed material should be in right proportion of replenishment rate of riverbed material.

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Chapter 20

Climate resilient microbes in sustainable crop production

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Abstract

Climate change poses a great threat to the sustainability in agricultural crop production. Such circumstances demand the use of improved agricultural practices, environment friendly and climate resilient technologies. Microorganisms, being ubiquitous and abundant in the soil environment, are the key players regulating the earth's biogeochemical systems. The enormous potential of these microbes is being recognized and scientific community around the globe is involved in significant research towards the selection and commercialization of the microbes of biotechnological and environmental relevance. These microbes may be helpful in sustainable crop production by providing protection to plants from harmful pests and pathogens, by enhancing plant growth, by alleviating environmental and nutritional stresses, thus facilitating plants to

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cope up with the different abiotic and biotic stress conditions in view of the changing climatic scenario and alleviating its dire consequences.

Keywords: Bacteria, Climate change, Mycorrhizae, Resilience, Soil microbes, Stress, Sustainable agriculture

Introduction

Microorganisms are the heart of all ecosystems. There is a huge diversity and abundance of microorganisms in soil; 1 gram of soil may contain more than 10^8 – 10^9 cells of bacteria, 10^7 – 10^8 cells of actinobacteria and 10^5 – 10^6 cells of fungi with thousands of different species (Microbes, 2010). These microorganisms are the key players of many soil functions and mediate 80–90% of the functions important in soil activities to maintain fertility of soil and perform various ecosystem services, including acquisition of plant nutrients, cycling of nitrogen and carbon, formation of soil etc. (Sacca *et al.*, 2017). Climate change is probably the most complex and challenging environmental problem faced by the world today. It is recognized as a global issue. The changing patterns of climatic parameters like rise in atmospheric temperature, changes in precipitation patterns, excess UV radiation and higher incidence of extreme weather events like droughts and floods are emerging major threats for the sustainable crop production (Tirado *et al.*, 2010). Climate change can have various consequences, ranging from global warming to local cooling, increased extreme weather events and shifting vegetation zones. All these changes will indirectly influence soil organisms and microbial processes (Philippot *et al.*, 2013). The Indian climate has undergone significant changes showing increasing trends in annual temperature with an average of 0.56°C rise over last 100 years (Rao *et al.*, 2009). In future, the climate associated stress events like high temperature, limited soil moisture and salinity stress will get magnified by climate change impacts (Singh and Bainsla, 2015). To mitigate the adverse impact of climatic change on productivity and quality of various crops, there is need to develop sound adaptation strategies. The future crop farming techniques and food production systems will have to be better adapted to a range of abiotic stresses such as greater heat accumulation, dwindling water and salinity availability as well as biotic stresses including pests and diseases, in order to cope with the consequences of progressively changing climate phenomena. In this scenario, climate smart agriculture sustainably enhances achievement of national food security and development goals (FAO, 2010). Due to the growing concern over climate change, it has become essential to successfully exploit the beneficial soil microbes and their interactions for enhancing the agrosystems resilience to climate change and for improving the soil fertility and health, in turn maximizing the crop production. In this review, various properties of soil microbes will be discussed which makes them important in agriculture keeping in view of the effects of the changing climatic scenario on crop production and the need to eliminate many problems associated with the use of chemicals in this sector.

Soil microbial communities- effect of climate change and their resilience

The direct effects of climatic change on microbial composition and function have been studied extensively by investigators. To predict the response of a microbial community to a disturbance, various drivers of the microbial community stability, including resistance and resilience have been studied (Shade *et al.*, 2012). Soil microbial communities may be more resilient to environmental change than their aboveground plant counterparts, and changes to soil microbial communities may occur only when abiotic variables are outside the range normally experienced by the communities (Cruz-Martínez *et al.*, 2009). Microbial communities respond to warming and other perturbations through resistance, enabled by microbial trait plasticity, or resilience as the community returns to an initial composition after the stress has passed (Allison and Martiny, 2008). Resilience is the capacity or ability of a system or individual to react (respond) to an external force (disturbance) while fulfilling some further conditions at the end of the response (outcome). The word 'resilience' is derived from Latin word *resilire* meaning 'to jump back'. The degree to which soil organisms are impaired after a stress can be defined as the resistance of the soil system, and the rate and extent of recovery is considered as its resilience (Doring *et al.*, 2015). The concept of resilience has become more important in the presence of climate changes, both in semi-natural and agricultural ecosystems. It has been referred to as a dynamic and relevant criterion of health across all levels and areas of agriculture (Doring *et al.*, 2015). For the growth and development of plants as well as microbes, soil is an excellent medium. Insight into the nature of the biological basis of resistance and resilience of soil functions has been growing. In fact, it has been suggested that resistance and resilience might be related to microbial communities and properties of the resident soil microorganisms (Griffiths and Philippot, 2013). The soil microbial communities are, indeed, an excellent way to study resilience as their response to disturbances can be relatively fast that is within days or weeks (Griffiths and Philippot, 2013; Cregger *et al.*, 2012). According to Allison and Martiny (2008), even if microbial composition is sensitive to a disturbance, the community might still be resilient and quickly return to its predisturbance composition. This may be due to several features of microorganisms like their fast growth rates, the rapid evolution through mutations or horizontal gene exchange. So, microbial communities could be among the fastest components of an ecosystem to respond to changing environmental conditions with relatively short generation times and rapid growth under favorable conditions. On the other hand, the high functional and genetic diversity, potentially rapid evolutionary rates and vast dispersal capabilities of microbes may mitigate responses to environmental change. Microbial community composition itself can be robust both to changing climate and to associated changes in plant production and species composition (Cruz-Martínez *et al.*, 2009).

Among bacteria and fungi, fungal communities showed the ability to dynamically adapt to changing environments without a loss of diversity (Yuste *et al.*, 2011). Fungal diversity was less sensitive to seasonal changes in moisture, temperature and plant activity than bacterial diversity.

Specific functional traits, for example, the ability to resist dehydration via synthesis of the sugar trehalose to maintain cell membrane integrity e.g., for drought resistance, the ability to use specific C or N forms that are released when a drought ends, might inform about resilience (Mouillot *et al.*, 2013). In contrast, more general stress-response pathways, such as the sporulation pathway of *Bacillus subtilis* (Higgins and Dworkin, 2012) may be universally useful for maintaining stability in the face of a variety of disturbances. Resistance and adaptation of microorganisms to increased temperature are most often owing to the synthesis of heat shock protein folding and unfolding other proteins. Interestingly, induction of heat shock proteins is triggered by exposure to other environmental stressors such as osmotic shock or the presence of heavy metals and aromatic compounds which provides a molecular basis for cross-protection where exposure to one disturbance increases resistance to a different disturbance (Ramos *et al.*, 2001).

Need for microbial inoculation

In general, there is a need for microbial inoculation as a component of agricultural practice because of loss of topsoil, soil infertility, poor plant growth, low yield index and insufficient diversity of indigenous microbes. Harnessing plant-microbe interactions will not only help in climate change mitigation but also strengthening the green economy for achieving economic stability. It leads to developing plant cultivars that have the potential to grow under the stress of warming climate and elevated CO₂ (Philippot and Hallin, 2011). Beneficial soil microorganisms can also offer substantial socio-economic benefits to the global economy by reducing the dependency on synthetic fertilizers and pesticides while supporting various ecosystem functions and processes. Therefore, soil environment can be manipulated with the beneficial microbes to: (i) increase nutrient availability for production of high yielding, high quality crops; (ii) protect crops from pests, pathogens, weeds; and (iii) manage other factors limiting production, provision of ecosystem services, and resilience to stresses like droughts (Lehman *et al.*, 2015).

Various soil microorganisms like plant growth promoting rhizobacteria (PGPR) have emerged has an environment-friendly approach to promote plant growth effectively under abiotic and biotic stress conditions. Moreover, various microbial inoculants that can facilitate plant growth are known to reduce the toxicity of heavy metals, contribute to nitrogen fixation, facilitate nutrient transformation, produce siderophores which help the plant to obtain sufficient levels of iron, synthesize indole acetic acid (IAA) and other plant hormones and provide protection against a range of different pathogens (Mohanty and Swain, 2018; Olanrewaju *et al.*, 2017).

In cultivated soils, the activity of soil microorganisms is an important determinant of effective nutrient cycling and plant growth (Kumar *et al.*, 2012). These PGPRs are being developed as efficient biofertilizers for commercial exploitation. Increased use of natural microbes in the form of biofertilizers, biopesticides, biofungicides, and so on can reduce the chemical load and sustain productivity. Moreover, the use of farm yard manure enhances resistance and resilience of soil microbial activity against heat stress as applying only nitrogen fertilizer may be weakening the

resistance and resilience of soil functions (Kumar *et al.*, 2013). Increased use of natural microbes in the form of biofertilizers, biopesticides, biofungicides, etc. can reduce the chemical load and sustain productivity in conservation agriculture which constitutes an integrative approach to address multiple challenges facing the agriculture and environmental sectors – enhancing productivity in the face of acute and widespread problems of resource degradation (soil erosion, declining water availability and quality, declining diversity) and increasingly stressed ecosystems and climate change (Singh and Reddy, 2013). It has been emphasized earlier, subsistence farmers, who face famine, would consider a successful technology to be one that produces some yield in the worst year rather than one that produces high yields in the best (Lal, 1987).

Role of soil microbes in plant growth nutrition

The growth and health of plants is dependent upon the availability of requisite composition and concentration of various macronutrients, micronutrients and trace elements in the soil (Hodges, 2010). It is also important that these nutrients should be present in a biologically available form to affect the growth and productivity of plants. For example, though phosphate and sulphate are available in abundance in the soil, but only the soluble ionic form of these nutrients is taken up by the plants using different mechanisms and the rest remains unutilized (Solomon *et al.*, 2003; White and Hammond, 2008).

Microorganisms play an important role in the mobilization and uptake of nutrients by the plants (Sahu *et al.*, 2018). Soil microorganisms like arbuscular mycorrhizal fungi (AMF) and plant growth-promoting rhizobacteria (PGPR) are known to positively affect plant health, growth, and nutrition. The balance of soil microbial population has been greatly disturbed by the excess use of chemicals to improve the crop yield. This has consequently affected geochemical cycling of nature and also led to environmental pollution. Their use was often suggested in order to reduce the input of chemicals in agriculture. To promote the yield and quality of crops and restore the soil nutrients for sustainable agriculture and environment, the use of microorganisms as bioinoculants is the better alternative for chemicals (Alori and Babalola, 2018).

Role of fungi

There are various groups of fungi like plant growth promoting fungi, endophytic, ectomycorrhizal, arbuscular that play an important role in increasing plant growth and obtaining nutrition through various means like solubilisation of phosphorus, production of plant growth promoting hormones, increased above ground photosynthesis etc. (Prakash *et al.*, 2015). Among these, arbuscular mycorrhizal (AM) fungi are an important component of the soil microbial community and form mutualistic associations with the roots of over 80% of all land plants and have a worldwide distribution (Öpik *et al.*, 2010). AM fungi are a group of beneficial microorganisms that are known for their obligate symbiotic associations with the roots of higher plants (Salvioli *et al.*, 2016) particularly members of phylum Glomeromycota with angiosperms (except

Pinaceae), bryophytes, pteridophytes and gymnosperms. Through symbiotic associations with plant roots, AM fungi facilitates mobilization and uptake of carbon, phosphorus, nitrogen, etc. (Smith and Smith, 2012; Walder *et al.*, 2012), as well as other essential minerals such as Zn, Mg, S, Ca, K, etc. (Mohammadi *et al.*, 2011; Alizadeh, 2012) and make them available for the growing plants besides their other benefits, for example, they improve water availability in plants, protect the plants from pests, provide tolerance to environmental stresses and serve a major role in biogeochemical cycling of nutrients in soil (Hashem *et al.*, 2018).

Arbuscular Mycorrhizae: AM fungi supply phosphorus and other nutrients to plants and fungi, in return, take carbohydrates from plants (van der Heijden *et al.*, 2016). Reduction in the carbon flow to the fungi reduces the absorption of phosphorus by AM (Abiala *et al.*, 2013) which also depends on the species of AM fungi. P is the most studied nutrient absorption by AM roots and its absorption is increased in plants associated with AM by 3–5 times more than direct root absorption and also when grown in soils low in P, AM-infected plant roots with mycorrhizal associations absorb and accumulate more P as compared to roots of plant without AM symbiosis (Smith and Smith, 2012). The several metres extended mycelia of AM increases surface of absorption many times to obtain the same nutrients which plant roots are trying from their proximate area. The fine structure of hypha than plant root helps it to penetrate within the soil and thus increases the surface area for absorption which helps in growth and development of associated plants (Olsson *et al.*, 2014). The easily available supply of nutrients in plants as a result of the AM plant symbiosis increases the photosynthetic rate and overall biomass of the plant as has been reported by studies in greenhouse-grown lettuce (Baslam *et al.*, 2013). Although P is the most studied nutrient absorption by AM roots, some reviews have also reported absorption of other nutrients (Mohammadi *et al.*, 2011; Alizadeh, 2012).

AM fungi have also been found to increase the uptake of nitrogen along with phosphorus, assist in N assimilation in plants (Zhu *et al.*, 2016) and induce better biological N fixation. The carbon (C) flux from the root to the fungus acts as a key trigger for N uptake and transport (Fellbaum *et al.*, 2012). A substantially greater belowground C drain was confirmed in mycorrhizal plants than in nonmycorrhizal plants on quantification of carbon fluxes using a novel CO₂ collection system (Slavíková *et al.*, 2017). The external hyphae may provide a significant delivery system for K, Cu and Zn in addition to P and N in many soils. The contribution of mycorrhizae to uptake of Cu, Zn, Mn and Fe by maize as influenced by soil P and micronutrient levels was evaluated by Liu *et al.* (2000) and variation in Zn, Cu, Mn, and Fe uptake by *G. intraradices* was reported.

Mycorrhizal fungi have been reported to interact with a wide range of other soil organisms, in the root, in the rhizosphere and in the bulk soil. Upon its association with other microorganisms, there is an improvement in the activity of AM. For example, the spore germination and root colonisation efficiency of AM is enhanced by the bacteria as reported by Miransari (2011). *Azotobacter chroococcum*, *Pseudomonas putida* and *Bacillus polymyxa* have been tested along with AM fungus *Glomus intraradices* on *Stevia rebaudiana* (Vafadar *et al.*, 2014). Other AM fungi like *Glomus fasciculatum* have been studied in association with bacteria to enhance plant growth (Singh *et al.*,

2012). Improvement in the plant growth, nutrient absorption, phytohormone and chlorophyll production and biomass (Hemavathi *et al.*, 2006) has been reported as a result of the synergy between AM and bacteria (Krüger *et al.*, 2012). The effect of AM fungi on growth and development of a variety of horticulture crop plants (Rouphael *et al.*, 2015) has been studied and described in fruits (Ortas, 2018; Rajesh Kumar *et al.*, 2015), vegetables (Ortas *et al.*, 2013; Baum *et al.*, 2015) ornamental crops such as *Petunia hybrida*, *Tagetes erecta*, *Chrysanthemum morifolium* (Schmidt *et al.*, 2015; Gouveia, 2016; Crişan *et al.* 2017) with respect to the effect of mycorrhizal application on growth and yield.

Role of bacteria

Bacteria have a number of direct and indirect beneficial effects promoting the growth in plants. The various direct effects of plant growth promoting bacteria include solubilisation of mineral nutrients such as phosphorus and potassium increasing their availability, nitrogen fixation, sequestration of iron by production of siderophores, production of plant growth regulators and synthesis of ACC-deaminase in stress control in plants and various indirect mechanisms which include depletion of iron, production of antibiotic compounds, synthesis of antifungal metabolites and extracellular cell wall degrading enzymes of phytopathogens like fungi, competition and induced systemic resistance (Alori and Babalola, 2018).

Bacteria in nutrient availability and plant growth: Bacteria increase the availability of macronutrients like N, P, K and micronutrients like Fe etc to plants for their growth and development. There is a significant role of bioinoculants in N cycling and its utilization by plants in soil (Gupta *et al.*, 2012). The biological nitrogen fixation has a great practical importance considering the use of nitrogenous fertilizers which has resulted in water pollution due to nitrates and eutrophication of water sources (Mekonnen and Hoekstra, 2015). A wide range of bacteria, can fix nitrogen which includes species of archaea, bacteria and cyanobacteria which may be symbiotic or free living (Dynarski and Houlton, 2018). The atmospheric nitrogen fixed as a result of free-living nitrogen-fixing bacteria and symbiotic association between rhizobia and legumes represents a renewable source of nitrogen and is the primary source of fixed nitrogen in land-based agriculture systems and are suitable alternates for inorganic N fertilisers in organic farming. The majority of leguminous plants forming symbiotic relationship with the members of genus *Rhizobium* and its relatives belonging to class Alphaproteobacteria as well as the phylogenetically diverse free-living nitrogen-fixing bacteria including *Acetobacter*, *Arthrobacter*, *Azoarcus*, *Azospirillum*, *Azotobacter*, *Bacillus*, *Burkholderia*, *Enterobacter*, *Herbaspirillum*, *Klebsiella* and *Pseudomonas*, are helpful in providing nitrogen to a wide variety of important crops. (Gyaneshwar *et al.*, 2011; Flores-Félix *et al.*, 2015).

Besides N, another nutrient that limits plant growth is Phosphorus. Most of the agricultural soils have large amounts of inorganic and organic phosphorus but only a very low concentration of P is available to plants, and there is deficiency of phosphorus in many soils (Zhu *et al.*, 2018). P form complexes with metal ions such as iron or aluminium in low pH soils (Kiflu *et al.*, 2017) and

calcium in high pH soils (Andersson *et al.*, 2016) that leads to its precipitation or adsorption in the soil (Herrera-Estrella and López-Arredondo, 2016). When P fertilisers are applied to soils, most added soluble P (about 75 %) forms insoluble phosphates that is become bound in soil, resulting in lower availability of P available for crop growth and yield.

Different bacteria, reported from different environments, play significant roles in the solubilization of inorganic phosphate and mineralization of organic phosphates. A number of bacteria belonging to genera *Achromobacter*, *Aerobacter*, *Agrobacterium*, *Bacillus*, *Burkholderia*, *Erwinia*, *Flavobacterium*, *Gluconacetobacter*, *Micrococcus*, *Pseudomonas*, *Ralstonia*, *Rahnella*, *Rhizobium*, *Serratia* and others convert insoluble form of phosphates to soluble forms (Alori *et al.*, 2017; Vyas *et al.*, 2010). They solubilize by the various mechanisms like by the production of organic acids, release of other chelating substances and inorganic acids, and by releasing phosphatase enzymes. The production of organic acids is the main mechanism for phosphate solubilization. The various organic acids produced by most of phosphate solubilizing bacteria during phosphate solubilization are gluconic acid, 2-ketogluconic, acetic, citric, glycolic, isovaleric, isobutyric, lactic, malonic, oxalic, propionic and succinic acids (Wei, 2018) which reduce pH and act as chelating agents, forming complexes with metal ions like calcium, aluminium or iron and release the phosphates which are then available to plants. The release of other chelating substances, inorganic acids such as sulphuric acid, nitric acid and carbonic acid, phosphatases including both acid phosphatase and alkaline phosphatase, phytase, phosphohydrolase are other mechanisms of phosphate solubilization by these bacteria enhancing the plant uptake of P and growth (Behera *et al.*, 2017a; Behera *et al.*, 2017b; Alori *et al.*, 2017; Liu *et al.*, 2018).

The population of phosphate-solubilising bacteria is more in the rhizosphere and found to be metabolically more active as compared with bacteria from non-rhizosphere and other locations (Wang *et al.*, 2017). Increased plant growth, biomass and yield of different crops and plants have been recorded upon the inoculation of phosphate-solubilising rhizobacteria (Rizvi *et al.*, 2014).

Supplementation of P in legumes has showed a positive response in leguminous plants like alfalfa, clover, common bean, cow pea and pigeon pea (Mitran *et al.*, 2018). Several root-nodulating bacteria of different legumes also solubilize phosphates (Qin *et al.*, 2011) and such bacteria show plant growth-promoting effect in non-legumes as well. Various inoculants are already available, and they have been used for many years without causing harm to the environment or end user (Abhilash *et al.*, 2016).

Another essential macronutrient required for plant growth is potassium. It is present in soil as an abundant element but exists mainly in bound forms. It plays significant roles in many metabolic processes like photosynthetic activity, synthesis of protein, and enzymes' activation and in imparting resistance to pests (Rawat *et al.*, 2016). Only 1-2 per cent of the K fertilizers applied to the fields become available to plants, the rest becomes bound with other minerals and hence not available to the plants (Prakash *et al.*, 2015). Potassium-containing minerals including clay minerals (illite, kaolinite) and rock-forming minerals such as feldspars (microcline, orthoclase) and mica (muscovite, biotite) contain potassium in bound form (Schön, 2015) which can be

solubilised by several soil microorganisms by secreting organic acids. These acids either dissolve potassium directly or indirectly by chelating silicon ions releasing K into the solution (Sharma *et al.*, 2016).

Different bacteria, namely, *Pseudomonas*, *Burkholderia*, *A. ferrooxidans*, *B. mucilaginosus*, *B. edaphicus*, *B. circulans*, and *Paenibacillus* spp. solubilize and release K from potassium-bearing minerals to an easily available form (Velázquez *et al.*, 2016; Basak *et al.*, 2017). The plant growth promoting activity of potassium solubilizing bacteria in different crops pepper, cucumber, maize, wheat, corn, cotton, rape, soybean etc has been reported by several workers (Singh *et al.*, 2010; Zahedi *et al.*, 2016; Prajapati and Modi, 2016). Microbial activity in soil plays an important role in favouring iron (Fe) uptake (Colombo *et al.*, 2014). Many of the proteins and enzymes such as nitrogenase, leghemoglobin and hydrogenase, involved in photosynthesis and nitrogen fixation have iron as an important structural component. Chelating agents produced by soil microbes called siderophores and by plants referred as phytosiderophores, solubilise and transport inorganic Fe (Saha *et al.*, 2016; Bocchini *et al.*, 2015). Siderophores chelate Fe^{3+} with high affinity resulting in an efficient bioavailable source of Fe for plants. Plant roots exude phenolic compounds under Fe-deficient conditions in soil which may lead to the selective modification of microbial flora in the rhizosphere. The development of a particular rhizosphere microbiome that favours more siderophore-producing microbes increases the availability of iron and its acquisition by plants (Pii *et al.*, 2016). Many bacteria, actinomycetes secrete siderophores including *Rhizobium*, *Azotobacter*, *Azospirillum*, *Alcaligenes*, *Pseudomonas*, *Enterobacter*, *Bacillus*, *Streptomyces* under low-iron conditions (Prakash *et al.*, 2015; Wang *et al.*, 2014). Various rhizobial strains have also been reported to release siderophores. The ability of these root nodulating bacteria in iron acquisition through siderophores is highly advantageous as iron is the structural component in many proteins involved in nitrogen fixation (O'Brian and Fabiano, 2010).

Role of microbes in stress control in plants

Plants are sessile organisms exposed to natural climatic or edaphic stresses and to environmental changes. The changing climatic scenario is supposed to have a surprising effect on agricultural production and farming practices as a result of these stresses. These involve both biotic and abiotic stresses can limit the growth and development of a plant (Irulappan and Senthil-Kumar, 2018). Various biotic stresses include infection by bacterial and fungal pathogens, viruses, insect predation and nematode infection. Abiotic stresses include high and low temperature, frost, drought, flooding, high salt concentrations, high metal concentrations, organic contaminants, mechanical wounding and excessive levels of radiation.

The stress tolerance in plants can be increased by applying the microorganisms and these techniques are increasingly being sought. Many studies have reported the important role of microorganisms like bacteria and fungi in improving plant health through increased protection against environmental stresses, either biotic (*e.g.*, pathogen attack) or abiotic (*e.g.*, drought,

salinity, heavy metals, organic pollutants) (Miransari, 2010; Glick, 2014). All of these stresses induce the plant to synthesize growth-inhibiting stress ethylene (Glick *et al.*, 2007). Many plant growth-promoting bacteria have been reported to synthesize the enzyme 1-aminocyclopropane-1-carboxylate (ACC) deaminase. When the plants are treated with such bacteria, they produce lower levels of stress ethylene as a consequence of the consumption of the ethylene precursor ACC by the enzyme (Glick, 2010; Glick, 2014). These treated plants are damaged/inhibited to a significantly lesser extent following a biotic or abiotic stress than are plants that are not treated with ACC deaminase-containing plant growth-promoting bacteria (Glick *et al.*, 2007).

Control of abiotic stress

It is known that abiotic stresses adversely affect plant growth, productivity and trigger morphological, physiological, biochemical and molecular changes in plants; often leads to massive, often complete crop failures. In hilly areas, for example, cold stress limits the agricultural productivity of plants.

Water stress: To address the climatic hazards and struggle against drought, plants develop several defense strategies; for example, mycorrhizal association with soil fungi. AM symbiosis like *Glomus intraradices*, *G. claroideum* etc. affects the water relations of host plants (Wu *et al.*, 2013; Mohammadi *et al.*, 2011). The effects of water stress and arbuscular mycorrhizal fungi *Glomus versiforme* on reactive oxygen metabolism and antioxidant production by citrus (*Citrus tangerine*) roots was studied by Wu *et al.* (2007). They showed that AM symbiosis helps in increments of enzymatic and non-enzymatic antioxidant productions which in turn help AM plants to enhance drought tolerance. Barzana *et al.* (2012) found that roots of AM plants enhanced significantly relative apoplastic water flow as compared with non-AM plants and this increase was evident under both well-watered and drought stress conditions. The presence of the AM fungus in the roots of the host plants was able to modulate the switching between apoplastic and cell-to-cell water transport pathways which could allow a higher flexibility in the response of these plants to water shortage according to the demand from the shoot. Hazzoumi *et al.* (2015) studied the influence of mycorrhizal fungi (*Glomus intraradices*) and water stress on the growth of basil plants (*Ocimum gratissimum* L.). The AM fungi stimulate growth and photosynthesis and drive the water status in plant at an optimal level. A decrease in levels of proline and phenolic compounds was noticed, confirming the role of mycorrhizal symbiosis in plant defense against biotic and abiotic stress.

Salinity Stress: Salinity is one of the most severe environmental stresses as it decreases crop production of more than 20% of irrigated land worldwide. AM fungi have been shown to improve plant tolerance to salinity and arbuscular mycorrhizal plants also have improved photosynthetic and water use efficiency under salt stress (Porrás-Soriano *et al.*, 2009). The significance of AM fungi in alleviating salt stress with improved host plant nutrition, higher K⁺/Na⁺ ratios in plant tissues and a better osmotic adjustment by accumulation of compatible solutes such as proline, glycine betaine, or soluble sugars was reported by Porcel *et al.* (2012).

According to Latef and Chaoxing (2011), AM fungi *Glomus mosseae* alleviate salt induced reduction of root colonization, growth, leaf area, chlorophyll content, fruit fresh weight and fruit yield of tomato plants and thus may protect tomato plants against salinity by reducing salt induced oxidative stress. Yaish *et al.* (2015) isolated and characterized endophytic bacteria some of which could solubilize potassium (K^+), phosphorus (PO_4^{3-}) and zinc (Zn^{2+}), from date palm (*Phoenix dactylifera* L.) seedling roots under saline conditions and found *Bacillus* and *Enterobacter* as the dominating genera. These strains also showed the ability to produce enzyme ACC deaminase and the plant growth regulatory hormone IAA, chelate ferric iron (Fe^{3+}) and produce ammonia which helped to promote the growth and development of date palm trees growing under salinity stress.

Heavy metal stress: The occurrence of heavy metals in the environment constitute a potential hazard for water sources, soils and plants. Although some metals serve as essential micronutrients for plants and are required for their growth and development like Zn, Cu, Fe, Mn, Ni, Mo and Co, their high concentration and long term existence in soils may have adverse impact on soil and water quality thus compromising sustainable food production. AM fungi have repeatedly been demonstrated to alleviate heavy metal stress of plants. They can filter out toxic heavy metals, act as a sink reducing the metal concentrations near roots and thus keep them away from the plants, protecting them from stress and metal toxicity (Hildebrandt *et al.*, 2007; Karimi *et al.*, 2011). Colonisation of plant roots by AM fungi considerably reduce the uptake of heavy metals into plant cells that may allow plants to thrive on heavy metal-polluted sites (Kumar *et al.*, 2018).

Control of biotic stress

Microbes play a major role in sustainable crop production by conferring disease resistance to crop plants against a wide range of pathogenic organisms (Coninck *et al.*, 2015) through their specialized and customized chemical secretions (Gourion *et al.*, 2015; Bonfante and Genre, 2015), thus reducing the stress in plants due to pathogens. Recently biocontrol of phytopathogenic nematodes using nematophagous microorganisms and biocontrol of weed with AM fungi have also attracted much attention.

Microbial control of phytopathogens and nematodes: Various strategies are employed by bacteria in the rhizosphere for control of plant root pathogens, in indirect way through competition for nutrients and space on the root (Pliego *et al.*, 2011), by induction of resistance in the host plant (Pieterse *et al.*, 2014) and in a direct way by their antagonistic activity against the pathogen via the production of biosurfactants, antibiotics (Raaijmakers and Mazzola, 2012; Mavrodi *et al.*, 2012), iron-sequestering siderophores or enzymes that hydrolyze the pathogen cell wall. Plant growth promoting bacteria which contain the enzyme ACC deaminase can modulate the level of ethylene in pathogen infected plants limiting the damage caused by the pathogen, may it be fungal/ bacterial/ nematodes (Glick, 2014; Nascimento *et al.*, 2016). The siderophores produced by rhizobacteria play role in suppressing the growth of fungal pathogens (Beneduzi *et al.*, 2012) which make the iron unavailable for fungal growth. Santos-Villalobos *et al.*, 2012

reported *Burkholderia cepacia* or its siderophore having the potential to be used as a biological control agent against *Colletotrichum gloeosporioides*, the causal agent of anthracnose in mango. For the control of pathogens such as *Pythium ultimum* on sugar beet, *Phytophthora infestans* on tomato, *Pythium* and *Rhizoctonia* spp. on bean, and *R. solani* and *Gaeumannomyces graminis* var. *tritici* on wheat, cyclic lipopeptides produced by *Pseudomonas* spp. play a great role (Mishra and Arora, 2018; Yang *et al.*, 2014). Phenazine-producing strain of *Pseudomonas aureofaciens* 1393 as an active ingredient of biopesticides Pseudobacterin-2[®] marketed in the Russian Federation and used for the control of a wide range of phytopathogens as well as for the induction of resistance to plant diseases in organic and conventional crops (Thomashow and Bakker, 2015).

The impact of AMF on the reduction of soil borne diseases has mainly been evaluated in studies on fungal pathogens such as *Phytophthora*, *Aphanomyces*, *Fusarium*, *Verticillium* etc causing root rots and lesions (Singh and Giri, 2017) and nematodes causing galls (Lamovsek *et al.*, 2013). Arbuscular mycorrhizal (AM) fungi can confer protection to host plants against some root pathogens by inhibiting their growth and enhancing plant nutrition and health. Several other mechanisms including the production of phytohormones, siderophores, accumulation of defensive plant compounds, expression of defense related genes and increasing the colonization of plant growth promoting rhizobacteria also play an important role in disease suppression (Pozo *et al.*, 2008; Lioussanne, 2010). Interaction between arbuscular mycorrhizal fungi as a bio-agent and *Rhizoctonia* root rot disease of common bean plant was investigated by Abdel-Fattah (2011) demonstrating that colonization of bean plants with AM fungi significantly increased growth and yield parameters, and mineral nutrient concentrations and reduced both disease severity and disease incidence. Different physical and biochemical mechanisms have been shown to play a role in enhancement of plant resistance against *Rhizoctonia solani*, namely, improved plant nutrition, improved plant growth, increase in cell wall thickening, cytoplasmic granulation, and accumulation of some antimicrobial substances (phenolic compounds and defense related enzymes). A diversity of microorganisms including fungi, bacteria, and viruses exist in nature that shows antagonistic activity against phytopathogenic nematodes which cause serious losses in a variety of agricultural crops worldwide. Nematophagous microorganisms employ a variety of physical, chemical, and biochemical mechanisms to attack nematodes (Lamovsek *et al.*, 2013). Several commercial products based on the bacteria and fungi have been developed to control the root-knot nematodes like *Meloidogyne* spp. (Lamovsek *et al.*, 2013; Kiriga *et al.*, 2018) viz. bacteria like *Pasteuria penetrans*, *Bacillus firmus*, *Burkholderia cepacia* and *Bacillus* spp., and fungi like *Purpureocillium lilacinus*, *Pochonia chlamydosporia* and *Myrothecium verrucaria*. Using two commercially available arbuscular mycorrhizal fungal (AMF) products based on *Funneliformis mosseae* and *Glomus dussii*, Tchabi *et al.* (2016) assess their effect on yam growth and ability to suppress nematode damage. The presence of AMF tended to lead to improved growth of yam as compared to non-AMF control plantlets.

Control of weeds: The environmental-friendly weed control methods that can contribute to effective weed management in sustainable agricultural systems are being explored due to the

problem of herbicide resistant in weeds as a result of the use of chemical control methods (Fialho *et al.*, 2016). Biological weed control refers to the action of biocontrol agents (parasites, predators or pathogens) to maintain weed population at a lower average density than would occur in their absence. AM fungi were found to suppress the competitiveness of the other type of plant population that is weeds in sunflower field. This ability of AM fungi can be exploited for biological control of weeds. AM fungi reduced the total biomass of a weed community and that this effect was even stronger in the presence of the crop sunflower (Rinaudo *et al.*, 2010). Veiga *et al.* (2011) investigated the effect of AM fungi (*Glomus intraradices*, *Glomus mosseae* and *Glomus claroideum*) on the growth of individual weed species and on weed-crop interactions and showed that AM fungi can negatively influence the growth of some weed species. Mycorrhizal weed growth reductions can be amplified in the presence of a crop. So, the maintenance and promotion of AM fungi activity may thereby contribute to sustainable management of agroecosystems.

Conclusion

The changing climatic scenario creates a great challenge to agricultural sustainability and requires an integrated approach for developing strategies in the years to come that aim at sustainable increase in agricultural production. Soil is a home to diverse microbial flora that plays key roles in ecosystem services. The existing agricultural management practices may affect their role in soil fertility and productivity in this changing climatic scenario. In the absence of potential management strategies to deal with the climate change, the microbes may lose their natural capacity to perform various biological activities like suppressing soil-borne plant pathogens, making nutrient pool in plant available forms etc, important for the growth, development, protection and productivity of crop plants. Harnessing plant-microbe interactions for the agricultural practices like integrated nutrient and soil management, integrated pest and weed management, organic agriculture involving the use of microorganisms in the form of bionoculants, biofertilizers, biopesticides, biological control of weeds etc along with other practices like conservation agriculture, use of cover crops, crop rotation, water and irrigation management practices etc, will help to contribute to climate change adaptation and building resistance and resilience in soil microbes.

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