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Contaminants in Agriculture

Sources, Impacts and Management

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Foreword

Contaminants caused by industrial activities, excessive use of pesticides, herbicides, chemical fertilizers, antibiotics, and pharmaceuticals containing heavy metals, sewage sludge, and improper disposal of waste into the soil, have become a major challenge that we need to overcome for a healthy environment. Such soils with toxic pollutants, apart from causing serious threat to all life-forms, alter plant metabolism, thus resulting in the reduction in crop quality and crop yield.

The assessment of risks of polluted soil on ecosystems and humans and the ways to reduce them have become the key subjects of concern for researchers. To address the problem, serious research into remediation processes has been carried out over the last 20 years. Various technologies have been developed for remediation of such polluted soils. The principles of phytoremediation techniques, immobilization of heavy metals, and soil washing are frequently listed among the best practices.

Remediation of heavy metal polluted soils is necessary to reduce the associated risks, make the soils available for agricultural production, enhance food security, and scale down land tenure problems arising from changes in the land-use pattern. Some plant species which grow profusely in a water-saturated soil and accumulate a spectrum of contaminants have been found to address the problem efficiently.

Accomplished scientists in the field of remediation have compiled and edited some very useful articles written by experts from different parts of the world and produced this book. It comprises 21 chapters grouped into four sections: Section A outlines the overview of contaminants in agriculture; section B illustrates sources of contaminants and their impacts on agriculture; section C discusses management strategies covering utilization, applications, and bioremediation of agricultural contaminants; and Section D focuses on approaches and challenges for crop protection and production from contaminated soils. This compendium provides extensive contributions from researchers in almost all aspects of agriculture and agronomy.

The editors have offered a good foundation of the subject for students, researchers, readers, plant growers, plant lovers, agronomists, agriculturists and all those who are concerned about soil and human health. I believe the book will prove to be a rich source of practical knowledge for all those involved and associated with the farming or processing of plants.

With my good wishes to the readers, I congratulate the editors, authors, and the publisher of this compendium.

Central University of Punjab R. K. Kohli
Bathinda (Punjab), India

Preface

Over the past few decades, the increase in global population and advancement in modern agricultural technology has amplified the demand for agricultural and exotic crops and livestock. Agricultural, horticultural, and other industrial activities are major causes of contamination in soils, sediments, and water bodies in the adjacent environments. Agricultural contaminants include organic and inorganic fertilizers, pesticides, herbicides, and insecticides, organic matter such as animal waste and decaying plant materials, irrigation residue like salts and trace metals, and microorganisms. Heavy metals are one of the most important factors of soil and water contamination.

Innovative management strategies are essential to maximize the benefits from the agricultural inputs while minimizing their off-site migration and impact on the receiving environments. In this regard, efficient management strategies and skills for the agricultural contaminants pave the way to combat the challenges to improve the production of agricultural crops. Application of targeted, sufficient, and balanced quantities of chemicals will be necessary for high yields without environmental penalty. At the same time, every effort should be made to improve the availability and use of secondary nutrients, micronutrients, organic fertilizers, and soil conservation practices to develop overall crop production in an efficient and environmentally sustainable manner, without sacrificing soil health and productivity.

Therefore, we must address these challenging issues rising day by day in the field of agriculture. Thus, we bring forth a comprehensive volume, *Contaminants in Agriculture: Sources, Impacts and Management*, highlighting the various prospects that are involved in current scenario. The book consists of 21 chapters categorized in different sections, consisting of review articles written by global experts. We are hopeful that this volume will meet the need of all researchers who are working or have great interest in that particular field. We are thankful to the Springer International Publishing AG, Switzerland, for the compilation of this scientific work. Heartfelt thanks are expressed to the team members (Eric Stannard, Nicholas DiBenedetto, Anthony Dunlap, and Arun Siva Shanmugam) for their dedication, sincerity, and friendly cooperation in producing this volume.

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

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

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About the Editors

M. Naeem is an Assistant Professor in the Department of Botany at Aligarh Muslim University, India. For more than a decade, he has devoted his research to improving the yield and quality of commercially important medicinal and aromatic plants (MAPs). His research focuses on escalating the production of MAPs and their active principles using a novel and safe technique involving depolymerized polysaccharides as well as the application of potent PGRs. His research also focuses on abiotic stress tolerance in medicinal plants. To date, he has successfully run three major research projects as the Principal Investigator sponsored by national funding agencies like the Department of Science and Technology, New Delhi, and the Council of Science and Technology UP, Lucknow. He has published more than 80 research papers in reputable national and international journals as well as 7 books. He has also participated in various national and international conferences and acquired life memberships to various scientific bodies in India and abroad. Based on his research contributions, he has been awarded a Research Associateship from the Council of Scientific and Industrial Research, New Delhi; a Yuva Vaigyanic Samman (2011) from the State Government of Uttar Pradesh; a Fast Track Young Scientist Award from the Department of Science and Technology, India; a Rashtriya Gaurav Award (2016) from the India International Friendship Society, New Delhi; a Young Scientist of the Year Award (2015), a Distinguished Young Scientist of the Year Award (2017); and a Best Scientist of the Year Award (2018) from the Scientific and Environmental Research Institute, Kolkata; and UGC-BSR Research Start-Up Grant (2018) by UGC, New Delhi.

Abid Ali Ansari is an Assistant Professor in the Department of Biology, Faculty of Science, University of Tabuk, Saudi Arabia. His research work is concerned with phytoremediation and eutrophication. He has a number of research articles of national and international repute to his credit. He has written ten edited books and a number of book chapters on varied aspects of his research. He has been awarded "Environmentalist of the Year 2011" and "Scientist of the Year 2014" by the National Environmental Science Academy, India, and "Research Excellence 2016 Award" by the University of Tabuk. He has also participated in various national and international conferences and acquired memberships to various scientific bodies (Saudi Biological Society, International Phytotechnology Society, and Society for Ecological Restoration).

Sarvajeet Singh Gill Assistant Professor, Centre for Biotechnology, Maharshi Dayanand University, Rohtak, India, has made significant contributions toward abiotic stress tolerance in crop plants. His research includes abiotic stress tolerance in crop plants, reactive oxygen species signaling and antioxidant machinery, gene expression, helicases, crop improvement, transgenics, nitrogen and sulfur metabolism, and plant fungal symbiotic interactions. Together with Dr. Narendra Tuteja at the International Centre for Genetic Engineering and Biotechnology (ICGEB), New Delhi, he worked on plant helicases and discovered a novel function of plant MCM6, PDH45, and p68 in salinity stress tolerance that will help improve crop production at sub-optimal conditions. A recipient of the Junior Scientist of the Year Award 2008 from the National Environmental Science Academy, he has edited several books and has a number of research papers, review articles, and book chapters to his name.

Part I
Overview of Contaminants in Agriculture

Organic and Inorganic Fertilizer Contaminants in Agriculture: Impact on Soil and Water Resources

I. Rashmi, Trisha Roy, K. S. Kartika, Rama Pal, Vassanda Coumar, S. Kala, and K. C. Shinoji

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1 Introduction

Nutrients are essential for crop growth and production. As plant growth involves 17 essential nutrient elements along with several other beneficial elements majority of which is supplied from soil, the replenishment of the elements taken up by the plants from soil becomes necessary for sustainable agriculture management. Therefore, in order to replenish nutrients in soil, various sources of amendments like inorganic fertilizers, organic manure sources like farmyard manure, municipal solid waste, distillery effluents, and food processing industry waste can be considered as a viable option for maintaining soil fertility. Both fertilizers and organic manures are the major source of nutrients for crop production in agriculture. In inorganic fertilizers such as urea, DAP (diammonium phosphate), and MoP (muriate of potash), nutrients are in inorganic forms and are easily accessible to crops. However, in organic manure, both organic and inorganic nutrient forms are present, which are slowly available to crops over a period of time. However, if we focus on how efficiently different nutrient elements are used as fertilizer formulations, it can be noted that in majority cases the efficiency of the applied fertilizers is way below 50%. This indicates that half of the applied fertilizer in most cases and more often almost 80–90% of the applied fertilizer remain unutilized by the plants and find entry into different sources like soil, water, and environment and become a source of contaminant. In the inorganic fertilizers, nutrient content is steady and does not vary much among various companies and is, therefore, more standardized. In contrast, organic manures vary in their nutrient content and composition depending on the feedstock or raw material used for compost preparation. Application of inorganic and organic fertilizers has both pros and cons. Indiscriminate use of inorganic fertilizers often results in increased risk of soil, water, and air pollution, which directly affects living beings. The inherent capacity of soil to produce crops in sustainable way is also hampered by imbalanced use of inorganic fertilizers. Therefore, improper management of both inorganic and organic fertilizers can detrimentally affect human health and ecological systems. According to FAOSTAT (2015), more than 50% of fertilizer is utilized by the United States, China, and India, which is visible by their agricultural and financial improvements. FAO (2016) also predicted that in the coming years, fertilizer consumption of Asian and Latin American countries would rise by 89%. Estimates of FAO highlight that supply of nutrients (N, P_2O_5, K_2O content in fertilizers) was 240 million tonnes at global level; however, nutrient requirement was 284 million tonnes in 2014, resulting in wide gap of nutrient scarcity for crop production. This high usage of fertilizers has resulted in buildup of nutrient stock in soil, leading to leaching and runoff loss affecting soil and water quality.

Both manure and fertilizers are essential for crop production, but indiscriminate use, rate of application, and improper storage can upshot contamination of environment. In recent times, the agriculture sources have become the major nonpoint source of pollution across the globe (www.epa.gov/nps/nonpoint-source-agriculture). Not only unmanaged use of fertilizers but also various other farm practices make agriculture as the dominant contributor to nonpoint source pollution. Various operations which lead to the contamination of the environment are as follows:

- Absence of proper soil and water conservation measures which leads to loss of soil and sediments through runoff.
- Poorly located or managed animal feeding.
- Excessive application of manures.
- Overgrazing practices.
- Excessive tillage operations or ploughing of the field at wrong time.
- Runoff from barnyards, feedlots, and croplands.

Many studies (Hanson 2002; Almasri and Kaluarachchi 2004) have revealed that higher crop production with indiscriminate use of fertilizers has become major source of water and soil pollution putting human health and ecological balance at risk (Khan et al. 2018). Fertilizers often contain certain heavy metals (HMs) such as chromium (Cr), cadmium (Cd), lead (Pb), arsenic (As), and mercury (Hg), and therefore, excess application on long term adversely affects the physical, chemical, and biological properties of soil. Beside soil health, crop metabolism is affected by accumulation of HMs, adversly affecting biochemical process resulting in collapse of cell organelles and plant death sometimes (Nagajyoti et al. 2010; Gupta and Sandallo 2011). Contaminants from fertilizers find their entry into food chain and, thus, can affect animal and human health (De Vries et al. 2002). Even application of huge amount amount of fertilizers during lawn making and maintenance also results in exposure of humans to different contaminants (Madrid et al. 2002). Eutrophication is a major pathway of nutrient entry into water bodies risking aquatic and human life. Runoff and soil loss due to rain, irrigation, etc. often result in heavy loading of nutrients and contaminants in water bodies. Among the nutrients, N and P are the major culprits which affect adversely water bodies. Some nutrients like N, on one hand, in the form of ammonium (NH_4^+) from fertilizer or manure is used by crops, whereas, on the other hand, other forms like ammonia (NH_3) gas is lost to the atmosphere contributing to greenhouse gas emission.

Mostly, soil gets contaminated as a result of human action when the concentration of chemicals that are not originally found in nature, nutrients, or elements in the soil exceeds naturally occurring levels. Thus, the chemicals have direct impact on functioning of the associated ecosystem and environment at an unacceptable level, it is called as soil pollution. Soil pollution brings detrimental changes in various soil properties, which adversely affects crop production, soil quality, human nutrition, and surrounding environment and thereby causes huge disturbance in the ecological balance (Tao et al. 2015). Application of precise dose of fertilizers is essential to supply optimum nutrient supply for crop production. Excessive application of fertilizers often leads to accumulate contaminants, which can adversely affect natural resources like soil, air, and water. All the above-mentioned factors strongly point out the significance of understanding the contamination of soil and water by various inorganic and organic fertilizers used for agricultural production. This chapter focuseson the various contaminants present in both fertilizers and manures and their influence on soil and water quality.

1.1 Inorganic Fertilizers: Consumption and Contaminants

Over the last few years, requirement of inorganic fertilizers increased worldwide with increase in crop production. There is a shift in the consumption pattern of fertilizers in many countries over a period of time. In Asian countries like India and China, fertilizer consumption increased rapidly; however, it almost remained constant in Western Europe and North America. As per various estimates by FAO, total fertilizer requirement is predicted to grow at 1.6% per annum globally. Demand for essential nutrients like N, P_2O, and K_2O is expected to grow by 1.5%, 2.2%, and 2.4%, respectively, from 2015 to 2020. This will result in an increase in the overall production and consumption of fertilizers in the next 5 years (FAO 2017). According to IFA (2017), with adoption of best management practices by farmers, it is hopeful that more efficient use of N and P fertilizers, followed by recycling and reusing of natural or organic nutrient sources, will tend to grow in coming years and emerge as a environment friendly pollution mitigation mechanism in agriculture.

In general, three major nutrients, N, P, and K, constitute a bulk of fertilizer industry, as these nutrients are essential for crop growth and development. It is estimated that among the three nutrients, N accounts for more than 60% of total nutrient utilized by crops followed by P and K. Compared to N fertilizer which is manufactured by chemical reaction between N from atmosphere and H from natural gas, phosphate and potash fertilizers largely involve digesting and mining activities (Arovuori and Karikallio 2009) of natural resources. As cited in many literatures, fertilizers, on one hand, were crucial element for green revolution, which resulted in significant increase in fertilizer production and consumption. There is no doubt that application of fertilizer has contributed greatly in raising agricultural productivity and reducing hunger worldwide (Erisman et al. 2008). This increase is shown in a study by Lu and Tian (2017) who reported an increase of 8 and 3 times in N and P fertilizer use. They also reported that during 1961–2013, an overall increase in fertilizer consumption resulted in improved N/P ratio to the tune of 0.8 $g\ N\ g^{-1}\ P$ per decade, highlighting the role of human on ecosystem services. Some of the studies indicate that indiscriminative use of fertilizers resulted in a number of environmental and ecological problems (Sutton et al. 2011; Lu and Tian 2017). Some of the common problems often encountered, such as soil acidification, salinization, ground water contamination, eutrophication, crop yield reduction, greenhouse gas emission, and air pollution, result in deterioration of natural resources, thereby hampering sustainable food production (Ju et al. 2009; Guo et al. 2010).

Imbalanced application of chemical fertilizers increases the chance of environmental contamination. Fertilizers that act as a source of macronutrients and micronutrients to crops are also rich in heavy metal, radioactive compounds, etc. and become a major source of contaminants in long run to soil and environment. For instance, inorganic fertilizer application can affect soil health by forming hard soil surface, reducing soil pH, decreasing microbial process, negatively affecting physical and chemical properties of soil, and thus indirectly influencing crop production. Similarly, with the emerging trend of organic farming in West and South East Asia,

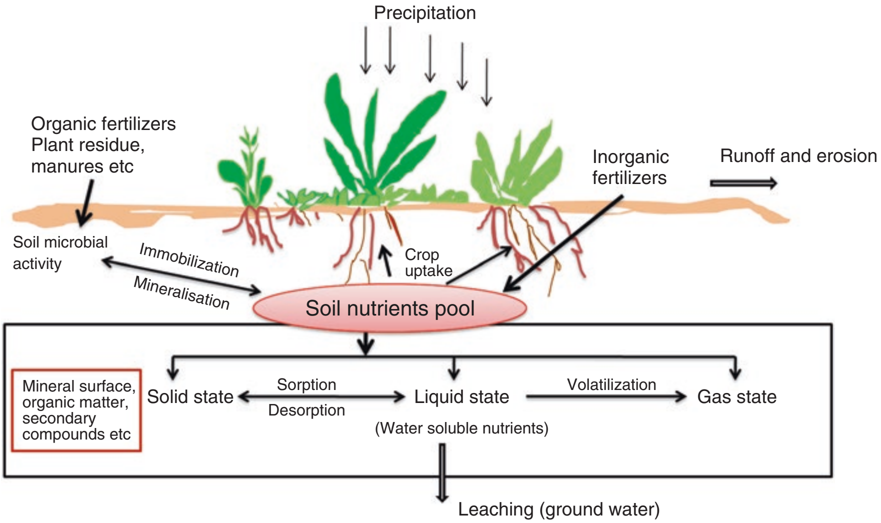

Fig. 1 Fate of organic and inorganic fertilizer behavior in soil

a lot of emphasis on the usage of organic fertilizers is promoted on larger scale across the world. But the major drawback in this system is the nonavailability of organic sources creating a wider gap between demand and supply. However, the organic fertilizers such as manures, crop residue, municipal solid waste (MSW), food processing industry waste, and others sometimes become the sink of various heavy metals, disease-causing pathogen, etc., which can have deteriorating effect on soil and water resources (Khan et al. 2018). Difference between organic and inorganic fertilizers is depicted in Fig. 1, showing the influence on soil and nutrient uptake.

Nitrogen and phosphorus are considered as backbone for any crop production system. Application of nitrogenous fertilizers in excess often results in various losses, such as leaching and volatilization, which not only reduces the nutrient use efficiency but also is an environmental threat. Nitrate is the major form of contaminants found in water bodies with excess application of N fertilizers. The second most consumed plant primary nutrient through fertilizers is phosphorus. The P is widely deficient in soil system, and 43% of world soils are scarce in available P needed for crop growth (Liu et al. 2012). The major problem with P fertilizers is the very low-use efficiency with only 10–15% of the applied fertilizer being utilized by the crop plant, while the rest remains in the soil or finds way into water bodies causing various environmental problems. In recent times, the consumption of fertilizer P increased by 3.2% from 2002 to 2010 (Lun et al. 2018). Phosphatic fertilizers manufactured from rock phosphate contain cadmium, and increased accumulation of Cd affects soil health. These contaminants might undergo some chemical changes and convert into different compound, which can be either more or less toxic to environment. In this context, sometimes HMs are easily absorbed by crops and tend to be accumulated in plant and animal body. Besides, soil properties and management also affect the fate of contaminants and decide whether they can be easily taken up by living forms. Soil properties such as soil texture, pH, organic matter, soil moisture, soil temperature, and heavy metals affect the accumulation of contaminants and their movement in soil–water system. Shayler et al. (2009) explained the mechanism of different behavior of contaminants in a system as follows:

(a) Some contaminants reach water bodies polluting surface and ground water.
(b) Some pollute air by escaping into atmosphere.
(c) Some pollutants bind tightly to soil surface and remain stable for years.

Many experts (e.g., Kolpin et al. 2002; Juhler et al. 2001; Battaglin et al. 2003) highlighted in environmental monitoring studies that EC is detected in various water body sources such as ground water, surface water, animal bodies like that of fish, and earthworm. Sometimes nutrient pollution is mainly caused by emissions from the agglomeration and industrial and agricultural sectors. Furthermore, in case of agglomerations, P emissions via household detergents play a significant role (ICPDR 2013). Nutrient discharge into water bodies can result from (i) point sources (in particular untreated/partially treated wastewaters) and/or (ii) diffuse sources (especially agriculture).

1.2 Organic Fertilizers and Contaminants

Organic fertilizers or manures are considered as biodegradable and are mostly from plant or animal origin. Most commonly used OMs include FYM, municipal solid waste, food industry waste, crop residue, different types of composts such as vermicompost, kitchen waste compost, distillery effluents, etc. According to Bruun et al. (2006) and Hargreaves et al. (2008), OM are used as fertilizers not only supply essential nutrients to plants but reduce chemical fertilizers requiement for micronutrients and eliminate the requirement of its consequent management or removal. Therefore, OMs are considered to be easiest way to recycle nutrient back to soil system. Besides acting as nutrient sources, OMs act as good soil amendments and conditioners and might reduce dependency on nonrenewable resources like fossil fuel for fertilizer production (Mondini and Sequi 2008). It has been stated that if OMs are utilized appropriately in crop production, then they are capable of supplying essential nutrients to crops. To revive barren or infertile soil, OMs are considered to be the best amendment and provide a better crop performance in agriculture (Soliva and Paulet 2001). Organic sources such as sewage sludge (SS) and animal manure are the most common organic wastes applied to soil either raw or composted. As suggested by many reports (Weber et al. 2007; Singh and Agrawal 2007), application of organic manures provides both macro- and micronutrients; improves organic matter, soil structure, bulk density, and other physical properties; and enhances microbial activities, resulting in efficient nutrient absorption by crops. Thus, proper utilization of different types of organic waste in crop production is encouraged rather than the conventional practices of applying inorganic fertilizers to carter productivity and soil health.

Generally, organic fertilizers are known for their slow release or transformation of nutrients, but the presence of contaminants such as HMs, other toxic compounds, and pathogen inoculums cannot be ignored (Petersen et al. 2003); besides, the bulky nature of OMs often results in high transportation costs. Especially, use of industrial by-products such as MSW, distillery waste, and fly ash often results in loading of HM besides PBTs (persistent, bioaccumulative, toxic chemicals) in soils and environment (cwmi.css.cornell.edu). Therefore, judicious and correct method of application of organic fertilizers should be strictly followed in order to avoid contamination of soil and water.

2 Contaminant Sources in Various Fertilizers and Manures

Contaminants from various inorganic and organic fertilizers are explained in this section. Various contaminants from fertilizer sources interfering with natural ecosystem deteriorate the soil, air, and water quality, thus directly affecting plants and animal life (Fig. 2). This section highlights the contaminants from the most commonly used N, P, and K fertilizers and organic manures and their ill effects on living forms and environment. Indiscriminate and long-term uses of inorganic and organic

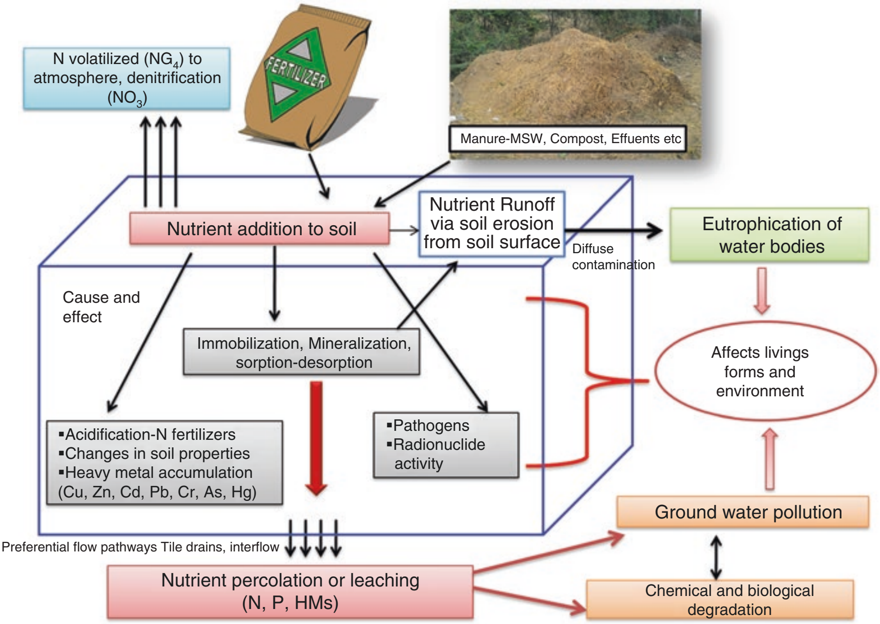

Fig. 2 Transformation of contaminants in inorganic and organic fertilizer in soil ecosystem

Table 1 Contaminants in fertilizers and manures

Inorganic fertilizers	Heavy metals	Others	References
N fertilizers	Cd	–	
P	Cd, As, Pb	Radionuclide like U, Ra, Sr	Khan et al. (2018)
K	Cl	–	
Micronutrients	As, Pb, Cd	–	MDH (2008)
Organic fertilizers			
Compost, biosolids, MSW	Cd, Zn, Ni, Pb, Hg, Cr, Cu	–	Smith (2009)

fertilizers result in accumulation of various contaminants, such as HMs and radionuclide (Table 1), thus raising environmental concerns by polluting natural resources especially soil, water, and atmosphere.

2.1 *Nitrogenous Fertilizers*

Despite the beneficial role of nitrogenous fertilizers in crop production, it is an undeniable fact that excessive N causes irreversible damage to our ecosystem. The consumption of N has increased from 12 Tg in 1960 to 113 Tg in 2010 to sustain agricultural production and feed the growing population globally (FAO 2016). Some ammonical N fertilizers such as ammonium nitrate and ammonium phosphate contain nearly 50–60 mg kg^{-1} of arsenic (As) (Li 2002). Besides As, higher accumulation of another HM like Cd was found in malt barely fertilized with ammonium nitrate especially in low N soils (Grant et al. 1996). Though barley increased with N fertilizers, Cd concentrations in grain were also increased due to the application of mono ammonium phosphate or KCl in consequent years of cultivation. Besides the addition of Cd to soil, nitrate form of N itself is a contaminant for water bodies. In India, several water bodies are affected by the nuisance of eutrophication, which is greatly caused by nutrient runoff from the adjoining agricultural fields. To name a few, Lake Udaisagar in Udaipur, Rajasthan (Vijayvirgia 2008), Dal Lake in Kashmir, Loktak Lake in Manipur, and Chilika Lake in Orissa (Patra 2012) were all affected by the problem of eutrophication. Most local water bodies adjoining agricultural fields are subjected to excess nutrient load coming as runoff from these fields. One latest study by Kritee et al. (2018) found that intermittently flooded rice farms in India emit 30–45 times more N_2O as compared to the maximum from continuously flooded farms, which predominantly emits methane. They suggest that co-management of water with inorganic nitrogen fertilizer and organic sources could reduce greenhouse emission by 90%.

Besides soil and water pollution, N fertilizers also affect air quality. The applied nitrogenous fertilizers are lost to the atmosphere in various gaseous forms like ammonia (volatilization), N_2O, and NO_x (denitrification). All these gases pollute the environment in various ways. The nitrous oxide (N_2O), in particular, is an important greenhouse gas (GHG) and has 6.2% contribution toward global warming. The persistence time of N_2O is 116 years with a global warming potential of 310 times in comparison to CO_2. Thus, with a meagre contribution of 6.2% in global warming in comparison to CO_2 (76%) and CH_4 (16%), it is one of the most potent threats to agriculture production and food security (Fagodiya et al. 2017). The nitrous oxide emission has increased steadily in the last two decades between 1990 and 2010 from 5.7 to 6.0 Tg N_2O per year with majority of the rise attributed to the intensification of agricultural practices involving increased fertilizer N application (Skiba and Rees 2014). Of the total N_2O emission, 36% is contributed by agricultural operations like fertilizer application and cultivation of farmlands (EPA 2010). The key factors, influencing nitrous oxide emission rates, are substrate availability (N), temperature (regulates the speed of the enzymatic reactions), pH, oxygen status, and also carbon for denitrification.

The National Oceanic and Atmospheric Administration (2009) has declared nitrous oxide as the second most potent ozone destroyer after chlorofluorocarbons (CFCs). In agriculture, N fertilizer is the main source of contamination, and other sources such as animal manure, sewage sludge, industrial process, and combustion reaction are major sources that release nitrous oxide to the atmosphere. Depletion of the protective ozone layer, which acts as a filter in removing the ultraviolet radiations, may cause various diseases like sunburn, cataract, genetic mutations, and cancer. However, depletion of ozone layer in the poles has resulted in more cooler springs and accentuated the contrast in temperature between poles and equator in the southern hemisphere. This contrast has caused stronger air circulation and more extreme storm events and can be considered as a direct consequence to climate change (Robinson 2014). The photochemistry of ozone was first described by Chapman (1930). Ozone is produced by the photolysis of O_2. The following reactions show the process of ozone formation.

$$O_2 + h\upsilon \rightarrow O + O \tag{1}$$

Followed by reaction of O and O_2,

$$O_2 + O + M \rightarrow O_3 + M \tag{2}$$

O and O_3 are quickly cycled between each other via

$$O_3 + h\upsilon \rightarrow O_2 + O \tag{3}$$

The ozone (O_3) again reacts with nascent oxygen and forms O_2.

$$O_3 + O \rightarrow O_2 + O_2 \tag{4}$$

Various reactive species in the atmosphere such as NO_x and ClOs react with the stratospheric ozone causing its depletion. The reactions in Eqs. 5 and 6 show how NO causes O_3 depletion.

When O_3 reacts with NO, the following reaction takes place,

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (5)$$

NO_2 is again recycled back to NO, and the chain reaction leading to O_3 degeneration continues.

$$NO_2 + O \rightarrow NO + O_2 \quad (6)$$

NO is recycled back to its original form, which makes it a very potent agent for O_3 depletion. The NO can typically destroy 10^3–10^5 molecules of O_3 before it is converted to some less reactive form (Lary 1997). Comparing the ozone depletion potential (ODP) of various greenhouse gases, the ODP weighted emission due to N_2O is the highest. In the present time also, the increased concentration of N_2O routed through anthropogenic activities would be the major O_3-depleting agent compared to the halocarbons (Ravishankara et al. 2009).

2.2 *Phosphatic Fertilizers*

Compared to N fertilizers, application of phosphatic fertilizers is of significance as they accumulate not only HMs but also radioactive materials like radionuclides of ^{238}U, ^{232}Th, ^{210}Po, ^{226}Ra, and ^{40}K (FAO 2009; Sonmez and Snmez 2007; Hassan et al. 2016). Along with metal impurities, rock phosphate (RP) used in fertilizer industries contains high concentrations of radionuclides from the ^{238}U decay series, such as U, Ra, and Rn (Lopez et al. 2010). Amendments like phosphogypsum (PG) are more radioactive than P fertilizers. Potential risk by exposure to radionuclide-enriched fertilizers through food consumption in human cannot be neglected (Rehman et al. 2006; Nowak 2013). Another study by Lopez et al. (2010) widely described the radioactive impact of U-series radionuclides in phosphate rock (during the industrial process) wastes on the environment. In contrast, several studies (Saueia and Mazzilli 2006; Righi et al. 2005) suggested negligible amount of radioactive contaminants in phosphate fertilizers. Release of by-products into environment from fertilizer industries is a serious threat to aquatic life, human beings, and other life forms, creating ecological imbalance in nature. One such instance was reported by Perianez et al. (1996) where 20% of the phosphogypsum was disposed to environmental systems until 1997 and was just considered as a waste management practices by industries.

Fluoride is closely associated with RP as majority of the mineral is present in the form of fluorapatite. While manufacturing commercial fertilizers, F is released into the atmosphere, which is recycled back to the earth's surface during rainfall. Also, phosphor-gypsum, a by-product from the P fertilizer industry, also leads to F contamination (Mirlean and Roisenberg 2007). In India, Unnao district in Uttar Pradesh is fatally affected by F contamination and has seen a rise in P fertilizer consumption by 5 lakh metric tonnes in the past one decade (www.downtoearth.org.in). Lead and cadmium contamination is another problem arising from excessive use of P fertilizers. Lin (1996) detected varying amount of HMs such as Cd 9.5–96.4 mg kg^{-1}, As 19.4–273.0 mg kg^{-1}, Pb 5.6–17.2 mg kg^{-1}, and Hg 0.01–0.42 mg kg^{-1} in rock phosphate and phosphorus fertilizers. In another study, triple superphosphate fertilizer application led to increased Cd concentration compared to other fertilizers (Atafar et al. 2010). Besides the primary nutrient fertilizers, arsenic (As) concentration in soil has increased due to zinc sulfate application. Phosphate fertilizers were important carrier of heavy metals such as Zn, Cu, and Cd in agricultural soils of England and Wales (Nicholson et al. 2003). In many scenarios, long-term application of P fertilizers results in accumulation of HMs and radionuclides, which could be potential threat to environment and organisms (Huang and Jin 2008).

2.3 Potassium Fertilizers

Potassium fertilizer such as KCl is commonly applied by farmers, and excess application of the fertilizer often leads to accumulation of Cl^- ions in soil. Some studies have shown that chloride anions accumulate to toxic levels in legumes. These contaminants are known to enter food chain through fertilizers or other chemicals used for food production. To avoid the adverse consequences of Cl^-, K_2SO_4 would be preferred as a fertilizer source (Khan et al. 2013). In another report, Grant et al. (1996) highlighted increased concentrations of Cd in malting barley due to KCl application. Fertilizers containing high level of sodium and potassium can have negative impact on soil properties such as soil pH, microbial life, and soil physical properties like structure and bulk density, which can hamper crop production (Savci 2012).

2.4 Organic Fertilizers

Heavy metals are the major contaminants in organic manures. Application of organic fertilizers (i.e., compost, sludge, or manure) to fields, especially agricultural crops, provides significant input not only of nutrients (i.e., nitrogen, phosphorus, sulfur, and micronutrients) but also of some heavy metals, some of them being toxic, such as cadmium or lead (Pinamonti et al. 1997; Lipoth and Schoenau 2007). Organic manures like sewage sludge can be used in agriculture provided, HMs content should be within threshold limits for soil application. In majority of conditions, organic fertilizers are usually considered “best,” but uncontrolled use of manures may cause environmental damage due to its high content of nitrogen released into the soil. Nitrogen present in the organic fertilizers transforms rather slowly into ammonium nitrate, and thus nitrate. Similar transformation happens with inorganic fertilizers, where urea converts into nitrate a little rapidly and more rapidly with ammonium nitrate fertilizers. The chemical transformation rate depends greatly on the soil microbial activity present in soil, and environmental conditions such as warmer temperatures and humidity favor this increased rate of transformation. Under high temperature especially during spring and summer, rapid conversion occurs compared to winter and dry conditions. The formed nitrate sometimes is absorbed by crops, and the excess is lost via leaching to subsurface depth, causing pollution of ground or surface water and sometimes resulting in eutrophication of water bodies.

Contaminant concentration should be kept in mind before planning for the reuse of waste materials as organic fertilizers. It is clear that continuous and long-term application of organic fertilizers from unknown sources often favors accumulation of HMs and other contaminants in soil and water system. Interaction of HMs and other contaminants with soil components provides a direct entry into food chain, and foods directly grown on such soils adversely affect animal and human health (Khan et al. 2008; Smith et al. 2009; Zhuang et al. 2009). Other studies by Smith et al. (2009) and Lopes et al. (2011) reported that heavy metal concentration in SS is 50–90% more than compost and 20 times more than manure (especially concentration of Cd and Pb). Industrial effluents from wastewater treatment plant of sewage sludge (or compost) are major sources of HMs concentrations, and the amount of pollutants varies depending on the composition of domestic waste and country origin (Bose and Bhattacharyya 2008: Egiarte et al. 2009). Organic manures such as vegetable fruit waste from food processing industries, municipal solid waste, or sewage sludge are some of common manure sources. Another waste source is from food markets rich in nutrient levels, organic matter, and moisture content (Varma and Kalamdhad 2015). In a similar study on food market wastes in Chimborazo Region of Ecuador, Jara et al. (2015) reported mean values of OM and $N–P_2O_5–K_2O$ as 77.3% and 2.5% ± 0.7% ± 3%, respectively. Though application of such organic waste or manures is a sustainable way to recycle nutrient and carbons into soil, precaution is needed to evaluate the possible source of contaminants present in such organic fertilizers before disposing into agriculture fields. This will not only prevent the entry of contaminants into food chain but also protect environment.

2.4.1 Heavy Metals: Major Contaminant in Organic and Inorganic Fertilizers

Soil is considered a long-term sink for toxic elements often referred to as heavy metals, such as Cu, Zn, Cd, Pb, Cr, As, and Hg. In India, heavy metal contamination in soil due to anthropogenic activity has been reported from different areas (Sachan 2007; Shanker 2005; Deka and Bhattacharyya 2009). In agriculture, soil is the major contributor of heavy metals, which includes liming materials, irrigation water, and sewage sludge as shown in Table 2. The HMs such as Cd, Cr, Zn, Pb, Cr, and As are highly contributed by inorganic fertilizers, pesticide, and organic sources in agriculture (Kelepertzis 2014; Toth et al. 2016).

Table 2 Total concentration of selected heavy metal in manures (ppm on dry weight basis)

Source	Arsenic	Cadmium	Chromium	Lead	Nickel	Copper
Cow manure	–	8	58	16	29	62
Poultry manure	0.35–110.5	–	0.6–19.6	–	–	3.5–13.5

Chhonkar (2003)

Table 3 Source of HM contaminants from inorganic and organic fertilizers in agriculture

Source	Heavy metal inputs	Contaminants	References
Inorganic fertilizers	Phosphate fertilizer	Cr, Cd, Cu, Zn, Ni, Mn, and Pb	Atafar et al. (2010), Sun et al. (2013), Toth et al. (2016), Kelepertzis (2014), etc.
	Nitrate fertilizer		
	Potash fertilizer		
	Lime		
Organic fertilizers	Animal manures	Zn, Cu, Ni, Pb, Cd, Cr, As, and Hg	Nicholson et al. (2003), Singh and Agrawal (2008, 2010), Niassy and Diarra (2012), Srivastava et al. (2015, 2016), Sharma et al. (2017), etc.
	Sewage sludge		
	Compost		
	Fly ash		

Srivastava et al. (2017)

Niassy and Diarra (2012) reported that sewage sludge, manure, and limes are major sources of cadmium enrichment. Repeated use of phosphatic fertilizers often results in deposition of HMs like Cd in soils. However, long-term application of sludge materials accumulates Cd, Cr, Ni, Pb, Cu, and Zn and builds up micronutrients like Cu, Mn, Cu, Co, and Zn (Srivastava et al. 2017). Land application of sewage sludge is one of the major contributors of heavy metal to the soil system (Srivastava et al. 2016; Sharma et al. 2017). Several studies had shown that both organic and inorganic fertilizers contribute to HM contamination as shown in Table 3. In a report by Daniel and Perinaz (2012), total urban solid waste generates nearly 68.8 million metric tonnes per year (TPY) or 1,88,500 metric tonnes per day (TPD). Out of the total, 9–10% of these wastes enter into agricultural land directly in the form of compost rich in heavy metals. This is a serious concern with the present data indicating higher accumulation of HMs by agricultural inputs directly influencing soil, water, air, and organisms. Threat or potential risks due to contamination by HMs, radionuclides, and other form of contaminants cannot be neglected in agriculture, though availability or transformation of these contaminants varies depending on soil type, input type, rate, mode of application, etc. Soil acts as a big reservoir for contaminant retention and degradation in long run protecting the environment and its ecosystem services so as to sustain several life forms. Besides negative effect on human, HMs also adversely affect soil microbial diversity, microbial-mediated process, and soil–microbe interaction (Gall et al. 2015; Rai et al. 2018). Soil faunae like invertebrates, small mammals, worms, and various agriculturally important

Table 4 Permissible HM content in soil and food material

Elements	World range of elements in nonpolluted soil (mg kg^{-1})	Maximum allowable limits of elements in fruits and vegetable (mg kg^{-1}) (*dry weight basis*)
Cd	0.07–1.1	0.2
Pb	10–70	0.3
Cu	6–60	40
Cr	5–121	2.3

Banerjee et al. (2010)

insects are affected by HM contamination (Bartrons and Penuelas 2017; Rai et al. 2018).

Soil type like those with high clay content have high buffering capacity which does not signify the effect of soil pH on bioavailability of metals and thus control metal chemistry in soils (Baldwin and Shelton 1999). The availability of metals for crop uptake from sewage sludge and other composts sometimes depends on intrinsic properties of the materials themselves. There is a need to develop more careful management scheme for experiments related for study of HM uptake by crops through compost and other sludge treatments (Smith 2009). Table 4 presents safe values for Cu, Pb, Cd, and Cr in fruits and vegetables recommended by WHO/FAO and range of heavy metals in nonpolluted soil.

Long-term application of excess organic manures with chemical fertilizers accumulates HMs like Cu, Zn, Cd, Cr, Pb, As, etc. in soils under vegetable fields of China (Huang and Jin 2008). They reported an increased accumulation of total Cu, Zn, and other heavy metals in soils with increase in vegetable production. Nicholson et al. (2003) reported the presence of high amount of HMs like Cu, Zn, Cd, other contaminants from P, and other fertilizers. In plants, Cd accumulation has a negative effect on N metabolism as it alters oxidant levels, resulting in oxidative stress with accumulation of active oxygen species (AOS), including superoxide radical (O^{2-}), hydroxyl radical (OH), and hydrogen peroxide (H_2O_2) (Gallego et al. 1996; Hassan et al. 2005). Cadmium accumulation in soil and its uptake by crops tend to induce stress in plants, thereby affecting the photosynthetic trait and its antioxidative pathway leading to growth reduction. Higher concentration of Zn usually present in sewage sludge and compost is relatively available and is easily transferred to plant tissues resulting in higher bioaccumulation (Speir et al. 2004). Bioaccumulation of HMs in plants interfere with metabolic pathways and biochemical reactions and directly affect photosynthesis, assimilation of biomolecules and elements, etc. (Kabata-Pendias and Pendias 1992), resulting in plant senescence and death.

With recent developments in agriculture, intensive cropping system is practiced by farmers, which forces excessive use of inputs such as fertilizers and pesticide in soil. These chemicals often leave residues in soil and get transported to water bodies, and thus contributes significantly to water and soil pollution (Almasri and Kaluarachchi 2004; Khan et al. 2018). Thus, pollution by contaminants has put human and animal life at risk, on the one hand, and environmental degradation, on the other hand. Fertilizers containing HMs such as Cr, Zn, Cd, Hg, and As from the raw materials contribute for higher accumulation of HMs in the soils (Huang and Jin 2008). Discriminate and blanket dose of fertilizer applied to crops results in HM buildup in soil and deteriorates soil functions, thereby adversely affecting crop growth and development. Such situations often affect both biochemical and physiological plant processes, leading to the degeneration of organelles and cells that may result in plant death (Nagajyoti et al. 2010; Gupta and Sandallo 2011). There are several studies that indicate that continuous and excessive application of inorganic and organic fertilizers will not only add nutrients to the soil but also considerable amounts of HMs in soil and plant systems. Some examples of heavy metal accumulation in soils of different experiments are shown in Table 5.

In last few decades, more emphasis has been put on the reuse of organic sources such as manure, distillery effluents, sewage/sludge water, and fly ash on agricultural field in order to reduce dependency on nonrenewable resources. Increasing population and urbanization had created more pressure for agricultural productivity with limited land use, and this has often pushed use of low-cost methods of applying such manure forms in soil, which has resulted in high buildup of HMs affecting adversely human health (Rai et al. 2019). Countries with high population like China, India, and African countries such as Zambia and Nigeria are using wastewater from sewage/sludge for irrigation without proper treatments, having direct impact on food quality and environmental issues. Long-term use of wastewater for irrigating crops in India showed accumulation of HM in plant tissues of food crops and poses health risk (Ghosh et al. 2012; Garg et al. 2014; Saha et al. 2015; Chabukdhara et al. 2016). However, in European and American countries, fertilizers, fungicides, and modern agricultural practices were responsible for HM contamination in food crops (Rai et al. 2019).

3 Fertilizers and Manures and Their Impact on Soil Health

3.1 Impact on Soil Properties

Both inorganic and organic fertilizers influence soil physical, chemical, and biological properties. The various soil properties influenced by the addition of inorganic fertilizers and organic manure are shown in Fig. 3. In this section, various soil properties influenced by inorganic and organic fertilizers application are explained.

3.1.1 Effect on Soil Physical Health

Some important physical indicators of soil are bulk density, water availability, hydraulic conductivity, compaction, pore size distribution, and soil surface cover. Soil structure is a dominant soil indicator used for crop production, which has direct influence on soil health. Application of fertilizers like $NaNO_3$, NH_4NO_3, KCl, K_2SO_4, and NH_4Cl deteriorates the structure (Savci 2012).

Table 5 Effect of various fertilizer containing HMs and their influence on soil properties

S. No.	Crop	Country	Source of fertilizer and manure, application rate	Effect of fertilizer and manure contaminants (HMs)	References
1.	Lettuce	China	Phosphate rock (PR) and triple superphosphate (TSP)	Average of 1% or less Cd was accumulated in lettuce tissue. Applications of the fertilizers at high rates could result in increased Cd accumulation in the soil over time	Huang et al. (2004)
2.	Potato–sugarbeet	Hamadan province of Iran	Pollution index was calculated for each element	Enhanced levels of As, Cr, Cu, Mn, Ni, and Pb in P-amended soils from sugar beet fields; Pb, Cr, As, and Cd for soils from potato fields; and Fe and Zn for soils from both potato and sugar beet fields	Cheraghi et al. (2012)
3.	–	Hesse, Germany	14 years of fertilizer application	Pseudo- and mobile metals (Cd, Cu, Mn, Pb, and Zn) in soils increased following 14 years of mineral fertilizer treatments (N, P, NP, and NPK). Long-term fertilizer use increased soil metal content, soil organic C, CEC, and decreased soil pH level	Czarnecki and During (2015)
4.	Land-use pattern (3): vegetable field, bare vegetable field, and grain crop field	Bejing, China	20 years of cultivation	Long-term use of excessive chemical fertilizers and organic manures in the bare vegetable field and the greenhouse vegetable field contributed to the accumulation of Cu, Zn, and other heavy metals in the soils. Cd pollution was relatively more serious in the bare vegetable field and the greenhouse vegetable field than that in the grain crop field	Huang and Jin (2008)
5	Soybean–wheat	Brazil	Phosphatic fertilizers and agricultural gypsum	Higher accumulation of uranium and Thorium radionuclides in soil where fertilizers; clayey texture retained more radionuclides than red latosol of mixed texture	Saleh et al. (2007)
6	Rice–wheat	India	Five levels of sludge, i.e., 0 (S0), 10 (S10), 20 (S20), 30 (S30), and 40 (S40) t ha^{-1}, applied to rice crop and wheat grown as residual crop with fertilizers	Improved rice and wheat yield; cd content in rice grain was above the Indian safe limit at 20 t ha^{-1} or higher levels of sludge application; significant buildup of P, S, Zn, Fe, and Mn in postharvest wheat soil at 40 t ha^{-1} sludge application	Latare et al. (2014)
7.	Animal feed and manure	England and Wales	Dairy and pig manure (85 samples)	Increment of about 5247 mg Zn, 1821 mg Cu, and 225 mg Ni per kg dry matter added to agricultural lands	Nicholson et al. (1999)