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

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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,

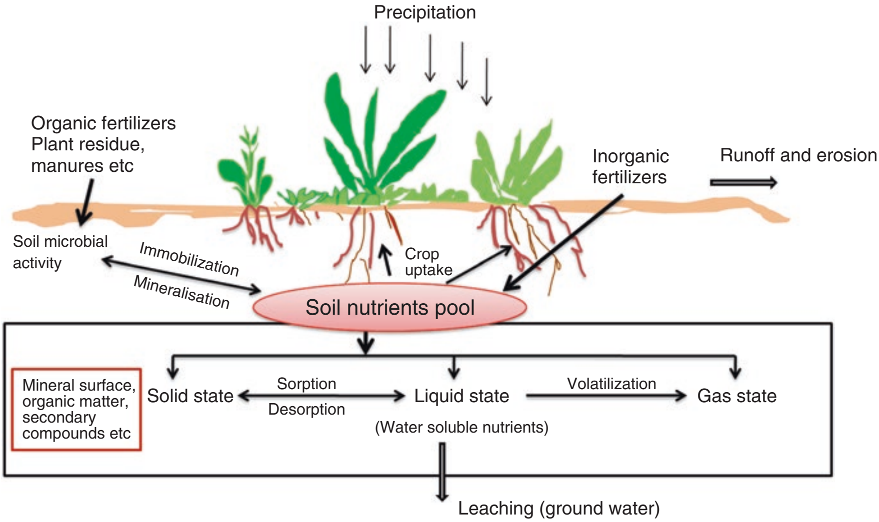

Fig. 1 Fate of organic and inorganic fertilizer behavior in soil

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

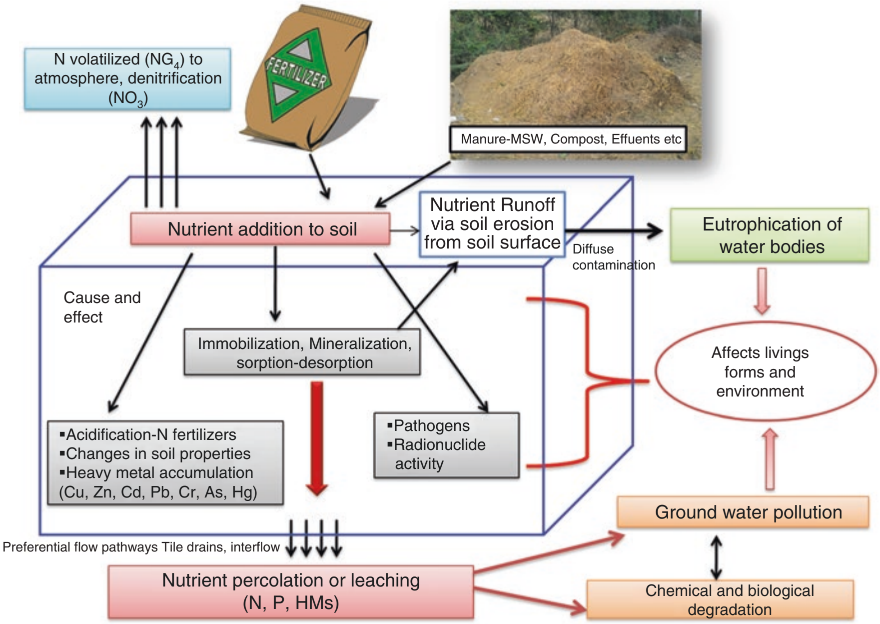

Fig. 2 Transformation of contaminants in inorganic and organic fertilizer in soil ecosystem

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)

8.	Animal feed and manure	China	Pig, cattle, and chicken feed and manure (224 samples)	Long-term agricultural application of animal manure increases the potential risk of cu pollution in soil and surface water.	Zhang et al. (2011)
				Mean Cu concentrations in pig, cattle, and chicken feeds were 179.8, 16.6, and 20.8 mg kg^{-1}, respectively. Cu concentrations in manures ranged from 1.5 to 1521.2 mg kg^{-1}	
9.	Pot experiment on herbaceous plants	Shanghai, China	Sewage sludge collected from waste water treatment plant	Long-term trials of sewage sludge application show accumulation of trace metals in the soil especially Ni and Cd; sewage sludge significantly affects heavy metal uptake by herbaceous plants	Dai et al. (2006)
10.	Column experiment (Composting of MADD)	Kent, UK	Biosolids namely fresh mesophilic anaerobic digested dewatered (MADD) sludge cake used, application rate of biosolids (250 kg N ha^{-1} $year^{-1}$)	Enriched the soil with Zn: 6 mg kg^{-1}, Cu: 2 mg kg^{-1}, Pb: 5 mg kg^{-1}, and Ni: 0.2 mg kg^{-1}	Gove et al. (2001)
				The movement of metals followed order Zn = Pb > Cu > Ni; composting or drying of MADD increases contamination of ground water	
11.	Silver beet	New Zealand	Composted sewage sludge for 4 years up to a maximum rate of 200 t ha^{-1} y^{-1}	Total heavy metal concentrations in the soil were high, but basal respiration, microbial biomass C, and anaerobically mineralizable N were significantly increased in the compost-amended plots relative to the control	Speir et al. (2004)
12	Long-term study: red beet, sugar beet, or barley	Woburn, England (23-year-old experiment)	Sewage sludge or composted sludge	Zn and Cu present in compost sludge organically bound fractions in compost-amended soil; there was no evidence of an increase in bioavailability of Zn and Cd to the crop plants with time	McGrath et al. (2000)
13	Barley	Toledo, Spain (5-year study)	Compost applied at two rates of 20 t ha^{-1} and 80 t ha^{-1} with mineral fertilizers	MSW compost increased microbial biomass; activities of the intracellular enzymes increased with the rate of compost addition; urease and phosphatase activities were reduced in compost-amended soil. Heavy metal toxicity was indicated as one possible cause of the inhibition of these enzymes	Garcia-Gil et al. (2000)

(continued)

Table 5 (continued)

S. No.	Crop	Country	Source of fertilizer and manure, application rate	Effect of fertilizer and manure contaminants (HMs)	References
14	Wheat	Tunisia (Short-term study)	MSW compost applied at 40 t ha^{-1} and 80 t ha^{-1}; farmyard manure was applied at 40 t ha^{-1} with or without chemical fertilizers	At 80 t ha^{-1}, plants showed an increase of heavy metal (Cu, Cd, Zn) content in all plant parts but did not affect crop yield and growth	Lakhdar et al. (2009)
15	Maize–soybean	China	10-year study; pig manure (0, 100, 250, and 500 kg total N ha^{-1} $year^{-1}$ for 8 years and 0, 10, 25, and 50 t of pig manure fresh weight ha^{-1} $year^{-1}$ for 2 years)	Serious accumulation of Cu and Zn in soil, total Cu and Zn concentrations increased by 204% and 107% at high application rates; Cu and Zn leaching occurred in the tested soil; Cu and Zn contents in plants parts were not affected by manure	Xu et al. (2013)
16	Tomato	Tunisia	Sewage sludge was mixed with the soil at 2.5%, 5%, and 7.5% (DW) proportions	Among the three HMs (Zn, Cu, and Cr), Zn had the highest capacity for transferring from soil into plants. Low metal translocation was observed from roots to leaves. The 7.5% SS dose decreased	Elloumi et al. (2016)
				Biomass production and caused a decline in chlorophyll content and stomatal conductance	

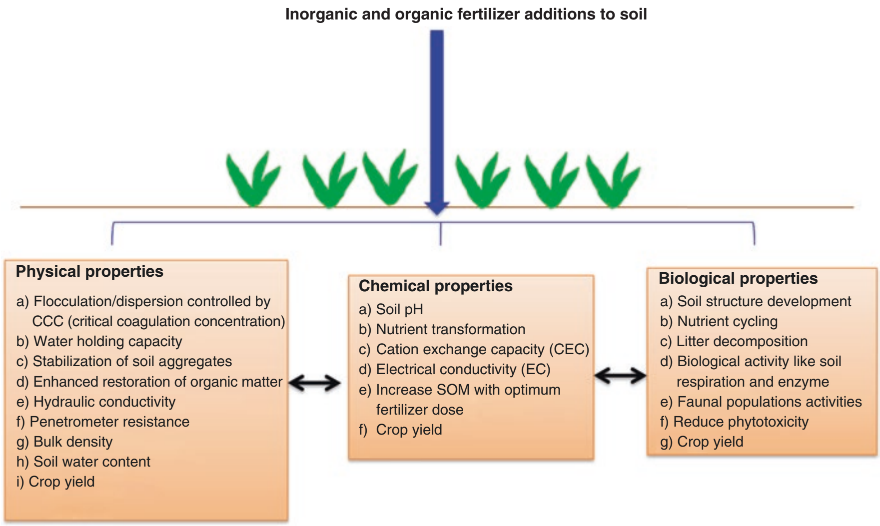

Fig. 3 Soil properties influenced by inorganic and organic fertilizers

Soil physical properties unlike chemical, are indirectly effected by fertilizers and manures. They contribute to better crop canopy, root distribution that directly effects physical properties like soil aggregation, bulk density, water movement etc. All the nutrients in the form of N, P, and K fertilizers directly play an important role in soil properties such as flocculation and dispersion depending on the composition of synthetic compounds. Both flocculation and dispersion are governed by critical coagulation concentration (CCC). As underlined by Sposito (1989), the lowest electrolyte concentration at which a soil suspension turns unstable and subjected to rapid flocculation or coagulation under a specific set of conditions is termed as CCC. Few studies indicate the benevolent impact of phosphatic fertilizers on soil physical properties (Thein 1976; Yeoh and Oades 1981a, b). Some of the properties improved by the addition of P fertilizers are lowering bulk density, enhanced water holding capacity, flocculation, etc. The addition of fertilizers is also known to improve stabilization of soil aggregates, which contributes significantly to the SOM stabilization. Similarly, application of fertilizers improved the mean weight diameter and aggregated stability of soil, which might be due to the phosphatic fertilizers binding the soil particles together (Marathe and Bharambe 2005; Selvi et al. 2005). However, Interweck et al. (1982) reported addition of ammonical fertilizers sometimes cause dispersion of soil colloids. But they did not observe any affect of ammonical fertilizer on soil physical properties like bulk density, penetration resistance, aggregate stability etc.

3.1.2 Effect on Chemical Properties

Important chemical properties such as soil pH, electrical conductivity (EC), soil nutrients interaction, and cation exchange capacity (CEC) govern soil suitability for crop production. Addition of excessive dose of chemical fertilizers to soil often leads to acidification and heavy metal and other contaminant accumulation, adversely affecting soil health.

Nitrogen in small amount is essential for crop growth; however, when used in excess, results in loss of nitrate through surface runoff, leaching (Bai et al. 2010; Lucas et al. 2011). Application of N fertilizers often increases acidification by converting NH_4^+ to NO_3^- in oxidation process, which generates H^+ and lowers the soil pH. In soil, oxidation of ammoniacal fertilizers is carried out by microorganisms that release ions causing acidity. Thus, conversion of fertilizer N to ammoniacal forms and nitrate forms substantially contributes to proton loading into soil reducing soil pH. Nitrification of ammonia, ammonium, and hydrolysis of urea releases $1H^+$ and $2H^+$ ions into soil system through microbes responsible for acidifying soil reaction (Khan et al. 2018). Interestingly, the assimilation of applied N fertilizers by crops in the form of nitrate-N and sulfate-S into organic forms, however, consumes H^+ ions, resulting in alkalinity of soil. There are number of studies illustrating the effect of N fertilizers on soil acidity (Chien et al. 2008; Jackie et al. 2011). The reduced pH increases Al solubility in soil, which becomes toxic for crop growth at pH <5.5. The study by Guo et al. (2010) in China reported that soil pH decreased significantly with application of excessive N fertilizer resulting in severe soil acidification, during 1980–2000. They also reported that application of N fertilizer released protons to the tune of 20–221 kg ha^{-1} $year^{-1}$, on the one hand, and base cation uptake contributed to additional 15–20 kg H^+ ha^{-1} $year^{-1}$ resulting in soil acidification, on the other hand. Chien et al. (2008) observed that application of various ammoniacal fertilizers changed soil pH in the following order: $(NH_4)_2SO_4$ < NH_4NO_3 < urea<control. In contrast, study by Darusman et al. (1991) observed no significant difference in soil pH when N was applied in the form of NH_3, NH_4NO_3, urea, and urea–NH_4NO_3 at rates ranging from 0 to 224 kg ha^{-1} during 20-year period. Chen et al. (2013) also described that soil acidification induced by N fertilizers is a serious threat for organisms and various ecosystem services. Soil acidification directly influences soil pH by increasing ions of Al and Fe in soil colloids and decreasing basic cations like Ca^{2+}, Mg^{2+}, and K that are essential for crops. Acidic soil impedes P availability to crops due to higher P fixation by forming insoluble Fe and Al phosphate compounds.

Another major aspect of inorganic fertilizers addition is its influence on soil organic matter (SOM) cycling. Triberti et al. (2008) highlighted the role of inorganic and organic fertilizer addition to C sequestration in cropping system. Compared to nonfertilized plots, addition of inorganic fertilizers with manures or crop residues improved soil carbon content and sequestration efficiencies in various cropping systems (Gong et al. 2009; Huang et al. 2010). Although SOC dynamics varies with climate and soil type, optimized fertilization with inputs and proper agronomic management are key factors that improve SOC buildup in soil. In contrast, few studies by Khan et al. (2007) and Mulvaney et al. (2009) suggested that continuous application of N fertilizers could result in net loss of organic N and organic C to the tune of 92% and 74%, respectively, from temperate and tropical regions. Balanced use of chemical fertilizers help in SOM build up compared to those without fertilizers applied during cropping system (Geiseller and Scoe 2014; Korschens et al. 2013)

3.1.3 Effect on Microbial Life

Soil biota highly influences soil health and is considered a prominent indicator for improving soil quality. The soil biological indicators govern various mechanisms, such as nutrient cycling, immobilization–mineralization, residue decomposition, soil respiration, and biomass addition.

Among microbial fauna, both bacteria and fungi play important role in nutrient transformation and govern the availability to plant roots. Immobilization and mineralization of nutrients from organic matter are highly influenced by soil microbial diversity that signifies the bioavailability of N, P, S, and few micronutrients essential for plants. Allison and Martiny (2008) in a review highlighted that 84% of 38 experiments indicated that microbial biodiversity is highly sensitive to N, P, and K fertilizers. Earlier studies underlined reduction in microbial population with the application of N fertilizers due to reduction in soil pH (Bittman et al. 2005).

Even symbiotic relationship of microorganisms with plants roots is also influenced by the availability of nutrients, for example, suppress *Rhizobium* activity in legumes with excess N fertilizers (Savci 2012). Reduction in microbial biomass P with 200 mg N kg^{-1} (ammonium sulfate) was reported by Saggar et al. (2000) during 168 days of incubation. Root colonization by arbuscular mycorrhizal fungi (AMF) was reduced with P and N application in long-term experimental studies (Ryan et al. 2000). However, inorganic fertilizers do not always suppress microbial community; instead, they indirectly help build up SOM. This improves microbial population and contributes to nutrient transformation and other benefits in soil system. Geiseller and Scow (2014) in their review paper reported 15.1% increase in soil microbial biomass carbon compared to control plots under long-term fertilizer use. This is quite clear that fertilizer application improves crop or plant biomass which adds back root exudates, plant parts back to soil and enhances microbial activity in a managed ecosystem.

3.2 Water Quality Issues Associated with Organic and Inorganic Fertilizers

Almost all the countries rely heavily on ground water for drinking water supply, livestock water, irrigating crops, industrial uses, and other uses. Scope of ground water contamination in many countries is very critical. Impact of fertilizer contaminants on water quality is a serious issue, which caters immediate attention worldwide. According to Organisation for Economic Co-operation and Development (OECD) countries, agricultural water quality has been identified as a major environmental issue and as a topic for policy analysis and is an issue of relevance across all OECD countries. The primary agricultural sector is mainly responsible for nitrate, phosphorus, pesticide, soil sediment, salt, and pathogen pollution of water from crop and livestock activities, but it can also play a role under certain farm practices in terms of improving water quality through a water purification function. Surface water is primarily affected through soluble contaminants via surface runoff or insoluble contaminants carried on soil particles during erosion events. However, ground water can be contaminated with pollutants through percolation, seepage, and infiltration rate. Water pollution from agriculture has associated costs in terms of removing pollutants from drinking water supplies, as well as damage to ecosystems and commercial fishing, recreational, and cultural values associated with rivers, lakes, ground water, and marine waters (Parris 2011). This nutrient enrichment of aquatic bodies is known as eutrophication, which results in an algal bloom by undesirable plants covering the water surface and decreases the biological oxygen demand that affects living things. The decomposition of organic matter from undesirable aquatic plants causes the water body to have depleted oxygen levels and restricts water use for fisheries, recreation, industry, and drinking. In most of the developing countries, lack of consistent and comprehensive database of contaminants from agrichemicals has made difficult to link nonpoint source of pollution and human activities. In many cases, extent of agricultural ground water pollution is generally less well documented than that of surface water, chiefly due to the costs involved in sampling ground water and because most pollutants take a longer time to leach through soils into aquifers. Among the various macronutrients used as fertilizers in agriculture, in particular nitrogen (N) and phosphorus (P) can cause eutrophication of surface waters. Further, their emission and discharge into coastal areas and the marine environment can significantly impact upon the status of those ecosystems. According to ICPDR (2013) during the period of 1988–2005, an average of about 35,000 and 400,000 tonnes of inorganic P and N, respectively, is transmitted into the Black Sea through Danube river each year. Some of the major contaminants and their impact on water quality are discussed below.

3.2.1 Nitrogen Contamination in Water Bodies

Nitrogen is the most important nutrient required by crops and highly vulnerable to losses causing contamination of surface and ground water resources. Nitrogen is converted into various forms of nitrate (NO_3^-), nitrite (NO_2^-), and ammoniacal (NH_4^+) forms before assimilation by crops and organisms. Nitrate is the most common form of N available in soil and loss from soil system to nearby water bodies. However, potential of nitrate in polluting the soil depends on soil type, N application rate, rainfall, irrigation, etc. Leaching is identified as a common mechanism through which N is lost from root zone and contaminating water reservoirs on large scale. Nitrate form of N is negatively charged and, therefore, does not bind to soil surface, and thus easily leaches through soil profile and finds entry into ground water or subjected to surface runoff polluting the water reservoirs. Nitrate accumulation at the surface and bottom soil layer is reported by Wang et al. (2015) who studied leaching and accumulation of NO_3^- in a simulated rainfall experiment. However, NO_3^- concentrations initially increased but later decreased sharply and stabilized with fertilization levels. They reported that soil was able to retain 50.53% of total nitrate applied during experiment. This indicated that precipitation or irrigation in such soils would increase threat for nitrate contamination through surface and subsurface flow into water bodies. As per US environmental protection agency and health organizations, the acceptable level of NO_3^-–N levels in drinking water should be less than 10 mg L^{-1} (EPAR 2001). However, high NO_3^-–N concentration in ground water of Japan was noticed due to application of N fertilizers (Kumazawa 2002). The NO_3^-–N concentration reached 100 mg L^{-1} in some wells posing high risk to human health. There are studies which illustrate spatial and temporal variation in N loss from fertilizers. In a study by Chen et al. (2016), significant linear correlation between total nitrogen (TN) and NO_3^- –N was observed in surface runoff.

Globally, nonpoint source of N pollution has gained attention due to its serious threat to aquatic and human life. It is estimated that agriculture itself contributes to nearly 75% of nonpoint source of pollution in the United States (Line et al. 1998). In Denmark, nearly 94% of nitrogen buildup in 270 water bodies was reported due to nonpoint source of pollution (Kronvang et al. 1996). In the Netherlands, agriculture contributed to nearly 60% of N buildup in water bodies through nonpoint sources (Boers 1996). In a recent study in China, Jiao et al. (2015) reported high accumulation of total phosphorus (TP) in areas with intensive agriculture practices in catchment areas of Miyun reservoir. They reported highest TN during winter season, but high concentrations of NH_4^+–N were observed during summer, and this clearly indicates the direct effect of season variations in N forms.

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) are all affected by eutrophication. Both USEPA and WHO (US Environmental Protection Agency (EPA) 1977; WHO 1958, 1985) have set threshold limit of NO_3–N as 10 and 50 mg L^{-1} nitrate for drinking water so as to prevent methemoglobinemia in infants. Under this condition, the NO_3^- in water enters the infant's body and is reduced to nitrite (NO_2^-), which in turn oxidizes the Fe^{2+} of hemoglobin to Fe^{3+}. The oxidized hemoglobin is incapable of binding with oxygen and thus causes anoxia and death of infants. The symptom is also referred to as "blue baby syndrome" as the blood color turns blue due to lack of oxygen. Nitrate is also known to be a carcinogen, which affects humans greatly. According to BIS (2012), the threshold limit of nitrate in drinking water is 45 mg L^{-1} in Indian situation. Almost 108.2 million people in India are exposed to more than 45 mg L^{-1} nitrate (Rai 2003). Thus, risk of nitrate contamination and diseases like cancer have become more common in India.

3.2.2 Nitrate Management in Ground Water

Several techniques of nitrate removal from ground water sources are now available with many industries and scientific organizations. The contaminated ground water is subjected to various processes to remove nitrate as explained by many authors (Khani and Mirzaei 2008; Bhatnagar and Sillanpaa 2011). Techniques such as (i) ion exchange process to remove nitrate ion from water, (ii) biological denitrification process, (iii) reverse osmosis, (iv) electrodialysis, (v) activated carbon and carbon nanotubes, (vi) montmorillonite and bentonite clays, and (vii) agricultural waste material (rice husk, wheat straw, sugarcane bagasse, etc.) are commonly utilized for nitrate removal. Other technique is management of soil organic matter to avoid nitrate leaching from fertilizers applied to soil. Thirty-year long-term experiment showed that 60–65% of applied N was assimilated by plant, 12–15% remained in soil organic pool, and 8–12% was lost to the ground water after 28 years of experiment. This shows the importance of organic matter management in soil to improve the efficiency of fertilizer N and prevent its leaching to the hydrosphere (Sebilo et al. 2013).

3.2.3 Phosphorus Contamination in Water Bodies

Unlike nitrogen, phosphorus is highly immobile in soil. Low availability of phosphatic fertilizers due to fixation to soil particles results in less leaching. Out of the total applied P, plants take up only 10–40% (Garg and Aulakh 2010). The remaining P accumulates in the soil over time and remains unused. According to Sharpley et al. (1994), soils with excessive use of animal manures, fertilizers, etc. containing more than 20 mg kg^{-1} soil solution P are subjected to surface runoff and leaching of P to water bodies. Tirado and Allsopp (2012) in a green peace report highlighted the alarming rates of P loss from field into water bodies. Due to inefficient management practices, nearly 33% of P is lost from soil by wind and water erosion. Poor P use efficiency of 15–30% of P fertilizer results in accumulation of excessive P in soil. Similarly, high rate of application and improper management of animal manure is a major pathway of P entering in water bodies. It is estimated that approximately half of manures applied to crop fields is lost to environment due to mismanagement of resources. Many studies including those of Zhang et al. (2004) and Wang et al. (2012) confirm the potential contamination of P as it is the limiting nutrient in fresh waters. Fig. 4 shows the P transformation pathways in soil water system. Surface runoff during soil erosion increases P losses from soil system to streams, rivers, lakes, and coastal regions (Eghball and Gilley 2001) and causes eutrophication from high bioavailability of soluble P in water bodies.

Water bodies enriched with P shows high algal blooms, reducing dissolved oxgyen, poor aquatic life, phenomena known as eutrophication. It is commonly observed in many developed and few developing countries with excessive application of manure and fertilizers use in agriculture. Phosphorus is considered as limiting nutrient in water bodies Correll (1998) because P concentrations below 10 and

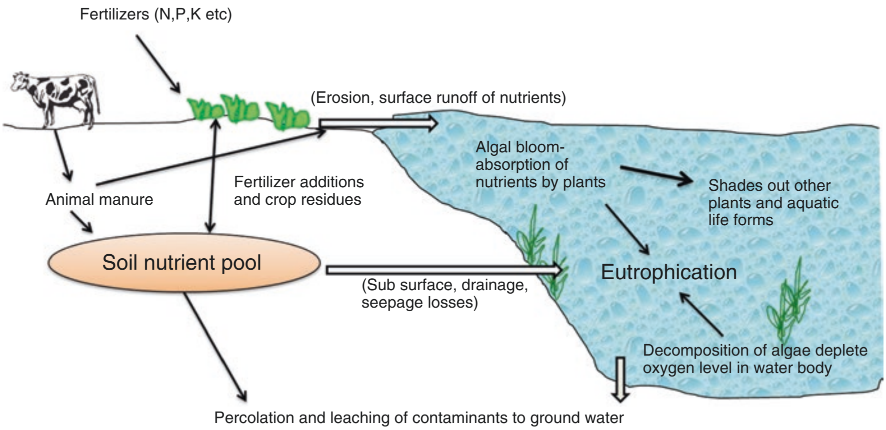

Fig. 4 Inorganic and organic fertilizers as source of contamination in water bodies

20 mg P L^{-1} supports fast growth of aquatic plants, phytoplanktons, etc. (Powlson 1998). Phosphorus had detrimental effect on drinking water quality. In a long-term fertilizer experiment of 16 years, continuous application P fertilizers led to leaching of 7–15% of applied P to ground water. Growth of microbes is a major problem in drinking water. The presence of low P levels like 1 ppm is known to increase microbial population. Miettinen et al. (1997) reported continuous growth of microbes up to 10 ppm P in water; however, the presence of other nutrients of HMs did not influence microbial growth. Higher P accumulation and downward P movement in long-term fertilizer experiments had been reported by Garg and Aulakh (2010) in 22 years of rice–wheat and 34 years of maize–wheat cropping systems in Punjab, India. They reported movement of 6–29% residual P below 30-cm soil depth and higher accumulation of P in subsurface soil layers. Another experiment on a peanut–sunflower system for 4 years showed 41% of P movement below 30-cm soil depth. Buildup and accumulation of P are significantly influenced by P management factors, such as application rate, mode of application besides soil type, depth, irrigation, and organic matter content, which govern P movement in soils.

Eutrophication conditions in water bodies develop with uncontrolled algal multiplication, and major contributor is nonpoint instead of point sources (Carpenter et al. 1998). The main reason for nonpoint sources is intensive fertilization of agricultural soils with P animal manure and fertilizers. Animal manure applied on N basis often results in high P buildup in many Western countries and is considered to be the major culprit for P loss via surface runoff (Eghball and Gilley 2001). Though P is highly susceptible to fixation by soil constituents, but many studies highlight that higher P application with animal manure or fertilizer could increase P level above threshold limit in water bodies. Such high P level causes eutrophication that cannot be reverted back within 1000 years to come (Bennett et al. 2001; Carpenter 2005). In agriculture and forest system, TP concentration varied from 0.01 to

2.47 mg L^{-1} in stagnant surface waters in China. However, higher concentration of TP was reported in surface flowing waters which ranged from 0.01 to 41.66 mg L^{-1} in forest and agriculture system, respectively (Xie et al. 2014). Organic P forms constitute 22–46% of total P and play important role in increasing algal blooms in rivers and other water bodies (Darch et al. 2014).

3.2.4 Organic Fertilizer and Water Quality

Organic manure provides essential crop nutrients and improves soil conditions by modifying aeration, water content, microbial biodiversity, organic carbon, nutrient cycling, etc., thereby significantly improving soil health. However, as a matter of fact, organic manures are also active sources that contribute to HM buildup, pathogenic microbes, nutrient accumulation, and subsequently polluting water bodies, which are serious concerns for human and environment health (Thurston-Enriquez et al. 2005; Jenkins et al. 2008). Improper and excessive application of manures often leads to high buildup of N and P that easily move out of root zone and penetrate to subsurface reaching ground water and polluting it. Surface runoff in such soils will carry N, P along with water flow during erosion causing eutrophication of water bodies nearby agriculture lands or livestock system. In agricultural fields, application of organic manures on regular basis (mostly N based) often acts as nonpoint source of water pollution. In many countries, organic fertilizers like animal manures are applied to the fields. Wastes generated from livestock, poultry, piggery, etc. are usually spread to the land leading to waste assimilation capacity and creating potential sites for ground water contamination, even when commercial fertilizers are also applied. N content in organic manure is either underestimated or ignored and is very critical for enhancing nitrate contamination in water bodies.

Municipal solid waste (MSW) and sewage sludge are other organic manures used in agriculture as soil ameliorant that improve physiochemical properties of soil and improve crop yield (Antonkiewicz and Pelka 2014). They also supply micronutrients and improve soil fertility. Heavy metals such as Cu, Cr, Zn, and Se accumulated above critical limit often interfere with living organisms at cellular levels (Zhao et al. 2012). In agricultural soils, MSW, organic manure, or industrial byproducts such as distillery effluents and fly ash often accumulates HMs in large quantities (Srivastava et al. 2017; Sharma et al. 2017). These organic chemicals and HMs enter into food chain and affect biochemical pathways, resulting in reduced cell growth and death of cells subsequently risking animal life (Khaliq et al. 2017). Poultry manures (PM) are recommended for crop production due to its high N content. However, Hill et al. (2005) suggested that higher dose of poultry manure increase bacterial count and nutrient content, which is susceptible to loss of nutrients (N) under rainfall or irrigation leading to eutrophication and becoming a serious source of contaminant. Poultry manure might be good option for improving soil health, but also it poses potential risk to surface water quality. Application time of manures also poses important risk with its transport via soil erosion and runoff along with soil type, topography, and climatic conditions. In hilly terrain (10% slope), application of PM leads to highest mean annual flow weighted runoff nutrient concentrations and loadings from potato fields. In addition to high nutrient loss from field, runoff samples recorded nearly 20–230% increase in *E. coli* population in water (Rees et al. 2011). Manure application to potato crop during fall time increases nutrient load in runoff samples of water.

In most of the agriculture fields, cattle, pig, and poultry manures are common organic fertilizers used for crop application in many countries. Nutrient concentrations of N, P, etc. vary largely depending on animal type, feed, and other management practices. Pagliari and Laboski (2012) reported that cows usually managed for meat and milk production contain 4.5–14.2 g kg^{-1} P and 2.8–15.0 g kg^{-1} P, respectively, which suggests that frequent monitoring is necessary for better manure management practices. Poultry manure is rich in N content, which may give rise to nitrate leaching. Cattle, poultry, and pig manures recorded Zn (180, 400, and 500 mg kg^{-1} dm, respectively) and Cu (50, 80, and 360 mg kg^{-1} dm, respectively) contents (Nicholson et al. 1999). According to Xiong et al. (2010), Cu is the widely used animal feed additive in China and results in soil Cu pollution. Huge increase in concentration of HMs from dairy, pig, and poultry manures over a period of 18 years was reported by Wang et al. (2013). They reported that HMs such as Cu, Zn, As, Cr, and Cd increased by 212, 95, 200, 791, and 63 in dairy manure, 771, 410, 420, 220, and 63 in pig manure, and 181, 197, 1500, 261, and 196 in poultry manure. Besides buildup of HMs, animal manures sometimes transmit antimicrobial-resistant bacteria raising the issue of environmental contamination as reported by Venglovsky (2009). Therefore, judicious application of such organic and animal manures is the only way to prevent contamination of soil and water resources and will enable to dispose the waste safely.

Municipal solid waste, sewage sludge, or biosolids are another form of organic manures that are easily available source of nutrients; however, they flush high dose of HMs and other contaminants to soil with land application. Biosolids are known to contain array of HMs like Cd, Cr, Cu, Ni, Pb, and Zn as contaminants (Lavado et al. 2005). These HMs are toxic to various life forms and create a number of environmental issues that interfere with the valuable provisional ecosystem services. Besides loss of nutrients, HMs are also lost from soils due to their high buildup and subsequent dilution from soil solution system instead of binding with organic matter and clay particles (Luczkiewicz 2006). Some studies highlight the improvement in soil fertility with the application of sludges; although the presence of HMs such as Cu, Zn, and Ni is essential, high concentrations of the same become toxic for microorganism and plants. Reduction in enzymatic activity and microbial biomass due to HM accumulation has been reported by Singh et al. (2012). However, other studies have reported improvement in soil properties with the application of MSW on field crops. Improvement in soil microbial activity, aggregate associated carbon, and reduction in bulk density with short-term application of MSW were reported by Mondal et al. (2015) in cowpea–wheat cropping system. Generally, MSWs are enriched with organic matter which acts as food and energy sources for heterotrophic microorganisms accelerating biomass C in soil. Sludges from paper, oil, and sugar industries recorded 50, 70, and 312 mg l^{-1} Pb, 3.7, 5.4, and 5.2 mg l^{-1} Cd, and 87,185, and 57 mg l^{-1} Zn, respectively (Machiraju 2011). High loading of HMs was recorded in Roca watershed of Nebraska, the United States, due to greater runoff flow during high rainfall period (Elrashidi et al. 2015). Negative effect of untreated sewage sludge or biosolids on HM content, pathogenic microbial population, and toxicity on other life forms has been reported in many studies (Natal-Da-Luz et al. 2009; Artuso et al. 2011). Therefore, there is a need to find more ecofriendly and sustainable ways to handle such organic manures for agriculture.

3.3 Impact of Contaminants on Human Life

Contaminants from various sources of inorganic and organic sources pose serious threat to plant, animal, and human life on one hand, at the same time affect environment quality (Huang and Jin 2008; Srivastava et al. 2017). These HMs not only decrease crop yield but also affect the soil properties, thereby deteriorating soil health. Heavy metal accumulation poses potential health hazard to human because of their entry into food chain through agriculture production. Fruits and vegetables are the major source of human nutrition after cereals. Some of common dangerous HMs such as Cr, Cd, Pb, As, and Hg are taken through food and are deleterious at high concentrations. Most of these HMs are thermostable and nonbiodegradable and, therefore, accumulate to toxic level in air, water, and soil (Sharma et al. 2007; Lokeswari and Chandrappa 2006). Rai et al. (2019) in review paper highlighted that daily intake of metals (DIM) and health risk index (HRI) values for a study was <1 indicating low risk; however, associated risk due to interaction of HMs with skin and inhalation cannot be neglected in human, in particular to children being most vulnerable. Currently, many studies worldwide had grabbed attention on risk assessment based on HMs in edible plant tissues (Antoniadis et al. 2017; Shahid et al. 2012a, b; Xiong et al. 2014). One important pathway of heavy metal entry into food chain is through the soil and water, which is polluted by agrichemicals. These HMs are then taken up by crops through roots and foliage, which is consumed by human and animals. Long-term exposure to HMs such as As and Cr targets the pulmonary organs, nervous system respiratory disorders, cancer, etc. Cd, the most common HM, is accumulated in soil by phosphatic fertilizers. HMs like Cu, Fe, Zn, and Cr (III) are essential for human metabolic process and play important role in several enzyme activity. However, other metals like As, Hg, Pb, and Cd are nonessential for human beings and classified as the most dangerous elements as per USEPA (Rai et al. 2019). These HM accumulations in animals include a few short-term effects, including vomiting, abdominal pain, and nausea. Few serious health disorders like cancer, liver and kidney damage, endocrine disruption, developmental retardation, and other diseases from severe exposure to toxic compounds have been reported by Mahurpawar (2015). Some papers have described several parameters like hazard quotient (HQ), translocation factor (TrF), health risk index (HRI), estimated daily intake (EDI), life time cancer risk (ILTCR), and bioaccumulation potential (BAP) as important indicators for determining risk assessment of metals and their interaction with soil and plants (Antoniadis et al. 2017; Xiong et al. 2016).

Other major contaminant is radionuclides that enter food chain through crops grown with P fertilizers. Phosphate deposits are usually enriched with radioactive and HM contaminants. Despite the positive effect of crop yield improvement with RP application, accumulation of radioactive elements such as Ur, Th, and Ra and their decay products has been reported in many studies (Lema et al. 2014; Khan et al. 2018). Eisenbud and Gesell (1997) suggested that long-time application of P fertilizers increased radionuclide levels in the soil. Phosphogypsum, a common by-product from P fertilizers, also contains substantial amount of radionuclides to contaminant soil environment. This type of by-product without testing applied to soil can directly affect human and animal health. Foods grown on such sites are very harmful as these contaminants interfere with metabolic process of plants that are consumed by human. Nowak (2013) highlighted the potential threat to human and animal exposed to radioactivity internally and externally by accumulation in different body organs. Continuous and excessive exposure often results in harmful health risks to human. Contaminants like soil- and water-borne pathogens from organic manure are also a potential risk for human, especially to those who handle the manures for field applications. Moreover, such pathogens and pests that once enter into agricultural soils are difficult to manage as they start their life cycle and get associated with crops and other host plants like weeds. Water is the reservoir for a number of contaminants in environment. Both inorganic and organic fertilizers when used indiscriminately by farmers are lost via runoff and leaching, thus contaminating water bodies, and are harmful for human and animals. This nutrient-enriched water is home for a number of pathogenic microbes and animals that spread disease epidemics affecting human health and are difficult to control. Pretreatment of such manures is an important step before land application.

The behavior and bioavailability of various contaminants present in inorganic and organic fertilizers vary depending upon the source, climatic conditions, application rate, method, agricultural practices, etc. Though various research studies have highlighted the critical levels for various contaminants like HMs and radionuclides, there is still a need for creating awareness among both producers and consumers associated with farming. It is, therefore, recommended that there should be proper monitoring of HMs, radionuclide, pathogens, and other contaminant forms in the fertilizers and manures, before application on fields in order to combat entry of pollutants in human food chain. Site-specific information which includes detailed knowledge of soil type, crops to be grown, and awareness level of farmers followed by the potential for transfer of contaminants to soil, water, air and reaching human should be know. These parameters would help in setting guide before loading pollutants in cultivable lands. The role of these contaminants is well understood with respect to human health risk in many studies. Therefore, environment friendly and economically feasible techniques could be utilized for remediation from the contaminants before its entry into food chain. Modern technologies like nanotechnology and creating awareness among farmers about contaminants associated with inorganic and organic fertilizers would not only reduce adverse effect of contaminants in food crops but could also improve their livelihood security.

4 Conclusion

This chapter explains the role of inorganic and organic fertilizers in agriculture and their adverse impact on soil and water quality. Fertilizers improve soil fertility by enriching it with essential nutrients for crops; however, they also contribute various contaminants to environment. Inorganic fertilizer is no doubt a backbone for agriculture, but sometimes, it is equally harmful when used indiscriminately by producers. Organic manures like compost and manures are known as soil conditioners as they supply plant nutrients but improve the physical and chemical properties of soil and improve the carrying capacity of soil health. Organic fertilizers such as MSW and biosolids generated from human waste are sources of nutrients but contain various toxic contaminants such as HMs, radionuclide, pathogen, and organic pollutants, which deteriorate soil and water quality. Compared to inorganic fertilizers, organic fertilizers are more beneficial for soil system, and therefore, measure should be taken to reduce concentration of contaminants in such materials before its transfer to crops.

Long-term and excessive application of inorganic fertilizers has adverse effect on soil properties and environment system. Continuos application of urea decrease soil pH, leaching losses into underground water, and volatilization loss. Another macronutrient P which is considered as major constraint in crop production is critical for water contamination. High P buildup often leads to surface runoff and leaching loss to water bodies causing eutrophication. Phosphatic fertilizers also accumulate HMs like Cd and radionuclide in soil system, which is considered to have adverse effect on human health. Similarly, repeated application of animal manure especially in many Western countries had resulted in contamination of water bodies and soil system, causing huge losses of nutrients. The contaminants from fertilizers and manures not only degrade water quality but also enter into food chain with direct effect on human health.

The use of manures and fertilizers free from contaminants, pathogen, and pollutants with minimum loss should be studied. Contamination via inorganic fertilizers and organic manures should be checked by various technologies like phytoremediation, applying lower or optimum dose of fertilizers, proper waste water treatment, use of models for analyzing and monitoring pollutant in soil, air, and water, public awareness programs, etc. However, agricultural emissions from diffuse sources are of even greater importance and could be analyzed using models. Integration of agricultural best management practices (BMPs) with other mitigation techniques for tackling different contaminants could be more economical and environment friendly so as to lower the risk of environmental pollution to a greater extent. Thus, the movement of active contaminants from soil to crops is to be minimized and suppressed for human health, welfare and environment security.

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