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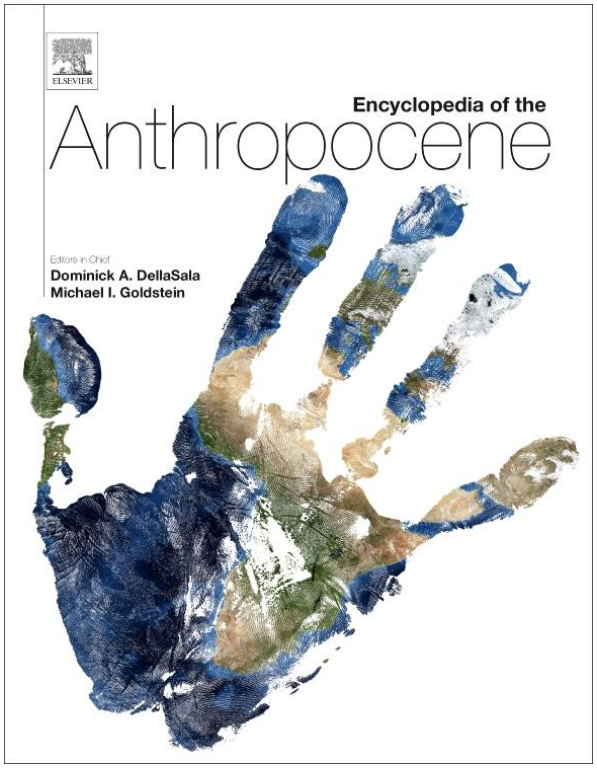


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# Fertilizers and Their Contaminants in Soils, Surface and Groundwater

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## Introduction

Fertilizers are integral part of current agricultural production as they provide essential mineral elements for positive crop growth and blossoming harvests. Even high yielding varieties of crop plants possibly do not reach to their full potential without getting a balanced dose of fertilizers. Fertilizers are broadly grouped in to two: (i) inorganic or chemical fertilizers which include nitrogenous, phosphatic, potassic, and complex fertilizers and (ii) organic fertilizers which comprise farm yard manure, bone meal, compost, green manure, etc. The increasing population forced agriculture intensification accompanied with additional use of fertilizers that have played vital role to meet the demand of food across the globe. During 1970s and 1980s, one-third of the increase in cereal production worldwide and half of the increase in India's grain production have been attributed to increased fertilizer consumption (FAO, 2013). It has been reported that to feed 6127.7 million populations in the year 2000 the consumption of nitrogen (N), phosphorus (P), and potassium (K), the key components of inorganic fertilizers, was 64.9, 25.9, and 18.2 kg $ha^{-1}$, respectively, which increased to 85.8, 33.2, and 20.4 kg $ha^{-1}$, respectively in the year 2014 when the world population reached 7243.8 million (FAO, 2013). Moreover, total fertilizer nutrient ($N+P_2O_5+K_2O$) consumption was estimated at 170.7 and 175.7 million tons in 2010 and 2011, respectively. The extent to which the world food production relies on the application of fertilizers can easily be understood as the estimated consumption of N, P, and K fertilizers is expected to increase from current consumption levels by 172%, 175%, and 150%, respectively by 2050. World fertilizer production is accompanied by an abrupt increase in the proportion of urea in world N production that comprises roughly 40% of all N fertilizers produced (Constant and Sheldrick, 1992). This boost in fertilizer consumption has resulted in a shift in the nutrient composition of runoff and leaching leading to deterioration of soil health, and quality of surface and groundwater.

Indiscriminate and long-term use of fertilizers has become a significant source of soil and water pollution (Hudak, 2000; Hanson, 2002; Almasri and Kaluarachchi, 2004) which put the pristine terrestrial and aquatic ecosystems downstream and human health at risk. Soils naturally contain heavy metals (HMs) such as cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), lead (Pb), etc., but excess application of fertilizers aggravate the situation by lowering the soil pH which facilitates HMs availability. Furthermore, fertilizers also contain a wide range of HMs from the source materials; therefore, application of these fertilizers adds more HMs to the soils (Huang and Jin, 2008). Excessive accumulation of HMs deteriorate the physical and biological characteristics of soil and adversely affect plant growth, and physiological and biochemical processes leading to the degeneration of organelles and cells that may result in plant death (Nagajyoti et al., 2010; Gupta and Sandallo, 2011). Consumption of such crops and crop products facilitates the entry of metals in the food chain where they impair our ecosystem, and human and animal health (Taylor and Percival, 2001; De Vries et al., 2002; Nagajyoti et al., 2010). Apart from agriculture, fertilizers are also extensively used to maintain and improve the beauty of home lawns, gardens, and parks. Thus, urban soils in park and residential areas may also have a significant impact on human health as they are directly exposed to HMs (Mielke et al., 1999; Madrid et al., 2002).

The nutrients present in fertilizers can be mobilized by rainfall; this results in the nutrient enrichment of surface water bodies, a condition known as eutrophication. Presence of excess nutrients allows luxurious growth of aquatic plants and algal blooms that causes depletion of dissolved oxygen which negatively affects aquatic life. The soluble forms of these nutrients supplied from fertilizers dissolve in water and are transported in solution through deep percolation of irrigation and rainfall waters to the groundwater where they make potable water supplies unsuitable for humans and livestock consumption (**Fig. 1**). Nitrogen-based fertilizers are considered the worst culprits of water pollution. In the soil, N is converted to ammonia (Speriran, 1996) which in turn is converted to nitrite ($NO_2^-$) and nitrate ($NO_3^-$) that is highly soluble and mobile and is loosely bound to soil particles. The nitrates are easily washed into surface water bodies by rain or leached into groundwater via soil and infiltrating water (Nolan et al., 2002a). The oxidation of $NO_2^-$ to $NO_3^-$ by dissolved oxygen in water leads to depletion of oxygen levels in water (Horita et al., 1997; **Fig. 1**). Consumption of $NO_3^-$-contaminated water causes methemoglobinemia or blue baby syndrome in infants and stomach cancer in adults (Wolfe and Patz, 2002; Nolan et al., 2002b).

Precise application of fertilizers to the plants gives promising results, however, the same fertilizers when used indiscriminately, pose serious threats to the environment and causes pollution of soil and water bodies. Therefore, it is highly desirable to understand the factors responsible for the fertilizer-induced contamination of soils and water system; and also to innovate ways that could effectively check the spread of this nonpoint source pollution without compromising growth and yield of crop plants. The present review is focused on fertilizers and their contaminants in relation to soil health, and quality of surface and groundwater.

## Fertilizers and Contaminants

Global food security owes much to the widespread use of mineral fertilizers. However, the commercially available fertilizers are blended with a range of trace metals, which are introduced into the soil along with the application of fertilizers (McLaughlin et al.,

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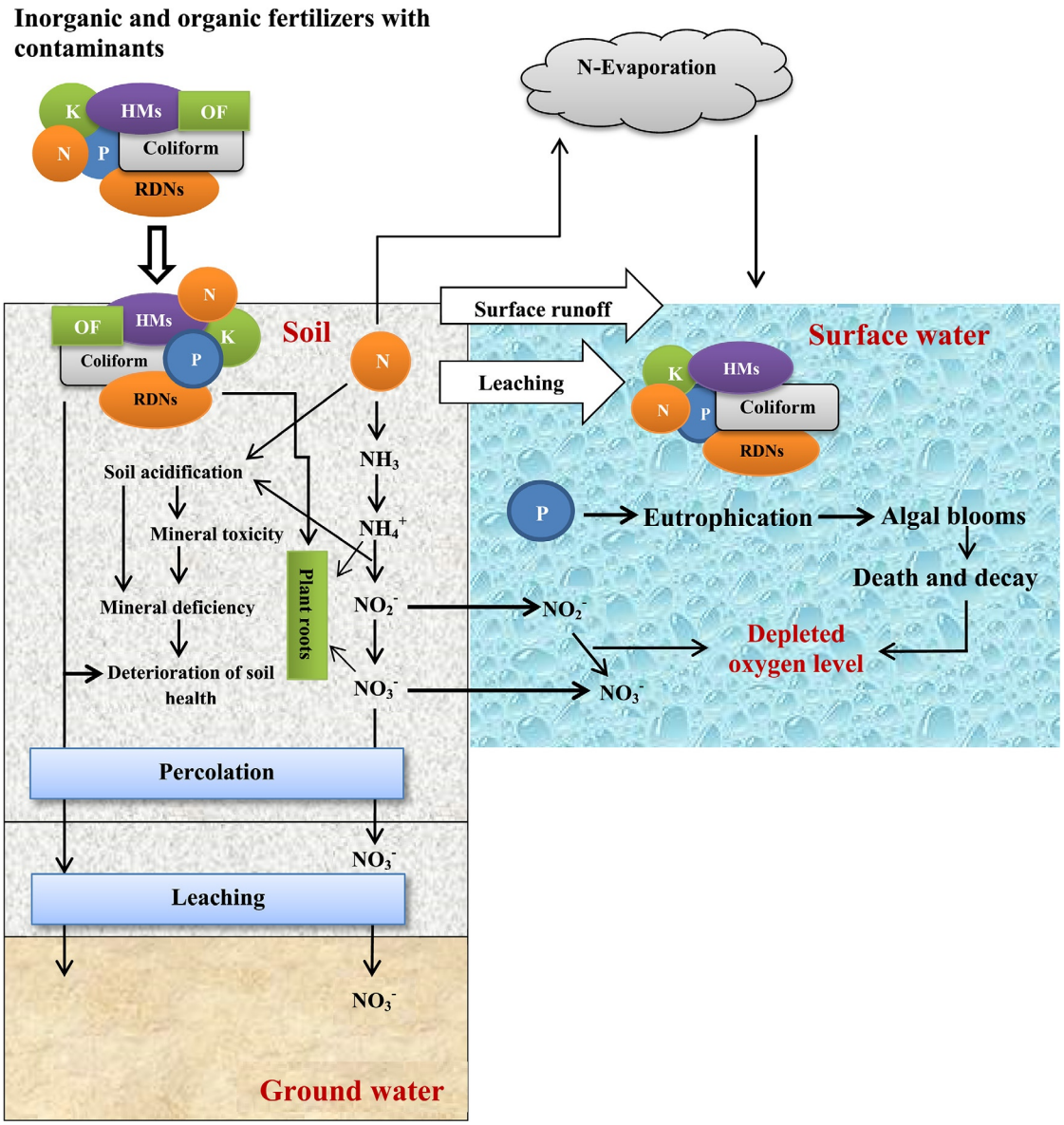


**Fig. 1** Impact of inorganic and organic fertilizers and their contaminants in soil, surface and groundwater. Application of inorganic fertilizers to the soil, along with mineral nutrients, adds HMs, RDNs, organic pollutants and pathogens to the soil. Nitrogen from applied fertilizers gets converted to $NH_3$ and $NH_4^+$ that oxidizes to $NO_3^-$ and produces protons ($H^+$) and decreases soil pH that results in the acidification of soil. Acidified soil causes mineral toxicity and mineral deficiency that ultimately results in the soil with poor health. $NO_3^-$ from the soil contaminates surface water and groundwater resources. Moreover, $NO_2^-$ also enters surface water and gets oxidized to $NO_3^-$ by dissolved oxygen in water which causes depletion of oxygen level in water. Phosphorous from the soil leaches to surface water bodies and causes eutrophication that results in algal blooms which on death and decay deplete the dissolved oxygen level. HMs, RDNs, and coliforms enter the food chain from soil through plants and water resources and adversely affect the ecosystem, and human and animal lives. *HMs*, heavy metals; *RDNs*, radionuclides; *OF*, organic fertilizers; *$NO_3^-$*, nitrate; *$NO_2^-$*, nitrite; *$NH_3$*, ammonia; *$NH_4^+$*, ammonium.

1996; Westfall et al., 2005). A high and significant dependency on fertilizers for sustainable crop production heightens environmental concerns as the issues of agricultural soil contamination become very important.

## Contaminants in Inorganic Fertilizers

Among inorganic fertilizers, phosphate fertilizers are the major source of contaminants as they may contain traces of Cd, Pb, As, Cr, fluorine (F), strontium (Sr), thorium (Th), uranium (U), zinc (Zn), etc. (Alloway, 1990; Al-Attar et al., 2012; Thomas et al., 2012; Raven et al., 1998). Certain levels of HMs are present naturally in soils which are contributed by weathering of parent materials. The contaminants in phosphate fertilizers owe their existence to its origin as almost all of the world's phosphate fertilizers are derived from phosphate rocks. During the process of production of different combinations of phosphate fertilizer products such as

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monoammonium phosphate (MAP), diammonium phosphate (DAP), triple superphosphate (TSP), and NPK mixes, these contaminants are inadvertently added to the agricultural soils. The analysis of As, Cd, and Pb concentrations in 29 rock phosphate samples collected from different locations from all over the world have mean concentrations of As, Cd, and Pb ranging from 0 to 7.1, 19.1, and 13.2 mg $kg^{-1}$, respectively (Hamamo et al., 1995; Raven and Loeppert, 1997). These metals (Cd, As, and Pb) are of most significant concern as they adversely affect human health and cause musculoskeletal problems. The concentration of Cd in P fertilizers varies greatly, depending on the phosphate rock source, single superphosphate (SSP) can contain from 2 to 40 mg $kg^{-1}$ Cd and TSP can have from less than 10 to over 100 mg $kg^{-1}$ Cd content (Robarge et al., 2004). Robarge et al. (2004) surveyed trace metal contents of various fertilizers of North America. They observed that concentration of Cd in DAP and MAP ranged from 16 to 22 mg $kg^{-1}$ and 19 mg $kg^{-1}$ in TSP, whereas, other fertilizer contained negligible amounts of Cd (<0.01 mg $kg^{-1}$).

Excessive and continuous use of fertilizers accumulates these contaminants in the soil to a level harmful to the environment (Atafar et al., 2010; Hariprasad and Dayananda, 2013; Yargholi and Azarneshan, 2014). Moreover, interaction between various elements produces several other toxic effects compared to that of single pollutants (Haiyan and Stuanes, 2003). In addition, irrigation water, pesticides, and organic amendments are other important sources of HMs in agricultural soils (Adriano, 2001; Nicholson et al., 2003). These harmful elements through bioaccumulation in plants join the food chain while the remaining enters water system through leaching and surface runoff (**Fig. 1**). HMs severely degrade soil quality, growth and yield of crop plants, quality of agricultural products, and pose serious threats to animals and humans (Gupta and Gupta, 1998; Singh et al., 2011). Availability of HMs in commercial fertilizers varies greatly. Modaihsh et al. (2004) analyzed the concentrations of Cd, Co, Cr, and Ni in commercially available inorganic fertilizers used in Saudi Arabia; they were lower than the tolerance limits and were in a range similar to those found worldwide. They concluded that the application of 80 kg P $ha^{-1}$, contributes 13 g of Cd $ha^{-1}$ to the soils of Saudi Arabia annually. Milinović et al. (2008) reported that contents of HMs varied significantly in different fertilizers depending on N:P:K ratio and fertilizer origin. Benson et al. (2014) reported higher concentration of Cu, vanadium (V), and Zn in superphosphate fertilizer, and elevated concentrations of Ni, Pb, and Cd were recorded in urea fertilizer.

The available information discussed above indicates that continuous application of P fertilizers will not only add nutrients to the soil but also significant amounts of Cd or other HMs. Several studies have been conducted to evaluate the effect of fertilizers on HM accumulation in soil. It has been reported that repeated application of fertilizers may lead to a gradual accumulation of HMs in agricultural soils over time (Loganathan et al., 1995; Chen et al., 2007). Loganathan et al. (1995) observed a significant correlation between P fertilizer application and Cd accumulation in plants. Huang et al. (2004) reported increased Cd accumulation in lettuce in response to the application of P fertilizer. Enrichment of Cd in the environment through the addition of phosphate fertilizers has gained huge attention as Tirado and Allsopp (2012) have estimated that 54%–58% of the Cd present in the environment originates from the supplementation of mineral phosphate fertilizers. The origin of Cd contamination in intensive agricultural soils in European countries can be traced back to the application of phosphate fertilizers; the data from the Forum of European Geological Surveys clearly showed that topsoil Cd levels follow the footprints of the distribution of $P_2O_5$ (Pan et al., 2010). In Chinese agricultural soils the addition of phosphate and compound fertilizers resulted in the yearly increment of 5%–30% in As and Pb and less than 8% in Cd concentrations, respectively, as noticed by Luo et al. (2009). Atafar et al. (2010) and Thomas et al. (2012) observed increased concentration of Cd, Pb, and As in cultivated soils due to fertilizer application. Cheraghi et al. (2012) investigated the effects of phosphate fertilizer application and different cultivation patterns on the HM content of agricultural soils. They observed 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. Jafarnejadi et al. (2013) reported that phosphate fertilizer rate and crop rotation have significant effects on soil physicochemical properties and on spatial variability of Cd species. Czarnecki and Düring (2015) observed that 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). However, contradictory reports are also available which showed no increase or minor increases in soil Cd content after phosphate fertilizer applications. Jeng and Singh (1995) observed that the increase in soil Cd content was very small after 70 years of phosphate fertilizer application, while Richards et al. (1998) did not notice any Cd enrichment in agricultural soils after 29 years of annual P additions at the rate of 0, 22.5, 45, and 90 kg $P_2O_5$ $ha^{-1}$. Similar results were also reported by Jones et al. (2002). Furthermore, it has been noted that P fertilizer input at a rate of 20 kg P $ha^{-1}$ may add Hg and Cr to the agricultural soils at levels approaching 0.01 and 25 g $ha^{-1}$ $year^{-1}$, respectively (Kongshaug et al., 1992; Kpomblekou and Tabatabai, 1994).

Phosphate fertilizers not only contain HMs but they also contain naturally occurring radioactive materials, such as the radionuclides $^{238}U$, $^{232}Th$, and $^{210}Po$, $^{226}Ra$, $^{40}K$ (FAO, 2009; Sönmez et al., 2007; Kara et al., 2004; Hassan et al., 2016). The principal constituent of phosphate rock is the $P_2O_5$-enriched mineral apatite in which radionuclides may be incorporated through ionic substitution or by adsorption. During mining and industrial processing these radionuclides are redistributed from phosphate ores to various products, by-products, and wastes of the phosphate industry. These radionuclides serve as source of radiation exposure to public health through phosphate fertilizers in agriculture, and by-products such as phosphogypsum (PG) in the building industry as well as in agriculture. The potential radiological risk owes to both external exposure and internal exposure through consumption of food grown on soil supplemented with radionuclide enriched fertilizers (Rehman et al., 2006; Nowak, 2013). Incorporation of radionuclides into the food chain via phosphate fertilizers has been considered of lesser concern, however; the by-product PG is considered as the main source of radionuclides. Continued and long-term application of phosphate fertilizers increases the radionuclide levels in the soil (Eisenbud and Gesell, 1997), surface and/or groundwater supplies (Spalding and Sackett, 1972; Zielinski et al., 1997). On the contrary, Santos et al. (1995), Sam et al. (1999), Righi et al. (2005), and Saueia and Mazzilli (2006) are of the opinion that long-term impact of fertilizers on radiological exposure is negligible.

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The concentration of radionuclides in fertilizers varies greatly depending on the parent rock. Several studies have been performed to test the availability of radionuclides in the fertilizers and their potential risk in plants, and human and animal health. The UNSCEAR (1988, 1993) indicates 1500 Bq $kg^{-1}$ as the average concentration of $^{238}U$ in phosphate deposits of sedimentary origin. Saleh et al. (2007) reported higher levels of $^{226}Ra$ and $^{232}Th$ in superphosphate fertilizer and suggested that high frequency of soil fertilization may lead to the accumulation of U and Th radionuclides in soil. They also observed that vegetables are the greatest contributors of $^{226}Ra$ and $^{40}K$, while meat gives the lowest rate of intake. Becegato et al. (2008) observed higher concentration of radionuclides in fertilized fields than in those where no fertilizers were used. They also reported that, due to higher adsorption capacity, clayey soils show greater concentration of radionuclides than sandy soils. Brahim et al. (2014) observed higher concentration of $^{238}U$ in phosphate fertilizers from Tunisia compared to the mean concentrations in the world resources of phosphate rocks. Hassan et al. (2016) measured the natural radionuclide concentrations of $^{226}Ra$, $^{232}Th$, and $^{40}K$ in different types of phosphate ores and fertilizers used in Egypt. They reported that the radiological hazards of the radium equivalent activities ($Ra_{eq}$), external and internal indexes and absorbed dose showed values greater than the worldwide safety limit. However, the values for annual effective dose were in the range of the worldwide average value (480 μ Sv $year^{-1}$).

In contrast, several studies showed negligible or no risk of radioactive pollution from phosphate fertilizers. For instance, Saueia and Mazzilli (2006) reported that higher concentrations of radionuclides showed negligible radiological impact. Righi et al. (2005) performed a study to assess radioactive pollution caused by a production plant of complex fertilizers. They reported that radioactive pollution from the production process was negligible due to avoidance of the production of PG, one of the main causes of radioactive pollution from the production of phosphate fertilizers (UNSCEAR, 1993; Bolívar et al., 1995; Haridasan et al., 2001). Saueia et al. (2013) reported that radionuclides present in the PG and SSP and TSP fertilizers are not available to the environment; therefore, their application in agriculture is safe.

## Contaminants in Organic Fertilizers

Organic fertilizers are naturally occurring compounds produced from waste matter or by-products, where only the physical extraction or processing steps are assisted by man (Huntley et al., 1997). Commonly used organic fertilizers include composted animal manure, compost, sewage sludge, food processing wastes, and municipal biosolids. They improve soil health and release nutrients to soils gradually. *De facto*, the recycling of organic residues as fertilizers and soil amendments in agricultural soils may curtail the utilization of nonrenewable resources and investments in excess energy (Mondini and Sequi, 2008). However, the use of organic fertilizers have many disadvantages such as the availability of organic N sources, existence of HMs and other toxic substances (Petersen et al., 2003), and the energy costs associated with transport and application.

Intensive animal production system uses animal feeds supplemented with essential elements and other nonessential metals which get incorporated inadvertently in animal manures (Sager, 2007; Moral et al., 2008; Zhang et al., 2012; Wang et al., 2015a,b). Use of animal manure as soil amendment and nutrient source has been a long tradition worldwide. However, recently the input of manure has been recognized as a major source of metal enrichment in soils. Nicholson et al. (1999) have estimated an annual increment of about 5247 mg Zn, 1821 mg Cu, and 225 mg Ni content to agricultural lands in England and Wales through animal manure application. Application of organic fertilizers not only adds HMs to the soil but also change the availability of metals and their uptake by the plants (Bolan and Duraisamy, 2003). Although, various soil properties (pH, clay type, chloride content, soil organic matter (SOM), Fe and Mn oxides) affect HM availability (McLaughlin et al., 2000), soil pH is the key factor that directly influences availability of HMs in the soil, and uptake by plants. Lower pH increases HM uptake by plants, while increasing pH boosts adsorption of HMs on clay and organic matter. Lime helps to maintain soil pH; therefore, liming will reduce bioavailability (Roberts, 2014). However, lime also adds Cd at the rate of 0.04–0.06 g Cd $ha^{-1}$ $year^{-1}$ (Sternbeck et al., 2011). Czarnecki and Düring (2015) found that continued long-term use of organic fertilizers increased metal content in soil, soil organic C, cation exchange capacity (CEC), and decreased soil pH level. They also observed that 8 years after cessation of fertilizer application, soluble metals were taken up by plants probably due to decreased pH level in long-term fertilized soil. The Cd-reducing property of organic matter works well at pH below 6.0, however, at pH 6.0–8.0 organic material increases Cd concentration in soil (Roberts, 2014). A case study on fertilizer and atmospheric inputs of Cd to agricultural soils in Sweden was performed by Sternbeck et al. (2011); they showed that annual Cd input was 0.8 g Cd $ha^{-1}$ $year^{-1}$ when P fertilizer was applied at the average rate of 22 kg $P_2O_5$ $ha^{-1}$. However from manure, net Cd input was 0.01 g Cd $ha^{-1}$ $year^{-1}$ which was nearly tenfold lower than the Cd concentration in P fertilizers. Queriolo et al. (2000) suggested that Pb uptake from soil to plants is promoted if soil contains less than 0.8% organic matter at pH < 6.7 and low phosphate concentrations. Zheng et al. (1997) reported that the combined application of organic materials with higher rates of lime was more effective in reducing Cd uptake by plants in Cd polluted acid soils compared to lime alone. CEC, a measure of soil fertility, is the property of soil to retain the cations on its surface. Sampanpanish and Pongpaladisai (2011) observed that Cd uptake by rice plants from soil treated with organic fertilizer was lower than with inorganic fertilizer because the presence of higher levels of organic matter in the soil enhances CEC which facilitates more Cd adsorption (Roberts, 2014) and thus enhanced HM retention in soil. These results corroborate the findings of Jones et al. (1987) who reported that wheat harvested from the long-term farm-yard manure supplemented plots contained lower Cd concentration than the wheat harvested from inorganic P fertilized plots. Elouear et al. (2016) also reported that sheep manure enhances immobilization of metals which resulted in decreased concentrations of Pb, Cd, and Zn in plant tissues.

Organic amendments such as sewage sludge contain a good amount of plant nutrients such as N, P, K, Ca, Mg, and Fe as well as other organic constituents (Martinez et al., 2003). On the other hand, they are also a rich source of toxic metals such as Pb, Cd, Ni, Cr, Hg, etc. (Dai et al., 2006; Singh and Agrawal, 2007). Furthermore, sewage sludge may contain Cd ranging from >1 to

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3650 mg $kg^{-1}$ (Alloway, 1990) which may add Cd to the land ranging from 30 to 40 g Cd $ha^{-1}$ $year^{-1}$ (Alloway and Steinnes, 1999). Extended use of biosolids/sewage sludge causes accumulation of HMs in the soil that can pollute surface water bodies through runoff and sediments (Evangelou, 1998; Elliot et al., 2002; Haiyan and Stuanes, 2003; Galdos et al., 2009). However, strong binding of HMs with the soil particles restricts them mainly to the topsoil with little downward movement to deeper layers and HMs are generally confined to 0–40 cm of soil layers (Haiyan and Stuanes, 2003; European commission, 2001). Łuczkiewicz (2006) observed that N compounds as well as HMs, originating from sewage sludge, can reach deeper than 0.8 m and contaminate potential shallow aquifers. Benítez et al. (2001) reported that application of different biosolids increased the total concentrations of HMs and the biosolids assisted the migration process of Cu, Zn, and Pb toward the lower soil layer and increased the uptake of Cu and Zn by wheat plants. On the contrary, Vaca et al. (2011) and Mondal et al. (2015) observed that sewage sludge improved soil health and crop yield with no environmental risks. Tsadilas et al. (1995) have noted the beneficial effects of sewage sludge application in many crops. However, the results from long-term trials of sewage sludge application show accumulation of significant quantity of trace metals in the soil (Dai et al., 2006). Gove et al. (2001) examined that application 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 $kg^{-1}$.

## Fertilizers and Soil Health

The efficiency of soils to perform their normal functions has deteriorated through different processes such as salinization, organic matter depletion, nutrient imbalance, anaerobiosis, and compaction. Therefore, for the protection and enhancement of sustainable agroecosystems, soil health should be urgently addressed. Soil health is defined as the capacity of the soil to carry out agronomic and environmental functions. A healthy soil is expected to be competent enough for water retention, carbon sequestration, plant productivity, waste remediation, and other functions. A sustainable ecosystem requires a continuous maintenance or enhancement of soil health. Monitoring of ecosystems depends on the use of indicators that must reflect soil processes, integrate different soil properties, and be sensitive to environmental changes. Soil health indicators are a combination of soil physical, chemical, and biological processes that are able to respond to altered soil conditions.

### Fertilizers Additions and Soil Physical Health

The important physical indicators of soil health include bulk density, water availability, compaction, porosity, and soil surface cover. The major plant nutrients applied to the soils are N, P, and K fertilizers that influence the soil conditions by regulating the flocculation-dispersion and/or coagulation processes. The process of flocculation/dispersion is regulated by critical coagulation concentration (CCC). The CCC is the lowest electrolyte concentration at which a soil suspension turns unstable and is subject to rapid coagulation or flocculation under a specific set of conditions (Sposito, 1989). If the salt concentration is below the CCC, dispersion occurs (Goldberg and Glaubig, 1987) while soil salinity level greater than 1.5 dS $m^{-1}$ provokes flocculation (Warrence et al., 2003). Usually, greater hydraulic conductivity is noted in a flocculated soil that is resistant to runoff and characterized by aggregate stability and pore space maintenance (Warrence et al., 2003). Poor hydraulic conductivity is observed in dispersed soil that is prone to runoff and shows aggregate instability and blockage of pore space by mobilized clay particles. However, soil physical properties emphatically respond to fertilizer applications via improved crop yields, enhanced restoration of organic matter, and increased SOM levels compared with unfertilized crops.

A number of studies indicate that the addition of phosphatic fertilizers have a benign impact on soil physical properties (Lutz et al., 1960; Thein, 1976; Yeoh and Oades, 1981a, b). The supplementation of phosphates to agricultural soils resulted in lower bulk density and higher soil moisture contents. Furthermore, results from the study of Lutz et al. (1960) confirmed the beneficial effect of phosphate additions to soil physical health as it enhanced the flocculation and water holding capacity of the soils. Formation and stabilization of soil aggregates in response to fertilizer additions have been studied extensively as soil aggregation contributes significantly to the SOM stabilization. The maintenance of SOM is especially crucial to plant-available nutrients in soils as it governs the status of retention and supply of mineral elements (Craswell and Lefroy, 2001). Thein (1976) noticed that the addition of phosphate fertilizers to the soil in the form of ammonium polyphosphate and triple superphosphate has no quantifiable impact on soil aggregation but phosphoric acid increases aggregate stability. Moreover, the supplementation of nitrogen in the form of ammonia adversely influences the formation of soil aggregates. It has been noted that the build-up of monovalent $NH_4^+$ could initiate the dispersion of soil colloids. Contrary to this, long-term field trials studying the effect of annual applications of $NH_4^+$ containing fertilizers have demonstrated that the estimated saturated hydraulic conductivity, penetrometer resistance, bulk density, soil water content, water stable aggregation, and compatibility were not significantly different in $NH_4^+$ fertilizer treated or control plots (Intrawech et al., 1982).

### Fertilizers Additions and Soil Chemical Health

Indicators of soil chemical health are consisted of soil pH, electrical conductivity, CEC, and plant available nutrients. Among these, soil pH is recognized as one of the crucial factor of soil chemical health. It affects a wide range of processes that includes soil nutrient bioavailability, plant primary production, soil microbial community structure and activity (Robson, 1989).

#### *Fertilizer additions and soil acidifications*

Most of the nutrients which are added to the soil are themselves not acidic but their reactions in soils lower soil pH. N fertilizers which were vital to the green revolution have been recognized as the major contributor of acidity to soils. The N fertilizer inputs in

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the form of ammonia and its subsequent transformations may substantially contribute to the proton loading to the soils (Van Breemen et al., 1987). In this context, the microbial oxidation of ammoniacal fertilizers is of considerable importance as the nitrification of ammonia, nitrification of ammonium, and hydrolysis of urea add $1H^+$, $2H^+$, and $2H^+$, respectively. Contrary to this, the assimilation of $NO_3^-$-N and sulfate-S to their organic forms generate alkalinity and consume protons.

Soil acidity may develop in response to nitrogen fertilizer addition when addition of N either exceeds the assimilation or storage by biotic components or SOM, respectively. Furthermore, the incomplete return of organic anions could also add to the acidification process. In China, Guo et al. (2010) noted that the application of heavy N fertilizer rates decreased soil pH substantially and resulted in a severe soil acidification, between the years 1980 and 2000. They observed that the N fertilizer application released 20–221 kg of $H^+$ $ha^{-1}$ $year^{-1}$, and base cations uptake contributed a further 15–20 kg $H^+$ $ha^{-1}$ $year^{-1}$ to soil acidification.

A number of studies have explored the impact of different N sources on the levels of soil acidity. In one of the pioneering work, Wolcott et al. (1965) reported that the acidifying effects of different N fertilizers were in the following order of magnitude; $(NH_4)_2SO_4 > NH_4Cl > NH_4NO_3 \approx$ anhydrous $NH_3 \approx$ urea > ureaform, when applied at the rate of 336 kg N $ha^{-1}$ annually for a period of 3 years. Later on, other studies have also confirmed this finding and have reported differences in the levels of acidification produced by the long-term application of different N sources (Bouman et al., 1995; Chien et al., 2008). Malhi et al. (1991, 2000) examined the effect of applying $(NH_4)_2SO_4$, $NH_4NO_3$, and urea on the levels of soil acidification during a 5- to 16-year period. The results showed that the order of the acidifying effects were $(NH_4)_2SO_4 > NH_4NO_3 >$ urea. A study by Bouman et al. (1995) evaluated the application of $NH_3$ and urea for 9 years and found that $NH_3$ resulted in greater acidity than urea. In a greenhouse trial during a 3-year period, Chien et al. (2008) observed that the change in soil pH followed the order $(NH_4)_2SO_4 < NH_4NO_3 =$ urea < control. However, the results from the study of Darusman et al. (1991) contradicted these findings. They did not observe any significant difference in the resulting 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 a 20-year period. Decrease in the pH of soil subsequently results in the enhancement of $Al^{3+}$ and $Fe^{2+}$ and depletion of essential basic cations such as $Ca^{2+}$, $Mg^{2+}$, and $K^+$ which hampers the normal growth and developments of the plants. Additionally, phosphate availability is also impeded in low pH soil due to the formation of sparingly soluble Al and Fe phosphates.

## Fertilizer Additions and SOM

SOM has been recognized as an important attribute of soil health. SOM is comprised of both the living and nonliving fractions. The living part includes soil microbial biomass and living roots while the nonliving part is made up of heterogeneous organic matter. SOM plays a vital role in aggregate stability and influences soil porosity, hence gas exchange reactions and water relations too. About 50% of the SOM is comprised of soil organic carbon (SOC) (Pribyl, 2010) and consists of labile, slow, and stable carbon pool. The equilibrium between addition and depletion of organic matter determines the levels of SOC. In chemically fertilized soils, the crop-derived C is the only leading C input. SOM serves as a key reservoir in the carbon cycle and as a repository of nutrients; and through its dominance on key fundamental biological and chemical processes it plays a significant role in nutrient release and availability (Henderson, 1995). Results from several studies have also demonstrated that the addition of synthetic mineral fertilizers improve the SOM level and the C sequestration in soils of highly managed multiple cropping systems in comparison to nonfertilized control plots (Triberti et al., 2008; Gong et al., 2009; Huang et al., 2010).

There are detailed evidences available which signify that the loss of N from the soil system is largely determined by the N status of the soil and N use of efficiency of the plants. C and N are predominant components of SOM and microbial C and N cycling are closely connected to each other; therefore, the factors affecting the status of C in the soil may also influence the reservoir of N in the soil. Glendining and Powlson (1995) analyzed the results of 45 long-term experiments ranging from 7 to 136 years in duration and mostly from temperate regions; they found that the long-term applications of N fertilizer increased total soil organic N compared to the no-fertilizer N treatments at 84% of the sites studied. However, contrary to this Khan et al. (2007) and Mulvaney et al. (2009) noted that a long-term trial of continuous input of fertilizer N triggered a net loss of soil organic N at 92% of the sites and a loss of soil organic C at 74% of the sites, situated in temperate as well as tropical regions. Paustian et al. (1997) summarized the available data on the effects of fertilizer N application on soil carbon concentration and observed a pattern where the supplementation of N to the soil increases the soil C. He attributed the fertilizer N-induced upsurge of soil C to the increased crop production and incorporation of crop residues along with the roots to the soil. The findings of $^{15}N$-tracer studies of Stevens et al. (2005) have demonstrated that the plant uptake of N is lower in chemically fertilized soil than native soil N. It has been noted that depletion in organic N depresses soil productivity and agronomic efficiency of fertilizer N (Mulvaney et al., 2009). Furthermore, fertilizer N-induced acidification and lowering of available soil moisture contents could curtail the expected benefits of mineral-N addition to the soils on SOM and may actually lower the rate of decrease of organic matter addition to the soil. Moreover of late, Geiseller and Scow (2014) and Körschens et al. (2013) proposed that balanced use of mineral fertilizers may actually increase SOM in comparison to plots receiving no fertilizers in long-term experiments.

## Soil Biological Health and Fertilizer Additions

Biological indicators of soil health give us information about soil structure development, nutrient storage, and biological activity. It includes nitrogen mineralization, soil microbial biomass, soil respiration, faunal populations, and rates of litter decomposition (Rice and Garcia, 1994; Sparling, 1997). Nutrient cycling in the agro-ecosystem is largely carried out by soil biota. These soil

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microorganisms play a vital role in soil processes encompassing through organic matter decomposition, nutrient cycling, and other chemical transformations. Bacterial and fungal populations particularly play a significant role in nutrient immobilization and mineralization as they are the constituents of the labile pool of nutrients such as C, N, P, and S.

Fertilizer additions to agricultural soils can influence soil biota via altering the populations of single organisms or total microbial biomass or soil biological activity such as soil respiration and enzyme activities. Furthermore the inputs of synthetic mineral fertilizers may induce osmotic effects especially in the vicinity of fertilizer granules or liquid injection points. Ammonia-based fertilizers are known to lower soil pH and may be toxic to soil organisms. Several authors have reported the reduction in microbial biomass when mineral N fertilizer was added (Ladd et al., 1994; Hopkins and Shiel, 1996; Šimek et al., 1999; Sarathchandra et al., 2001; Bittman et al., 2005). Altogether, it has been observed that greater availability of essential mineral elements depresses the activity of symbiotic organisms. For instance, higher mineral N and soluble P concentrations decreases $N_2$-fixation by rhizobia and retards the degree of infectivity of mycorrhizal fungi to host plants, respectively. Earlier studies had found that the addition of 500 mg P $kg^{-1}$ soil as calcium diphosphate resulted in an increase in microbial P and soil respiration; however, microbial N remained uninfluenced (Haynes and Swift, 1988). In a laboratory incubation study Saggar et al. (2000) have noted that the addition of 200 mg N $kg^{-1}$ to soil as ammonium sulfate enhanced N mineralization but reduced microbial P during the 168 days of incubation. The application of ammonium fertilizer promoted the development of a population of soil nitrifiers, which was preferred over methanotrophs for niche environments within the soil. While nitrifiers could also oxidize methane, their rates of oxidation are significantly slower than those of methanotrophs (Bedard and Knowles, 1989).

Supplementation of fertilizers to the soils may also cause shifts in microbial community structure (Ruppel and Makswitat, 1999; Wardle et al., 1999; Marschner et al., 2003). Relative alterations in microbial C, N, and P may give important clues regarding shifts in the composition of the microbial community. In short-term experiments, the addition of fertilizer N did not alter community composition (Waldrop and Firestone, 2004; Avrahami et al., 2003) but longer-term incubation of 16 weeks resulted in considerable microbial community shifts (Avrahami et al., 2003). Marschner et al. (2004) concluded that the relative abundance of substrates in root exudates determines community composition. Donnison et al. (2000) noted that soil fungi responded differently to the addition of mineral fertilizers. Ryan and Ash (1999) and Rubio et al. (2003) observed that the addition of mineral N did not affect arbuscular mycorrhizal fungi (AMF); however, the gradual increase in mineral P input reduced the rate of root length colonization. Moreover, in a long-term trial, Ryan et al. (2000) found that AMF root colonization was remarkably reduced in response to mineral P and N inputs.

Organic fertilizers act as slow release materials where the components of organic fertilizers are slowly decomposed in soils. They hike the C, N, and other nutrients in soils and thereby concurrently cater to the needs of the microbial biomass which have usually low available C. Organic fertilizers have more pronounced effects on soil microbial biomass and activities than inorganic fertilizers (Hopkins and Shiel, 1996; Parham et al., 2002, 2003; Plaza et al., 2004). They usually increase soil microbial biomass (Peacock et al., 2001; Parham et al., 2002; Kaur et al., 2005; Ebhin Masto et al., 2006), $CO_2$ evolution (Ajwa and Tabatabai, 1994), and enzyme activities (Crecchio et al., 2001; Kandeler et al., 1999). In general, the addition of compostable organics to the soil increased microbial populations. Addition of humic substances encourages microbial activity directly by supplying essential nutrients and carbon substrate, and increasing uptake of nutrients across cell walls (Valdrighi et al., 1996). Differential responses to the supplementation of humic acid have been observed which ranges from boosting effects on aerobic bacterial growth to little effects on actinomycetes to no effect on the growth of filamentous fungi (Vallini et al., 1993; Valdrighi et al., 1996). The variable microbial responses to humic acid additions have been ascribed to the molecular weight of the humic acids. The application of lower weight fractions of humic acids triggers higher microbial growth than the higher molecular weight fractions (Garcia et al., 1991). Interestingly Vallini et al. (1997) have noted that the nitrifiers (chemotrophs) are incapable of using humic acids as an alternative carbon and energy source. However, Filip and Tesarova (2004) have suggested that microbial activity may even be suppressed if humic acid is the only carbon source.

## Fertilizers and Water Quality

Deterioration of water quality is one of the most serious global environmental problems. Agriculture including livestock is considered to be the largest nonpoint source of water pollution. Fertilizer leaching, runoff from agricultural fields, manure from concentrated livestock operations, and aquaculture are the largest agricultural nutrient sources.

### Inorganic Fertilizers and Water Quality

The global applications of N and P fertilizer in agriculture have increased eightfold and threefold, respectively, since the early 1960s (Constant and Sheldrick, 1992; Caraco, 1995; Matson et al., 1997; Smil, 2001). Nutrients from applied fertilizers are transported into nearby streams and lakes through rain water, erosion, irrigation channels, and seepage. These nutrients also contaminate underground water supplies through leaching and adversely affect the physicochemical properties of water (Shamrukh et al., 2001; Obire et al., 2008; Namdev et al., 2011). Nutrient enrichment of water bodies creates a condition known as eutrophication; eutrophic water bodies support the growth of undesirable aquatic plants and surface blooms of cyanobacteria (blue-green algae). 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. Schroeder and Balassa (1963) for the first time reported the presence of

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HMs as impurities in commercial fertilizers. Presence of HMs in fertilizers has been further confirmed by various studies (Brigden et al., 2002; Sampanpanish and Pongpaladisai, 2011; Benson et al., 2014). These HMs are transported to the nearby water bodies and pose severe threat to aquatic ecosystem and make water bodies unsuitable for consumption.

The most common impairment of waters is mainly caused by excessive inputs of N and P. Nitrate-N ($NO_3^-$-N) is a highly soluble and mobile form of N which loosely binds to soil particles, and therefore is of great concern in groundwater contamination through leaching (**Fig. 1**). On the other hand, P strongly adsorbed by soil particles, does not leach to groundwater readily but is of major concern in runoff to surface water such as lakes, streams, etc. However, potassium (K) is not a limiting nutrient in water; therefore, nutrient-associated water quality problems are mainly concerned with N and P. Agricultural land use activities directly influence $NO_3^-$ concentration in groundwater (**Fig. 1**). Oenema et al. (2005) observed that $NO_3^-$ leaching to groundwater and N and P discharges to surface waters are related to N and P surpluses, hydrological condition, land use, and soil type. They also reported that a decrease in N and P surpluses in agriculture decreased N and P leaching to groundwater and surface water. Wang et al. (2015a, b), in a simulated rainfall experiment, evaluated $NO_3^-$ accumulation and leaching in surface and groundwater. They added fertilizer to the soil 10 min before the rainfall and observed an increase of $NO_3^-$ concentration in surface flow; the concentration rapidly decreased and gradually stabilized at a low level during the remainder of the experiments. Eight days after the 12 rainfall experiments, they reported that soil had retained 50.53% of the total $NO_3^-$ applied. They concluded that $NO_3^-$ residues mainly existed at the surface and in the bottom soil layers that may lead to dangerous pollution for surface and groundwater.

### *Nitrogen (N) inputs in waters*

Fertilizers are the most significant source of N contamination of ground and surface waters. Of the applied nitrogenous fertilizers to soil, only 50% is used by the plants, 2%–20% is lost through evaporation, 15%–25% reacts with organic compounds in the soil and the remaining 2%–10% penetrates surface and groundwater (Korkmaz, 2007; Sönmez et al., 2007). A portion of N lost through evaporation enters water bodies through atmospheric deposition. Nitrogen in soil exists in the form of $NO_2^-$, $NO_3^-$, ammonium ($NH_4^+$), ammonia ($NH_3$), and organic nitrogen (organic-N) (**Fig. 1**). Of these N forms, $NO_3^-$ the highly mobile species, is mainly responsible for N losses from soils through leaching (Tesoriero et al., 2000). Being negatively charged, $NO_3^-$-N is not attracted to the negatively charged soil particles and is water soluble; it can travel long distances and easily enter groundwater or surface water through drainage, leaching, soil erosion, or runoff (**Fig. 1**). There exists a strong correlation between the traveling distance of $NO_3^-$ and increased phytoplankton productivity (Mallin et al., 1993). Interactions of N and iron (Fe) influence the structure of plankton community (DiTullio et al., 1993) and may cause encystment of dinoflagellates (Doucette and Harrison, 1991). It has been noted that inclusion of $NO_3^-$ to surface water occurs mainly via discharge of groundwater through baseflow (Devlin et al., 2000; Bachman et al., 2002). Therefore, to protect surface water quality it is necessary to prevent groundwater contamination. Similar to the agriculture systems, fertilizer industries also play a significant role in adding nutrients waste to groundwater as well as to surface water bodies. Obire et al. (2008) reported extremely adverse impacts on the physico-chemical and bacteriological water quality characteristics of a creek as a result of the discharge of poor quality effluent from the fertilizer company.

Fertilizer losses from cropland exhibit temporal and spatial variations. Chen et al. (2016) observed that surface runoff of total nitrogen (TN) and $NO_3^-$-N show a significant linear correlation. They also observed that application of fertilizer in spring and autumn enhanced the concentrations of TN and $NO_3^-$-N, whereas concentrations decreased rapidly after the peak values in spring but declined slowly in autumn. Jiao et al. (2015) studied the spatial and seasonal variations in nutrient concentrations in the upper catchment of the Miyun reservoir, China. They reported that total phosphorus (TP) concentrations were higher in catchments that had a higher proportion of cultivated land than in those with less cultivated land. Jiao et al. (2015) also observed that TN concentrations were highest in the autumn and were higher in the autumn and winter than in the other seasons, whereas, $NH_4^+$-N concentrations were higher in the summer than in the other seasons. On the other hand, TP concentrations were highest in summer and gradually decreased in the autumn and winter. These results are in agreement with the findings of Miao et al. (2012) and Li et al. (2013) who suggested that cropland is the main source of sediments and nutrients because of frequent disturbances of the land surface and relatively low vegetation cover. Kim et al. (2008), using a mass balance approach, studied total mass of N discharged from various sources in Korea. They reported that total N input in Korea was $1194.5 \times 10^3$ tons N year$^{-1}$. Nitrogen discharged into rivers was estimated as $408–422 \times 10^3$ tons N year$^{-1}$ that included 41% of N from agricultural areas. Wise and Johnson (2011), using Spatially Referenced Regressions on Watershed (SPARROW), observed that annual nutrient yields were higher in watersheds on the wetter side of the Cascade Range compared to watersheds on the drier side. Study also showed that most of the nutrient load was contributed by the combined input from agriculture, point sources, and developed land rather than natural nutrient sources. Shen et al. (2011) reported that agricultural activities cause large seasonal variation in $NO_3^-$ loading to groundwater. They observed a sudden increase in $NO_3^-$ loading to groundwater after fertilizer application and shallow groundwater had the highest contamination of $NO_3^-$. They concluded that a large proportion of N fertilizer was not used by the crops and leached into the groundwater via irrigation, causing long-term groundwater contamination. Jeyaruba and Thushyanthy (2009) compared the concentration of $NO_3^-$-N in groundwater in different cropping systems such as upland crops, mixed crops, banana, and paddy. They observed a good correlation between cropping system and $NO_3^-$-N concentration in groundwater. High $NO_3^-$-N concentration of groundwater was observed in upland cropping system which was followed by cultivation of mixed crops; however, no significant difference was observed between upland and mixed crops. There was significant difference between upland and mixed crops to banana and paddy land use. But there was no significant difference between paddy and banana. Thus, it indicates that cropping system but not the crop has significant impact on $NO_3^-$-N concentration of groundwater.

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Several studies showed that poor surface water quality in several rivers in China was attributable to fertilizer use and industrial wastewater discharge (Zhang et al., 2010; Chen et al., 2014). Jimoh et al. (2003) studied the timing of fertilizer application on the concentrations of $NO_3^-$, phosphate, and dissolved oxygen in surface waters and groundwater. They observed that before fertilizer application, $NO_3^-$ level in surface waters downstream of the area under irrigation was 0.0 mg $L^{-1}$; it reached 74.1 mg $L^{-1}$ after fertilization, while the phosphate level rose from 1.2 to 19.2 mg $L^{-1}$ during the same period. The level of dissolved oxygen in the downstream section was too low to support flora and fauna. On the other hand, Maghanga et al. (2013) observed no relationship between the time of fertilizer application and surface water $NO_3^-$-N levels. Sun et al. (2015) observed lower pH and dissolved oxygen level and higher values of chemical oxygen demand and biological oxygen demand in regions densely populated and interspersed by intensive agriculture activities or urbanization.

### *Phosphorus inputs in waters*

Among soil nutrients, P is considered to be highly immobile and binds tightly to soil particles with the least leaching. P is not readily available and plants use it inefficiently, taking up only 5%–10% of the applied (Loehr, 1974; Richardson et al., 2009). In terms of a global budget, P accumulation in the world's soils is greater than its removal in harvested crops and meat; this results in an imbalance between P input and output. Moreover, repeated application of fertilizers results in excessive accumulation in the soil; therefore, much of the unused P is left behind in the soil. Common P sources include rock phosphate, manure, and compost. It is considered that accumulation of P content in soil beyond 20 mg $kg^{-1}$ leads to enhanced P runoff and leaching rather than contributing to increased crop production (Sharpley et al., 1994). After long-term fertilization in paddy ecosystems, a positive correlation between soil P and surface water TP was also reported by Wang et al. (2012).

#### Phosphorus fertilizers and eutrophication

As mentioned above, P tightly binds with soil particles; therefore, any factors that increase soil erosion will also increase P runoff (Eghball and Gilley, 2001; Uusitalo et al., 2000) to streams, rivers, lakes, and coastal regions and cause eutrophication (**Fig. 1**). Eutrophication is followed by the uncontrolled growth of phytoplankton and algal blooms which depletes oxygen owing to decomposition of organic matter that put aquatic lives at risk (Pickney et al., 2001). Phosphorus is considered to be the primary limiting nutrient in eutrophication (Correll, 1998) and concentrations as low as between 10 and 20 μg P $L^{-1}$ are sufficient to support luxurious growth of phytoplankton, aquatic plants, and algal blooms (Powlson, 1998). Turbidity is an optical determination of water clarity (EPA, 2012); excessive growth of aquatic plants and their decomposition products makes water turbid which appears cloudy, murky, or colored which inhibits the penetration of light to deeper layers. Submerged plants that hardly receive sunlight die, decompose, and consume more oxygen which further exacerbates the low dissolved oxygen level in the water (**Fig. 1**). Extreme depletion of oxygen leads to the death of other more sensitive organisms and the formation of "dead zones" as in the Gulf of Mexico. Highly eutrophic waters used for drinking can develop obnoxious taste and odor problems and contain water-soluble neuro- and hepato-toxins that can be harmful to humans and livestock (Lawton and Codd, 1991). Miettinen et al. (1997) studied the effect of P on bacterial growth in drinking water. They observed that addition of phosphate-P ($PO_4$-P), even as low as 1 μg $PO_4$-P $L^{-1}$, increased microbial growth in drinking water produced from surface or groundwater. Microbial growth was increased up to a concentration of 10 μg of $PO_4$-P $L^{-1}$, however, other inorganic nutrients did not significantly affect microbial growth.

Although, eutrophication results from the combination of point and nonpoint sources, point sources have been replaced by nonpoint sources of nutrients (Carpenter et al., 1998). Among the nonpoint sources of eutrophication, intensive fertilization of agricultural soils has been considered as the key source of P. Excessive inputs of P began in the middle of the 20th century (Carpenter et al., 1998; Bennett et al., 2001) and it could take 1000 years or more to recover from eutrophication caused by the agricultural over-enrichment of soils (Carpenter, 2005). It was an International Congress of Limnologists in 1974 that led to a resolution emphasizing the critical role of P in eutrophication (Wetzel, 1975). Xie et al. (2014) analyzed the concentration of TP in still and flowing surface water of typical agro- and forest ecosystems in China. They noticed significantly higher TP concentrations in agro-ecosystems than those in forest ecosystems both for still and flowing surface water with no seasonal variation in TP concentration. They reported that concentrations of TP ranged from 0.01 mg $L^{-1}$ (forest ecosystems) to 2.47 mg $L^{-1}$ (agro-ecosystems) for still surface waters, and from 0.01 mg $L^{-1}$ (forest ecosystems) to 41.66 mg $L^{-1}$ (agro-ecosystems) for flowing surface waters, respectively. Darch et al. (2014) reported that organic P comprised 22%–46% of the total P and that organic P causes a significant risk of eutrophication. Additions of P to any water body leads to greater acceleration in growth than the additions of N or any other nutrients (An and Park, 2002; An, 2003). Uhlmann and Albrecht (1968) stated that freshwater organisms are 15 times more susceptible to changes in P levels than to changes in N. However, these findings are not in agreement with the studies of Goldman et al. (1990) who reported that increased N and P together stimulate the growth of phytoplankton in fresh water.

## Organic Fertilizers and Water Quality

Organic fertilizers are extensively used as a soil amendment and fulfill the nutrient requirement of crops (Brady, 1974). In addition to providing nutrients, organic fertilizers maintain soil aeration, moisture, and nurture the growth of soil microorganisms. On the other hand, organic manure contains fecal coliforms, HMs, nutrients that enter water bodies and degrade water quality and pose serious threats to the environment and public health (Thurston-Enriquez et al., 2005; Jenkins et al., 2008). Most of the organic agricultural systems use compost or manures as N source and the rates of manure application are based on crop N requirements. Therefore, a farmland with successive years of manure or compost application will generally accumulate excess P (Mikkelsen, 2000;

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Lotter, 2003; Qian et al., 2004). In contrast, other studies show a decrease in P concentration in organic production systems (Mader et al., 2002; Gosling and Shepherd, 2005). Generally, N and P present in the manure, accumulate in the soil and may contribute to increased $NO_3^-$ levels in groundwater and eutrophication of surface waters. Therefore, agriculture fields, supplemented with manures, also act as potential nonpoint source of water pollution.

Successive applications of high rates of dairy manure or sewage sludge can increase the risk of surface and groundwater pollution (Mohammadi et al., 2009; Rees et al., 2011). Various studies have been conducted to test the harmful effects of various types of manure on water quality parameters. Yanan et al. (1997) observed that application of organic manure did not increase N recovery by crops; organic manure reduced $NO_3^-$-N accumulation in the soil profile, but the total $NO_3^-$ leaching was larger. Tymczyna et al. (2000) analyzed groundwater samples collected near a pig farming operation; they contained about tenfold higher $NO_3^-$-N and $NH_4^+$-N concentrations than the permissible limits. They also observed that river water showed a significant degradation in water purity. Hill et al. (2005) studied the effect of animal waste application on biological and physicochemical characteristics of runoff water using simulated rainfall events. They observed a significant increase in bacterial and nutrient concentrations after the simulated rainfall events which could contribute to water pollution. Mishra et al. (2006) observed that the application of manure causes significant edge-of-field nutrient losses, if rainfall occurs soon after application. Poultry manure is considered to be one of the sources that enhances SOM and improves soil fertility. On the other hand, poultry manure may act as a serious contaminant and pose potential risks to surface water quality. Mohammadi et al. (2009) reported that organic fertilizer increased the water extractable and bioavailable P content of soil. Rees et al. (2011) studied the effects of time of poultry manure application on soil erosion and runoff water quality. They applied manure in late fall, preplanting, and prehilling (PH) on 11% and 8% slope plots. Their results showed that fresh poultry manure applications at the rate of 4 Mg $ha^{-1}$ had no effect on annual runoff, but significantly reduced the May to October runoff when manure was applied in PH stage on 11% slope compared to the F stage on 8% slope. Fall manure applications significantly increased flow-weighted yearly runoff concentrations of nutrients, whereas, PH treatment lowered nutrient losses, runoff, and soil loss. They also reported increased concentrations of *Escherichia coli* in runoff after manure application. Rainfall events play a significant role in transporting human pathogens through water runoff from biosolids-applied fields to surface water supplies and shallow groundwater (Kudva et al., 1998; Sinton et al., 2007).

Biosolids (treated sewage sludge), the by-products of waste water, are easily available and a cheap source of nutrients and organic matter. Application of biosolids is a cost-effective method to boost soil quality and plant growth and for the disposal of treated sludge. Although, biosolids are a valuable source of nutrients, they contain lower N, P, and K contents compared to commercial fertilizers (Niemi and Niemi, 1991). Besides, sewage sludge also contains undesirable HMs, organic chemicals, and pathogens. Sewage sludge-amended soils irrigated with high rates of water causes leaching of nutrients and their further transport through the soil column to potential shallow aquifers. The nutrients and HMs through runoff and sediments enter water bodies and promote growth of algae and cause a wide array of water quality problems (Łuczkiewicz, 2006). HMs from soil, in diluted form and adhering to clay and organic matter colloidal particles, are transported to surface water bodies through runoff and sediments (Evangelou, 1998; Quinton et al., 2001; Haiyan and Stuanes, 2003; Galdos et al., 2009). Galdos et al. (2009) observed a decrease in volumes of water and sediment lost by runoff after sewage sludge application; however, trace metal concentration in the runoff water and sediment increased. In a 2-year study (dry and wet years), Elrashidi et al. (2015) observed element loading into Salt Creek in the Roca watershed, Nebraska, United States, they reported greater loading during the wet year than the dry year, and that greater precipitation during the wet year increased the negative impact of runoff from soils.

## Conclusions

The information presented in this review indicates that fertilizers, in addition to boosting the agriculture sector, cause contamination of soils and waters. Fertilizers contain vital nutrients required for soil improvement and proper growth of crop plants. Being extremely vital for agriculture, fertilizers are equally harmful to the environment, human, and livestock. In addition to mineral nutrients, they also contain various contaminants including HMs and radionuclides. Along with inorganic fertilizers, organic fertilizers also add potentially harmful and toxic metals, organic pollutants, and pathogens to soils and waters. However, organic fertilizers are more conducive to soil health as they increase the nutrient status, moisture content, aeration, soil microbial diversity, and organic matter. Organic fertilizers should be processed properly to make them free from undesirable metals, organic chemicals, and pathogens before application to soil.

Repeated long-term applications of fertilizers causes an accumulation of nutrients in the soil which, through leaching and surface runoff, enter the groundwater and surface water resources and make water unpalatable and harmful for consumption. For instance, P from agriculture fields enters surface water bodies and causes eutrophication which results in algal blooms and degraded water quality. Moreover, fertilizers also add HMs to the soil that are taken up by the plants and enter the food chain where they affect human and animal lives. Nitrogen from nitrogenous fertilizers gets converted to $NO_3^-$ and becomes a potentially fatal contaminant when leached into groundwater sources. Therefore, to cope with the adverse effects of fertilizers and their contaminants, it is necessary to develop crop varieties that utilize the available nutrients efficiently. The future research should be directed to develop fertilizers with minimum contaminants and to explore the optimum dose of fertilizers for a particular crop with minimum losses to the environment. Fertilizer-induced contamination of soil and water can also be minimized by adopting various control measures such as phytoremediation, application of lowest possible dose of fertilizers, wastewater treatment, nutrient monitoring, and mathematical models, public awareness, and legislations.

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