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Behavior of Inorganic Contaminants Associated with Agricultural Fertilizers and Their Impact on Soil and Plant Ecosystems

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Abstract: Inorganic fertilizers are subjected to an easy breakdown in soil compared to organic manures and, therefore, easily contaminate soil, water, and air. The major source of contamination is from nitrogenous and phosphatic fertilizers, which affect soil properties, runoff cause water contamination, or sometimes escape to atmosphere affecting air quality thereby enhanced contribution to greenhouse gases contributing to climate change. The contaminants associated with various kinds of fertilizers became an important issue due to its hazardous effect on soils, plants and human health. Also the indiscriminate use of fertilizer and manures with improper handling and storage facilities, etc. often result in degradation of natural resources, releasing contaminants into soil, air, and water which directly impact human health. High buildups of Potential Toxic Elements (PTEs) like Cr, Cd, Pb, Ni, Hg and F in the soil are often associated with an excess application rate of manures and fertilizers in agriculture. Various contaminants have a direct effect on soil properties, such as a reduction in soil organic carbon, high accumulation of salts, compaction, surface crusting, and imbalance of essential nutrient and the most effective factors of contaminates solubility in soils are: the total and available form of the element, pH, organic matter, calcium carbonate, clay content, and cation exchange capacity. However, plant species and cultivars have a great role and significantly varied in the uptake of contaminants and their impact on the crop quality. This article is an attempt to summarize self-experiences and international published documents on the behavior of various inorganic contaminants such as fluorine, cadmium and lead found in fertilizers used in agricultural farming.
Keywords: Source Contaminants, Chemical Fertilizers, Consumption, Contaminants impacts on soils and plants

INTRODUCTION

Organic and Inorganic Fertilizers beside agricultural amendments applied in different soil ecosystems contain significant amounts of PTEs as contaminants, transferred into food chain and adversely affect human health and livestock as well as natural ecosystems. Human health risk assessments are a key part of creating reasonable and prudent regulations for permissible levels of metals in fertilizers. The levels of PTEs in fertilizers and agricultural amendments are thus subject to soil contamination; consequently, regulators need to balance the benefits of economical fertilizers with the risks posed by excessive levels of metals in these essential products.

The main objective of this work is to review the most important and recent publications on the soil contamination by heavy applications of fertilizers and related amendments that contains significant concentrations of PTEs as cadmium Cd, Fluorine F and lead Pb. 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 thermo-stable and no biodegradable and, therefore, accumulate to toxic level in air, water, soil and plant.

CONSUMPTION OF FERTILIZERS IN EGYPT:

Fertilizer consumption in Egypt was reported at 54.82 % in 2016, according to the World Bank collection of development indicators, compiled from officially recognized sources. Egypt, actual values, historical data, forecasts and projections were sourced from the World Bank in May of 2020. In Egyptian

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farming, fertilizer Consumption was calculated per Hectare of Arable Land data was reported at 645.457 kg/ha in Dec 2015.

Figure 1. Fertilizer consumption (%) of fertilizer production in Egypt sourced by the World Bank (2020)

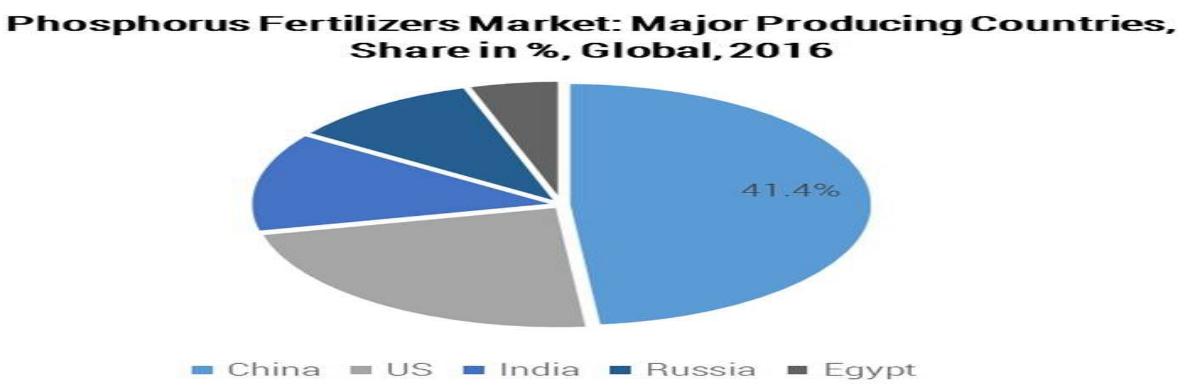

Figure 2. Global phosphorus fertilizer market 2016

This records a decrease from the previous number of 724.236 kg/ha for Dec 2014. The data reached an all-time high of 724.236 kg/ha in 2014 and a record low of 432.533 kg/ha in 2002. Figure 1&2, represents the consumption of fertilizers in Egypt until the year 2016.

Poor farming practices can cause soil erosion and loss of soil fertility. Efforts to increase productivity by using chemical fertilizers, pesticides, and intensive irrigation have environmental costs and health impacts. Fertilizer consumption (% of fertilizer production) in Egypt was 54.82 as of 2016. The highest value over the past 14 years was 82.89 in 2003, while the lowest value was 34.33 in 2009 Figure 3. This finding perhaps could be related to understanding the injury of heavy application of chemical fertilizers**.**

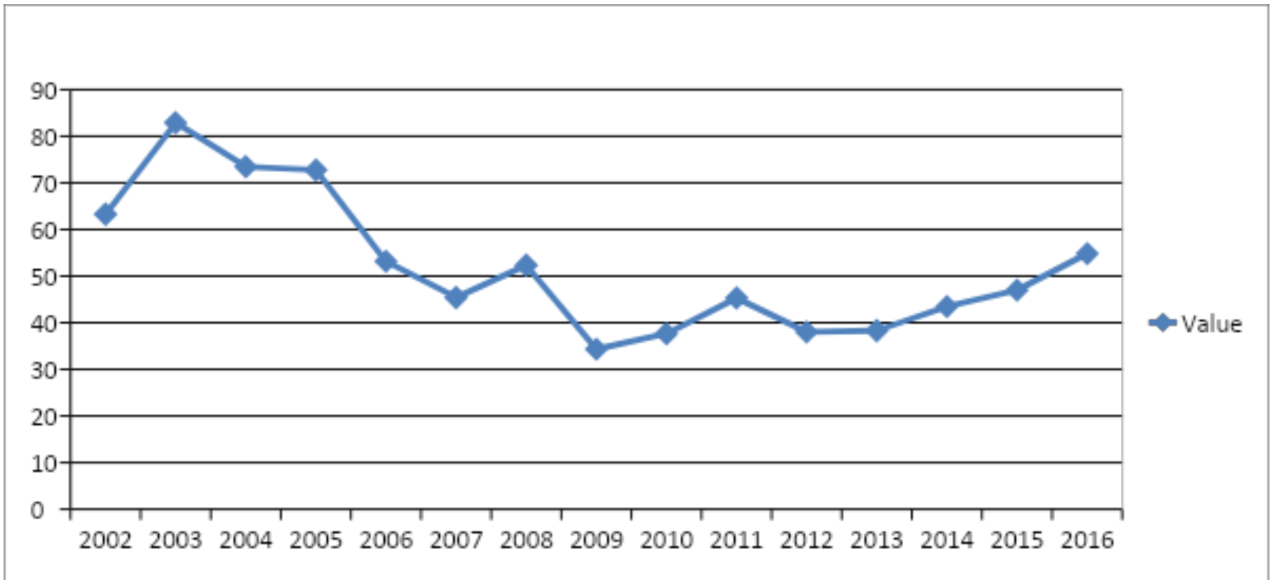

Figure 3. percentage of fertilizer consumption in Egypt compared to fertilizer production (Source, FAO **2013** electronic files and web site)

PROBLEMS OF HEAVY APPLICATIONS OF AGRICULTURAL FERTILIZERS

Camilia (2001) studies on the effects of wide use of different fertilizers, commercially prepared, and the resultant effect of their accumulation on plant and soil and behavior of indicated fertilizers was evaluated through studies for the elements contaminating the common commercial fertilizers used in the local market; the mobility of such elements in soil as well as responses of developed plants were also included. 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 (Almasri and Kaluarachchi, 2004) which put the pristine terrestrial and aquatic ecosystems downstream and human health at risk. Soils naturally contain PTEs (HMs) such as cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), lead (Pb) and Fluorine (F) etc., but excess application of fertilizer consumption measures the quantity of plant nutrients used per unit of arable land. Fertilizer products cover nitrogenous, potash, and phosphate fertilizers (including ground rock phosphate). The average values of some PTEs and fluorine in some materials especially phosphate fertilizers compared with farmyard manure and sewage sludge are recorded in Table, 1.

The excessive nitrogen fertilizer applications have sometime lead to pest problems by increasing the birth rate, longevity and overall fitness of certain agricultural pests, such as aphids. Further, excessive use of fertilizers emits significant quantities of greenhouse gas into the atmosphere. Over-fertilization of a vital nutrient can be detrimental, as "fertilizer burn" can occur when too much fertilizer is applied, resulting in drying out of the leaves and damage or even death of the plant. In many industrialized countries, overuse of fertilizers has resulted in contamination of surface water and groundwater. There is no single correct mix of inputs to the agricultural land, as it is dependent on local climate, land quality, and economic development; appropriate levels and application rates vary by country and over time and depend on the type of crops, the climate and soils, and the production process used.

Table 1. Average of extractable PTEs and other potentiality toxic elements in earth crust, phosphate fertilizers, rock phosphates (RP), compared with averages in farmyard manure and sewage sludge (mgkg^{-1}).

Element	Earth Crust	Phosphate fertilizer	Rock phosphate	Farmyard manure	Sewage Sludge
Cd	0.5	0.1-170	1-90	0.1-0.8	0.4-2.1
Co	30	---	0.2-21	---	0.5-1.4
Cr	200	---	6-327	---	---
Cu	100	1-300	20-98	2-172	10-38
F	270	23000	20000-40000	---	---
Ni	80	7-38	9-51	2.1-30	> 30
Pb	16	7-225	<1-51	1.1-27	> 25
Zn	50	50-1450	<2-2412	15-566	50-610

Source (Curtis & Smith (2002).

Potential Toxic Elements (PTEs) in used fertilizers

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 (Figure 4). This section also highlights the contaminants pathways created 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 fertilizers result in accumulation of various contaminants, such as HMs (Table 2), thus raising environmental concerns by polluting natural resources especially soil, water, and atmosphere.

Gathering of PTEs in biosphere may take place by both natural and human activities (Figure 1), While, weathering of rocks is the chief natural source of heavy metal contamination in the environment, the anthropogenic sources include mining, smelting operations, and agricultural activities (Herawati et al. 2000).

According to (Rashmi, *et al.,* 2020), inorganic and organic fertilizers are crop food considered as indispensable sources of nutrients to the agriculture ecosystem. These crop foods, besides supplying essential nutrients and acting as soil conditioners, pose potential pollution risk in agriculture and might contain significant amount of contaminants. Indiscriminate use of fertilizer and manures, improper handling and storage facilities, etc. often result in degradation of natural resources, releasing contaminants into soil, air, and water which directly impact human health. Inorganic fertilizers are subjected to easy breakdown in soil compared to organic manures and, therefore, easily contaminate soil, water, and air. 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. (Thomas *et al.,* 2012).

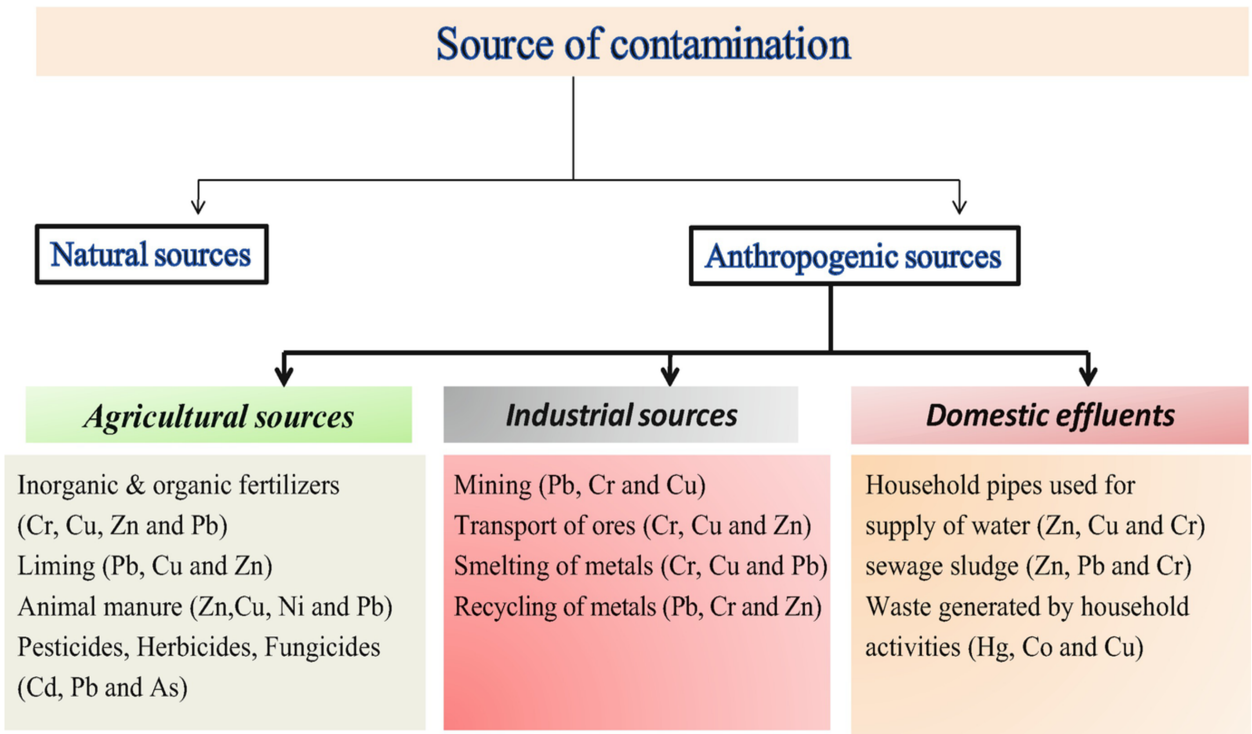

Figure 4. Natural and anthropogenic sources of PTEs and their composition

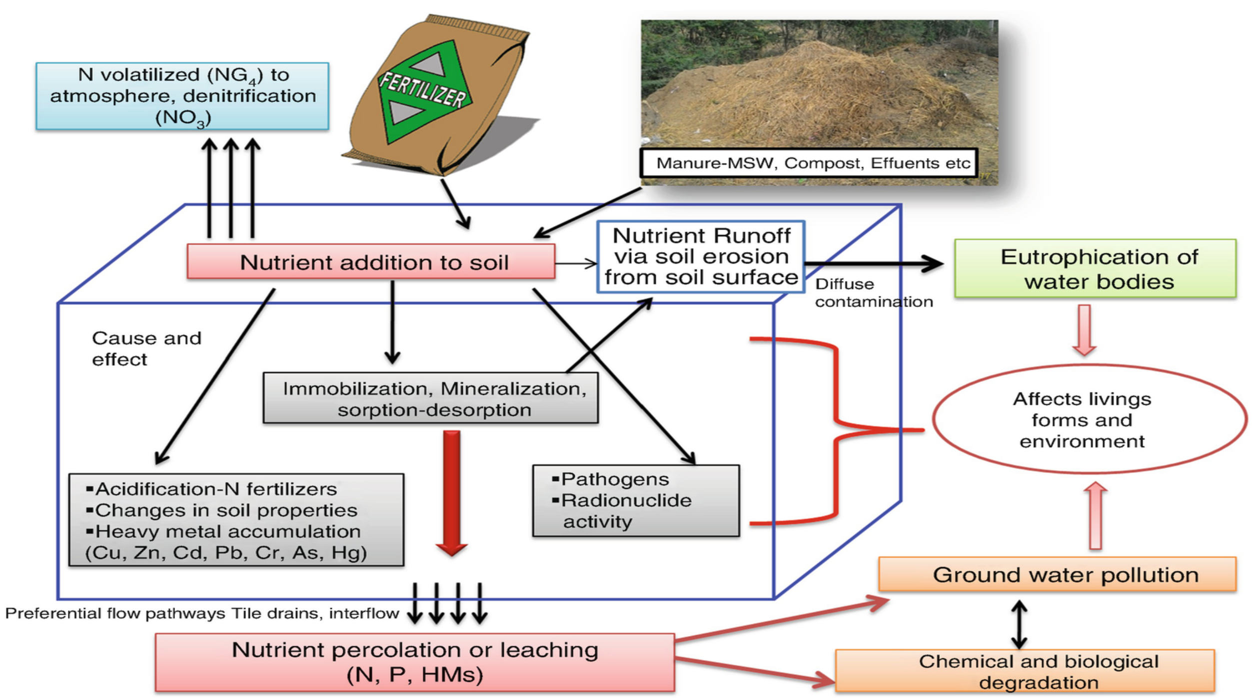

Figure 5. Pathways of contaminants found in organic and inorganic fertilizer applied in soil ecosystem

Table 2. Contaminants in fertilizers and manures applied in agricultural soils

Inorganic fertilizers			
	PTEs	**Others**	**References**
N fertilizers	**Cd, Ni ,Pb**	**–**	**Benson et al. (2014)**
P	**Cd, As, Pb, F**	**Radionuclide like U, Ra, Sr**	**Khan et al. (2018)**
K	**Cl**	**–**	
Micronutrients	**As, Pb, Cd**	**–**	**MDH (2008)**
Organic Fertilizer			
Compost, bio solids, MSW	**Cd, Zn, Ni, Pb, Hg, Cr, Cu**	**–**	**Smith (2009)**

Khan, *et al.,* 2018 mentioned that Major source of contamination is from nitrogenous and phosphatic fertilizers, which affect soil properties, runoff cause water contamination, or sometime escape to atmosphere affecting air quality thereby enhanced contribution to greenhouse gases contributing to climate change. High buildup of PTEs like Cr, Cd, Pb, Ni and Hg in soil is often associated with excess application rate of manures and chemical fertilizers in agricultural farming. There can have deteriorating effect on soil and water resources. Difference between organic and inorganic fertilizers in their behaviors is depicted in Figure 6.

Agricultural crops are the most important dietary source of nutrients as it contains protein, carbohydrates, vitamin, fibers, minerals, essential metals etc. and also contain antioxidants (Islam *et al.,* 2018), but it becomes harmful to human as it accumulates PTEs in their tissue when grown in the contaminated soil. Both natural and anthropogenic interventions have been considered for the release of PTEs into the environment that can pollute soil, water, and plants including other compartments of the ecosystem and eventually affect human health and well-being (Ahmed *et al.,* 2015). The activities such as rapid industrialization, vehicular exhaustion, wastewater irrigation, sludge application, and the use of large quantities of agrochemicals such as metal-based pesticides and fertilizers are the sources of toxic metals contamination.

The risks associated with metal pollution in foods are of great concern in last decade, particularly in agricultural crops such as rice, cereals, vegetables, and fruits. Consumption of metal contaminated foods pose serious health problems that range from shortness of breath to several types of cancers (Islam *et al.,* 2017), therefore, the environmental safety of foods against metals pollution is exclusively crucial to human health.

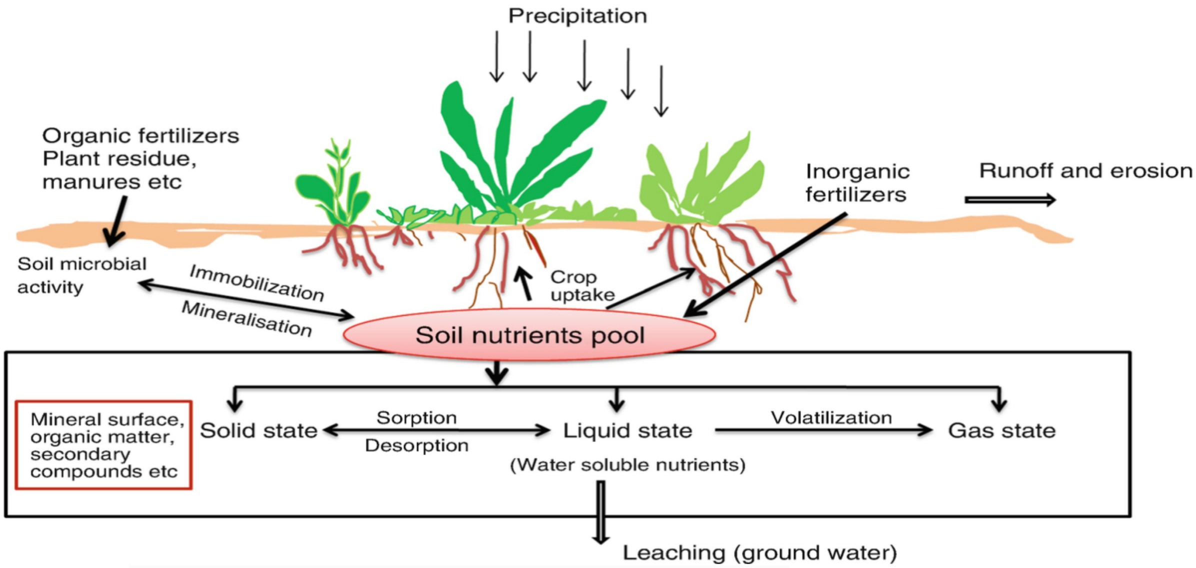

Figure 6. Fate of organic and inorganic fertilizer behavior in soil (Source by Khan, *et al.,* 2018)

Curtis and Smith (2002) stated that phosphate fertilizers contain a range of potentially toxic impurities that can accumulate in the soil, including arsenic, cadmium, chromium, fluorine, strontium, thorium, uranium and zinc. Of these, cadmium is the element of most concern, because it creates the greatest potential risks to animal health, food quality and soil quality.

Rock phosphates also contain relatively high levels of fluoride, ranging from 1,900 to 42,400 ppm. The environmental significance of fluorine accumulation in soils and crops from phosphate fertilizers has so far not received as much attention as heavy metal contamination. El-Kherbawy *et al.* (2014) studied the contents of PTEs in three groups of Egyptian commercial phosphate rock collected from different mines applied in Egyptian agricultural lands.

The chemical characterizations of different types are presented in table(**3**). As shown in the table, significant concentrations of Pb, As, Co and Zn were observed in these types of rock phosphate. The heavy applications of these types in agricultural soils will led to future pollution problems with inorganic pollutants. 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. Excessive and continuous use of fertilizers accumulates these contaminants in the soil to a level harmful to the environment (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 (Nicholson *et al.,* 2003). 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.

Table 3. Total contents of PTEs (mg kg-1) found in commercial phosphate rock samples applied in Egyptian soils

Rock Phosphate types	**Cd**	**Pb**	**Zn**	**As**	**Co**
G1					
El Sebaiya east 24	7.1	56.9	215.6	90.76	49.2
El Sebaiya west 27	6.8	42.9	199.5	94.4	54.4
G2					
Hamraween(1) 27	7.1	69.7	266.4	105.84	25.7
Hamraween(2)28	8.1	64.7	305.6	107.18	51.7
Hamraween(3)30	8.5	60.9	319.1	109.52	47.7
G3					
Oroba	11.7	50.8	299.2	97.14	30.2
Abu tartur	3.2	72.8	128.4	108.44	48.6

Cheraghi *et al.,* (2012) reported the relationship between the effects of phosphate fertilizer application and different cultivation patterns on the HM contents in agricultural soils. They observed significant levels of As, Cr, Cu, Mn, Ni, and Pb in P-amended soils cultivated with sugar beet and significant concentrations of Pb, Cr, As, and Cd in soils cultivated with potato plants. In addition, heavy application of phosphate fertilizer with different rates and crop rotation, led to significant effects on soil physicochemical properties and on spatial variability of Cd species Jafarnejadi *et al.,* (2013). In the same trend Czarnecki and Düring (2015) observed that pseudo- and mobile metals (Cd, Cu, Mn, Pb, and Zn) in soils increased after 14 years of mineral fertilizer treatments (N, P, NP, and NPK).

EFFECT OF ORGANIC WASTES APPLIED IN FARMING ACTIVITIES ON PTES CONTENTS IN AGRICULTURAL SOILS

Chemical, biochemical and biological composition of sewage sludge applied to agricultural soils could be the main source in soil contamination. These materials are rich with organic material and elements considered nutrients to plants, particularly P fertilizer.

Awad *et al.,* (1995) evaluated the environmental aspects of sewage sludge application on the grow

th and mineral contents, especially PTEs of apple seedlings grown on newly reclaimed soil. They stated that Pb and Ni in apple seedlings leaves and fruits were slightly increased but not to the toxic level, while Cd was relatively unaffected.

Rabie *et al.*, (1996) found that the concentrations of PTEs in the filtrated sewage effluent at Helwan were; 0.7 to 2.5 ppm for Fe, 0.3 ppm for Mn and 0.2 ppm for Zn. Abd El-Sabour *et al.*, (1996) added that the concentration of PTEs in the filtrate of Cairo sewage effluent at El-Gabal El-Asfar farm were 0.81 ppm for Fe, 0.23 ppm for Zn, 0.06 ppm for Cu, 0.02 ppm for Co and 0.014 ppm for Pb. The total contents of those PTEs in the suspended particulate being 20.7ppm for Fe, 22.2 ppm for Zn, 0.7 ppm for Cu, 0.3 ppm for Co and 0.3 ppm for Pb.

The addition of sewage sludge to soils may be an inexpensive and effective alternative to the methods applied currently (mineral fertilization, manure etc.). In spite of the undisputable advantages resulting from the application of sewage sludge in agriculture, it also involves some serious threats. Among those we should mention the presence of pathogens, PTEs and organic pollutants. In the current scenario of increasing global population, the generation of solid wastes like bio solids is bound to increase remarkably. Improper and unscientific disposal of bio solids results in several environmental issues such surface and groundwater contamination, degradation of land, and food chain contamination. Delibacak, *et al.,* (2020) added that International as well as national guidelines on the carrying capacity of toxicants in bio solids composts should be set and stringent monitoring of such guidelines should be enforced in agricultural use of bio solids.

IMPACT OF FERTILIZERS CONTAMINANTS ON SOILS AND PLANTS ECOSYSTEMS

Soil is considered a long-term sink for toxic elements often referred to as PTEs, such as Cu, Zn, Cd, Pb, Cr, As, and Hg. PTEs contamination in soil due to anthropogenic activity has been reported from different areas (Sachan 2007; Deka and Bhattacharyya 2009).

Fertilizer use recommendations are based on experiments carried out by the Egyptian Ministry of Agriculture. The rates recommended by the Ministry of Agriculture are averages, not tailored to specific crop needs in a specific area. In practice, neighboring farmers use different rates of fertilizers for the same crop. However, farmers applied higher values of fertilizers assuming that increasing of fertilizers will increase the crop production.

Taha *et al.,* (2004) have carried out a detailed investigation on pollution sources and related environmental impact in the new communities southeast Nile Delta, Egypt. They concluded that pollution caused deterioration of ground water quality due to the misuse of fertilizers and pesticides especially in the old lands according to PTEs retention in such soils and using of low quality waters in soils new industrial cities. Fish and Johnson (2003) stated that PTEs bind to surfaces by several mechanisms. Metals exhibit typical cation-exchange behavior on clay minerals; ions such as Cd^{2+} and Pb^{2+} are attracted to layer silicates by electrostatic forces. However, these metals must compete with more abundant major cations for the available exchange sites, so a large degree of metal partitioning onto exchange sites is not expected. Sorption of metals on metal oxides (such as hydrous ferric oxide) is generally far more important and can be expressed as a surface-complexation reaction of the type:

$$Fe\text{--}OH] + Cd^{2+} = Fe\text{—}O\text{--}Cd]^{+} + H^{+}.$$

Poder (2004) concluded that the vegetative growth of maize and sunflower plants cultivated in PTEs contaminated soils was not dramatically reduced compared to the control plants and that for Cu and Pb the concentration in the leaves was above the normal range. Moreover, the above-ground biomass, the grain and the seed of maize and sunflower plants were not suitable for human and/or animal consumption.

Potential toxic elements such as Cd, Cr, Zn, Pb, Cr, and As are highly contributed by inorganic fertilizers, pesticide, and organic sources in agriculture (Kelepertzis 2014 and Toth *et al.,* 2016), plants (Saber et al 2014).

Low quality of irrigation water, pesticides, and organic amendments are important sources of HMs in agricultural soils (Nicholson *et al.,* 2003). 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. Cheraghi *et al.,* (2012) Reported that 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). 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 is easily absorbed by crops and tends 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 PTEs affect the accumulation of contaminants and their movement in soil–water system.

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).

Fluorine is ubiquitous in the environment with most deriving from natural sources, these being: normal weathering processes resulting in F release from rocks and minerals, volcanic activity and marine aerosol emission, together with biomass burning, being in part natural. However, there are several sources of anthropogenic ally-derived F which in some areas represent a threat to the biosphere. Anthropogenic sources can be broadly subdivided into those deriving from industrial processes, which include coal fired power generation, brick making and ceramic manufacture, aluminum production and phosphate fertilizer production, and those deriving from agricultural practices such as phosphate fertilizers and sewage sludge application, and the use of F containing herbicides and pesticides etc.(Ron Fuge, 2019).

Camilia and Zaghloul (2007) studied F desorption accumulation of fluorine in six soils represent light texture soils having different percentage of $CaCO_3$ and receiving different quantities of P fertilizers. Specifically, fluorine occurs in these soils created from continual agricultural applications of phosphate fertilizers for more than 15 years through the kinetic approach. The standard division analysis applied in this work, indicated that Fluorine concentration in soil had very strong positive correlation with total concentration of soil P, reflecting the link between P fertilizer applied and F accumulation in soils. In addition, the total content of F as well as the extractable fraction in the soil samples studied exceeded the critical values for plant growth.

The major control on the litharge chemistry of F is the similarity of the F^- and the OH^- ions with ionic radii of 131 pm and 135 pm, respectively (Li *et al.,* 2017). Due to this similarity the F^- ion easily substitutes for the OH− ion in rock forming minerals. It is, therefore, not surprising that hydroxyl-containing silicates and apatite are the major hosts of F in the lithosphere.

Addition of excessive dose of chemical 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 (Khan et al. 2018), under such situation PTEs could be found in the soil ecosystem will be more bioavailable for plants.

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).

In agriculture, soil is the major contributor of PTEs from application of low quality water; sewage effluents and heavy application of fertilizers are shown in Table 4.

Table 4. Total concentration (ppm) of selected heavy metal in manures ((based on oven dry weight basis, Chhonkar 2003)

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**

SOIL FACTORS AFFECTING SOLUBILITY OF FERTILIZER CONTAMINANTS IN SOIL ECOSYSTEM

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.

Imbalanced or heavy application of chemical fertilizers increases the chance of environmental contamination by PTEs. 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. Excessive and continuous use of fertilizers accumulates these contaminants in the soil to a level harmful to the environment (Hariprasad and Dayananda, 2013; Yargholi and Azarneshan, 2014).

Organic matter plays a prominent role in the formation of stable complexes with certain divalent metal ions by chelation phenomena, such stable complexes being responsible for the migration and accumulation of metal organic compounds in soil and easily to be uptake by cultivated plants.

There is a temporary effect around the fertilizer e.g. high pH from urea hydrolysis. Superphosphate has some residual acidity form manufacture and but this is again just a temporary affect around the granules. Such temporary effects can be significant e.g. increased risk of ammonia volatilization risk around urea pills due to high pH and increased risk of phosphorus reaction. Ammonium phosphate fertilizers (MAP, DAP) in many soils (e.g. higher pH) can release volatile ammonia causing seed injury if in proximity to the seed but longer term they can be acidifying particularly if applied in excess of requirements.

Longer term effects of chemical fertilizers can include leaching of nitrate and sulfate which will leach some base cations, causing acidification unless the nitrate and sulfate supply in the fertilizer is balanced by base cations anyway e.g. calcium nitrate or calcium sulfate (the latter as is the main sulfate form in superphosphate). So even urea, which has a temporary high pH effect around the pill has a medium capacity to acidify the soil, MAP and DAP more acidification potential and ammonium sulfate even more.

The most acidifying fertilizer commonly applied is elemental sulphur ("artificial" or natural) which has around three times the acidifying potential by weight as calcium carbonate has pH lifting potential.

Extra plant growth (e.g. of legumes) caused by the fertilizer may also result in some acidification over time. Chemical fertilizer forms of phosphorus tend to not have the same liming effect as natural reactive phosphate rock as this has more calcium and a calcium carbonate component.

The direction of pH change can sometimes be similar in soils of different starting pH but have different consequences. In acidic soils, acidification will often be thought of as detrimental or requiring correction with liming. But, as an example, Tagliavini et al 1995 reported in alkaline soils that the acidifying effect of ammonium sulfate may be beneficial (to metal trace element nutrition) as compared to use of non-acidifying calcium nitrate.

Arne and Jóska (2009) mention that Major changes in soil pH are related to (1) conversions of fertilizer constituents involving protons (release or consumption), (2) losses from the system through leaching and gaseous losses, and (3) plant uptake in exchange/alongside with protons (4) also account for uncertainty in the effects of fertilizers on soil pH. While the oxidation/nitrification of ammonium releases protons and acidifies the soil, the uptake of the nitrate generated by this process by crops and/or denitrification consumes protons, while leaching does not. Hence the acidification due to ammonium sulphate is the stronger the more N is leached. In addition, manure increase soil pH, as crops absorb more cations (positive charges) than anions (negative charges). The balance is made up – simplified – by carboxylic acids. When these along with the organic matter are broken down again, this process consumes protons and hence increases soil pH.

In general, changing of soil pH from heavy application of fertilizers will drastically influenced PTEs bioavailability in soil ecosystem and this phenomenon could be important to be applied in phytoremediation of PTEs in contaminated soils (Saber et al. 2019) or minimizing the hazards of inorganic pollutants bioavailability.

Crop factor also influenced PTEs bioavailability in the soil ecosystem. The stronger acidification of legumes is valid, but not caused by the N2 fixation as such. As an uncharged molecule it doesn't affect the proton balance of this symbiotic system. But legumes tend to absorb less anions (nitrate), and the cations surplus uptake strongly acidifies the soil.

Temperature plays a significant role in the adsorption of PTEs. Increase in temperature increases the rate of adsorbate diffusion across the external boundary layer. The solubility of PTEs increases with an increase in temperature, which improves the bioavailability of PTEs (Bandowe *et al.* 2014). However, the actions of microorganisms increase with rise in temperature at a suitable range, and it enhances microbial metabolism and enzyme activity, which will accelerate bioremediation. The stability of microbes-metal complex depends on the sorption sites, microbial cell wall configuration, and ionization of chemical moieties on the cell wall configuration, and ionization of chemical moieties on the cell wall.

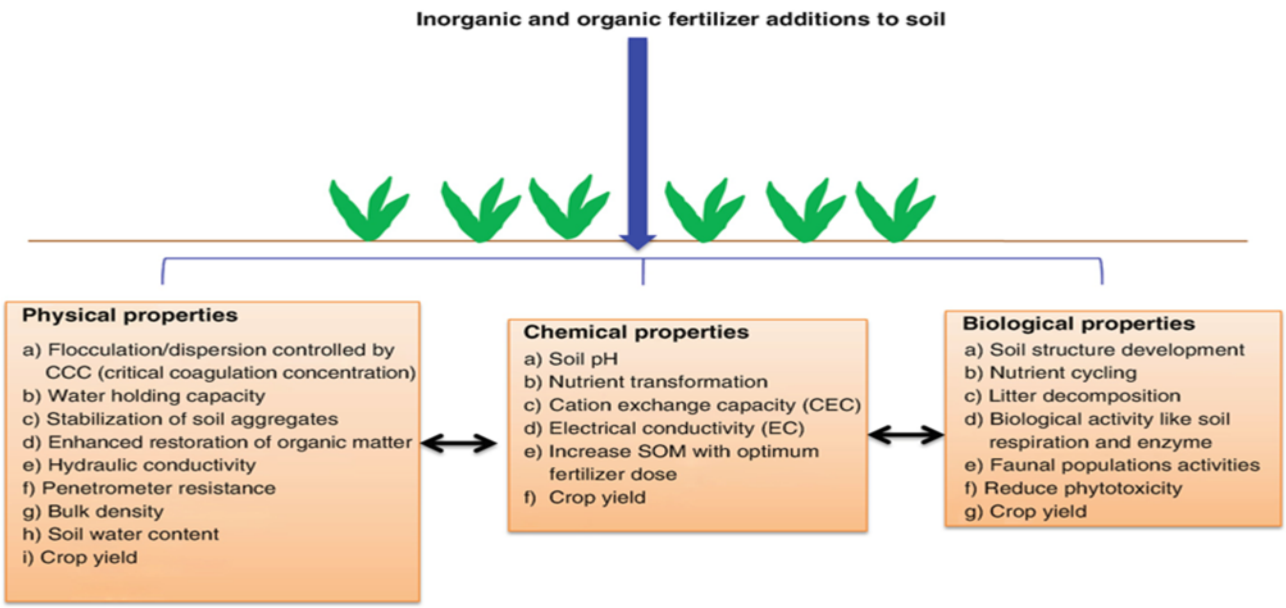

Figure 7. Soil properties influenced by inorganic and organic fertilizers (Source, Rashmi, *et al.*2020)

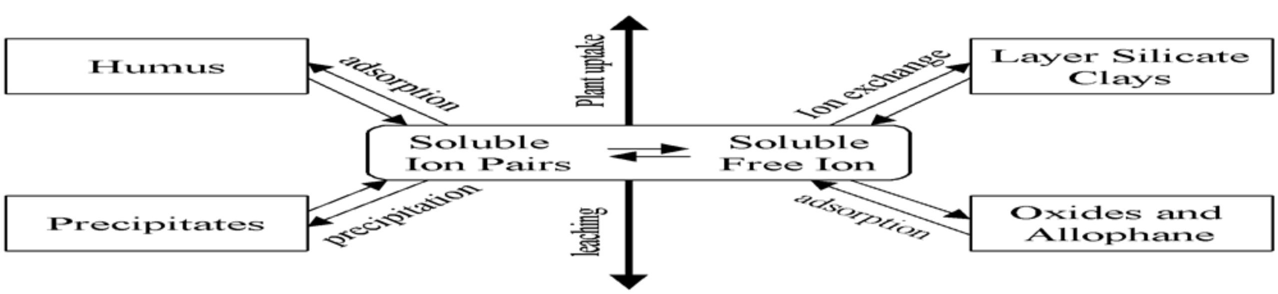

Figure 8. Dynamic interactive processes governing solubility, availability and mobility of elements in soils [(c.f. McBride (1994)]

PLANT FACTORS AFFECTING POLLUTANTS OF FERTILIZERS BIOACCUMULATION IN CULTIVATED CROPS

The bioavailable/mobile fraction of PTEs can be taken up by plants and other living organisms, Figure8. (Sammut *et al.,* 2010). The metals enter the plants from the soil mainly via the root (Pourrut *et al.,* 2011). Foliar heavy metal uptake by crops cultivated near metal recycling industries is also reported to be a major path of metal entrance to plants (Schreck *et al.,* 2013). The entrance of metals from soil to roots is not direct; rather they are first adsorbed on plant roots, followed by binding to carboxyl groups of uranic acid around the roots, or directly to the mucilage polysaccharides of the rhizoderm cell surface (Pourrut *et al.,* 2011). Several processes/steps are involved in the uptake of metals by plants including: desorption of metal from soil particles, transport of metals towards plant roots, uptake of metals by roots, and translocation of metals towards shoot (Saifullah *et al.,* 2009). Cadmium is relatively more available for plant uptake because it is predominantly found in soil solution or bound to the solid phase (Verbruggen *et al.,* 2009).

Different crop species accumulate Cd to different degrees if grown on the same soil, and on highly contaminated soils a change of plant species or cultivar may be the only management approach which will permit crop growth. Bioavailability of a metal in the soil is the part of the total metal content that is readily available or made available in a dynamic manner over time to an organism from its direct environment (Pauget *et al.,* 2012).Plants in relation with PTEs were divided into two sections. The 1st represented by hyper accumulator plants such as Canola (Zn, Cu and Ni), Indian mustard (Ni and As) [Saber et al., 2016], and non-hyper-accumulator plants represented by most of editable plants.

Leafy vegetables such as silver beet, spinach, lettuce, are Cd accumulators, whereas cereals tend to exclude Cd from their grain. While the relative differences between cultivars noted are often significant enough to warrant inclusion of Cd as a selection factor in breeding programs. Root exudates have an important role in the acquisition of several essential metals and some PTEs such as Pb, As, Cd. For example, some grass species can exude from roots a class of organic acids called phytosiderophores, which were shown to significantly enhance the bioavailability of soil-bound of PTEs such as Fe, Zn, and Cd (Awad and Romheld 2000).

EFFECT OF RELEASED PTES FROM HEAVY APPLICATION OF FERTILIZERS ON NUTRIENTS BIOAVAILABILITY

Higher levels of Ni induced the remobilization of macronutrients compared to normal Ni concentrations (Léon *et al.,* 2005), whereas a reduction in the remobilization of stored barley seed phosphorus reserves was reported due to the decrease in the activities of acid phosphatase, α-amylase, and alkaline phosphatase in endosperms mainly due to the concentrations of Cd and Cu (Kalai *et al.,* 2014) during germination.

Moreover, Cu and Cd enhanced soluble protein and sugar content and caused lipid peroxidation even at the lowest dose, and caused an accumulation of proline, fundamentally in radicles (Kalai *et al.,* 2014).

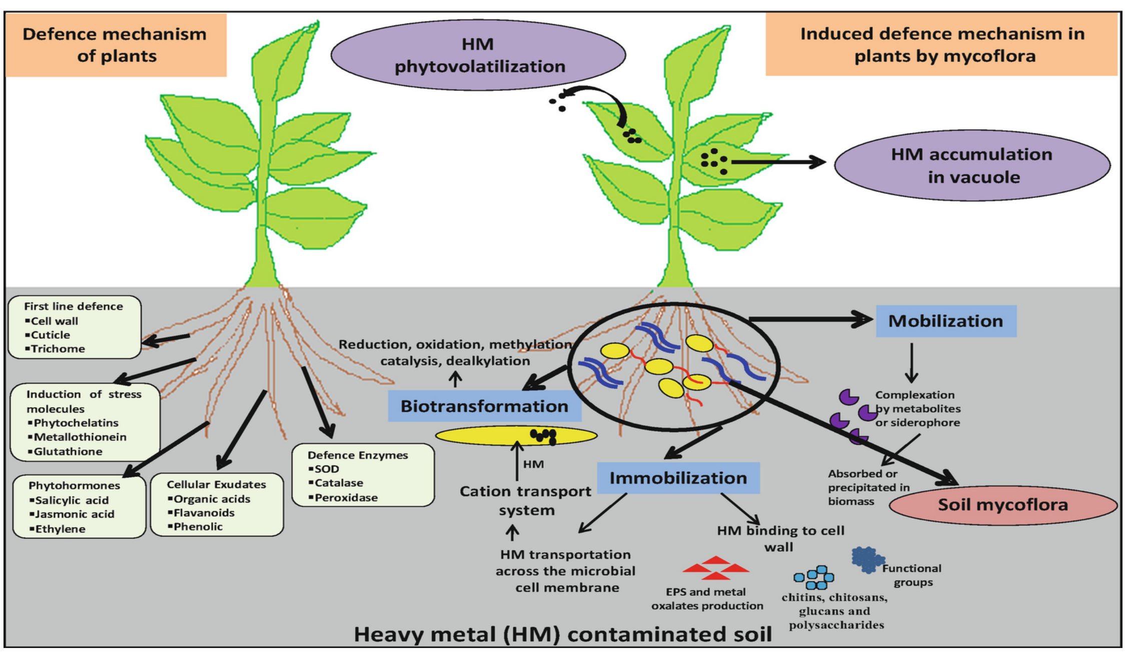

Figure 9. Fate of organic and inorganic fertilizer behavior in soil. Source Singh, *et al.* (2018)

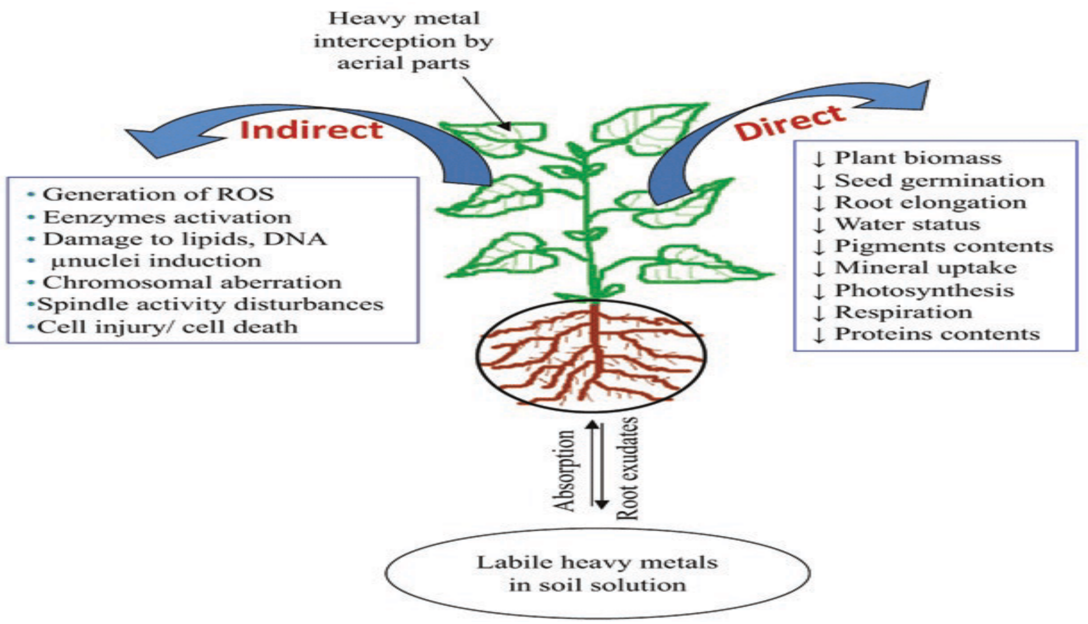

Figure 10. PTEs uptake by plant roots and possible direct and indirect toxic effects resulting in reduced crop production.

The decrease in seed germination of barley after exposure to Cu or Cd is not a result of reduced water uptake by seed tissues, but may be due to a failure in reserve remobilization from the endosperm (Kalai *et al.,* 2014). Increasing concentrations of Cu, Cr, Co, Ni, Mn, Pb, and Zn metals reduced the germination percentage in different crops (Wang *et al.,* 2014) and this reduction in germination rate was related to the restricted oxygen uptake and physiological disorders in the supply of food reserves (Márquez-García *et al.,* 2013). These HMs not only decrease crop yield but also affect the soil properties, thereby deteriorating soil health.

CONCLUSIONS

Potential toxic elements PTEs can be found naturally in the Earth's crust and fertilizers prepared from earth materials. Also, Potential toxic elements could be distributed to various parts of the environment or through human activities through the heavy application of agricultural fertilizers, which represent the important part of environmental pollution. One of the most environmental concerns about soil pollution with inorganic pollutants present in fertilizers is its serious impact on human health, especially in the last decade. PTEs enter plants grown through the roots from the soil solution and move to the food chain. Different studies imply most of the absorbed PTEs may be stored in the roots where they are deposited in the form of insoluble metal salts, where they are fixed by negatively charged presents inside the cell wall, or deposited in the space between cells, or accumulate in the gaps. It may pass to the stem or fruits and this causes many negative effects that lead to lower crop productivity and final product pollution. The intensive use of inorganic or even organic fertilizers is fraught with risks in Egyptian agricultural activities, especially if these fertilizers contain high concentrations of these toxic elements.

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