

## Review Article

<https://doi.org/10.20546/ijcmas.2018.705.067>

## Soil Pollution with Lead: Geochemistry, Food Safety Issues and Reclamation Options - A Review

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### ABSTRACT

Lead (Pb) exposure is estimated to account for 0.6% of the global burden of disease with the highest burden in developing regions. Lead is considered as general protoplasmic poison, which is slow acting, cumulative and subtle. The use of leaded gasoline, discharges from industrial activities and other sources, and deposition by rainfall or dry fall can greatly influence the availability of Pb in soil, water, and other environments. Most of the Pb in plants and soil surface are anthropogenic origin. As many of the Pb pollutants are indispensable for human life, soil contamination with lead is not likely to decrease in near future. Severe Pb contamination in soils may cause a variety of environmental problems including loss of vegetation, groundwater contamination, and Pb toxicity in plants, animals, and humans. The cation exchange capacity, pH, organic matter, clay and CaCO<sub>3</sub> content can be considered as the most important factors affecting Pb adsorption capacity of soils. Lead may cause the toxic effects on gastrointestinal, muscular, reproductive and neurological systems. Pb is having long half-life in biological systems and plants facilitate entry of Pb in food chains of man and animals. It may enter into our body through ingestion of food or through the blood stream (Johnson, 1998). Recently, accumulator plants for reclaiming Pb polluted soils have increasingly been used. Also, application of phosphate has been reported to be effective in immobilising Pb in soil, leading to reduction in its transfer from soil to plant. Among various reclamation techniques applied for heavy metal, phytoextraction has emerged as less costly, effective method of in situ reclamation. Use of synthetic chelates has improved phytoextraction. Lead with synthetic chelate forms soluble bio-available compounds which may leach down the soil profile and cause ground or water contamination. Hence, approaches of re-vegetation and reclamation, involving both ameliorative and adaptive strategies to allow plant establishment and encourage subsequent vegetation, have emerged.

#### Keywords

Soil Pollution,  
Lead,  
Geochemistry,  
Food Safety

#### Article Info

##### Accepted:

07 April 2018

##### Available Online:

10 May 2018

### Introduction

Lead (Pb) is a naturally occurring toxic heavy metal found in the earth's crust. Its widespread use has resulted in extensive environmental contamination, human exposure and significant public health problems in many

parts of the world. Lead is a cumulative toxicant that affects multiple body systems and is particularly harmful to young children. WHO has identified lead as one of the ten chemicals of major public health concern, needing action to protect the health of workers, children and women of reproductive

age. As many of the lead pollutants are indispensable for human life, soil contamination with lead is not likely to decrease in the near future. It is non-biodegradable, toxic heavy metal and it has become a global health issue. Due to strong binding of most trace metals to soil constituents, and their limited transport, trace metals have long residence time in soils (Hesterberg, 1998) and concentrations can become elevated above background levels and threaten plant, animal, and environmental health. As many of the Pb pollutants are indispensable for human life, soil contamination with lead is not likely to decrease in near future (Yang *et al.*, 2000). The Pb loading rate in soil exceeded its natural removal rate by approximately 20-fold or more (Nriagu, 1990).

### **Sources of lead in soil**

The terrestrial abundance of Pb indicates a tendency for Pb to concentrate in the acid series of magmatic rocks and argillaceous sediments in which the common Pb concentrations range from 10 to 40 ppm, while in ultramafic rocks and calcareous sediments its range is from 0.1 to 10 ppm. The average abundance of Pb in the Earth's crust is estimated at about 15 ppm. In the terrestrial environment, two kinds of Pb are known: primary and secondary. Primary Pb is of geogenic origin and was incorporated into minerals at the time of their formation, and secondary Pb is of a radiogenic origin from the decay of U and Th. The ratio of Pb of various origins is used for dating the host materials. Other anthropogenic sources including old house paints, tetraethyl lead in gasoline, water coming from leaded pipes, melting and smelting industries, sewage and sludge, contaminated water are responsible for depositing lead on soil.

In 2004, an estimate of 3.15 million tonnes of lead were extracted from earth's crust by

human and brought into circulation by society. The only comprehensive assessment of global anthropogenic lead release to soil and waste dates back to 1983 which estimated that 6,00,000 to 16,60,000 tonnes of lead directed to waste deposits or released to soil. Around 2,00,000 to 2,60,000 tonnes of lead is again deposited from atmosphere to land. At least 10 % of the consumption is accumulated in landfills.

### **Forms lead in soil**

The form of Pb emitted by automobiles is rapidly gets transformed to  $PbSO_4$  in the atmosphere.  $PbSO_4$  is quickly converted by soil chemical processes to other, non-crystalline, species of Pb. In calcareous soils,  $PbSO_4$  and  $PbCO_3$  forms are generally present, but it contributes for <5% of the soil Pb.  $Pb^{4+}$  cannot persist in soils because it is reduced to  $Pb^{2+}$ . Also,  $PbSO_4$  cannot persist because it is readily oxidized. Lead tends to accumulate in the surface ground layer and its concentration decreases with soil depth. Lead concentrations decrease rapidly in soil with distance from streets and highways. Soils characterized by high amount of organic matter, swelling clay mineral and calcareous subsoil are suitable medium to immobilize a significant lead pollution. Lead is commonly reported to be the least mobile amongst the other heavy metals (Kabata-Pendias, 1993). The largest part of lead is bound to the residual phases (42%), and 19% and 27% of lead to the organic matter and Fe-Mn oxides, respectively. The role of exchangeable and specifically adsorbed lead is the less significant (12%). In the horizon with high clay mineral content (B horizon) the role of residual phases increases (56%), while the amount of lead bound to Fe-Mn oxides decreases (22%), and its amount bound to organic matter is the same (20%) as compared to the A1 horizon. The role of exchangeable and specifically adsorbed lead in this horizon is negligible (2%). In the carbonate containing

C horizon the amount of lead bound to residual phases is the most significant (63%). The role of organic matter slightly decreases (16%), while the amount of lead bound to Fe–Mn oxides is the same (21%) as compared to B horizon. There was no measurable lead in the exchangeable and specifically fraction in the C horizon

According to the experiment carried out by Johnson *et al.*, (1998), it was seen that organic Oa horizon contained maximum concentration of labile Pb. Among the mineral horizon, Bs1 horizon contained maximum concentration of Pb. Overall with increasing depth, concentration of Pb was found to be in more tightly bound form. Organically bound form of Pb is more in the upper Oa horizon whereas amorphous oxide bound was found in maximum concentration in the lower C horizon. Inorganically bound form of Pb was more in the lower C horizon as compared to other horizon. Exchangeable+ soluble form of Pb which is the most easily available form of Pb was present in upper Oa horizon. The concentration of heavy metals in the solution phase is of major importance for all ecological considerations because plants take up the available metals from the soil solution, and the transport of metals within the soil or even to the groundwater also depends on the metal concentration of the solution phase. However, the processes which determine the concentration of heavy metals in the soil solution are not yet fully understood. Changes in soil water content, departures from equilibrium or steady-state to non-equilibrium conditions, and changes in the activity of microorganisms which influence redox conditions, contents of soluble chelating agents, and the composition of soil atmosphere require simultaneous consideration. These processes moderate the reactions of heavy metals such as precipitation- dissolution, adsorption-desorption, and complex and ion-pair

formation in relation to the pH and thus influence the distribution of the various metal species in the solid phases of the soil and in the soil solution.

### **Factors affecting mobility of Pb in soil**

The cation exchange capacity, pH, organic matter, clay and CaCO<sub>3</sub> content can be considered as the most important factors responsible for the adsorption capacity of soils for Pb (Adhikari and Singh, 2003). Various factors affecting mobility of Pb in soil are enlisted below

- pH
- Soil organic matter
- Soil granulometry
- Phosphorus addition
- Presence of CaCO<sub>3</sub>

### **Lead in ocean**

Recent work on lead suggests that the ocean may provide a central role for lead transport and distribution along the Eurasian Basin boundaries of the Arctic Ocean (AMAP, 2004). The residence time of lead in surface water, which is relatively short (<5 years), is still long enough to permit transfer of contaminant lead from the North Atlantic and Nordic Seas into the Arctic (Macdonald *et al.*, 2005) (Table 1).

### **Lead determination in soil**

After collection of soil sample, it is disaggregated, sieved and dried. Then Pb is extracted using various extractants. After extraction, instrumental analysis is done. Neutral salt extraction with CaCl<sub>2</sub>, NH<sub>4</sub>Cl (Qian *et al.*, 1995) (Krishnamurti *et al.*, 2000) and NaNO<sub>3</sub> (Gupta and Aten, 1993) provide the most useful indication of metal phytoavailability and is more effective for estimating plant availability. Extractable Pb in

soil generally provides better indication of Pb availability to plants (Risser and Baker, 1990; Krishnamurti *et al.*, 1995).

### **Fate of lead and its transport in agriculture**

The fate and toxicity of trace metals in soils is dictated by the chemical form in which they are present within soils. These general forms include water soluble metals (i.e., free ions, inorganic or organic complexes), exchangeable metals, metals precipitated as inorganic compounds, metals complexed with humic materials, metals bound to hydrous oxides and layer silicate minerals, metals precipitated as insoluble sulfides, and metals bound within the structure of primary minerals (Gambrell, 1994). Lead may enter into the food chain either by deposition on surface of edible part of plant or it may get deposited on soil surface and finally enters to the plant part by uptake of plant root. Automobile exhausts, old house paint, bullets, batteries, e-waste etc are among the various sources of Pb which gets deposited either on plant or on soil surfaces. Lead contamination in paddy soils resulted in soil fertility deterioration and rice yield and quality decline (Majer *et al.*, 2002). Paddy is also staple food of most of the world's population.

### **Lead uptake by plant**

Lead is available to plants from soil and aerosol sources. Lead uptake studies in plants have demonstrated that roots have ability to take up significant quantities of Pb while simultaneously greatly restricting its above ground translocation to plant (Lane and Martin., 1977). Lead moves predominantly into the root apoplast and thereby in a radial manner across the cortex and accumulates near the endodermis. The endodermis acts as partial barrier to the movement of root and shoot. This may in part account for the reports of higher accumulation of Pb in roots as

compared to shoots (Sharma and Dubey, 2005). It appears that casparian strips of endodermis are the major limiting factor restricting Pb transport across endodermis into the central cylindrical tissue. This provides evidence that Pb moves into symplast. In general, the apparent concentration of Pb in aerial parts of the plant decreases as the distance from plant increases. This occurs due to greater localization of Pb in the cell walls of root than any other plant part. It is seen that accumulation of Pb in different plant parts can be as follows: Root > Shoot > Grain.

In this experiment it was seen that accumulation rate decreased with increasing the concentration of Pb in soil. Thus vegetation showed high relative uptake in area of low soil concentration and low relative uptake in areas of high concentration. It also showed that there is no direct correlation with the amount of Pb present in the soil and the amount taken up by plant (Table 2).

### **Lead in food**

Foods such as fruits, vegetables meat, seafood soft drink and wine may contain significant amount of lead. Cigarette smoke also contains small amounts of lead. As per literature review it is found that has no essential function in the human body, it can merely do the harm after uptake from, air, or water. Lead can cause several unwanted effects such as a rise in blood pressure, kidney damage, Brain damage, Decline fertility of men through sperm damage, diminishing learning ability of children, Behavioral disruption of children, etc. (Tiwari *et al.*, 2013). In older food basket surveys, the influence of lead-soldered tin cans used for storage of food was noticeable. Glazes on ceramics, earthenware, bone china, and porcelain often contain lead and are a potential source of exposure. Vitamin C, Thiamine, taurine (a vitamin B<sub>6</sub>/cysteine derivative), folate, vitamin B<sub>12</sub>, garlic and the

amino acids methionine and glycine may offer significant advantages to lead exposed individuals with few risks. Calcium, iron, zinc, and selenium along with vitamins B<sub>6</sub>, D and E offer large advantages along with significant offsetting risks at high doses. Good intakes of phosphorus, magnesium, copper and glutamic acid (glutamate) offer possible smaller advantages with little risk. It must be emphasized that a combination of these nutrients is needed to offset lead's diverse impacts, though if one were to nominate a single nutrient it would probably be vitamin C since, in spite of some inconsistent results, it has strong, widespread impacts combined with minimal risks for most individuals (the main exception would be individuals with high iron levels, since it increases iron absorption).

### **Lead in human**

Lead poisoning is also called plumbism, colica pictonum or saturnism. Lead is toxic to humans and affects virtually every system in the body. In 1995 the WHO named skin and muscle as the only two systems left unharmed by Pb exposure. Pb mainly enters human body through the digestive tract and respiratory tract, and then goes into the blood circulation in the form of soluble salts, protein complexes or ions, etc. 95% of the insoluble phosphate lead accumulates in bones. Pb is strongly pro-organizational. It affects and damages many of the body organs and systems, such as kidney, liver, reproductive system, nervous system, urinary system, immune system and the basic physiological processes of cells and gene expression (Su *et al.*, 2014). Young children are particularly vulnerable to the toxic effects of lead and can suffer profound and permanent adverse health effects, particularly affecting the development of the brain and nervous system. Lead also causes long-term harm in adults, including increased risk of high blood pressure and kidney damage. Exposure of pregnant women to high levels of lead can

cause miscarriage, stillbirth, premature birth and low birth weight, as well as minor malformations. Research has shown that some Pb minerals are poorly absorbed by humans (PbS, chloropyromorphite, while some others are readily absorbed (PbCO<sub>3</sub>). Perhaps the most important factor in Pb absorption is the presence of food in the stomach/ intestine when the Pb source is present.

Several research teams evaluated Pb isotope absorption by human volunteers fed Pb with meals or specific foods, or on fasting. On fasting, soluble Pb is absorbed at 50–80%, usually assumed by EPA to be 50% for Pb acetate. But when the Pb is ingested with a meal, 1 hr before a meal, or up to 4 h after a meal, absorption falls to the range of 2–5% of dose (Heard and Chamberlain, 1982; Heard *et al.*, 1983; James *et al.*, 1985). Particular food ingredients ingested with Pb can greatly reduce Pb absorption, especially Ca (Blake and Mann, 1983); Ca is believed to compete with Pb absorption by a Ca-transport protein in the small intestine, but also to form coprecipitates with phosphate and Pb. Pb incorporated in kidney or spinach had quite low bioavailability to adults (Heard *et al.*, 1983).

As noted earlier, a meta-analysis of the contribution of soil versus house dust to blood Pb of urban children has shown that house dust was considerably more important (Lanphear *et al.*, 1998). Several groups noted that Pb in mining site soils caused less increase in blood Pb than did Pb in smelter site soils (Steele *et al.*, 1990). Davis *et al.*, (1993) found galena and anglesite (PbSO<sub>4</sub>) with rindings in mine waste soils at Butte, MT. The dissolution of PbSO<sub>4</sub> was found to be inherently slow compared to the time needed for clearance of the stomach and intestine of children, helping to explain why this form of Pb caused less uptake into blood (Table 3).

**Table.1** Common values for Pb concentration (ppm) in various environmental media

Material	Concentration	Range
<b>Igneous Rock</b>	15	2-30
<b>Sandstone</b>	7	1-31
<b>Limestone</b>	9	-
<b>Shale</b>	20	16-50
<b>Coal</b>	16	Upto 60
<b>Fly Ash</b>	170	21-220
<b>Soils (agricultural)</b>	-	2-300
<b>Fresh water (µg/L)</b>	3	0.06-120
<b>Sea water (µg/L)</b>	0.03	0.03-13
<b>Sewage, sludge</b>	1832	136-7627

**Table.2** Lead content in root and shoot of rice seedling of 10 and 20 days in presence of different concentration of Pb(NO<sub>3</sub>)<sub>2</sub> in sand culture

Age of seedling (days)	Concentration of Pb (µM)	Pb content(µmol Pb/g DW) in root	Pb content (µmol Pb/g DW) in shoot
<b>10</b>	0	0	0
	500	0.16	0.06
	1000	0.72	0.22
<b>20</b>	0	0	0
	500	0.80	0.38
	1000	1.22	0.72

(Verma and Dubey, 2003, Chopin and Alloway, 2007)

**Table.3** Blood lead levels associated with specific biological responses in children

Blood lead level (µg/dL)	Effect
<b>8</b>	Subtle neurological impairment
<b>10</b>	ALAD inhibition
<b>15-20</b>	Erythrocyte protoporphyrin elevation
<b>&lt;25</b>	Verbal IQ, mental development, physical size, and age at physical milestones such as first step, hearing thresholds, and postural sway
<b>40</b>	Increased urinary ALA excretion, anemia coporphyrin elevation
<b>50-60</b>	Cognitive (central nervous system) deficits
<b>50-60</b>	Peripheral neuropathies
<b>80-100 (acute level)</b>	Encephalopathic symptoms

(Hettiarachchi *et al.*, 2004)

## **Reclamation of lead in soil**

### **Physical remediation**

Replacement of contaminated soil, soil removal and soil isolation

### **Chemical remediation**

Application of  $\text{CaCO}_3$   
Application of phosphate

### **Bioremediation**

Phytoremediation

### **Recycling of lead batteries**

In India, which state that it is now the responsibility of each battery manufacturer, importer, assembler and recycler to ensure that the number of used lead-acid batteries collected is equal to the number of new lead-acid batteries sold.

Lead batteries, accounting for 78% of reported global consumption in 2003.

By applying best available techniques for recycling, < 0.1 % of the lead is lost by the recycling activities.

### **Controlling lead release from the sources**

Reducing consumption of raw materials and products that include lead as an impurity.

Substitution (or elimination) of products, processes and practices containing or using lead with lead-free alternatives.

Controlling lead releases through low-emission process technologies and cleaning of off-gases and wastewater.

Management of lead-containing waste.

## **Phytoremediation**

It describes the treatment of environmental problems (bioremediation) through the use of plants that mitigate the environmental problem without the need to excavate the contaminant material and dispose of it elsewhere. Phytoremediation has become an effective and affordable technological solution used to extract or remove inactive metals and metal pollutants from contaminated soil. Phytoremediation includes phytostabilisation, phytoextraction, phytovolatilisation, rhizofiltration etc.

Phytoextraction - To hyperaccumulate heavy metals in plant biomass.

Phytostabilization - Immobilisation of heavy metals in the soil or ground water through absorption or accumulation by roots.

Rhizofiltration - Adsorption/absorption of contaminant into plant roots present in solution surrounding root.

Pb is the least mobile heavy metal. Because Pb is very strongly bound in almost all types of soil, its phytoextraction is rather limited. When Pb is taken up by plants, its translocation to above-ground parts is very poor. The major proportion of Pb is concentrated in root tissues.

### **Phytoextraction**

Phytoextraction is a soil remediation technique involving plants that concentrate heavy metals in their shoots, which may be removed from the area by harvest. Lead phytoextraction, using plants to extract Pb from contaminated soils, is an emerging technology. Calculations of soil Pb mass balance suggest that this technology will be economically feasible only if systems can be developed to employ high biomass plants that

can accumulate greater than 1% Pb in their shoots (Huang *et al.*, 1997).

### **Chemically enhanced phytoextraction**

It has been demonstrated that Pb is rapidly accumulated in the roots if Pb is bioavailable in the plant growth media; however, only a small proportion of absorbed Pb is translocated to shoots. For most Pb-contaminated soils that we have studied, Pb in soil solution is usually less than 0.1% of total soil Pb. Thus, the Pb availability to plants is limited. Furthermore, for plants grown in these soils, Pb translocation from roots to shoots was less than 30% for the best Pb translocating plants (Huang *et al.*, 1996, Jones *et al.*, 1973, Kumar *et al.*, 1995). Two major limitations to the Pb phytoextraction are the low Pb bioavailability in soil and the poor Pb translocation from roots to shoots. A key to Pb phytoextraction is to increase and maintain Pb concentrations in the soil solution. Chelates have been used in soils and nutrient solutions to increase the solubility of metal cations in plant growth media and are reported to have significant effects on metal accumulation in plants (Grath *et al.*, 2002) (Huang *et al.*, 1997)

### **Current approaches to revegetation and reclamation of Pb contamination**

Though application of synthetic chelates have shown promising effect on enhancing the translocation of metal contaminants from soil to above ground plant part; more particularly soil, synthetic chelates also increase the solubility of metal contaminants which can lead to leaching of metal to deep below the ground and thus contaminating ground water. Further reclamation of mined soil where probability of Pb contamination is more, revegetation can be a useful tool for stabilizing the contaminated soil. A range of reclamation techniques is available for

metalliferous substrates but only through the use of vegetation to stabilise mine wastes can complete longterm rehabilitation be achieved. Successful revegetation can be a permanent and visually attractive solution and, at the same time, be relatively inexpensive. A vegetation cover can be effective in providing the necessary surface stability to prevent wind-blow of contaminated particulates, and in reducing water pollution by interception of a substantial proportion of incident precipitation (Tordoff *et al.*, 2000). Vegetation can return a large proportion of percolating water to the atmosphere through transpiration, thus reducing the concentrations of soluble heavy metals entering watercourses.

Lead is circulated in the environment, mainly due to anthropogenic activities. Poisoning in the environment has achieved global concern due to its toxic effect on the living organisms. Soil serves as both source and sink of Pb. It's availability in soil is governed by organic matter, pH, kind of clay, presence of CaCO<sub>3</sub>, etc. Plants derives bio-available Pb and accumulates Pb in root region, it's translocation to above root portion is very low. Phyto-remediation, chemical remediation and re-vegetation with application of suitable amendments and appropriate management practices near areas with high Pb concentration are efficient techniques in remediation of contaminated soils.

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**How to cite this article:**

Neelam Yadav, Ankita Trivedi, S.S. Yadav, D.K. Yadav, V.K. Yadav and Nagesh Yadav. 2018. Soil Pollution with Lead: Geochemistry, Food Safety Issues and Reclamation Options - A Review. *Int.J.Curr.Microbiol.App.Sci*. 7(05): 528-538.  
doi: <https://doi.org/10.20546/ijcmas.2018.705.067>