LEAD: THE HEAVY METAL IN SOIL WATER AND PLANT ENVIRONMENT

S.K. KHATIK, RISIKESH THAKUR AND G.D. SHARMA

Department of Soil Science and Agricultural Chemistry
J.N. Krishi Vishwa Vidyalaya, Jabalpur 482 004, M.P., India

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ABSTRACT

Contamination of soils by heavy metals is of widespread occurrence as a result of human agricultural and industrial activities. Among heavy metals, lead is a potential pollutant that readily accumulates in soils and sediments. The lead (Pb) concentration in soil range from 2 to 200 ppm, plants 0.1 to 10 ppm, water 0.04 to 0.10 ppm in drinking water and in ground water 0.015 to 0.075 ppm and air 0.1 to 5 ppm. The sources of lead are containing fertilizers, sewage and sludge, industrial wastes which contains many ppm of lead. Although lead is not an essential element for plant growth but its get easily absorbed/adsorbed and gets accumulated in different plant parts. Uptake of Pb in plants is regulated by pH, particle size and cation exchange capacity of the soils as well as root exudation and other physico-chemical parameters. Excess Pb causes number of toxicity symptoms in plants eg. stunted growth, chlorosis and blackkening of root system. In human health is causes diseases like Apathy, Insomina, Coma and >30 ppm of lead exposure claim the life of animal by gastro-intestinal pH, stage of lactation or pregnancy. Remediation of soils contaminated with Pb using phytoremediation and rhizofiltration techniques appear to have great potential for cleaning of Pb – contaminated soils.

INTRODUCTION

Lead is a metallic element found everywhere in the environment (Soil, water and plant) as a pollutant because of huge industrialization. Apart from the
natural weathering processes, Pb contamination of the environment has resulted from mining and smelting activities, Pb contaminated paints, gasoline and explosives as well as from the disposal of municipal sewage sludge enriched in Pb (Chaney and Ryan, 1994). Smelting and gasoline combustion primarily cause air pollution with the lead particles reaching the soil through dry and wet deposition (Balt and Bruggenert, 1978; Milberg et al. 1980). Pb input in the environment continues to be one of the most serious global environmental and human hazards. As many of the Pb pollutants are indispensable for modern human life, soil contamination with Pb is not likely to decrease in the near future (Yang et al. 2000). Humans started its use in some forms since prehistoric time. While lead has a wide use in daily human life but, it creates ill effects on human health. High levels (>30 ppm) of lead exposure can be claim the life of animals.

Significant increases in the Pb content of cultivated soils has been observed near industrial areas. Pb tends to accumulate in the surface layer and its concentration decreases with soil depth (de Abreu et al. 1998). Soils contaminated with Pb cause sharp decreases in crop productivity thereby posing a serious problem for agriculture (Johnson and Eaton, 1980).

It occurs naturally in all soils and waters. Plant absorb soil lead through their roots, hence all plants contain small amount of lead (0.1-10 ppm). The relationship between soil and plant lead varies to much. It is impossible to predict accurately how much lead a plant will uptake, when grown on a soil containing a high concentration of lead.

**Position in the periodic table**

Lead (atomic number 82, atomic mass 207.21) has on outer electronic configuration of 6s6p2 and belongs to carbon family or IV A group of the periodic table. In soil the ionic form of lead which is absorbed by plants are Pb2+ and Pb4+ plants easily absorbed Pb2+ ion as compared to Pb4+ because less energy is required for absorption of Pb2+ as compared to Pb4+.

**Source of lead**

Pb is the major pollutant in the environment. Besides natural weathering processes the main sources of Pb pollution are exhaust fumes of automobiles, chimneys of factories using Pb, effluents from the storage battery, industry, mining and smelting of Pb ores, metal planting and finishing operations, fertilizers, pesticides are additives in pigments and gasoline (Eick et al. 1999). Figure 1 shows various sources, which contribute to Pb pollution in the environment. Sewage sludge containing large quantities of lead and other metals is regularly discharged on to field and garden soils due to increasing trends in urbanization (Paivoke, 2002). Mine water also transports a large amount of fine - grained sediments contaminated with Pb (Laxen and Harrison, 1977).

**Anthropogenic sources**

Lead pollution of the environment occurs through anthropogenic activities such as -

- **Lead based paints**
- **Gasoline**
- **Insecticides**
- **Fertilizers**
- **Industries wastes**

(Preyea, Frank 1999)

**Lead - based paints**

It (containing up to 50% lead) was widely used up to the Mid 1940s because it was more durable than the non lead-based paint of the day. Estimates indicate that 90% of homes built before 1940 contain lead paint. Use of lead -based paints declined during 1950s and was banned for home use in 1978. Industrial uses of high - lead paint are still allowed. Flaking, chalking or other disturbance of lead - based paints on exterior surfaces of buildings and other structures create lead - rich that fall on to near by soil and increase soil lead content.

**Gasoline**

Tetraethyl lead [Pb(CH3)4 ] and tetramethyl lead [Pb(C2 H5 )4 ] are added to gasoline to increase the octane rating. It is an inexpensive and effective octane -booster and antiknock compound. About 75% of gasoline lead was emitted exhaust pipes. In urban areas automobile exhaust contributes substantially to the atmospheric pollution Pb compound are major pollutants emitted by automobiles. Plants growing near highways are usually exposed to more lead than other localities.

**Insecticides**

Lead arsenate (Pb AsO4 ) was a popular insecticide during the first half of the 20th century because of its low toxicity to plants and great effectiveness for controlling insect pests. The most common use for control of codling moth in commercial apple orchards. Smaller but still substantial amounts were used on deciduous tree fruits other than apple. Repeated application of lead arsenate over time caused lead and arsenic to accumulate in soil. Lead arsenate was banned on most food crops in the U.S. in 1988 and on all food crops in 1991.

**Industries wastes**

Industrial uses includes manufacture of electrodes, batteries, glass wares, newsprint inks etc. Pb - affected soils contain Pb in the range of 400-800 mg kg−1 soil whereas in industrialized areas the level may reach upto 1000 mg Pb kg−1 soil (Angelon and Bini, 1992).

**Fertilizers**

In a long term field experiment (41 years) involving regular application of mineral fertilizers to crops of sunflower or barley followed by oat - winter rye in rotation, revealed that the fertilizers increased the level of mobile forms of Pb in the soil and also its uptake by the crops (Stefanov et al. 1995). Some selecte, dertilizers and soil amendments given in Table 1.

**Inorganic minerals of lead**

Lead is on element forming approximately 0.002 % of the Earth’s crust. The
most important minerals are:
Galena : PbS (major source of lead)
Cerusite : PbCO₃
Crocoite : PbCrO₄
Pyromorphite : Pb₅(PO₄)₃Cl

Uses of lead
On an estimate of the year 1987, out of total produced lead 60% lead was used for making batteries, lead pipes, cables, newsprint ink, anti-clock agents in automobiles fuel, pesticides, lead based paints etc. On an average 25-40% of the lead reused throughout the world is obtained by recycling from the lead wastes.

Environmental behavior
Lead is one of the heavy major heavy metal, which are potentially toxic to both plants and animals. Lead occurs naturally in the environment. Due to huge industrialization which increased the concentration of the lead in Water, Air, Soil, Half life, Food chain.

Water
Surface water forms an accumulation sink for lead compounds. Insoluble lead compounds sink and are adsorbed in the sediment or accumulate on suspended matter (in particular the clay fraction). Aquatic plants likewise accumulate lead. The biochemical oxidation of organic substances is inhibited at lead concentrations above 0.1 mg/L, fauna is depleted by concentrations above 0.2 mg/L and 0.3 mg/L is the threshold for fish toxicity (trout and white fish) (DVGW, 1985).

Table 1
Lead (Pb) concentration in some industrial area of M.P. (Pithampur & Dewas)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters</th>
<th>Pithampur industrial area, district Dhar M.P.</th>
<th>Dewas industrial area, dist Deewan. M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Factory sludge</td>
<td>2.90-16.39</td>
<td>0.0-33.55</td>
</tr>
<tr>
<td>2.</td>
<td>Nallah sludge</td>
<td>3.12-22.0</td>
<td>4.39-4.73</td>
</tr>
<tr>
<td>3.</td>
<td>Soil</td>
<td>0.72-20.52</td>
<td>0.96-3.32</td>
</tr>
<tr>
<td>4.</td>
<td>Water</td>
<td>1.32-1.91</td>
<td>1.00-1.27</td>
</tr>
<tr>
<td>5.</td>
<td>Plant</td>
<td>3.7-53.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2
Lead (Pb) concentration in Indore city of M.P.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters</th>
<th>Indore city</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nallah sludge</td>
<td>3.10-12.65</td>
</tr>
<tr>
<td>2.</td>
<td>Soil (0-15 cm)</td>
<td>0.12-14.90</td>
</tr>
<tr>
<td>3.</td>
<td>Soil (15-30 cm)</td>
<td>0.00-11.87</td>
</tr>
<tr>
<td>4.</td>
<td>Sewer water</td>
<td>1.46-1.53</td>
</tr>
<tr>
<td>5.</td>
<td>Plant</td>
<td>9.60-1.27</td>
</tr>
</tbody>
</table>


Table 3
Lead concentration in selected fertilizers and soil amendments

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Fertilizers / Soil amendments</th>
<th>Pb ( ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rock phosphate</td>
<td>4.6-29.2</td>
</tr>
<tr>
<td>2.</td>
<td>Triple super phosphate</td>
<td>11.1-13.2</td>
</tr>
<tr>
<td>3.</td>
<td>Ammonium nitrate</td>
<td>&lt;0.40</td>
</tr>
<tr>
<td>4.</td>
<td>Dairy manure</td>
<td>7.5</td>
</tr>
<tr>
<td>5.</td>
<td>Poultry manure</td>
<td>6.0-8.4</td>
</tr>
<tr>
<td>6.</td>
<td>Swine manure</td>
<td>7.0-11.0</td>
</tr>
<tr>
<td>7.</td>
<td>Municipal waste</td>
<td>28.0</td>
</tr>
<tr>
<td>8.</td>
<td>Sewage sludge</td>
<td>65.0</td>
</tr>
</tbody>
</table>


Table 4
Important lead compounds which is used

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compounds</th>
<th>Chemical formula</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Oxides</td>
<td>PbO</td>
<td>Glass making</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb₃O₄</td>
<td>Rust inhibitor for iron</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PbO₂</td>
<td>Oxidising agent</td>
</tr>
<tr>
<td>2.</td>
<td>Streater</td>
<td>Pb(C₁₇H₃₅COO)₂</td>
<td>Stabilizer in PVC compounds</td>
</tr>
<tr>
<td>3.</td>
<td>Tetra acetate</td>
<td>Pb(CH₃COO)₄</td>
<td>Oxidising agent</td>
</tr>
<tr>
<td>4.</td>
<td>Tetra alkyls</td>
<td>Pb(CH₃)₄</td>
<td>Anti knock agent in fuel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb(C₂H₅)₄</td>
<td>(lead compounds- organic)</td>
</tr>
<tr>
<td>5.</td>
<td>Oleastes</td>
<td>Drying accelerator for oil based paints</td>
<td></td>
</tr>
</tbody>
</table>

Source: WHO, 1987

Table 5
Lead production for most important lead producing and consuming Countries, 1987.

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine production (contained Pb), 10⁶t</th>
<th>Refined production (primary and secondary), 10³t</th>
<th>Refines consumption, 10³t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soviet Union</td>
<td>510.0</td>
<td>780.0</td>
<td>775.0</td>
</tr>
<tr>
<td>Other Eastern Block</td>
<td>503.7</td>
<td>623.9</td>
<td>665.5</td>
</tr>
<tr>
<td>Australia</td>
<td>486.2</td>
<td>220.7</td>
<td>65.0</td>
</tr>
<tr>
<td>Canada</td>
<td>413.4</td>
<td>225.8</td>
<td>102.9</td>
</tr>
<tr>
<td>United States</td>
<td>318.3</td>
<td>1027.9</td>
<td>1202.8</td>
</tr>
<tr>
<td>Peru</td>
<td>192.0</td>
<td>70.8</td>
<td>21.9</td>
</tr>
<tr>
<td>Mexico</td>
<td>177.1</td>
<td>185.1</td>
<td>99.6</td>
</tr>
<tr>
<td>Total World</td>
<td>3389.3</td>
<td>5631.4</td>
<td>5622.5</td>
</tr>
</tbody>
</table>


Groundwater is adversely affected by soluble lead compounds (e.g. lead chloride, nitrate). Nevertheless, it has been established that drinking water that passes through lead pipes may contain high lead concentrations (depending on the groundwater). Lead is not chemically affected by deoxygenated water. In lead pipes, carbonated water forms lead carbonate deposits on the inner pipe surface.
Lead is found in all foodstuffs and fodders because it is ubiquitous. Vegetable foodstuffs generally contain more lead than animal products. This is the result of their special exposure dust precipitations containing lead cling to the surface of plants and are thus consumed. In higher life forms, the maximum concentrations are found in internal organs such as the liver and kidneys. The increase in concentration is as follows in aquatic systems: water < fish < sediment (DVGW, 1985).

Most humans absorb lead through their food (roughly 440-550 µg per day) and drinking water (some 20 µg per day) (DFG, 1982). At places where lead is produced or processed, atmospheric pollution is an additional problem. Approximately 30-50% of the lead inhaled remains in the lungs (WHO, 1987), the rest is absorbed by the body and usually deposited in the bones.

Uptake of lead
Soil microorganisms may affect heavy metal availability by the process of biosorption, bioaccumulation and solubilization. It was shown by Marshner and Coworkers (1996) that ectomycorrhiza could influence uptake transport and toxicity to Pb in Norway spruce plants.

Pb is available to plants from soil and aerosol sources, Pb uptake studies in plants have demonstrated that roots have on ability to take up significant quantities of Pb whilst simultaneously great restriction restricting its translocation to above ground parts (Lane and Marthin, 1977). This notion was overturned by Miller and Koeppe (1971) who demonstrated that Zea mays L plants could translocate and accumulate significant quantities of Pb in the leaves in a concentration dependent manner. Pb accumulate in the surface layers of soils and therefore it is difficult to reliably measure the portion of soil Pb.
directly available to plants. Its availability depends mainly on soil conditions. Pb binds to organic material in the soil. Soil particle size and cation exchange capacity as well as plant factors such as root surface area, root exudates, mycorrhization and rate of transpiration affect the availability and uptake of Pb (Davies, 1995).

The absorption of Pb (as Pb) in soil follows the langmuir relation and increases with increasing pH between 3.0 to 8.5 (Lee et al. 1998). However, Blaylock and Coworkers (1997) reported that in soil with a pH between 5.5 and 7.5 Pb solubility is controlled by phosphate (PO₄³⁻) or carbonate (CO₃²⁻) precipitates and very little Pb is available to plants. Pb present in the soil is nearly always tightly bound to organic colloidal material in a precipitated form, all of which serve to reduce the uptake of Pb by plant roots.

**Lead toxicity in plants**

The visual non specific symptoms of Pb toxicity are rapid inhibition of root growth, stunted growth of the plant and chlorosis (Burton et al. 1984). Pb phytotoxicity leads to inhibition of enzyme activities, disturbed mineral nutrition and water imbalance. These disorders upset normal physiological activities of the plant. At high concentration Pb eventually leads Pb to cell death (Ernst, 1998; Seregin and Ivanov, 2001).

Pb toxicity inhibits germination of seeds and retards growth of seedlings. Pb decreases germination percent, germination index, root/shoot length, tolerance index and dryness of roots and shoots (Mishra and Choudhri, 1998). High concentrations of Pb (1 mM) caused 14 to 30% decreased germination in rice seeds and reduced the growth of seedlings by more than 13 to 45% (Verma and Dubey, 2003).

**Remediation of lead contaminated soils**

The remediation of Pb contaminated soils represents a significant challenge to many industries and government agencies. To date Pb-contaminated sites have been remediated through a relatively narrow range, of engineering based technologies (Salt et al. 1995). Heavily contaminated soils have primarily been excavated, stabilized with cement and then placed in secured landfills. This process is expensive and requires additional site restoration. Some remediation of lead contaminated soils are given below:

**Phytoremediation**

During recent years the concept of using plants to remediate heavy metal contaminated sites (called phytoremediation) has received greater attention (Vassil et al. 1998, Jarvis and Leung, 2002). Phytoremediation may involve either phytostabilization or phytoextraction. Phytoextraction involves the use of plants to remove the contaminant from contaminated soils. The concept of using plants to accumulate metal for subsequent processing is both technically and economically attractive.

For practical reasons, the shoot Pb concentration is the most important physiological parameter for evaluating Pb- phytoextraction potential of plants (Huang and Cunningham, 1996). It has been shown that Pb accumulation in roots is significantly higher than in shoots, possibly because of the low Pb translocation from roots to shoots (Cunningham et al. 1995, Verma and Dubey, 2003). Plant species with higher shoot/root Pb concentrations are more efficient in Pb translocation. *Thlaspi rotundifoliun* plants have been reported to accumulate 130-8200 mg Pb kg⁻¹ shoot dry weight (Reeves and Brooks, 1983).

Because of its slow growth rate and small biomass however, this species is not suited for phytoreextraction of Pb from contaminated soils. Some cultivars of *Brassica juncea* containing 760 µM Pb (Kumar et al. 1995). It was reported by Huang and Cunningham (1996) that the Pb concentration in the shoot of corn was significantly higher than that of the best Pb - accumulating *Brassica juncea* cultivars when the plants were grown on a Pb contaminated soil.

**Rhizofiltration**

Another promising clean-up technology appears to be rhizofiltration, which involves use of plant roots to remove contaminants such as heavy metals from contaminated water (Dushenkov et al. 1995). A high level of Pb deposition is seen in corn root tips as revealed by histochemical and electron; microscopy studies. When the seedlings are incubated in a medium containing 0.66 mM Pb for 19 days (Tung and Temple, 1996), a strong deposition of Pb occurs on the branches in the seedlings (Tung and Temple, 1996). Malkowski and coworkers (2002) also showed that corn plants treated with 10⁻³ M Pb accumulated 138, 430 mg of Pb per kg of dry weight in root tips compared to 26,833 mg in the rootbasal part. Since the first 8 mm of the apical root accounts for approximately 50%of the Pb accumulated by the entire root system (Malkowski et al. 2002), it appears that the plant with a more, branched root system will take up more Pb and other heavy metals compared to plants with longer andJess branched root systems.

**Chelation**

Results from chelation experiments indicate that Pb concentration in the shoot can be increased dramatically when the soil Pb concentration is increased by adding, a synthetic chelate to the contaminated soil, the synthetic chelate EDTA forms a soluble complex with many metals, including Pb (Kroschwitz, 1995) and can solubilize Pb from soil particles (Vassil et al. 1998). Application of EDTA to Pb-contaminated soils has been shown to induce the uptake of Pb by plants causing Pb to accumulate more than 1% (w/w) of the shoot dry biomass (Huang and Cunningham, 1996, Huang et al. 1997). Large Pb particles cannot easily cross the casparian strip due to their size and charge characteristics but once they form a complex with chelators such as EDTA, their solubility increases, the particle size decreases and they become partially ‘invisible’ to those processes that, would normally prevent their unrestricted movement such as precipitation with phosphates and carbonates, or binding to the cell-wall through mechanisms such as cation exchange (Jarvis and Leung, 2002). It is important to point out that the addition of chelates to the soil has to be done in a carefully controlled manner so as not to mobilize Pb into ground water or otherwise promote its off-site migration (Huang and Cunningham, 1996).
Fertilizers
Use of phosphate containing soil amendments such as triple super phosphate sometimes can reduce plant uptake of soil lead, by causing leaf phosphate minerals of very low solubility to form, e.g. Triple super phosphate.

Liming
Plant lead concentrations typically decrease with increasing soil pH. Amend acidic soils contaminated with lead with agricultural lime i.e. calcium carbonate (CaCO₃) or dolomite (MgCO₃·CaCO₃) to pH 7 or greater. Maintain soils containing lead at pH 7 to minimize plant uptake of lead element. It is difficult to reduce the pH of soils that contain free lime (also know as caliche), which have a pH of 8 or greater. Using an acidic fertilizer formulation such as one containing nitrogen as ammonium or urea will help reduce soil pH over time.

Organic matter
Maintain a soil organic matter level near 8%. Added organic matter to soil, in soils with high lead levels, adding one third by volume organic matter will significantly reduce lead availability. Organic compounds find lead and make it less available to the plant. When adding organic matter the pH should also be maintained above 6.5. Good source of organic matter include composted leaves, natural (nm acid) peat and well rotled manure. Avoid leaf mulch obtained along high ways or city streets as it may contain higher than normal lead levels. Normally organic matter will reduce plant uptake of soil lead.

Soil scraping
Replacement of uppermost contaminated soil (depth : 0-15 cm) from cultivated field. The maximum amount of lead was absorbed/adsorbed by soil in clay - humus complexes. By scraping of contaminated soil highest quality of Pb can be removed from the soil and become suitable from growing the crops. One to two times further cleaning by phytoremediation or rhizofiltration leads to removes the traces amount of Pb from soil and then crop produce become edible for animal consumption.

CONCLUSION
Pb has gained considerable attention as a potent heavy metal pollutant due to the growing anthropogenic pressure on the environment, Pb contaminated soils show a sharp decline in crop productivity. Pb is taken up by plants mainly through the root system and party, in minor amounts through the leaves. Inside the plants Pb accumulates primarily in the root but a part of it is translocated to the aerial portions. Soil pH, soil particle size, cation exchange capacity as well as plant factors such as root surface area, root exudation and mycorrhizal transpiration rate affect the availability and uptake of lead. It is potentially toxic if present at high concentrations. Soil factors such as high cation exchange capacity, Alkaline pH, High organic matter and P-content in soil decreases Pb uptake by plants.

Visual non specific symptoms of Pb toxicity are stunted growth, chlorosis and blackening of the root system. Emerging clean up technologies for remediation of Pb such as phytoremediation and rhizofiltration have the potential to provide environmentally sound and economically viable remedies for the cleaning of Pb-contaminated soils. Liming reduces the availability of lead due to decrease the solubility and its uptake by plants. Phosphatic fertilizers and organic matter also helpful to reduced the Pb concentration in soil.

REFERENCES