



Review

A critical review on speciation, mobilization and toxicity of lead in soil-microbe-plant system and bioremediation strategies



Anamika Kushwaha, Nidhi Hans, Sanjay Kumar, Radha Rani*

Department of Biotechnology, Motilal Nehru National Institute of Technology, Teliyarganj, Allahabad, Uttar Pradesh, India

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ABSTRACT

Lead accumulation in soils is of serious concern in agricultural production due to the harmful effects on soil microflora, crop growth and food safety. In soil, speciation of lead greatly affects its bioavailability and thus its toxicity on plants and microbes. Many plants and bacteria have evolved to develop detoxification mechanisms to counter the toxic effect of lead. Factors influencing the lead speciation include soil pH, organic matter, presence of various amendments, clay minerals and presence of organic colloids and iron oxides. Unlike, other metals little is known about the speciation and mobility of lead in soil. This review focuses on the speciation of lead in soil, its mobility, toxicity, uptake and detoxification mechanisms in plants and bacteria and bioremediation strategies for remediation of lead contaminated repositories.

1. Introduction

Heavy metals are a group of elements having density higher than 7 g cm^{-3} . Heavy metals/metalloids include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), selenium (Se), nickel (Ni), silver (Ag), and zinc (Zn). Other less common metallic contaminants include aluminium (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U). Of these, lead is the most toxic contaminant whose extensive use has caused environmental and human problems in many parts of world. Elemental lead is odourless, silver-bluish-white in color, soft, highly malleable, ductile and relatively poor conductor of electricity. It is frequently used in many industrial processes. Common anthropogenic sources of lead contamination in environment include mining, smelting of ores, burning of coal, effluents from storage battery industries, automobile exhausts, metal plating, leather tanning, finishing operations, fertilizers, pesticides and from additives in pigments and gasoline. Though, heavy metals are important both industrially and biologically, due to their non-biodegradable nature, they are steady in environment and pose a serious threat to it and their excessive deposition in the soil can cause serious damage to soil ecosystem.

Soils is a heterogeneous mixture of different organic and organo-mineral substances including, clay minerals, oxides of iron, aluminum, and manganese, humic substances, and other solid components as well as a variety of soluble substances. Speciation and mobility of heavy metals depends on the binding processes for them in soils, which vary with the composition of the soils, the soil reaction, and redox

conditions. Metals may form different species depending upon its binding with various soil compounds, reacting surfaces, or to external or internal binding sites with different bonding energies.

Lead (Pb) is one of the ubiquitously distributed most abundant toxic elements in soil without biological function. It is recognized as a chemical of great concern in the new European REACH regulations (EC 1907/2006; Registration, Evaluation, Authorization, and Restriction of Chemicals). It is largely found in dispersed form in rock formations. Its concentration in igneous and sedimentary rocks are: 2–18 mg/kg in Basaltic igneous, 6–30 mg/kg in Granite igneous, 16–50 mg/kg in Shales and Clays, 7–150 mg/kg in Black shales and $< 1\text{--}30 \text{ mg/kg}$ in sand stones (Cannon et al., 1978). Its increasing level in soil environment has adverse effects on soil microbial diversity and on growth and metabolism of plants. Plants experience oxidative stress upon exposure to lead that leads to cellular damage and disturbance of cellular ionic homeostasis. It impairs plant growth, root elongation, seed germination, seedling development, cell division, transpiration, chlorophyll production, lamellar organization in the chloroplast (Sharma and Dubey, 2005; Gupta et al., 2010; Maestri et al., 2010). Besides that, it can be accumulated in different parts of plants and there by enter in food chain. Lead can affect any organ in the body but most sensitive parts are developing nervous system, hematological and cardiovascular system, reproductive system and kidney. Children are more vulnerable to lead poisoning than adults. Its accumulation over time in human bodies can cause serious illness which include headache, short-term memory loss, mental confusion, sense of unreality, distorted perception, pain in muscles and joints, and gastro-intestinal upsets, food

* Corresponding author.

E-mail addresses: radharani@mnnit.ac.in, raadharani1982@gmail.com (R. Rani).

intolerances, allergies, vision problems, chronic fatigue, fungal infections etc. Therefore, contamination of agricultural soil by lead is significant from environmental and nutritional point of view.

Irrespective of certain regulatory steps executed and practiced to restrict the release of lead pollutants into soil ecosystem, contamination levels are still alarming (Ghosh and Singh, 2005). Chemical, and physical methods for remediation of lead contaminated soil are highly expensive and ineffective and may cause conspicuous destruction of soil structure, fertility and other properties, thus are not suitable for practical applications. Hence, work has been ongoing to develop cost-effective and high-efficiency technologies for the remediation of lead contaminated sites (Chatterjee et al., 2011). Immobilization or stabilization, mobilization by washing soil with metal chelators, and phytoremediation techniques are reported among the best demonstrated available technologies (BDATs) for remediation (Wuana and Okieimen, 2011). In the present review various bioremediation strategies by plants, such as phytostabilization, phytoextraction and rhizofiltration, and by bacteria such as biosorption/complexation and precipitation has been discussed for remediation of lead contaminated repositories.

2. Natural reservoirs of lead

The average abundance of lead in earth's crust is approximately 15 mg/kg which is equivalent to approximately 14 g of lead per ton of rock. The lead contents of the common rock types, range from about 30 mg/kg (granitic rocks, rhyolite and black shale) to about 1 mg/kg (evaporite sediments, basalt and the ultramafic igneous rocks like dunite) (Lovering, 1969). Due to the high silica and potassium content in igneous and metamorphic rocks, lead content is relatively high (Wedepohl, 1956). Researchers have found that 70–95% of the total lead present in rocks is present in K-feldspar plus plagioclase (Tauson and Kravchenko, 1956; Zlobin and Gorshkova, 1961). Some of the minerals of granite rocks, principally those containing radioactive elements (for example, monazite, xenotime, uraninite, thorite, zircon, allanite, titanite) contain greater concentrations of lead. Sedimentary rocks contain comparatively small amount of lead, average lead concentration, 32 mg/kg for carbonaceous shale, 23 mg/kg for siltstone, mudstone, claystone, and noncarbonaceous shale, 17 mg/kg for sandstone, and 11 mg/kg for limestone and dolomite.

Although lead comprises of more than 200 known minerals, most of these are very rare. The common silicate minerals found in igneous rocks are potash feldspar; plagioclase feldspar and muscovite mica; pyroxenes, amphiboles, and biotite mica; and quartz. The common minerals of chemically precipitated sedimentary rocks (calcite, dolomite, gypsum, and halite) normally contain less than 10 mg/kg lead. The lead content of the sedimentary clay minerals is extremely variable but is commonly in the order of 10–20 mg/kg (Lovering, 1969).

3. Anthropogenic sources of lead

Lead occur naturally in the soil environment from pedogenetic processes of weathering of parent materials in trace levels (< 1000 mg/kg) and rarely toxic (Kabata-Pendias and Pendia, 2001; Pierzynski et al., 2000). Cause of increase in environmental levels of lead more than 1000-fold over the past years, is mainly anthropogenic. Major sources of lead pollution include unwarranted use of lead containing substance in our daily life like lead based paints (contain lead chromate), lead glazed ceramics, lead-based solder (used to join copper pipe, brass and chrome plated brass faucets) etc. Moreover, extensive lead ore mining, tailings and smelting has caused high levels of soil environment contamination. High levels of lead has been detected in plants and soils adjacent to smelting works. In addition, several pesticides containing substantial amount of lead like lead arsenate are widely used in horticulture and agriculture. Aerial emission of Pb from the combustion of petrol containing tetraethyl lead contributes substantially to the content of Pb in soils in urban areas. Fig. 1 describes the

sources of lead and its entry in soil-plant-microbial system.

Due to excessive use of lead in man-made products and industrial processes, it has become a common contaminant in urban areas. High levels of lead have been reported by many workers in area near to highways, approximately 30 m zone is at risk of high contamination which also depends on traffic density. High levels of lead in soil (upto 7000 mg/kg) and dust (up to 12,000 mg/kg) have been reported in areas near to lead mines and smelting zone. According to USEPA, permissible level of lead in soil is 400 mg/l and Bureau of Indian Standard have recommended an acceptable limit of lead is 0.01 mg/l in drinking water.

4. Lead species, mobility and availability in soil

In soil, lead are adsorbed initially by fast reactions, followed by slow adsorption reactions and then are redistributed into different chemical forms with varying bioavailability, mobility, and toxicity (Shiowatana, 2001). This distribution is controlled by reactions of lead in soils such as (i) mineral precipitation and dissolution, (ii) ion exchange, adsorption, and desorption, (iii) aqueous complexation, (iv) biological immobilization and mobilization, and (v) plant uptake (Wuana and Okieimen, 2011).

In soils, lead may occur as a free metal ion, complexed with inorganic constituents (e.g., HCO_3^- , CO_3^{2-} , SO_4^{2-} , and Cl^-), or may exist as organic ligands (e.g., amino acids, fulvic acids, and humic acids); alternatively lead may be adsorbed onto particle surfaces (e.g., Fe-oxides, biological material, organic matter, and clay particles) (Uzu et al., 2009; Sammut et al., 2010). Anthropogenic sourced lead generally accumulates primarily in the surface layer of soil, and its concentration decreases with depth (Cecchi et al., 2008). The migration and distribution of lead within the soil result from combinations of factors that include chemical processes such as oxidation and reduction reactions, adsorption of cations on the exchange complex, chelation by organic matter and by other metal oxides and cycling by vegetation. Because of its strong binding with organic and colloidal materials, it is believed that only small amounts of the lead in soil are soluble, and thereby available for plant uptake (Kopittke et al., 2008a, 2008b; Punamiya et al., 2010). Most of these processes are in turn influenced by the regional factors involved in soil formation- climate, biota, topography, and, especially, parent material, all operating through time (Amundson et al., 2015).

Factors influencing lead speciation include soil pH, soil type, particle size, organic matter, presence of organic colloids and iron oxides, cation exchange capacity (CEC), and the amount of lead in soil, presence of various amendments (Silveira et al., 2003).

4.1. Soil pH

Soil pH plays a crucial role in lead persistence in soil. As soil pH plays significant role in retention of lead by soils, hence pH significantly affects the lead solubility and bioavailability. At alkaline pH, lead is principally found as lead carbonates and phosphates which is insoluble in nature while at acidic pH, lead exist as free ionic species. Martinez and Motto (2000) reported that soil pH below threshold (< 5.2 ± 0.2) solubility of lead increases thus increased its bioavailability. In one study, plants grown in soils to which lead had been added took up more lead from acid soils than alkaline soils, but the effect was confounded somewhat by differing amounts of organic matter (MacLean et al., 1969). Finzgar et al. (2007) found negative correlations between total lead and pH in all soil horizons except the A2 horizon (horizon devoid of Fe and Al oxides and clay). The effect of pH may be the indirect consequence of microbiological activity which in turn controls the oxidation and reduction of iron and manganese (Olaniran et al., 2013; Hodgson, 1963). Studies on the distribution of the heavy metals within the soil profile based on pH alone may fail to give consistent results. Instead, the sorption-desorption exchange process should be viewed in

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