World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:12, No:4, 2018

Lead in The Soil-Plant System Following Aged Contamination from Ceramic Wastes

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***Abstract*—**Lead contamination of agricultural land mainly vegetated with perennial ryegrass (*Lolium perenne*) has been investigated. The metal derived from the discharge of sludge from a ceramic industry in the past had used lead paints. The results showed very high values of lead concentration in many soil samples. In order to assess the lead soil contamination, a sequential extraction with H_2O, KNO_3, EDTA was performed, and the chemical forms of lead in the soil were evaluated. More than 70% of lead was in a potentially bioavailable form. Analysis of *Lolium perenne* showed elevated lead concentration. A Freundlich-like model was used to describe the transferability of the metal from the soil to the plant.

***Keywords*—**Bioavailability, Freundlich-like equation, sequential extraction, soil lead contamination.

I. Introduction

THE heavy metal contamination of soil is one of the most pressing concerns in the conservation of the environment. Various sources of contamination are responsible for a buildup process of metals in soil: aerial deposition, waste disposal, agricultural practices, etc. [1], [2]. When a metal reaches the soil, it distributes among the soil phases, and the linkage with the solid phase occurs through sorption processes both on the mineral matrix (clays, oxides, hydroxides) and on the organic matrix (humic substances). Bonds of various nature and strength are formed between heavy metals and soil surfaces [3].

The release of the metal from the soil surfaces to the liquid phase takes place in response to changes in the chemical environment of the soil. Once released into the liquid phase, the metal can move freely through transport processes (diffusion, dispersion, etc.) and it can be absorbed by the plants. The same transport mechanisms can convey the metal even if it is linked to very small colloidal particles. During the transport, the contaminants may be subject to further reactions (oxidation reduction, hydrolysis, photolysis, degradation, etc.) which may modify both their toxicity and bioavailability. In general, plants can absorb heavy metals present in the soil solution that are mobile or potentially bioavailable. In the bioavailability processes, the step from the solid phase to the soil solution is governed by the specific characteristics of the soil that influence the chemical forms of the metals in the soil environment [4].

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In this paper, the source of contamination was the uncontrolled disposal of industrial wastes sludge containing lead based paints and derived from a ceramic factory.

Lead (Pb) can enter the food chain through the ingestion of contaminated edible products at various levels, depending on its chemical forms and soil characteristics which determine its bioavailability. Lead is not an essential element and can negatively affect both human health and the environment [5], [6].

To evaluate the potential risk to environments and the food chain, chemical forms of Pb were evaluated by sequential extraction procedure, which identifies the most mobile species of greater concern as regards the long-term contamination. Furthermore, to describe the transfer from soil to plants, a model based on a Freundlich-like equation was evaluated.

II. Materials and Methods

A. The Site

Uncontrolled disposal of sludge from a decommissioned ceramic industry produced a great contamination of the soil near the factory. Wastes containing lead based paints were discharged into unlined ditches, which overflowed and flooded the soil. Very high levels of lead were detected in soil. The contaminated area, once used for agricultural purposes, was located at short distance from the old abandoned factory, from which it was separated by some ditches without banks. In the past, soil tillage was performed in order to obtain field convexity with the creation of bumps and depressions. During frequent floods, the contaminated water of the ditches flooded these depressions. In many parts of the contaminated area, the soil still had a violet color derived from ceramic paints, despite the fact that more than 20 years have passed since the dismantling of the factory. The area was mainly vegetated with perennial ryegrass (*Lolium perenne*) species that grew spontaneously. Soil contamination was not uniformly distributed, with zones of high concentration of lead surrounded by uncontaminated zones.

B. Sampling and Analysis

Sampling points were selected at different distances from the unlined ditches where the sludge was disposed, with a network scheme in order to cover the whole area of 10 000 m^2 near the factory. The soil samples collected at each sampling point, derived from five subsamples, were mixed, air-dried and ground to pass through a 2-mm sieve before analysis.

Soil pH was determined using a glass electrode at a soil/water ratio of 1:2.5 [7], cation exchange capacity (CEC) using barium chloride (pH = 8.1) [8], and texture (sand, silt,

and clay) by the pipette method [9]. Organic matter was determined by wet combustion [10]. The soil was a sandy loam classified as "Typic Psammaquesnt" which contained on a dry weight basis 13.8% clay, 29.2% silt, 55.5% sand, 0.9% organic matter, 5.3 pH and 14.4 $cmol_{(+)}kg^{-1}$ cation exchange capacity.

At each sampling point, vegetable samples were also collected, then transported to the laboratory in plastic bags and separated into tops and roots. The aerial parts of plants were washed with distilled water. The samples were air dried at 50 °C and then crushed and ground to pass a 2-mm sieve. Only the aerial parts were analyzed.

Soil and vegetable samples were digested in aqua regia, and Pb was determined by ICP-OES with a Liberty AX Varian spectrometer. Potential risks from the contaminated soil were estimated by investigating the chemical forms of metal. In the soil samples, the chemical forms of lead were determined by a sequential extraction procedure (SEP) with H_2O, KNO_3 1M and EDTA 1% with a ratio soil solvent 1:5. Three replicates of samples were carried out for each extraction step [11].

C. Quality Assurance and Quality Control

Quality assurance and quality control were performed by testing two standard solutions (0.5 and 2 mg L^{-1}) every 10 samples. CRM ERM – CC141 for soil and CRM ERM - CD281 for plants were the certified reference materials used. The values obtained for CRM ERM – CC 141 were 32.5±1.2 mg kg^{-1} Pb, which was in good agreement with the certified values of 32.2±1.4 mg kg^{-1} Pb. For CRM ERM - CD281, the values obtained were 1.71±0.14 mg kg^{-1} Pb, which was also in good agreement with the certified values of 1.67±0.11 mg kg^{-1} Pb. The detection limit for Pb was 5 μg L^{-1} and recovery of spiked samples (5%) ranged from 95% to 101% with a relative standard deviation (RSD) of 1.87% of the mean.

III. Results and Discussion

To provide a detailed evaluation of the potential hazard for human health and environment, total concentration of Pb in the contaminated site has been integrated also by a sequential extraction procedure to determine the mobility and bioavailability of Pb. The method of sequential extraction is widely used to ascertain chemical speciation of heavy metals in soils [11]-[13]. The adopted sequential extraction has been successfully used in contaminated soils to evaluate the possible transfer of metals from soils to plants. The water-soluble and exchangeable fraction of lead is considered immediately available to plant uptake, whereas the metal extractable by EDTA can be considered as mobilisable and potentially bioavailable.

The total and extractable Pb concentrations are reported in Table I.

In the area, a great variability of Pb total content in soil samples was discovered. The values ranged from 40 mg kg^{-1} to 5000 mg kg^{-1}. Subsamples showed the contrary satisfactory homogeneity. Sample n. 14 located outside the contaminated field contained 44 mg kg^{-1} Pb and was considered as reference non-polluted soil. Samples 6, 8, and 10 showed similar Pb concentration (about 40 mg kg^{-1}), thus 44 mg kg^{-1} could be considered as the original content of the soil. The highest values of lead concentration (from 1550 to 5250 mg kg^{-1}) were detected in samples 1, 2, 3, 4, 7 both near the factory and the unlined ditches. The soil of these samples was characterized by a pink violet color till a depth of 20 cm. Further high values (from 576 to 1192 mg kg^{-1}) were found in samples 5, 9, and 11, far from the factory. Also these soil samples were pink violet colored. The concentration values could be explained taking into account the slope of the field. Samples 5, 9, and 11 were located in the depressions created by soil tillage, which were crossed as a preferential route by the overflow. Samples 12 and 13 showed higher values if compared to uncontaminated samples, but visual examination did not show any particular color. These higher values could be ascribed to the influence of the near motorway. Concerning the results from the sequential extraction procedure, it is worth noting that soluble (H_2O) and exchangeable (KNO_3) forms are drastically reduced with respect to total content.

TABLE I
Mean Values of Total and Available (KNO_3 and EDTA Extractable) Pb Concentrations in Soil Samples.

Sample	Total	KNO_3	EDTA	Total extractability (%)
8	40	19	13	80.0
14	44	25	12	84.1
6	49	22	18	81.6
10	54	19	16	64.8
12	77	17	35	67.5
13	121	25	62	71.9
9	576	53	290	59.5
5	731	50	523	78.4
11	1192	59	830	74.6
2	1550	22	860	56.9
1	1780	20	840	48.3
3	2220	20	1100	50.5
4	3070	19	2000	65.8
7	5250	58	3250	63.0

Data are expressed as Mg Kg^{-1} on a dry weight basis. The amount extractable in water was always negligible and not reported in the table.

No water soluble lead was recovered in any samples, while concentration of metal in exchangeable form is the same in polluted and unpolluted samples, suggesting that the metal is not retained by soil with ionic linkages. Extraction with EDTA, which is able to break also covalent linkages, dissolved relevant quantities of the metal also in those samples where the total content was higher due to the contamination by ceramic sludge.

The strength of binding of Pb with the different soil components determines its bioavailability and the risk associated with its presence in the ecosystem. The potential hazards evaluation was carried out by calculating the potential bioavailability, which is determined by the percentage of the sum of metal extractable by the different reagents of the SEP with respect to the total concentration.

$$Total\ extractability = 100 \times \frac{\sum(Pb_{H2O}+Pb_{KNO3}+Pb_{EDTA})}{Pb_{Tot}}$$

Total extractability indicates the possibility of Pb to be released from the soil solid phase into the soil solution from which it can be taken up by plants. The data are reported in Table I.

Thus, the sequential extraction procedure is useful in providing information on the mobility and chemical availability of Pb in soil.

It is important to remark that the distribution of Pb in the different SEP fractions is strictly dependent on the characteristics of the soils such as pH, organic matter content, and CEC. Soil pH plays an important role in the distribution of Pb in the various fractions, for example Pb becomes more mobile as pH decreases. In all soil samples, Pb existed mostly in the EDTA extractable forms.

The Pb content in the above ground part of *Lolium perenne* plants grown in the contaminated sites ranged from about 7 mg kg^{-1} to about 37 mg kg^{-1}. The trend of the plant uptake of Pb in relation to the soil concentration of the metal is described in Fig. 1.

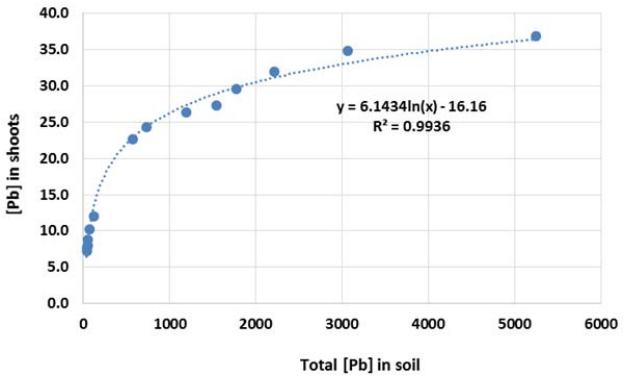

Fig. 1 Relationship between total Pb concentration in different soil samples and Pb content in the shoots of *Lolium perenne* plants. Data are expressed as mg kg^{-1} on a dry weight basis

The transfer of inorganic ions from soil to plants can be interpreted using transfer models, and Freundlich-like equation has been often used to describe the uptake of contaminants by plants [14]-[16].

The Freundlich-like equation (1) for plant uptake is:

$$q = KC^{\frac{1}{n}} \quad (1)$$

where q is the contaminant concentration in plants (mg kg^{-1}), and C is the concentration (mg kg^{-1}) of contaminants in the soil. In the Freundlich-like equation, K can be considered as an index of uptake ability, whereas the value of 1/n is indicative of the strength of absorption.

Even if a Freundlich-like equation can be usefully used to study absorption of metals by plants, plant uptake cannot be considered a biosorption process, in which a contaminant is adsorbed on a non-living biomass. Biosorption process in fact derives from the presence of functional groups able to interact with the contaminant on the adsorbing surfaces of non-living biomass. On the contrary, plant uptake involves living plants and a physiological contaminant transport mechanism, which depends on the plant species. Thus, the Freundlich-like equation is used only as an operational tool to describe plant uptake. In this case, no thermodynamic significance can be attributed to the parameters K and 1/n, which can be used only as indicative of the ability of plant to uptake Pb from the soil.

To describe the trend of plant uptake vs soil total Pb concentration, a Freundlich-like equation has been used. The data obtained from the equation are reported, in the logarithm form, in Fig. 2. The data are very well fitted to a straight line.

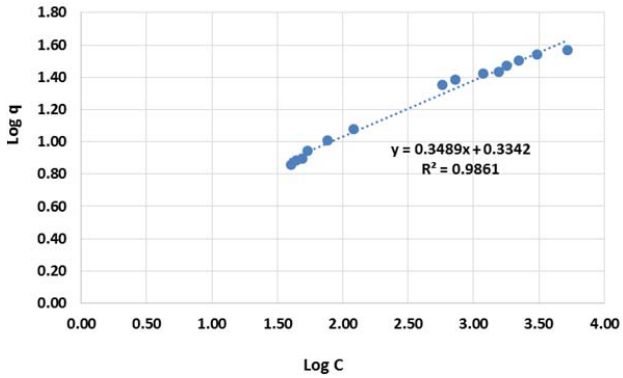

Fig. 2 Freundlich-like equation for the shoots uptake of *Lolium perenne* (q) in relation to different soil total Pb concentration (C)

Considering the trend of Pb uptake with respect to the amount extractable by EDTA, the pattern of the curve (Fig. 3) is similar to the trend of plant uptake vs soil total Pb concentration.

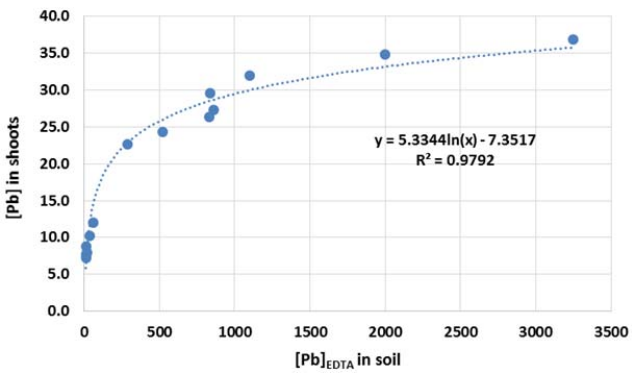

Fig. 3 Relationship between Pb extracted by EDTA in different soil samples and in the shoots of plants. Data are expressed as mg kg^{-1} on a dry weight basis

If the data are expressed by the Freundlich-like equation in the logarithm form, they fitted a straight line as reported in Fig. 4.

In the evaluation of plant Pb uptake models, there are no differences in using total Pb concentration or EDTA extractable Pb. These results can be ascribed to the acidic pH of soil, which greatly promote the Pb extractability with EDTA, whose values are linearly related to the total concentration. Soil pH does not affect extraction in H_2O and KNO_3 because lead in soluble and exchangeable form has almost completely disappeared due to aging processes.

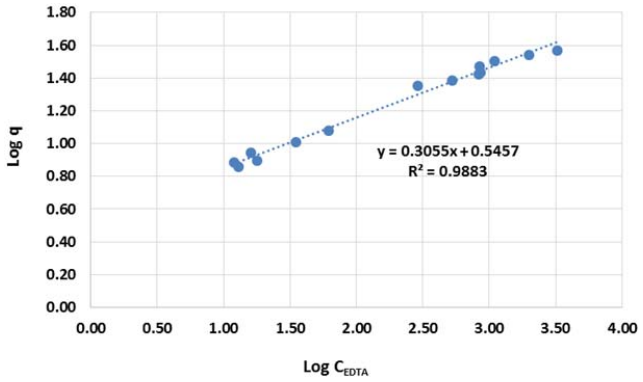

Fig. 4 Freundlich-like equation for the shoots uptake of *Lolium perenne* (q) in relation to different Pb concentration extracted by EDTA in soil (C_{EDTA})

IV. Conclusion

Total Pb pollution in most samples far exceeded the Italian soil concentration level of 400 mg kg^{-1} beyond which it is necessary to proceed with a risk assessment procedure in order to evaluate the soil contamination. Plants growing in the area near the decommissioned factory appeared to be at risk due to the amount of Pb taken up and to the high Pb bioavailability. For the soil of the contaminated area under investigation, characterized by very different contaminant concentrations, a Freundlich-like model could be used as support to predict the uptake of lead by plants.

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