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Leaching Behaviour of Lead as Influenced by Pore Volume and Solution Composition under Contrasting Soil Types

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ABSTRACT

Automobile emissions and sewage irrigation are the major sources of lead pollution in the urban environment. The studies on the leaching pattern of Pb at different pore volume intervals showed that, Vertisols need 7-8 times of effluent passes on the land to be contaminated. Whereas, in Alfisols, after the second time of effluent passing on the land, it starts moving downwards, thereby, contaminating the soil in the rhizosphere region and the ground water with Pb. The various ions present in the effluent may enhance/reduce the mobility of Pb in soils. The ions like Ca^{2+} , NO_3^- and Cl^- enhanced Pb mobility, whereas CO_3^{2-} and PO_4^{2-} were found to decrease Pb mobility in both contrasting soil types. The effect of different ionic species in decreasing order of Pb mobility in soils was as follows; $\text{Ca}^{2+} > \text{NO}_3^- > \text{Cl}^- > \text{CO}_3^{2-} > \text{PO}_4^{2-}$. The mobility of Pb was well pronounced in Alfisols when compared to Vertisols. The practical consequence of these findings warrants some attention to soil compaction modification in the effluent disposal site to minimize certain soluble metals contained in solid waste leachate. These findings will enable the industrial policy makers to take decision about the specificity of soil types for particular type of industry construction.

Key words: Lead, leaching, solution composition, pore volume

INTRODUCTION

Automobile emissions and sewage irrigation are the major sources of lead pollution in the urban environment. Lead, a toxic heavy metal, is introduced into the environment mostly from petrol driven vehicles. Lead comes in the category of those trace elements which are known to be toxic even when present in traces. Lead in the tetraethyl $[(\text{CH}_3\text{CH}_2)_4\text{Pb}]$ form is used as an antiknock additive to gasoline to increase its octane number.

In India, lead concentration that forms a component of inorganic fraction in particulate matter exceed the WHO guidelines of $0.5 \mu\text{g m}^{-3}$ in seven cities viz., Ahmedabad, Bombay, Calcutta, Delhi, Hyderabad, Kanpur and Kochi (NEERI, 1995). The health concerns with Pb contaminated soils arise mostly from plant metal accumulation through soil particles and dust ingestions by humans, especially children (McBride and Bouldin, 1984). Lead poisoning remains one of the most common environmental hazards inspite of good body scientific knowledge on its toxicity and control measures. The clinical manifestations of lead poisoning in adults may present as chronic anemia, general malaise, easy fatigability, kidney failure and brain drainage. In developing countries like India, over 95% of urban sewage and electroplating effluent as well as bicycle industry effluents,

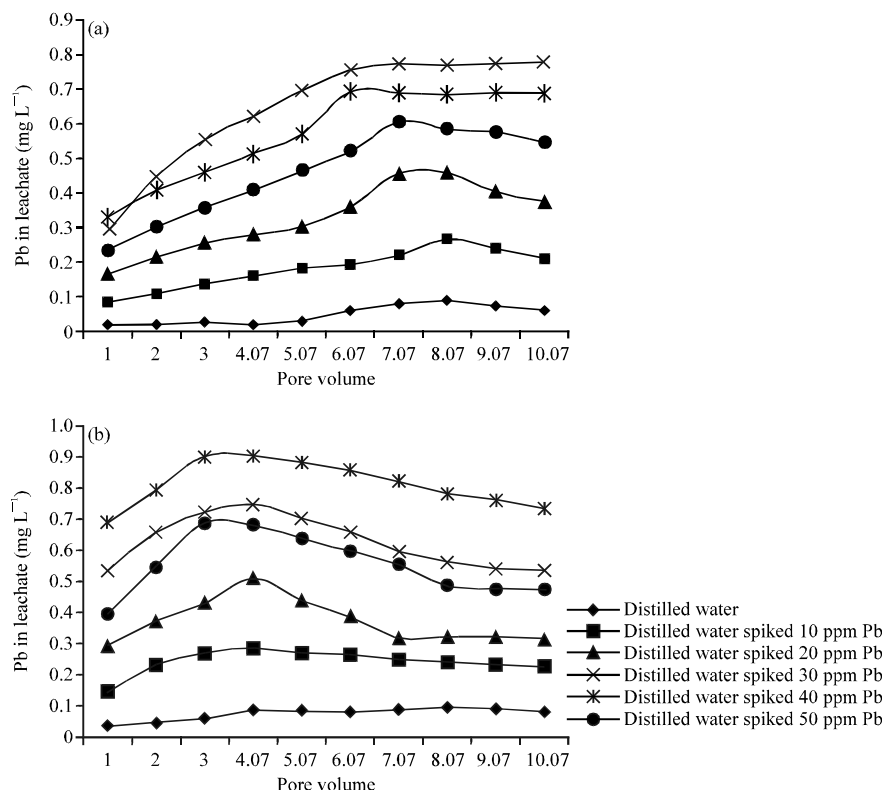


Fig. 1(a-b): Leaching pattern of Pb in soils at different pore volumes, (a) Vertisole and (b) Alfisol

containing Pb wastes which are being discharged as untreated into rivers, bays, soil, water and air, causes a major human health hazard. A sorption-desorption phenomena, which operates at the solid-liquid interface, play an important role in controlling the concentration of lead in ambient solution. The information on lead transport, transformation, the knowledge of kinetics of adsorption and mobility are the useful environment guidelines to prevent the potential toxic hazards of lead in soil (Fig. 1). On perusal of literature, a comprehensive study on effect of pore volume and solution composition on lead mobility is totally lacking. Lead accumulates near the surface of the soil. Hence, the root system of crops is affected and ultimately enters into food chain. Unless checked, it may grow to crisis proportion and threatening the sustainable development of the country.

METHODOLOGY

Leaching study

Experimental setup: The mobility of Pb in soil in orders of contrasting characters viz., Vertisols and Alfisols were evaluated by conducting leaching study under various pore volumes. The pore volume is defined as the total pore space of the soil monolith. One pore volume was calculated by subtracting the initial weight of the dried soil from the weight of the saturated soil after the initiation first drippings.

The columns of 35 cm length and 5 cm diameter were used. A Whatman No. 42 filter paper was placed at the bottom of the PVC tube and the end was tied with muslin cloth. Above the filter paper, a layer of 2 cm thickness sand was placed. On the top of the filter paper, the PVC tubes were

packed with two layers of experimental soils which differ in their bulk densities (1.3 and 1.2 mg m^{-3}) to simulate the field condition. The entire setup was mounted on a funnel containing conical flask wherein the eluates were collected. The experimental soils, Vertisol and Alfisol contained 4.5 and 1% organic matter, respectively.

Preparation of working solution: The deionized water spiked with different concentrations of Pb ($10, 20, 30, 40$ and 50 mg kg^{-1}) in $\text{Pb}(\text{NO}_3)_2$ were used as a working solution. The Pb levels were fixed based on their maximum content permitted in the soil (50 mg kg^{-1} for Pb). To facilitate leaching, each of this working solution was applied to the top of each column manually. The eluate was collected for each pore volumes upto ten pore volumes. The EC and pH of each eluate were measured.

The concentration of Pb in the eluate samples was determined by using AAS. From the concentrations of metal and the volume of each eluate fraction, the quantities of metal transported through the soil column were calculated.

Mobility affected by ionic species: An incubation and column experiments was carried out to know the effect of solution composition (index cations and anions) on Pb mobility. To examine the mobility of Pb as affected by solution compositions i.e., index cations like Ca^{++} and anions like Cl^- , SO_4^{2-} , PO_4^- , NO_3^- and CO_3^{2-} were selected. Since, Ca^{++} the dominant cation and Cl^- , NO_3^- , SO_4^{2-} , PO_4^- and CO_3^{2-} the dominant anions were observed as plenty in the contaminated soils. The Pb salts were mixed with chloride free soil to reach the final concentrations of 250 mg kg^{-1} since the initial total Pb concentration was 250 mg kg^{-1} . Since the initial soil Ca concentration was $15,000 \text{ mg kg}^{-1}$, the solutions containing varied levels of calcium (Ca^{++}) i.e., $10,000$ and $20,000 \text{ mg L}^{-1}$ were prepared. The fixed Cl^- and NO_3^- , SO_4^{2-} , PO_4^- and CO_3^{2-} levels were 500 and 1000 mg kg^{-1} , since the initial Cl^- , NO_3^- , SO_4^{2-} , PO_4^- and CO_3^{2-} concentrations were $690, 980, 724$ and 605 mg kg^{-1} , respectively. The volume of these solutions should approximately represent the volume of water required for maintaining the field capacity moisture.

Treatment details

Soil types: S_1 -Alfisol was taken as coarse textured soil and S_2 -Vertisol as fine textured soil:

- $\text{T}_1 = \text{Cl}^- \text{ free soil} + 250 \text{ ppm Pb}$
- $\text{T}_2 = \text{Contaminated soil} + 250 \text{ ppm Pb}$
- $\text{T}_3 = \text{T}_1 + 500 \text{ ppm Cl}^-$
- $\text{T}_4 = \text{T}_1 + 1000 \text{ ppm Cl}^-$
- $\text{T}_5 = \text{T}_1 + 500 \text{ ppm NO}_3^-$
- $\text{T}_6 = \text{T}_1 + 1000 \text{ ppm NO}_3^-$
- $\text{T}_7 = \text{T}_1 + 500 \text{ ppm PO}_4^-$
- $\text{T}_8 = \text{T}_1 + 1000 \text{ ppm PO}_4^-$
- $\text{T}_9 = \text{T}_1 + 500 \text{ ppm CO}_3^{2-}$
- $\text{T}_{10} = \text{T}_1 + 1000 \text{ ppm CO}_3^{2-}$
- $\text{T}_{11} = \text{T}_1 + 10,000 \text{ ppm Ca}^{++}$
- $\text{T}_{12} = \text{T}_1 + 20,000 \text{ ppm Ca}^{++}$

The experimental design was Factorial Complete Randomized design (FCRBD) and the treatments were replicated twice. This study included two sub experiments:

Incubation experiment: The experimental soils were incubated for three weeks after imposing the above treatments. The moisture was maintained at field capacity throughout the incubation i.e., in alternate days, the total weight and loss of weight were measured which represents the moisture loss and was adjusted by adding same mass of water. After incubation, the soils were used for leaching study.

Column experiment: Cylindrical PVC tubes (diameter 5 cm) were used as soil columns. In each column, two layers of soil, each of 10 cm height with a bulk density of 1.3 (bottom) and 1.2 (top) mg m^{-3} were maintained.

Before packing the soil in the tube, a What man No. 42 filter paper was placed and tied with a muslin cloth at the bottom. Over this, a layer of gravels to a height of 3 cm was placed. Approximately 5 cm spacing was provided at the top for the application of deionized water in which the flow was controlled manually. These columns were mounted on plastic funnels provided with conical flasks for the collection of leachates. The soil columns were leached using measured quantities of deionized water, which were added slowly until the soil column became saturated and the retention time was noted. The leachates from each leaching were analyzed for pH, EC, Cl^- , NO_3^- , PO_4^{2-} , SO_4^{2-} , CO_3^{2-} , Ca^{2+} and Pb. Section wise soil samples were also taken at the end of the experiment at different bulk densities in the soil columns and were analyzed for total and DTPA Pb.

RESULTS AND DISCUSSION

Leaching behavior of lead in soil: This experiment examined the potential for metal leaching of solutions comprising the graded concentrations of Pb.

Vertisols: The mean concentration of Pb in leachate of 50 mg Pb L^{-1} spiked columns exceeded 0.72 mg Pb L^{-1} after the 7.07 pore volumes of leachate but was less than 0.11 mg Pb L^{-1} for deionized water alone passed columns after similar leachate volumes. The maximum rate of Pb break through (i.e., the BTC inflexion point) for all the Pb concentrations occurred after six pore volumes of leachate had been collected. However at lower concentration, Pb (10 and 20 mg Pb L^{-1}) on average required a greater volume of leachate to reach the BTC inflexion point. The earliest occurring inflexion point (in terms of leachate volume) was noticed in Vertisols particularly for higher concentrations. Unlike the Alfisols, there was little or no initial lag phase, with rapid increase in the Pb concentration of leachate occurring almost immediately after leaching commenced (Fig. 1).

Break Through Curves (BTC) for Vertisols, in particular the 50 mg Pb L^{-1} spiked solution passed columns were less sigmoid and more exponentially shaped curves. This was consistent with a significant degree of preferential leaching occurring in these soils. Comparing BTC shapes, although initially there was a sharp increase in Pb concentration over the first part, this did not continue the rate of increase declining considerably after the first 3 pore volumes. As a consequence, the shape of the plotted Vertisol experimental data appeared exponential rather than sigmoidal.

On examination of Pb Break Through Curves (BTCs) for the Vertisols, it appears to show two main components or stages in their construction. The first shows rapid break through of solute in the initial stages of leaching but the second, a marked slowing down of this after about 7.07 pore volumes (1 pore volume = 1 time effluent pass). This suggested that Pb is being sorbed from solution passing through the smaller pores and this depleted solution is diluting the flow from

Table 1: Effect of treatments on the total and DTPA-extractable Pb (mg kg⁻¹) in the lead spiked incubated soils

Treatments	Total Pb	DTPA Pb
Alfisol (S₁)		
T ₁	199.850	21.850
T ₂	170.500	11.350
T ₃	173.500	13.750
T ₄	189.500	14.500
T ₅	185.000	16.500
T ₆	198.500	19.150
T ₇	99.350	7.300
T ₈	88.160	7.150
T ₉	103.750	8.300
T ₁₀	97.300	9.850
T ₁₁	207.450	19.800
T ₁₂	214.800	20.500
Vertisol (S₂)		
T ₁	210.350	24.800
T ₂	198.450	9.170
T ₃	185.200	15.350
T ₄	189.350	18.350
T ₅	201.300	11.950
T ₆	225.850	13.800
T ₇	83.000	5.300
T ₈	71.500	4.150
T ₉	95.200	6.300
T ₁₀	108.750	6.050
T ₁₁	219.300	25.850
T ₁₂	220.350	27.300
CD	0.050	0.050
S	0.357**	ns
T	0.874**	0.747**
S×T	1.236**	1.056**

preferential leaching, thus restricting the rate of solute concentration increases. This was in line with the findings of Carey *et al.* (1996) and Avudianayagam *et al.* (1999). Evidences suggested that Pb sorption is time dependent and the increase in solute residency times within soils will increase retention of Pb (Table 1).

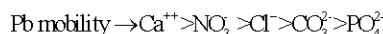
Alfisol: The experimental data displayed well-defined sigmoidal shaped curves. Leachate Pb concentrations reached approximately 90% of the input (0.88 mg Pb L⁻¹) after 4.04 pore volume, but neither Vertisols reached such a high final Pb concentration. There was little initial lag phase until two pore volumes of leachate had been collected. After that rapid increased in Pb concentration was noticed upto 7.07 pore volumes. After seven pore volumes, there was no increase in the Pb concentration in the leachate. The mean concentration of Pb exceeded 0.88 mg Pb L⁻¹ after first seven pore volumes of leachate in 50 mg Pb L⁻¹ spiked deionized water passed columns but was less than 0.09 mg Pb L⁻¹ for deionized water alone passed columns after similar leachate volumes.

Comparing BTC shapes, the sharp rises observed in leachate Pb concentrations after a small initial lag phase of two pore volumes and finally attained a steady state for all concentrations indicated that retention or hold back of Pb was minimal in Alfisol when compared to Vertisol.

While examining the BTCs for Pb in Alfisols, early break through occurs before 4.04 pore volumes. The leachate Pb concentration reached approximately 90% of the input concentration after 7.07 pore volumes. This was in agreement with the findings of Abreu *et al.* (1999). They stated that the rapid movement of solute through preferential flow paths can cause early break through of the metallic ion such as Pb^{++} in Alfisol.

Lead mobility in soil: The Pb mobility varied for different ionic species and for various soils. The differences in Pb mobilization pattern were observed for various ionic species for two different soils. In general, Pb mobility was found to be fastened in Alfisols than in Vertisols. This might be due to the influence of soil properties on Pb mobilization. The similar results were obtained by Dowdy *et al.* (1999). Among the different ionic species, Pb mobility was increased for cationic species than anionic species. While seeing the behavior of anionic species on Pb mobilization, NO_3^- anion recorded the highest Pb mobility followed by Cl^- , CO_3^{2-} and PO_4^{2-} . The PO_4^{2-} anion had less capacity to mobilize Pb from the soil.

In general, the Pb mobility for two types of soils subjected for three times leaching followed similar pattern for different ionic species. It was as follows:



The Ca^{++} ions had high efficiency to desorb/mobilize the strongly sorbed Pb^{++} from soil. Since the ionic radius of Ca^{++} ($0.99 \text{ \AA}$) could be well comparable with the ionic radius of Pb^{2+} ($1.10 \text{ \AA}$) and can be easily replaced Pb^{++} from the adsorbed site through cation exchange reaction (Zhu and Alva, 1993; Amrhein and Strong, 1990; Smolders *et al.*, 1998). They reported that, the deicing salts such as Calcium Magnesium Acetate (CMA) could result in Pb mobilization as neutral ion pairs with carbonate because of the decomposition of acetate under aerobic condition.

The effect of Cl^- ion in mobilizing Pb from the soil was well understood by the explanations given by Khan *et al.* (2000). They found that the highest mobility of trace elements may be attributed to the presence of Cl^- ions which are capable of electron withdrawing (I-effect) tendencies. Thus, the active sites of this molecule, low in electron density, in turn deactivating the molecule for interacting to the metal ion, resulting in their greater mobility.

The effect of CO_3^{2-} on Pb mobilization was well evidenced. Though CO_3^{2-} and PO_4^{2-} had less Pb mobilization effect when compared to Cl^- , NO_3^- and Ca^{2+} , their effect was seen in a meager quantity in Alfisol than in Vertisol. This may be due to the formation of insoluble Pb compounds as $PbCO_3$ and $Pb_3(PO_4)_2$ as reported by Nriagu (1978). He also stated that precipitation or dissolution of an appropriate sparingly soluble compound is the primary mechanism for Pb immobilization that controls the activity of Pb in the equilibrium solution. The same finding was further strengthened by the reports of Diyab *et al.* (2001). They found that phosphates and carbonates of Pb compounds are weakly soluble and quite stable in numerous soils (Fig. 2).

While viewing the Pb content in the leachates of three leaching, they are in the decreasing order as follows:

Pb content in 1st leaching > 2nd leaching > 3rd leaching

The similar trend was obtained for both soils. This might be due to the more desorbing nature of deionized water at early days of leaching on the loosely bound Pb^{2+} in the exchange complex with

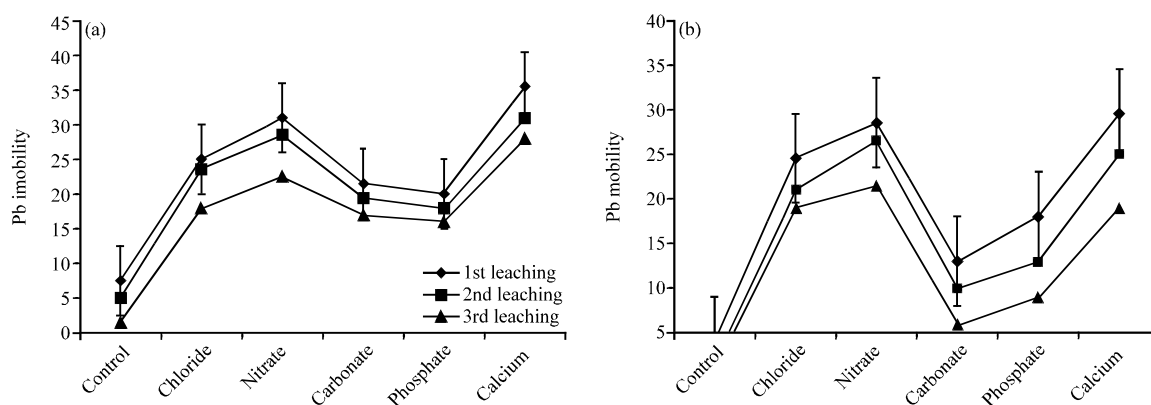


Fig. 2(a-b): Effect of ions on lead mobility in soil, (a) Alfisol and (b) Vertisol

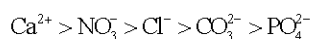
vander Waals forces. This leads to desorb/mobilize more Pb^{2+} from the soil at the early stages of leaching. During 2nd and subsequent leaching, the desorption action of deionized water is on the tightly bounded Pb^{2+} on the exchange site which in turn desorbs low amount of Pb^{2+} from the soil. This was akin to the results of Caprie *et al.* (2001).

The scrutiny of results obtained from path analysis revealed that Ca^{++} , Cl^- , NO_3^- , PO_4^{2-} and CO_3^{2-} showed positive direct effect on Pb mobility in both the soils. The pH had an indirect effect through various ionic species on Pb mobility.

CONCLUSION

- The studies on the leaching pattern of Pb at different pore volume intervals showed that, in Vertisols, it needs 7-8 times of effluent passes on the land to be contaminated. Whereas, in Alfisols, after the second time of effluent passing on the land, it starts moving downwards, thereby contaminating the soil in the rhizosphere region and the ground water with Pb
- The practical consequence of these findings warrants some attention to soil compaction modification in the effluent disposal site to minimize the certain soluble metals contained in solid waste leachate
- These findings will enable the industrial policy makers to take decision about the specificity of soil types for particular type of industry construction. The heavy textured soils were highly suitable for construction of electroplating industries that release effluents containing mobile metals like Ni, Cd, Cr and Cu, whereas the light textured soils are not suited for the effluents containing mobile metals
- The ions like Ca^{2+} , NO_3^- and Cl^- enhanced Pb mobility, whereas CO_3^{2-} and PO_4^{2-} were found to decrease Pb mobility in both soil types

The effect of different ionic species in decreasing order of Pb mobility in soils were as follows:



The mobility of Pb was well pronounced in Alfisols when compared to Vertisols.

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