

Formation and Leaching of Lead Species from a Sandy Loam Alluvial Soil as Related to pH and Cl:SO₄ Ratio of Leachate

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ABSTRACT

In a laboratory experiment, solutions of PbCl₂ alone and/or in combination with CrCl₃ and Cr₂(SO₄)₃ @ 10 mg L⁻¹ of each metal, dissolved in canal water, were applied onto soil while canal water alone was the control treatment. Four pore volume (PV) of solutions were applied @ one PV at each installment while the fifth PV was only canal water to all the soil columns. After infiltration of each PV, leachates were collected and analysed. The activity of lead as Pb²⁺ ions in leachates was the highest followed by that of PbCO₃ and Pb(OH)₂. Activities of PbCO₃ and Pb(OH)₂ were inversely while that of Pb²⁺ ion was positively related to pH of leachate. The effect of Cl to SO₄ ratio (Cl:SO₄) on the leaching pattern of Pb(OH)₂ and PbCO₃ species was negligible between the ratio of 0.4 to 0.6. At higher Cl:SO₄, after a small drop, it increased dramatically. However, there was no change in the removal of Pb²⁺ as α_{Pb} with an increase in Cl:SO₄ from 0.4 to 0.9. The activities of all the three forms of Pb²⁺ gradually decreased first from leachate L₁ to L₃ and then increased up to L₅. However, this aspect of Pb²⁺ behaviour with time needs more detailed and specific studies.

Key Words: Lead; Activity; Soil solution; pH; Chloride; Sulphate

INTRODUCTION

Mobility and bio-availability of metals in soil depend upon its chemical transformations and thus both are of great concern with human health. The chemistry of Pb²⁺ in soil can be explained on the basis of specific, non-specific and exchange adsorption; the insolubilization and formation of ion pairs/complex ions. However, few data are available to prove the relative importance of these mechanisms, particularly under the agro-climatic conditions of Pakistan. Although, formation of different Pb species in response to ionic concentration and composition, and the system pH may affect retention or removal of Pb from a soil.

Lagerwerff and Brower (1973) studied the exchange reaction of Pb²⁺ with Al³⁺, Ca²⁺ and Na⁺ in three soils. In the Na⁺-system, Pb²⁺ was found to precipitate and solubility of solid Pb²⁺ phase i.e. precipitates of Pb(OH)₂, was found to increase with a decrease in pH and/or concentration of NaCl. Equilibrium batch studies using pH as master variable by Santillan-Medrano and Jurinak (1975) showed that hydroxide, carbonate and phosphate as important compounds of Pb²⁺ which controlled its activity in solution. Schnitzer and Kerndorf (1981) found that Pb²⁺ and Cr³⁺ formed hydroxides above pH 6 in water and hydrolysis constants for Pb²⁺ was -7.82. In addition, presence of Cl⁻ and SO₄²⁻ could affect the activity of Pb²⁺ in the soil system. Thus an attempt has been made to estimate the forms of Pb²⁺ in soil solution and their leaching pattern as affected by soil pH and Cl:SO₄ ratio.

MATERIALS AND METHODS

A sandy loam soil (Table I) was collected from 15 cm surface layer of a field. After passing through 2 mm sieve, 3.5 kg was filled in PVC lysimeters.

Table I. Analysis of soil used for the experiment

Characteristic	Amount	Characteristic	Amount
EC _e , dS m ⁻¹	1.90	Cl ⁻ , mmol _c L ⁻¹	2.65
SAR, (mmol L ⁻¹) ^{1/2}	1.14	SO ₄ ²⁻ , mmol _c L ⁻¹	14.95
pH _s	7.58	CaCO ₃ , %	2.60
Pb ²⁺ , µg kg ⁻¹	2081.00	Clay, %	16.20
Cr ³⁺ , µg kg ⁻¹	1733.00	Organic matter, %	0.46

The treatments included canal water (EC= 0.24 dS m⁻¹, Ca²⁺ =1.0, Mg²⁺ =0.8, Na⁺ =0.6, HCO₃⁻ =0.9, Cl⁻ =0.7, SO₄²⁻ =0.8 mmol_c L⁻¹, Pb²⁺ =320 µg L⁻¹), application of PbCl₂, PbCl₂ + CrCl₃ and PbCl₂ + Cr₂(SO₄)₃ solutions made in canal water. The concentration of Pb²⁺ in treatment solutions was 10,000 µg L⁻¹ excluding their concentration in canal water. Solutions equal to 4 PV were applied to respective lysimeters and for the 5th PV canal water was added. The PV was calculated with the help of formula:
$$\text{Pore volume (PV)} = (M_w \times BD_s) / (M_s \times D_w) \times \pi r^2 l$$
where, M_w = loss in weight (g) of soil on oven-drying, BD_s = Bulk density of soil as Mg m⁻³. M_s = mass of saturated soil paste (g), r = radius of soil columns value = 5.5 cm, and l = length of soil columns = 25 cm

The soil solutions were allowed to infiltrate under gravitational influence. Leachate was collected after infiltration of each PV and analysed for cations/anions (Page *et al.*, 1982). The soluble Pb^{2+} was determined by atomic absorption spectrophotometer (model Varian SpectraAA 250 plus). Activity of Pb^{2+} species was calculated following Santillan-Medrano and Jurinak (1975) i.e. $p\alpha[Pb] = -\log\gamma_{Pb} [Pb]$, where Pb is in moles Leachate⁻¹

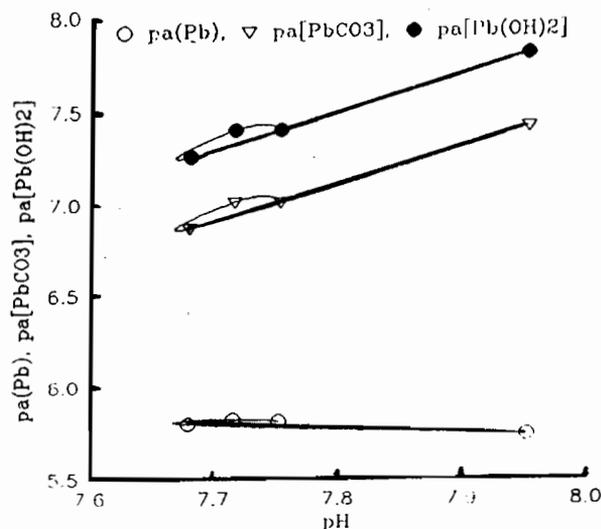
$$p\alpha[Pb(OH)_2] = 2pH - 8.1 \text{ and}$$

$$p\alpha[PbCO_3] = 2pH + \log P_{CO_2} - 5.33$$

RESULTS AND DISCUSSION

Activities of $PbCO_3$ and $Pb(OH)_2$ were inversely related while that of Pb^{2+} ion was positively related to pH of leachate, i.e. $-\log$ of activity increased for the former two species and that of the latter one decreased with an increase in pH and vice versa (Fig. 1). Lead activity ($p\alpha_{Pb}$) measured by Kalbasi *et al.* (1995) in lead arsenate contaminated soils ($pH_{1,2} = 7.30$ to 8.50) ranged from 7.21 to 9.37. Hem (1973) reported that in many natural surface waters, Pb^{2+} activities were regulated by either $PbCO_3$ or $Pb_3(OH)_2(CO_3)_2$. The activity of Pb^{2+} as $Pb(OH)_2$ and $PbCO_3$ in the present study conforms well with the findings of Santillan-Medrano and Jurinak (1975). The $p\alpha_{Pb}$ calculated by them was about 6.0 for $PbCO_3$ and about 7.0 for $Pb(OH)_2$ which was more at higher pH. The decrease in the activity of Pb as $PbCO_3$ and $Pb(OH)_2$ with an increase in pH shows that Pb^{2+} begins to precipitate in the form of $Pb(OH)_2$ and $PbCO_3$ as the pH of the system increases. Swallow *et al.* (1980) observed that

Fig. 1. pH affects Pb species concentration in leachates



precipitation of Pb^{2+} started at $pH > 6$ in the form of $Pb(OH)_2$. The $p\alpha_{Pb}$ as Pb^{2+} ions in this study is relatively less than that observed by Kalbasi *et al.* (1995). It could be due to the absence of Cl^- ions in the system they studied while present solutions contained a lot of Cl^- ions (0.73 to 3.17 mmol L^{-1}) which might have contributed to the activation of Pb^{2+} in the form of $PbCl^+$ and $PbCl_2^0$ ion pairs as was observed by Hahne and Kroontje (1973) and Giardano *et al.* (1983).

The effect of Cl^- to SO_4^{2-} ratio ($Cl:SO_4$) on the leaching pattern of $Pb(OH)_2$ and $PbCO_3$ species were negligible between the ratio of 0.4 to 0.6. At higher ratio, after a small drop, it increased dramatically (Fig. 2). However, there was no change in the removal of Pb^{2+} as $p\alpha_{Pb}$ with an increase in $Cl:SO_4$ from 0.4 to 0.9. In general, the variation in the formation and removal of Pb species in response to $Cl:SO_4$ was the same as were the changes in pH of the soil-water system. Hence, it appears that both the pH and $Cl:SO_4$ effects have been overshadowing each other. In the present study, SO_4^{2-} was the dominant anion which induced Pb^{2+} precipitation as $PbSO_4$ while passing through the soil system resulting in decreased concentration or increased $p\alpha[Pb(OH)_2]$ and $p\alpha[PbCO_3]$ in leachates. Olsen and Skogerboe (1975) reported precipitation of Pb^{2+} as $PbSO_4$ in a soil containing SO_4^{2-} ions. The activity of Lead as Pb^{2+} ion in leachates was the highest followed by that of $PbCO_3$ and $Pb(OH)_2$ (Fig. 3). Whereas, the activities of all the three forms of Pb^{2+} gradually decreased first from leachate L_1 to L_3 and then increased up to L_5 . This appears due to more interactions and addition of Pb^{2+} into soil. However, this aspect of Pb^{2+} with time needs more detailed and specific studies.

Fig. 2. Cl:SO₄ affects Pb species concentration in leachates

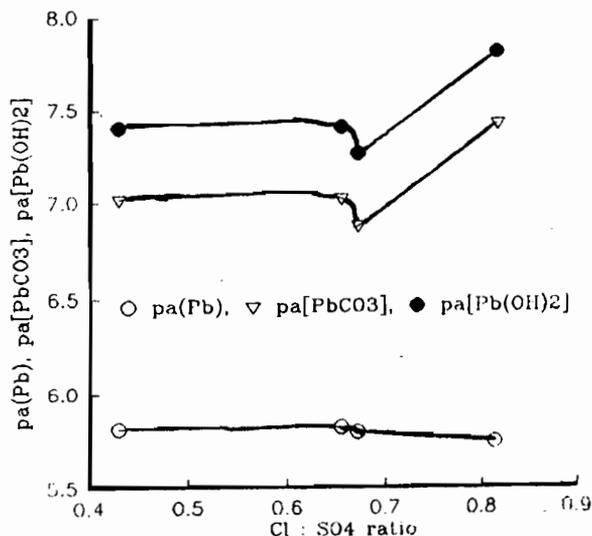
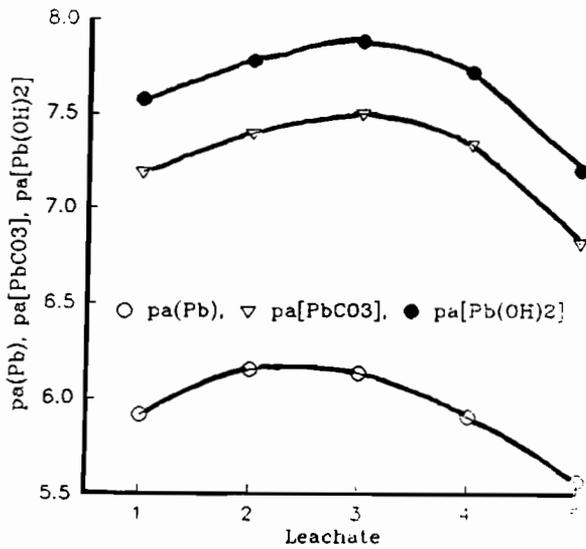


Fig. 3. Removal of Pb species in different leachates**CONCLUSIONS**

The removal in leachate remained highest as Pb^{2+} followed by $PbCO_3$ and $Pb(OH)_2$ as a function of pH, $Cl:SO_4$ and passage of time. The observation is of significance to decrease the Pb^{2+} contamination of the subsoil water by inducing the formation of $PbCO_3$ and $Pb(OH)_2$ compounds through appropriate/suitable chemical manipulation of the soil-water system.

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