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Lead Adsorption and pH Interactions in Brazilian Oxisols

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Abstract. Adsorption reactions in the mobility and availability of lead (Pb) in soils are important because of its potential for contamination of humans and animals. Considering the lack of information of this nature in variable charge soils, this paper aimed to study the chemical and physical properties of soils collected in five points the margin of a highway to analyze the reactions of these three soils at different pH values and four concentrations of lead, applied in the form of nitrate, and to correlate the properties of the soil and the results obtained. We analyzed different chemical and physical properties of soils and the levels of lead, before and after 60 days to start the experiment. The soils under study were classified as medium texture and clay and lead values found are within the range of natural levels in the soil. The interaction effects were only observed between the treatments containing higher doses of lead nitrate added and pH adjusted to 6.5.

Keywords: Adsorption, Lead, pH interactions, Oxisols.

1. Introduction

Lead (Pb) is a heavy metal potentially toxic to humans and animals. Therefore, its use tends to be restricted in order to minimize the risks from their accumulation in soils, water and air. The increasing use of land transport powered by fossil fuels has caused a significant increase in environmental pollution on land areas adjacent to roads. During the road's cycle life are produced by the materials used to build it and the movement of vehicles, compounds that may contaminate the environment [1]. The final fate of heavy metals is its accommodation and infiltration in soils and sediments. Heavy metals are often accumulate in the top soil layer and is then accessible to the roots of plants. The soil has a great capacity to retain heavy metals, however, if this capacity is exceeded, the metal availability in the middle penetrate the food chain of living organisms or are leached, jeopardizing the quality of the groundwater system [2]. The retention of these metals in soil can occur in different forms, being regulated mainly by specific adsorption phenomena (forming inner sphere complex, which are covalent bonds) or non-specific adsorption (resulting in outer sphere complex, which links are ionic) [3]. The understanding of the processes of adsorption and desorption of metals are essential to the remediation of contaminated areas, as well as prevention of future contamination [4]. Therefore, this study aimed to characterize the soils margins of a highway, located in the Brazil and the influence of four levels of lead and three different pH soil values.

2. Experimental Development

2.1. Methodology

Samples of the surface layer (0-20 cm) of Oxisols were collected in five equidistant points (A, B, C, D and E), along Route MG-050, located in Minas Gerais State, Brazil, chosen based on economic importance and size of the catchment area. These samples came from areas not known to be subject to intentional contamination with lead. We analyzed the levels of phosphorus (P), potassium (K^+), calcium (Ca^{2+}),

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magnesium (Mg^{2+}), aluminum (Al^{3+}), potential acidity (H+Al), exchange capacity effective cation (t), capacity cation exchange at pH 7.0 (T), percent aluminum saturation (m%), percent base saturation (V%), organic matter (OM), pH (measured in water) and texture. All analyzes were done according to international methodologies [5].

To evaluate the mechanism of specific adsorption on the retention of lead in these soils, we applied four doses (0, 50, 100 and 500 mg) of lead nitrate ($Pb(NO_3)_2$) for each pound of soil from every point of sampling. As the pH and the time provided directly influence the availability of chemical elements, the experiments were conducted on three soil pH values (4.5, 5.5 and 6.5) previously adjusted with calcium hydroxide ($Ca(OH)_2$) or hydrochloric acid (HCl). The research was conducted in a greenhouse, totaling 60 treatments, each one with 4.5 kg of soil in pots and placed in this location where the humidity was maintained at 60%. Prior to the experiment and after 60 days of incubation, the samples were analyzed for soil determine the quantities of lead adsorbed, using USEPA 3051B method. This method [6] use 1 g of soil digested with 10 mL of concentrated HNO_3 in open block digester during 10 minutes at 95 ± 5 °C. The samples were cooled and after the addition of another 5 mL of HNO_3 again brought to the digester heating block at 95 ± 5 ° C for 2 hours. They were then cooled and added to 2 mL of distilled water and 3 ml of H_2O_2 (30%). They were then conducted again to the block digester for another 2 hours at 95 ± 5 ° C. Subsequently, the samples were cooled and received 5 ml of HCl and 10 ml of distilled water were heated for 5 minutes at 95 ± 5 °C. The aliquots were filtered and analyzed by atomic absorption spectrophotometer. Finally, data were submitted to Tukey's statistical test using the SAS software.

2.2. Results and Discussion

The results of chemical analysis of soils and the total content of lead, before the start of the experiment are shown in Table 1.

Table 1: Chemical characterization and levels of lead in soil sampling points of the side of Route MG-050.

Point	pH	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	t	T	P	K	Pb	V	m
		---------------------- cmol dm^{-3} ----------------------						--- mg dm^{-3} ---		mg kg^{-1}	------- % -------	
A	6.1	10.7	0.7	0.0	1.9	11.6	13.5	3.2	67	38.64	86.2	0.0
B	6.2	2.9	1.3	0.0	2.3	4.4	6.7	1.1	73	29.18	65.3	0.0
C	5.9	2.7	0.5	0.3	1.7	3.6	5.0	1.7	64	27.24	66.6	8.3
D	6.1	5.1	1.1	0.0	2.1	6.4	8.5	3.2	92	36.44	75.6	0.0
E	6.6	9.6	16.1	0.0	1.5	26.1	27.5	1.1	131	21.97	94.6	0.0

Although Oxisols characterized by being acid soils, old, weathered, there were no detectable amounts of aluminum. Higher levels of pH, calcium and magnesium can be explained by the soil sampling sites were close to areas of limestone mining. The lead content are found within the range of natural soil levels normally found between 10-100 mg kg^{-1} [4,7,10].

The Figure 1 shows the texture analysis results. The soils of the points B, D and E were classified as "medium textured" soils. The point C soil was classified as "sandy soil" and Point A soil as the "clayey soil". Oxisols represent about 45.7% of the Brazil soils and are described as highly weathered, deep, non-hydromorphic, high clay content (between 50 and 80%) and low fertility [7]. The differences in texture, possibly explain the natural contents of lead higher at Point A because the metal tends to adsorb this fraction of the soil. The clay influences the adsorption of metals due to the presence of oxides of Fe and Al (gibbsite, goethite, Fe and Al oxides free and amorphous) in the clay fraction [8,9].

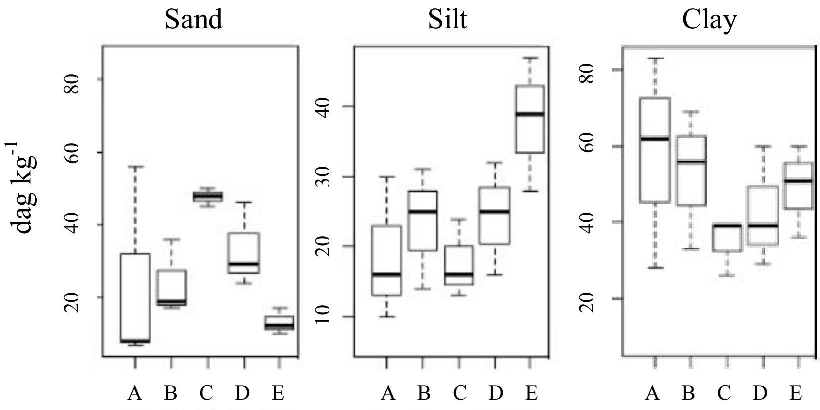

Fig. 1: Sand, silt and clay boxplot diagram in the five sample points (expressed in dag kg^{-1}).

Irrespective of point, Table 2 shows the average values found for each of the lead amount of lead added, pH and Tukey’s statistical test.

Table 2: Results and statistical analysis of the amount of Pb and pH found.

Doses of Pb added (mg kg^{-1})	Pb average found (mg kg^{-1})	Tukey’s statistical test	pH adjusted	Pb average found (mg kg^{-1})	Tukey’s statistical test
0	42.22	c			
50	180.84	cb	4.5	440.25	a
100	276.77	b	5.5	513.96	a
500	1498.57	a	6.5	544.59	a

Note: Means followed by the same letter do not differ by Tukey’s statistical test at 5% level.

Statistical differences were observed only among the treatments that received different doses of lead. Separately, there was no influence of pH on the amounts of lead adsorbed by soil. The highest values of lead found in the zero dose in relation to those found before the experiment are due to pH changes that increased the availability of lead. Table 3 shows the effect of the interaction between pH and different amounts of added lead.

Table 3. Mean values (expressed in mg kg^{-1}) and Tukey's statistical test of the interaction effects between pH and the levels of Pb.

Dose of Pb added	pH 4.5	Tukey’s statistical test	pH 5.5	Tukey’s statistical test	pH 6.5	Tukey’s statistical test
0	41.04	b	34.92	b	50.68	b
50	182.49	b	171.74	b	188.31	b
100	317.69	b	219.85	b	292.77	b
500	1219.75	a	1629.35	a	1646.60	a

Note: Means followed by the same letter do not differ by Tukey’s statistical test at 5% level.

Although the quantities of lead are adsorbed increased as the pH increased, it was observed that the interaction effects occurred only the dose of 500 mg kg^{-1} of lead nitrate. This shows that these soils, pH influence the adsorption of lead only in higher doses. From the results, the formulated following regression equation:

$$Y = -2650 + 2.94 * DOSE + 52.2 * pH$$

where Y is the lead content in the soil samples (mg kg^{-1}), DOSE corresponds to levels of lead which have been added (0, 50, 100 or 500 mg kg^{-1}) e pH corresponds to the three pH values studied (4.5, 5.5 or 6.5). The high value of R2 (0.86) indicates a strong correlation between the values added to the vessels and between the adsorbed amounts, assigning a secondary role to the pH in smaller doses. Other authors papers [10,11] corroborate the results found in this study.

3. Conclusions

The analysis of soils collected in five points the margin of Route MG-050 showed no signs of lead poisoning. The chemical characterization showed no abnormalities and small chemical variations in the attributes analyzed can be attributed to variations in texture and pH. When these soils were subjected to different pH values and levels of lead, applied in the form of nitrate, their interactions are expressed only in higher doses.

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