

Majors Soil Classes of the Metropolitan Region of Curitiba (PR), Brazil: II - Interaction of Pb with Mineral and Organic Constituents

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ABSTRACT

The interaction between heavy metals and soil constituents is one of the most important factors influencing the potential for ground water pollution. To study Pb behavior, samples of soils were incubated with a salt solution containing this metal. The experimental units consisted of plastic bags, partially opened with 0.1 dm³ of soil with three replications. After incubation, samples were subjected to sequential and selective extractions. Lead retention, measured by the maximum adsorption capacity of the soil, was relatively high with values ranging from 6,439 to 22,148 mg kg⁻¹. The sequential and selective extractions showed that Pb adsorption was stable where the metal was found mainly in organic matter, Fe and Al oxides, and residual forms (specific adsorption). The capacity of the soils to retain Pb, thereby increasing the leaching potential of the metal, was in the sequence of: Histosol - Oxisol - Inceptisol.

Key words: Humic fraction, Fe and Al oxides, sequential extraction procedure, specific adsorption

INTRODUCTION

Major aspects of soil pollution by heavy metals are related to accumulation and transport processes. When chemical elements are applied to soil, they can reach soil solution and follow distinct pathways (i.e., adsorbed to particles of the solid phase, be complexed, form precipitants, leached or absorbed by the plants; Sposito, 1984). These processes are influenced by soil chemical, physical, and mineralogical characteristics. The study of the heavy metal reactions with soil constituents is mainly related to adsorption. This is a key factor influencing soil capacity to remove them from soil solution thereby making the heavy

metals unavailable to plants and minimizing ground water contamination.

Metal-soil solid phase interaction occurs through electric charges present on the secondary minerals and on the humic components, and varies with the considered constituent type. Metal adsorption in 1:1 clay mineral can take place at O²⁻ and OH⁻ sites on the external surface or at the broken edges of the mineral (Swift and McLaren, 1991). Similarly, the adsorption on the oxides, hydroxides and oxyhydroxides of Fe and Al can happen through electrostatic forces or through bonds with a high covalent character (specific adsorption) (Naidu et al, 1998). Furthermore, the non-specific adsorption or electrostatic interaction (common

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with 2:1 secondary minerals, such as montmorillonite) involves lower energy which facilitates metal exchange by other polyvalent cations thus enhancing the risk of groundwater pollution.

Metal-organic complexes play a major role in metal reactions in the superficial horizons of the soil profile. Carboxylic and phenolic groups are present in large numbers in humic and fulvic acids and involve high energy bonds (Harter and Naidu, 1995). In addition, organic compounds are directly related to acidification processes, complexation, precipitation, and oxi-reduction reactions, influencing heavy metal solubility and stability in the soil.

Like clay mineralogy and organic matter content, soil pH also has a large influence on the adsorption and mobility of heavy metals which can affect the concentration of these elements in soil solution (King, 1988). Elliott et al. (1986) postulated that under acid conditions, the adsorption phenomenon dictates Pb bioavailability, while solubility, precipitation and complexation control bioavailability under neutral or alkaline conditions. The acidity influence can vary among metals and the pH of maximum adsorption is related to the constant of the first product from metals hydrolyzed (Schwertmann and Taylor, 1989). Thus, hydrolyzed Pb is more adsorbed than the free ion. In addition, Pb can form compounds with chlorite, sulfate, sulfite, and phosphate. Santillan-Medrano and Juriank (1975) observed that in lime soils, $PbCO_3$ probably controls Pb solubility, while in non-lime soils, its solubility was dominated by $Pb(OH)_{2(s)}$, $Pb_3(PO_4)_{2(s)}$, $Pb_4O(PO_4)_{2(s)}$ and $Pb_5(PO_4)_3OH_{(s)}$ species.

The objective of this study was to investigate Pb interaction with organic and mineral constituents of samples collected from major soils classes located in the metropolitan region of Curitiba, Paraná State. A further objective of this study was to define the susceptibility of these soils to Pb pollution and potential ground water contamination.

MATERIALS AND METHODS

The studied area was in the metropolitan region of Curitiba city – Parana State, located in Southern Brazil. This region, known as the First Paranaense Plateau, is located between the Serra do Mar Mountain and Devoniana Cliff in the hydrographic

basin of Alto Iguaçu River; the area has an average altitude of 920 m (IPPUC, 1991). The regional geologic formation, dating from the Quaternary Period, formed by fluvial sediments is called the Guabirota Formation (Bigarella and Salamuni, 1962). This formation consists of poorly consolidated sediments such as claystones and sandstones (Salamuni and Stellfeld, 2001). In general, the Guabirota Formation gave rise to the clayey soils, with occurrence of expansive clays, but with contributions of the silt and sandy fractions (Santos, 2002).

The most common soils observed in the metropolitan region are Cambisol. This soil class comprise around 60 % total area, followed by Latosol (17%), and Organosol (10.5%) (EMBRAPA, 1984, 1999). Three soil profiles representing these major soil classes were selected at Experimental Farm of Canguiri (Federal University of Paraná) located in the Pinhais city (PR) (UTM 688000 west, 719000 south, zone number 22). Soil samples were collected from each soil profile (Histosol – H horizon, Oxisol – A and B horizons and Inceptisol – A, B and C horizons). (Table 1), air dried and split into two parts. The first portion was sieved (2 mm) and used for general soil characterization (physical and chemical properties) and to determine the maximum adsorption capacity of Pb (MAC). The second portion was sieved (3.6 mm) and incubated in a $Pb(NO_3)_2$ solution which was subjected to fractionated extraction methods for heavy metals.

The physical analyses of the soils consisted of particle-size, using the pipette method (EMBRAPA, 1997), and field capacity, using the funnel method (Jorgensen, 1995). Soil chemical characterization (i.e., pH, exchangeable base content, and potential acidity) was done as described by Pavan et al. (1992).

The MAC was determined at a controlled pH of 5.5 to assure higher Pb adsorption; 0.3 g of soil was placed in a centrifuge tube with 20 mL of 5 mmol L⁻¹ $Ca(NO_3)_2$ solution (Pierangeli, 1999). The pH was adjusted to 5.5 (if necessary) by adding 7 mmol L⁻¹ $Ca(OH)_2$ or 7 mmol L⁻¹ HNO_3 solutions. Then a solution of 0.45 mmol L⁻¹ $Pb(NO_3)_2$ was added to each tube (prepared in 5 mmol L⁻¹ $Ca(NO_3)_2$) to bring the final volume to 30 mL. The tube was sealed and subjected to 12h cycles of shaking and resting for 72h. The solutions were then centrifuged until the supernatant liquid was completely clear. The supernatant was analyzed for Pb using an atomic

absorption spectrophotometer. This process was repeated (8 times) with the remaining content of the tubes until the adsorption was lower than 2% on average (Pierangeli, 1999). The amount of Pb adsorbed was calculated as the difference between the added Pb and what was remaining in solution after equilibrium. The MAC was determined by summing these contents. Total soil Pb content was determined by HF, HNO₃, H₂SO₄, and HClO₄ extraction as described by Lim and Jackson (1986). The second part of experiment was designed to establish the soil forms of Pb. The experiment was conducted under greenhouse conditions. Experimental units consisted of partially opened plastic bags with 0.1 dm³ of soil arranged in a completely randomized design with three replicates. Each sample received an equivalent rate of 40% of its MAC (Table 1) that had been previously determined in the first part of the experiment. The 3.6 mm sieved soil sample bags received Pb(NO₃)₂ applied as a solution and were incubated for 60 days (Gomes et al. 1997). During the incubation period, the sample moisture was maintained between 80 and 100% of field capacity to favor the process of metal diffusion in the soils. After incubation, the samples were dried, homogenized, and sieved (2 mm). To study the reaction of Pb with soil constituents, the selective and sequential chemical extractions procedures proposed by Mann and Ritchie (1993) and Gomes et al. (1997) (Fig. 1) were used.

The mineralogical analyses data (reported by Pires, 2004), soil granulometry and chemical determinations were submitted to statistics analyses using simple correlations (Pearson) with the SPSS program for Windows 10.0. The following significance levels for *r* values were used: *, significant at the 0.05 probability level; **, significant at the 0.01 probability level and; ***, significant at the 0.001 probability level.

Table 1 - Rates of Pb applied in six soil samples from metropolitan area of Curitiba city - Paraná State - Brazil¹

| Sample No. | Brazilian classification | U.S. Taxonomy ² | Horizon | Sample depth | Pb |
|------------|--------------------------|----------------------------|---------|--------------|---------------------|
| | | | | cm | mg kg ⁻¹ |
| 1 | Organosol | Histosol | H | 0-60 | 6,957 |
| 2 | Latosol | Oxisol | A | 0-30 | 3,356 |
| 3 | Latosol | Oxisol | Bw | 30-220 | 2,704 |
| 4 | Cambisol | Inceptisol | A | 0-34 | 3,201 |
| 5 | Cambisol | Inceptisol | Bi | 34-99 | 3,088 |
| 6 | Cambisol | Inceptisol | C | 99-200 | 3,007 |

¹ Dose of metal corresponding to 40% of the maximum adsorption capacity.

² Approximate correlation with U.S. Soil Taxonomy.

RESULTS AND DISCUSSION

General soil characteristics

Some physiochemical soil parameters (i.e., total organic carbon, clay content and CEC) which reflect soil heavy metals adsorption capacity are shown at Table 2. All soils were acid with pH ranging from 4.3 to 5.4. It is well established that, at this pH range, adsorption is the most important metal reaction occurring in the soil (Elliot et al., 1986). As a result of low soil pH, Al saturation was high, especially for the Histosol and Inceptisol (i.e., values above 50%). Exchangeable Al content was clearly influenced by the weathering process (Table 2). The most intensely weathered samples (Oxisol - A and B horizons and Inceptisol - A horizon) had lower values compared to other samples; Pires (2004) suggested that weathering favored gibbsite formation.

The superficial negative charges associated with the humic fraction of the Histosol increased the CEC to values somewhat comparable to the Inceptisol (Table 2). Also, the organic matter influence was observed within the Oxisol profile, where there was a marked decrease in total CEC from the A to B horizon.

The high activity of the clay fraction (T values) derived from the Guabirotuba Claystone Formation was observed in the C horizon of the Inceptisol (Table 2). This could be associated with the presence of 2:1 clay minerals (vermiculite and smectite). Working with the same soil types, Pires (2004) found (in all horizons) hydroxy-interlayered vermiculite (HIV) as well as vermiculite in separated phases in the B and C horizons of the Inceptisol.

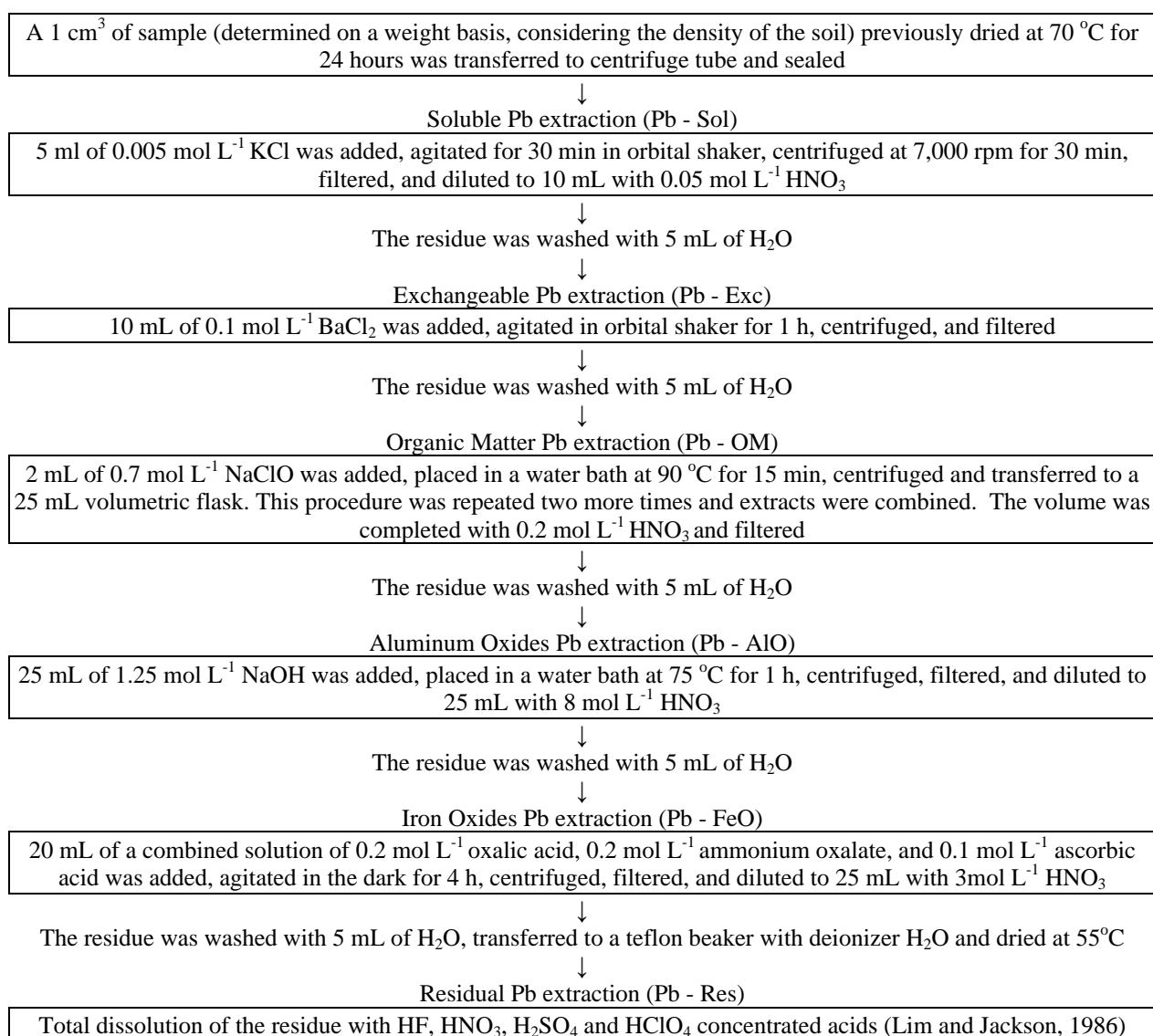


Figure 1 - Sequential and selective extraction of Pb in the soil.

Pires (2004) observed the predominance of kaolinite in the clay fraction of the soils (contents above 700 g kg^{-1}), followed by gibbsite, goethite, hematite, and amorphous Fe and Al oxides. Further, Lima et al. (1997) and Boszczowski (2001), working in soils from the Metropolitan Region of Curitiba, found that kaolinite was also the most abundant clay mineral. The transformation of minerals with high CEC (2:1 minerals) into minerals with low CEC (kaolinite and Fe and Al oxides), as a consequence of weathering, resulted in lower values of cation exchange capacity in Oxisol samples compared to the Inceptisol samples (Table 2).

Pb maximum adsorption capacity of the soil (MAC)

Due to the low native Pb content of the soils (Table 3), there was no significant interference in the determination of the MAC. Another important factor is that a major portion of total Pb is found in the mineral structure and thus out of the soil sorption complex. The MAC values for Pb varied widely from 6,439 to 22,148 mg kg^{-1} (Table 3). These results were similar to those found in USA soils (Zimdahl and Skogerboe, 1977; Harter, 1979); these reports found values of Pb MAC ranging from 3,108 to 29,008 mg kg^{-1} and 1,450 to

52,629 mg kg⁻¹, respectively. The ranges are also comparable to 2,115 to 19,465 mg kg⁻¹ for Brazilian soils reported by Pierangeli (1999). The wide variation in Pb MAC was expected and can

be explained by the large differences in soil chemical and mineralogical properties.

Table 2 - Chemical and granulometric analysis of six soil samples from metropolitan area of Curitiba city - Paraná State - Brazil¹

| Sample No | U.S. Taxonomy | Horizon | pH H ₂ O | Al ⁺³ | H + Al | Mg ⁺² | Ca ⁺² | K ⁺ | Effective CEC | Total CEC |
|-----------|---------------|---------|---------------------|------------------|--------|------------------|------------------|----------------|---------------|-----------|
| | | | | | | | | | | |
| 1 | Histosol | H | 4.3 | 6.5 | 26.8 | 0.3 | 0.8 | 0.1 | 7.7 | 27.9 |
| 2 | Oxisol | A | 4.9 | 1.4 | 10.5 | 0.7 | 1.7 | 0.1 | 3.9 | 13.0 |
| 3 | Oxisol | Bw | 5.3 | 0.5 | 5.0 | 0.3 | 0.6 | 0.0 | 1.4 | 5.9 |
| 4 | Inceptisol | A | 5.2 | 2.5 | 13.1 | 1.2 | 2.0 | 0.1 | 5.8 | 16.4 |
| 5 | Inceptisol | Bi | 5.1 | 5.9 | 19.0 | 0.3 | 0.5 | 0.1 | 6.8 | 19.9 |
| 6 | Inceptisol | C | 5.4 | 11.7 | 25.6 | 0.8 | 1.1 | 0.2 | 13.8 | 27.7 |

| Sample No | U.S. Taxonomy | Horizon | V | m | T | Organic Carbon | Clay | Silt | Sand |
|-----------|---------------|---------|------|------|------|----------------|------|------|------|
| | | | | | | | | | |
| 1 | Histosol | H | 4.1 | 85.2 | 41.7 | 93.6 | 669 | 252 | 79 |
| 2 | Oxisol | A | 19.2 | 36.0 | 28.4 | 27.5 | 457 | 221 | 322 |
| 3 | Oxisol | Bw | 15.1 | 36.0 | 9.8 | 5.7 | 604 | 174 | 222 |
| 4 | Inceptisol | A | 20.1 | 43.2 | 27.2 | 35.3 | 602 | 90 | 308 |
| 5 | Inceptisol | Bi | 4.4 | 87.0 | 40.7 | 8.8 | 488 | 257 | 255 |
| 6 | Inceptisol | C | 7.5 | 85.0 | 77.8 | 3.9 | 356 | 418 | 226 |

¹Chemical characteristics determined according methodologies propose by Pavan et al. (1992). Calculations according to EMBRAPA (1999): effective CEC = Ca²⁺ + Mg²⁺ + K⁺ + Al³⁺; total CEC or CEC determined on pH 7,0 = Ca²⁺ + Mg²⁺ + K⁺ + Al³⁺ + H⁺; V (bases saturation) = (Ca²⁺ + Mg²⁺ + K⁺)x100/ total CEC; m (aluminum saturation) = Al³⁺x100/effective CEC; T (clay fraction activity) = total CEC x100 /clay content.

Soil organic carbon strongly influenced Pb MAC since a strong correlation was found between these two factors ($r = 0.96^{***}$); this confirms a high affinity of this metal for the humic fraction components (Malavolta, 1967; Abd-Elfattah and Wada, 1981; Gomes et al., 1997). As a result of soil organic matter variation, the highest Pb MAC was observed in the H horizon of the Histosol and its values decreased with depth in the other soil classes (Table 3).

In relation to the clay fraction mineralogy (Pires, 2004), a strong relationship between kaolinite content and Pb adsorption capacity was observed ($r=0.80^*$). This suggested a high kaolinite influence on the soil chemical properties since it is the most abundant mineral in the clay fraction of the studied soils. However, despite crystalline Fe and Al oxides being recognized as major influences on metal adsorption phenomena (Pierangeli, 1999; Fontes et al., 2001), nether Al oxides (gibbsite) nor Fe oxides (hematite and goethite) were related to Pb MAC.

However, our results showed enhanced metal adsorption with diminishing oxide crystallinity, since the Fe₂O₃-AO/Fe₂O₃-DCB ratio [AO -

amorphous Fe and Al oxides extraction with 0,2 mol L⁻¹ ammonium oxalate (McKeague, 1978)/DCB - crystalline Fe oxides extraction with dithionite-citrate-bicarbonate (Mehra and Jackson, 1960)], an indication of the degree of crystallinity, was highly correlated with Pb MAC ($r=0.99^{***}$). The relationship observed can be explained by the increase in surface area and number of adsorption sites with diminishing mineral crystallinity (McKeague, 1978).

Another parameter which confirms the inverse relation between mineral crystallinity and metal adsorption was the width at half maximum height (WHH) of the (111) goethite reflection and Pb MAC ($r = 0.90^*$). According Fitzpatrick and Schwertmann (1982), lower goethite crystallinity (which has higher WHH values) corresponds directly to higher specific surface and, consequently, higher metal adsorption.

Pb content obtained from sequential extractions

Higher pollution risks of groundwater are associated with Pb in the soil solution and with the predominance of non-specific sites of adsorption

(exchangeable fraction). These sites are mainly present in the 2:1 clay minerals. The soluble Pb content (soil solution) varied from 140.9 to 613.1 $\mu\text{g cm}^{-3}$ (Table 4). The most

pronounced effect of clay mineralogy was an inverse relation between Pb solution content and Gt specific surface ($r = -0.94^{**}$).

Table 3 - Maximum adsorption capacity and total contents of Pb under natural conditions from six soil samples from the metropolitan area of Curitiba city - Paraná State - Brazil

| Sample No | U.S. Taxonomy | Horizon | Natural total content | Maximum adsorption capacity |
|-----------|---------------|---------|-----------------------|-----------------------------|
| | | | | mg kg^{-1} |
| 1 | Histosol | H | 2.1 | 22,148 |
| 2 | Oxisol | A | 0.6 | 8,420 |
| 3 | Oxisol | Bw | 1.1 | 7,248 |
| 4 | Inceptisol | A | 1.2 | 8,286 |
| 5 | Inceptisol | Bi | 0.8 | 7,041 |
| 6 | Inceptisol | C | 0.6 | 6,439 |

The relatively high Pb content in soil solution (even at the 40% soil MAC rate – Table 1) may be attributed to the differences in the experimental conditions of the two determinations (i.e., MAC and Pb incubation for sequential extractions). The MAC was obtained under buffered conditions of soil pH (5.5); whereas, the soil incubation with Pb solution was done under natural soil pH values (4.3 to 5.4 - Table 2) which can diminish the negative charge formation from pH dependent sites on colloid surfaces. Furthermore, the equilibrium solution with high Pb concentration was renewed 8 times during MAC determination. The successive addition and removal of solution provided cations replacement on the colloid by for Pb, then the cations were removed with the solution. The application of a lower rate of Pb (40 % of the MAC) once without leaching (Pb incubation), resulted in a higher competition between the Pb and the soil cations (especially given the high natural Al^{3+} content; Table 2).

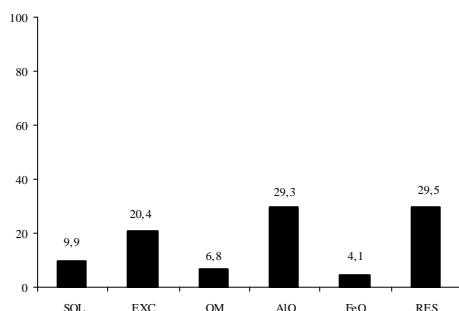
In the exchangeable Pb fraction (Pb-Exc – Fig. 1), the metal content ranged from 468 $\mu\text{g cm}^{-3}$ (Oxisol B horizon) to 1,086 $\mu\text{g cm}^{-3}$ (Histosol H horizon - Table 4). The Pb-Exc was also high in the C horizon of the Inceptisol (1,045 $\mu\text{g cm}^{-3}$). As a result, there was a high correlation between the Pb-Exc and clay fraction activity and total CEC ($r = 0.82^*$ and 0.99^{***} , respectively). The Pb-Exc content increased with sample depth for the Inceptisol (Table 4) since the inferior horizons were less weathered and had higher total CEC values (Table 2), associated with the presence of vermiculite (Pires, 2004). Combined values of Pb in soil solution and exchangeable forms indicated values close to 30 % for the A horizon and 40 to 50 % for the B and C horizons (Fig. 2); this can be interpreted as a higher susceptibility of the subsuperficial horizons (vs. the A horizon) to soil contamination and potential metal loss by leaching.

Table 4 - Contents of Pb extracted by sequential treatments of six soil samples from the metropolitan area of Curitiba city - Paraná State - Brazil (after incubation)¹

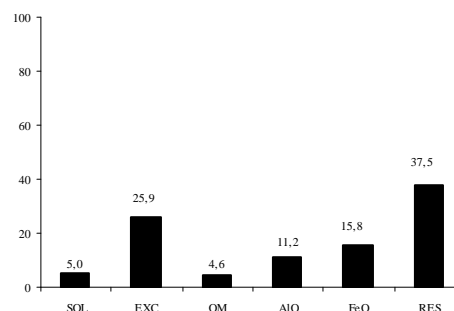
| Sample No | U.S. Taxonomy | Horizon | Soluble | Exchange | Organic matter | Aluminum oxides | Iron oxides | Residual |
|-----------|---------------|---------|---------|----------|----------------|-----------------|-------------|----------|
| | | | | | | | | |
| 1 | Histosol | H | 525.0 | 1,086.0 | 362.7 | 1,562.7 | 217.0 | 1,571.9 |
| 2 | Oxisol | A | 291.2 | 621.2 | 66.1 | 259.3 | 590.2 | 1,067.4 |
| 3 | Oxisol | B | 613.1 | 468.0 | 13.4 | 103.8 | 646.7 | 765.0 |
| 4 | Inceptisol | A | 140.9 | 730.8 | 130.8 | 316.3 | 446.5 | 1,062.3 |
| 5 | Inceptisol | B | 234.4 | 863.4 | 12.9 | 118.1 | 537.5 | 508.6 |
| 6 | Inceptisol | C | 468.0 | 1,044.7 | 1.3 | 45.0 | 664.4 | 581.4 |

¹Using sequential extraction methods as described by Mann and Ritchie (1993) and Gomes et al. (1997).

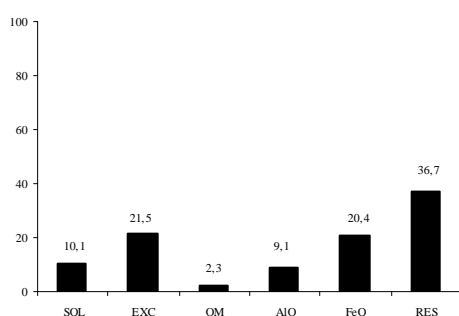
(a) H Horizon – Histosol



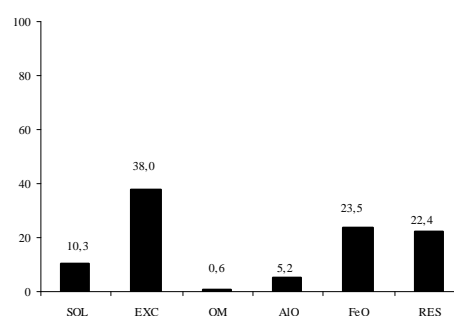
(d) A Horizon – Inceptisol



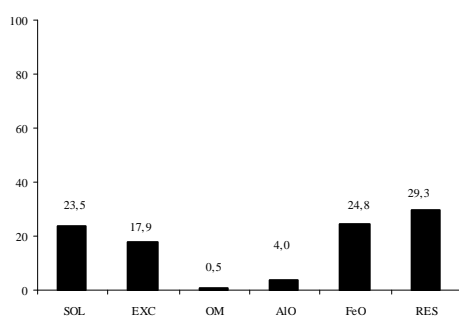
(b) A Horizon – Oxisol



(e) B Horizon – Inceptisol



(c) B Horizon – Oxisol



(f) C Horizon – Inceptisol

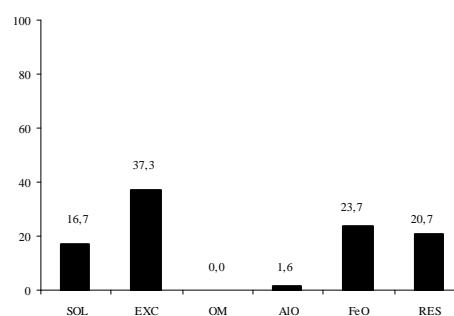


Figure 2 - Relative contribution (percentage) of soluble (Sol), exchangeable (Exc), organic matter (OM), Al oxides (AlO), Fe oxides (FeO) and residual (Res) forms to total Pb extracted in the sequential soil sample analyses.

As expected, more Pb was extracted by NaClO (Pb - organic matter) from the Histosol and from the A horizon of the Oxisol and Inceptisol (Table 4) due to the abundance of organic matter (r between Pb-OM and organic carbon content = 0.99^{***}). However, the general contribution of organic matter to Pb soil forms was low with a maximum value of 6.8 % for the Histosol (Fig. 2).

The highest Pb - Al oxides (Pb-AlO) were observed in the Histosol H horizon (Table 4) and can be attributed to the higher concentrations of amorphous Al minerals under hydromorphic conditions (Wowk, 2003; Pires, 2004).

Ammonium oxalate and oxalic acid extractors were applied to the sequential extraction (Fig. 1), mainly, for Pb bonded in amorphous Fe and Mn

oxides removal through complexation reactions (Shuman, 1985). The correlation between the Pb - Fe oxides (Pb-FeO) and the organic carbon content ($r=0.94^{**}$) and between Pb-FeO and Pb-OM ($r=-0.82^*$), indicates competition between organic matter and Fe oxides for the metal adsorption.

The Pb forms which were resistant to all previous extractions were determined by sample total digestion (Pb - Residual). There are several possible Pb sources in this residue. Pb could be inherited from the parent material found in the silicate minerals' structure and Fe and Al oxides in the different soil fractions. Another source is Pb strongly adsorbed to the humic fraction and crystalline Fe and Al oxides; the extraction of these was only partial due to the nature of the treatments used (Fig. 1). For example, the complete extraction of Fe oxides can only be obtained by use of a stronger reducing agent as in the dithionite-citrate-bicarbonate method (DCB). A further source is Pb adsorbed specifically to the hydroxyl edge of the kaolinite octahedral sheet. In the sequential analysis proposed by Mann and Ritchie (1993) and Gomes et al. (1997), there was no specific method for this mineral extraction.

The Pb residual was the most abundant form in four of the six samples. This may indicate a fast transformation of the incubated metal into a stable form. Since there was significant correlation between Pb-Res and organic carbon content ($r=0.94^{**}$), a major portion of the residual fraction (Pb-Res) probably originated from the humic fraction which was resistant to NaClO extraction. In addition, the highest concentrations of Pb-Res were observed in the H horizon of the Histosol, and the A horizons of the Oxisol and Inceptisol (Table 4). Furthermore, the low solubility forms (Pb-AlO, Pb-FeO and Pb residual) represented more than 60 % of the total Pb in the surface horizon (Fig. 2), showing the importance of stable forms of Pb. In general, the Pb adsorption in the Oxisol was more stable than that of the Inceptisol.

CONCLUSIONS

1. The Pb retention (measured as the maximum adsorption capacity of the soil - MAC) was relatively high, with values ranging from 6,439 to 22,148 mg kg⁻¹, and defined by organic matter and amorphous Fe and Al oxide contents.
2. The sequential and selective extractions indicated that Pb adsorption was stable since the

metal was found mainly in organic matter, Fe and Al oxides, and residual forms (specific adsorption) with low exchangeable contents.

3. The capacity of the soils to retain Pb was in the decreasing sequence of: Histosol - Oxisol - Inceptisol, thereby increasing the leaching potential of the metal. Although this study added to what the MAC and Pb sequential extractions are important to identify the soil fragility, more work that takes into account other soil morphological, physical, and chemical aspects is needed to properly define the potential for heavy metal ground water pollution.

RESUMO

A interação entre os metais pesados e os constituintes orgânicos e minerais do solo é um dos fatores mais importantes para definir o potencial de contaminação das águas subterrâneas. Para estudar o comportamento do Pb em solos da região metropolitana de Curitiba, estado do Paraná, amostras das classes Organossolo, Latossolo e Cambissolo foram submetidas a análises físicas e químicas, e incubadas com soluções de sais desse metal. A dosagem utilizada correspondeu a 40% da Capacidade Máxima de Adsorção de Pb do solo (CMA). O ensaio foi conduzido na Universidade Federal do Paraná, em condições de casa de vegetação, no período de 29 de outubro a 29 de dezembro de 2003. O delineamento experimental foi em blocos ao acaso, com três repetições e as unidades experimentais corresponderam a sacos plásticos parcialmente abertos com 0,1 dm³ de solo. Após o período de incubação (60 dias), as amostras foram submetidas a extrações sequenciais e seletivas, na seguinte ordem: 1) KCl 0,005 mol L⁻¹; 2) BaCl₂ 0,1 mol L⁻¹; 3) NaClO 0,7 mol L⁻¹; 4) NaOH 1,25 mol L⁻¹; 5) ácido oxálico 0,2 mol L⁻¹, oxalato de amônio 0,2 mol L⁻¹ e ácido ascórbico 0,1 mol L⁻¹; 6) ácidos fluorídrico, nítrico, sulfúrico e perclórico concentrados. O teor de Pb foi determinado por espectrofotometria de absorção atômica. A adsorção de Pb, estimada pela CMA, foi alta, com valores entre 6.439 a 22.148 mg kg⁻¹, influenciada, principalmente, pelos teores de matéria orgânica e óxidos de Fe e Al de baixa cristalinidade no solo. As extrações sequenciais e seletivas evidenciaram que a adsorção de Pb foi estável, onde o metal foi encontrado principalmente associado à matéria orgânica, óxidos de Fe e Al e ao resíduo dos

tratamentos (adsorção específica). Verificou-se a seguinte ordem decrescente da capacidade dos solos em adsorver Pb, aumentando o potencial de lixiviação do metal: Organossolo - Latossolo - Cambissolo. Contudo, adicionalmente à CMA e distribuição do Pb nos diferentes constituintes do solo, para definir a fragilidade dos mesmos à poluição por metais pesados, são necessários estudos complementares, destacando-se aspectos morfológicos (profundidade do solo, altura do nível freático, porosidade, etc.), físicos (compactação, velocidade de infiltração da água, etc.) e químicos (reações de precipitação, complexação, etc.).

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