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Lead in Soils in Paint Contaminated Residential Sites at San Antonio, Texas, and Baltimore, Maryland

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Lead (Pb) is a toxic metal that can be harmful to humans when ingested or inhaled, particularly to children under the age of six. Lead poisoning can cause a number of adverse human health effects, but is particularly detrimental to the development of children (USEPA, 2005). Lead induces a multitude of physiological, biochemical, and behavioral dysfunctions. The greater absorptive capacity of the gastrointestinal tracts of children puts them at much higher risk than the adults (ATSDR, 2000). Soil ingestion by hand-to-mouth activity (i.e., geophagia) is a major source of lead exposure to children. Primary sources of Pb pollution in soils include industrial activities, vehicular emissions, coal burning, refuse incineration, pesticide applications, and paints applied to structural surfaces (Alloway and Ayres, 1997). Lead in paints is the principal source of human exposure to environmental Pb in the U.S. (ATSDR, 2000). Despite efforts made to reduce residential exposure to Pb (including setting a maximum allowable Pb content in paint of 0.06% in 1977), there exists a significant number of housing facilities in every city in the U.S. that were built prior to the implementation of that policy.

San Antonio is 8th largest city in the U.S. with over 50% of the houses built before 1950. There are 340,532 pre-1978 housing units in San Antonio, accounting for 57% of the total housing units in the city (U.S. Census, 2000). Baltimore is another large metropolis with severe environmental Pb problems, with a Pb poisoning rate four times the national average (Rioux, 2001). The number of houses built prior to the 1950's in Baltimore is close to 530,000. The likelihood of Pb contamination in the yards of these homes from Pb paint is 95%. Approximately, an estimated 976,000 homes were built in between 1950-1978, with 75% of these homes with likely Pb-based paint (Rioux, 2001). Children living in these houses are at the greatest risk of exposure, as crawling on the ground and playing in the backyards can result in ingestion and inhalation of soil- and dust-borne lead (USEPA, 2001). Because Pb is highly immobile in soils, concerns about chronic human exposure to soils persist to date, despite the fact that the use of Pb-based paints was banned 25 years ago (Finster et al., 2003). Several investigations have found that natural and anthropogenic factors, such as weathering, chipping, scraping, sanding and sand blasting of painted pre-1978 structures induce human exposure to Pb via soils (Gulson et al., 1995).

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Soil Pb cleanup is traditionally done by soil removal for off-site disposal, which is extremely expensive and rather impractical for cleaning up residential properties. As a result, *in-situ* biological remediation techniques, such as phytoremediation is becoming popular in recent years. The technique is environment-friendly, inexpensive, and visually unobtrusive. However, effective remediation of Pb-contaminated residential soils using a specific plant system is an immensely complex task, whose success depends on a multitude of factors that includes the nature and extent of metal contamination, soil chemistry, metal availability, and the ability of the target plant to uptake the Pb from the soil (Datta and Sarkar, 2004).

Success of phytoremediation depends, in addition to total concentrations of soil Pb, on a thorough understanding of the physical and chemical properties of the soil. The primary objective of this work was to establish the soil Pb levels in contaminated residential sites of San Antonio, TX; and Baltimore, MD. The secondary objective was to assess certain important soil physico-chemical properties like soil pH, carbonate level, and clay content of these soils that need to be understood prior to the developing a phytoremediation strategy.

MATERIALS AND METHODS

Ten residential sites built prior to 1978 in each location (San Antonio, TX; and Baltimore, MD), all with lead-based paint contamination were selected. For each site, 3 composite soil samples were collected from the sides of the houses, which are likely to have the highest Pb concentration. Each composite soil sample was a mixture of 4 samples taken at a depth of 0 to 6 inches from 4 locations within each housing unit. Handling of the soil samples followed the 1981 EPA/CE-81-1 protocol (Plumb, 1981). Soils were air dried, disaggregated with gentle grinding using a mortar and pestle, and sieved to provide a fraction < 2mm.

Total Pb in the soils was determined using EPA Method 3050B (USEPA, 1996). Soils were extracted with Mehlich- 3 extractant solution in a 1: 8 soil: extractant ratio and were analyzed to estimate plant-available Pb concentrations (Mehlich, 1984). A Perkin Elmer Elan 9000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used for Pb determination. Soil pH was measured in water at a soil/water ratio of 1:1 (Sparks, 1996) using a pH/ion/conductivity/°C meter (Oakton Ion 510 Series, OAKTON Instruments, Vernon Hills, IL). Particle-size composition of each soil sample was determined using the pipette method (Sparks, 1996). Gravimetric Method for loss of carbon dioxide was used to determine the carbonate content in soils (Sparks, 1996).

Soil analyses were carried out in triplicate. Recoveries of 90 - 110% of spikes and external standards were considered acceptable. Repetitive or additional measurements of soil pH, clay and carbonate content, and soil Pb levels on all soils were performed following the established laboratory QA/QC procedures. Statistical analyses (descriptive statistics) were performed using JMP IN 5.1 (SAS Inc., USA). Treatment means were statistically differentiated using a student-t test at the $p < 0.05$ level.

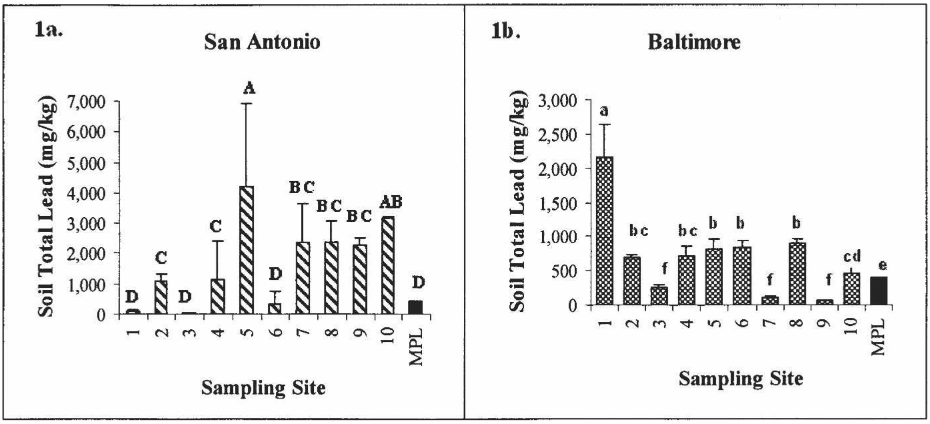

Figure 1. Total soil Pb concentrations in paint contaminated housing sites in: a) San Antonio, TX; and b) Baltimore City, MD. MPL indicates the maximum permissible Pb level (400 mg Pb/ kg soils) identified by the USEPA (2001). Values labeled with different letters are significantly different at $p < 0.05$.

RESULTS AND DISCUSSION

Total soil Pb values for the contaminated San Antonio sites averaged 1,697 mg/kg, with the highest concentration of 4,182 mg/kg (Figure 1a). The range of soil Pb concentration was between 36 mg/kg and 4,182 mg/kg, with a median value of 1,706 mg/kg. Total soil Pb content averaged 697 mg/kg at the contaminated residential sites in Baltimore, with a maximum value of 2,165 mg/kg Pb (Figure 1b). The range of soil Pb concentration was between 60 mg/kg and 2,165 mg/kg, with a median value of 696 mg/kg. The soils from the residential sites that were built after the ban on Pb-based paint had Pb at concentrations ranging from non-detectable to 5 mg/kg soil (data not shown). The typical Pb levels in natural surface soils vary, but the average is reported to be 20 mg/kg (Kabata-Pendias and Pendias, 1992). About 70% of the soils from both San Antonio and Baltimore that were studied have total soil Pb concentrations above the USEPA's permissible limit of 400 mg Pb /kg soil (USEPA, 2001).

The Mehlich-3 extraction solution allows for determining the plant-available metal concentrations in soils (Mehlich, 1984). The Mehlich-3 extractable Pb concentrations ranged between 9% and 46% of total soil Pb in San Antonio (Figure 2a). The values were typically much higher in Baltimore soils where it ranged between 17% and 66% (Figure 2b). Nine sites out of 10 in Baltimore had Mehlich-3 extracted Pb concentrations greater than 20% of total soil Pb. In contrast, less than 50% of the number of sites in San Antonio that were sampled had plant-available Pb concentrations greater than 20% of total soils Pb.

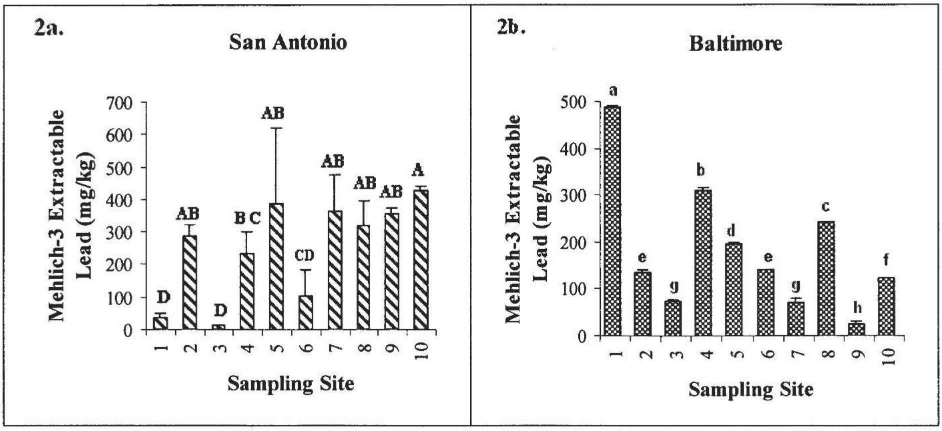

Figure 2. Plant available Pb concentrations determined using the Mehlich-3 extractant from Pb-based paint contaminated housing sites in: a) San Antonio, TX; and b) Baltimore City, MD. Values labeled with different letters are significantly different at $p < 0.05$.

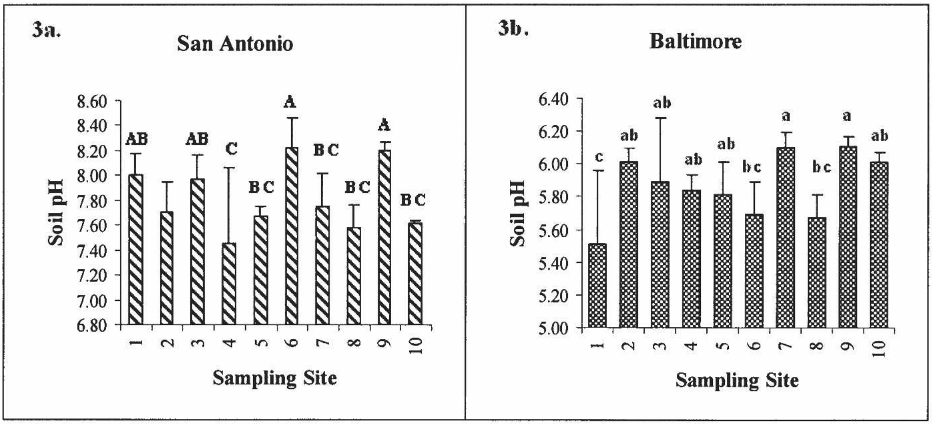

Figure 3. Soil pH of Pb-based paint contaminated residential sites under study from: a) San Antonio, TX; and b) Baltimore City, MD.

Hence, despite the higher levels of total Pb concentration in the San Antonio soils, the extractable fractions for plant uptake were lower compared to the Baltimore soils. Thus, soil physico-chemical properties influencing the Pb dynamics need to be adequately considered while developing suitable phytoremediation strategies for cleanup and proper management of Pb contaminated soils.

One of the most important factors controlling metal fractionation in soils is soil pH. Lead adsorption on soil components is typically controlled by soil pH, which controls the surface charge of the adsorbent as well the degree of ionization and

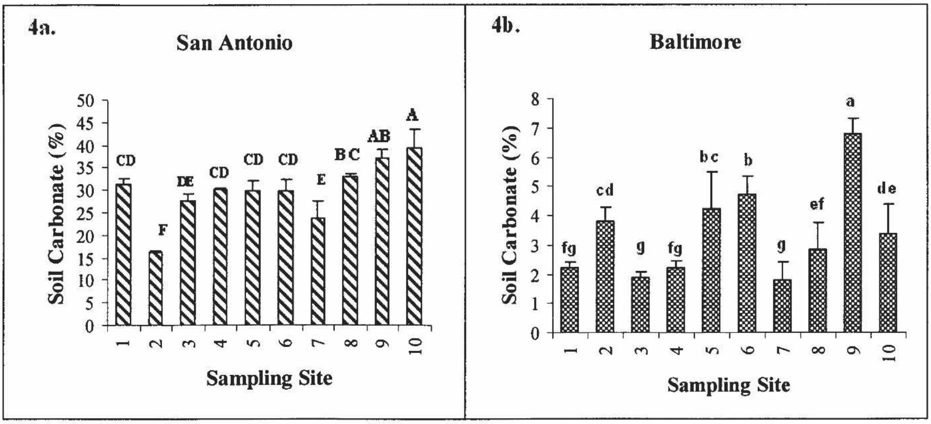

Figure 4. Soil carbonate levels in Pb-based paint contaminated residential sites under study from: a) San Antonio, TX; and b) Baltimore City, MD.

speciation of metal cations, such as lead (Elliot and Huang, 1981). San Antonio soils are typically alkaline in nature (pH ranging from 7.5 to 8.2), while Baltimore soils are acidic (pH ranging from 5.5 to 6.1) (Figure 3). The median pH is 7.73 in San Antonio soils, whereas in Baltimore soils, it is 5.84. In the acidic soils, Pb is likely to be in a more mobile form and/or bound to the oxidizable fractions (Elliot and Huang, 1981), which are potentially phytoavailable. Hence, Pb is likely to be more available for plant uptake in Baltimore soils. It has been shown that Pb adsorption on soils increases as pH increases above 6.0 (Pierangeli et al., 2001). Lead retention in soils as a function of pH is closely related to the decrease in concentration of H^+ ions, which are in competition with Pb cations. Consequently, negative charges on soils at higher pH values increase the potential of adsorption of metal cations, such as Pb. Gomes et al. (1997) found that among the heavy metals studied, Pb presented the highest affinity towards clay minerals. This phenomenon is influenced by the soil pH and total Pb content of soils (Sanchez-Camazano et al. 1998).

Sorption of divalent metal ions, such as those of Pb is more favored in soils with high pH, high organic matter, high cation exchange capacity, and high clay content (Reed et al., 2002). High level of carbonate results in increased adsorption of divalent metals to certain soil fractions with negative surface charge, making the metals less available for plant uptake (Zhenbin et al., 2001). The carbonate content ranges from 16% to 40% in San Antonio soils, whereas it is only 2% to 7% in the Baltimore soils (Figure 4). The high carbonate content of the San Antonio soils enhances the soil pH favoring Pb adsorption, as well as might promote the precipitation of Pb, thereby making it less available for plant uptake. Our results show that plant extractable lead among the studied soil samples varied especially as a function of pH and carbonate contents of the soils. The San Antonio soils have a median value of 27% carbonates; hence, it is expected that a significant fraction of the total Pb in soils will be bound to the

Table 1. Soil texture as percent clay, silt and sand contents in the Pb-based paint contaminated soils collected from San Antonio, TX.

Residential Site #	Clay (%)	Silt (%)	Sand (%)
1	4.34 ± 0.9	30.5 ± 0.8	65.1 ± 0.1
2	17.8 ± 1.7	56.8 ± 1.5	25.4 ± 0.2
3	12.3 ± 2.2	57.7 ± 1.2	30.0 ± 1.1
4	20.5 ± 0.8	43.1 ± 0.4	36.4 ± 1.3
5	6.77 ± 0.1	43.2 ± 0.2	50.1 ± 0.1
6	3.52 ± 0.4	30.4 ± 0.5	66.1 ± 0.1
7	5.96 ± 0.2	70.6 ± 0.3	23.5 ± 0.5
8	8.48 ± 0.3	63.4 ± 0.3	28.2 ± 0.6
9	46.3 ± 2.2	43.2 ± 1.4	10.5 ± 0.8
10	60.5 ± 6.7	25.4± 5.5	14.0 ± 1.1

All data are shown as mean ± standard deviation of three replicates.

Table 2. Soil texture as percent clay, silt and sand content in the Pb-based paint contaminated soils collected from Baltimore, MD.

Residential Site #	Clay (%)	Silt (%)	Sand (%)
1	1.76 ± 0.1	24.6 ± 0.3	73.7 ± 0.5
2	2.60 ± 0.1	27.3 ± 0.5	70.1 ± 0.5
3	2.10 ± 0.1	33.1 ± 1.5	64.8 ± 1.6
4	4.89 ± 0.3	19.5 ± 1.4	75.6 ± 1.6
5	5.29 ± 0.1	62.8 ± 0.2	32.0 ± 0.2
6	4.65 ± 0.2	9.03 ± 0.6	86.3 ± 0.8
7	4.61 ± 0.1	58.1 ± 1.2	37.3 ± 1.1
8	2.12 ± 0.0	50.1 ± 0.3	47.8 ± 0.3
9	4.61 ± 0.1	48.9 ± 1.2	46.5 ± 1.4
10	4.09 ± 0.1	61.1 ± 1.1	34.8 ± 1.2

All data are shown as mean ± standard deviation of three replicates.

carbonates. In contrast, the Baltimore soils have very low carbonate contents and low pH values, potentially resulting in higher plant available Pb forms.

The clay fraction of the soils typically adsorbs 20% to 30% more metals than the entire soil because of the increased amount of fines, such as organic matter and amorphous oxides, hydroxides, etc. associated with the clay fraction. The finer particles generally have higher adsorption capacities because of the increased specific surface (Ban˜uelos and Ajwa, 1999). The San Antonio soils have higher clay contents ranging from 3.5% to 60.5% (Table 1). Baltimore soils have a much lower clay fraction, ranging between 1.8% and 4.9% (Table 2). Soils with higher clay contents are expected to have lower concentrations of phytoavailable Pb, as Pb gets stabilized in the surface soil horizon by forming complexes on the surface of clay minerals through hydrolysis reactions that produce non-exchangeable forms. This study suggests that plant available Pb forms in the San Antonio soils could be negatively influenced by their high clay contents.

Several other soil parameters, such as cation exchange capacity, soil salinity, soil organic matter (SOM), iron and aluminum oxides, calcium and magnesium salts, and phosphorous compounds are known to have a significant influence on the speciation of heavy metals such as Pb (Sanchez-Camazano et al. 1998). Knowledge of the various soil properties that influence the geochemical forms of Pb in soils is essential to develop innovative technologies to improve plant uptake of lead. This knowledge is the key to understanding the potentially phytoavailable fractions of Pb, as well as the amount of Pb that might be potentially remobilized under certain environmental conditions. This will result in an improved efficiency of a given phytoremediation program geared towards minimizing soil Pb -induced environmental and human health risks. More in-depth investigations on the relative influences of the various soil properties on the soluble and exchangeable Pb forms are currently in progress in our laboratory.

In order to plan and carry out effective phytoremediation of Pb-based paint contaminated residential soils, information on the Pb phases in soils is extremely useful. Because of their acidic pH, low clay content and low carbonate content, it appears that the Baltimore soils will have higher concentrations of soluble and exchangeable lead relative to the San Antonio soils, which are alkaline, clayey, and rich in carbonates, properties that promote Pb retention. This suggests that Pb is likely to be more available for plant uptake in the Baltimore soils, and a chemically (chelate)-catalyzed phytoextraction strategy will be potentially necessary for the San Antonio soils that require Pb to be remobilized from their soil-bound forms, thereby making it more available for plant uptake.

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