Heavy Metals in the Environment

Effect of Biosolids Processing on Lead Bioavailability in an Urban Soil

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ABSTRACT

The potential for biosolids products to reduce Pb availability in soil was tested on a high Pb urban soil with biosolids from a treatment plant that used different processing technologies. High Fe biosolids compost and high Fe + lime biosolids compost from other treatment plants were also tested. Amendments were added to a Pb-contaminated soil (2000 mg kg^{-1} Pb) at 100 g kg^{-1} soil and incubated for 30 d. Reductions in Pb bioavailability were evaluated with both in vivo and in vitro procedures. The in vivo study entailed feeding a mixture of the Pb-contaminated soil and AIN93G Basal Mix to weanling rats. Three variations of an in vitro procedure were performed as well as conventional soil extracts [diethylenetriaminepentaacetic acid (DTPA) and $Ca(NO_3)_2$] and sequential extraction. Addition of the high Fe compost reduced the bioavailability of soil Pb (in both in vivo and in vitro studies) by 37 and 43%, respectively. Three of the four compost materials tested reduced Pb bioavailability more than 20%. The rapid in vitro (pH 2.3) data had the best correlation with the in vivo bone results ($R = 0.9$). In the sequential extract, changes in partitioning of Pb to Fe and Mn oxide fractions appeared to reflect the changes in in vivo Pb bioavailability. Conventional extracts showed no changes in metal availability. These results indicate that addition of 100 g kg^{-1} of high Fe and Mn biosolids composts effectively reduced Pb availability in a high Pb urban soil.

INGESTION OF lead-contaminated soils is one of the primary factors responsible for elevated blood Pb in children (Mielke, 1999). Although incidences of blood Pb above the current guideline of 10 μg dL^{-1} have generally decreased, occurrences of elevated blood Pb are still common in urban areas. In 1988, the Agency for Toxic Substances and Disease Registry estimated that more than 3 million children ages 6 mo to 5 yr living in metropolitan areas had blood lead levels greater than 15 μg dL^{-1} (Agency for Toxic Substances and Disease Registry, 1988). The report also stated that soil Pb concentrations greater than 500 to 1000 mg kg^{-1} were associated with increased child blood Pb. Median concentrations of Pb in inner city soils are greater than 1000 mg kg^{-1}, suggesting that elevated Pb in soils is at least partially responsible for the observed elevated blood Pb in children living in urban areas (Angle et al., 1974).

The relationship between the mineral form of Pb and its bioavailability has been demonstrated in in vivo and in vitro trials. Feeding studies, with immature swine (*Sus scrofa*) as well as weanling rats (*Rattus* spp.) as human surrogates, have shown that the mineral form of Pb, fed both in a soil matrix and as pure minerals, can alter the rate of Pb adsorption (Baltrop and Meek, 1975; Freeman et al., 1996; Ruby et al., 1999). Lead bioavailability to immature swine from 19 untreated substrates collected from 8 sites ranged from 0.01 to 90% (Casteel et al., 1996a–d, 1997, 1998a–c). Differences in Pb bioavailability were attributed to the presence of different mineral species using an in vitro procedure (Medlin, 1995). These results suggest that lead bioavailability in soils can be manipulated by changing its mineralogy.

Currently, removal and replacement of contaminated soils is the most commonly used remedial option for high Pb soils (Berti and Cunningham, 1997). Removal and replacement is not economically or environmentally feasible to carry out in high density urban areas. Research to limit the bioavailibility of Pb in situ has focused on the addition of soil amendments to alter the Pb chemistry in place. Much of this work has focused on the formation of pyromorphite through the addition of P amendments (Cotter-Howells and Caporn, 1996; Ma et al., 1995; Pearson et al., 2000). While P addition has been shown to be effective, there are environmental concerns related to high rates of P amendments, such as the potential for increased eutrophication in adjacent water bodies (Sharpley and Beegle, 1999).

Other amendments have also demonstrated the ability to reduce Pb bioavailability. The addition of manganese along with P to soil has reduced both in vivo and in vitro Pb availability over the addition of P alone or Mn alone (Hettiarachchi et al., 2000). The addition of "iron rich" material, a high Fe by-product from titanium processing, reduced in vitro extractable Pb in several Pb-contaminated soils (Berti and Cunningham, 1997). The importance of soil organic matter in limiting Pb availability has also been demonstrated (Strawn and Sparks, 2000). The application of biosolids materials (by-product of municipal wastewater treatment) may offer an alternative option. Recent studies indicate that application of biosolids or biosolids compost can reduce the bioavailability of soil Pb (Brown and Chaney, 1997; Brown et al., 1999). This is reasonable, given that biosolids often have high concentrations of Fe and P (g kg^{-1}) and Mn (mg kg^{-1}), and generally contain >50% organic matter.

While the addition of P to Pb-contaminated soils has

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Abbreviations: AAS, atomic adsorption spectrometry; DTPA, diethylenetriaminepentaacetic acid; PBET, physiologically based extraction test.

a quantifiable endpoint (formation of pyromorphite), the mechanisms responsible for the observed reduction in Pb availability in Fe-, Mn-, or biosolids-amended soils are not clear. It is generally thought that the adsorption reaction, potentially leading to precipitation, is responsible for the observed decrease in Pb bioavailability. Biosolids contain high levels of organic matter and P that may contribute to the observed ability to limit metal solubility (Li et al., 2000). In addition, biosolids generally contain high concentrations of Fe and Mn. In some cases Fe is added to biosolids in percent concentrations to aid in dewatering. The alternating aerobic and anaerobic conditions in wastewater treatment plants combined with the high organic matter and Fe content of biosolids suggest that the formation of ferrihydrite is favored and the crystallization of this oxide may be inhibited. Ferrihydrite has been shown to form surface inner sphere complexes with Pb (Scheinost et al., 2001). Over time, as this oxide is aged, surface adsorption may lead to precipitation of a more crystalline, Pb-bearing Fe oxide.

Characteristics of biosolids vary depending on the stabilization process used to meet standards for pathogen reduction prior to land application. Biosolids can be treated with slaked lime for dewatering and pathogen reduction. Use of this material can result in increased soil pH. This is often desirable since increased soil pH is associated with decreased metal phytoavailability. While the observed decrease in plant uptake of metals may not correspond to a similar decrease in bioavailability to animals, it may be that a high lime material would neutralize the acidity in the gastric system and limit the amount of Pb that comes into solution. Composting biosolids (done to produce a material that can be used without restrictions) results in the transformation of organic compounds to a higher fraction of humic and fulvic acids. As discussed, each of these components may also contribute to the biosolids' ability to limit metal bioaccessibility. By understanding the unique qualities of different biosolids products, it may be possible to maximize in situ reductions in bioavailability by applying biosolids with particular characteristics. In addition, reduction of Pb bioavailability, through the application of biosolids or biosolids products, may offer an economically feasible alternative to current remediation technologies for Pb-contaminated urban areas.

This study was conducted to determine the effects of different biosolids processing methods on the ability of biosolids to reduce Pb availability in an urban soil. Biosolids products were selected for the study to evaluate the importance of (i) stabilization through the composting process, (ii) the role of calcium carbonate, and (iii) the importance of inorganic oxides in reducing Pb availability. Changes in Pb bioavailability were assessed through in vivo (using weanling rats) as well as in vitro procedures. In addition, agronomic soil extracts were used to determine whether potential changes in bioavailable Pb would be reflected in the extractable pool of this metal.

MATERIALS AND METHODS

Soil and Amendment Characteristics

Soils Collection, Preparation, and Analysis

Soil for the study was collected from a home garden in Baltimore, MD. The garden had been identified as containing high soil Pb by the Kennedy Krieger Foundation (engaged in helping children with undue Pb absorption in Baltimore, MD). There was no history of Pb smelting, refining, or battery recycling in the neighborhood where the soil was collected. Approximately 40 kg of soil was collected (top 10 cm) from garden that was immediately adjacent to the house. Soil was air-dried and sieved through a 2-mm stainless steel sieve. The soil was analyzed for total carbon and nitrogen by combustion (25 and 1.6 g kg^{-1}). Particle size analysis with the hydrometer method (American Society for Testing and Materials, 1985) classified this soil as loamy sand. Cation exchange capacity of the soil was measured as 14.7 $cmol_c$ kg^{-1} (Chapman, 1965). The soil and soil amendments were analyzed for total metal concentrations with the aqua regia procedure and the filtrate was analyzed with flame atomic adsorption spectrometry (AAS) with deuterium background as appropriate (McGrath and Cunliffe, 1985; Table 1). The source of high soil Zn (977 mg kg^{-1}) was not clear. All other elements were within normal range for soils (Brady and Weil, 2002). Carbon, N, and P concentrations were not indicative of excessive fertilization or mulching.

Biosolids Amendments

Biosolids amendments for the study were generated at the Onondaga County Drainage and Sanitation Department's wastewater treatment facility in Syracuse, NY. Biosolids from the New York facility are a combination of primary and secondary sludges that are anaerobically digested and then dewatered with a belt press to achieve a solids content of approximately 220 g kg^{-1} (22%). New York biosolids materials tested included digested raw, digested and dewatered, ashed, N VIRO (N-Viro, Toledo, OH) (heat-pasteurized through addition of slaked lime), and composted biosolids (Richards et al., 1997). In addition to the compost produced at the Syracuse POTW, compost (90%) + lime [10% $Ca(OH)_2$], high Fe compost (Back River POTW, Baltimore), and compost + lime +

Table 1. Total metal concentrations of the high Pb urban soil and the biosolids amendments used. The soil was 2.53% C and 0.16% N.

Treatment	Zn	Cd	P	Cu	Mn	Ca	Pb	Fe
					mg kg^{-1}			
Soil	977	<0.5	795	54	418	7 574	2 135	26 900
Raw	613	8.7	29 590	542	334	45 870	135	68 100
Pellet	640	9.3	28 420	560	333	40 530	158	67 500
Ash	980	11	34 080	1 009	689	84 670	145	86 750
N VIRO	180	3.2	9 600	139	280	338 100	94	17 000
Compost	468	5.3	21 630	359	458	31 810	134	49 600
High Fe compost	800	10.8	27 390	348	867	29 560	240	99 000
High Fe compost + lime	320	3.4	14 610	185	1 557	164 410	135	58 900

Table 2. Select properties of the soil amendments and amended soils used in the study. Active Fe and Mn oxide measurements (ammonium-oxalate extractable) are for the soil amendments only. All other measures were conducted on the amended soils following a 30 d incubation.

Treatment	Active Fe oxide	Active Mn oxide	DTPA Pb	$Ca(NO_3)_2$ Pb	pH
	mg kg^{-1}				
Soil only			**321**	**0.42**	**6.74**
Raw	**67 890**	**324**	**499**	**0.53**	**6.67**
Pellet	**66 370**	**203**	**471**	**0.70**	**6.92**
Ash	**54 630**	**290**	**600**	**0.45**	**7.34**
Compost	**48 890**	**394**	**584**	**0.51**	**6.01**
Compost + lime			**499**	**0.53**	**6.67**
N VIRO	**13 820**	**60**	**308**	**0.69**	**8.21**
High Fe compost + lime	**52 230**	**854**	**576**	**0.31**	**7.71**
High Fe compost	**113 900**	**693**	**492**	**1.24**	**4.98**

Fe (COMPRO, Washington, DC) were also included in the study. They were included to determine the relative importance of Fe and carbonate in biosolid composts in inactivating soil Pb.

All compost amendments were added to the soil at a 10% dry weight ratio to reach a total mixture weight of 1.25 kg (i.e., 1.125 kg dry soil was mixed with 125 g dry compost). This application rate is common when biosolids are used for restoration (Sopper, 1993). All of the biosolids processing products were added at a rate equivalent to that of the biosolids constituent in the Syracuse compost mixture. This rate was determined by analysis of total Pb in the biosolids amendments. The total Pb in the raw and pelletized material averaged 10% higher than the Pb in the New York compost, that is, composting had diluted the biosolids by 10%. To correct for this difference and maintain a constant rate of biosolids addition, using 100 g compost per kg soil as a basis, the dry weight loading rate for the pellets and the raw biosolids was decreased by 10% (i.e., raw and pellitized biosolids were added at a rate of 112.5 g biosolids to 1.138 kg soil). After addition of amendments, deionized water was added to bring the soils to field capacity. The amended soils were kept covered at field capacity for 30 d at 25°C. Soils were thoroughly mixed weekly during incubation. Following the 30-d incubation period, soils were air-dried and sieved through a 1-mm stainless steel sieve. This size fraction was used to assess the risks posed by both dust adhesion to hands as well as pica behavior where children directly ingest greater quantities of larger soil particles. Available and extractable metals in the amended soils were measured on the air-dried, sieved soils, using both the diethylenetriaminepentaacetic acid (DTPA) procedure and 0.01 *M* $CaNO_3$ extract (Brown et al., 1994; Lindsay and Norvell, 1978). The DTPA extraction was done with a 5 m*M* DTPA, 10 m*M* $CaCl_2$, and 0.1 *M* triethanolamine solution added to soils at a 2:1 ratio. The $CaNO_3$ extract was done with a 2:1 solution to soil ratio with a 2-h shaking time. Lead concentrations in these extracts were measured with AAS. Amorphous or active oxides were measured with the ammonium oxalate method (Loeppert and Inskeep, 1996). Soil pH was measured with a 2:1 deionized water to soil volume ratio. Samples were incubated with intermittent stirring for 1 h before measurements were made (Table 2). A sequential extract (Berti and Cunningham, 1997) was followed to determine changes in partitioning of soil Pb as a result of amendment addition (Fig. 1). Solutions from the sequential extraction were analyzed with inductively coupled plasma–atomic emission spectroscopy (ICP–AES). Properties of the biosolids amendments are presented in Tables 1 and 2.

In Vivo Study with Rats

Test Rats

Eighty-four (7 rats × 12 treatments) weanling male Sprague–Dawley rats (Harlan Sprague–Dawley, Indianapolis, IN), approximately 3 to 4 weeks old and weighing approximately 50 to 60 g, were randomly divided into 12 dietary groups according to the soil treatments. They were housed individually in stainless steel cages with wire-mesh bottoms in a temperature- and humidity-controlled (20°C, 55% humidity) room with 12-h periods of alternating light and dark with artificial illumination (fluorescent light). A color-coding system was used to designate the rat dietary treatments. All animal care and handling conformed to the National Institutes of Health guidelines (National Institutes of Health, 1985).

Diet Preparation

Sieved control and amended soils were mixed with rat diets at a rate of 5% dry weight. AIN93G Basal Mix (95%) was used as the rat diet for the study (Harlan Teklad [Madison, WI] Catalog no. TD 96107). The basal mix without cellulose is designed for use at 950 g kg^{-1} in a modified AIN-93G diet. Lead acetate (Sigma Chemical Company [St. Louis, MO] Catalog no. L-3396) was used as an addition to the basal mix to provide a calibration of the tissue Pb response to a Pb salt considered to be 100% bioavailable (Mahaffey et al., 1977). Lead acetate was added to the diet at two rates: 11 and 20 mg kg^{-1}. These rates were selected to reflect the probable bioavailability of the Pb in the control soil (USEPA, 1994). In this case, the Pb acetate rates used overpredicted the bioavailability of Pb in the control soils. Lower rates would have been more appropriate to compare the relative availability of salt-added Pb to soil Pb. Total Pb in the soils and the diet samples are reported in Table 3.

For the control diets sand was used in lieu of soil. The sand acted as an inert material in the diet and was intended to be comparable with the soil being tested, providing a fiber source with minimal additional adsorptive capacity. Previous studies have shown that addition of soil to rat diets that included Pb acetate reduced adsorption of Pb (Chaney et al., 1989). Lead acetate was dissolved in distilled deionized water. A solution was then sprayed over the surface of the premixed sand in amounts that equaled the prescribed final concentrations of lead. The sand was then mixed until it was homogeneous. A small amount of AIN93G diet was added to the sand, lead–sand, or soil in three sequential additions. Following each addition, the mixture was homogenized with a Hobart (Troy, OH) mixer. This was done to reduce the density of the sand or soil component prior to incorporation with the bulk of the AIN93G diet. This mixture was then added to the remainder of the AIN93G in small amounts and mixed to apparent homogeneity after each addition. After addition of the last of the sand, lead–sand, or soil mixtures the bowl was "rinsed" with small amounts of the diet mix and returned to the Hobart mixer. This rinsing was repeated two more times to assure that all lead and sand or soil were incorporated in the diet.

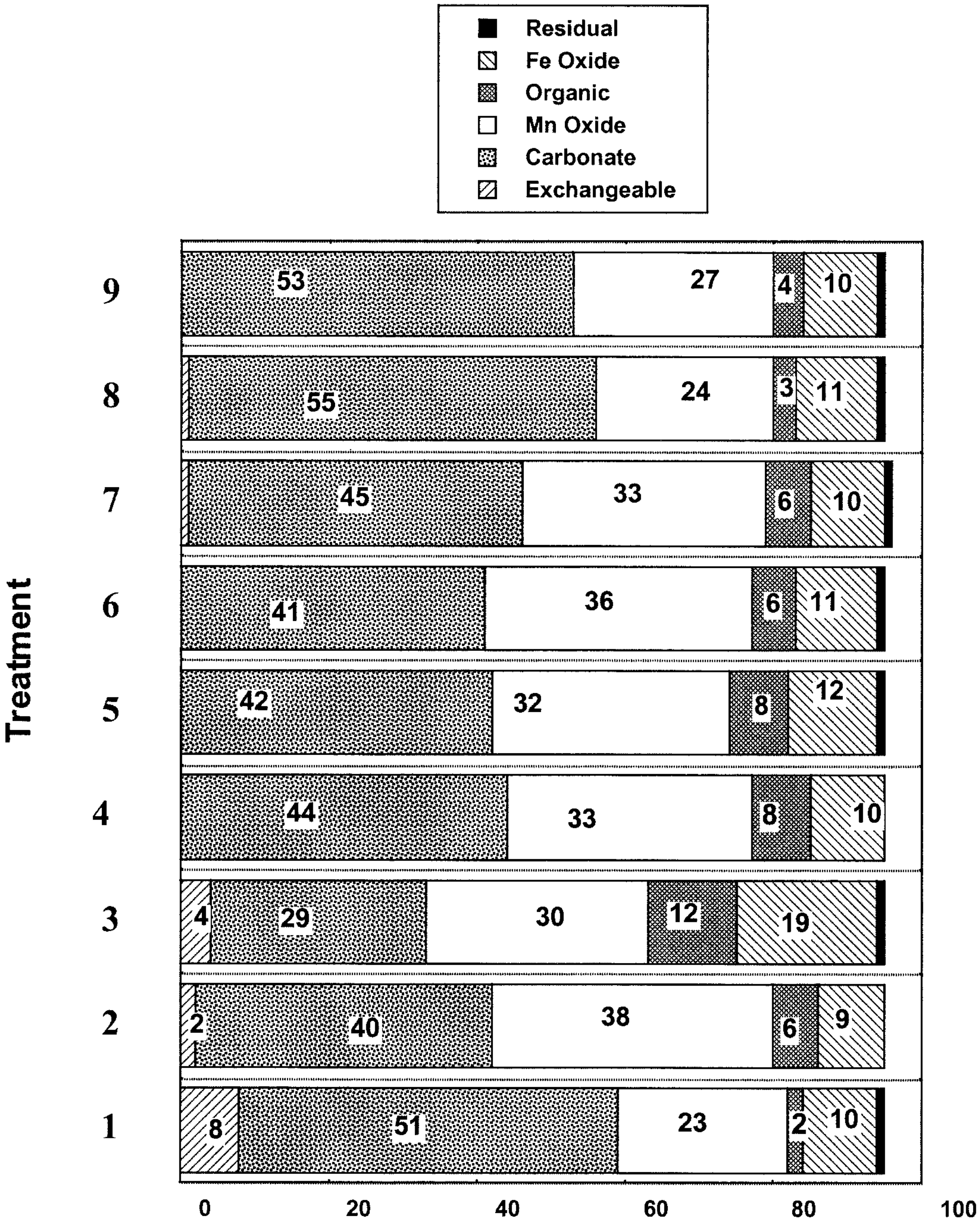

Fig. 1. Partitioning of soil Pb by the Berti and Cunningham procedure (1996) after soils had been amended and incubated for 30 d. Treatments were as follows: 1, control soil; 2, compost; 3, high Fe compost; 4, high Fe compost + lime; 5, compost + lime; 6, raw biosolids; 7, pellet biosolids; 8, ashed biosolids; 9, N VIRO biosolids.

Each soil or sand diet was then mixed on the Hobart mixer for two hours.

Analytical Procedures

The rat body weights and daily food intakes were measured to accurately determine the amount of lead consumed by each rat. Total food intakes were determined for each animal by weighing food cups before and after consumption. Unconsumed food was discarded at this time. Grids were placed in each food cup to minimize spillage. Spillage was estimated by checking the amount below each cage biweekly before cages were changed or paper was replaced. Distilled-deionized water was available on demand for the duration of the study. This eliminated the possibility that elements that may be present in tap water, such as Ca, would affect Pb adsorption (Mahaffey et al., 1977). Raised, wire-mesh floors were used to minimize coprophagy. At the end of 35 d, following an overnight fast, animals were sacrificed by decapitation after being anesthetized with CO_2. Immediately after decapitation, organs were removed, weighed, and washed in ice-cold saline solution. They were then frozen at −70°C until analysis. The entire femur was excised and generally, the right femur was analyzed for minerals. The entire liver was excised and weighed. One gram of sample was analyzed for minerals. Both kidneys were collected and weighed, but only one was used for analysis, with the second serving as backup. Soft tissue was removed by

Table 3. Concentration of lead in diets, soils, and rat bone tissue from the feeding study. Diets were mixed to contain 5% of the test soils. Soils were sieved to <1 mm after incubation with the biosolids products before mixing with the basal control diet AIN-93G rat diet. Rats were sacrificed after 35 d.

Treatment	Soil Pb	Diet Pb	Bone Pb	Liver Pb	Kidney Pb
	mg kg^{-1}				
Control diet		0.0g†	0.56g	0.02e	0.50f
Lead Acetate 1		11.3f	33.9f	0.9d	6.66e
Lead Acetate 2		19.7e	66.6e	1.1d	8.54ed
Soil	2135abcd	125.3a	145a	3.1a	14.62a
Raw	2099abcd	82.4cd	87.5bcde	1.8c	12.81bcd
Pellet	2034bcd	84.3cd	86.7cde	1.8c	10.15bcde
Ash	2086abcd	89.3c	97.3bcd	1.9bc	12.53bcd
N VIRO	1559d	70.6d	111b	2.5ab	17.43a
Compost	1768cd	116.7ab	105bc	2.3bc	13.7abc
Compost + lime	2662a	90.1c	91.2bcd	2.0bc	9.61cde
High Fe compost	2576ab	100.6bc	73.3de	1.9bc	9.85cde
High Fe compost + lime	2309abc	99.2bc	81.8cde	2.0bc	10.41cde

† Means followed by the same letter are not significantly different according to the Duncan Means Separation test ($p < 0.05$).

scraping the bone with a scalpel and rinsing with physiological saline. All tissue and bone samples were dry-ashed before analysis. Blood was collected in heparinized tubes and immediately placed on ice. Blood was refrigerated until analysis for minerals. Duplicate samples of the bone, blood, liver, and kidney were analyzed for Pb, Ca, Cd, Mg, Fe, Mn, Cu, and Zn by inductively coupled plasma–mass spectrometry (ICP–MS) or by AAS after dry ashing and digestion with nitric acid and hydrogen peroxide (Hill et al., 1983).

In Vitro Study

Chemical Extraction of Lead from the Incubated Soils

In vitro extractability (bioavailability) of the amended soils (Table 4) was measured with two main procedures, the gastric phase of the physiologically based extraction test (PBET) procedure developed by Ruby et al. (1996) and a simplified PBET procedure (Brown and Chaney, 1997). For all in vitro extractions soil was added to an extracting solution at a 1:100 ratio. The gastric phase of the PBET was performed with a 2.5 g soil to 250 mL solution at 37°C for 1 h. The extracting solution (1.25 g pepsin, 0.50 g citrate, 0.50 g malate, 420 μL lactic acid, and 500 μL acetic acid in 1 L deionized water, pH corrected to 2.0 by addition of 12 *M* HCl) was heated to 37°C prior to soil addition. Temperature was maintained by submersing the extraction vessels in a circulating, heated water bath. Samples were stirred continuously during the extraction with magnetic stir bars in the extraction vessels. Solution pH was checked every 10 min during the extraction and corrected by addition of 12 *M* HCl. After 1 h, samples were filtered through Whatman (Maidstone, UK) #40 filter paper and analyzed for Pb with AAS.

Table 4. Results of three in vitro procedures including the physiologically based extraction test (PBET) and a modified version of the PBET at two pH levels, done on the high Pb urban soil, which had been incubated for 30 d with a variety of biosolid treatments. All soils were added to extracting solutions at a ratio of 1 g to 100 mL. Results shown are means ± standard error for each procedure ($n = 3$).

Treatment	Rapid in vitro, pH 2.30	Rapid in vitro, pH 1.50	PBET, pH 2.0
	mg Pb L^{-1} extract		
Soil	6.93 ± 1.3	20.4 ± 1.4	16.7 ± 1.4
Raw	4.19 ± 0.8	14.66 ± 0.5	16.8 ± 2.1
Pellet	3.84 ± 0.4	13.3 ± 0.3	11.3 ± 0.5
Ash	4.71 ± 1.0	15.2 ± 0.7	11.8 ± 1.2
N VIRO	2.41 ± 0.4	7.13 ± 0.2	13.6 ± 0.5
Compost	4.22 ± 0.8	14.0 ± 1.9	12.5 ± 0.9
Compost + lime	4.71 ± 0.1	14.9 ± 0.7	13.1 ± 1.3
High Fe compost	3.18 ± 0.6	13.0 ± 1.2	8.84 ± 1.4
High Fe compost + lime	2.53 ± 0.4	11.6 ± 1.2	14.9 ± 1.0

In addition to the standard PBET procedure described above, a simplified version of this extraction (rapid PBET) was performed at two pH levels (1.50 and 2.30) (Brown and Chaney, 1997). In the rapid PBET, the same extracting solution was used; however, pH was not controlled during the extraction. The rapid PBET procedure allows a much greater number of treatments to be tested at one time period. For both rapid in vitro procedures, samples were placed in a 37°C shaking water bath for 1 h at 120 rpm. After 1 h, samples were filtered through Whatman #40 filter paper and analyzed by AAS. The final pH of the extracting solution was also measured. In the pH 1.5 extraction, the final pH of the solution ranged from 1.53 to 1.64 for all soils except the N VIRO treated soil. For this soil, the final pH of the extracting solution was 3.10. For the pH 2.3 extraction, a similar pattern was observed with the final pH ranging from 2.43 to 3.3 in all treatments except the N VIRO soil, in which the final pH ranged from 4.08 to 5.34. The elevated pH observed in the N VIRO treatments is the result of the high rate of calcium carbonate equivalent materials used in the N VIRO process to achieve pathogen reduction in the biosolids. Solutions were analyzed for Pb with AAS.

RESULTS AND DISCUSSION

Rat Feeding

The different treatments had no effect on the average daily food intake, mean body weight, or the weight of the individual organs of the rats. Average food intake in the final week of the study ranged from 15.4 g in the unamended soil treatment to 16.6 g in the compost + lime and compost + lime + Fe treatments. The body weight of rats ranged from 244 g in the N VIRO treatment to 261 g in the control and Pb acetate treatments. In addition, there was no treatment effect on the Ca and Zn concentration of bone and liver tissue. There was some variation in liver Fe concentration, with the control (689 mg kg^{-1}) and high Fe compost (731 mg kg^{-1}) soil treatments having the highest Fe values (other soil treatments ranged from 422–567 mg kg^{-1}). Calcium concentration in the kidney tissue was increased in the N VIRO treatment (440 vs. 358 mg kg^{-1} control soil). These differences may be the result of the higher Fe concentrations in the compost and high Ca in the N VIRO treatment.

Table 5. Observed reduction in bioavailability compared with the control soil after a high Pb urban soil was amended with a range of biosolids amendments including biosolids composts as measured by bone Pb in weanling rats and a range of in vitro procedures. Negative numbers indicate an increase in bioavailability relative to the unamended soil.

Treatment	Bone Pb	Rapid in vitro, pH 2.30	Rapid in vitro, pH 1.50	PBET, pH 2.0
	%			
Raw	8	8	−9	−53
Pellet	10	18	3	0.00
Ash	6	5	−2	−10
N VIRO	−36	38	38	−44
Compost	23	35	26	20
Compost + lime	12	6	−1	−9
High Fe compost	37	43	21	34
High Fe compost + lime	29	54	28	−12

Evaluation of the percent reduction in Pb bioavailability is typically calculated as follows:

$$\text{(bone Pb} - \text{bone Pb in amended soil)/ bone Pb in unamended soil} \quad [1]$$

For this study, Eq. [1] was adjusted to reflect differences in total Pb concentrations in the rat diets. The equation used for this study was:

$$\text{(bone Pb/diet Pb in unamended soil)} - \text{(bone Pb/diet Pb in amended soil)/ (bone Pb/diet Pb in unamended soil)} \quad [2]$$

Results of the study (using Eq. [2]) indicate that the Pb in the unamended soil was 75% less bioavailable than the Pb acetate–amended diets. This observed decrease in bioavailability is within the range that has been reported for Pb in soil in comparison with Pb acetate (Chaney et al., 1989). In addition, several of the biosolids amendments significantly reduced the bioavailability of soil Pb as measured by the bone Pb concentrations in the rats (Table 3). Bone, liver, and kidney values are presented. For this study, results from these organs are comparable. Bone values for rats are potentially the best indicator of Pb uptake as they reflect exposure over time. Blood was only sampled from rats at sacrifice. Blood values can exhibit biphasic behavior that can be interpreted only with multiple sacrifice times (Freeman et al., 1996). Bone values are used as a basis to compare treatment efficacy. Other measures of changes in Pb bioavailability (soil extracts and in vitro measures) are evaluated in relation to the observed changes in bone Pb.

The reduction in bioavailability of Pb in the different soils is defined as the change in the portion of total Pb that is absorbed from the treated vs. untreated soil (Eq. [2]) (Table 5). The observed reduction was most pronounced for the composts tested. The percent reductions in Pb bioavailability in various compost-amended soils over the control ranged from 12% in the compost + lime treatment to 37% in the high Fe compost. The percent reduction in bioavailability in the noncomposted biosolids products ranged from 6% in the ashed material to 10% in the pelletized biosolids. It is possible that the longer chain organic compounds present in the composts were partially responsible for this reduction over the uncomposted biosolids (Brady and Weil, 2002). The sequential extraction (Fig. 1) showed a shift in partitioning to the organic fraction from the control soil (2% associated with organic) to the compost-amended soils (6–12%). This shift was less pronounced in the noncomposted biosolids amendments (3–6%). Humic substances formed during composting may have formed stable complexes with the soil Pb that remained intact in the gastric system of the rats. A recent study showed that soil organic matter was responsible for the complexation of the slowly desorbed fraction of Pb in soil solution (Strawn and Sparks, 2000). However, it is not clear how Pb behavior in a soil system relates to its behavior in the gastric tract.

The addition of lime appeared to increase Pb bioaccessibility. In the highest Ca treatment (N VIRO–treated soil; Table 1), Pb bioavailability was increased over the control (+36%). Lime addition to the compost also reduced its effectiveness (23 vs. 12%; Table 5). Metal phytoavailability is generally decreased with increasing soil pH. However, the results from this study show an opposite trend. The pH of the high Fe compost soil mixture was 5.00, the most acidic of all soil treatments. It also had the greatest reduction in bone Pb with a 37% reduction in bioavailability over the control soil. The N VIRO–amended soil had the highest pH, 7.80. The Pb in the N VIRO–amended soil was more bioavailable (36% increase) than the Pb in the control soil. The sequential extraction also indicated that a high portion of Pb in the N VIRO treatment was associated with the carbonate fraction (55 vs. 51% in the control soil and 30% in the Baltimore treatment). Although this type of extract is not a quantitative indication of a change in mineral form, the operationally defined increase does suggest a mineral shift. This may be related to the formation of Pb carbonates as opposed to simply a function of soil pH and reduced solubility of Pb. Lead carbonate minerals are relatively soluble with the log K equal to 4.65 (Lindsay, 1979). High concentrations of Ca in the N VIRO and compost + lime treatment may have shifted the stability of existing soil Pb minerals and precipitated a portion of the total Pb as Pb carbonate. This may have come into solution in the gastric system of the rats and resulted in higher bioavailability of the soil Pb. The subsequent solubility of additional Ca may not have been sufficient to inhibit Pb adsorption. Similar results were observed by Berti and Cunningham (1997) when Portland cement (also high in Ca) was added to Pb-contaminated soils. They observed an increase in the Pb associated with carbonates

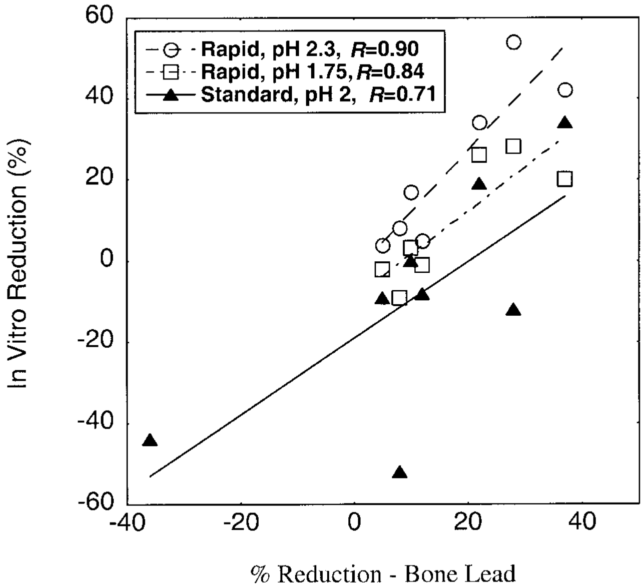

Fig. 2. Correlation in percent reduction in bioavailability of Pb in treated soils as compared with control soil between bone Pb in weanling rats and two in vitro procedures, one conducted at two pH levels. In both rapid procedures, one outlier point (N VIRO) soil has been deleted from the dataset.

during the sequential extraction of the amended soils. Using the standard version of the PBET extraction, they also observed that cement addition increased bioavailability of Pb over control soils. These results suggest that although increasing soil pH through the addition of $CaCO_3$ can decrease Pb solubility, it is important to ensure that the reduction in Pb solubility is not the result of the formation of Pb carbonate minerals.

It appears that amorphous Fe and Mn oxides in the composts were partially responsible for the observed reduction in Pb bioavailability. The sequential extraction shows an increase in partitioning to the Mn oxide fraction for all treatments (excluding ash) that also showed an in vivo reduction in bone Pb (Fig. 1). Oxalate-extractable Mn was also highest in the two most effective treatments (high Fe compost and high Fe compost + lime, 37 and 29% reduction in bone Pb) (Table 2). Manganese oxides have been shown to irreversibly adsorb Pb (McKenzie, 1980). Manganese addition, both in combination with P and singly, has been associated with a reduction in Pb availability using the PBET extraction procedure (Hettiarachchi et al., 2000). The results from this study confirm the ability of Mn oxides to reduce Pb bioavailability that was indicated in earlier studies. They also suggest that the observed reduction in the high Fe + lime compost may have been increased had the biosolids used for the compost feedstock not been lime stabilized. The presence of high levels of Ca in the other amendments resulted either in an increase in Pb bioavailability over the control (N VIRO) or a decrease over the same amendment without lime (compost vs. compost + lime). It may be that a compost material with high Mn oxide content and no added Ca would further limit Pb bioavailability.

Both the oxalate-extractable Fe and the Pb associated with Fe was significantly greater in the high Fe compost treatment. However, differences in oxalate-extractable Fe were not associated with a change in partitioning to this fraction in the sequential extract for other treatments. For the high Fe compost treatment, a doubling of the oxalate-extractable Fe (compared with all other treatments excluding the N VIRO treatment, where the value was about 10% of the high Fe compost) was comparable with the observed increase in partitioning of this fraction in the sequential extract. This treatment also showed the greatest reduction in bone Pb in the in vivo portion of the study (Table 5). Similar results were observed by Berti and Cunningham (1997) when high Fe materials (total Fe = 200 g kg^{-1}) were added to Pb-contaminated soils at 20 to 100 g kg^{-1}. In that study, Fe addition was associated with a change in Pb repartitioning during the sequential extraction. The trend was most pronounced in the highest rate (100 g iron rich material kg^{-1} soil) of amendment addition. A decrease in PBET Pb over the control soil was also observed for this treatment. These results are in agreement with Pb adsorption studies that have been conducted with different Fe oxides (Martinez et al., 1999; Sauve et al., 2000). These studies found that oxides with high surface area, such as ferrihydrite, provide a highly effective adsorptive surface and that, even under extreme conditions, this adsorption is not completely reversible. Ferrihydrite is generally formed under moist conditions in the presence of high amounts of organic matter. It is one of the first oxides to precipitate from solution (Cornell and Schwertmann, 1996). These types of conditions are prevalent in wastewater treatment facilities, suggesting that the Fe in the biosolids would be present partially as ferrihydrite. Additional work to characterize the nature of the oxides in the biosolids and the relationship between the type of oxide and the Pb adsorption capacity is needed. However, the results from this study suggest that the high amorphous Fe and Mn concentration of the composts, in combination with some type of organo–Pb complexation, may play a significant role in Pb adsorption, resulting in reduction in Pb bioavailability in soils.

In Vitro Assays in Comparison with Animal Feeding

The results of the standard in vitro procedure (Ruby et al., 1996) did not correlate as well as the rapid in vitro procedures to the bone Pb data from the rat feeding (Fig. 2, Table 5). The R^2 value for the standard in vitro procedure vs. bone Pb was 0.71 and 0.66 when the N VIRO soil was excluded. The rapid in vitro procedures were much better correlated with the bone data with the exception of the N VIRO–amended soil. This treatment raised the final pH of the gastric solution to 3.20 and 4.56 in the low and high pH procedures, respectively. The marked increase in solution pH may have been responsible for the overestimation in reduction in Pb availability observed in the in vitro procedure. If this data point is removed from the regression analysis, R^2 values for the pH 1.50 and 2.30 procedures were 0.84 and 0.90. Although other soil amendments modified the final pH of the gastric solution when the extraction was run at pH 2.30, these deviations were 1 log unit or less. It is possible that a range of pH modification is acceptable with the modified procedure, though an acceptable range has yet to be determined. Nevertheless, these results indicate that the modified in vitro procedure may provide a more accurate measure of changes in in vivo bioaccesibility as a result of soil treatment than the standard procedure of Ruby et al. (1996).

It would appear that normal soil extraction methods are not appropriate for assessing soil Pb availability to humans. The results of both the $Ca(NO_3)_2$ and the DTPA extractions had no relationship with the results from the in vivo and in vitro trials (Table 2). Although the $Ca(NO_3)_2$ extract has been used to accurately assess the phyto- and bioavailable fraction of several metals in contaminated sites (Basta and Sloan, 1999; Conder et al., 2001), it does not appear suitable to gauge the bioavailable fraction of Pb in soil. The same may be said for the DTPA procedure.

CONCLUSIONS

Results from this initial study indicate that the addition of biosolids composts, particularly those high in oxalate-extractable Fe and Mn, have the potential to reduce the bioavailability of soil Pb. Both animal feeding trials and in vitro laboratory assays confirmed these results. The sequential extraction used in the study also indicated that an increase in Pb partitioning to Fe and Mn oxides, along with increased organic complexation, were observed in the amendments that showed the greatest decrease in Pb bioavailability. However, it would be desirable if a more quantitative tool, such as X-ray adsorption spectroscopy (XAS), could confirm this shift in partitioning. Sequential extractions and XAS have been used in a laboratory incubation with a high Pb soil and apatite amendment to examine changes in Pb mineralogy as a result of amendment addition (Ryan et al., 2001). In this study, the sequential extraction appeared to alter Pb partitioning during the extraction procedure. The XAS was a more appropriate tool to quantify changes in Pb mineralogy. However, use of XAS on a compost-amended high Pb soil in a field setting did not identify a clear end point (Scheckel and Yang, 2001). Results showed a change in partitioning to what the authors described as the absorbed fraction. It may be that this technique has not been sufficiently developed to quantitatively assess changes in partitioning when a range of mechanisms are involved.

Without quantification of the mineralogical changes that resulted in reduced Pb availability in compost-treated soils, it is not possible to predict whether all compost materials would have a similar capacity. It is also not possible to predict the longevity of the observed reduction. A complete understanding of the mechanisms responsible for the observed reduction would facilitate the production of a compost with enhanced binding capacity. Attaining this type of understanding, along with field validation of the laboratory results, should be the next phase of additional research. However, even without this, results do suggest that amendment of high Pb urban soils with high rates of biosolids compost (particularly those that are produced without high rates of lime addition) will reduce Pb availability. Reductions may be on the order of 20 to 35% over unamended soil.

Use of biosolids compost may be especially beneficial in treating Pb-contaminated soils in inner city areas, where the greatest number of children are affected by elevated blood Pb levels and where there is currently no existing mechanism to remediate Pb contamination. Since all urban areas produce biosolids, it is possible that locally available biosolids could be composted and applied to home gardens to provide a cost-effective means to reduce the threat posed by elevated soil Pb. This is currently being done in Baltimore on a trial basis. Results from this program should provide useful information for other municipalities.

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