

Geochemical Behavior of Lead in an Alfisol and an Ultisol at High Levels of Contamination

Jeffrey L. Howard and Grazyna Sledzinski

Department of Geology, Wayne State University, Detroit, MI 48202

ABSTRACT: The behavior of Pb in the A and B horizons of an Alfisol from Michigan and an Ultisol from Virginia was studied to determine the effects of “shock” loading. Combined sequential extraction-sorption isotherm analysis (CSSA), a relatively new and little tested method, was used in the study. After spiking to simulate severe contamination (~3000 to 60,000 mg/kg), CSSA revealed unexpectedly high levels of exchangeable Pb in the A horizon of the Alfisol and in both horizons of the Ultisol, and showed that the sorption capacities of the phases commonly responsible for fixation of Pb at low to moderate levels of contamination were exceeded. Carbonate sorbed the bulk of the Pb in the Alfisol B horizon and has a high sorption capacity in both soils, despite the presence of other phases with a strong affinity for Pb. Thus, when shock loading occurs (e.g., at a shooting range or dump sites), the highly contaminated A horizons of both soils are expected to pose a serious toxic hazard to humans, and groundwater contamination is possible in association with the Ultisol. CSSA proved useful for determining the sorption capacities of the individual phases while together in a natural soil system and therefore is a valuable method for predicting the attenuation capabilities of soils.

KEY WORDS: sequential extraction, sorption isotherms, soil contamination, heavy metals.

I. INTRODUCTION

Lead is one of the most commonly encountered heavy metals in contaminated soils, and it is the one most often found at hazardous-waste sites (Sims *et al.*, 1986). Lead is a toxic heavy metal of environmental concern because of its tendency to bioaccumulate and damage the skeletons, internal organs, and nervous systems of animals (Luoma, 1983; Chaney *et al.*, 1988; Gunn *et al.*, 1988). Lead also may enter the food chain by way of plants, but this is generally considered to be a much less significant pathway than animal uptake (Kabata-Pendias, 1984; Alloway and Ayres, 1993).

Many studies have been made of soils containing low to moderate levels of Pb contamination. This is typically the result of anthropogenic enrichment via agricultural amendents (e.g., sewage sludge) and airborne deposition in urban settings. In

both cases, the levels and rates of Pb loading are low. Few studies have been made of severely contaminated soils. High levels of contamination may result from airborne deposition downwind from smelters, by decomposition of Pb shot at shooting ranges, and from refuse at battery recycling plants or dump sites. Airborne deposition rates are probably low in general, but published (Jorgensen and Willems, 1987) and proprietary data indicate that the breakdown of Pb shot occurs rapidly and causes “shock” loadings. Presumably, this also occurs when battery parts decompose, but no published studies of this phenomenon are known to us. It is important that shock loadings at high levels be studied because the behavior of Pb is likely to be quite different from that when loading rates and levels are low.

The purpose of this investigation was to characterize the behavior and fate of Pb at high levels of contamination under conditions of shock loading. Combined sequential extraction-sorption isotherm analysis (CSSA), a relatively new and little tested method, was used in the study. An Alfisol was contrasted with an Ultisol to explore a wide range of soil characteristics. Following the method of Salim *et al.* (1993, in press), the soils were first spiked with solutions containing high levels (1000 to 8000 mg/l) of Pb and sorption isotherms were constructed for the bulk soil samples. The soils were subsequently subjected to sequential extraction analysis, and sorption isotherms were then constructed for each individual targeted form. This paper discusses the Pb partitioning and sorption capacities of whole soils and the individual phases composing them. Only shock loadings by Pb are considered; the effects of prolonged accumulation at low loading levels, and of competition with other metals, were not studied.

II. PREVIOUS WORK

Lead is usually a minor constituent of Earth materials, the average concentration in uncontaminated soils being less than about 50 mg/kg (Nriagu, 1978; Shacklette and Boerngen, 1984; Adriano, 1986; Davies, 1990). Previous studies show that low to moderate levels of Pb contamination (~100 to 1000 mg/kg) are common in soils as a result of the addition of agricultural amendments (Page, 1974) and airborne deposition in urban settings (Motto *et al.*, 1970; Ward *et al.*, 1977; Parker *et al.*, 1978; Harrison *et al.*, 1981; Gatz *et al.*, 1981; Miller *et al.*, 1983; Miller and McFee, 1983; Gibson and Farmer, 1986; Yassoglou *et al.*, 1987). High levels of contamination (>1000 mg/kg) have been documented in soils affected by smelting (Marten and Hammond, 1966; Buchauer, 1973; Lagerwerff *et al.*, 1973; Wagner and Siddiqi, 1973; Temple *et al.*, 1977; Beyer *et al.*, 1984), by Pb ammunition at shooting ranges (Jorgensen and Willems, 1987), and by battery recycling plants (Elliott *et al.*, 1989). The average concentration of soil Pb at hazardous waste sites is about 300 mg/kg (Eckel *et al.*, 1985), but levels ranging up to 466,000 mg/kg have been reported (Sims *et al.*, 1986).

Lead and other heavy metals in soils generally can be found in a variety of forms exhibiting different degrees of bioavailability and mobility. The geochemical

partitioning may be determined by sequential extraction analysis (Tessier *et al.*, 1979). This method has been widely used (Martin *et al.*, 1987; Forstner, 1993), but previous studies are mainly limited to soils and sediments containing low to moderate concentrations of Pb. We know of only one published study dealing with severely contaminated soil (Elliott *et al.*, 1989). Sorption isotherm analysis is a useful technique for characterizing the adsorption characteristics and capacities of Earth materials (Kinniburgh, 1986). This technique has often been used to examine the sorption characteristics of Pb (Scudato and Estes, 1975; Griffin and Au, 1977; Zimdahl and Skogerboe, 1977; Harter, 1979; McKenzie, 1980; Farrah *et al.*, 1980; Aualiitia and Pickering, 1987), but these studies have been limited to studies of whole soils, or individual soil components in isolation. Salim *et al.* (1993) found that by combining the sequential extraction and sorption isotherm methods, it is possible to characterize the sorption characteristics of individual phases while together in a natural system. However, their study was restricted to one particular type of sediment.

III. MATERIALS AND METHODS

The Alfisol samples used in this study were collected at a rural site along I-96 near Howell, MI, about 60 km northwest of the city limits of Detroit. The sampling site is 100 m downwind from the highway in an open pasture. A carbon steel bucket auger was used for sampling. The A_p and B_t horizon samples represent the 0 to 15 cm and 31 to 45 cm depth intervals, respectively. The Ultisol samples were collected 350 m north of the junction of state highways 619 and 662 in rural Dinwiddie County, VA. Samples were obtained from a hand-dug pit. The A_p and B_t horizon samples represent the 0 to 20 cm and 21 to 42.5 cm depth intervals, respectively. The soil samples were air dried and gently ground to obtain the <2-mm fraction by sieving. Each sample was then characterized in terms of color, particle size distribution (pipette method), pH (1:1, soil:water), organic matter content (Walkley-Black method), Fe-oxide content (determined by measuring Fe in step 5 below and converting to weight percent FeOOH), carbonate content (determined gravimetrically by leaching 10-g soil samples with 100 ml of 10% HCl for 24 h), and clay mineralogy. The mineralogical composition of the clay fraction was determined by X-ray diffraction analysis using a Rigaku RU 200 rotating anode power diffractometer after pretreatment to remove soluble salts, carbonates, organic matter, and Fe-oxides (Kunze, 1965). The proportions of clay minerals present were estimated using the method of Weir *et al.* (1975).

After the basic characteristics of each soil were determined, each sample was characterized by sequential extraction analysis (as described below) to determine partitioning at background levels. Subsequently, severe contamination was simulated by spiking 2.5-g soil samples with 40 ml of solutions containing the following concentrations of Pb: 500, 1000, 3000, 4000, 5000, 6000, and 8000 mg/l. These

solutions were prepared using $\text{Pb}(\text{NO}_3)_2$. The samples were mixed on a wrist shaker for 7 d. Previous kinetic studies on clayey glacial sediments in Michigan (Salim, 1994) suggest that Pb approaches equilibrium after this time. The Pb concentrations in these supernatants were used to construct sorption isotherms for the bulk samples. After spiking and removal of supernatants, the remaining soil solid components were subjected to sequential extraction analysis. The procedure used is based on the methods of Chao (1972), Tessier *et al.* (1979), and Miller *et al.* (1986). Sequential extraction procedures are affected by a certain amount of nonselectivity and readsorption; hence, the steps are actually operationally defined in terms of the particular phases targeted. The targeted forms, extractants, and equilibrium times, respectively, were as follows:

- Step 1 (exchangeable): 20 ml 1 M MgCl_2 , 1 h
- Step 2 (carbonate occluded): 20 ml 1 M NaOAc, 5 h
- Step 3 (Mn-oxide occluded): 20 ml 0.1 M $\text{NH}_2\text{OH-HCl}$ + 0.01 M HNO_3 , 30 min
- Step 4 (organically bound): 20 ml 0.1 M $\text{K}_4\text{P}_2\text{O}_7$, 24 h
- Step 5 (Fe-oxide occluded): 20 ml 1 M $\text{NH}_2\text{OH-HCl}$ + 25% (v/v) HOAc, 4 h

Reagents were prepared from analytical-grade chemicals using distilled-deionized water. After each individual step was performed, the supernatants were obtained by centrifugation, acidified to $\text{pH} < 2.0$, and placed in acid-washed polypropylene bottles. All extractions were carried out in triplicate, and Pb was determined by flame atomic absorption spectrophotometry using a Varian AA-1275 instrument equipped with a deuterium lamp background correction. Relative standard deviations of analytical results are $\leq 20\%$.

IV. RESULTS AND DISCUSSION

A. Soil Characterization

Southeastern Michigan, where the Alfisol (Typic Hapludalf, soil series unknown) was sampled, is characterized by a humid-temperate (mesic) climate. The soil parent material is sandy calcareous glacial till of Wisconsinan age, and soil genesis has taken place over approximately the last 11,000 years (Hansel *et al.*, 1985). The soil is moderately well drained and relatively uniform as a function of depth. The thickness of the solum is about 75 cm. Table 1 shows that the Alfisol A horizon is sandy loam, whereas the B horizon is sandy clay loam. Both horizons have brown (10YR) hues. The pH of both horizons is slightly acid. Carbonate and Fe-oxide contents are low, but there is a significant increase in the carbonate levels in

TABLE 1
Characteristics of the Soil Types Studied and Michigan Glacial Lake Sediments

Sample type	Color ^a	pH	%						Clay mineralogy ^b
			Sand	Silt	Clay	FeOOH	Carb.	Org. mat.	
Alfisol A hor.	10 YR 6/4	5.3	56.8	27.3	15.9	0.07	0.01	1.70	I ₆₂ V ₁₀ K ₈ Q ₈ F ₈ C ₄
Alfisol B hor.	10 YR 6/4	6.0	40.2	25.3	34.4	0.15	1.40	0.50	I ₆₆ V ₁₀ K ₁₀ Q ₄ F ₇ C ₃
Ultisol A hor.	10 YR 5/4	6.2	73.3	14.1	12.6	2.30	0.8	0.75	ND ^c
Ultisol B hor.	5 YR 5/6	5.6	51.9	6.0	42.1	6.60	0.6	0.38	K ₅₅ CV ₃₀ G ₉ S ₅ I ₁
Glacial lake sed. ^d	2.5 YR 5/6	7.8	18.0	32.0	50.0	0.15	25.6	0.74	I ₆₁ K ₁₃ C ₈ O ₁₈

^a Dry.

^b I, illite; K, kaolinite; C, chlorite; O, quartz + feldspar + hornblende + calcite; CV, chloritized-vermiculite; V, vermiculite; G, gibbsite; S, smectite; Q, quartz; F, feldspar.

^c Not determined.

^d Data from Salim et al. (1993); average of four samples.

the subsoil. Organic matter content is average and decreases with depth. The clay mineralogy of both horizons is very similar. The predominance of illite implies that the cation exchange capacity (CEC) is moderate to low.

The Ultisol samples are from the inner Coastal Plain province of southeastern Virginia, where the climate is humid-temperate (thermic). The soil parent material is sandy alluvium of Pliocene age (Carpenter and Carpenter, 1991), and the profile is a very well drained Plinthic Paleudult (Varina Series) with a solum 83 cm thick. Table 1 shows that the quantities of FeOOH in both the A and B horizons are quite high, as expected for such an old soil. The presence of carbonate is apparently the result of artificial liming; Coastal Plain soils are typically thoroughly leached and strongly acidic. The clay fraction contains mostly kaolinite, chloritized-vermiculite, and gibbsite. This implies that the CEC is very low.

B. Background Levels of Lead

The results of sequential extraction analysis (Table 2) show that the Pb in the Alfisol A horizon is associated mostly with the organic and carbonate-occluded fractions, with lesser amounts in the exchangeable, Fe-oxide-occluded, and Mn-oxide-occluded fractions. In the B horizon, most of the Pb is in the organic fraction, suggesting that some downward movement of Pb has occurred as a result of illuviation. The total background Pb content of the Alfisol is within the range of 5 to 22 mg/kg, comparable to the results of Kessler-Arnold and O'Hearn (1989), who reported that the average total Pb content of southeastern Michigan soils ranges from 10 to 18 mg/kg. Background concentrations of Pb in Quaternary sediments of the Great Lakes region are also generally below about 25 mg/kg (Fitchko and Hutchinson, 1979; Konkel, 1979; Mudroch *et al.*, 1988; Salim *et al.*, 1993).

The Ultisol has lower levels of Pb than the Alfisol, especially in the A horizon. Sequential extraction data (Table 2) show that the Pb is mainly in the Fe-oxide-occluded form in both horizons, probably due to the high levels of Fe-oxides present. Organically bound Pb has a higher concentration in the A horizon, and the carbonate-occluded fraction contains higher levels of Pb in the Ultisol B horizon. Overall, the total background levels of Pb are between 4.0 and 10.0 mg/kg. Tidball (1976), Shacklette and Boerngen (1984), and Holmgren *et al.* (1993) have also reported that the Pb content of soils in the Atlantic Coastal Plain is generally low, with concentrations equal to or less than 14 mg/kg.

C. Lead Distribution at High Levels of Contamination

The spiked Alfisol and Ultisol soil samples sorbed large quantities (~3000 to 60,000 mg/kg) of Pb (Table 3). The sequential extraction data show that the

TABLE 2
Sequential Extraction Analysis of Background Levels of Lead

Soil type	Targeted form												Summed total mg/kg
	Exchangeable		Carbonate occl.		Mn-oxide occl.		Organic		Fe-oxide occl.		Residual		
	mg/kg	% ^a	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	
Alfisol A hor. ^b	3.6	16.1	5.1	22.9	1.1	4.9	8.7	39.0	3.5	15.7	BDL	0	22.3
Alfisol B hor. ^b	0.4	7.7	0.9	17.3	0.3	5.8	3.0	57.7	0.4	7.7	BDL	0	5.2
Ultisol A hor.	BDL ^c	0.0	0.8	7.7	BDL	0.0	1.6	15.4	8.0	76.9	ND ^d	0	10.4
Ultisol B hor.	BDL	0.0	1.3	31.7	0.4	9.8	0.6	14.6	1.8	43.9	ND ^d	0	4.1

^a Percentage of summed total.

^b Data from Howard and Sova (1993).

^c BDL, below detection limit.

^d ND, not determined.

TABLE 3
Sequential Extraction Analysis of Lead After Spiking

Spike concentration (mg/l)	Targeted form												Summed total sorbed (mg/kg)	Total sorbed by bulk sample (mg/kg)	% difference in summed vs. bulk totals ^b
	Exchangeable		Carbonate occl.		Mn-oxide occl.		Organic		Fe-oxide occl.						
	mg/kg	% ^a	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%			
Alfisol A Horizon															
500	2,837.6	67.7	997.6	23.8	109.6	2.6	183.2	4.4	60.8	1.4	4,188.8	4,724.8	11.3		
1,000	3,242.4	66.0	1,245.6	25.4	130.4	2.7	226.4	4.6	65.6	1.3	4,910.4	6,036.8	18.7		
3,000	3,854.4	68.7	1,221.6	21.8	214.4	3.8	248.8	4.4	73.6	1.3	5,612.8	11,035.2	49.1		
4,000	3,904.0	68.4	1,248.0	21.9	180.8	3.2	295.2	5.2	80.8	1.4	5,708.8	7,252.8	21.3		
5,000	3,964.0	70.1	1,069.6	18.9	258.4	4.6	279.2	4.9	84.8	1.5	5,656.0	9,172.8	38.3		
6,000	4,061.6	69.1	1,365.6	23.2	124.8	2.1	253.6	4.3	68.8	1.2	5,874.4	9,595.2	38.8		
8,000	4,353.6	67.9	1,562.4	24.4	167.6	2.6	265.6	4.1	64.8	1.0	6,414.0	10,395.2	38.3		
Alfisol B Horizon															
500	306.4	4.6	5,522.4	83.3	192.0	2.9	421.6	6.4	184.0	2.8	6,626.4	7,988.2	17.0		
1,000	298.4	2.6	8,688.0	76.7	839.2	7.4	1,104.0	9.7	400.0	3.5	11,329.6	15,954.2	29.0		
3,000	584.0	1.5	34,604.0	91.2	1,048.0	2.8	1,288.0	3.4	420.0	1.1	37,944.0	47,520.0	20.2		
4,000	672.0	1.6	38,500.0	91.2	1,056.0	2.5	1,632.0	3.9	464.0	1.1	42,224.0	52,272.0	19.2		
5,000	778.4	1.7	41,021.6	91.1	1,072.0	2.4	1,648.0	3.7	524.0	1.2	45,044.0	54,980.8	18.1		
6,000	653.6	1.4	43,500.0	91.1	1,272.0	2.7	1,768.0	3.7	544.0	1.1	47,737.6	52,811.2	9.6		
8,000	506.4	1.0	46,280.0	90.5	1,332.0	2.6	2,284.0	4.5	712.0	1.4	51,114.4	59,280.0	13.8		
Ultisol A Horizon															
500	1,621.6	61.1	805.6	30.4	94.4	3.6	58.4	2.2	72.0	2.7	2,652.0	3,099.2	14.4		
1,000	1,741.6	63.0	808.0	29.2	110.4	4.0	43.2	1.6	63.2	2.3	2,766.4	3,760.0	26.4		
3,000	1,896.0	62.9	880.0	29.2	138.4	4.6	34.4	1.1	64.0	2.1	3,012.8	6,336.0	52.4		
4,000	2,056.0	55.5	1,341.6	36.2	145.6	3.9	64.8	1.7	98.4	2.7	3,706.4	5,472.0	32.3		
5,000	2,056.0	58.4	1,184.0	33.6	168.8	4.8	40.8	1.2	69.6	2.0	3,519.2	7,792.0	54.8		
6,000	2,128.0	56.9	1,298.4	34.7	171.2	4.6	58.4	1.6	84.8	2.3	3,740.8	10,576.0	64.6		
8,000	2,277.6	53.6	1,629.6	38.4	184.0	4.3	61.6	1.4	92.8	2.2	4,245.6	4,448.0	4.6		

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Ultisol B Horizon													
500	1,989.6	72.7	600.0	21.9	44.8	1.6	27.2	1.0	73.6	2.7	2,735.2	3,643.2	24.9
1,000	2,258.4	70.9	776.0	24.4	56.0	1.8	28.8	1.0	67.2	2.1	3,186.4	4,523.2	29.6
3,000	2,888.0	72.3	936.0	23.4	62.4	1.6	33.6	0.8	72.8	1.8	3,992.8	8,011.2	50.2
4,000	2,640.0	63.0	1,312.0	31.3	88.8	2.1	56.8	1.4	95.2	2.3	4,192.8	6,720.0	37.6
5,000	3,208.0	66.3	1,384.0	28.6	96.0	2.0	52.8	1.1	100.0	2.1	4,840.8	8,452.8	42.7
6,000	2,748.0	55.5	1,912.0	38.6	106.4	2.2	67.2	1.4	113.6	2.3	4,947.2	9,883.2	51.0
8,000	3,410.4	67.6	1,384.0	27.4	77.6	1.5	52.8	1.0	118.4	2.3	5,043.2	6,016.0	16.2

^a Percentage of summed total sorbed.

^b Calculated as $100 \cdot (\text{total sorbed by bulk sample}) \cdot (\text{summed total sorbed}) / \text{total sorbed by bulk sample}$.

sorbed Pb in the Alfisol A horizon is mostly in the exchangeable (~68% of summed total) and carbonate-occluded (~21% of summed total) fractions. It was expected that significant levels of exchangeable Pb would be present because this form typically increases with increasing pollution as other phases become overloaded (Engler, 1980; Forstner and Wittman, 1981; Forstner, 1989). However, it is surprising that more Pb is not organically bound because this form is prominent at background levels (Table 2) and is often predominant in soil surface horizons (Zimdahl and Skogerboe, 1977; Berrow and Mitchell, 1980; Miller and McFee, 1983; Miller *et al.*, 1983; Adriano, 1986; Davies, 1990). The association of Pb with carbonate, especially in the Alfisol B horizon, is expected because Pb has often been found in the carbonate fraction of calcareous soils (Sposito *et al.*, 1982; Gibson and Farmer, 1984, 1986; Yassoglou *et al.*, 1987; Howard and Sova, 1993). The results are also similar to those of Elliott *et al.* (1989), who studied a soil containing about 200,000 mg/kg Pb and found most of the metal in an acid-soluble (presumably carbonate-occluded) form. In contrast with Harter (1979), who found a good correlation between Pb sorption and vermiculite content, the differences in the levels of exchangeable Pb in the A and B horizons of the Alfisol studied here are probably due to differences in organic matter content because the proportions of vermiculite in the clay fractions of both horizons are about the same (Table 1).

Unlike the Alfisol, the distribution of the Pb in the Ultisol is about the same in both horizons (Table 3). The Pb is found mainly in exchangeable (~58% of summed total) and carbonate (~30% of summed total) forms. The differences in the levels of exchangeable Pb in the two horizons correspond better with differences in clay content than with organic matter content (Table 1). This is attributable to the low levels of organic matter present. As noted above, the association of Pb with carbonate is not surprising, and both clay and carbonate content have previously been found to be good predictors of Pb retention by soils (Korte *et al.*, 1976; King, 1988). More Pb is associated with carbonate in the spiked samples than at background levels (Table 2), probably because lime was recently added as an agricultural amendment. The presence of lime suggests that Pb may be precipitating as a separate carbonate phase, although further study is needed to document this reaction. Iron-oxide content is usually a good predictor of Pb retention by soil (Jenne, 1968; Korte *et al.*, 1976; King, 1988), probably because oxides have a strong specific sorption affinity for Pb (McKenzie, 1980; Aualiitia and Pickering, 1987). The oxides in the Ultisol (Plinthic Paleudult) studied may have a low affinity for Pb partly because the soil pH (5.6 to 6.2) is below the zero point of charge (pH 8.5) of Fe-oxides (Dragun, 1988); a positive surface charge precludes cation exchange reactions involving Pb. Elliott *et al.* (1986) noted that removal of Fe-oxides from a Plinthic Paleudult reduced the soil ZPC from 6.0 to 2.3 and increased the sorption of heavy metals. Another contributing factor may be the predomi-

nance of hematite and (or) goethite in the Ultisol studied. Well-crystallized Fe-oxides are thought to have less of an affinity for Pb than freshly precipitated and less crystalline forms (Dragun, 1988), and Aualiitia and Pickering (1987) have shown that specific sorption by hematitic and goethitic iron ores is limited at pH values less than about 6.0.

Table 3 also compares the summed total determined by sequential extraction with the total obtained using the bulk sample. The comparison shows that the summed total sorbed is always less than the bulk total sorbed. This is probably partly the result of the inevitable loss of a small amount of solid material when the samples are washed with deionized water between each step in the sequential extraction procedure, and partly due to random sample variability. The differences range from 4.6 to 64.6% (average of 30.2% with a standard deviation of 15.9%). These differences are somewhat greater than those of 20% reported by Harrison *et al.* (1981). It is also evident from the results in Table 3 that the proportions of the Pb sorbed by each individual phase are more or less the same despite the range in concentrations used. Hence, a better estimation of the actual amounts of Pb in each targeted phase could theoretically be obtained using the relative proportions in each phase and the bulk totals as a correction factor.

Table 4 indicates that the quantities of Pb sorbed by each of the bulk samples for both soils decrease with increasing spike concentrations, as expected. The decrease of the sorption is probably because there are only a limited number of sorption sites in the soils for this particular metal. The Alfisol B horizon stands out as having sorbed almost all of the Pb added up to a spiking solution concentration of 3000 mg/l. Carbonate is clearly of prime importance in controlling the Pb in the soils studied. Lime also has been recognized for many

TABLE 4
Quantities of Lead Sorbed by Bulk Soil Samples

Spike concentration (mg/l)	Sample type							
	Alfisol				Ultisol			
	A horizon		B horizon		A horizon		B horizon	
	mg/kg	% ^a	mg/kg	%	mg/kg	%	mg/kg	%
500	4,724.8	59.1	7,988.2	99.8	3,099.2	38.7	3,643.2	45.5
1,000	6,036.8	37.7	15,954.2	99.7	3,760.0	23.5	4,523.2	28.3
3,000	11,035.2	23.0	47,520.0	99.0	6,336.0	13.2	8,011.2	16.7
4,000	7,252.8	11.3	52,272.0	81.7	5,472.0	8.6	6,720.0	10.5
5,000	9,172.8	11.5	54,980.8	68.7	7,792.0	9.7	8,452.8	10.6
6,000	9,595.2	10.0	52,811.2	55.0	10,576.0	11.0	9,883.2	10.3
8,000	10,395.2	8.1	59,280.0	46.3	4,448.0	3.5	6,016.0	4.7

^a Percentage of total added in spiking solution.

years as an excellent immobilizing agent for the remediation of sites contaminated by heavy metals (John, 1972; Korte *et al.*, 1976).

D. Sorption Isotherms of Bulk Samples

Figure 1 shows that the Alfisol B horizon is characterized by an H-type isotherm, whereas the other sample isotherms are of the L-type. The H-type isotherm is usually produced by either significant van der Waal's interactions contributing to the sorption process, or by a highly specific interaction between the solid phase and the sorbing substance (Dragun, 1988). The results of sequential extraction analysis (Table 3) suggest that the carbonate phase is responsible for the strong affinity of the Alfisol B horizon for Pb. McBride (1979) has shown that carbonate sorbs Mn by a combination of precipitation and specific adsorption; presumably, the same relations are true for Pb. L-type isotherms reflect a strong affinity at low concentrations, but less affinity at higher levels due to a limiting number of sorption sites and a decrease in sorbing surface as the excess of sorbate increases (Sposito, 1984). This isotherm shape is thought to be produced when physisorption or ion exchange is dominant, and is characteristic of layer silicate minerals and organic matter (Farrah *et al.*, 1980; Adriano, 1986). Thus, the observed isotherm shapes (Figure 1) concur with sequential extraction results (Table 3), indicating the importance of clay content and (or) organic matter in controlling Pb sorption in the Alfisol A horizon and in both Ultisol horizons.

E. Sorption Isotherms of Individual Fractions

Using CSSA, Salim *et al.* (1993) showed that it is possible to construct isotherms not only for bulk sediment samples, but for individual phases as well. This is done

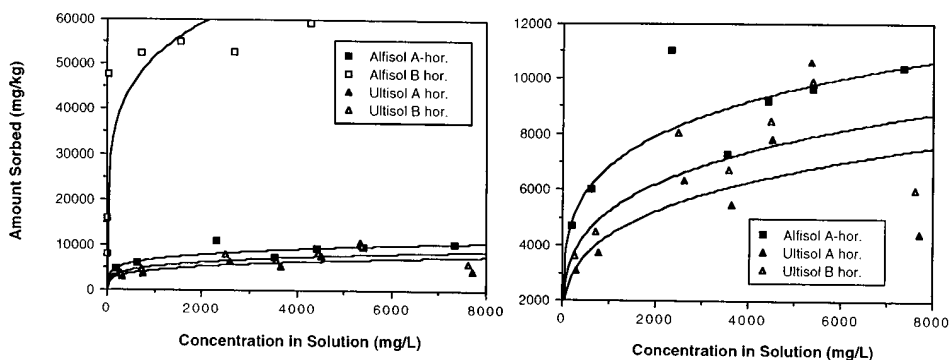


FIGURE 1. Lead sorption isotherms for bulk samples. Plot at right corresponds to that at left but at expanded scale.

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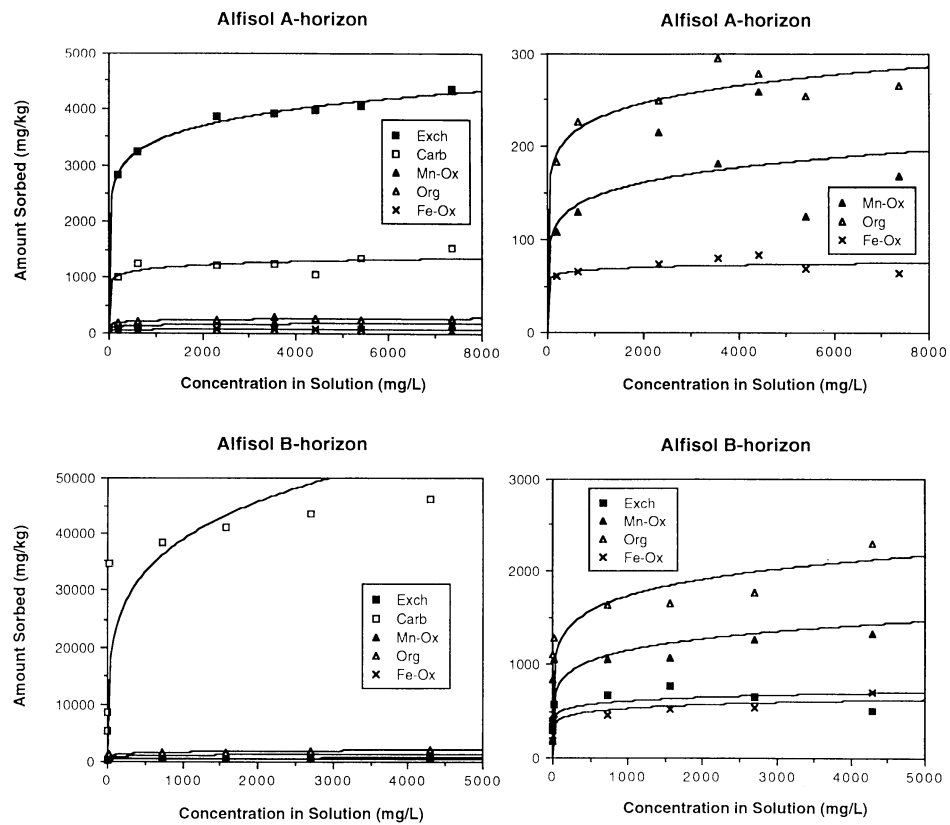


FIGURE 2. Lead sorption isotherms for each form targeted by sequential extraction analysis. Plots at right correspond to those at left but at expanded scale.

by plotting the amounts recovered in each step of the sequential extraction procedure after spiking against the corresponding equilibrium solution concentration determined using the bulk sample. This approach has a definite advantage over previous methods, which have relied on bulk samples or single pure phases in isolation, because it allows sorption capacities to be determined for individual phases while together in a natural mixture. Figures 2 and 3 show that it is also possible to build isotherms successfully for most of the individual fractions examined in this study. Correlation coefficients indicate that there is a good fit to the Freundlich equation (Table 5) in many cases. The poorest fit generally seems to be associated with the oxide-occluded fractions, similar to the findings of Salim *et al.* (1993). This problem is perhaps attributable to the small quantities of oxides present, thereby resulting in greater scatter among samples.

The shapes of the isotherms for individual fractions are similar to those of the corresponding bulk samples. Thus, with the exception of the H-type isotherm

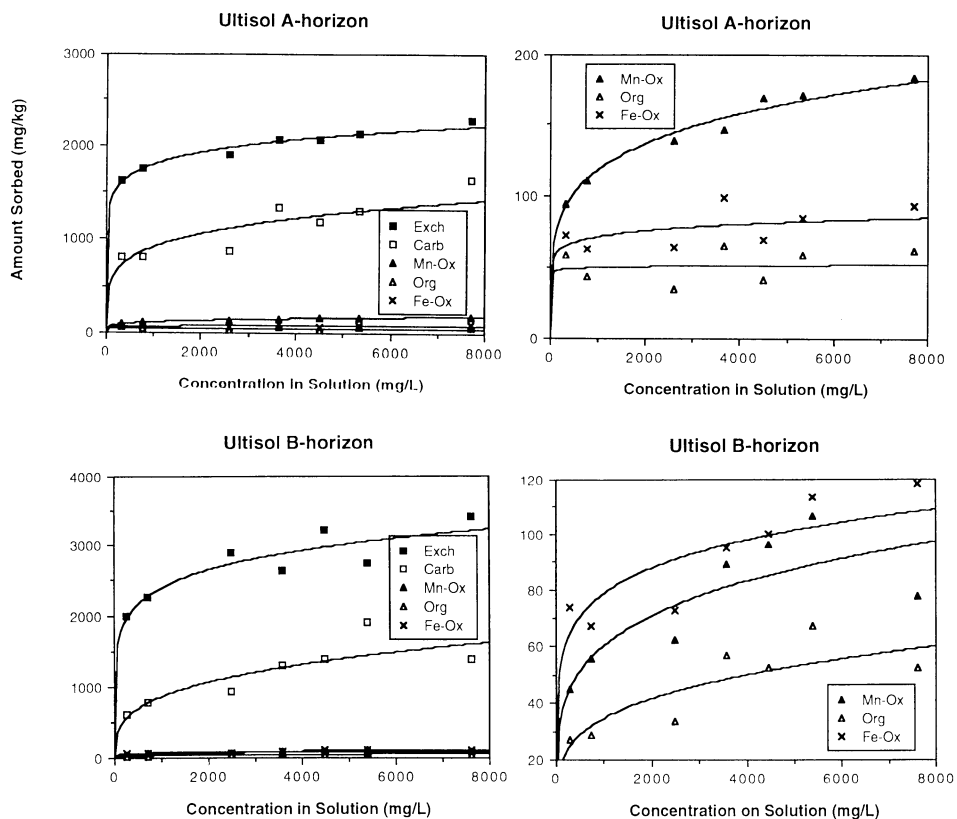


FIGURE 3. Lead sorption isotherms for each form targeted by sequential extraction analysis. Plots at right correspond to those at left but at expanded scale.

derived for the carbonate fraction of the Alfisol B horizon, the isotherms for the individual fractions generally appear to be of the L-type. As noted previously, the shapes of isotherms are thought to reflect the type of sorption mechanism taking place, with H-type and L-type isotherms representing chemisorption and physisorption, respectively (Sposito, 1984; Dragun, 1988). However, care must be exercised when interpreting and comparing isotherm shapes because it is not possible to distinguish sorption and precipitation using isotherm data alone (Sposito, 1984), and because the isotherm shapes depend on such factors as the scales used in plotting and the relative proportions of phases in the samples. To the extent that sorption mechanisms are reflected in the shapes of the isotherms in Figures 2 and 3, there is no indication of specific adsorption by oxides, even in the Ultisol B horizon.

Table 5 shows that there is an excellent fit between the data and the particular form of the Langmuir equation used; hence, estimated sorption capacities were obtained not only for bulk samples, but for individual phases as well (Table 6). The

TABLE 5
Correlation Coefficients (R) for Freundlich and Langmuir Sorption Isotherms

Soil type	Targeted Form							Bulk sample
	Exchangeable	Carbonate occl.	Mn-oxide-occl.	Organic	Fe-oxide occl.			
	Freundlich Isotherms							
Alfisol A horizon	0.99	0.67	0.58	0.89	0.54		0.88	
Alfisol B horizon	0.83	0.93	0.79	0.89	0.89		0.91	
Ultisol A horizon	0.98	0.87	0.99	0.10	0.55		0.71	
Ultisol B horizon	0.92	0.92	0.88	0.88	0.83		0.83	
	Langmuir Isotherms							
Alfisol A horizon	1.00	0.97	0.94	1.00	0.99		0.98	
Alfisol B horizon	0.99	1.00	1.00	0.98	0.98		1.00	
Ultisol A horizon	1.00	0.96	0.99	0.93	0.97		0.88	
Ultisol B horizon	0.98	0.95	0.96	0.96	0.98		0.94	

TABLE 6
Sorption Capacities Obtained From Langmuir Isotherms

Soil type	Targeted Form							% difference in summed vs. bulk totals ^a
	Exchangeable (mg/kg)	Carbonate-occl. (mg/kg)	Mn-oxide-occl. (mg/kg)	Organic (mg/kg)	Fe-oxide-occl. (mg/kg)	Summed total (mg/kg)	Bulk Total (mg/kg)	
Alfisol A horizon	4,353.5	1,479.9	161.3	270.3	67.6	6,332.6	10,437.3	39.3
Alfisol B horizon	526.3	46,168.1	1,321.7	2,152.8	666.7	50,835.6	58,207.2	12.7
Ultisol A horizon	2,300.0	1,678.4	192.3	62.1	92.6	4,325.4	5,452.6	20.7
Ultisol B horizon	3,353.4	1,657.9	90.1	62.1	125.0	5,287.6	7,007.7	24.5
Glacial lake sed. ^b	264.6	217,865.0	100.0 ^c	1,164.0	476.2	219,869.8	180,500.0	-17.9

^a Calculated as 100 [(total sorbed by bulk sample) - (summed total sorbed)]/total sorbed by bulk sample.

^b Data from Salim et al. (1993).

^c Estimated value.

total sorption capacities obtained by summing the capacities of each individual fraction show good agreement with those measured directly using bulk samples. This successful mass balance implies that the individual capacities are reasonably accurate. The differences in sorption capacities (summed total vs. bulk total) average about 23%, comparable to results reported by Salim *et al.* (1993) for Michigan glacial lake sediments. Except for the Alfisol B horizon, the sorption capacity of the exchangeable fraction is greatest, and it is clear that the capacities of the other fractions have been exceeded after spiking. This accounts for the observed predominance of exchangeable forms of Pb under conditions simulating severe contamination. Farrah *et al.* (1980) obtained the adsorption capacities of illite, kaolinite, and montmorillonite for Pb using “pure” samples. With their data, and the proportions of clay and clay mineral types in the Alfisol B horizon (Table 1), an approximate adsorption capacity of about 5600 mg/kg is calculated for the exchangeable fraction using montmorillonite to conservatively estimate the adsorption capacity of vermiculite. Because the observed capacity is only 526 mg/kg (Table 6), this result suggests that an evaluation of the attenuation capability of a part of a soil based on “pure” phases may be overestimated by an order of magnitude or more.

The bulk sorption capacity of the Alfisol A horizon for Pb (10,437 mg/kg) is somewhat lower than the capacities of other Michigan soils (10,712 to 15,656 mg/kg) characterized by Zimdahl and Skogerboe (1977), and of Alfisols in Pennsylvania and New York (14,248 mg/kg and 25,792 mg/kg, respectively) reported previously by Harter (1979). The B horizon of the Alfisol studied stands out as having the capacity to sorb the greatest levels of Pb. This is obviously due to the carbonate fraction, which itself is able to occlude 46,168 mg/kg of the Pb, or about 90% of the summed total. However, an even higher sorption capacity (180,500 mg/kg) was obtained by Salim *et al.* (1993) for calcareous sediments containing about 25% carbonate (Table 1). The sorption capacities obtained for the Ultisol studied (5453 to 7008 mg/kg) are within the range of those reported previously (Harter, 1979) for Ultisols in Maryland and Pennsylvania (4536 mg/kg and 16,432 mg/kg, respectively).

V. SUMMARY AND CONCLUSIONS

The behavior of Pb in the A and B horizons of a Michigan Alfisol and a Virginia Ultisol was studied by CSSA after spiking to simulate severe contamination. All of the samples sorbed large quantities (~3000 to 60,000 mg/kg) of Pb. CSSA showed that Pb is predominantly in an exchangeable form in the A horizon of the Alfisol and in both horizons of the Ultisol because the sorption capacities of the phases commonly responsible for the fixation of Pb at low to moderate levels of contamination are exceeded. Carbonate sorbed the bulk of the Pb in the Alfisol B horizon and has a high sorption capacity in both soils, despite the presence of other

phases with strong affinities for Pb. The exchangeable form is mobile and bioavailable (Luoma, 1983; Gunn *et al.*, 1988; Dragun, 1988). Hence, these results suggest the following scenarios in the event of severe Pb contamination: (1) the A horizons of both soils are expected to pose a serious toxic hazard to humans either directly by ingestion or indirectly because of bioaccumulation in the food chain, (2) groundwater contamination is possible in association with the Ultisol because Pb in the B horizon is mobile, and (3) no groundwater contamination is expected in association with the Alfisol because Pb in the B horizon is immobilized by fixation reactions involving carbonate precipitation. Although it was anticipated that significant quantities of exchangeable Pb would be present at high levels of contamination, the magnitudes observed were unexpected because at low to moderate levels of contamination, Pb is commonly immobilized in soils by fixation reactions involving organic matter and oxide minerals.

In recent years, there has been great interest in the effects of heavy metals resulting from the land disposal of untreated wastes such as sewage sludge, municipal wastewater, landfill leachates, dredged sediments, and oil refinery wastes. Hence, many investigations have been carried out to determine which properties are important for predicting the attenuation capabilities of soils and for regulating the surface applications of such wastes. These studies have relied on samples of whole soils or of individual components in isolation. The former approach is limited by the fact that no information is gained regarding the actual partitioning of metals in various forms; the latter by the fact that interactions among phases cannot be documented. The CSSA approach is superior because it overcomes both of these limitations; however, further studies are needed. Only shock loadings by Pb were investigated in this study, and the geochemical behavior of Pb may not necessarily be the same in the presence of other metals or if high levels are achieved by a gradual buildup through low loading levels over a prolonged period of time. The results may be applicable at heavily contaminated sites where rapid loading probably does occur, such as shooting ranges and hazardous waste dump sites.

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