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Sequential Extraction Analysis of Lead in Michigan Roadside Soils: Mobilization in the Vadose Zone by Deicing Salts?

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ABSTRACT: Sequential extraction analysis was used to characterize the geochemical partitioning of Pb in roadside soils of the Detroit, MI area. Four soil profiles (10, 30, 60, and 100 m from road) were sampled at 15-cm intervals to a depth of 75 cm at each of five locations along an urban-rural transect. The observed concentrations increase with increasing traffic volume and proximity to the highway, indicating that vehicle emissions are the principal source of Pb. Concentrations in roadside soils of urban sites (>100,000 vehicles per 24 h) are 10 to 15 times greater than the background level of 12 to 22 mg/kg found at rural sites. Sequential extraction data show that the Pb is mainly in carbonate and oxide forms in the most heavily contaminated soils; organically bound forms tend to predominate elsewhere. Both surface and subsurface horizons of soils are polluted at urban sites where translocation in the vadose zone is suggested by elevated levels of Pb to depths of 75 cm. Mobilization is attributed primarily to partial dissolution of organic matter by excess NaCl derived from highway deicing salts and complexation of Pb with organic chelates. Mobilization appears to be occurring in soils up to 60 m from the highway at urban sites.

KEY WORDS: sequential extraction, lead contamination, urban soils, leaching, ground water.

I. INTRODUCTION

A 1974 EPA mandate requiring the use of unleaded fuel in all new automobiles has resulted in significant reductions of Pb emissions in the U.S. (USEPA, 1990). However, leaded gasoline is still burned in older vehicles, which may account for as much as 30% of vehicular air pollution in some areas, and many other countries have yet to regulate the use of leaded fuels (World Resources Institute, 1990). Lead and other toxic heavy metals are among the chief constituents of urban runoff (Cole *et al.,* 1984; Marsalek and Schroeter, 1988), much of which is derived from streets and highways (Johnston and Harrison, 1984; Lygren *et al.*, 1984; Hoffman *et al.*, 1985; Harrison and Johnston, 1985; Stoltz, 1987). These metals are found at elevated levels in roadside soil and vegetation (Cannon and Bowles, 1962; Chow, 1970; Lagerwerff and Specht, 1970; Ward *et al.*, 1977; Muskett and Jones, 1980; Ho and Tai, 1988) where they accumulate both as a result of surface runoff and airborne deposition. There is also evidence that most of the Pb found in urban street dusts is derived from highways rather than residences (Hopke *et al.,* 1980; Linton *et al.,* 1980; Gulson *et al.,* 1981), and even the Pb content of some urban household dusts is significantly related to traffic volume and proximity to a highway (Culbard *et al.,* 1988). Once released into the roadside environment, Pb is persistent; hence, there is growing concern over highways as nonpoint sources of pollution.

Using single-extractant determinations and total concentrations, early studies established a clear correlation between the heavy metal content of roadside soil and traffic volume, road age, or proximity to a highway (Singer and Hanson, 1969; Lagerwerff and Specht, 1970; Chow, 1970; Motto *et al.*, 1970; Page *et al.*, 1971; Ward *et al.,* 1977; Muskett and Jones, 1980). It was also determined that although PbBrCl is the principal component of exhaust from vehicles using leaded gasoline, it is rapidly converted into other compounds (Pierrard, 1969; Ter Haar and Bayard, 1971). However, the fate of the metal in roadside soils was less clear (Olson and Skogerboe, 1975; Zimdahl and Skogerboe, 1977; Biggins and Harrison, 1980). Later investigations have provided more definitive documentation of the geochemical partitioning of heavy metals in street dusts and roadside and urban soils with sequential extraction methods (Harrison *et al.,* 1981; Miller and McFee, 1983; Gibson and Farmer, 1984, 1986; Garcia-Miragaya, 1984; Yassoglou *et al.,* 1987). These studies have shown that the bulk of anthropogenic Pb in roadside soils is typically immobilized by fixation reactions involving organic matter or carbonate and oxide minerals. Thus, Pb is expected to be concentrated in the surface horizons of roadside soils where it poses little threat to ground water.

Most previous studies have used soil samples collected within 15 cm of the ground surface (many no more than about 3 cm deep) and within about 50 m of the road. The purpose of this study was to determine the geochemical partitioning of Pb in roadside soil samples at greater depths below the soil surface and at greater distances from the highway. Preliminary results suggested that Pb had been mobilized in the vadose zone at the contaminated urban sites studied, and it was hypothesized that chlorides derived from deicing salt were responsible. Hence, these soils and several background samples were subsequently analyzed for evidence of salt contamination using water-soluble Na as an indicator. Sodium was chosen over measuring Cl directly because the latter is known to be leached very rapidly (Hanes *et al.,* 1976), whereas Na is more likely to be retained on exchange sites.

II. MATERIALS AND METHODS

Five sites located approximately 40 km (25 miles) apart were studied along an urban-rural transect in the Detroit metropolitan area (Figure 1). The locations, construction dates, and traffic volumes at the areas sampled are given in Table 1. Site 1 is located just upwind from the juncture of two major freeways, and the others along a major interstate highway. Undisturbed soils were studied except

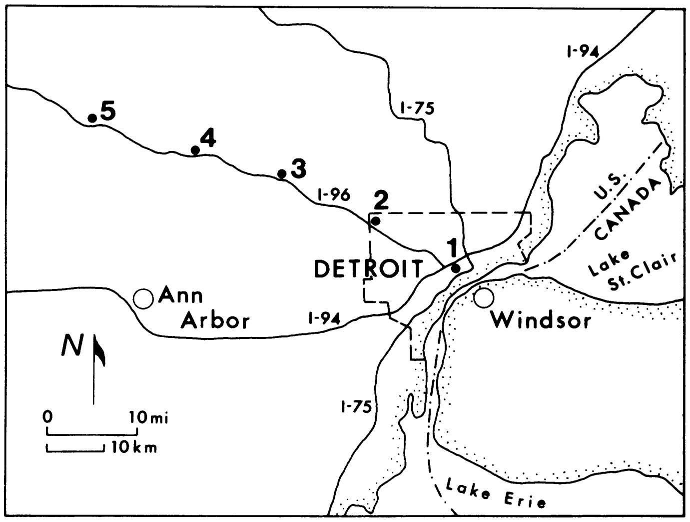

FIGURE 1. Locations of soil sampling sites in southeastern Michigan. Dashed line indicates Detroit city limit.

TABLE 1
Highway Construction Dates and 1990 Traffic Volumes at the Sites Studied

Site location	Constructed	Traffic volume (vehicles per 24 h)
I-94 at Hwy. 10	1955	145,700 (119,200)[a]
I-96 near Hwy. 24	1977	131,900
I-96 near Novi Rd.	1957	105,200
I-96 near Kent Lake Rd.	1957	96,400
I-96 near Chilson Rd.	1963	49,500

[a] Additional traffic volume for Hwy. 10.

Source: Michigan Department of Transportation. 1992. Personal communication.

along highway shoulders (≤10 m from the road) and at site 1 (≥30 m from road), which was fill constructed by Wayne State University in 1966. Metropolitan Detroit has a population of 4 million people and a normal annual precipitation of 80 cm. All soils were sampled at 0- to 15-, 16- to 30-, 31- to 45-, 46- to 60-, and 61- to 75-cm depth intervals, and at distances of 10, 30, 60, and 100 m on the downwind side of each highway using a carbon steel bucket auger. The dominant vegetation at each site was grass; hence, the only obstructions to the wind were occasional small bushes or trees. The soil samples were air dried and the <2-mm fraction obtained by sieving. Each sample was characterized for particle size distribution (pipette method) and organic matter content (Walkley-Black method). Each bulk sample was split to obtain a 10-g subsample that was ground to <0.5 mm in an agate mortar and pestle, and then split to obtain 2.5-g duplicate samples for chemical analysis. The sequential extraction procedure used is based on the methods of Chao (1972), Tessier *et al.* (1979), and Miller *et al.* (1986). It is recognized that no sequential extraction procedure is perfectly selective and that problems exist with resorption (Rendell *et al.,* 1980; Tipping *et al.,* 1985; Kheboian and Bauer, 1987); nevertheless, the utility of the technique is widely accepted. The sequential extraction procedure was done using 2.5-g samples of soil and 20 ml of extracting solution. The targeted forms, extractants, and equilibration times are as follows:

- Step 1 (water soluble): 20 ml distilled-deionized H_2O, 16 h.
- Step 2 (exchangeable): 20 ml 1 *M* $MgCl_2$, 1 h
- Step 3 (carbonate occluded): 20 ml 1 *M* NaOAc, 5 h
- Step 4 (Mn-oxide occluded): 20 ml 0.1 *M* NH_2OH-HCl + 0.01 *M* HNO_3, 30 min
- Step 5 (organically bound): 20 ml 0.1 *M* $K_4P_2O_7$, 24 h
- Step 6 (Fe-oxide occluded): 20 ml 1 *M* NH_2OH-HCl + 25% (v/v) HOAc, 4 h
- Step 7 (residual or silicate occluded): (0.2 g soil) 1 ml aqua regia + 6 ml HF + 2.8 g boric acid heated at 130°C for 2 h in Parr digestion bomb

Each sample was extracted by mixing with a wrist-action shaker, and the supernatants collected by centrifugation. All extracts were acidified to pH <2.0 with 1 *M* HNO_3 and analyzed for Pb by flame atomic absorption spectrophotometry using a Varian AA-1275 instrument equipped with a deuterium lamp background correction. The water-soluble extracts from the sequential extraction procedure also were analyzed for Na, the carbonate-occluded extracts for Ca, Mn-oxide-occluded extracts for Mn, and Fe-oxide-occluded extracts for Fe. These data were converted to weight percent Fe-oxide (FeOOH), Mn-oxide (MnO_2), and carbonate ($CaCO_3$) and used to estimate phase concentrations. Phase concentration factors (PCFs) were calculated as the ratio of the weight percentage of Pb in a given form (determined by sequential extraction) to the weight percentage of the form in the sample. According to this method (Forstner and Patchineelam, 1980), Pb enrichment of a form is indicated by a PCF >1, whereas PCFs ≤1 indicate no enrichment. Background levels of water-soluble Na were estimated using duplicate samples from two surface soils collected in wooded areas within the city of Detroit. Analytical precision for the chemical data is generally ≤20% (relative standard deviation).

III. RESULTS AND DISCUSSION

A. Soil Characterization

The soils found at each site studied are relatively uniform as a function of both depth and distance from the highway; representative profiles are described in Table 2. Sites 1, 2, and 3 (Figure 1) are on a nearly level glacial outwash plain underlain by alluvial sand and gravel, and lacustrine silt and clay. These soils are moderately well to somewhat poorly drained, yellowish-brown (10 YR), calcareous sandy loam and loam. The fill at site 1 is composed of a mixture of loamy A and B horizon material and contains occasional artifacts such as brick, cement, burnt wood, coal clinker, and unidentifiable metallic fragments. Sites 4 and 5 are on gently sloping moraines underlain by sandy glacial till. The soils here are similar to those above, but somewhat better drained and less calcareous. Limestone pebbles are generally found at all sites, and the presence of weathered mafic rock fragments at site 3 is reflected in brown (7.5 YR) hues. Fe and Mn oxides are generally low, but elevated levels of water-soluble Na are common in the pedons studied, especially near the highway and at urban sites. Solum thicknesses are generally ≤75 cm, and the undisturbed soils classify mainly as Inceptisols. The parent materials for the soils are of Wisconsinan age, and soil genesis has taken place over approximately the last 13,000 years.

B. Lead in Surface Horizons

The results of chemical analysis (Table 3) show that the soils at the urban sites studied (1, 2, and 3) are polluted with Pb. This is based on the fact that total lead concentrations at these sites are 10 to 25 times greater than those at rural locations 4 and 5 (Figure 1). Concentrations in surface horizons 100 m from the road at the rural sites indicate an apparent background level of 12 to 22 mg/kg (Table 3). This is similar to the 10 to 18 mg/kg average range reported by Kessler-Arnold and O’Hearn (1989) for southeastern Michigan soils. Lead contents generally decrease with increasing distance from the highway at urban sites; hence, the principal

TABLE 2
Characteristics of Representative Soil Profiles (100 m from Road)

Depth (cm)	Color	pH	Sand	Silt	Clay	FeOOH (wt. %)	MnO_2	Carbonate	Org. Mat.	Na[a] (mg/kg)
Site 1										
0–15	10 YR 3/1	7.6	61	21	18	0.08	<0.01	0.1	4.5	79[b]
16–30	10 YR 6/2	7.6	62	20	18	0.10	0.01	1.2	4.6	59
31–45	10 YR 5/4	7.8	55	24	21	0.11	0.01	1.2	4.8	58
46–60	10 YR 5/6	7.4	50	26	24	0.11	<0.01	1.2	4.0	48
61–75	10 YR 5/3[c]	7.2	50	30	20	0.10	<0.01	1.0	2.6	151
Site 2										
0–15	10 YR 3/2	7.6	72	22	6	0.07	0.01	0.3	3.4	10
16–30	10 YR 6/2	7.6	68	21	11	0.09	0.01	0.4	3.1	17
31–45	10 YR 4/3[c]	7.7	29	41	30	0.19	0.01	0.5	5.6	27
46–60	10 YR 6/4[c]	7.5	24	70	6	0.20	0.05	0.1	3.0	29
61–75	10 YR 5/4[c]	7.8	12	45	43	0.21	0.06	0.1	1.1	25
Site 3										
0–15	10 YR 4/2	7.0	64	26	10	0.05	<0.01	0.05	1.1	10
16–30	10 YR 5/1[c]	6.8	73	19	8	0.03	<0.01	0.01	0.1	70
31–45	10 YR 5/6[c]	7.4	60	30	10	0.05	<0.01	0.02	<0.1	74
46–60	10 YR 5/6[c]	7.6	36	38	26	0.12	<0.01	0.03	<0.1	15
61–75	10 YR 6/1[c]	7.8	66	19	15	0.11	<0.01	0.50	0.1	13
Site 4										
0–15	10 YR 5/1	5.4	79	16	5	0.04	0.04	<0.01	1.3	10
16–30	7.5 YR 7/4	5.6	86	10	4	0.03	0.02	<0.01	1.1	9
31–45	7.5 YR 4/4	5.7	86	10	4	0.07	0.02	<0.01	0.3	14
46–60	7.5 YR 4/4	7.2	79	11	10	0.12	0.03	<0.01	0.7	13
61–75	7.5 YR 4/6	7.4	82	16	2	0.11	0.03	1.3	0.6	9
Site 5										
0–15	10 YR 4/3	5.9	61	29	10	0.05	0.01	0.01	2.4	8
16–30	10 YR 4/3	6.0	66	24	10	0.05	0.01	<0.01	1.7	10
31–45	10 YR 6/6	6.4	74	17	9	0.04	<0.01	<0.01	0.7	12
46–60	10 YR 5/6	6.3	85	9	6	0.04	<0.01	<0.01	0.6	11
61–75	10 YR 5/6	6.5	87	8	5	0.04	0.01	<0.01	0.4	9

[a] Average background level (water soluble) at two urban sites = 9 ± 3 mg/kg.
[b] Values are for water-soluble fraction.
[c] Mottling present.

source of Pb contamination is obviously vehicle emissions. The total concentrations measured here are much lower than some reported previously (Garcia-Miragaya, 1984; Harrison *et al.,* 1981; Yassoglou *et al.,* 1987; Ho and Tai, 1988).

TABLE 3

Selected Sequential Extraction Data for Pb at the Sites Studied

	Targeted form														
	Water soluble		Exchangeable		Carb.-occl.		Mn-occl.		Organic		Fe-occl.		Residual		
Depth (cm)	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	Summed total (mg/kg)
Site 1: 10 m from Road															
0–15	1.5	0.4	2.7	0.7	153.1	40.9	2.3	0.6	6.9	1.8	138.2	36.9	70.0	18.7	374.7
31–45	0.4	0.6	0.6	0.9	8.9	13.1	1.0	1.5	9.5	14.0	2.4	3.5	45.0	66.4	67.8
61–75	0.2	0.3	0.6	1.0	6.3	10.0	0.6	1.0	10.0	15.8	1.6	2.5	43.8	69.4	63.1
Site 1: 100 m from Road															
0–15	BDL	0	0.3	0.5	4.1	6.3	0.6	0.9	11.3	17.4	7.5	11.5	41.2	63.4	65.0
31–45	0.2	0.1	0.5	0.4	33.4	24.3	1.0	0.7	8.1	5.9	37.0	26.9	57.5	41.8	137.7
61–75	0.2	0.2	0.4	0.4	26.8	25.2	0.9	0.8	10.5	9.9	21.3	20.0	46.2	43.5	106.3
Site 2: 10 m from Road															
0–15	1.2	0.7	1.0	0.6	54.9	31.5	1.4	0.8	8.0	4.6	47.8	27.4	60.0	34.4	174.3
31–45	0.7	1.2	0.4	0.7	8.0	13.5	1.1	1.9	9.4	15.9	0.9	1.5	38.8	65.4	59.3
61–75	0.2	0.4	0.4	0.8	4.3	8.5	0.9	1.8	6.5	12.9	0.6	1.2	37.5	74.4	50.4
Site 2: 100 m from Road															
0–15	BDL	0	0.1	0.2	6.0	9.8	0.7	1.1	9.8	16.0	4.8	7.8	40.0	65.1	61.4
31–45	BDL	0	0.1	0.2	1.9	3.3	0.6	1.1	6.4	11.2	6.9	12.1	41.2	72.2	57.1
61–75	BDL	0	BDL	0	0.4	0.7	0.5	0.9	4.6	8.3	3.7	6.7	46.2	83.4	55.4
Site 3: 10 m from Road															
0–15	1.9	0.6	3.1	0.3	197.6	63.4	2.1	0.7	4.7	1.5	22.1	7.2	77.5	25.1	309.0
31–45	0.7	0.4	0.4	0.2	51.5	27.3	1.1	0.6	7.0	3.7	73.0	38.7	55.0	29.1	188.7
61–75	1.0	0.4	1.8	0.6	103.3	36.9	2.0	0.7	4.6	1.6	98.6	35.2	68.8	24.6	280.1
Site 3: 100 m from Road															
0–15	0.2	0.9	BDL	0	3.4	15.1	0.3	1.3	11.1	49.3	1.3	5.8	6.2	27.6	22.5
31–45	0.6	1.5	0.2	5.1	1.6	4.1	0.2	0.5	4.5	11.6	0.6	1.5	31.2	80.2	38.9
61–75	0.1	1.0	BDL	0	2.2	22.2	0.2	2.0	5.4	54.0	2.0	20.0	BDL	0	9.9
Site 4: 10 m from Road															
0–15	0.5	1.2	0.4	0.9	5.0	11.8	1.4	3.3	7.7	18.2	9.8	23.2	17.5	41.4	42.3
31–45	0.5	7.9	0.2	3.2	1.1	17.5	1.3	20.6	3.0	47.6	0.2	3.2	BDL	0	6.3
61–75	0.5	6.0	0.2	2.4	1.0	11.9	1.1	13.1	5.1	60.7	0.5	6.0	BDL	0	8.4
Site 4: 100 m from Road															
0–15	0.3	2.4	2.7	22.0	0.4	3.3	1.4	11.4	6.6	53.7	0.9	7.3	BDL	0	12.3
31–45	0.3	3.9	0.5	6.6	0.8	10.5	0.6	7.9	5.0	65.8	0.4	5.3	BDL	0	7.6
61–75	BDL	0	BDL	0	0.4	4.0	BDL	0	3.7	36.6	1.0	9.9	5.0	49.5	10.1

TABLE 3 (continued)
Selected Sequential Extraction Data for Pb at the Sites Studied

	Targeted form														
	Water soluble		**Exchangeable**		**Carb.-occl.**		**Mn-occl.**		**Organic**		**Fe-occl.**		**Residual**		**Summed total**
Depth (cm)	**mg/kg**	**%**	**mg/kg**	**%**	**mg/kg**	**%**	**mg/kg**	**%**	**mg/kg**	**%**	**mg/kg**	**%**	**mg/kg**	**%**	**(mg/kg)**
Site 5: 10 m from Road															
0–15	0.2	0.8	0.1	0.4	7.1	29.8	BDL	0	9.8	41.2	4.1	17.2	2.5	10.5	23.8
31–45	0.1	1.4	BDL	0	0.9	12.2	BDL	0	5.3	71.6	1.1	14.9	BDL	0	7.4
61–75	0.2	3.8	BDL	0	0.9	17.0	BDL	0	2.8	52.8	1.4	26.4	BDL	0	5.3
Site 5: 100 m from Road															
0–15	0.3	1.3	3.6	16.1	5.1	22.9	1.1	4.9	8.7	39.0	3.5	15.7	BDL	0	22.3
31–45	0.2	3.8	0.4	7.7	0.9	17.3	0.3	5.8	3.0	57.7	0.4	7.7	BDL	0	5.2
61–75	0.2	5.7	0.2	5.7	0.5	14.3	0.4	11.4	2.0	57.1	0.2	5.7	BDL	0	3.5

Note: BDL, below detection limit.

However, those data are for samples of the upper 5 cm of soil or less. We sampled the upper 15 cm; therefore, concentrations in the upper 5 cm could be greater by a factor of perhaps three to five times because of dilution. Although site 1 is affected by the heaviest volume of traffic (Table 1), site 3 has nearly the same total amount of Pb, apparently because site 1 was disturbed by construction during 1966. Overall, total Pb concentrations correlate positively with traffic volume and road age. Chemical analysis of coal clinker fragments from site 1 showed significant levels of Pb (85 ± 5 mg/kg), whereas that in concrete and brick samples is negligible. Only small quantities of clinker are present, however, and the systematic decrease in Pb concentration with increasing distance from the highway suggests that this material is not the principal source of Pb in the soils studied.

Sequential extraction analysis shows that the bulk of the Pb at sites 1, 2, and 3 is occluded mainly in carbonate and oxide phases, with lesser amounts in the residual and organic fractions (Table 3). These results are similar to those reported for roadside soils elsewhere (Harrison *et al.,* 1981; Yassoglou *et al.,* 1987). Harrison *et al.* (1981) demonstrated that $PbSO_4$ is extracted primarily by $MgCl_2$ (step 2 in this study), which comprises only a minor component of the soils studied here. Hence, this is not the predominant form of Pb present as reported in other studies (Olson and Skogerboe, 1975; Linton *et al.,* 1980; Biggins and Harrison, 1980). Lead is present mainly as carbonate and Fe-oxide phases near the highway, whereas organic forms predominate farther away, as shown by a three-component plot (Figure 2) of oxide-occluded (Fe- and Mn-oxide-occluded forms combined, Ox), carbonate-occluded (Ca), and organically bound Pb (Or). PCFs were calculated (Table 4) to determine whether these trends

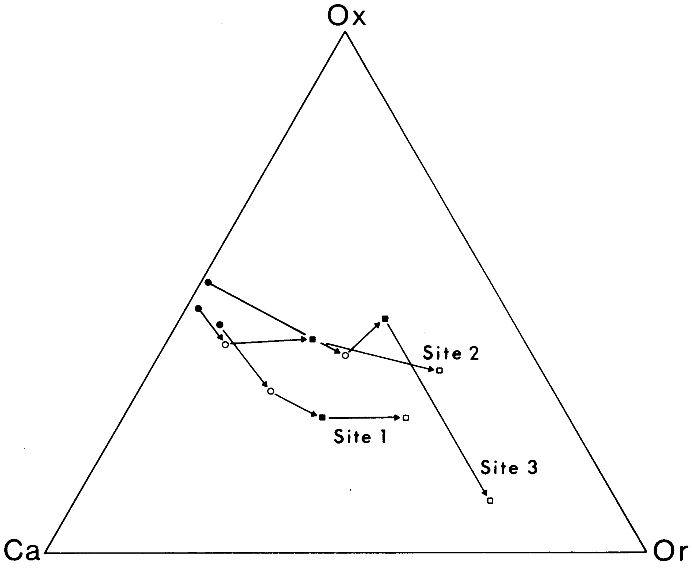

FIGURE 2. Ternary diagram (figure reads the same as a “textural triangle”) showing the geochemical partitioning of Pb in surface horizons. Ox, oxide occluded; Ca, carbonate occluded; Or, organically bound. Distances from highway: 10 m, solid circles; 30 m, open circles; 60 m, solid squares; 100 m, open squares. Values are normalized percentages of summed total.

are due to enrichment, or simply because of differences in the relative abundances of host phases. PCFs decrease with increasing distance from the highway for oxide and increase with increasing distance for organic phases. Such systematic variations suggest Pb enrichment, whereas variations for carbonate are random and imply differences because of the abundance of this phase. Soil characterization data (not shown) indicate that carbonate contents increase with increasing proximity to both the highway and urban Detroit. This may indicate that at least some of the carbonate was derived from, or formed as a result of reactions with, particles of anthropogenic origin, although the remainder is probably of natural origin, as shown by the presence of limestone pebbles in soil profiles. This interpretation is consistent with the findings of Ter Haar and Bayard (1971), who demonstrated that much of the PbClBr emitted as auto exhaust is converted into $PbCO_3$ and $(PbO)_2PbCO_3$ within 18 h, possibly as a result of photolytic reactions with atmospheric CO_2 (Pierrard, 1969). At the rural sites studied, similar trends in chemical partitioning are observed at site 4 (Table 3). However, at site 5, there is no difference in partitioning as a function of distance from the highway, suggesting that background levels are present.

TABLE 4
Phase Concentration Factors for Pb in Different Host Phases of Surface Horizons

Distance from road (m)	Site 1	Site 2	Site 3	Site 4	Site 5
	(dimensionless)				
			Carbonate		
10	29.3	26.2	32.4	197.0	17.5
30	15.1	17.2	383.3	220.0	420.0
60	29.6	15.1	102.0	[a]	810.0
100	63.0	32.7	300.0	[a]	2290.0
			Oxide		
10	535.7	208.9	337.7	265.0	172.0
30	159.3	109.6	282.2	36.0	47.5
60	215.0	88.0	278.1	93.0	135.7
100	156.2	112.5	142.0	234.0	343.0
			Organic		
10	0.9	1.2	1.3	26.0	11.5
30	2.4	2.2	3.2	2.3	7.4
60	3.0	4.1	10.4	17.8	36.5
100	3.9	4.7	44.6	41.3	16.3

[a] Indeterminate because no carbonate detected.

The relative magnitudes of the PCF values observed (oxide > carbonate > organic matter) correspond with the chemical affinity sequences of different phases for Pb recognized elsewhere (Forstner and Wittmann, 1981; Adriano, 1986). The large PCFs associated with oxide are usually attributed to the very strong specific adsorption affinity of such minerals for Pb (Jenne, 1968). However, part of the oxide-occluded Pb may represent pedogenic lead oxide precipitates decomposed by reduction during sequential extraction steps 4 and 6. Organic matter PCFs are comparatively low, but significant enrichment may have occurred as a result of chelation. Carbonate may be enriched through either chemical precipitation or adsorption (McBride, 1979); however, the exceptionally high values observed cannot be resolved within the limits of analytical error.

C. **Lead Distribution with Depth**

The subsurface soil horizons at urban sites 1, 2, and 3 (Figure 1) are also polluted with Pb (Table 3). Total concentrations are commonly five to ten times background level even at the 75-cm depth, and especially within 30 m of the road. An anthropogenic origin is suggested by the general increase in Pb concentration with increasing proximity to both the soil surface and the highway found in water-soluble, exchangeable, carbonate-occluded, and oxide-occluded fractions. The complete data set, only part of which is shown in Table 3, was used to obtain mean values for soil profiles by averaging together values from all depths. The results (not shown) suggest that an overall trend exists of decreasing Pb content with increasing distance from urban Detroit. Between-site comparisons by analysis of variance suggest that the differences in Pb content between polluted urban and nonpolluted rural sites are statistically significant (Table 5).

Soil organic matter has a strong chemical affinity for Pb; hence, the metal usually accumulates in the surface horizons of contaminated soils (Berrow and Mitchell, 1980; Miller and McFee, 1983; Miller *et al.*, 1983; Adriano, 1986; Davies, 1990). The fact that Pb concentrations in subsurface horizons at the urban sites studied are generally far above background level, and in some cases are greater in one or more subsurface horizons than in the surface layer, suggests that mobilization has occurred. Three possible mechanisms for solubilization of Pb, interpreted to be in order of decreasing importance, are as follows: (1) complexation with organic chelating agents, (2) complexation with Cl derived from highway deicing salts, and (3) complexation with CO_3 derived from carbonate dissolution.

The bulk of subsurface Pb in the urban soils studied is in oxide-occluded and carbonate forms, with lesser quantities in residual and organic fractions (Table 3). Figure 2 shows that oxide-occluded and carbonate Pb tends to increase, and organically bound Pb decrease, in surface horizons with increasing proximity to the highway. Table 3 shows a similar trend with respect to increasing proximity to soil surface; hence, organically bound Pb often is the dominant form in the subsurface. At rural sites 4 and 5, this form generally predominates at all depths. It is well known that dissolution of soil organic matter occurs in the presence of

TABLE 5
Calculated F-Values for Comparisons of Soil Profile Means at Sites 1 to 5 by Analysis of Variance

Distance from road (m)	Water-sol. and exch.	Carb.	Oxide occl.	Org.	Residual	Total
10	4.3[a]	4.1[a]	3.5[a]	3.3[a]	1.5	4.6[a]
30	1.0	10.5[b]	7.6[b]	6.1[b]	3.1[a]	5.8[b]
60	4.1[a]	3.2[a]	5.3[b]	2.3	104.0[b]	18.4[b]
100	1.6	8.7[b]	12.6[b]	3.3[a]	60.5[b]	27.5[b]

[a] Significant difference ($\alpha = 0.05$; F = 2.87).
[b] Highly significant difference ($\alpha = 0.01$; F = 4.43).

excess salts (Mortensen, 1965), and this is believed to be a common cause of mobilization of sediment-bound heavy metals in estuaries with chloride concentrations of ≥200 mg/l (Salomons and Mook, 1980). This has been attributed to oxidation in the presence of microorganisms and complexation of the released metals with chloride or ligands from the decomposing organic matter (Forstner, 1989). Amrhein *et al.* (1992) have proposed a similar mechanism for mobilizing Pb in contaminated highway soils. The observed decrease in organically bound Pb with increasing proximity to the highway and soil surface, and with increasing traffic volume, suggests that soil organic matter is decomposing because of road salt applications. Thus, chelation with partially decomposed organic matter is probably a major factor contributing to the observed mobility. Evidence for this is clearest in surface horizons (Figure 2), and it can be found up to 60 m from the road at urban sites. The main source of the salt is probably spray from the traffic; however, Hanes *et al.* (1976) report that salts may move laterally, either by surface runoff or lateral subsurface flow, for considerable distances even on nearly level ground. Lead initially deposited in close proximity to the highway and later mobilized could presumably migrate laterally by the same mechanism.

In areas where road salt is used heavily as a deicing agent, contamination of ground water by Na is a serious problem (Hanes *et al.*, 1970; Huling and Hollacher, 1972; Murray and Ernst, 1976; Pilon and Howard, 1987), and mobilization of Pb in contaminated roadside soils is suspected because chlorides are known to complex with and solubilize many heavy metals (Hahne and Kroontje, 1973; Doner, 1978; Amrhein and Strong, 1990). Approximately 100,000 tons of road salt (NaCl) are applied annually in the Detroit metropolitan area (Michigan Department of Transportation, 1992; personal communication); hence, it is possible that the observed mobilization is partly the result of Pb complexation with Cl. The urban soil profiles studied contain elevated levels of water-soluble Na based on a comparison with the rural soils and two urban soil samples collected from sites located away from major roads (Table 2). Using a 1:1 soil-to-solution ratio, the upper range of water-soluble Na observed in this study (150 to 264 mg/l) corresponds to chloride levels in the soils which are, or have been, in the range of 200 to 400 mg/l. Hahne and Kroontje (1973) report that solubilization of Pb occurs as metal-Cl^+ and metal-Cl_2 complexes at chloride concentrations of 35 and 350 mg/l, respectively. Thus, the apparent mobility of Pb in the vadose zone is possibly due to displacement of Pb from exchange sites by Na through mass action, and complexation of Pb with excess Cl. Because highway deicing salts are rapidly leached in the months following application (Hanes et al., 1976) and sampling in this study took place in November, Na and Cl levels during the previous winter were probably much greater. Oliver *et al.* (1974) and Hanes *et al.* (1976) have shown that Cl levels in roadside soils and urban snow may be one or two orders of magnitude greater than the maximum levels found in this study.

The soils in which Pb mobilization is greatest are also those containing the highest levels of carbonate measured. Judging from pH measurements (Table 2), the soil solutions in the vadose zone are undersaturated with respect to $CaCO_3$, which implies production of CO_3 through mineral dissolution. The observed solubility is possibly partly the result of mobilization as a Pb-CO_3 complex. However, the fact that the $PbCO_3$ form consistently increases with increasing proximity to the highway (Table 3) implies that Pb is being immobilized possibly by adsorption onto carbonate. The contribution of CO_3 complexation, therefore, is difficult to assess.

No drastic changes in soil type are present in the transect investigated; however, some differences are evident among the soils shown in Table 2. The urban sites sampled are somewhat richer in both clay and carbonate, and higher in pH, than the rural sites. Two of the urban sites are also higher in organic matter content than the other sites. An increase in pH or in clay and/or organic matter content will theoretically reduce Pb mobility. Because Pb mobility appears to be greatest at the urban sites and least at rural sites, these soil properties probably are not the main factors controlling Pb distribution. Furthermore, if the data are normalized to correct for grain size effects, it is clear that the urban soils are greatly enriched in Pb of probable anthropogenic origin.

Solubilization by complexation with Cl, CO_3, and/or organic chelates also accounts for the fact that water-soluble and exchangeable components of Pb are present in many of the soil profiles studied (Table 3). Both components show strong, positive linear correlations with total Pb that are significant at the 99% level. These forms are thought to be found only in soils and sediments which are heavily polluted (Fuller *et al.,* 1976; Engler, 1980; Pickering, 1981; Forstner, 1985), and both are considered highly bioavailable (John, 1972; Tessier and Campbell, 1979; Gunn *et al.,* 1988). The presence of a water-soluble component suggests that the adsorption capacity of the soil has been exceeded, but the maximum Pb content of any single horizon observed in this study is 374.7 mg/kg, and the summed total for all horizons in the most contaminated profile is only 1068 mg/kg. Both values are well below the estimated adsorption capacity of 5.2×10^{-5} mol Pb per gram of soil (10,774 mg/kg) based on the data of Zimdahl and Skogerboe (1977), who analyzed a Michigan soil with properties similar to those in this study. For a 1:1 soil-to-solution ratio, the water-soluble Pb levels measured are far in excess of the 50 μg/l drinking water standard (USEPA, 1976). Subsurface horizons at sites 1, 2, and 3 are commonly mottled, indicating a fluctuating water table and saturated conditions for at least some period of the year (Simonson and Boersma, 1972); thus, some ground water contamination may be taking place.

An unexpected result of this study is that residual Pb concentrations were found to increase with increasing levels of contamination (Table 3). This form of Pb is generally considered to be that which is lattice bound within silicate minerals and should therefore be unaffected by anthropogenic contributions to the total Pb pool. Gibson and Farmer (1986) also found that residual Pb increased with increasing total Pb in urban soils elsewhere, and concluded that either an unidentified, highly insoluble phase had been present or Pb was simply carried over from a previous extracting solution. Forstner and Wittmann (1981) have suggested that if the ratio of solid mass to extracting solution volume is excessive, the system may overload, thereby leading to carryover problems. Analysis of the sequential extraction data from this study shows that there is a very strong, positive linear correlation ($r^2 = 0.89$) between Fe-oxide-occluded (step 6) and residual (step 7) Pb levels. However, it is unclear whether this reflects carryover or the presence of an unidentified residual phase of anthropogenic origin. It has been suggested that Pb is often in a phosphate form in contaminated soils (Lagerwerff and Brower, 1973; Santillan-Medrano and Jurinak, 1975; Nriagu, 1978), but it is uncertain where in the extraction scheme used that such a phase would be recovered. Excess salts may cause dissolution of soil silicate minerals (Dragun, 1988); hence, it is theoretically possible that anthropogenic Pb recovered in the residual fraction may have been in the form of reprecipitated amorphous silicate.

IV. SUMMARY AND CONCLUSIONS

The urban roadside soils studied were found to be contaminated to greater depths and at greater distances from the roadway than expected. The concentrations of Pb in roadside soils of urban sites were found to be 10 to 15 times greater than the background level of 12 to 22 mg/kg observed at rural sites. The observed correlation between elevated Pb concentrations and traffic volume, road age, proximity to the highway, and soil depth indicates that the principal source of contamination is vehicle emissions. Both surface and subsurface horizons of soils at urban sites are polluted with Pb. Mobilization in the vadose zone is implied by elevated Pb levels to depths of 75 cm and by the presence of a water-soluble Pb component. The principal cause of Pb mobilization appears to be complexation with organic chelating agents. These are probably being generated by partial dissolution of soil organic matter due to the presence of excess NaCl derived from highway deicing salts. This is suggested by the elevated levels of water-soluble Na measured and the fact that Pb is mainly in carbonate and oxide forms in the most heavily contaminated soils, whereas organically bound forms tend to predominate elsewhere. Mobilization is also attributable to displacement of Pb from exchange sites by excess Na and possibly some complexation with Cl and/or CO_3. Further studies are needed to determine the exact mechanism of mobilization and the nature and extent of possible ground water contamination by Pb.

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