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SPATIAL DISTRIBUTION OF TRACE METALS IN DELAWARE COUNTY, INDIANA, SURFACE SOILS

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ABSTRACT: Soils in urban areas and in proximity to industrial facilities may become contaminated with trace metals via atmospheric deposition. Soil material was sampled from two depths (0-5 cm and 10-25 cm) within a grid network throughout Center Township, Delaware County, Indiana, and analyzed for concentrations of lead (Pb), cadmium (Cd), zinc (Zn), chromium (Cr), and nickel (Ni). Their concentrations were compared with local and global background levels to determine the extent, if any, of metal contamination from atmospheric deposition. Elevated concentrations of Pb, Cd, and Zn (203.9, 2.5, and 275.2 mg/kg, respectively) were detected, indicating anthropogenic contamination. Lead concentrations were significantly higher ($p < 0.05$) in the surface horizon than in the subsurface. Concentrations of most metals were typically highest near the city center. As a result of sequential chemical extraction of selected soils, the majority of the Pb and Cd was found to occur in residual forms, considered immobile in soil, while Zn, Cr, and Ni occurred in carbonate and organically bound forms, both of which are only slightly bioavailable. These data indicate that the majority of the metals under study pose little, if any, environmental and/or public health hazard from contact with lawns, garden plots, and soil.

KEYWORDS: Atmospheric, cadmium, chromium, deposition, fractionation, lead, nickel, zinc.

INTRODUCTION

Numerous studies (Pichtel, *et al.*, 1997; Maskall, *et al.*, 1996; Kabata-Pendias and Pendias, 1992; Uminska, 1988; Tam, *et al.*, 1985; Czarnowska, *et al.*, 1983; Miller and McFee, 1983) have documented evidence of soil contamination as a result of atmospheric deposition from industrial activity and vehicular emissions. Deposited metals may pose an environmental and/or public health threat, depending on factors such as metal species and the chemical and physical properties of the recipient soils.

Lead battery recycling plants, lead smelters, foundries, and auto-related facilities release lead (Pb), cadmium (Cd), and zinc (Zn) into the biosphere via stack emissions, leaching from waste piles, and dispersion of fugitive emissions (Mattigod and Page, 1983; Förstner, 1995). The use of leaded gasoline was an additional source of atmospheric lead. Although banned in the United States in 1978, leaded gasoline serves as a historical source of soil Pb. Chromium (Cr), nickel (Ni), Cd, and Zn are also released from fossil fuel combustion and from other metallurgical activities, including electroplating.

Dispersion and subsequent accumulation of metals from industry and vehicular emissions can be distributed in various ways. First, a point source of land contamination may occur as a localized elevated concentration surrounded by concentric areas of successively lower concentrations. Second, the distribution can occur as an elliptical area of high concentration along the direction of the prevailing wind (Förstner, 1995; Davies, 1983). Finally, metal concentrations can be distributed vertically (that is, within the soil profile as a function of depth).

In contaminated soils, Pb and Cd compounds are typically concentrated in the upper soil horizons (Hindy, 1991; Buchauer, 1973; Munshower, 1977; Miller, *et al.*, 1983), while Zn, Cr, and Ni compounds tend to be more evenly distributed throughout the profile, indicating a greater mobility in the soil (Little and Martin, 1972). The environmental mobility and bioavailibility of Pb, Cd, Zn, Cr, and Ni in urban soils is dependent upon the physicochemical forms in which the metal is associated in the soil profile (Harrison, *et al.*, 1981). Sequential extraction procedures provide qualitative evidence regarding the forms of the associations of these metals and, thus, of their mobility and bioavailibility (Sposito, *et al.*, 1982; LeClaire, *et al.*, 1984).

The city of Muncie, Indiana, located in Center Township, Delaware County, has been heavily industrialized, housing metal-related facilities for over a century. A systematic soil sampling design was established to determine the average concentrations of Pb, Cd, Zn, Cr, and Ni within the Township. From these data, contour plots were prepared to illustrate the spatial distribution of metal concentrations. These plots were then compared to historic city and road plans and to the prevailing wind direction in order to correlate concentrations with possible sources. The metals were also evaluated for mobility; that is, whether they are retained mostly on the soil surface, or whether they migrate to levels deeper in the soil profile, and the extent to which these metals migrate from a source by way of atmospheric transport.

EXPERIMENTAL METHODS

Center Township (T20N, R10E), Delaware County, Indiana, was divided into 25 equal-sized quadrants (1.2 miles x 1.2 miles). Three replicate soil samples were collected near the center of each quadrant using a 2.5 cm (1 in) diameter stainless steel soil probe. Samples were collected at two depths, 0-5 cm and 10-25 cm, to examine the extent of metal contamination in the shallow soil profile. Sampling was conducted as far as practical from roadways to avoid localized contamination by Pb from the past use of leaded gasoline. Sampling locations included parks, gardens, vacant lots, schoolyards, and churches. In order to assess the presumed background levels of each metal, triplicate samples were taken at both depths approximately three miles north, south, east, and west of Center Township.

Soil samples were prepared for total metal analysis by air drying for 1 week at ambient temperature. The dried samples were crushed and passed through a 2-mm mesh (#10) sieve. Soils were digested for total metals content using a hot HNO_3 method (Miller, *et al.*, 1983; Harrison, *et al.*, 1981; Ure, 1991; Thompson, 1983). A 0.5 g sample was digested in 10 ml of hot (100° C) 16M HNO_3 for 16 hours in a Hach Digestahl reactor. After overnight digestion, five to eight 1 ml aliquots of 30% H_2O_2 were added to oxidize resistant organic matter. The solutions were filtered into 50 ml volumetric flasks using Whatman #1 filter paper, each extract was brought to volume (50 ml), the extracts were acidified with HNO_3, and they were stored at 4° C until analysis. Concentrations of soluble Pb, Cd, Zn, Cr, and Ni were measured via atomic absorption spectrophotometry (AAS; Perkin-Elmer model 2240, Norwalk, Connecticut; Perkin-Elmer, 1982).

Samples collected in quadrant 18 (SE 1/4, NE 1/4, Sec. 21) had elevated concentrations of all five metals at both depths. Chemical fractionation of soil Pb, Cd, Zn, Cr, and Ni followed the sequential extraction procedure outlined by Sposito, *et al.* (1982). Sposito's method involves sequential extraction of an air-dried soil sample with 0.5M KNO_3 (16h), deionized H_2O (2h; extracted three times and combined), 0.5M NaOH (16h), 0.05M Na_2EDTA (6h), and 4M HNO_3 (16h at 80° C). Metals extracted by KNO_3 and H_2O are assumed to be exchangeable and soluble, respectively. These metals represent the most labile and bioavailable fraction in the soil (LeClaire, *et al.*, 1984). The NaOH is assumed to remove organically bound metals, and EDTA should extract metals from inorganic precipitates. The NaOH and EDTA fractions represent potential reserves of bioavailable metals. Metals removed by HNO_3 are an estimate of residual, nonlabile metals or sulfides (Sposito, *et al.*, 1982). All soil extracts were centrifuged for 15 min. at 3000x g; the supernatant was decanted and analyzed for metal concentrations using AAS.

Soil pH was measured using a pH meter with a glass electrode paired with a calomel electrode. Soil was mixed with deionized H_2O at a 2:1 (v/w) liquid:solid ratio, and the method of McLean (1982) was used.

Total organic carbon (TOC) content was measured on the 0-5 cm samples collected from each quadrant using a loss on ignition method (Nelson and Sommers, 1982). For this method, from 3 g to 5 g of soil (weighed out to 0.0001 g) was placed in a porcelain crucible and dried at 105° C for 1 hour. The sample was then placed in a muffle furnace at 360° C for 2 hours to fully oxidize the organic portion of each sample. Total organic carbon was expressed as the percent of weight lost by ignition in the muffle furnace.

Summary statistics for the metal concentrations in each quadrant were calculated using DATADESK (Data Description, 1997) on a Macintosh Performa 636 personal computer with a Windows operating system. Analyses of variance and *t*-tests were also conducted ($p < 0.05$) using DATADESK.

Contour plots of the mean metal distribution for the 0-5 cm depth were prepared using SURFER (Scientific Software Group, 1994). A grid representing the township was split into 5 rows and 5 columns representing the 25 sampling quadrants. The mean concentration for each metal was entered into the center nodes of each quadrant. Contour plots were developed by SURFER using a Krieging statistical method. The plots were then exported as .dxf (digital exchange format) and imported into ARCINFO (Environmental Systems Research Institute, Inc., 1994a) to be georeferenced to the actual dimensions of Center Township on a digitized map. This procedure allows for the contour plots to be overlaid onto U.S. Geological Survey topographic maps of the Muncie area using ARCVIEW software (Environmental Systems Research Institute, Inc., 1994b).

RESULTS AND DISCUSSION

The soil pH of the Township samples ranged from 5.9 to 8.0 (Table 1). The average pH was 7.4, which is comparable to pH 6.8 observed for local background samples. The pH for Indiana soils averages 5.5 - 6.0 (U.S. Department of Agriculture, 1972). In east-central Indiana, the predominance of calcitic and dolomitic bedrock results in high carbonate soil types. Czarnowska, *et al.* (1983) noted that soil contamination results in an alkaline soil pH. Soil reaction (*i.e.*, pH) has an effect on the degree of metal solubility and displacement in the soil profile (Czarnowska, *et al.*, 1983). At the pH range observed in Indiana, most metals will tend to precipitate (Kabata-Pendias and Pendias, 1992; Lindsay, 1979). The organic matter content ranged from 2.1% to 10.3% (Table 1) with an average value of 6.1%. The 10.3% organic matter value occurred in quadrant 18 and may be due to the presence of carbonaceous wastes (*i.e.*, slags and/or dense non-aqueous phase liquids).

SPATIAL DISTRIBUTIONS OF SOIL METALS

Lead. The highest surface soil Pb concentrations occur in or near the city center (Figure 1), and in isolated locations, concentrations exceed 460 mg/kg. Soil Pb decreased to 81 mg/kg outside the township limits, which approximates mean local background levels (114.2 mg/kg). Soil Pb concentrations differ significantly ($p < 0.05$) within the surface horizon. These data concur with the results of other studies (Pichtel, *et al.*,1997; Czarnowska, *et al.*, 1992; 1983) that urban Pb concentrations tend to be highest in the city center and/or industrial zones.

The average Pb levels both in the township (Table 1) and local background samples were higher than the global baseline level of 20 mg/kg Pb in surface soils (Kabata-Pendias and Pendias, 1992). Miller and McFee (1983) found that soils in industrialized northwestern Indiana contained 500 mg/kg Pb, several orders of magnitude greater than global baseline levels. Long distance transport from metallurgical industries can significantly increase elemental concentrations in the soil surface (Steinnes, 1984). Certain relatively volatile metals, including Pb, are preferentially concentrated in the smallest particle size fractions occurring in airborne particulate matter (Steinnes, 1983). Additionally, high soil Pb may result from heavy vehicular traffic using leaded gasoline over many decades. High Pb levels were noted along three major roads into Muncie (Figure 1). These roads, running northwest, east, and southwest of downtown, were the original

Table 1. Soil pH, total organic carbon, and total metal concentrations throughout Center Township, Delaware County, Indiana.

Parameter	Depth (cm)	Mean	*p* Value	Max	Min
pH	0-5	7.3 ± 0.6	n/a[1]	8.0	5.9
TOC[2] (%)	0-5	6.1 ± 2.0	n/a	10.3	2.1
Pb (mg/kg)	0-5	203.8 ± 35.9	*[3]	466.3	81.1
	10-25	172.2 ± 28.9		344.8	53.9
Cd (mg/kg)	0-5	2.48 ± 0.2	ns[4]	4.0	1.8
	10-25	2.21 ± 0.2		3.1	1.5
Zn (mg/kg)	0-5	275.2 ± 85.7	ns	2750.0	126.1
	10-25	210.1 ± 37.9		509.6	108.2
Cr (mg/kg)	0-5	9.7 ± 1.4	ns	17.0	4.0
	10-25	8.6 ± 1.4		20.9	3.0
Ni (mg/kg)	0-5	25.0 ± 2.5	ns	49.0	16.7
	10-25	26.8 ± 2.2		42.7	16.7

[1] n/a = Not applicable.

[2] TOC = Total organic carbon.

[3] * = Significant at $p < 0.05$.

[4] ns = Not significant.

thoroughfares into the city. Lead concentrations in roadway soils and rights-of-ways were in the range of 140-540 mg/kg (Ward, *et al.*, 1977; Tam, *et al.*, 1987).

The distribution of Pb in the lower soil horizon (10-25 cm; data not shown) differs significantly ($p < 0.05$) from its distribution in the upper horizon. This difference is presumably the result of the low solubility and thus low mobility of Pb at neutral-high pH (Maskall, *et al.*, 1996; Davies, 1983). The low mobility and high surface retention of Pb in the environment has been documented by a number of researchers (Maskall, *et al.*, 1996; Kabata-Pendias and Pendias, 1992; Harrison, *et al.*, 1981; Davies, 1983). Therefore, Pb will not easily leach into the subsurface nor is it expected to occur in the same pattern as it does on the surface. A variety of factors will influence subsurface Pb concentrations, including soil pH and organic matter content, which varied from 5.9 to 8.0 and 2.1% to 10.3%, respectively (Table 1). Furthermore, soil oxidation-reduction potential and the presence of complexing ions will influence mobility or retention (Kabata-Pendias and Pendias, 1992).

Lead speciation in the surface soil of quadrant 18 was: carbonate > residual >> organically bound > soluble > exchangeable (Figure 2). For the 10-25 cm

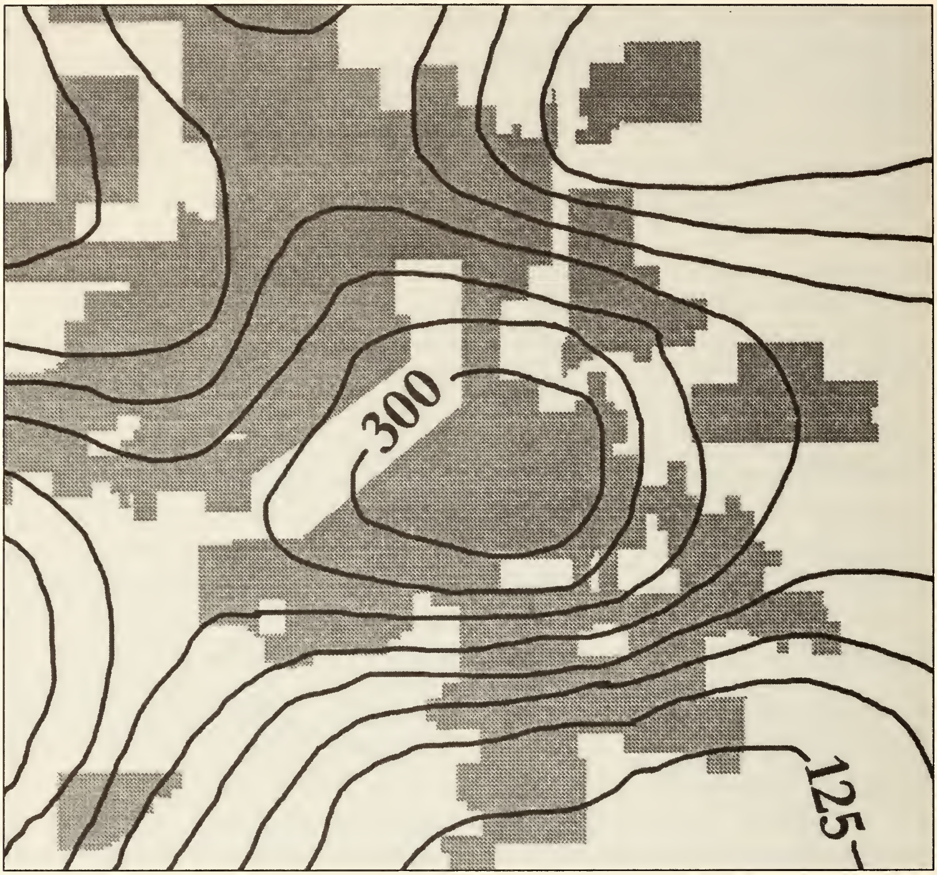

Figure 1. Contour plot of surface soil Pb concentrations (mg/kg; contour interval = 25 mg/kg).

samples, the order was: carbonate >> residual > soluble > organically bound > exchangeable. This order agrees with the results of Pichtel, *et al.* (1997) that carbonate and residual/sulfide are the dominant Pb species in anthropogenically affected soils. High soil pH tends to precipitate Pb as insoluble carbonates, oxides, and hydroxides. Kabata-Pendias and Pendias (1992) also reported the occurrence of Pb carbonates as the dominant Pb species in roadside soils, indicating that anthropogenic Pb should not be very mobile or bioavailable (Maskall, *et al.*, 1996).

Cadmium. Soil Cd levels reached a maximum of 3.2 mg/kg near the city center and decreased to 2.0 mg/kg at the edge of Center Township (Figure 3). The highest Cd readings (4.0 mg/kg) occurred at isolated points in the vicinity of well-established industries. The reported levels are much higher than the local background concentration (0.14 mg/kg). Miller and McFee (1983) found that soils in industrialized northwestern Indiana contained 10 mg/kg Cd, many orders of magnitude greater than background levels. According to Uminska (1993),

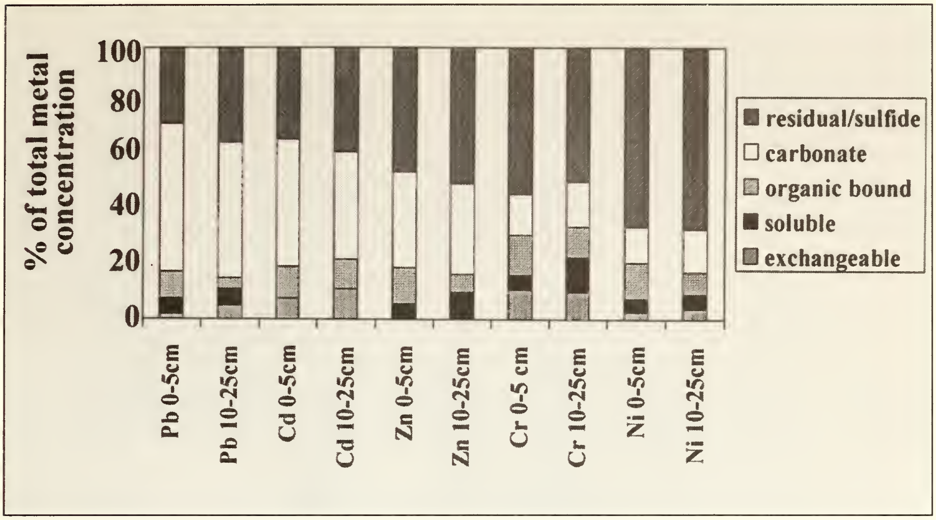

Figure 2. Distribution of soil metal species from a sequential extraction of quadrant 18.

soils with Cd concentrations greater than 1 mg/kg were probably anthropogenically contaminated.

Cadmium in the surface soil occurs primarily as carbonates and follows this order: carbonate > residual/sulfide > organically bound > exchangeable >> soluble (Figure 2). This same order was observed at the lower depth with the exception that carbonate = residual/sulfide. Pichtel, *et al.* (1997) concluded that in areas heavily contaminated with Cd, the greatest proportion of soil Cd occurred as carbonates, organically bound, and exchangeable. Organically-bound Cd is an indication of anthropogenic contamination (Asami, *et al.*, 1995).

The majority of soil Cd is expected to be immobile in the township soils. Mobility of the potentially labile carbonate species is dependent on pH. At pH values above 7.5, any Cd sorbed to soil material is highly immobile (Buchauer, 1973; Hindy, 1991; Kabata-Pendias and Pendias, 1992). Furthermore, sulfide/residual Cd species are immobile in soil.

Zinc. Soil Zn concentrations in the surface horizon ranged from 126 to 2750 mg/kg (Table 1). Local background levels average 126.1 (0-5 cm depth) and 108.2 (10-25 cm), and worldwide concentrations range between 15 and 125 mg/kg (Kabata-Pendias and Pendias, 1992). The highest Zn contours (Figure 4) are located in the area of established industries. Miller and McFee (1983) found that soils in industrialized northwestern Indiana contained 2000 mg/kg Zn, a value1-2 orders of magnitude greater than the background levels. Robberecht, *et al.* (1983) found 2160 mg/kg Zn in soil surrounding a non-ferrous metal industry.

The two Zn distributions (0-5 cm and 10-25 cm) are not significantly different ($p < 0.05$). Zinc is reported to be mobile and equally distributed throughout the soil profile (Kabata-Pendias and Pendias, 1992; Davies, 1983).

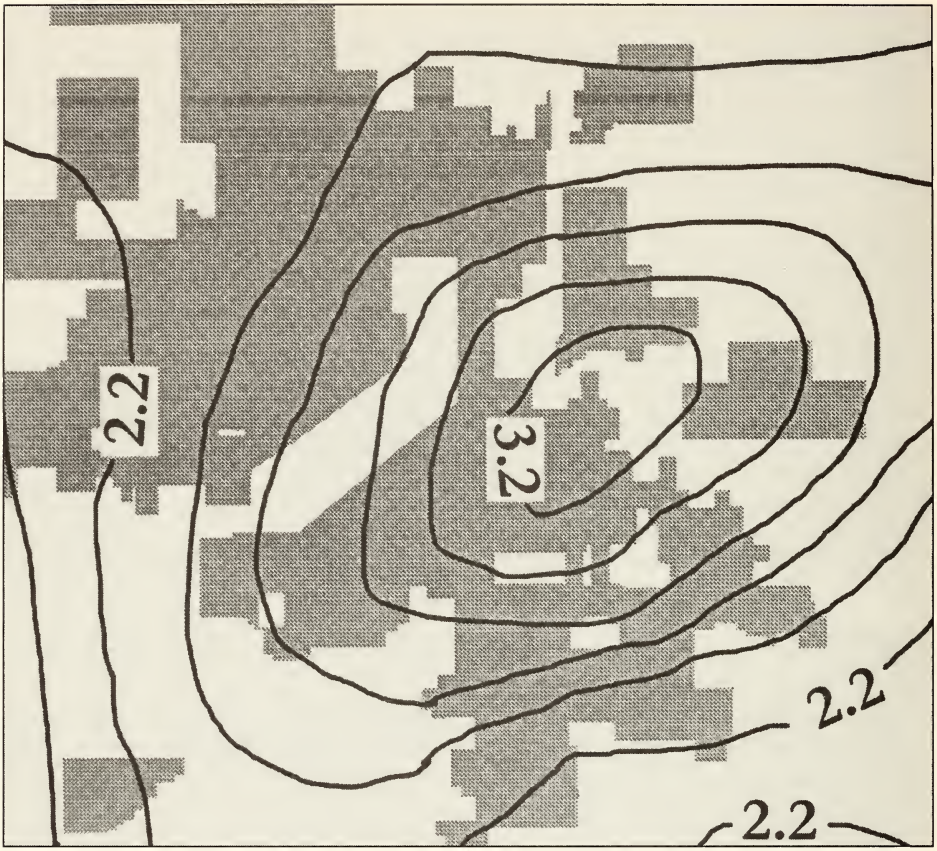

Figure 3. Contour plot of surface soil Cd concentrations (mg/kg; contour interval = 0.2 mg/kg).

Speciation of Zn in the surface soil occurred as: sulfide/residual > carbonate > organically bound > soluble > exchangeable (Figure 2). At the 10-25 cm depth, the order of Zn speciation was: sulfide/residual > carbonate > soluble > organically bound > exchangeable. These results are similar to findings which demonstrated that Zn occurs primarily in the residual/sulfide fraction of contaminated urban soils (Pichtel, *et al.*, 1997). Based on the predominance of the residual fraction, soil Zn is not expected to leach significantly as sulfide/residual species are non-labile. Zinc occurs naturally as ZnS; it also occurs as carbonate precipitates as a result of neutral to high soil pH.

Chromium. Chromium concentrations in Center Township surface soils ranged from 4 to 17 mg/kg (Figure 5, Table 1). Local background levels averaged 9 mg/kg for the surface horizon and 6 mg/kg for the subsurface. The global mean for soil Cr is 54 mg/kg (Kabata-Pendias and Pendias, 1992). Pichtel, *et al.* (1997) measured a maximum of 69 mg/kg in soils from Warsaw, Poland, and Czarnowska, *et al.* (1983) found numerous surface soils in excess of 40 mg/kg.

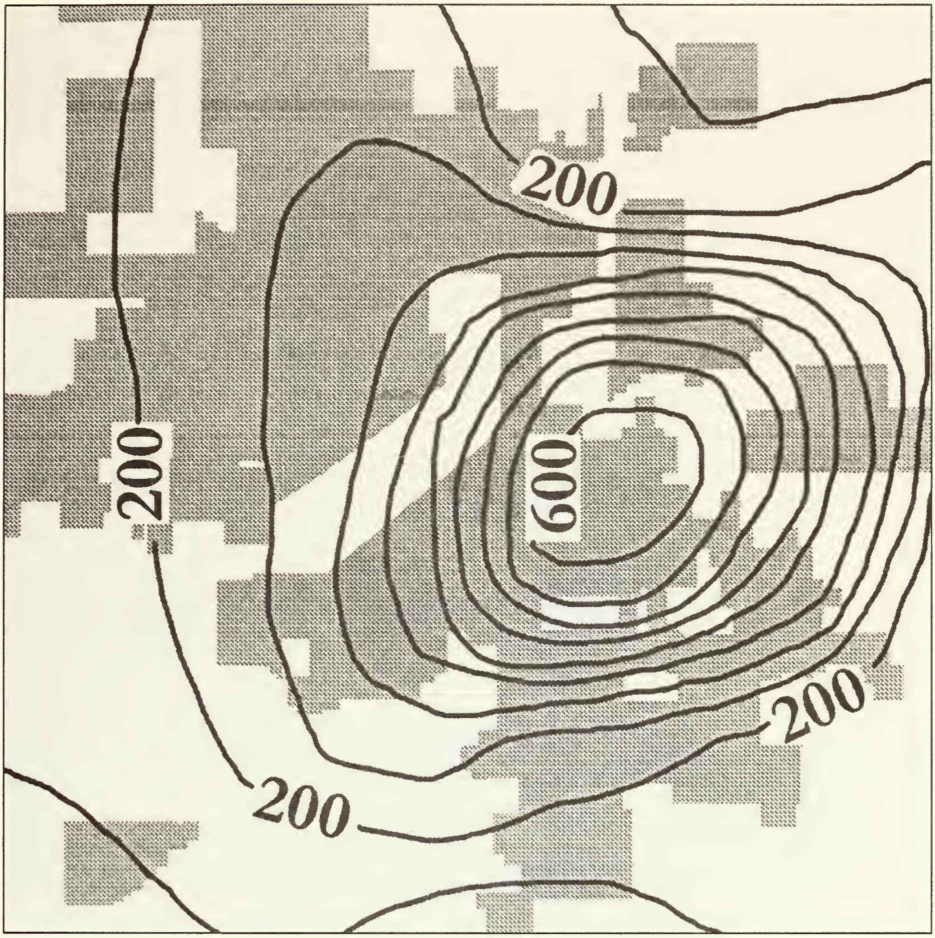

Figure 4. Contour plot of surface soil Zn concentrations (mg/kg; contour interval = 50 mg/kg).

No significant variation occurred among Cr means for either the surface or subsurface, and no significant difference in Cr concentrations was found between the two sampling depths. The average Cr concentration decreased from 9.7 mg/kg to 8.6 mg/kg as the depth increased from 0-5 cm to 10-25 cm.

Surface soil Cr was distributed as: sulfide/residual >> organically bound > exchangeable > carbonate > soluble. The 10-15 cm Cr speciation was: sulfide/residual >> soluble > carbonate > organically bound > exchangeable. The predominance of sulfide/residual Cr in urban soils was also reported by Pichtel, *et al.* (1997). Anthropogenic Cr additions from the atmosphere to soil most commonly result in two Cr species, hydrous oxide bound and organically bound (Kabata-Pendias and Pendias, 1992). Therefore, atmospheric deposition of Cr in Center Township plays a minor role when compared to the presence of residual, non-labile Cr, presumably arising from soil parent material.

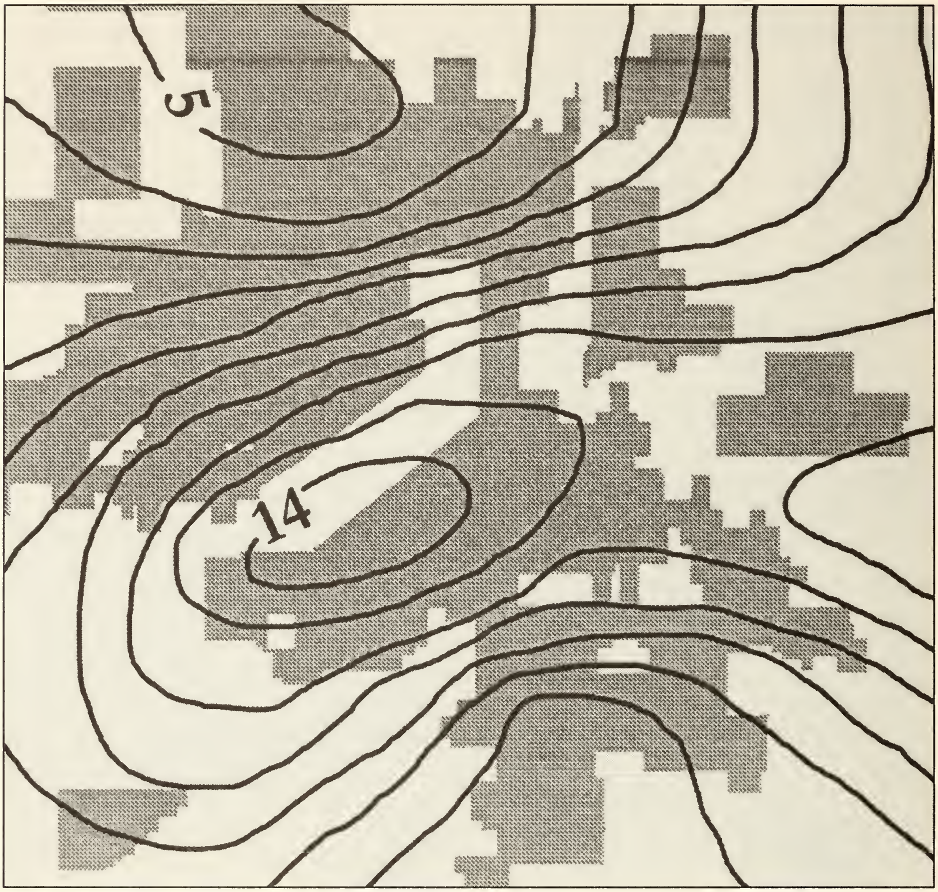

Figure 5. Contour plot of surface soil Cr concentrations (mg/kg; contour interval = 1 mg/kg).

Nickel. Soil Ni concentrations ranged from 32 mg/kg near the downtown to 18 mg/kg south of Muncie (Figure 6). An average Ni concentration of 25.0 mg/kg was observed for the 0-5 cm samples. However, no significant within-group variation occurred. Soil Ni values were lower than local background levels (39.8 mg/kg). Surface soils in the U.S. range in Ni content from < 5 to 150 mg/kg (Kabata-Pendias and Pendias, 1992).

The Ni distribution at the two soil depths was the inverse of all other metals tested in that the greater average Ni concentration (26.8 mg/kg) occurred in the soil collected from the 10-25 cm level; however, the difference between distributions was not significantly different. Nickel concentration often increases with increasing depth in the soil profile (Davies, 1983). As a result of weathering, Ni is easily mobilized. The Ni cation, Ni^{2+}, is stable in an aqueous environment, allowing for migration over long distances in the soil (Kabata-Pendias and Pendias, 1992). The Ni cation may eventually be coprecipitated as Fe and Mn oxides (Sparks, 1995).

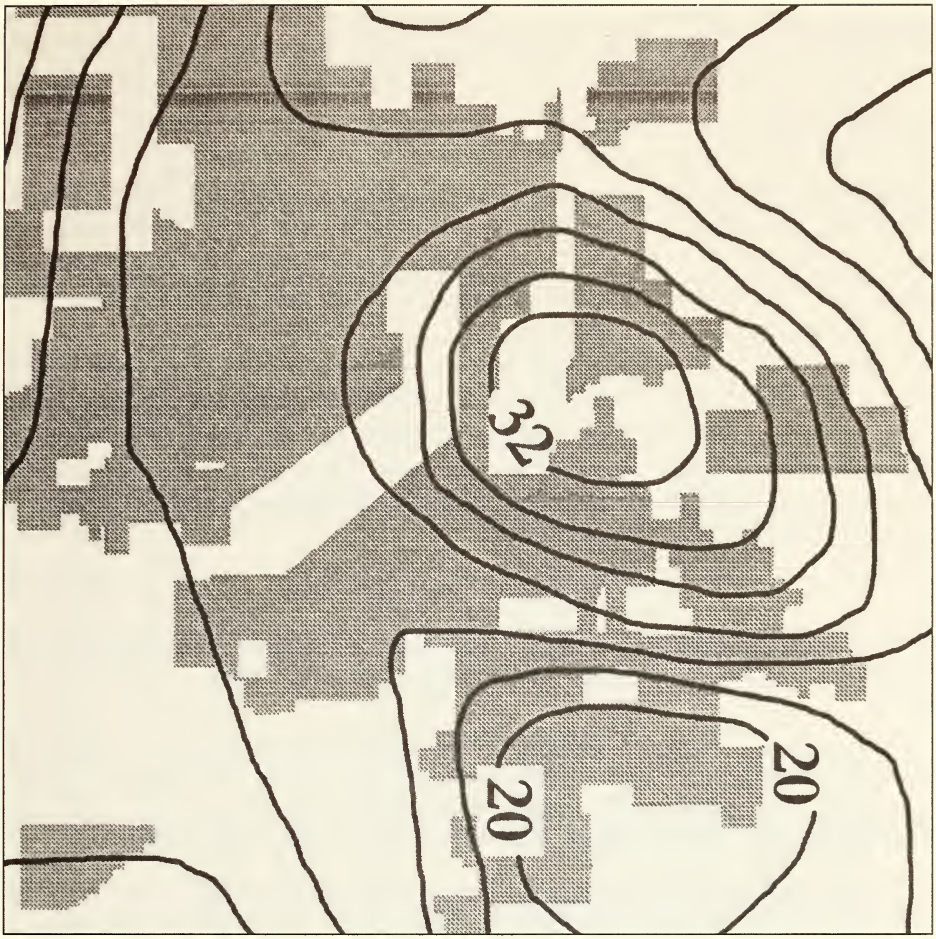

Figure 6. Contour plot of surface soil Ni concentrations (mg/kg; contour interval = 2 mg/kg).

Sequential extraction analysis at the 0-5 cm level resulted in a distribution of: sulfide/residual >> carbonate > organically bound > soluble > exchangeable (Figure 2). This order also held for the 10-25 cm level. Nickel has a strong affinity for sulfur, and in terrestrial rocks, Ni occurs mainly as sulfides, arsenides, and ferromagensium complexes (Kabata-Pendias and Pendias, 1992). Nickel is also associated with carbonates, phosphates, and silicates.

SUMMARY AND CONCLUSIONS

Center Township was assessed for the degree of metal contamination, if any, that resulted from long-term atmospheric deposition. Elevated Pb concentrations were detected as compared to background (*i.e.,* outside township) levels. Levels of soil Cd and Zn were also higher than background values, which indicates anthropogenic contamination. Most of the surface and subsurface contamination occurs in the city center and in areas of well-established industry. Aside from Pb, metal concentrations did not significantly differ between the two depths.

The minimal leachability of metals in circumneutral pH soils and the tendency of metals to accumulate in the organic material of surface soils is important in terms of potential environmental hazard. Only in highly contaminated soils or in acid, permeable soils are anthropogenic metals found deeper than 5-8 cm below the surface. Once soils become contaminated with metals, they are likely to remain until removed by soil erosion rather than leaching (Davies, 1983). This feature of contaminated soil may have adverse health implications due to human exposure to surface dusts.

As a result of sequential extraction of soils from selected sites, much of the Pb and Cd was found to occur as residual, which is considered immobile in soils, and Zn, Cr, and Ni occurred as carbonate and organically bound forms, both of which are only slightly bioavailable. These data indicate that the majority of the metals measured pose little environmental and/or public health hazard from contact with lawns, garden plots, and soil.

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