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Zinc and Cadmium in Illinois Surface Soils

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ABSTRACT

Zinc and Cd are important in soil ecosystems making knowledge of their contents significant to understanding soil characteristics including productivity, toxicity and nutrient quality of biomass. This study determined contents of Zn and Cd in surface soils (Ap, A1, or A11) sampled throughout Illinois. For assay, the soil materials were digested in a mixed acid under pressure and the finish for Zn was inductively coupled plasma emission spectroscopy and for Cd was inductively coupled plasma mass spectroscopy. The geometric mean total Zn was 60 mg kg^{-1} (n=150, geometric deviation (GD) = 1.46) and total Cd was 0.287 mg kg^{-1} (n=72, GD = 1.64). Zinc tends to be highest in soils developed in thin to moderately thick loess overlying Wisconsinan till and in north central Illinois where Zn may have been derived from Zn-bearing minerals in limestones and dolomites. Zinc contents are relatively low in Albaqualfs of south-central Illinois. Cadmium contents tend to be high in soils of the Green River Lowland and Rock River Hill Country of northwest Illinois. Low Cd levels are associated with soils developed in thick loess adjacent to the Mississippi River and in relatively highly weathered Albaqualfs of south central Illinois. There is some indication that loesses blown from the Wabash and Ohio valleys are slightly higher in Cd content than in loess from the Mississippi Valley. The mean Cd content found in this study was lower than means of other studies of Illinois surface soils. There is no relationship between the contents of Zn and Cd in this suite of samples. About half ($R^2 = 0.448$) of the content of Zn was explained by a multiple linear equation of clay and organic C contents. Most of the Zn difference is explained by clay content. No significant relationship of Cd was found with either clay or organic C contents. The mean of the log ratio of Zn to Cd was 204.

INTRODUCTION

Zinc and Cd are important trace elements in the biosphere. Zinc plays significant roles in enzymes of plants and animals and its concentrations in compartments of the soil-plant-animal web have been much studied both from the standpoint of a limiting nutrient in short supply and as a toxic element in abundance (e.g., Prasad, 1993). Cadmium is taken up to varying degrees by plants thereby entering the food chain (e.g., Das et al., 1997). Cadmium is a potent toxin for animals (Friberg et al., 1974) and the element has been increased in concentration in certain ecosystems by industrial operations and by disposal of domestic and industrial wastes (Elliott and Stevenson, 1977; Torrey, 1979). Some naturally high soil levels of Cd are associated with organic-rich black shales and sulfide-bearing ore deposits (Tourtelot, 1970).

The general distribution of soil orders in Illinois (Fehrenbacher et al., 1984) amounts to Alfisols, developed under mixed, deciduous hardwood trees, occurring on rolling topography adjacent to rivers and streams, on the hilly landscape of the dissected Ozark Plateau that occurs across the southernmost 40 to 80 km of Illinois, and south of the Wisconsinan glacial boundary on rather level topography of Illinoian glacial drift that is overlain with loess. Mollisols, developed under tall-grass prairie, occur on level to gently rolling prairies over about the northern half of the state. Seventy-nine percent of the aereal extent of upland soils have loess at least in their surficial horizon (Fehrenbacher et al., 1986). Soil development is closely related to thinning of loess with distance from riverine source areas. Consequently loess thickness can be related to taxonomic, chemical, and physical characteristics of soils in belts of loess of contrasting thickness (e.g., Bray, 1934; Smith, 1942; Fehrenbacher et al., 1986). These belts tend to parallel the Mississippi, Illinois, Wabash, and Ohio river valleys that were loess sources.

This study is a part of a long-term characterization of the constitution of Illinois soils (e.g., Jones and Beavers, 1966; Jones, 1986; Jones, 1989; Jones, 1991). The results provide base-level data for Zn and Cd expected in surface soils of the different soil regions of Illinois. The findings also provide further insight into provenance and elemental nature of the glacial deposits that are the parent materials of almost all of Illinois soils. The results also identify potential areas for subsequent detailed study.

METHODS

One hundred fifty samples of surface horizons of upland soils were analyzed for Zn and 72 were analyzed for Cd. The samples came from the soil-sample archive maintained by the College of Agricultural, Consumer and Environmental Sciences, University of Illinois. This archive contains samples collected for soils investigations throughout the 20th century. Sampling sites distributed across the state were selected to be representative of soil development and parent materials. The uppermost surficial sample – usually the A1, A11, or Ap horizon – of a given soil profile was studied. Mollisol and Alfisol soil orders, mostly with fine or fine-silty particle-size classes are represented. The mixed mineralogic class is most common except in northeastern Illinois where a thin loess layer overlies drift and the illitic class is common. The sampling sites are nearly identical to those locations shown in the map of study of Ba in Illinois soils (Jones, 1986). Virgin and cultivated soils were sampled.

The air-dry sample was crushed and passed through a 2-mm screen. Subsequently a carefully split subsample was ground in an agate mortar and pestle to <250 μm. About 0.54 g of sample weighed to the fourth place was digested in a solution containing HNO_3, HCl, HF, and H_3BO_3 (CEM, 1991). The digestion was carried out in a microwave oven programmed to deliver 100% power for 1 min. followed by 50% power for 20 min. This power sequence was repeated two times for a total of 63 min. digestion. Zinc determination was performed by inductively coupled plasma emission spectroscopy in the Microanalytical Laboratory of the School of Chemical Sciences, University of Illinois at

Urbana-Champaign. The coefficient of variation of three duplicate analyses of random samples was 4.97% and was 2.51% for three samples of National Institute of Standards and Technology (NIST) Standard Reference Material 2709 (San Joaquin soil). The mean Zn content of three analyses of NIST 2709 was 105.4 mg kg^{-1} which compares with the certified value of 106 ± 3 mg kg^{-1}. Cadmium analysis was done by inductively coupled plasma-mass spectroscopy of the acid digestate. These analyses were performed by the Illinois Waste Management and Research Center, Illinois Department of Natural Resources. The coefficient of variation of four duplicate analyses was 17.99% and 8.79% for three replicate analyses of NIST 2709. The mean Cd content of NIST 2709 analysis was 0.41 mg kg^{-1} which compares with the certified value of 0.38 mg kg^{-1}.

An isopleth map of Zn was drawn by the Geospatial Analysis and Modeling Section of the Illinois State Geological Survey using ArcView GIS software version 3.0a (ESRI, Redlands, CA). A grid of 243 rows and 136 columns amounting to a cell size of 6.7 km^2 was superimposed on the Illinois state map. Cells empty of data within the grid were assigned values using the spline interpolator method. Finally, using data-filled cells, smoothed isopleths were drawn using a weighting factor and the nearest 40 points to any given cell to fit the isopleth curve. No Cd isopleth map was drawn because of the few data points. Compositional data were analyzed using procedures in SAS® software release 8.1© (SAS Institute Inc., Cary, NC).

RESULTS AND DISCUSSION

The Zn analyses were distributed log normally (Fig. 1; Kolmogorov D = 0.119; P > D is < 0.01), whereas, the Cd data are neither clearly normal (Fig. 2; Kolmogorov D = 0.093; P > D is 0.12) nor log-normal (Kolmogorov D = 0.090; P > D is 0.15) distributions. Data for the log-normal distribution are presented herein. The geometric mean content of Zn was 60 mg kg^{-1} (GD, 1.46) soil and Cd was 0.287 mg kg^{-1} (GD, 1.64) soil.

An isopleth map of Zn is presented in Fig. 3. Zinc contents tend to be low in the southern half of Illinois except for an area about 35-km wide of loessial soils adjacent to and parallel with the Wabash River (Fehrenbacher et al., 1986). A significant amount of the loess in this band was blown westward from the Wabash alluvial plain as has other loess at the sate border in east central Illinois where a band of loess up to 25-km wide and as much as 200-cm thick accumulated in which surface soils have > 110 mg Zn kg^{-1}. This latter area of Zn concentration is drawn by the plotting program as completely enclosed by isopleths, whereas, the isopleths probably extend into Indiana following loess isopachs. North trending bands of > 80 mg kg^{-1} occur 25 to 40 km E of the Mississippi River in west central and in central Illinois 100 to 150 km E of the Illinois River. These areas reflect larger amounts of clay in surface soils relative to coarser soils in thicker loess to the west. As described later, clay content explains a large portion of the variance of Zn in this study. The relatively highly weathered Albaqualf soils in south central Illinois bear low Zn, 30-mg kg^{-1} or less. These texture-contrast soils are not only weathered and leached (Wilding et al., 1963) but clay as well as organic C contents of the surface horizons are low so Zn adsorption is low relative to that in Mollisols of adjacent soil areas. The highest level with most continuous extensive occurrence of Zn occurs in north central Illinois with >100 mg Zn kg^{-1}. Here, Ordovician-age rocks of the Plattville and Galena groups (Willman, 1975) and a limited area of outcrop of Cambrian-age rocks, largely sandstones, outcrop and were most recently glacially eroded. These rock sequences contain numerous limestones and dolomites that may contain accessory Zn minerals, principally sphalerite.

Inspection of a map of Cd concentrations (not shown) indicates several generalizations regarding local Cd levels. Like Zn, lowest Cd levels occur in the Albaqual soils of southeast Illinois. Highest Cd concentrations occur in the northern half of Illinois in soils of the Green River Lowland and Rock River Hill Country. Soils developed in thick and moderately thick loess derived from the Mississippi River valley have low Cd.

Comparison data for central tendency statistics for other Zn and Cd studies relevant to this study are presented in Table 1. The geometric mean content of Zn amounting to 60 mg kg^{-1} found in Illinois surface soils compares with the geometric mean of 48 mg kg^{-1} found by Shacklette and Boerngen (1984) in 1239 samples collected at about 20-cm depth from sites throughout the conterminous United States. For localities east of the 96th Meridian, Shacklette and Boerngen (1984) reported 40 mg kg^{-1}. For a study of Missouri surface soils (0 to 15 cm), Connor and Shacklette (1975) reported a geometric mean of 49 mg kg^{-1} (GD = 1.55). Logan and Miller (1983) reported an arithmetic mean content of 75 mg Zn kg^{-1} soil for 239 surface soils sampled in 7 Ohio counties. Karathanasis and Seta (1993) reported an arithmetic mean Zn content of 42.4 mg kg^{-1} (s = 47.5) for 27 surface horizons sampled in 15 Kentucky counties. The Illinois EPA Office of Chemical Safety (1994) presented mean contents of Zn and Cd for surface soils of adjoining counties comprising five areas of clustered urbanized counties conforming to different Metropolitan Statistical Area classifications (Table 1). Surface soil samples from all counties (n = 26) in this urban category had an arithmetic mean Zn content of 137.9 mg kg^{-1} (median = 95.0 mg kg^{-1}; n = 106) compared with 76.3 mg kg^{-1} (median = 60.2 mg kg^{-1}; n = 140) for all other or not-urbanized counties (n = 76). The arithmetic mean Zn content for all samples from these two areas was 102.9 mg kg^{-1} (median = 67.4 mg kg^{-1}; n = 246). Results of the Missouri and the two Illinois studies suggest that the content of Zn in an Illinois surface soil not affected by human-related inputs of Zn will contain about 60 mg Zn kg^{-1}.

The geometric mean content of Cd amounting to 0.287 mg kg^{-1} found in Illinois soils compares with the geometric mean of 0.175 mg kg^{-1} (GD = 2.70) determined by Holmgren et al. (1993) in 3045 samples of surface soils of the conterminous United States. Among this latter sample suite, the geometric mean Cd content of 131 samples from Illinois amounted to 0.181 mg kg^{-1}. Cadmium analyses of 243 Illinois surface soils by the Illinois EPA (Illinois EPA and Office of Chemical Safety, 1994) resulted in a much higher arithmetic mean Cd content of 0.97 mg kg^{-1} (median = 0.50 mg kg^{-1}; n = 245). This mean content compares with a slightly lower mean of 0.73 mg kg^{-1} (median = 0.50 mg kg^{-1}) for a sample subset of 139 locations beyond urbanized areas. There is no apparent explanation for the much higher levels reported by the Illinois EPA compared with contents found in this study. Logan and Miller (1983) found an arithmetic mean Cd content of 0.2 mg kg^{-1} in their study of surface soil in 7 Ohio counties.

Data for clay and for organic C contents were available for some of the samples assayed for Zn and Cd. Clay and organic C analyses were performed by analysts in the soil characterization laboratory of the former Agronomy Department (later, Crop Sciences Department) over the long time interval that the samples were collected. The data became a large archive of soil analyses. Organic C analyses were performed, at least from about 1950, by the acid-dichromate digestion procedure closely following method 6A1a (USDA et al., 1996) and clay content was determined, also from about 1950 but probably dating earlier, by the pipet procedure (Method 3A1, USDA et al., 1996). Among the data (taken in their logarithmic forms), there are significant linear regressions for Zn for 77 samples with clay data ($R^2 = 0.361$, $P < .0001$) and for 118 samples with data for organic carbon ($r^2 = .321$, $Pr < .0001$). The multiple linear regression (Fig. 4) with these independent variables yields somewhat less than half of the explanation in Zn variation among 69 samples ($R^2 = 0.448$, $P < .0001$). Of this relationship, clay contributes 0.355 to the model R^2. In contrast, neither clay nor organic carbon have significant regressions with Cd. The regression of the ratio of log of Zn to Cd with the log of clay content was highly significant ($n = 38$, $P = .001$) but with a low coefficient of determination ($r^2 = 0.254$) , whereas, the regression of the ratio with log organic carbon was substantially lower ($n = 53$, $r^2 = .062$, $P = .071$). Zinc sorption to clay minerals, especially smectites and vermiculites, is greater than Cd (Tiller et al., 1984) which can explain some of the observation of the direct relationship of ratios with clay content. In their survey of United States surface soils Holmgren et al. (1993, Table 9) found significantly more Zn in fine texture classes; e.g., 14.9 mg Zn kg^{-1} in loamy sand compared with 98.0 mg Zn kg^{-1} in clay. Cadmium content also increased substantially in finer texture classes.

The mean of the log ratio of Zn to Cd in this study amounted to 204. Holmgren et al. (1993) reported higher ratios among their samples from Illinois with the range of 250 to 299.

SUMMARY

Geometric mean contents of Zn and Cd amounted to 60 mg kg^{-1} and 0.287 mg kg^{-1}, respectively. No close relationship occurred with loess thickness and attendant weathering and soil development except Cd may have weathered and leached from surface horizons of Albaqualfs. Clay content explains more variance in Zn content than organic C does and neither of these variables explains Cd content in this sample suite. There was no consistent relationship of Zn content with Cd content. However, the log of the ratio of Zn to Cd as a function of clay content increased significantly, confirming earlier observations of stronger adsorption of Zn than Cd to smectite and vermiculite. Mean contents of Zn are comparable to other studies of Illinois sample suites but Cd content found in this study is lower.

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Figure 1. Histogram of total Zn occurring in Illinois surface soils. Data are reported in 5 mg kg^{-1} increments or bins. Normal (solid line) and log-normal (dashed line) distributions are fitted to the data.

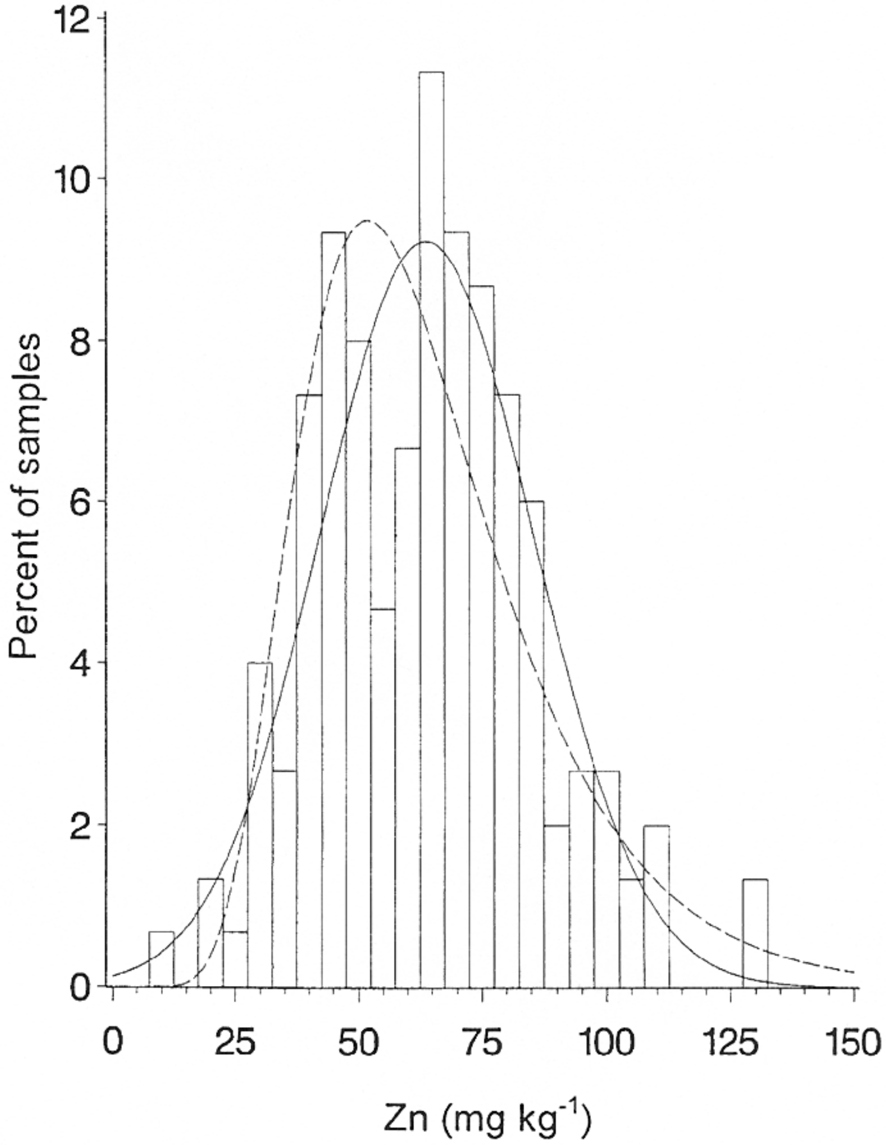

Figure 2. Histogram of total Cd occurring in Illinois surface soils. Data are reported in 0.025 mg kg^{-1} increments or bins. Normal (solid line) and log-normal (dashed line) distributions are fitted to the data.

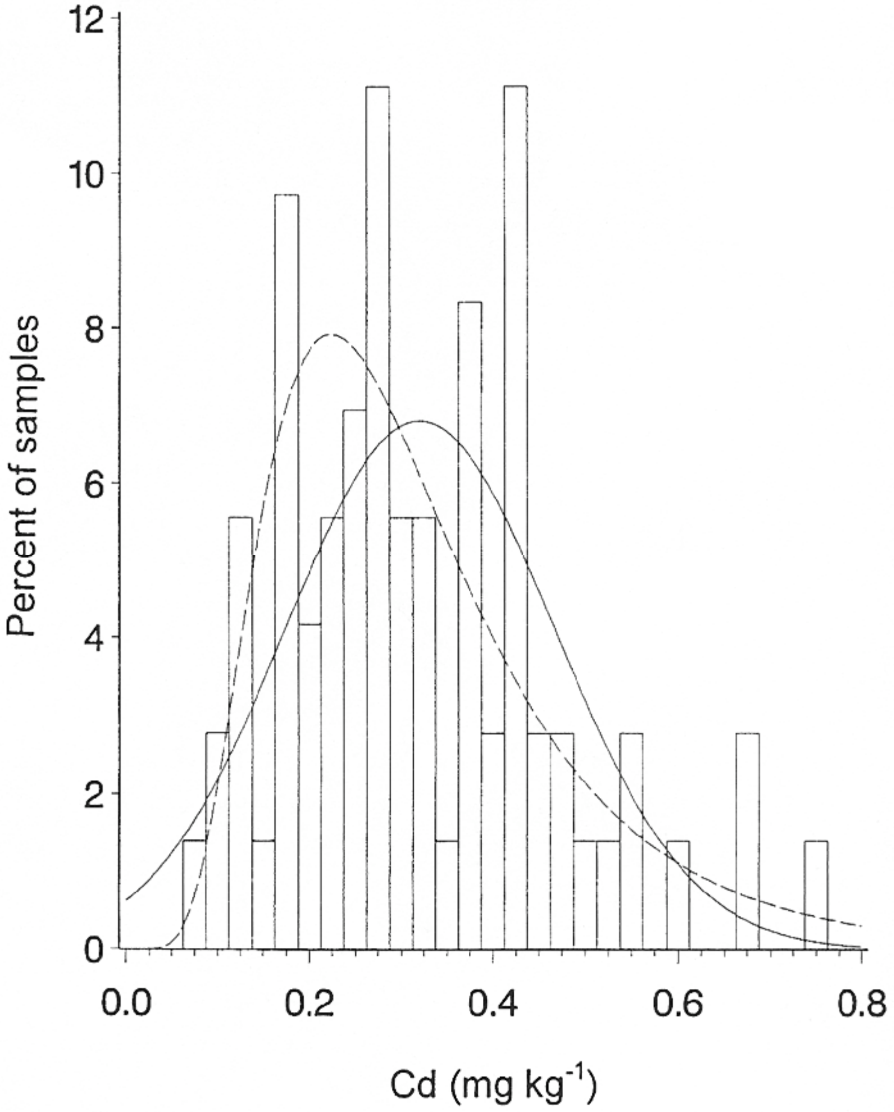

Figure 3. Isopleth map of Zn in Illinois surface soils. Isopleth interval is 10 mg Zn kg^{-1}.

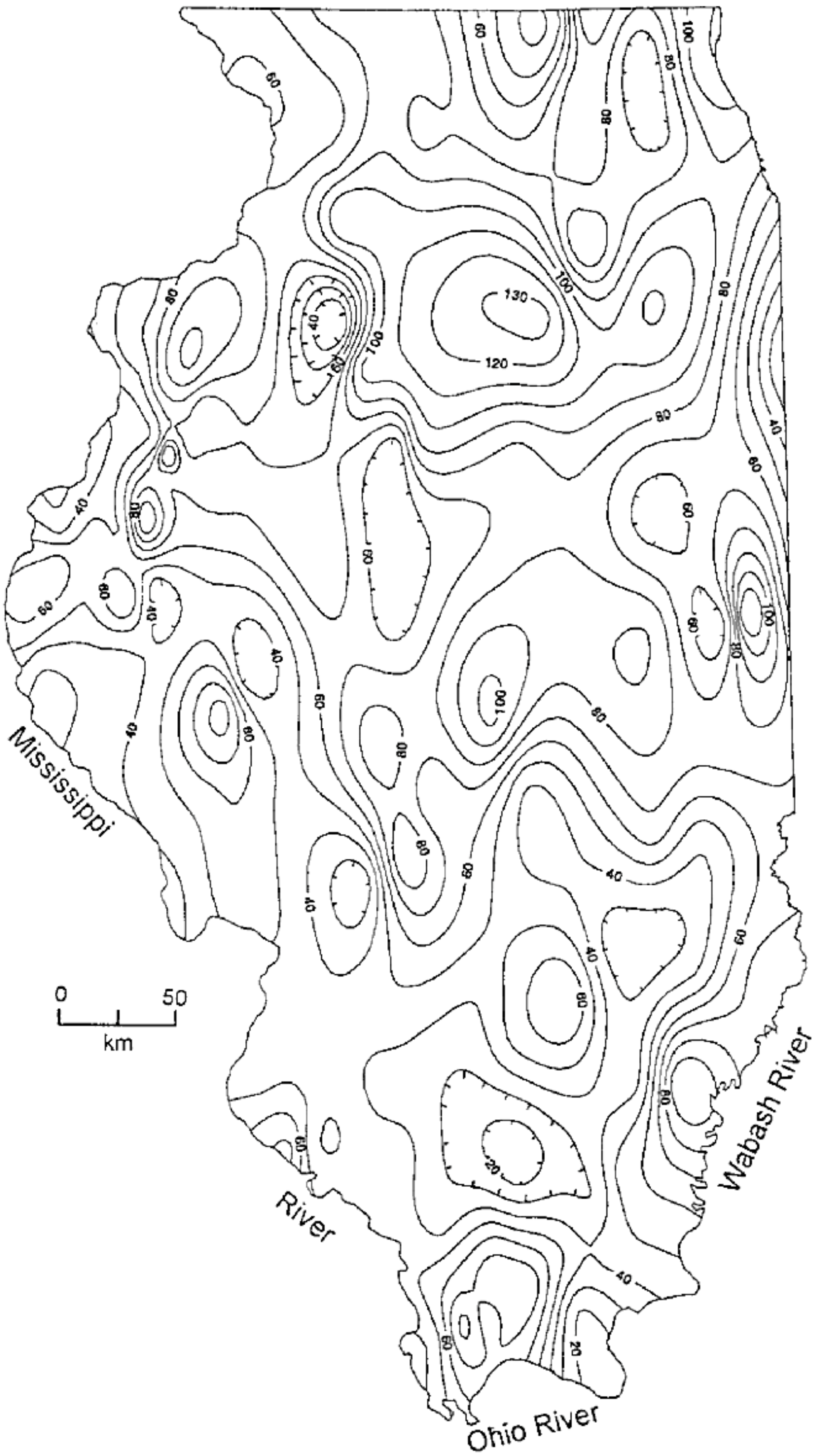

Figure 4. Multivariate surface for total Zn in Illinois soils as a function of clay and organic C contents. Axes are log base n. The equation for the surface is: Zn = 1.2723 + 0.2516 Organic C + 0.4052 clay content.

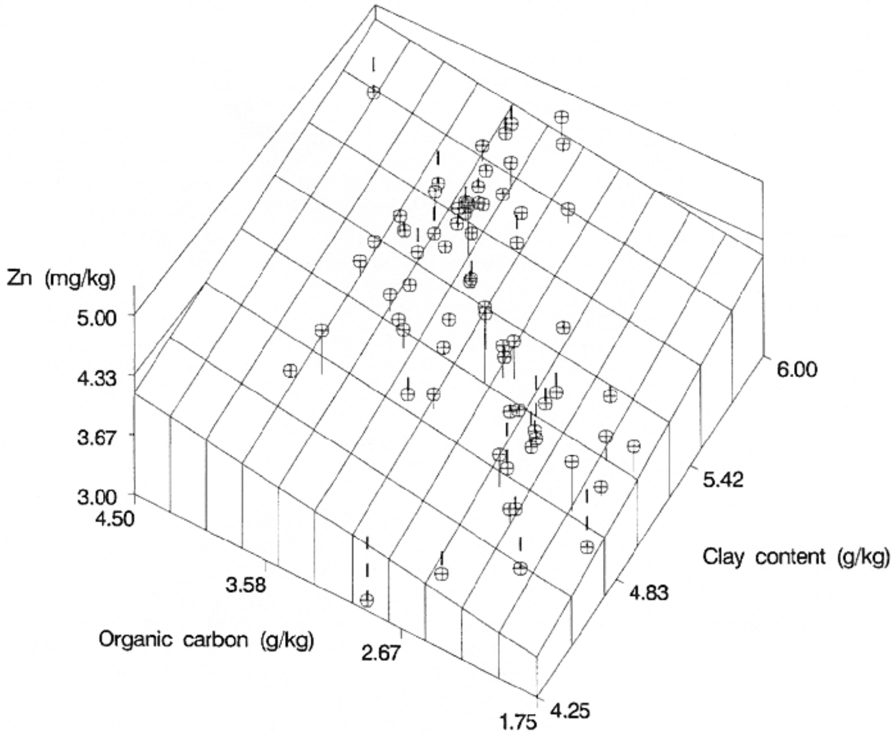

Table 1. Contents of Zn and Cd in Illinois, Missouri, Ohio, and Kentucky surface soils. The data are geometric means except as noted.

Sampling scheme	Zn	Cd	Source
	- - - mg kg^{-1} (n) - - -		
Statewide	60 (150)	0.287 (72)	This study
Statewide	52.4 (131)	0.81 (131)	Holmgren et al. (1993)
Statewide	102.9† (246)	0.97† (245)	Illinois EPA Office of Chemical Safety (1994)
Counties in MSA‡	137.9† (106)	1.3† (104)	Illinois EPA Office of Chemical Safety (1994)
Counties not in MSA	76.3† (140)	0.73† (139)	Illinois EPA Office of Chemical Safety (1994)
Missouri	49 (1140)	n.d.	Connor and Shacklette (1975)
Ohio	75† (239)	0.2† (237)	Logan and Miller (1983)
Kentucky	42.4†(27)	n.d.	Karathanasis and Seta (1993)

† Arithmetic mean

‡ Metropolitan statistical areas