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Soil geochemical signature of urbanization and industrialization – Chicago, Illinois, USA

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ABSTRACT

The concentrations of 45 elements in ambient (not obviously disturbed) surface soils were determined for 57 sites distributed throughout the city of Chicago, Illinois in the upper Midwestern United States. These concentrations were compared to soils from 105 sites from a largely agricultural region within a 500-km radius surrounding the city and to soils collected from 90 sites across the state of Illinois. Although the bulk composition of the Chicago urban soils reflects largely natural sources, the soils are significantly enriched in many trace elements, apparently from anthropogenic sources. The median concentration of Pb in Chicago soils is 198 mg/kg, a 13-fold enrichment compared to regional concentrations. Zinc (median 235 mg/kg), Cu (59 mg/kg), and Ni (31 mg/kg) are also enriched from 2- to 4-fold in Chicago soils and all four elements show strong mutual correlations. These elevated concentrations are most likely related to vehicular and roadway sources and represent uneven distribution across the city as airborne material. Other airborne particulate material from a combination of fossil fuel combustion, waste incineration, and steel production may contribute to apparent elevated concentrations in Chicago soil of Fe (median 2.9%), Mo (5 mg/kg), V (82 mg/kg) and S (0.09%). Chicago soils are enriched from about 1.6- to 3-fold in these elements. Enrichments in P and Se may be caused by direct addition of phosphate fertilizer to parklands, lawns and gardens. The density of the sampling (1 site per 10 km²) is inadequate to define the distribution of the observed enrichments within the city or to predict soil compositions for most of the areas between sample sites, but does provide a statistically significant signature of the history of urban and industrial activity within the city in contrast to the surrounding agricultural lands.

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1. Introduction

Soils can act as receptors and accumulators of many trace elements, including those that may be added by atmospheric deposition of anthropogenic derivation. Anthropogenically altered soils provide an integrated record of numerous processes over time and hence are not well suited for studies of specific sources of elements, but rather record the net effects of human activities over long periods. Comparison of soils in urban areas with surrounding rural areas allows an assessment of the degree of anthropogenic modification to urban soils. Although all soils in the region probably bear some imprint of human activities and no longer reflect purely natural conditions, regional soils provide a baseline against which potentially more intense human activity in urban areas can be judged. Because urban soil integrates information on the history of urbanization and industrialization of a city, it should be expected that each city would have its own characteristic soil geochemical signature determined by that history. A comparison of some recently published urban soil studies suggests this may

indeed be so. In this paper, the geochemical signature of soils within the city of Chicago, Illinois, a major metropolis in the upper Midwestern United States, are reported and the interplay of factors that have led to the current soil composition speculated upon.

Modifications of natural soil chemical compositions caused by intense human activities in urban areas have been widely reported. Most commonly studied modifications involve enrichments in trace elements that can be damaging to environmental processes and human health. Examples of recent urban area vs. background studies in the United States include New York City (Pouyat and McDonnell, 1991), New Orleans, Louisiana (Mielke et al., 2000), Detroit, Michigan (Murray et al., 2004), Indianapolis, Indiana (Filippelli et al., 2005), and Champaign, Illinois (Zhang, 2003).

The data used in this report were collected originally for a study of the concentration and distribution of polycyclic aromatic hydrocarbons (PAHs) within the city of Chicago and a possible correlation with inorganic components in the urban soils. Surface soils were collected at 57 sites, all within the boundary of the City of Chicago, Illinois, in 2001 and 2002. Data on non-urban soils of the region, to which Chicago soils are compared, are from two sources: (1) soils from 105 sites within a 500-km radius of Chicago extracted from a larger data set on soils of the United States,

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referred to as the Shacklette data in this report (Boerngen and Shacklette, 1981) and (2) soils from 90 sites across the state of Illinois (Zhang and Frost, 2002), both surveys being of largely agricultural regions. The data on the Chicago soils was reported by Kay et al. (2003) and a general interpretation of the results is in Kay et al. (2008). In this report compositional variation is examined in more detail and the possible link of Chicago soil compositions to several classes of anthropogenic activities is discussed. The location of Chicago and Shacklette sample sites is shown in Fig. 1. Chicago soils have been analyzed for a robust suite of 45 major and trace elements so that changes in both bulk soil compositions and trace elements can be examined. Statistically significant differences between Chicago and regional soils are examined in terms of both natural and anthropogenic processes. As expected, based on published studies of many other urban areas, surface soils in Chicago exhibit significant enrichments in a large suite of elements. The interpretation suggests that some enrichments are related to natural geological differences between the Chicago area and the surrounding region. Most, however, seem best explained by anthropogenic modifications to soils largely from atmospheric deposition from a variety of sources. Potential causes of modifications are discussed in a general sense, but no attempt is made to ascribe specific element enrichments or specific highly enriched samples in terms of any single process, source, or activity.

Analysis of spatial variability of soil compositions within the city shows that the sample density of this study, ca. 1 sample site per 10 km², does not provide adequate resolution of the spatial variability to allow extrapolation of compositions from a single sample to surrounding areas with confidence. Thus, although the data clearly document a significant anthropogenic modification of soil chemistry within the city compared to regional baseline compositions, they cannot be used to infer areas within the city of consistently elevated trace element content.

2. Overview of the city of Chicago

The city of Chicago, Illinois occupies an area of 606.2 km² and lies along the southwestern shore of Lake Michigan. In 2006, the population of the city was 2,872,790 and the greater metropolitan area, including residential and industrial land use, housed 9,661,840 people. The city was incorporated in 1837 with a population of about 30,000 but grew rapidly to more than 1,000,000 people by 1890 in spite of a devastating fire that destroyed much of the city in 1871. The city reached a maximum population of roughly 3.6 million in the 1950s before declining to its present population. The present city is largely a business and financial center along with extensive residential areas. Previous heavy industry

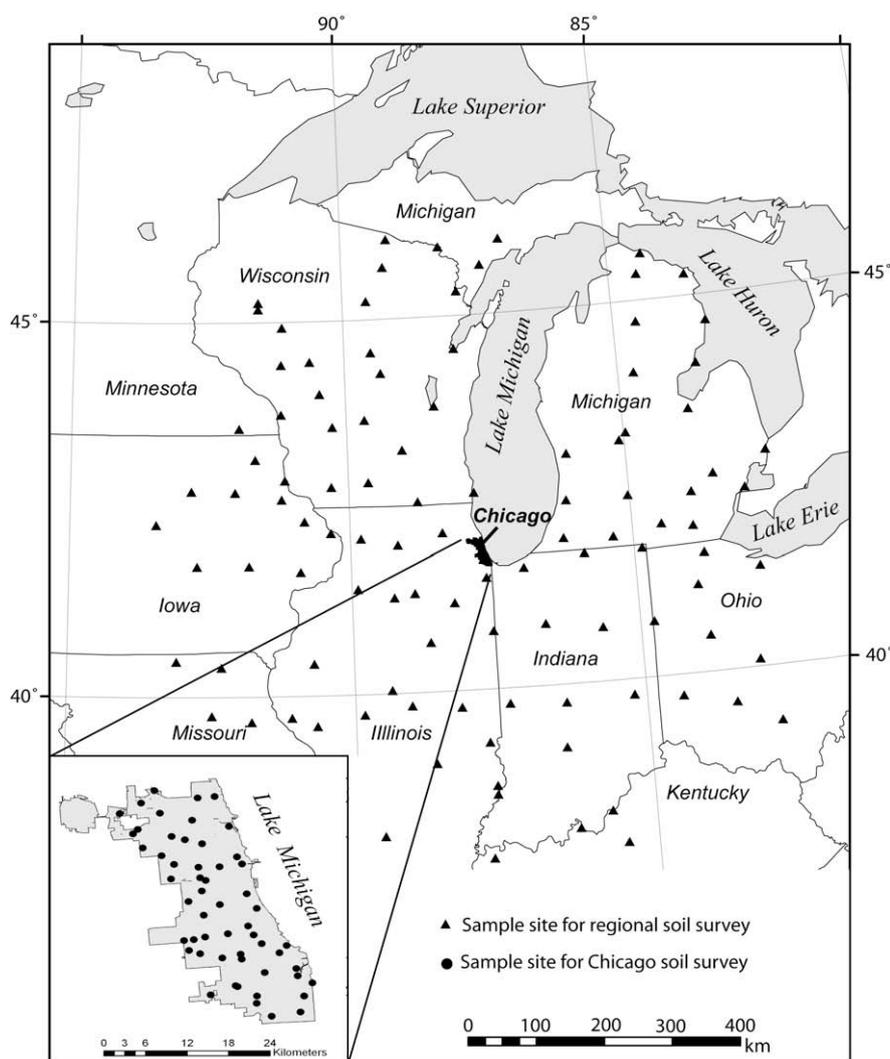


Fig. 1. Map showing location of regional soil sample sites (Boerngen and Shacklette, 1981) within 500 km of Chicago and sites within the city of Chicago sampled for this study.

has largely moved to surrounding areas where production of chemicals, metals, machinery and consumer electronics, along with publishing and food processing, are major activities. Nevertheless, significant brownfield areas remain in the city.

3. Methods

The Chicago soil survey was conducted in 2001 and 2002 and is described in detail in Kay et al. (2003). The survey was designed primarily to examine soils for concentrations of PAHs, and the inorganic constituents discussed here were determined as an adjunct to that activity. Sample sites were selected by a computer-generated random technique from a large population of potential sites (Kay et al., 2003). The potential sites were property owned either by the City of Chicago, including libraries, fire stations, and police stations, or by Commonwealth Edison, an electric utility company. Soils were collected by Tetra Tech EM, Inc. (2001) in accordance with the Illinois Environmental Protection Agency approved field sampling plan and included the uppermost 15 cm of soil. Sites and samples were selected to avoid obvious contamination and human disturbance. One field duplicate was taken at every tenth sample site and analyzed.

Chemical analyses were performed on the <0.18-mm fraction of the soil, after a 4-acid, near-total digestion. Methods for handling and analysis are provided by Arbogast (1996). Analyses were performed at XRAL Laboratories in Toronto, Ontario, Canada, using techniques developed by the US Geological Survey (USGS), and at the USGS laboratories in Lakewood, Colorado. Inductively coupled plasma-atomic emission spectrometry provides quantitative data on a suite of 40 elements (Briggs, 2002). In addition, total C was

measured using an automated C analyzer (Brown and Curry, 2002a) and carbonate C using coulometric titration (Brown et al., 2002b). Total S was determined using an automated S analyzer (Brown and Curry, 2002b) and Hg by cold-vapor atomic absorption spectrometry (Brown et al., 2002a). Arsenic and Se were determined by hydride generation atomic absorption spectrometry (Hageman et al., 2002).

Calibration of the analyses was performed by standardizing with digested rock reference materials and a series of multi-element solution standards. Data were deemed acceptable if recovery was within the range of 85–115% at five times the lower detection limit and the calculated relative standard deviation (RSD) of the duplicate samples was no greater than 15% for all elements except Hg, Se and As. For these elements, recovery within the range 80–120% and an RSD no greater than 20% was considered acceptable. All analytical data is reported in Kay et al. (2003).

The suite of analytical techniques used to analyze Chicago soil provides data for 45 elements. Five elements are present at concentrations below detection limits in all samples. These and their detection limits are Ag (2 mg/kg), Au (8 mg/kg), Ho (4 mg/kg), Ta (40 mg/kg), and U (100 mg/kg). These elements are not further discussed. Four additional elements, Bi (50 mg/kg), Cd (2 mg/kg), Eu (2 mg/kg) and Sn (50 mg/kg), occur in less than detectable concentrations in more than 1/3 of the samples. These elements are likewise excluded for further consideration. The remaining 36 elements occur at detectable concentrations in at least 2/3 of samples and are included in the following statistical analyses. Non-detect values are replaced with a value of 50% of the detection limit. Table 1 provides medians and percentiles for these elements. Because many elements display distributions that vary significantly

Table 1
Median and percentile compositions of Chicago and regional soils. "Non-detect" is indicated as the number of analyses below the limit of detection (LOD).

Element	Non-detect	LOD	Chicago 25%	Chicago 50%	Chicago 75%	Regional 25%	Regional 50%	Regional 75%	Chicago 50%/Regional 50%
Al (%)	0		3.45	5.33	6.06	3	5	7	1.1
Ca (%)	0		1.73	3.21	4.76	0.37	0.55	0.7	5.8
Fe (%)	0		2.5	2.9	3.64	1	1.5	3	1.9
K (%)	0		1.31	1.84	2.25	1.18	1.55	1.83	1.2
Mg (%)	0		1.15	1.7	2.77	0.15	0.3	0.5	5.7
Na (%)	0		0.46	0.53	0.63	0.7	0.7	0.7	0.8
P (%)	0		0.05	0.08	0.1	0.02	0.03	0.04	2.7
Ti (%)	0		0.16	0.24	0.28	0.15	0.3	0.3	0.8
Ccarb (%)	0		0.5	1.1	2.35				
Corg (%)	0		3.04	4.91	7.17				
S (%)	9	0.05	0.05	0.09	0.13				
As (ppm)	0		10.2	13.2	17.7	3.35	5.8	8.8	2.3
Ba (ppm)	0		387	445	498	300	500	700	0.9
Be (ppm)	8	1	1	2	2	0.7	0.7	1.5	2.9
Ce (ppm)	0		24	51	63				
Co (ppm)	0		9	11	13	5	7	13.7	1.6
Cr (ppm)	0		52	65	78	20	50	70	1.3
Cu (ppm)	0		39	59	91	7	15	30	3.9
Ga (ppm)	0		10	15	17	7	10	15	1.5
Hg (ppm)	0		0.08	0.19	0.39	0.05	0.08	0.15	2.4
La (ppm)	0		18	28	33	20	30	50	0.9
Li (ppm)	0		22	32	42	10	19	26	1.7
Mn (ppm)	0		384	495	636	200	300	700	1.7
Mo (ppm)	5	2	3	5	6	2	2	2	2.5
Nb (ppm)	0		7	10	11				
Nd (ppm)	0		14	24	30				
Ni (ppm)	0		25	31	43	7	15	20	2.1
Pb (ppm)	0		71	198	470	10	15	20	13.2
Sc (ppm)	2	2	6	9	11	5	7	10	1.3
Se (ppm)	2	0.2	0.7	0.8	1.2	0.2	0.4	0.6	2.0
Sr (ppm)	0		98	106	123	70	100	150	1.1
Th (ppm)	14	6	5	8	9	5	8	10	1.0
V (ppm)	0		61	82	93	30	50	70	1.6
Y (ppm)	0		13	17	18	10	20	30	0.9
Yb (ppm)	0		1	2	2	1.5	2	5	1.0
Zn (ppm)	0		112	235	494	40	50	62	4.7

from normal distributions, the summary is presented as medians and percentile values rather than as means and standard deviations. In Table 2, results are given as means, which are used below to compare Chicago soils to the Illinois data set for which compositions are reported as arithmetic means.

Data on regional soils are from two sources. First, data for samples within a 500-km radius of Chicago were extracted from the Shacklette data (Boerngen and Shacklette, 1981). The Shacklette data set for the conterminous US contains geochemical data from soils and other regolith collected and analyzed beginning in 1958 and continuing until about 1976. The samples were collected at a depth of ca. 20 cm from sites that, insofar as possible, had surficial materials that were very little altered from their natural condition and that supported native plants. The <2-mm fraction of the samples was chemically analyzed by a variety of techniques in the USGS laboratories in Denver, Colorado. Details of the survey are given by Shacklette and Boerngen (1984). Second, soils from 90 sites across the state of Illinois were analyzed and summary statistics reported (Zhang and Frost, 2002). Samples were analyzed from both A and B horizons. The A-horizon data have been used for the comparison because those samples were taken between 10 and 20 cm below the surface and overlap with the 0–15 cm depth range of the Chicago samples. In addition, Hg concentrations were reported for 101 samples covering approximately the southern two thirds of the state of Illinois (Dreher and Follmer, 2004). These two sources are referred to as the Illinois data set. Neither the Shacklette nor Illinois data sets provide a perfect comparison with the Chicago soil data because of differences in sampling, preparation, and analytical techniques, discussed in more detail below, but both data sets reveal differences with Chicago soils that exceed possible variability introduced by these differences in techniques.

4. Geologic setting

4.1. Chicago

The city of Chicago is built mostly on a veneer of Pleistocene (Wisconsin) glacial deposits that overlie dolomite of Silurian age. Glacial deposits include lacustrine clay and silt and coarser lake and beach sand and dune sand. Extensive areas are also underlain by lodgement till and frontal moraines formed by an ice lobe than advanced out of the Lake Michigan basin (Hansel and Johnson, 1992, 1996). Material was deposited between 23 and 10 ka BP. Bedrock consists of flat-lying carbonate, dominantly dolomite, of Silurian age (Willman, 1967). The nature of presettlement soils within the city is not known in detail. In general, soils are classified as silty and clayey, generally poorly drained, that have formed on glacial till and lake sediment, and sandy and loamy upland soil formed on glacial outwash and sandy lake sediment. The parent materials for all soils are the glacial deposits rather than bedrock (Mapes, 1979). The dominant soil order is entisols, soil with no diagnostic horizons and little alteration from parent material (Natural Resources Conservation Service, 1998).

4.2. Region

The 500-km-radius region surrounding Chicago contains a variety of geologic and pedologic conditions, some of which vary considerably from the immediate Chicago area. The entire area lies within the generally low relief region of the Great Plains and, with the exception of a few of the southernmost sample sites, has been glaciated during the Pleistocene. Thus, nearly all soils are developed on the nearly continuous cover of glacial deposits and related

Table 2

Comparison of mean element concentrations of Chicago soils with mean concentrations in Shacklette and Illinois soils. Ratios for trace elements are rounded to the nearest integer value.

Element	Chicago mean	Shacklette mean	Illinois A mean	Chicago/Shacklette	Chicago/Illinois	Shacklette/Illinois
As (ppm)	19.55	6.50	9.00	3.0	2.2	0.7
Hg (ppm)	0.64	0.14	0.03	4.5	19.4	4.3
Al (%)	4.80	4.86	5.08	1.0	0.9	1.0
Ca (%)	4.07	0.83	0.65	4.9	6.3	1.3
Fe (%)	3.30	1.85	2.38	1.8	1.4	0.8
K (%)	1.76	1.56	1.75	1.1	1.0	0.9
Mg (%)	2.48	0.40	0.50	6.2	5.0	0.8
Na (%)	0.52	0.73	0.57	0.7	0.9	1.3
P (%)	0.09	0.04	0.06	2.0	1.4	0.7
Ti (%)	0.22	0.28	0.42	0.8	0.5	0.7
Ba (ppm)	427	499	568	1	1	1
Ce (ppm)	47		67		1	
Co (ppm)	11	9	11	1	1	1
Cr (ppm)	71	44	56	2	1	1
Cu (ppm)	150	18	28	8	5	1
Ga (ppm)	14	13	11	1	1	1
La (ppm)	26	36	33	1	1	1
Li (ppm)	31	20	19	2	2	1
Mn (ppm)	583	460		1		
Mo (ppm)	6	2		2		
Nb (ppm)	10					
Nd (ppm)	25					
Ni (ppm)	36	16		2		
Pb (ppm)	395	19	29	20	14	1
Sc (ppm)	9	8	8	1	1	1
Sr (ppm)	114	122	103	1	1	1
Th (ppm)	9	8	9	1	1	1
V (ppm)	76	61	85	1	1	1
Y (ppm)	16	21		1		
Zn (ppm)	397	54	74	7	5	1
Se (ppm)	1	0		2		
Total C (%)	7.61	2.55		3.0		
S (%)	0.13					
CO ₃ C (%)	1.92					
Organic C (%)	5.78		1.84		3.1	

loess rather than bedrock. With the exception of a few of the northernmost sample sites, the underlying bedrock is a variety of Paleozoic flat lying sedimentary rocks, dominantly clastic, but also with locally dominant carbonate rocks. Precambrian crystalline rocks underlie northern Wisconsin and northern Michigan. The area is dominantly agricultural and the dominant soil orders are alfisols and mollisols (Natural Resources Conservation Service, 1998).

5. Results

5.1. Chicago

Summary statistics for 35 elements in Chicago soils are given in Tables 1 and 2. The complete analytical data is available in Kay et al. (2003).

5.2. Regional data

The Shacklette data were processed by the same techniques as the Chicago data to exclude elements which occur below detection limits. Medians and percentiles are also shown in Table 1 and means in Table 2. The Shacklette data set lacks information on five elements (carbonate C (Ccarb), organic C (Corg), S, Nb and Nd) present in the Chicago data. Therefore, comparisons of Chicago and regional soils are restricted to the 30 remaining elements that are common to the two data sets. Analytical techniques used for some elements in the Shacklette data reported concentrations in discrete integer values rather than continuously distributed values. As a result, medians and percentile values are artificially rounded. This aspect of the data must be taken into account in attempting precise comparisons of the two data sets.

The Illinois data are available only in summary form (Table 2), mostly arithmetic means, ranges, and standard deviations, so are not treated as rigorously as the Shacklette data in the comparison. They do, however, provide important additional means of comparing Chicago soils to soils across an adjacent, largely agricultural region. They also have the advantage of being collected from a depth range that overlaps that of the Chicago samples, thus minimizing possible depth-related variations that might influence comparison with the Shacklette data.

5.3. Differences between the Chicago and regional surveys

There are several important differences between the Chicago and regional surveys that should be considered when comparing soil compositions. To what extent might these differences affect the comparability of the three data sets? Samples for the Shacklette survey were taken from a depth of about 20 cm compared to Chicago soils, which were a composite of the upper ca. 15 cm. Thus, many of the Shacklette samples may include material from the zone of illuviation below the surface soil horizon. The Chicago samples are commonly from unzoned soils. The Illinois samples used in the comparison are "A-horizon" soils collected at 10–20 cm depth. Thus, there is a difference in average sample depth of the three surveys of 10–15 cm from the shallowest (Chicago) to deepest (Shacklette). Table 2 presents a comparison of means for Illinois and Shacklette soils. The maximum variation for any single element between the two data sets is 30% except for Hg. Thus, it appears that depth differences between these two data sets produced, at best, minor variations. Because the depth of Chicago samples overlaps with that for Illinois samples, it is further concluded that variations related to depth are also small in comparing Chicago soil to either regional data set.

Another potentially important difference is the size fraction analyzed. Both the Shacklette and Illinois surveys analyzed all

material with a particle size <2 mm (sand and finer particles) whereas the Chicago analyses were performed on a finer fraction consisting of the <0.18-mm fraction (silt and finer particles). These different grain-size fractions could cause chemical variations in that the mineralogy, and thus chemical compositions, of the size fractions may differ. In particular, exclusion of the sand-sized fraction, as in the Chicago soils, might result in an increase in the proportion of clay minerals vs. quartz, which could result in significant increases in concentrations of components that are commonly present dominantly, although not exclusively, in clays, such as Al, K, Li and Sc, or trace elements that might bind to clay particles. Of these four elements, only Li shows a substantial difference between Chicago and regional soils, being enriched by a factor of 1.6–1.7 in Chicago soils compared to Shacklette and Illinois soils (Tables 1 and 2). Aluminum, K, and Sc have mean concentrations that vary by a maximum of 10% between the three data sets. Thus, an increase in the proportion of clay minerals in material analyzed from Chicago soils might account for a small increase in components that occur with clays, but the effect should be much smaller than the major differences discussed below for many elements.

The three surveys were conducted at different times. Chicago soils collected in 2001–2002 are the most recent. Illinois soils were collected in 1992. The Illinois portion of the Shacklette survey was conducted over an 11-a period from 1961 to 1972. Could there be temporal changes in regional soils which affect comparisons between the Chicago samples and the older regional samples? Comparing the Illinois and Shacklette means in Table 2 shows that, with the exception of Hg, the means for all elements vary by a maximum of about 30% between the two data sets. Even if all of this variation was ascribed to temporal changes in composition, an unlikely event, it appears that such changes over the 17–30 a between the two surveys is minor and that the composition of regional soils does not change over time at a rate that could substantially affect the comparison of recent Chicago soils to older regional data sets.

Finally, the analytical techniques used were different between the surveys. The Shacklette survey was performed over a period of more than 10 a and several different techniques were employed (Shacklette and Boerngen, 1984). All were different from the techniques used in the Chicago survey. Likewise, the Illinois survey techniques differed from both the Chicago and Shacklette surveys. Although sensitivities and detection limits varied between techniques, all analyses were calibrated to established geochemical standards and there is no reason to suspect that there is any inherent analytical bias in the data. Thus, while acknowledging that the comparison of the Chicago data set with the Shacklette and Illinois data is not precise, the differences between Chicago soils and soils from the surrounding region are so pronounced for many elements that differences cannot be explained solely by variations in sampling and analytical techniques. Rather, the differences show that the urban soils of Chicago contain a signature of compositional alteration that is not present in the surrounding region.

5.4. Comparison of Chicago and regional soil chemistry

A simple way to examine gross differences in the three data sets is the ratio of medians or means for each element (Fig. 2 and Table 1). Many elements exhibit significant enrichment in Chicago soils compared to the regional compositions (Fig. 2). Compared to the Shacklette data, Chicago soils are enriched about 13× in Pb and 6× in Ca and Mg. Other prominently enriched trace elements include Zn (4.7×), Cu (3.9×), Be (2.9×), P (2.7×), Mo (2.5×), Hg (2.4×), As (2.3×) and Se (2×). A test for significant differences in the two sets was performed using the Kruskal–Wallis nonparametric test, which avoids complications introduced by the non-normal nature of many element distributions. For all of the above

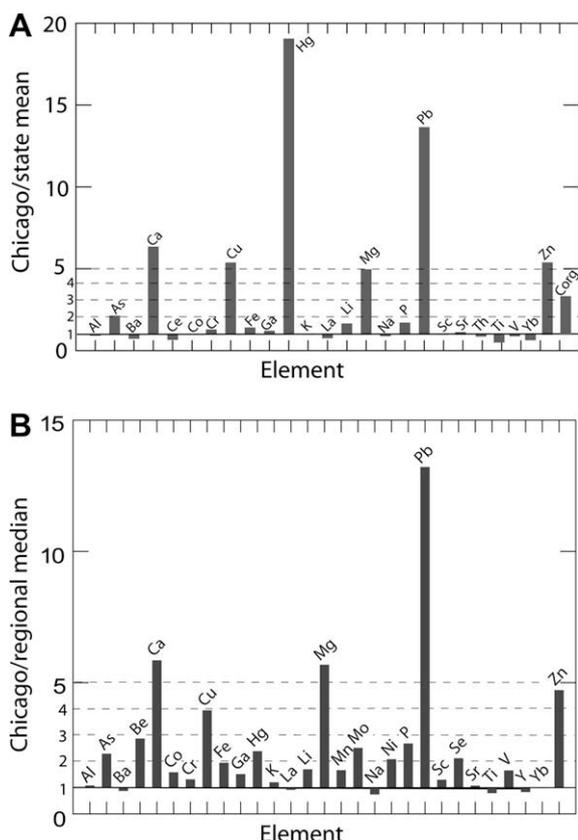


Fig. 2. (A) Anchor bar chart comparing mean concentrations of Chicago soils with Illinois soils for 25 elements that are common to the two data sets. (B) Anchor bar chart comparing median concentrations of Chicago soils with Shacklette soils for 29 elements that are common to the two data sets.

elements, results indicate a statistically significant difference at a probability of $P < 0.001$. Other elements showing apparent enrichments between $1.5\times$ and $2\times$ are Co, Fe, Ga, Li, Mn and V. All show high probabilities of significant differences between Chicago and the Shacklette soils by the Kruskal–Wallis test. There are no elements in the data sets that show significant depletion in Chicago. The lack of element depletions may be a result of variations in quartz content, whereby quartz in Chicago soils is somewhat lower as a result of higher carbonate mineral content. Silicon is not one of the elements included in the analyses.

Comparison of Chicago soils to the Illinois samples gives somewhat similar results. Calcium, Mg, Pb, Zn and Cu are enriched by a factor of 5 or greater in Chicago soils. Mercury shows an extreme enrichment, much greater than that shown in the Shacklette comparison, but this derives from the skewed distribution of Hg in Chicago soils so that the mean is strongly influenced by a few very high concentrations. Data from a study of Hg in Illinois soils (Dreher and Follmer, 2004) indicates that the median Hg (not explicitly given) does not vary greatly from the mean. A comparison of Hg medians for Chicago and Illinois would likely indicate an enrichment of $2\text{--}3\times$ in Chicago, similar to the comparison with Shacklette data. Organic C is enriched by a factor of about three in Chicago soils relative to Illinois soils. Organic C is not reported as part of the Shacklette data.

6. Interpretation

Principal component factor analysis with varimax rotation was used to examine gross similarities and differences in inter-element relationships between the two data sets. For both data sets, a large

percentage of the total variation can be explained by a small number of factors. For the Chicago soils, five factors account for 72% of the total variability, and for the Shacklette soils, four factors account for 66% of the variability. The element groupings that make up the factors vary between Chicago and the surrounding region suggesting that chemical changes consequent to urbanization and industrialization play a significant role in the composition of Chicago soils. For Shacklette regional soils, the factors are largely interpretable as natural element groupings expected from mineral components of the region. Although these factors are also present in Chicago soils, reflecting the natural component of the soils, the Chicago soils also contain factors which seem best explained by various anthropogenic modifications. Some these are discussed in more detail below.

6.1. Elevated Ca and Mg in Chicago

One of the most prominent element enrichments in Chicago soil is a 5- to 6-fold enrichment shown by both Ca and Mg compared to both Shacklette and Illinois soils. Because both elements are major components of dolomite, and because dolomite is the principal bedrock type both beneath the city and beneath adjacent Lake Michigan, the source area for much of the glacial deposits on which Chicago soils are developed, this enrichment may be a natural feature. High correlations among Ca, Mg and carbonate C (Fig. 3), the three principal constituents of dolomite, suggest that variations in dolomite content between Chicago soils and regional soils account for at least part of the enrichments in Chicago. Factor analysis indicates that variations in carbonate minerals accounts for *ca.* 11% of the total chemical variability in Chicago soils. Factor analysis of Shacklette soils also reveals a strong factor that is controlled by carbonate minerals that accounts for *ca.* 13% of regional variability. This factor is expressed by strong correlations between Ca, Mg and Sr (carbonate C is not included in the Shacklette analyses). An additional potential source of these elements is concrete and mortar, which commonly occur in urban soils (Bridges, 1991). The current information does not allow an assessment of the relative importance of naturally occurring carbonate minerals vs. anthropogenic additions.

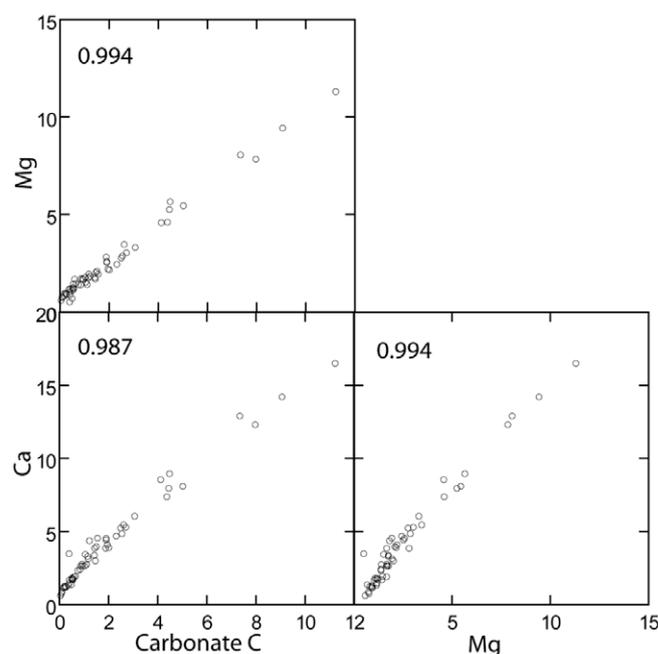


Fig. 3. Scatter plot matrix for Mg, Ca, and Ccarb in Chicago soils and Pearson correlation coefficients for element pairs.

6.2. Elements related to clay minerals

Both the Chicago and Shacklette data sets produce strong factors expressed by correlations of elements common in clay minerals. This clay factor accounts for 30% of the variability in Chicago soils and 32% of the variability in the Shacklette data set. Fig. 4 shows a scatter plot matrix and Pearson correlation coefficients for six elements (Al, K, Ga, Li, Sc and V), which have especially strong correlations in Chicago soils apparently caused by their mutual occurrence in clay minerals. In the Shacklette data, the clay factor also includes the elements As, Cu, Fe, Ni and Cr, all elements that are common in trace amounts in clay minerals or adsorbed to them. In the Chicago soils, these elements do not appear in the clay factor, but rather are expressed in separate factors, which may indicate that anthropogenic factors have overwhelmed natural factors in the distribution of these elements as discussed in following sections.

6.3. Chicago anthropogenic factors

The most prominent enrichment of a trace element in Chicago soils is Pb, which along with Zn, Cu and Ni, forms a factor accounting for ca. 8% of the total variability. Fig. 5 shows Pearson correlation coefficients for these four elements plus S. In nature, these elements all show a strong affinity to bind chemically with S and have a distribution that correlates strongly with S content. The Chicago soils, however, do not show this strong correlation even though S is probably enriched in Chicago soils. Correlation coefficients of the four elements with S range from 0.476 to 0.573 suggesting that their occurrence is controlled, at least in part, by factors other than the occurrence of natural sulfide minerals. Furthermore, there is no known natural source in the Chicago region that could account for the 13-fold increase in Pb concentration over regional background. Shacklette soils also show a weak correlation between Pb and Zn (Pearson correlation coefficient = 0.492), but both Cu and Ni appear to occur mostly in clay minerals as de-

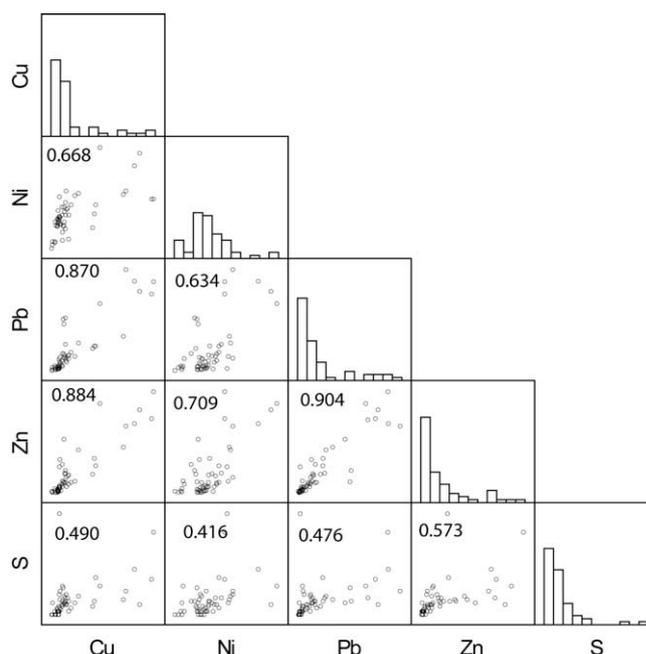


Fig. 5. Scatter plot matrix for elements in Chicago soils that may be controlled by vehicular particulate deposition.

scribed above. Neither the Shacklette nor Illinois data contain S analyses, so a direct comparison to Chicago is not possible. The enrichments of these four trace metals in Chicago thus appear to be dominantly of anthropogenic causes, a topic expanded on in the following section.

Chicago soils produce a strong factor, accounting for 18% of the total variability, which reflects mutual correlation between organic

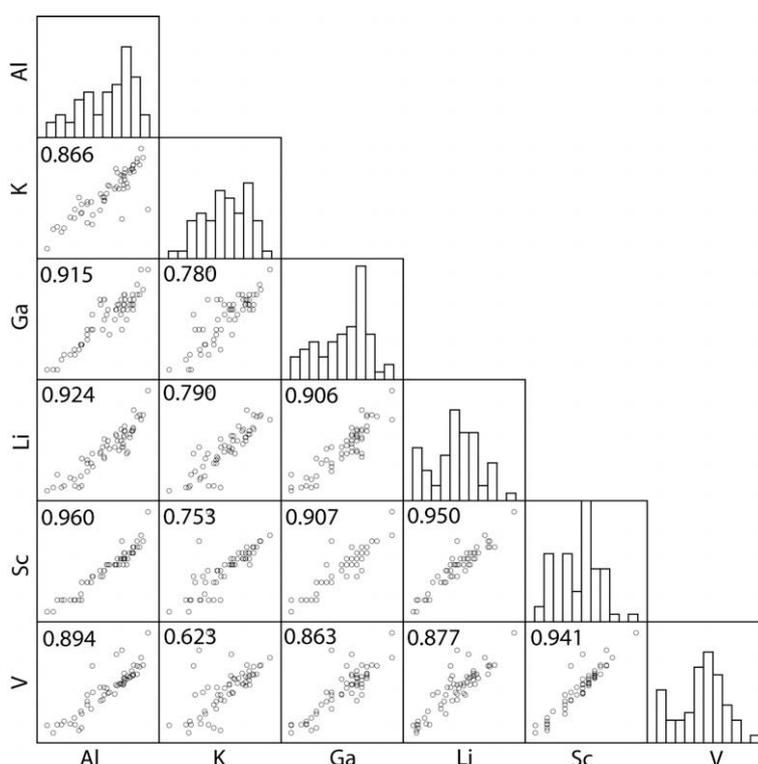


Fig. 4. Scatter plot matrix and Pearson correlation coefficients for six elements in Chicago soils that are common in clay minerals.

C, Fe, Mo, Nb and S. An additional factor defined by a strong correlation between Cr and Mn accounts for an additional 8%. Fig. 6 shows the correlation between all seven of these elements. Vanadium is added to Fig. 6 to illustrate its positive correlation with most of these elements in addition to its affinity for the elements associated with clays. Correlations vary from weak (0.229 for Mn vs. Corg) to strong (0.897 for S vs. Corg). For Shacklette soils, there is no data on organic C and S. Iron is strongly correlated with clay minerals, Mo shows a weak affinity for carbonate minerals and Nb shows a weak correlation with P and Se. The occurrence of this prominent element grouping in Chicago soils may be a signal of anthropogenic modifications of soil by additions of materials from a wide variety of potential sources. The correlation of Corg, Fe, Mo, V and S seen in Chicago could occur in nature, for instance in pyritic black shales. Black shales are not present in bedrock of the immediate Chicago area, but probably underlie part of Lake Michigan about 50 km north of the city based on projection of onshore geologic units. The black shales are relatively thin and comprise only a few percent of the total bedrock sequence, so they would be at best a small fraction of the bedrock source for Chicago glacial deposits. For elements common to the Chicago and Shacklette data sets (Fe, Cr, Mn, Mo and V), there is a modest enrichment in Chicago soils over the regional baseline that varies from 1.3× for Cr to 2.5× for Mo. Compared to Illinois data, Chicago soils are enriched in Fe by a factor of 1.4, Cr by a factor of 1.3, and Corg by a factor of 3.2. The Illinois data do not include Mn and Mo. Chicago soils are slightly depleted in V relative to Illinois soils by a factor of 0.9. The element correlations and magnitude of the enrichment in Chicago by additions of natural materials such as black shale seems unlikely. Carbon, Fe, Mo, Mn, Cr, V and Nb are all major or trace components of steel, so their correlation might signal metal-

lic waste additions to soil, but other possible causes are discussed below.

Phosphorus and Se show enrichments of 2.7 and 2.0, respectively, in Chicago soils relative to Shacklette soils. Phosphorus has a 1.7-fold enrichment relative to Illinois soils. Selenium is not reported in the Illinois data. Phosphorus and Se concentrations have a Pearson correlation coefficient of 0.699 in Chicago. Shacklette soils also show a strong correlation of 0.728. Neither element shows a strong correlation with any other element in the data sets, so their correlation may indicate a single source that controls their concentration and enrichment in Chicago. Phosphatic fertilizer is a common anthropogenic source for P enrichment. Phosphorites, the geologic source for P in fertilizers, are commonly enriched in Se. Globally, phosphorites exhibit an 8-fold enrichment in Se relative to average shale and USA phosphorites are even more enriched (Altschuler, 1980). Thus, the P–Se enrichment and correlation may be a geochemical signal of soil alteration by fertilizers that have been used more intensely in Chicago than in the surrounding agricultural regions.

Mercury is enriched 2.4-fold in Chicago relative to Shacklette soils, likely the result of anthropogenic inputs. The extreme enrichment relative to Illinois soils indicated in Fig. 2A is likely a statistical artifact resulting from comparing means, the only parameter reported for Illinois soils, rather than medians. As discussed above, comparing medians would likely indicate enrichment similar to that relative to Shacklette soils. In natural soils, Hg tends to bind strongly with organic C molecules (Skylberg et al., 2000) and there is commonly a strong correlation of the two elements. In Chicago soils, the two are virtually independent of each other (Pearson correlation coefficient = 0.02) indicating that Hg in Chicago soils is behaving in a geochemical manner different from that in natural

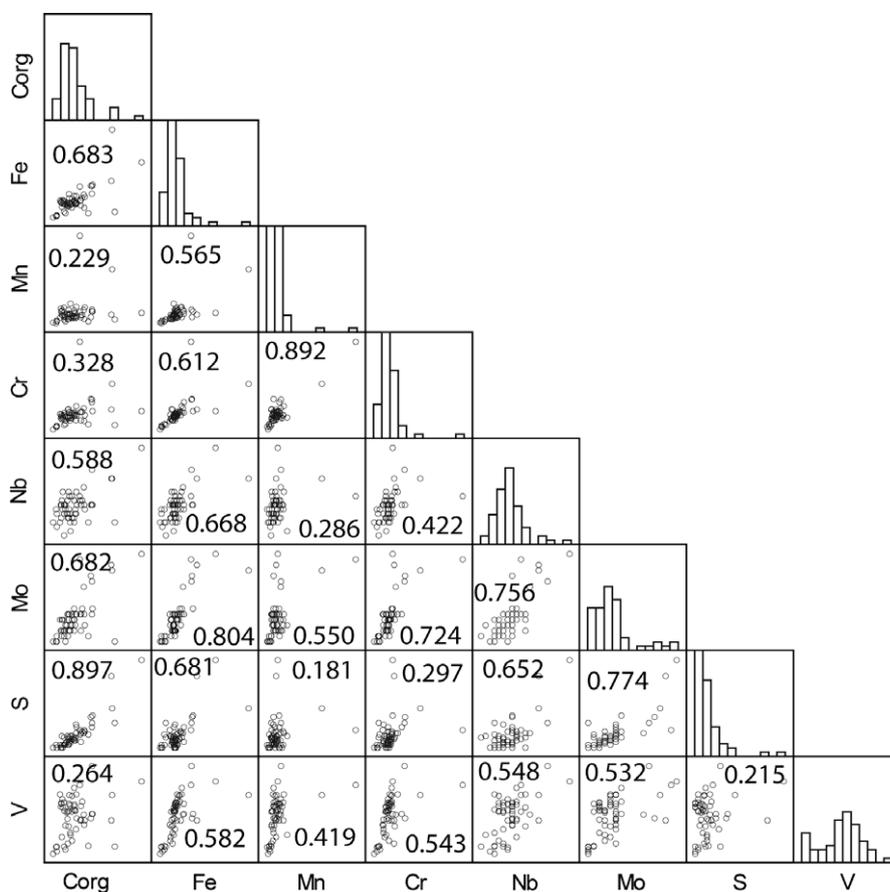


Fig. 6. Scatter plot matrix and Pearson correlation coefficients for eight elements in Chicago soils that may be controlled by industrial particulate deposition.

settings. There are no significant correlations between Hg and any other element in the Chicago data set indicating that Hg enrichment is a result of processes that operate largely independently of other human activities assigned to other element factors or soil processes.

7. Discussion

The present data document that there are significant differences in the chemical composition of soils within Chicago relative to the surrounding agricultural region, a result expected in light of results from many other urbanized areas, including areas within the upper Midwestern USA (Parker et al., 1978; Zhang, 2003; Murray et al., 2004; Filippelli et al., 2005). Unlike many studies that have concentrated on a limited suite of elements, commonly trace elements of interest for human health, the large suite of elements in the present study allows a more comprehensive evaluation of both natural and anthropogenic aspects of soils in Chicago. The data set of Chicago soil chemistry is biased because industrialized and obviously disturbed sites were avoided, so it is not representative of the city as a whole. Rather, it represents commonly occurring ambient soil compositions that are not obviously impacted by site-specific influences, and thus, are soils typically encountered by the population of the city.

7.1. Natural variability

The bulk chemistry of Chicago soils appears to reflect mostly natural geologic and pedologic factors rather than anthropogenic modifications. Although Chicago soils differ strongly from regional soils for some major elements, there are naturally occurring factors that account for these differences. Specifically, the strong enrichments of Ca and Mg in Chicago soils can be explained by underlying geology. The bedrock beneath Chicago is almost entirely dolomite and the glacial materials that form the parent material for the soils is also enriched in dolomite. Although dolomite is a common rock type in the region, it is generally subordinate to sandstones, siltstones, and shales. Likewise, a suite of elements including Al, K, Ti, Ce, Co, Ga, La, Li, Nd, Sc, Y and Yb appear to be controlled by clay content of the soils. None of these elements is strongly enriched relative to regional concentrations in either the Shacklette or Illinois data. The maximum enrichment is 1.6 for Co and 1.5 for Ga. Other elements do not vary significantly from re-

gional backgrounds indicating that the clay content of Chicago soils is similar to that of the surrounding region. The carbonate and clay factors defined by principal component analysis account for more than 60% of the total compositional variability within the city showing that, even in heavily urbanized environments, natural processes remain the dominant influence on soil composition.

7.2. Anthropogenic overprints

Anthropogenic influences are also significant for many elements and, for some, may dominate the soil compositions in the city. As documented above, there are three groupings of elements defined by mutual positive correlations of concentrations and clearly defined principal components, which reflect anthropogenic influences. No attempt is made to ascribe anthropogenic soil alterations to specific sources or activities, but rather some general classes of potential sources that may have a widespread influence across the city are suggested. The sample sites were selected to avoid obviously contaminated soils, and thus, the observed differences between Chicago soils and regional soils probably reflect widely dispersed common activities within the city or atmospherically dispersed pollution rather than unique point source contamination.

A study of airborne particulate matter in Chicago was conducted in 1981–1982 (Scheff et al., 1984). The chemical composition of particles that they reported are shown in Table 3 and are compared to ambient soil compositions of both the Shacklette and Illinois data sets. The particulate matter shows very high enrichments in 10 elements compared to regional soils. The three highest enrichment factors are for Pb (384), Cu (106), and Zn (72). These are also the three elements that show the strongest enrichments in Chicago soils relative to regional soils, strongly suggesting that addition of particulate matter to soils is a major factor in accounting for the high concentration of these elements in Chicago. Seven other elements, including Ca, Mg, Na, As, Cr, Ni and Se have enrichment factors of particulate vs. regional soils ranging from 5 to 54. These seven also show substantial enrichments in Chicago soils.

Atmospheric deposition of trace metals has been shown to significantly alter the composition of undisturbed soils in urban areas. For instance, a 4-fold increase in concentration of Pb and 2-fold increases in Ni and Cu have been documented along a rural to urban gradient near New York City in soils supporting native forest veg-

Table 3

Comparison of element concentrations in Chicago airborne particulate matter and concentrations of those elements in regional soils.

Element	Chicago particulate ^a	Shacklette soil ^b	Illinois soil ^b	Particulate/soil ^c
Al	22,200	48,810	50,800	0.5
Ca	43,400	8260	6500	5.3
Fe	29,500	18,540	23,800	1.6
K	13,300	15,660	17,500	0.8
Mg	22,900	4020	5000	5.7
Na	40,100	7320	5700	5.5
As	48	7	9	6.9
Ba	560	499	568	1.1
Co	25	9	11	2.8
Cr	1170	44	56	26.6
Cu	1900	18	28	105.6
Mn	1130	4580		0.2
Ni	282	16		17.6
Pb	7290	19	29	383.7
Se	27	0.5		54.0
V	122	61	85	2.0
Zn	3900	54	74	72.2

^a Chicago particulate = mean of total suspended particulates in ppm (Scheff et al., 1984).

^b Shacklette and Illinois soils = arithmetic mean in ppm.

^c Particulate/soil = particulate mean/Shacklette mean.

etation (Pouyat and McDonnell, 1991). Similarly, concentrations of Pb, Zn, Cu and Cd in undisturbed soils under natural vegetation in heavily industrialized East Chicago, Indiana, immediately east of the city of Chicago, vary from 20 to 100 times higher than soils at a rural site 67 km away (Parker et al., 1978). Implicit in these observations is that there are relatively local sources for anthropogenic particulates that affect the urban areas more intensely than the surrounding region. Recent investigations show this is also the case in Chicago. In the southeastern part of the city, significant inputs of dust from nearby steel mills, and coal dust account for high concentrations of Fe, Cr, Mn, Ca, S and Se in airborne particles (Sweet et al., 1993). On a broader scale, the dry depositional flux of anthropogenic elements (Cu, Mn, Pb, Cr, C and Cd) was shown to be roughly 5–10 times higher in Chicago than at two other non-urban sites in the region (Holsen et al., 1993). Therefore, the high concentrations of elements such as Pb, Zn, Cu, and Ni that we have observed in our Chicago data seem likely to be caused by deposition of atmospherically transported material that may have nearby point sources but have been dispersed to varying degrees across the city.

The study of Chicago particulate matter also provided profiles for potential sources of particulate matter and provided an estimate of the relative importance of several potential natural and anthropogenic source categories for airborne particulates at that time (Scheff et al., 1984). These profiles are useful in examining possible sources for the element enrichments that have been observed in Chicago soils. Because soils are long-term repositories for many elements that are delivered to them by atmospheric deposition, their compositions are an integration of many processes, which likely changed in character, location and intensity during the roughly 150-year history of urbanization and industrialization preceding this study. Hence, soils are not particularly well suited to identification of specific soil-altering activities. Nevertheless, the data do identify several specific compositional trends that appear to record different types of anthropogenic modifications.

Lead, Cu, Zn and Ni have been repeatedly shown to be related to vehicular pollution in many parts of the world (Lagerwerff and Specht, 1970; Bignal et al., 2004) and this source seems a likely contributor to the elevated concentrations observed in Chicago. The source profile developed by Scheff et al. (1984) for “mobile sources” based on results from highway tunnel tests, contains high concentrations of Pb and Zn. Copper and Ni are also included, but at concentrations lower than in several other source profiles. Copper, Zn and Pb are all common constituents of various vehicle components. Wear of tires and brake pads and dispersion of lubricants have been shown to be strong contributors of loading of Pb, Zn and Cu in urban runoff (Davis et al., 2001). Roadway emissions have been shown to include elevated concentrations of these metals in several urban areas, for instance in Milwaukee, Wisconsin, a major metropolitan area about 100 km north of Chicago (Lough et al., 2005). Tail pipe emissions may also be important. The Pb content of soils along two of the major freeways in Chicago was measured in the early 1970s at a time when leaded gasoline was still in wide use (Khan et al., 1973). Lead concentrations in soils as high as 7600 mg/kg were found and a strong correlation between Pb content of soil and traffic volume was documented. The concentration of Pb declined significantly within 30 m of the roadway. There seems little doubt that during the period of leaded gasoline use vehicle exhaust was a major contributor to Pb in soils near major roadways, but its broader influence on the city is not clear. Khan et al. (1973) observed that Pb concentration in the soils along the two major freeways showed a strong seasonal variation suggesting that Pb added to soil from vehicle exhaust may be highly labile and is quickly removed from its original depositional site. The importance of Pb from leaded gasoline exhaust in the present data, collected 15 years after the cessation of leaded gasoline use, is not clear.

Nevertheless, the very strong correlations between Pb, Zn, Cu and Ni in Chicago soils suggests the likelihood of a common causative factor, and vehicle emissions of various types seem a likely source.

A detailed study of Pb distribution in soil within a 4-block residential area of Chicago (140 m × 260 m) (Shinn et al., 2000) showed that a set of 62 samples (equivalent to a sampling density of ca. 1700 sites per km²) allowed prediction of Pb concentration in unsampled areas within the study area. It also demonstrated high variability within that small area (175–7953 mg/kg). The study concluded that the Pb distribution was controlled by two factors: (1) variations in traffic volume and (2) varied potential point sources within the study area. The study avoided buildings that may have been treated with Pb-based paint, another widely recognized source of soil Pb. Based on the combination of the above-cited studies and the present data, it is suggested that excess Pb and the correlated elements Zn, Cu and Ni in Chicago soils are largely derived from vehicular sources, but that airborne transmission of these metals is of short enough distance that a large variability of their concentrations exists within the city.

Models of source apportionment for suspended particulates reported by Scheff et al. (1984), in addition to “mobile sources”, identified significant contributions from three additional sources: (1) fly ash from fossil fuel combustion; (2) stack emissions from refuse combustion; and (3) emissions from steel production. Chemical profiles for these sources contain notably high concentrations of: (1) Cr, Cu, Fe and Mn for steel production; (2) Pb, S and Zn from refuse combustion; and (3) Ni, S and V from oil fly ash, and S and Se from coal fly ash. All of these sources exist (or existed) in and around Chicago. Model results from Scheff et al. (1984) indicate that, for the period of their study, coal combustion was the dominant source for anthropogenic airborne particles, being roughly comparable or slightly greater than vehicular sources, and roughly twice as important as steel production and refuse incineration.

In comparing these results to the Chicago soil chemistry, it is notable that the elements that are most characteristic of these three sources are enriched in Chicago soils. Thus, all three sources identified from airborne particulate studies may play a role in causing this enrichment. The regional data do not include S analyses for most samples. However, a recent study of soils from two continental-scale transects in the USA and Canada determined a median S concentration of 300 mg/kg for surface soils and little regional variation (Smith et al., 2005), suggesting that Chicago soils may be enriched in S about 3-fold over regional background. Of the sources of airborne particulates identified by Scheff et al. (1984), only fly ash from coal combustion and particulate emissions from refuse combustion contain high S. One or both of these sources appear to account for the increased S concentration if it is ascribed totally to particulate deposition. High concentrations of Cr, Cu, Mn and Fe are characteristic of steel mill particle emissions, but this source may play a minor role, at best, in Chicago soil compositions. The particles that were analyzed in the 1980s had concentrations of Fe and Mn that do not differ greatly from regional soils. Copper enrichments in Chicago seem largely attributable to vehicular sources as discussed above. Because the Fe and Mn enrichments are relatively small and because the two elements may be very mobile in soil-forming environments, the cause for these enrichments in Chicago seems not uniquely defined by the present study.

Mercury shows a 2.4× increase in Chicago soils relative to the Shacklette baseline, probably resulting from enhanced atmospheric deposition from local sources. A survey in the mid 1990s (Landis et al., 2002) found that the atmospheric concentration of Hg in precipitation was a factor of 2, and in particulates a factor of 6, times higher in the Chicago area than in surrounding regions. This increase was ascribed to local Hg releases to the atmosphere. In Chicago soils, Hg enrichment appears to be independent of the processes and sources discussed above for other elements. Mercury

concentration has no significant correlation with any element in the Chicago data set. This may reflect the complexities of Hg transport, deposition and sequestration, which differ substantially from other elements. One notable aspect of Hg in Chicago soil is the lack of correlation with organic C and S concentration in contrast to natural settings where there is commonly a strong correlation of these elements in surface soil. The Illinois data set shows a weak correlation (0.28) between Hg and organic C in A-horizon soils (Dreher and Follmer, 2004) compared to 0.02 for Chicago soils. Although much of the Hg increase in the city probably relates to widespread atmospheric deposition, a few extreme values, ranging up to 13 mg/kg, may indicate the existence of occasional site-specific contamination even at sites that are otherwise not obviously disturbed.

Increased P (2.7 \times) and Se (2.0 \times) concentrations in Chicago soils may be an example of direct physical additions to soil rather than atmospheric deposition. As discussed above, a logical source for P enrichment is the application of phosphatic fertilizer to lawns and gardens. Selenium, which correlates strongly with P in these soils, is also enriched in some fertilizers, suggesting that at least part of the Se enrichment could be caused by fertilizer application. Selenium is typically enriched also in coal fly ash, which may contribute to the Se content of Chicago soils.

7.3. Spatial variability

The data examined were to test the scale of spatial variability and the degree to which this relatively widely spaced sample design allows predictions of soil chemistry in unsampled areas of the city. Only the distribution of Pb, the trace element that shows the greatest enrichment and is probably the principal element of concern for human health, was examined. Examining the data with variography and kriging indicates that most variability within the city occurs at a scale that is not captured by the data. Semivariograms indicate a range of influence of a sample that is far shorter than the average sample spacing. Interpolated surfaces for Pb concentration produced by kriging do not agree well with the concentrations at sample sites. It is concluded that the data are not adequate to accurately map the distribution of Pb, and probably other elements, within the city. A study using much higher sample density (ca. 1700 sites per km²) was reported by Shinn et al. (2000). Sixty-two samples were collected within a 4-block residential area of Chicago. Variography for Pb concentrations indicated a range of influence of about 70 m for individual samples and a predictive surface could be generated by kriging. The study showed extreme variability within the small study area. Concentrations of Pb ranged from 175 to 7953 mg/kg compared to 13–1910 mg/kg for the present city-wide survey. A survey of Pb in New Orleans soil (Mielke et al., 2000) used an average sample density of about 25 sites per km² to produce a stable kriged surface of Pb variability across the city. In contrast, the sample density of the present survey is about 1 site per 10 km². It is suggested that urban soil studies can be of two types varying in purpose and magnitude. Using sample site densities similar to the Chicago survey provides valid summary statistics on the urban area and can be used to make general inferences of the relative importance of various anthropogenic inputs to soils. However, mapping intra-city variability of elements in a manner that allows site-specific predictions of element concentrations is a task that may require sample site densities one to two orders of magnitude greater than the present survey.

8. Conclusions

Ambient (not obviously disturbed) soils within the city of Chicago are significantly enriched in a spectrum of elements com-

pared to soils in the surrounding agricultural region. Some enrichments (Ca and Mg) have a natural cause produced by the underlying bedrock, which is largely dolomite in contrast to widespread clastic rocks that underlie a majority of the region. Clay minerals are also an important controlling factor on Chicago soils and, together with carbonate minerals, these naturally-occurring minerals account for about 60% of the chemical variability of the urban soils.

Most of the enrichments appear to have an anthropogenic cause produced by a variety of activities during the roughly 150-year period of intense urban and industrial land use. Deposition of particulate matter from a variety of sources provides a potential source for most of the observed enrichments. Lead, Zn, Cu, and Ni concentrations are all significantly elevated compared to soils in the surrounding region and the concentrations of these four elements are strongly correlated with each other. These enrichments are most likely caused by vehicular and roadway particulate matter that is unevenly distributed across the city. Iron, Mo, V and S concentrations are elevated in Chicago soils and their concentrations also correlate with each other and with organic C, Cr, Mn and Nb. Comparing these elements to compositions of potential particulate matter sources, a combination of coal fly ash, oil fly ash, waste incineration, and steel mill emissions appears to account for these enrichments. Mercury concentration is also elevated in the city and its concentration is independent of other elements, suggesting either that there is a unique Hg source or that its geochemical behavior, and hence its soil sequestration, is very different from other elements. Phosphorus and Se concentrations are both significantly enriched in Chicago and strongly correlated. In contrast to most other elements, P and Se concentrations may be a result of direct soil additions through use of phosphate fertilizer.

Analysis of spatial variability of soil compositions in the city, based on Pb concentrations, indicates that the sampling density is inadequate to map soil compositional variations and to predict compositions in unsampled areas. The data set, however, provides statistically significant information on median compositions of soils in the city. It provides a general definition of the degree of alteration produced by the history of urbanization and industrialization, and allows an assessment of the relative importance of several classes of anthropogenic soil alteration.

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