Baseline concentrations of trace elements in residential soils from Southeastern Missouri

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Abstract Anthropogenic sources of pollution can significantly contribute to elevated concentrations of toxic elements in soils. A preliminary survey of trace elements content and their availability in residential soils from New Madrid County, Missouri was undertaken. Mean elemental concentrations (mg kg^{-1}, dry wt) of sixty two soil samples were: As 6.6, Be 0.8, Cd 1.6, Co 9.7, Cr 24.5, Cu 18.1, Fe 9951, Mn 298, Ni 15.6, Pb 48.8, V 42.1, Zn 95.5 and Hg 0.05. The US EPA preliminary remediation goals (PRGs) was only exceeded by As (7 % of samples) and V (8% of samples). The Missouri average background values were exceeded by Pb (69%), Zn (31%), Cu (27%), As (23%), Be (19%), Co (18%), Ni (16%), V (8%) and Mn (2%). Crustal enrichments (EF$_c$) for As (97), Cr (6), Cu (10), Pb (121), V (7), and Hg (17) were highest for North Lilbourn soils. Fractionation experiment revealed that Fe (54–79%) was in the residual phase while Zn (70–90%), Mn (88–92%), As (59–81%) and Pb (63–79%) were potentially available in soils. Factor loadings of the element concentrations on principal components 1, 2 and 3 accounted for over 81% variance of the data set. The factor loadings suggested that apart from natural contributions of trace elements to the soils, human activities possibly accounted for other inputs in soils.

Introduction

Pollution and contamination of soils by toxic elements in various regions of the World is a consequence of human activities. Humans are constantly exposed to soil containing harmful trace elements through, inhalation of dusts, dermal contact and ingestion. Assessment of trace elements content of soil (Ljung et al. 2006; Imperato et al. 2003) and the risks due to exposures (De Miguel et al. 2007; Rieuwerts et al. 2006) are important in environmental management decisions and overall protection of human health. Elemental concentrations in soil arise from both natural processes and anthropogenic pollution sources (Dœlsch et al. 2006). Trace elements such as zinc, manganese, chromium, copper, cobalt, and iron are beneficial to plants and humans but toxic effects may manifest at high concentrations. Other trace elements such as beryllium, arsenic, cadmium, lead, and mercury are known to have no beneficial biological functions in humans. Beryllium exposure causes berylliosis, arsenic exposure causes skin and nail pigmentation and cancers, cadmium affects the liver and mercury impacts the central

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nervous system. In particular, childhood lead poisoning remains a major environmental health problem in United States and other parts of the world. Most children are poisoned as a result of exposure to harmful levels of lead-contaminated dust, deteriorated lead-based paint, and lead-contaminated soil in and around home environments (US EPA 2004a). According to Mielke and Reagan (1998), lead in soil is the primary causative agent for concern in addressing the population of children at risk of lead poisoning. Children are often more susceptible to chemical exposures because of their often hand-to-mouth activity and greater gastrointestinal absorptions more than adults (Calabrese et al. 1997). Assessment of trace elements availability and mobility in soil is related to their potential occurrence of adverse effects to the ecosystem and in exposure evaluations in humans.

Missouri is the number one lead producing State in United States since 1907 and most of the lead mining and smelting activities are located in Southeastern Missouri (Missouri Department of Health 2004). Residential soils have been contaminated in the past due to lead mining. For example, a 52 acre lead smelter facility at Herculaneum, Missouri, was operated for over 100 years before decontamination and clean-up of soils near homes were instituted in the 1990s (US EPA 2001). Agricultural and metal smelting and even atmospheric transport of materials due to lead mining can contribute to the levels of trace elements in residential soils. New Madrid County was ranked 11th in Missouri with the worst record of environmental releases (Scorecard 2004). The areas under study, North Lilbourn, Lilbourn and Howardville, a few miles from the Mississippi river were covered by water until the late nineteenth century. The water was later drained for settlement and farming activities. Most residents in Howardville, Lilbourn and North Lilbourn are poor and live in substandard housing. For many decades these communities faced environmental hazards due to lack of funding to support infrastructures and maintain housing. Environmental threats in these cities include lead, radon, and carbon monoxide from substandard housing, inadequate water and wastewater treatment, water contamination by fertilizers and pesticides and presence of disease vectors (US EPA 2003a). Current concern to some residents in New Madrid County include asthma and allergies, drinking water quality, blood lead levels (BLLs), and household and solid wastes problems (US EPA 2006). Lead paint has been associated with poor housing and therefore New Madrid County is classified as a targeted lead screening area by Missouri Department of Health. A survey conducted suggests that 2,700 Missouri children under the age of six had elevated blood lead (Missouri Department of Health 2004).

Trace elements in soils from Southeastern Missouri may have contributions from agricultural activities, metal smelting operations, vehicular emissions and atmospheric depositions. This study is independent of the Missouri Department of Health BLLs survey, but was undertaken to provide first time knowledge of the trace element content and their distribution in residential soils from New Madrid County. Human exposures to toxic trace elements through direct contact, inhalation and ingestion may increase and the risk due to exposures may be more significant for children hence the objective of this study was to establish the concentrations of arsenic, beryllium, cadmium, cobalt, copper, chromium, iron, lead, manganese, nickel, vanadium, zinc and mercury in New Madrid County residential soils and to evaluate the availability of the elements in the most contaminated soils because of the health risks they could pose to humans.

Materials and methods

Study area and samples collection

The study areas were Howardville, North Lilbourn, and Lilbourn in New Madrid County, Southeast Missouri. Figure 1 shows the aerial location of the study areas in the State of Missouri. The Southeast of Missouri lies in the Mississippi embayment and the soils geology was derived from the Tertiary and Quaternary Periods (Cenozoic Era). Most of the ground cover of this period consisted of alluvial (stream deposited) clays, sand and gravels (with a few poorly consolidated sandstones); glacial (ice deposited) tillites and gravels, and eolian (wind blown) clays and loess. A total of 62 soil samples were collected randomly from topsoils in Howardville, North Lilbourn and Lilbourn at a depth of 10 cm using cleaned hand augur. Soil samples were collected from undisturbed residential areas to avoid potential contamination from other sources. Soil samples were placed in clean polyethylene sampling bags, coded at the various sampling sites for

Fig. 1 Aerial map of sampled areas in the State of Missouri
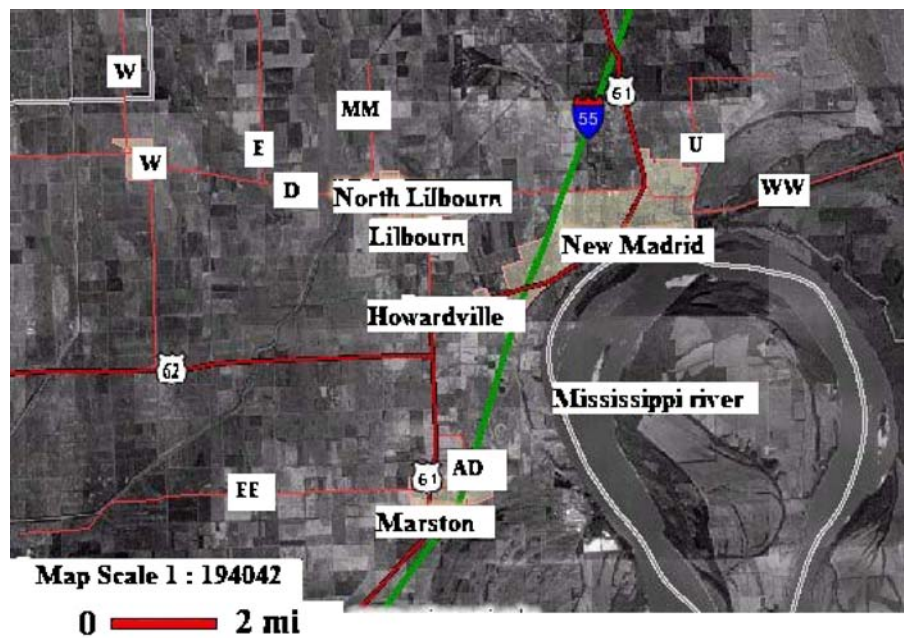
easy identification and transported to the laboratory. Samples were dried at 60°C and sieved to collect the <2 mm grain size fraction.

Soil properties and total element determination

About 0.5 g of sieved soil samples (<2 mm) were accurately weighed and placed in acid washed microwave Teflon digestion vessels. Each weighed sample was digested with nitric acid (15 ml), perchloric acid (2 ml) and hydrofluoric acid (2 ml) under the following microwave program: Step 1: 105°C for 2 min and hold 5 min at 1,000 W; Step 2: 140°C for 3 min and hold 5 min at 1,000 W; Step 3: 180°C for 5 min and hold 5 min at 1,000 W. The digest considered a total leach was quantitatively transferred from each digestion vessel into a standard flask and made up to 25 ml with deionized water. The inductively coupled plasma-optical emission spectrometer (ICP-OES) was calibrated using multi-element standards (SPEX Certiprep, NJ, USA) containing As, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn. For quality control purpose, SRM 1944 (New York New Jersey sediments) and SRM 2709 (San Joaquin soil) purchased from NIST (Gaithersburg, MD, USA) were used in precision, accuracy and method validation. The ICP-OES was automatically recalibrated after every 10 analytical

runs and known standards were analyzed as part of the quality check. The recovery rates for the elements analyzed were in the range of 90–102% for SRM 2709 and 94–104% for SRM 1944.

The direct mercury analyzer (DMA 80) purchased from Milestone Inc. (Connecticut, USA) was used for total mercury measurements in soil samples. Soil sample was weighed into a nickel boat previously analyzed as blank. Weighed sample was passed into the DMA 80 and the process of drying, decomposition, amalgamation and atomic spectrophotometer detection at 254 nm. The DMA condition was as follows: drying temperature 300°C, drying time 60 s, decomposition temperature 850°C, decomposition time 180 s, purge time 60 s, and amalgamation time 12 s. Quality assurance and calibration of DMA was conducted with SRM 2709. SRM 2709 was analyzed as unknowns after every 10 runs and the percentage recovery for ranged between 100.1 and 100.7%.

For pH determination, 10 gm portion of soil was weighed into a clean beaker and 25 ml deionized water (1:2.5) was added. The mixture was stirred with a clean glass rod and the soil slurry was allowed to equilibrate for 30 min (McClean 1982). The soil texture was determined by the hydrometer method (Foth 1984), moisture was by drying at 105°C and organic matter was measured gravimetrically by loss-on-ignition (LOI) at 450°C (Blume et al. 1990).

Bulk powders of representative samples of New Madrid County soils were analyzed at University of Missouri using a Scintag Pad X-Ray Diffractometer (XRD). The X-ray source was a copper anode operating at 40 kV and 35 mA using a Cu Ká radiation (1.54 Å) and a Ni filter. X-ray data were collected between a scanning range 3°–35° 2-theta at a rate of 1° 2-theta/min and a step size of 0.01° 2-theta. The slits were 0.5 mm (divergence) and 0.2 mm (receiving). Data obtained was processed using MacDiff software (version 4.2.5) to establish baseline intensity, smooth counts, correct peak positions (relative to quartz) and calculation of peak intensities and peak areas.

Trace elements availability in soils

Selective releasing of elements bound in soil geochemical phases (exchangeable: EX, carbonate: CAR, iron/manganese oxides/sulphides: OX, organic matter: OM and residual: RES) under decreasing pH and increasing oxidizing conditions were conducted using sequential extracting procedure by Tessier et al. (1979). From the total elemental concentrations obtained for the 62 residential soils, we evaluated element distribution in 14 samples with the highest element content. Selected soils were dried at 60°C to remove moisture and later sieved to collect the <0.5 mm fraction. Representative samples were sequentially extracted with 1 M NaOAc at pH 8.2 to remove exchangeable cations (Step I), 1 M NaOAc/HOAc at pH=5.0 for carbonate bound metals (Step II), 0.04 M $NH_2OH \cdot HCl$ in 25% HOAc for metals bound to iron and manganese oxides (Step III), H_2O_2/HNO_3 for organic-/ sulphides bound metals (step IV) and $HCLO_4/HF$ for residual metals (Step V). The levels of As, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the five chemical forms were measured with the ICP-OES (Varian-Pro CCD Simultaneous ICP-OES, Varian Inc., California, USA) after calibration with appropriate diluted standards.

Statistical analyses

The descriptive statistics of the analytical data was carried out on Statistix 8 for Windows analytical software (Analytical Software, Tallahassee, FL 32317, USA) and the skewness of analytical data was tested by the Shapiro–Wilk normality test ($P<0.05$). The result of the test showed that the analytical data was non-normally distributed. The Spearman rank correlation test was then adopted to reduce problems of non-normality of analytical data and correlation coefficients were calculated to see the interrelations among the different elements. Multivariate analysis encompassing principal component analysis (PCA) and analysis of variance (ANOVA) were applied to extract information from the analytical data. By plotting the principal components, one can view interrelationships between different variables, detect and interpret any patterns, groupings, similarities or differences from the elemental concentrations of data obtained. Furthermore, through correlation loading plots, elements with high associations or high correlations suggested similar origins. The Unscrambler version 9.2 (Camo Inc., Woodbridge, NJ, USA) and SAS 9.1 for Windows were used for the PCA analysis. Prior to conducting the PCA, all analytical data consisting of a matrix of 13 variables (elemental concentrations) × 62 samples were normalized and centered.

Results and discussion

Soil properties

The averages obtained for pH, particle size (PS) distribution, moisture, and OM across the sampling sites are given in Table 1. Soil pH was acidic (pH=4.5–5.5, 3% of samples), slightly acidic (pH=5.6–6.5, 25% of samples), neutral (pH=6.6–7.5, 36% of samples), slightly alkaline (7.6–8.5, 30% of the samples) and alkaline (pH=8.6–9.5, 1% of the samples). Acidic soil condition promotes leaching and depletion of nutrients and trace elements from soils. Organic matter (OM) across the study areas ranged from 1.1–14.3% with North Lilbourn posting the highest value. OM retains trace elements but element release can significantly increase under decreasing pH condition. Moisture content of the soils was generally less than 6%. The soils were generally sandy as classified by the USDA soil texture triangle (US EPA 1991). North Lilbourn had the highest average clay and silt content while Howardville soils had more average sand content. Soil texture affects soil structure, chemistry and porosity. The mineralogy (X-ray diffraction analysis) of soil samples from North Lilbourn and Lilbourn indicated

Table 1 Averages (ranges) of soil properties and trace elements concentrations (mg/Kg dry wt.) in soils across three Missouri cities

Parameter	Howardville (n=20)	North Lilbourn (n=22)	Lilbourn (n=20)	Missouri background[c]	US EPA PRG[d]	Dutch Reference[e]
pH	6.94±0.92 (4.50–8.1)	7.05±0.81 (5.09–8.6)	6.91±0.75 (5.92–8.01)			
Moisture[a]	2.4±0.9	5.2±3.6	4.4±2.0			
OM[a]	4.5±3.0 (4.50–8.1)	7.1±3.0 (2.3–14.3)	5.4±2.9 (1.1–10.1)			
PS[a]	C: 2.2, S: 88.8, Si: 8.96	C: 7.4, S: 79.3, Si: 13.1	C: 3.8, S: 86.41, Si: 9.8			
As	6.28 (0.00–27.47)	8.40 (0.00–28.53)	4.81 (0.00–18.54)	10	22	29
Be	0.71 (0.22–1.38)	0.96 (0.58–1.24)	0.69 (0.37–0.94)	1.0	150	
Cd	1.33 (0.00–4.96)	2.01 (0.38–4.83)	1.49 (0.32–3.91)		39	0.8
Co	8.71 (3.85–17.14)	11.59 (5.78–39.86)	8.55 (4.13–12.35)	12	900	10
Cr	19.60 (3.98–45.87)	32.24 (17.28–46.26)	20.99 (7.27– 36.49)	50	210	100
Cu	11.01 (3.62–27.91)	28.67 (9.42–95.15)	13.50 (2.79–39.28)	19	2,900	36
Fe[a]	0.93 (0.35–1.9)	1.2 (0.64–1.7)	0.8 (0.39–1.2)	2.47	2.3	
Mn	271.3 (96.19–928.3)	357.1 (195.4–970.5)	260.6 (105.9–404.1)	940	3,200	
Ni	13.63 (6.15–26.56)	17.37 (12.55–26.45)	15.60 (7.28–26.87)	20	1,600	35
Pb	31.61 (9.93–76.89)	71.70 (19.58–186.6)	40.91 (9.71–83.36)	23	400	85
V	36.26 (13.58–83.1)	55.28 (20.3–80.5)	33.31 (16.73–56.3)	72	78	
Zn	60.4 (8.9–230.6)	109.4 (14.7–425.5)	115.2 (11.9–631.3)	53	23,000	140
Hg[b]	23.1 (3.8–82.9)	82.8 (18.2–776.0)	34.9 (7.6–76.7)		23,000	300

[a] Moisture, organic matter (OM), particle size (PS) and Fe are expressed in percent; *C* clay, *S* sand, *Si* silt

[b] *Hg unit* μg/kg

[c] Missouri average background values (US EPA 2003b)

[d] US EPA PRG: United States preliminary remediation goals (PRG) or soil screening values (US EPA 2004b)

[e] Dutch target reference value: based on concentration found in nature where only the contamination is from atmospheric deposition (Kabata-Pendias and Pendias 1992).

the presence of clay minerals, feldspar, quartz and calcite. However, Howardville soils contained mainly quartz, feldspar and trace clay minerals. XRD diffractograms of soils from the study areas are shown in Fig. 2. The order of abundance of the minerals was: North Lilbourn: Quartz (44%)>feldspar (11%)>clay (45%)>calcite (trace); Lilbourn: Quartz (57%)>feldspar (18%)>calcite (11%)>clay (14%); and Howardville: Quartz (77%)>feldspar (20%)>clay (trace). New Madrid County soils are in the floodplains and they generally contained low calcite and high quartz. Norra et al. (2006) reported similar findings in the soils of Germany. Quartz is the second most common mineral in the earth's crust and a constituent of granite, sandstone and limestone. Feldspar minerals are composed of aluminosilicates in the form $NaAlSi_3O_8$ or $CaAl_2Si_2O_8$ and Calcite (calcium carbonate) is a constituent of limestone.

Baseline concentrations of trace elements in soils

The overall mean, median (mg kg^{-1}, dry wt) and ratio of mean to median values of 13 trace elements in the sixty two soil samples analyzed are given in Table 2. The low average-to-median ratios indicated less extreme values. It is difficult to apportion these elements in soils analyzed to specific sources but natural phenomena and possible contributions from major human activities may be significant. To assess the natural background concentrations of elements in soils and the possible elevation of elemental content in soils, we compared the results of this study with normal ranges in the literature, earth crust element levels (Mason and Moore 1982), Missouri average background values (US EPA 2003b), the conterminous United States baseline values (Shacklette and Boerngen 1984), the US EPA preliminary remediation goals (US EPA 2004b) limits for residential soils and the Dutch target concentrations (Kabata-Pendias and Pendias 1992). The US EPA remediation goals were provided to assess toxicity risks in residential areas and ultimately address human health risks due to exposures to trace elements. It was not possible to compare element concentrations in the top and deeper soil layers because of the heavy movement of soil in these areas over the years.
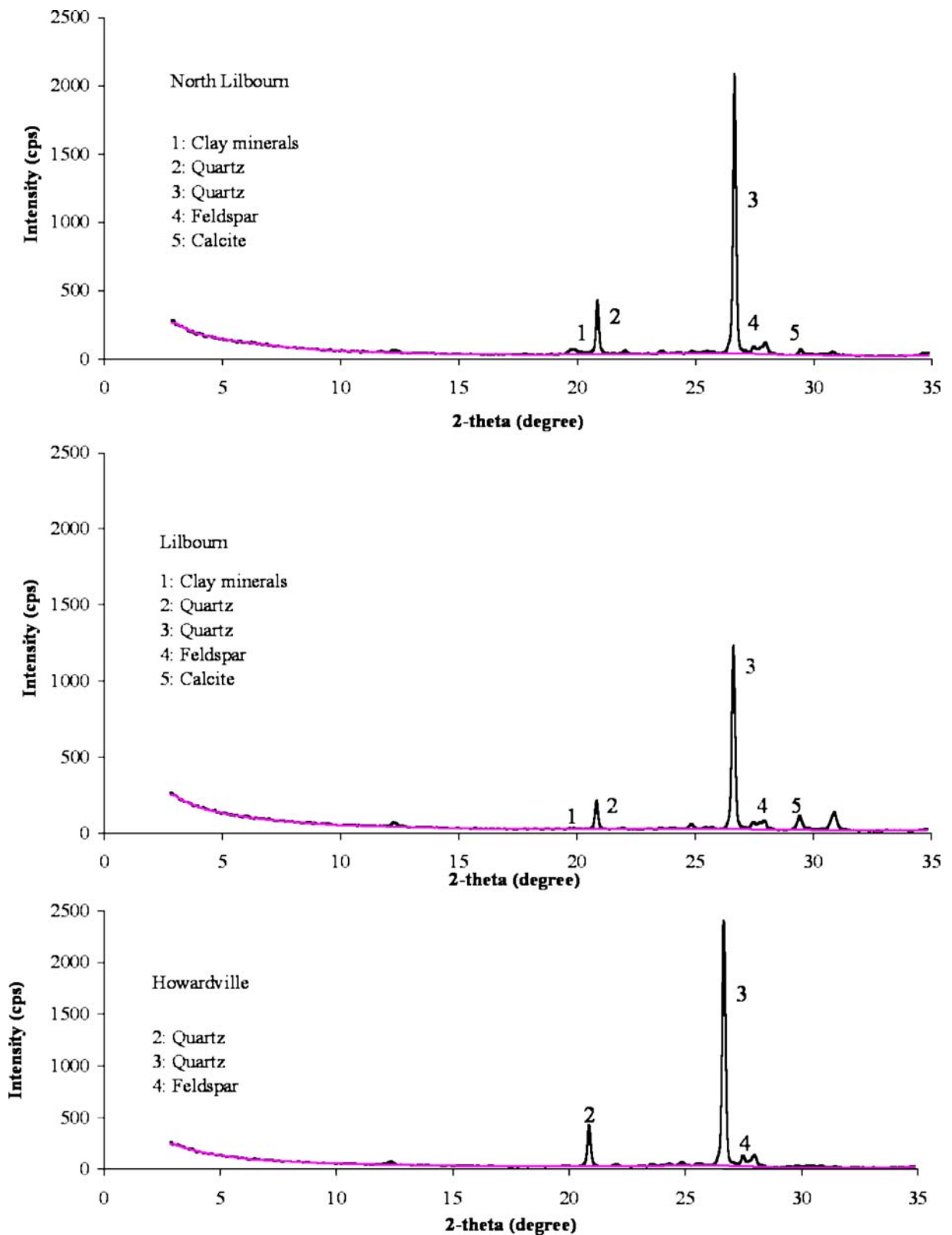
Fig. 2 Bulk powder XRD diffractogram of Southeast Missouri soils

Table 2 Mean trace element concentrations (mg kg^{-1}) in Missouri soils in comparison with other soil baseline values

Element	This study			USA[a]	Madrid[b]	Luxembourg[c]	China[d]	Earth crust[e]
	n=62			n=1,318	n=346	n=81		
	AM±SD	Median	Mean/Median	AM	AM	AM	AM	AM
As	6.56±8.57	3.77	1.74	7.20	10	58	8.39	1.8
Be	0.79±0.25	0.79	1.0	0.92				2.8
Cd	1.62±1.38	0.92	1.76		0.1	0.8	0.14	0.2
Co	9.68±4.96	9.18	1.05	9.10		24	7.46	25
Cr	24.53±10.60	24.53	1.0	54	15	124	51.92	100
Cu	18.08±16.72	12.48	1.45	25	9.5	32	8.66	55
Fe	9951±3925	10,426	0.95	26,000		94,000		50,000
Mn	298.27±172.88	259.84	1.15	550	333	1,364		950
Ni	15.59±4.75	15.24	1.02	19		70	19.0	75
Pb	48.83±39.76	37.79	1.29	19	17	44	9.12	13
V	42.06±20.43	38.23	1.1	80		338		135
Zn	95.49±116.56	65.87	1.45	60	39	224	40.37	70
Hg	0.05±0.10	0.03	1.67	0.09	0.033	na	0.047	0.08

AM arithmetic mean; *SD* standard deviation

[a] Shacklette and Boerngen 1984 (digestion procedure was not given)

[b] De Miguel et al. 2007 (2:2:2 HNO$_3$/HCl/H$_2$O digestion)

[c] Horckmans et al. 2005 (HCl/H$_2$SO$_4$/HF/HNO$_3$ digestion)

[d] Hu et al. 2006 (As and Hg: aqua regia digestion; Se: HNO$_3$/HCLO$_4$/HF; other heavy metals: HNO$_3$/HCl/HCLO$_4$/HF)

[e] Mason and Moore 1982.

In comparison, the percentages of samples that exceeded the Missouri average background concentrations (Table 1) were as follows: As (23%), Be (19%), Co (18%), Cu (27%), Mn (2%), Ni (16%), Pb (69%), V (8%) and Zn (31%). Similarly, As (7% of samples) and V (8% of samples) exceeded the respective US EPA preliminary remediation goals limit for residential soils. With the exception of cobalt, lead and zinc, the averages for As, Be, Cr, Cu, Fe, Mn, Ni, and V in this study were below the conterminous United States baseline values (Shacklette and Boerngen 1984: Table 2). However, the averages observed for As, Cd, Pb and Zn in this study were higher than the corresponding values in the earth's crust (Mason and Moore 1982). The baseline values reported for China were equally exceeded by the averages posted for Cd, Co, Cu, Pb and Zn in this study. Even the concentrations found in nature where only the contamination is from atmospheric deposition (Dutch soil target values: Table 1) were also surpassed for Cd (54%), Co (48%), Cu (9%), Pb (11%), and Zn (12%). Compared with other background values, the averages of Cd, Cr, Cu, Pb, Zn and Hg in this study were consistently higher than the values reported for natural soils of Madrid, Spain (De Miguel et al. 2007). Furthermore, the averages for Cd and Pb were greater than the corresponding values for Luxembourg background soils (Horckmans et al. 2005). It is pertinent to note that differences existed in the acid digestion conditions (Table 2) used by Shacklette and Boerngen (1984), Horckmans et al. (2005), and De Miguel et al. (2007).

The elemental concentrations in soils from Southeast Missouri varied across the three study sites (Table 1). North Lilbourn samples generally had higher average concentrations of As, Be, Co, Cr, Cu, Fe, Pb, Mn, V, Zn, and Hg than other study sites. The higher clay content in North Lilbourn soils possibly acted as sinks or adsorption sites for trace elements in soils. The highest lead level (186.6 mg kg^{-1}) observed for North Lilbourn soil was approximately eight times the Missouri background (23 mg kg^{-1}). The samples from this area were from old housing units of about 50 years old. Six North Lilbourn samples (NL2, NL3, and NL5) within less than 0.1 mile recorded the highest lead levels ranging from 101.7–186.6 mg kg^{-1}. Three Lilbourn samples (L3) from a daycare soil had lead values ranging from 13.8–48.2 mg kg^{-1}. Also soils

(L4) from an elementary school recorded lead levels in the range 12.2–19.2 mg kg^{-1}. The highest arsenic concentration (NL3: 28.53 mg kg^{-1}) in North Lilbourn soil was approximately three times the Missouri average (10 mg kg^{-1} dry wt). Arsenic levels posted for a daycare soil (L3) ranged from 4.5–10.2 mg kg^{-1}. The most abundant trace elements were Fe (AM: arithmetic mean=12,293 mg kg^{-1}), Mn (AM: 357.1 mg kg^{-1}) and Zn (AM: 115.2 mg kg^{-1}) in North Lilbourn soils. Vanadium was highest in Howardville soils (HV1: 83.1 mg kg^{-1} and HV8: 80.6 mg kg^{-1}) and North Lilbourn soils (NL10: 80.3 mg kg^{-1} and NL11: 80.5 mg kg^{-1}). The averages recorded for arsenic, Be, Cr, Co, Fe, Mn, Ni and V were below the respective Missouri background values and the US EPA PRGs. Except for one sample (NL9) that recorded 0.77 mg kg^{-1}, other samples were below worldwide mercury background level of <0.4 mg kg^{-1} (Kabata-Pendias and Pendias 1992). We believe that the sources of trace elements in soils probably were from diffuse points. Vehicular pollution is less in the sampled areas compared to big cities. These areas were and still remain predominantly agricultural lands. Therefore, application of commercial fertilizer and pesticides over time may elevate trace elements concentrations in soils above natural background levels. Also atmospheric depositions from lead ore smelting activities in the region could contribute to the level of trace elements in soils. Probably lead in soils originated from fertilizer use and arsenic was likely derived from application of arsenical pesticides. Other minor sources may include wood preservative chemicals, fallouts from thermal and coal fired power plants, metallurgical activities and natural processes. Apart from natural sources, increasing levels of vanadium in these soils may arise from combustion of fossil fuels, burning and disposal of coal wastes, metallurgy and smelter operations. Sources of zinc in soils analyzed probably originated from fertilizer applications.

Soil enrichments

Enrichment factor may be used to assess changes in element concentrations on the top soil layer based on differences in the element levels between the upper and deeper horizons. Due to the constant moving of soils where gardening and agricultural activities are prominent, it may be difficult to determine anthropogenic contributio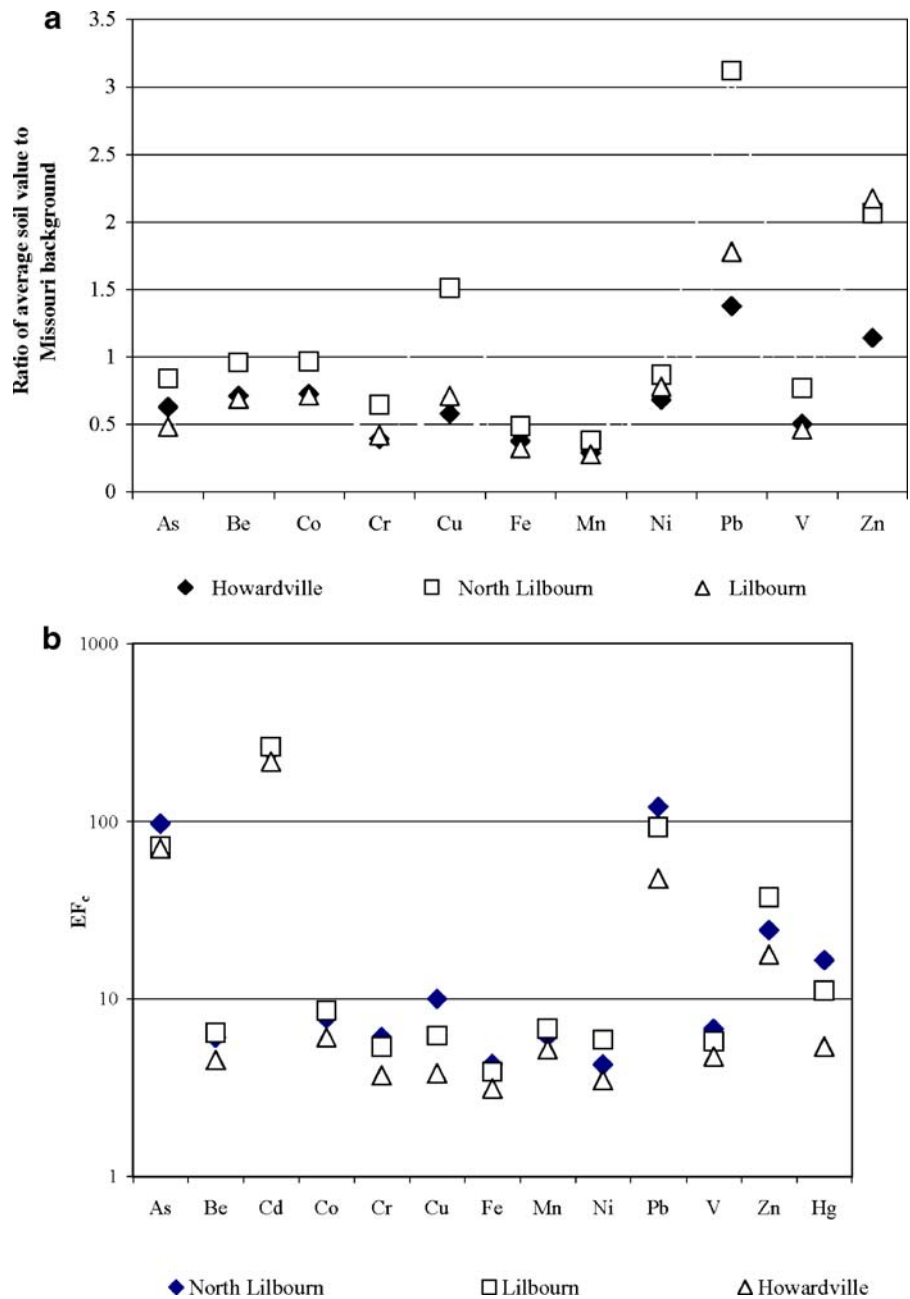ns of trace elements on the top soil layer. In this study, we attempted to show the ratio of the average soil concentrations in the areas studied to the Missouri State background values and the values reported for the earth crust. We note that variations may exist in soil data obtained from one place to another because of differences in mineralogy, clay and organic matter content, grain size effects, pH and other environmental factors. The ratio of soil averages in this study to the corresponding Missouri average background values is shown in Fig. 3a. Missouri background values were not available for Cd and Hg. The highest ratio (3.1) was recorded for lead in North Lilbourn area.

Soil modification or changes may be derived through crustal enrichment factors (EF$_c$) using this equation: EF$_c$=(C_x/C_{Al})$_{soil\ sample}$/(C_x/C_{Al})$_{reference\ soil}$, where (C_x/C_{Al})$_{sample}$ is the ratio of the concentration of a test element to the concentration of aluminum in the sample and (C_x/C_{Al})$_{reference\ soil}$ is the same ratio but with a reference soil (Yay et al. 2007). Elemental concentrations of the earth crust (Table 1) and aluminum as a reference element was used in calculation of EF$_c$. Aluminum was adopted because it is one of the largest components of soil and the modification of aluminum by other anthropogenic sources is difficult (Yay et al. 2007). The calculated EF$_c$ for Missouri soils analyzed are given in Fig. 3b and it was highest for cadmium (EF$_c$ from 218 to 265) at the three areas of study. North Lilbourn generally posted the highest enrichments for As, Cr, Cu, Pb, V, and Hg while Howardville soils had the lowest enrichments.

Analysis of variance and Spearman rank correlations

The one-way analysis of variance (ANOVA) revealed that significant variation ($P<0.05$) existed in the levels of Be, Cr, Cu, Fe, Ni, Pb, V, and Hg across the study sites. The Spearman rank correlations between soil properties (pH, and organic matter) and trace element content in soils analyzed are given in Table 3. For all samples ($N=62$), soil pH and arsenic correlated poorly with OM, Be, Cd, Co, Cr, Cu, Fe, Mn, Pb, V, Hg and Zn content. However, moderate to strong associations varying from 0.42–0.77 at $p<0.001$ were found between OM and Be, Cu, Cd, Cr, Fe, Ni, Pb, V, Hg and Zn. Iron also associated strongly ($p<0.001$ and $r^2>0.6$) with Be ($r^2=0.91$), Co ($r^2=0.81$), Cr ($r^2=0.74$), Cu ($r^2=0.62$), Mn ($r^2=0.61$), Ni ($r^2=0.69$), V ($r^2=0.90$) and moderately with Zn

$(r^2=0.52)$. Other moderate and strong relationships were: Mn–Cr (0.49), Mn–Ni (0.47), Ni–Cr (0.83), Co–Cr (0.68), Co–Cu (0.59), Co–Mn (0.76), Co –V (0.85) and Co–Hg (0.76).

In Howardville soils, pH and arsenic values had poor correlation with OM and the elements analyzed. Iron had significant relationships ($p<0.01$) with most of the elements (Fe–Be: 0.93, Fe–Co: 0.94, Fe–Cr: 0.87, Fe–Cu: 0.6, Fe–Mn: 0.78, Fe–Ni: 0.87, Fe–V:

0.92). Manganese was strong with beryllium (0.69), OM (0.63), Co (0.74), Cr (0.72) at $p<0.01$ and moderate with Cu (0.59) and Hg (0.5) at $p<0.05$. Organic matter acted as sinks for copper (0.69), Hg (0.75), Pb (0.7), and Zn (0.66). In North Lilbourn soils, organic matter was significantly ($p<0.02$) associated with Pb (0.74), Cd (0.59), Cr (0.57), Cu (0.7) and Hg (0.59). Lead was also significantly correlated ($p<0.01$) with cadmium (0.76) and copper

Table 3 Spearman rank correlations of soil properties and elements' concentrations in soils

	pH	As	Be	Cd	Co	Cr	Cu	OM	Fe	Mn	Ni	Pb	V	Hg
As	0.12	1												
Be	0.09	0.00	1											
Cd	0.23	0.30**	0.04	1										
Co	0.03	−0.04	0.82***	−0.05	1									
Cr	0.24	0.15	0.82***	0.38**	0.68***	1								
Cu	0.25*	0.13	0.70***	0.50***	0.59***	0.86***	1							
OM	0.02	0.12	0.53***	0.42***	0.34**	0.67***	0.77***	1						
Fe	0.04	−0.02	0.91***	−0.05	0.81***	0.74***	0.62***	0.52***	1					
Mn	−0.32**	−0.05	0.60***	−0.08	0.76***	0.49***	0.40**	0.37**	0.61***	1				
Ni	0.26*	0.17	0.77***	0.28*	0.75***	0.83***	0.79***	0.49***	0.69***	0.47***	1			
Pb	0.07	0.14	0.33**	0.57***	0.21	0.54***	0.75***	0.70***	0.26*	0.15	0.43***	1		
V	0.03	−0.08	0.93***	−0.04	0.85***	0.79***	0.64***	0.49***	0.90***	0.73***	0.73***	0.21	1	
Hg	−0.05	−0.04	0.33**	0.34**	0.76***	0.43***	0.67***	0.67***	0.28**	0.20	0.34*	0.79***	0.28*	1
Zn	−0.04	−0.04	0.54***	0.02	0.57***	0.54***	0.63***	0.55***	0.52***	0.53***	0.57***	0.43***	0.59***	0.48***

Number of samples=62, *OM* organic matter;
* Correlations are significant at the 0.05 level (2 tailed); ** Correlations are significant at the 0.01 level (2 tailed), *** Correlations are
  significant at the 0.001 level (2 tailed).

(0.64). For Lilbourn soils, iron was highly associated with beryllium, OM, Co, Mn, Ni, V and Zn (r^2 ranged from 0.65 to 0.88). Manganese also associated moderately or strongly with beryllium, Co, Cr, and Cu. Arsenic and pH were poorly correlated with all the elements. Lead was moderately correlated with Ni (0.48), Be (0.47), Co (0.37) and Fe (0.31) but weak with arsenic. Organic matter usually formed complexes with trace elements in soil (Kabata-Pendias and Pendias 1992; Berthelsen et al. 1994). Most of the elements were associated to some degree with the iron/ manganese oxides and oxyhydroxides phases. The association of each element with some soil properties and other elements may be influenced by their origins or nature in soil. The interrelationship of these elements was projected on the principal components for further information.

Distribution of trace elements in soils

Figure 4 shows the percentages of the potentially available trace element fractions in soils analyzed. The order of the average trace element abundances in the first four fractions (EX, CAR, OX and OM) was: Fe>Mn>Zn>Pb>As>Cu>Ni>V>Cr>Co>Be>Cd (Howardville), Fe>Mn>Zn>Pb>Cu>As>Cr>Ni> Co>V>Cd>Be (North Lilbourn), and Fe>Mn>Zn> Pb>Cu>As>Cr>Ni>Co>V>Cd>Be (Lilbourn). Arsenic in the potentially available fractions for the three areas under study ranged from 59–81%. Cadmium was found in all the phases as was also observed by Ramos et al. 1994. Zinc in the potentially available fractions ranged from 70–90% across the study areas but 42–53% was accounted for by the oxide fractions. Other dominant elements in the oxide fractions were manganese (69–81%) and cobalt (30–56%). Iron oxides are generally known to have great affinity for selective adsorption of cobalt (Kabata-Pendias and Pendias 1992).

Chromium was moderately labile in the soils and between 42–50% was found in the RES portions. Nickel distribution in the RES portion of the soils ranged from 36–55%. Nickel was also distributed in the OX and OM fractions (OX≤32%, OM≤29%). In all the sites, copper distribution was highest in the OM phase (Howardville: 31%, Lilbourn: 57% and North Lilbourn: 53%) and the RES phase varied from 30 to 37%. Lead distributed significantly in both the OX and OM portions (Howardville: 59%, Lilbourn: 62%, and North Lilbourn: 62%) and the RES fraction. The levels of Pb in the RES portion were as follows: Howardville ≈ 21%, Lilbourn ≈33%, and North Lilbourn ≈37%. Iron (54–79%) and vanadium (49– 80%) were highly predominant in the RES fraction. Except for Howardville soils, beryllium associated

Fig. 4 Percentage of available fractions in Southeast Missouri soils
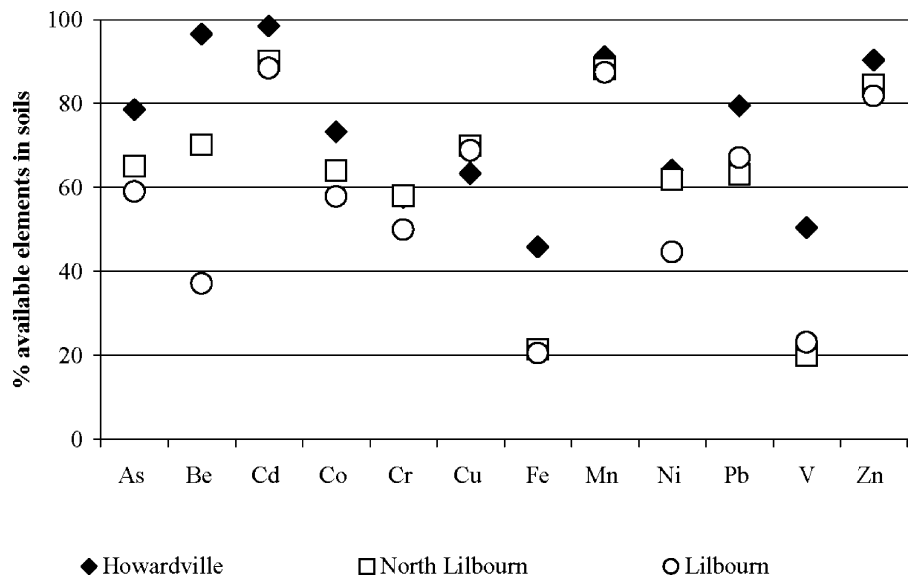
more (≈80%) with OM and the RES soil fractions. Generally and irrespective of the study area, arsenic, cadmium, lead, manganese and zinc had the lowest retention in the soils. Prevailing environmental conditions at the study areas may not promote the availability of the elements in the OX and OM fractions of soils. However, the elements in the EX and CAR fractions may be more available in the

Table 4 Factor loadings after varimax rotation for thirteen trace elements concentrations

Variable	Lilbourn			North Lilbourn			Howardville		
	Factor1	Factor2	Factor3	Factor1	Factor2	Factor3	Factor1	Factor2	Factor3
pH	0.07	*0.32*	0.22	−0.26	−0.27	0.03	0.00	−0.16	−0.3
Organic matter	−0.20	0.21	−0.16	0.19	*−0.32*	−0.06	0.25	*−0.07*	−0.01
Quartz	0.11	*0.4*	−0.02	0.15	−0.02	−0.01	−0.02	0.04	*−0.57*
Feldspar	−0.13	0.21	−0.24	0.08	−0.04	*−0.54*	−0.24	−0.05	0.26
Clay	−0.04	*−0.31*	0.37	−0.11	−0.23	0.31	0.18	*−0.38*	0.10
Calcite	0.03	*−0.38*	0.06	−0.16	0.09	0.29	0.00	0.00	0.00
As	−0.22	−0.03	*−0.45*	−0.19	0.05	*0.56*	−0.07	0.25	*0.58*
Be	*−0.3*	−0.13	0.22	*0.36*	0.09	−0.04	0.29	0.23	0.05
Cd	0.22	−0.03	*0.45*	−0.16	*−0.34*	−0.22	0.01	*−0.52*	−0.22
Co	*−0.31*	−0.17	0.10	*0.34*	0.18	−0.01	0.29	0.21	0.08
Cr	−0.21	0.22	*0.33*	0.28	0.24	−0.13	*0.31*	−0.05	−0.06
Cu	*−0.3*	0.26	0.17	0.19	*−0.35*	0.07	0.28	0.20	0.02
Fe	*−0.32*	−0.09	−0.11	*0.40*	−0.01	0.00	0.27	0.27	0.01
Hg	−0.2	0.27	−0.07	0.11	*−0.35*	0.14	0.21	−0.26	0.2
Mn	*−0.3*	−0.19	−0.09	0.25	0.28	−0.11	*0.32*	0.01	0.04
Ni	*−0.30*	−0.07	0.23	*0.33*	−0.2	0.00	*0.32*	−0.04	0.01
Pb	−0.2	*0.31*	0.19	−0.01	*−0.39*	−0.04	0.23	*−0.33*	0.24
V	*−0.32*	−0.16	−0.01	*0.32*	0.2	−0.07	*0.31*	0.18	−0.05
Zn	*−0.33*	0.11	0.07	−0.19	−0.01	*0.47*	0.19	0.26	−0.11
Eigenvalues	7.78	5.27	2.35	6.09	5.94	2.25	9.42	2.69	1.88
Explained var.	41.0	27.7	12.4	32.1	31.3	11.9	52.3	14.9	10.4
Cumul. % var.	41.0	68.7	81.1	32.1	63.3	75.2	52.3	67.3	77.7

Factor loadings exceeding the absolute value of 0.3 are printed in italics; *Cumul.* cumulative; *Var.* variance.

natural soils analyzed of New Madrid County. The potentially available trace elements may pose a threat to the health of humans through exposures from soil ingestion, dermal contact and inhalation of dusts.

Factor analysis and origin of elements in soils

Factor analysis (FA) was applied to the analytical data obtained to see the distribution and interrelationships of the elements and minerals at the study areas. Principal component analysis (PCA) of the 13 variables showed some relationship of the elements with one another. PCA 1, 2 and 3 with eigenvalues >1 explained over 75% of the total variance of the data set across the sites (Table 4). A closer look at the loadings suggested possibly different origins of the elements in the data set. The soils of Lilbourn had loadings greater than 0.3 on PC1 for beryllium, Co, Cu, Fe, Mn, Ni, V, and Zn. Lesser correlation was recorded for lead, Cr, As and Hg on PC1 (loadings <0.3). These elements as discussed earlier were associated with organic matter and feldspar. PC2 had associations of Cr, Cu, Hg and Pb with one another and these were influenced by pH and quartz content. On PC3, the clay minerals controlled the beryllium, Cd, Cr, and Ni concentrations in Lilbourn soils. For North Lilbourn soils, PC1 showed associations of beryllium, Co, Cr, Fe, Ni, V and Mn with one another (range of loadings 0.32–0.4). These elements also related weakly with quartz content (loadings ≈0.2). On PC2, clay minerals and organic matter influenced the levels of cadmium, Cu, Ni, Pb and Hg. On PC3, Zn and As were closely related to one another and to the amount of clay in soils. In Howardville sample area, with the exception of Cd and As, all the elements were related to organic matter and clay content (PC1 with loadings ≈0.2). PC2 had arsenic, Be, Co, Cu, Fe, V and Zn with positive loadings of at least 0.2. Clay minerals and Cd, Pb and Hg were also directly correlated (loadings ≈0.26–0.52). PC3 showed the close association of arsenic with Pb and feldspar. Generally, elements on PC1 across all the sites related to the soil minerals such as the iron/manganese oxides and oxyhydroxides fractions of the parent soil material. PC2 was also related possibly to anthropogenic sources associated with fertilizer applications and contributions from atmospheric deposits (Galena is the principal lead ore mined in the region for over a century and it is associated with silver, zinc, copper, cadmium, bismuth,

arsenic, antimony and traces of mercury). Other lead sources may include chips of old paint from buildings and vehicular emissions. PC3 may be influenced by pesticide applications such as lead arsenate pesticide use since these were farming areas.

Conclusions

Baseline concentrations of trace elements in Southeast Missouri soils were established in this study. The ratios of the average values obtained for the elements to the Missouri corresponding Missouri background values were not highly pronounced except for lead with a factor of 3.1 in North Lilbourn. According to the US EPA PRGs, toxicity risks were only apparent for a few samples containing arsenic (7%) and vanadium (8%). The variations in trace element levels across the study areas may be influenced by the intensities of various human activities, soil types and chemistry and environmental conditions. Factor analysis indicated that the soils were derived from the parent soil materials and from anthropogenic inputs. Fertilizer and pesticides applications probably contributed to the natural soils of New Madrid County. The US EPA and other stakeholders have contributed to the improvement of basic infrastructures in the region, reduction of water quality problems and overall empowerment of the cities studied through education and participation. Environmental management strategies and policies will help to curtail exposures of humans to toxic elements.

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