ORIGINAL PAPER

Bioavailability of trace metals in brownfield soils in an urban area in the UK

Catherine R. Thums · Margaret E. Farago · Iain Thornton

Abstract Thirty-two brownfield sites from the city of Wolverhampton were selected from those with a former industrial use, wasteland or areas adjacent to industrial processes. Samples (<2 mm powdered soil fraction) were analysed, using inductively coupled plasma–atomic emission spectrometry (ICP–AES) for 20 elements. Loss on ignition and pH were also determined. A five-step chemical sequential extraction technique was carried out. Single leach extraction with 0.12 M hydrochloric acid of Pb, Cu and Zn in soil was determined as a first approximation of the bioavailability in the human stomach. Some of the sites were found to have high concentrations of the potentially toxic elements Pb, Zn, Cu and Ni. The partitioning of metals showed a high variability, however a number of trends were determined. The majority of Zn was partitioned into the least chemically stable phases (steps 1, 2 and 3). The majority of Cu was associated with the organic phase (step 4) and the majority of Ni was fractionated into the residue phase (step 5). The majority of Pb was associated with the residue fraction (step 5) followed by Fe–Mn oxide fraction (step 3). The variability reflects the heterogeneous and complex nature of metal speciation in urban soils with varied historic histories. There was a strong inverse linear relationship between the metals Ni, Zn and Pb in the readily exchangeable phase (step 1) and soil pH, significant at $P < 0.01$ level. There was a significant increase ($P < 0.05$) in the partitioning of Cu, Ni and Zn into step 4 (the organic phase) in soils with a higher organic carbon content (estimated by loss on ignition). Copper was highly partitioned into step 4 as it has a strong association with organics in soil but this phase was not important for the partitioning of Ni or Zn. The fractionation of Ni, Cu and Zn increased significantly in step 3 when the total metal concentration increases ($P < 0.01$). The Fe–Mn oxide fraction becomes more important in soils elevated in these metals, possibly due to the scavenging of metals by oxides. Cu and Pb extracted by HCl was statistically similar to the sum of the metals in steps 1 to 4 ($P < 0.01$) and HCl available Zn was statistically similar to the sum of Zn in steps 1 to 3 ($P < 0.01$). Step 4 (the organic phase) was not an important phase for Zn, so it was concluded that any Cu, Zn and Pb present in soil in a nonresidue phase would be potentially available for uptake into the human system once soil has been ingested.

Keywords Brownfield soils · Sequential extraction · Lead · Zinc · Copper · Nickel

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Introduction

Urban geochemical mapping in the UK has been described and discussed by Fordyce et al. (2005) for 21 cities, including the city of Wolverhampton, which is known to exhibit high concentrations of potentially harmful elements (PHEs) (Kelly et al. 1996; Kelly 1997; Fordyce et al. 2005).

Wolverhampton, with a population of around 236,600, lies to the north east of Birmingham in the West Midlands, UK (Fig. 1) and covers an area of 6,945 hectares. The geology of Wolverhampton is divided by the Western Boundary Fault that separates Triassic sandstones in the north-northwest and Carboniferous coal measures in the southeast (Hains 1969). The Carboniferous coal bands have been extensively worked, leaving a modified landscape and a disrupted soil profile (Bridge et al. 1997). The Triassic sandstones and Permian–Carboniferous sandstone and mudstone sequences to the north of the Western Boundary Fault are covered by a layer of locally derived glacial till, up to 12 m thick in places (Hains et al. 1969; Bridge et al. 1997).

The region has had mining and metal processing activities since the 16th century, which were geographically constrained to the local coal and iron stone resources. There are no major river systems in the city; and the building of a canal network in the late 18th century and a rail network in the mid 19th ?tul?> century provided important transport links for industry. Linear industry grew adjacent to the infrastructure served by canal wharfs and rail lines. Urban development during the industrial revolution of the 18th and 19th centuries was responsible

Fig. 1 United Kingdom indicating the location of Wolverhampton

for the conversion of the agricultural market town into a regionally important manufacturing and commercial centre. The landscape was still predominantly rural, until urban development schemes during the 1920s and 1930s attracted manufacturing companies such as bicycle, vehicle and aircraft producers along with the associated component industries, and residential development to house the workforce (Upton 1998). Residential housing in this region has since developed over, or adjacent to, sites of former mining and metal processing industries. The industrial activity was dominated by the manufacturing of steel, metal component parts, metal plating, galvanising and the paint and pigment industry (Upton 1998). Industrial development has declined in the UK over the last 40 years, a trend reflected in Wolverhampton, but the region has modernised towards electronics and component-based industries. Metal-based industries still play an important role in the local economy with the UK's only Cu refinery located a few kilometres to the east of the Wolverhampton administrative boundary (Upton 1998; EA 2001). A regional road-building scheme in the southeast has improved transport links with the West Midlands and the rest of the UK; redevelopment of former industrial areas and the canal network, used now for recreational activities, are part of the ongoing regional development scheme.

Former industries, many now closed, and the land and buildings used for other, including residential, purposes, have left a legacy of contamination by potentially hazardous elements (PHEs). Atmospheric and terrestrial contamination enhances the concentrations of many PHEs in the urban environment. Thus the geological input of trace metals into urban soils has been exceeded by anthropogenic input through industrialisation and urbanisation, resulting in elevated metal concentrations (Thornton 1991; Facchinelli et al. 2001; Fordyce et al. 2005). The geochemical signature of urban ground, which is often disturbed and reused as land use changes, is usually very different from that of the surrounding rural areas, and soils frequently have an elevated pH due to the large amounts of cement and concrete used in construction. Urban gardens and parks, which might appear undisturbed, show enhanced concentrations of PHEs from atmospheric emissions from industrial and utility point sources and traffic, urban runoff, littering and changes in land use (Ander et al. 2001; Fordyce et al. 2005).

The impact of specific human activities has been reported in a number of surveys. The proximity to industrial activity such as factories, scrap metal yards, battery plants, waste ground and repair garages was found to significantly increase the level of Pb in adjacent garden soils and house dusts (for example: Davies et al. 1987; Rieuwerts et al. 2000; Ander et al. 2001; Fordyce et al. 2005). Kelly et al. (1996) reported a spatial variation in metal concentration from surface and subsurface soils in Wolverhampton, higher values being reported in areas on or adjacent to former or contemporary industrial activity. The influence and nature of the adjacent road, the property age and the degree of recent redecoration, particularly the contribution of Pb-rich paint chips from stripping and sanding of internal and external surfaces, were found to be significant factors influencing Pb levels in and around UK houses (Thornton et al. 1985; Davies et al. 1987; Culbard et al. 1988).

The classical infectious diseases of childhood have been overtaken by a group of conditions to which pollutants in the environment may be contributing (ATSDR 2002), examples include asthma (CDC 1998), childhood cancer (Zahm and Devesa 1995) and autism or autistic spectrum disorder (ASD) (Palmer et al. 2006). Elevated ASD prevalence in urban areas versus rural areas (Palmer et al. 2006; Williams et al. 2006) suggests an environmental contribution, and an association between heavy metal exposure and ASD has been suggested (Lidsky and Schneider 2005). Nataf et al. (2006) have demonstrated that coproporphyrin levels were elevated in children with autistic disorder relative to control groups. Precoproporphyrin, a specific indicator of heavy-metal toxicity, was also elevated in autistic disorder. That chronic exposure to lead and mercury can contribute to developmental and behavioural disabilities in children is well documented (for example, Myers et al. 1997; Landrigan et al. 2002; Szpir 2006). For lead, impairment can occur even at relatively low levels (Canfield et al. 2003). Although currently children's blood lead should be below 10 µg/dL, Canfield et al. (2003) suggest that "there may be no threshold for the adverse consequences of lead exposure" and they estimate that considerably more children are adversely affected by exposure to environmental Pb than had been estimated. Manganese in excess affects the adult brain but has also

been implicated in diminished intellectual function in children (Wasserman et al. 2006).

Thus the enhanced concentrations of many PHEs in the urban environment and their bioavailability are of interest, particularly in the area of the health of children. Fordyce et al. (2005) point out that the potential hazards posed by PHEs depend on a number of factors including concentration, chemical form and bioavailability. This study aims to assess the concentrations of Pb, Cu, Zn and Ni and the factors influencing their variability and bioavailability in soil sampled from Wolverhampton, UK. This paper reports the results for samples from 32 brownfield sites, sampled under a National Environmental Research Council (NERC) URGENT project as detailed in the paper by Thornton et al. in this volume, which describes investigations of mineralogy and chemical speciation, plant uptake and Pb isotopic source apportionment studies by a research consortium from Imperial College, London, NERC Isotope Geosciences Laboratory, British Geological Survey and the University of Nottingham.

Metals form chemically stable species and associations with major soil constituents, which leads to accumulation in soil (Davies 1990). The least chemically stable fraction is considered the most available to environmentally sensitive receptors. Assessing metal availability is an important part of an exposure and risk assessment; identifying the factors affecting the available portion are therefore important parameters in the assessment of risk. The physicochemical form of a metal in soil is an important control to mobility and bioavailability (West et al. 1999). Metals are regarded as stable if they are incorporated into the silicate lattice or become associated to secondary authigenic precipitates such as carbonates, amorphous Fe–Mn oxides and insoluble phosphates, which fix the metals in soil. Metals become strongly bonded to the surface layer of organic matter, Fe–Mn oxides and clay minerals. Surface adsorption can lead to the metals becoming incorporated into the host by chemosorption. Weaker electrostatic bonding with soil particles is less chemically stable and metals are regarded as more available. Assessments of metal availability are made by measuring the portion of total metal in a soluble or readily exchangeable phase (Ure et al. 1993). Soluble metal species occur as free metal ions $[M^{n+}]$ and neutral molecules of organic and inorganic compounds (Thornton et al. 1985). It is

the free metal ion that is regarded as the most available for plant uptake; the activity has been predicted by total metal concentration and pH for $[Ni^{2+}]$, $[Cu^{2+}]$, $[Zn^{2+}]$ and $[Pb^{2+}]$ (Japony and Young 1994; Sauvé et al. 1996; Ge et al. 2000). Soil pH, redox potential, the number of ion exchange sites and competing cations for ion exchange sites, are all factors that have been found to influence the availability of metals in soils.

Chemical sequential extraction methods are used to determine the distribution of metals in operationally defined phases (Tessier et al. 1979; Rauret et al. 1999). This study uses a method of Tessier et al. (1979) for the partitioning of metals in river sediments, and adapted for the determination of multielement analysis in soil samples analysed by inductively coupled plasma-atomic emission spectrometry (Li et al. 1995a, b). The limitations of chemical extractions to assess metal speciation occur due to the simplification of an open system by a reagent-defined experiment. The partitioning of elements are therefore dependent on the procedures used and are referred to as "operationally defined" (Tessier et al. 1979; Rauret et al. 1999).

Single-chemical extraction techniques assess the proportion of total metal that is available for a specific environmental receptor. The first approximation of Pb that is bioaccessible in the stomach of the human gastrointestinal tract is assessed by a weak HCl solution (Gibson and Farmer 1984; Gulson et al. 1994).

Methods

Thirty-two brownfield sites, including two allotments, were sampled in 1999–2000 for the NERC URGENT project "Studies into metal speciation and bioavailability to assist risk assessment and remediation of brownfield sites in urban areas" (grant reference number GST/03/2251). A composite surface soil (0–15 cm) sample was taken from 20–25 subsamples from a 20 m × 20 m square using a Dutch auger. To determine total metal concentration the soil samples were air dried at 30°C for 2–3 days, disaggregated, sieved to <2 mm and milled to a fine powder for acid digestion with HNO_3–$HClO_4$ (Thompson and Walsh 1983). Soil pH was determined from the <2 mm fraction in a 10:1 ratio of

deionised water to soil. The standard method of loss on ignition (LOI) was used to estimate organic carbon content. A known weight of the <2 mm soil is placed in 105°C to expel moisture, weighed again and placed at 450°C to burn off organic matter. The weight loss is expressed as a percentage of the moisture free soil. The samples underwent wet digestion in HNO_3–$HClO_4$ using the method of Thompson and Walsh (1983) before the determination of the "total" concentrations of Li, Na, K, Be, Mg, Ca, Sr, Ba, La, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, P, S and As by inductively coupled plasma–atomic emission spectrometry (ICP–AES). Total concentrations and results of extractions are reported in this paper for the elements Ni, Cu, Zn and Pb.

Sequential chemical extractions follow the established method of Tessier et al. (1979) modified for analysis of soil samples by ICP–AES by Li et al. (1995a, b). Five chemical reagents determine the fraction of an element brought into solution under different chemical conditions. Step 1, 0.5 M $MgCl_2$ at pH 7.0; step 2, 1.0 M CH_3CO_2Na at pH 5.0; step 3, 0.04 M $NH_2 \cdot OH \cdot HCl$-in 25% CH_3CO_2H; step 4, 30% H_2O_2 at pH 4.0; and step 5, 70% HNO3–60% $HClO_4$–40% HF. The first step extracts the metals in readily exchangeable sites by a weak electrolyte solution of magnesium chloride under neutral pH conditions. The step 2 reagent, sodium acetate at pH 5.0, dissolves carbonate species and releases ions specifically adsorbed onto pH-dependent exchange sites. The third step uses hydroxylammonium chloride to reduce amorphous oxide and hydroxides of Fe, Mn and Al, with an addition of acetic acid to keep the dissolved component in solution. The fourth step oxidises organic matter and sulphides using a hot hydrogen peroxide attack at pH 4.0. The last step dissolves the residue phases by an attack of nitric, perchloric and hydrofluoric acids; this step dissolves the clay fraction, phosphates, residue organic material, sulphides, slag material, alloys and other chemically resistant compounds from anthropogenic sources.

Single-chemical extraction approximates the fraction extracted during soil ingestion in the human large intestine. A solution of 0.12 M HCl is agitated with soil in a 10:1 acid to soil ratio at room temperature for 2 h (Gulson et al. 1994; Rieuwerts et al. 2000). Elemental determination of the total, sequential and single extraction solutions was carried

out using inductively coupled plasma–atomic emission spectrometry (ICP–AES).

A standard quality control procedure for total and sequential extractions was followed after Thompson and Howarth (1976) and Gill and Ramsey (1997). Certified reference materials, blanks and random duplicate samples were incorporated into the analytical run. Two soil reference materials from the National Institute of Standards and Technology were used: SRM 2709 and SRM 2710. The total element analysis gave an acceptable level of bias and precision (<5%) for all elements analysed. The majority of elements show a recovery of less than 100%, in the sequential extraction procedure, which is partially accounted for by a loss of material during the sequential analytical procedure, which involves several stages of washing and the transferal of material (Rubio and Ure 1993). Reagent blank measurements were used to determine the detection limit for elements in each step. A value of three times the standard deviation of the instrumental detection limit for duplicate reagent blank measurements was taken as the analytical detection limit. Samples with a low total concentration of Pb have had the values replaced by the analytical detection limit in steps 1 and 2, limiting the determination of metal partitioning between the first two steps for samples with a low total Pb concentration.

Results

Total concentrations of Ni, Cu, Zn and Pb

Descriptions of the sites are given in Table 1, descriptive statistics for the concentrations of Ni, Cu, Zn and Pb in the 32 urban brownfield soils are given in Table 2 and results for pH and LOI are given in Table 3. Table 2 shows that the concentrations of the metals Ni, Cu, Zn and Pb are positively skewed and some values are anomalously high. Geochemical data are typically strongly skewed, the existence of unusually high concentrations is a very common characteristic, and outliers may often originate from another population from the main body of data (Reimann and Filzmoser 2000; Reimann et al. 2002). Samples with a high metal concentration are of most interest to environmental investigations, and therefore it is important to retain these values in the data set.

Box plot diagrams indicating the ranges of Ni, Cu, Zn and Pb concentrations in the Wolverhampton brownfield soils are shown in Fig. 2. The site W6 was classified as an extreme value for the elements Ni, Cu and Zn (an extreme value has a concentration >3 times the variance of the box) and an outlier for the element Pb (an outlying value has a concentration >1.5 times the variance of the box). Site W3 was classified an outlier for Cu and Zn. Site W7 was an outlier for Cu, Zn and Pb, whereas site W10 was classified as an outlier in the distribution of Pb and W29 on outlier for Cu only. In Fig. 3 the nine sites with the highest concentrations of Ni, Cu, Zn and Pb are represented.

Soil properties

Values for pH and loss on ignition are given in Table 3. Soil pH ranges from 4.2 to 8.2 with a median value of 6.4. Loss on ignition is an approximation of the percentage of organic carbon in soil. The organic content of urban brownfield soils is between 3% and 51% with a median of 9%. Both parameters are important variables in modelling the behaviour of trace metal solubility and bioavailability in soils.

Sequential extractions

The partitioning of Ni, Cu, Zn and Pb across the five-step extraction scheme is shown in Table 4 and illustrated in Fig. 4. The geometric means and ranges are nonparametric (Kolmogorov–Smirnov test). Percentages of the total extracted in each step were used to construct the box plots shown in Fig. 4. Box plots are useful in nonparametric statistics because they use the 25th median and 75th percentiles to illustrate the box and thus the distribution around the central tendency. As the data are skewed, the median values are different from the geometric means, thus orders shown in the figure and the table may be different. This is especially true for zinc because it has a very great variability, which was found to be high over all steps of the sequential extraction. The majority of Zn was partitioned into steps 3 and 5 and decreased in the order 3, 5 > 2 > 4 > 1. The majority of Pb was partitioned into step 5 and 3 decreasing in the order 5 > 3 > 4 > 2 > 1. The majority of Ni is partitioned into step 5 (>70%). The majority of Cu was partitioned into step 4, followed by step 5.

Table 1 Site details for urban brownfield sites and two allotments in Wolverhampton

Site	East	North	Address	Land use	Previous land uses & local industrial activity
W1	391030	301170	Oxley Golf Course	Recreation	Previous use; agricultural
W2	388450	300860	Staffordshire Golf Course	Recreation	Previous use; agricultural
W3	393690	297700	East Park	Recreation	Previous use; coal mine-pit area
W4	392516	297240	Major Street	Recreation	Previous use; buildings unknown use
W5	393730	296530	Old Gas Works	Rough ground	Previous use; gas works & railway
W6	394463	295095	Coseley Nature Reserve	Recreation	Previous use; landfill site British Waterways
W7	394960	295960	Dudley Street	Rough ground	Previous use; metal works unknown use
W8	395069	296834	Bilston Wood	Woodland in industrial area	Woodland
W9	390170	301290	Aldersley Recreation	Recreation	Adjacent to rifle range, railway
W10	391330	301090	Ripon Road	Waste ground adjacent to tyre factory	Tyre factory on site of former enamel works
W11	390810	296710	Needlewood Close	Residential garden	
W12	388240	295750	Hilston Avenue	Ground under pylon	Residential area
W13	392760	295760	Hilston Road	Recreation	Previous use; coal mining
W14	392830	299710	Powel Street Nature Reserve	Recreation	Adjacent to railway
W15	388910	299580	Valley Park Reserve	Nature reserve	Adjacent to railway-canal
W16	392380	295460	Ettingshall Park	Recreation	Previous use; colliery spoil heap
W17	391240	297580	Drayton Street Recreation Ground	Recreation	Adjacent to industrial site
W18	395139	299384	Watery Lane 1	Rough ground	Adjacent to galvanising plant, sewage plant
W19	395086	299157	Watery Lane 2	Rough common ground	Adjacent to galvanising plant, Previous use; sewage plant
W20	396601	301123	Lichfield Road	Rough common ground	Adjacent to canal
W21	393960	299860	Bentley Bridge 1	Rough ground	Adjacent to metal works & light industrial park
W22	394570	299977	Bentley Bridge 2	Rough ground	Adjacent to metal works & light industrial park
W23	395400	299670	Bentley Bridge 3	Rough ground	Adjacent to steelworks
W24	394680	299830	Neachells Lane Wood	Rough ground & woodland	Adjacent to steelworks
W25	394210	298970	Strawberry Lane	Rough ground	Adjacent to industrial sites & railway
W26	394600	298750	Neachells Bridge	Rough ground	Adjacent to industrial units
W27	392681	298701	Qualcast Road	Rough ground	Adjacent to & previous use & steel works
W28	391701	301816	Steel Drive	Rough ground	Adjacent to tyre factory & metal works
W29	391780	300120	Fowlers Park 1	Woodland	Adjacent to municipal incinerator & canal
W30	392026	300217	Fowlers Park 2	Recreational	Adjacent to municipal incinerator & canal
W31	389201	296799	Windsor Avenue	Allotment	
W32	392200	297100	Howell Road	Allotment	

Table 2 Descriptive statistics for the concentrations of, Ni, Cu, Zn and Pb in urban brownfield soils (concentration in µg/g)

	Ni	Cu	Zn	Pb
n	32	32	32	32
Mean	49	209	531	206
Median	36	88	283	120
SD	53	415	815	197
Skewness	4.0	4.8	4.5	1.6
Minimum	14	17	70	14
Maximum	318	2370	4670	768
Percentiles				
25th	23	58	169	75
75th	60	195	541	281
95th	172	1188	2401	745

Table 3 Descriptive statistics for pH and loss on ignition (LOI) in urban brownfield soils

	Soil pH	LOI
n	32	32
Median	6.4	9%
Range	4.2–8.2	3–51%
SD	1.2	9

Extraction by 0.12 M HCl

Samples from 30 brownfield sites were extracted with 0.12 M HCl. The two allotment sites were not included since it was possible that soil treatment and importation by the allotment holders would influence the bioavailability. Results for the extraction of Cu, Zn and Pb by 0.12 M HCl for the 30 sites are given in Table 5. More than 25% of the samples for Ni were on or below the analytical detection limit, therefore Ni is not included in the table.

Discussion

Table 2 and Figs. 2 and 3 show that the concentrations of Cu, Zn, Ni and Pb vary greatly in the sites investigated. The four sites with the highest total concentrations of these four metals were W6, W7, W10 and W3. W6, now designated as a nature reserve, was previously a landfill site and used for dumping dredged canal sediment. W7 was the site of a metal works. Site W10 was used formerly by an enamelling works and a tyre factory. W3, now
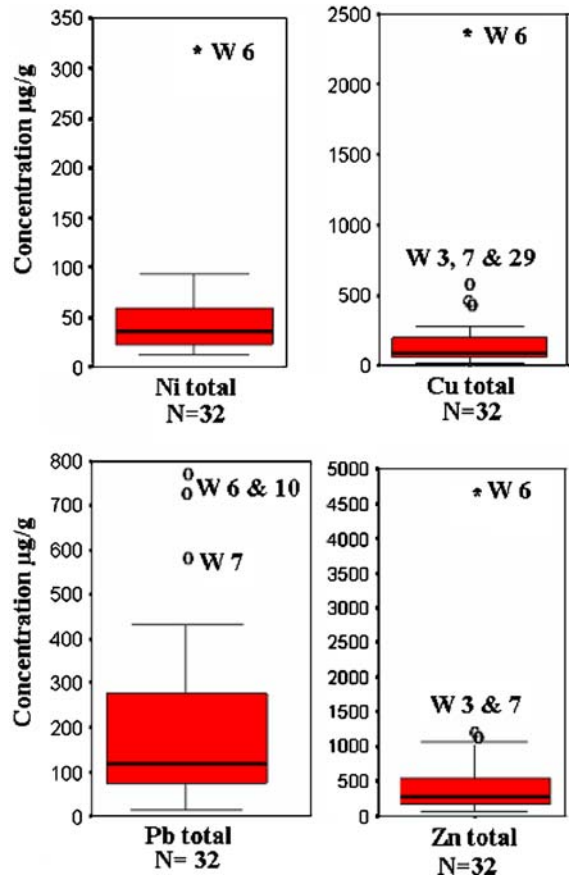
Fig. 2 Box plot diagram indicating the range of Ni, Cu, Zn and Pb concentration in urban brownfield soils ($n = 32$)
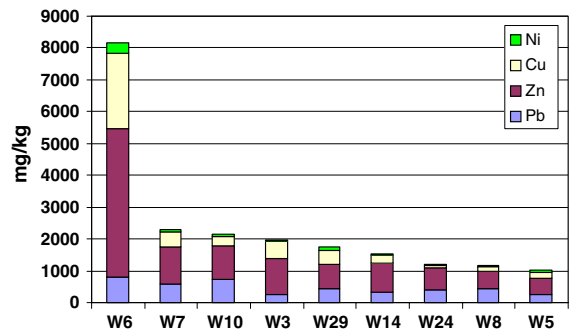
Fig. 3 The nine most contaminated brownfield sites, showing concentrations of Ni, Cu, Zn and Pb

designated as a recreation area, was a former colliery site. Thus the concentrations of these elements in soils are highly influenced by historical land use, and all the sites are within areas of former or contemporary industrial activity.

Table 4 Geometric mean, median and range for, Ni, Cu, Zn and Pb in steps 1–5 of the sequential chemical extraction (concentration in µg/g) $n = 32$

Step		Ni	Cu	Zn	Pb
1	GM	0.5	0.8	7.5	1.5
	Median	0.28	0.7	11.7	1.0
	Range	<0.3–7.3	0.2–9.8	<0.6–114	<0.9–9.7
2	GM	1.6	2.4	31.3	9.8
	Median	1.4	2.6	37.7	11.7
	Range	<0.8–35	<0.3–45	1.0–218	<2.7–125
3	GM	4.1	4.2	74.0	23.5
	Median	3.3	5.8	76	27
	Range	0.9–127	<0.2–551	3.9–528	2.9–156
4	GM	3.1	31.6	18.1	17.4
	Median	2.6	34.3	16.1	20.2
	Range	1.1–22	1.9–716	1.5–269	2.0–119
5	GM	19.6	23.0	55.1	32.6
	median	25.0	26.0	64.1	36.0
	Range	1.5–89	1.9–342	12–327	1.6–665

GM, geometric mean; range, minimum and maximum values; < denotes limit of detection for particular step

The UK government's contaminated land exposure assessment (CLEA) model (DEFRA-EA 2002a) considers the exposure to contaminants from the direct and indirect ingestion and inhalation of soils (DEFRA-EA 2002b) and has defined generic soil guideline values (SGV) for As, Cd, Cr, Pb, Hg, Ni and Se (DEFRA-EA 2002c). Values for Ni and Pb are shown Table 6. Eleven of the 32 sites exceed the SGV of 50 µg/g for Ni and three sites exceed the 450 µg/g for Pb (DEFRA-EA 2002d).

The available or labile metal pool is a generic term that is used to describe the fraction of metal that is potentially available for uptake into a biological receptor. It has been defined (Young et al. 2005) as that metal in the solid phase of the soil that is immediately capable of buffering the metal ion activity in the soil solution. These authors point out that the functions of the labile pool may include slow interactions with nonlabile phases or metal associations, and the control over bioavailability following direct ingestion. Chemical extraction schemes are often used to quantify labile metal pools, and multistep sequential extractions enable the identification of the main chemical associations of metals in soil. Despite limitations in the selectivity of exact soil phases, the partitioning of metals is of value in the assessment of metal mobility and persistence in contaminated soil (Gibson and Farmer 1986; Young et al. 2005).

The partitioning of metals across the five-step extraction scheme has high variability in urban soils, and the trends found in this work were comparable to those in published surveys. Gibson and Farmer (1986) reported the majority of Zn partitioned into the carbonate, moderately reducible and residual phases, Cu into the organic phase and Pb into the moderately reducible and residual phases. These authors concluded that the distinct partitioning pattern of heavy metals in urban soils was of value in establishing the main chemical associations of the heavy metals in the solid phase. In the urban brownfield soils of Wolverhampton a higher proportion of Zn was found to occur in the relatively soluble phases, steps 1 and 2, as compared with Cu, Pb and Ni, which were associated with the more resistant phases (Table 4, Fig. 4).

Correlation coefficients were calculated between the results of the sequential extractions and the soil pH, organic carbon content (LOI), and total metal concentrations using Spearman's correlation coefficient (r'), as this is suitable for nonparametric data, and the results are shown in Table 7. A strong positive relationship between two variables is indicated by two asterisks at the 99% significance level or $P < 0.01$. A weaker but still significant relationship is indicated by a single, at the 95% significance level or $P < 0.05$. The sign of the coefficient indicates the direction of the relationship. The partitioning of Ni, Cu, Zn and Pb in step 1 increases as soil pH decreases. This relationship is significant, implying that in more-acidic soils there is a higher proportion of exchangeable metals. The partitioning of Zn into step 2 increases in soils that are more alkaline. This may be the competitive adsorption of Zn in soils with a high pH at the expense of other cations.

The loss on ignition of the soil (LOI) approximates the amount of organic matter, which is an important property in the binding of trace metals in soil (Plant and Raiswell 1983; Rieuwerts et al. 1998). The step 4 reagent, hydrogen peroxide, is designed to break down organic-metal compounds (Tessier et al. 1979; Li et al. 1995a). The partitioning of Ni, Cu and Zn increases in step 4 as the organic carbon content of soil increases. It is inferred that the organic phase becomes more
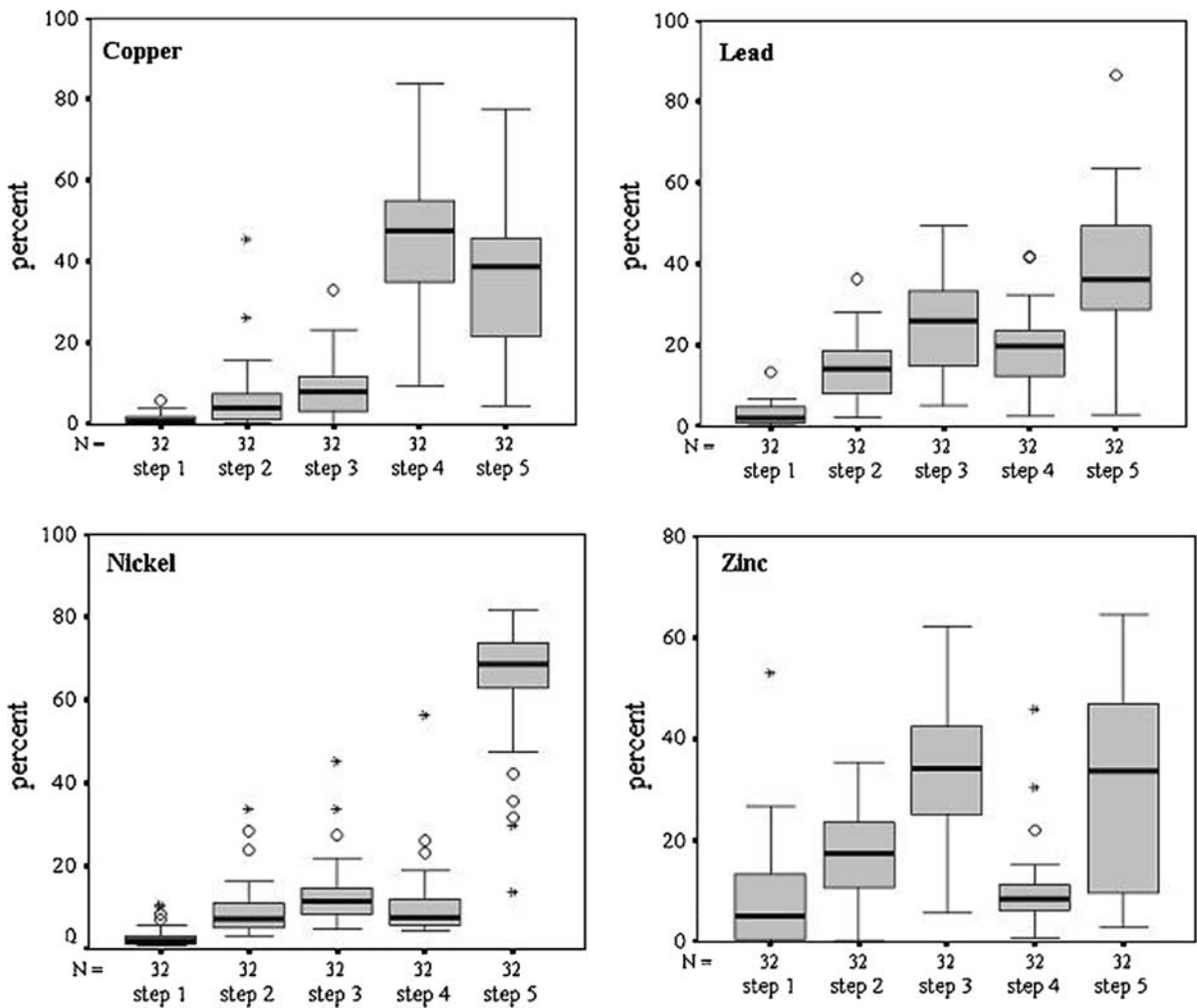
Fig. 4 Box plot diagrams illustrating the partitioning (percentages) of Cu, Zn, Ni and Pb across a five-step sequential extraction procedure

important for Ni, Cu and Zn in organic-rich soil. This is particularly the case for Cu, where a high percentage of total Cu is partitioned into step 4, the organic phase (median 48%, range 10–84%). Soils high in organic carbon have a positive relationship with total Pb; however, as there was no significant correlation between Pb in step 4 and the organic carbon content, it is suggested that it is possible that Pb-organic complexes were not extracted by step 4 reagents, and so the occurrence of the species may be underestimated by this method.

To test if there was a greater partitioning into one phase in more contaminated soil a correlation between the total metal concentration and the partitioning of metals was performed (Table 8). The

partitioning of Ni, Cu and Zn increases in step 3, the Fe–Mn oxide phase, in soils elevated in these metals. The partitioning of Pb in step 1 appears to decrease in soils more contaminated with these metals.

The partitioning coefficient of metal into the readily exchangeable fraction (step 1) has been calculated from

Partitioning into step 1 =

$$\frac{\text{Concentration of metal in step } 1 \, (\mu g/g)}{\text{Total concentration of metal in soil } (\mu g/g)}.$$

There is a strong inverse relationship between the partitioning of Zn into step 1 and soil pH ($P = 0.00$). The partitioning of Ni into step 1 also has a strong inverse relationship with soil pH whilst Pb and Cu have a

Table 5 Summary statistics for the concentrations of Cu, Zn and Pb in 30[a] urban brownfield soils, extracted by 0.12 M hydrochloric acid (concentrations reported in µg/g)

	Median	Geometric mean	Range	Standard deviation
Cu	41	44	6–1660	297
Zn	103	112	13–3100	563
Pb	67	67	10–389	91

[a] Two allotment sites were not included

Table 6 Soil guideline values for Pb and Ni (µg/g) (DEFR-EA 2002d)

Land use	Pb	Ni
Residential with plant uptake	450	50
Residential without plant uptake	450	75
Allotments	450	50
Commercial/industrial	750	5000

weaker relationship, although they are still significant at 95% at the significance level ($P = 0.03$ and $P = 0.05$, respectively). The partitioning of metal into the readily exchangeable fraction may be a useful measure of potential bioavailability and mobility in soil.

The brownfield sites represent a range of land-use types and reflect the variability of metal partitioning in urban soils. The patterns of fractionation for Pb are shown in Fig. 5. It is apparent that very little of the Pb is solubilised in step 1. Lead in soil from site W21 (rough ground, adjacent to metal works and light industrial park) is all solubilised in steps 1–4, whereas that from site W22 from the same area (Table 1) has a different pattern of fractionation, demonstrating inhomogeneity in both intersite and intrasite soils (see also Thornton et al. 2008 in this volume).

The patterns of fractionation for two sites (W6 and W14) are shown in detail in Fig. 6. These two sites are designated as nature reserves and are used for recreation, including play sites for young children. Soil from the site W6 has high concentrations of Cu, Ni, Zn and Pb (Fig. 3 and Table 2). The majority of total Pb (768 µg/g) was found in the least available residual fraction. The total Cu concentration (1663 µg/g) was found to be fractionated into the most available steps 1, 2 and 3; however, the Fe–Mn oxide phase, step 3 was found to be an important phase for Ni, Cu and Zn. W14 is adjacent to a railway, managed as a nature reserve with vegetation cover of trees and grasses. The soil has a low pH (5.8) and an estimated 50% organic carbon

Table 7 Significant correlation between metal partitioning in sequential extractions and the soil pH, LOI and total metal concentration ($n = 30$, two allotment sites excluded)

			Step 1	Step 2	Step 3	Step 4	Step 5	Total metal concentration
Ni	pH	r'	−0.82**		0.47**			0.47**
		Sig.	0.00		0.01			0.01
	LOI	r'				0.39*		
		Sig.				0.05		
Cu	pH	r'	−0.35*					
		Sig.	0.05					
	LOI	r'			−0.40*	0.39*		0.59**
		Sig.			0.02	0.02		0.00
Zn	pH	r'	−0.89**	0.51**	0.50**			
		Sig.	0.00	0.01	0.01			
	LOI	r'				0.50*		0.51**
		Sig.				0.02		0.00
Pb	pH	r'	−0.52**					
		Sig.	0.00					
	LOI	r'						0.52**
		Sig.						0.00

* Significant at $P < 0.05$ (statistically significant at the 5% level)

** Significant at $P < 0.01$ (statistically significant at the 1% level)

Table 8 The correlation between total metal concentration and the partitioning of metals (%) in sequential extraction steps $(n = 30)^a$

		Correlation coefficient between total metal concentration and the partitioning of metals in steps 1, 2, 3, 4 and 5 (calculated as a percentage)				
Ni total	r'	−0.178	−0.025	**0.594****	−0.211	−0.133
	Sig.	0.345	0.897	0.001	0.263	0.483
		Cu step 1	Cu step 2	Cu step 3	Cu step 4	Cu step 5
Cu total	r'	−0.178	−0.143	**0.523****	0.096	−0.228
	Sig.	.347	.451	.003	.614	.226
		Zn step 1	Zn step 2	Zn step 3	Zn step 4	Zn step 5
Zn total	r'	−0.182	0.281	**0.528****	0.248	−0.504
	Sig.	0.335	0.133	0.003	0.186	0.005
		Pb step 1	Pb step 2	Pb step 3	Pb step 4	Pb step 5
Pb total	r'	**−0.469****	−0.099	−0.159	−0.084	0.268
	Sig.	0.009	0.604	0.402	0.658	0.152

** Significant at $P < 0.01$ (statistically significant at the 1% level)

[a] Two allotment sites were not included
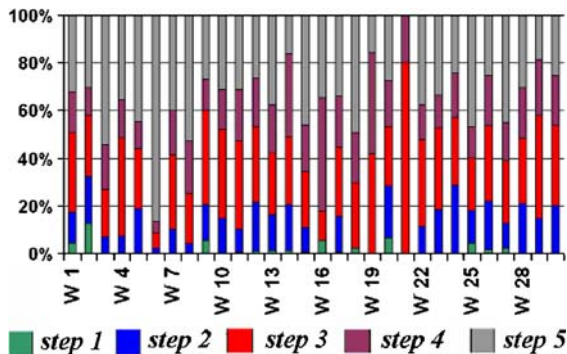
Fig. 5 Partitioning of Pb into five steps for 30 brownfield sites in Table 1 (two allotments not included)

content. Only a small proportion of the Pb is in the residual fraction. Nickel and Zn were found to be comparatively high in step 1. The partitioning of metals into the organic fraction (step 4) was found to be more important than the Fe–Mn oxide fraction, particularly for Ni, Cu and Pb.

Extraction with 0.12 M hydrochloric acid has been used to approximate bioaccessible Pb, the fraction of total Pb available for absorption in the human stomach from ingested soil. Single leach extraction schemes have been designed to model human stomach acidity; however they are not necessarily a true representation of the bioavailable fraction (Davis et al. 1994). Lead binds strongly to humic materials in soil, and is less

soluble in the acidic conditions in the stomach than is the Pb bound to Fe and Mn oxides (Chaney et al. 1988). In the alkaline conditions in the duodenum both OM and Fe oxides strongly bind Pb (Chaney et al. 1988). A better assessment of Pb bioavailability would be obtained using the physiologically based extraction test (PBET) (Ruby et al. 1996), where Pb is extracted in both acid and alkaline conditions simulating those in both stomach and duodenum. However in this work only the acidic conditions were simulated.

There are significant positive correlations between the concentration of metal extracted by 0.12 M HCl (Table 5) and the total concentration of the elements. Spearman's correlation coefficients were high and positive; Cu $r' = 0.93$ $(P < 0.01)$, Zn $r' = 0.96$ $(P < 0.01)$ and Pb $r' = 0.94$ $(P < 0.01)$. The proportion of Cu and of Pb extracted by 0.12 M HCl was found to be statistically similar to the sum of Cu and Pb in steps 1, 2, 3 and 4, respectively; the proportion of 0.12 M HCl extractable Zn was statistically similar to the sum of Zn in steps 1, 2 and 3. The results are presented in Table 9, with significance indicated at the $P < 0.01$ level. Step 4 was not an important phase for Zn (median 9%) therefore it can be concluded that the availability of Cu, Zn and Pb once soil had been ingested into the GI tract was equivalent to the nonresidual phases (step 5); all other species are potentially available for uptake.

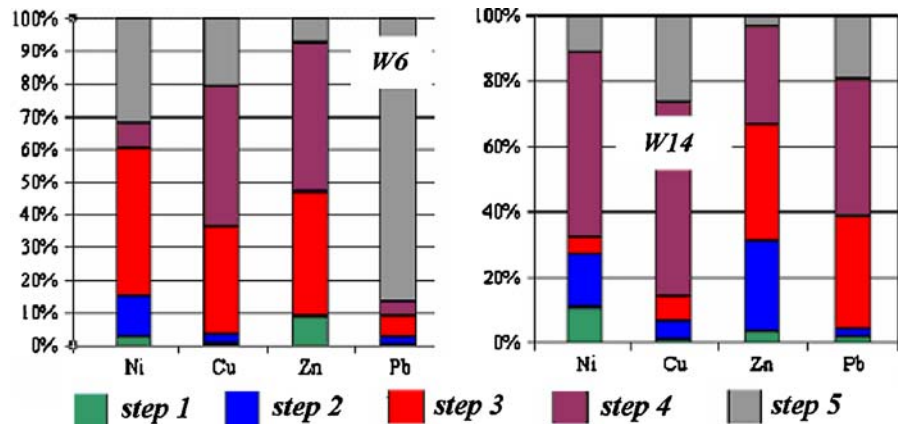**Fig. 6** Partitioning of Ni, Cu, Zn and Pb in sites W6 and W14

Table 9 A comparison between metal partitioning by two chemical extraction methods

Method	Geometric mean (μg/g)	Correlation and significance level r' (sig.)
Cu partitioned into 0.12 M HCl	45	0.87 (0.00)
Cu partitioned into sum of steps $1 + 2 + 3 + 4$	49	
Zn partitioned into 0.12 M HCl	112	0.82 (0.00)
Zn partitioned into sum of steps $1 + 2 + 3$	137	
Pb partitioned into 0.12 M HCl	67	0.95 (0.00)
Pb partitioned into sum of steps $1 + 2 + 3 + 4$	66	

The integrated exposure uptake biokinetic (IE-UBK) model for Pb blood levels in children was developed for the US Environmental Protection Agency to estimate the blood lead (PbB) levels in children exposed to Pb contamination from several sources (IEUBK model 2002). The IEUBK model was run [using model default values as recommended (IEUBK 2002)] and using site-specific "total" Pb concentration in soil from 30 urban brownfield sites. In the first run the default value for bioavailability (30%) was used. In the second run the site-specific HCl availability value was used. The results show blood Pb (PbB) level (in μg/dL) for a hypothetical child, or population of children, between the ages of 1 and 2 years. Blood Pb levels in children should not exceed 10 μg/dL, (US EPA 1994).

Using the default estimate of bioavailability (30%), it was found that children exposed to the urban brownfield soils in this study would not exceed blood lead levels of 10 μg/dL. However, when the experimental values of the availability from the HCl extractions for each site was used, there were three sites where blood lead levels were predicted to exceed the 10 μg/dL threshold value. The sites were

W6, W10 and W24. Sites W6 and W10 have high total soil Pb concentration (Pb_{Total} 768 and 732 μg/g respectively), and exceed the SGV for residential development (DEFRA-EA 2002d). The sites have measured HCl availability of 35% and 39%, respectively. W24 has a moderately high Pb_{Total} 401 μg/g and a high HCl extractability of 97%. Although the mean Pb concentration at site W24 does not exceed the SGV for residential development, the high bioavailability means that the Pb is a potential hazard should the site be redeveloped for residential purposes in the future. Since lead exposure even at relatively low levels below 10 μg/dL can pose a hazard to children, leading to intellectual impairment (Canfield et al. 2003), it appears necessary to carry out bioavailability tests for Pb, in addition to total concentrations, before brownfield sites in urban areas are developed for residential housing.

Conclusions

The high variability of partitioning across the five-step schemes can be attributed to the variability of

anthropogenic activity controlling metal source and the soil properties. Soils with higher total Zn have a greater partitioning in the more environmentally available phases. Soils with a higher total Ni, Cu and Pb have higher concentrations of these metals in the residue phases, suggesting that the anthropogenic input is in a chemically resistant form or that the anthropogenic metals form insoluble solid phases. Strong organic-metal complexes are released during oxidation of organic matter in step 4, thus the partitioning of Ni, Cu and Zn increases in step 4 as the organic carbon (measured by LOI) content of soil increases, particularly for Cu. where a high percentage of total Cu was partitioned into step 4, the organic phase (median 48%, range 10–84%).

The partitioning of Ni, Cu, Zn and Pb in step 1 increases as soil pH decreases, whereas the partitioning of Zn into step 2 increases with soil pH. Using HCl availability, there were three sites where children exposed to the soil by hand-to-mouth activity would be predicted to exceed the 10 μg/dL threshold blood lead concentration. The sites were W6, W10 and W24 (Table 1).

It can be concluded from the results that estimates of PHE content, concentration and bioavailability is site specific, and depends on the historical land use. The potential bioavailability and bioaccessibility of the elements studied here is dependent on soil properties, such as carbon content and pH. It is recommended that bioavailability tests, particularly for Pb, be carried out before brownfield sites in urban areas are developed for residential housing.

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