

# The chemistry and parent material of urban soils in Bristol (UK): implications for contaminated land assessment

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**Abstract** An earlier survey of topsoil from parks and allotment in the city of Bristol (UK) revealed the presence of relatively high levels of “pseudo-total” Cd, As, Cu, Pb and Zn, with Cd and As exceeding present UK soil guidelines. This follow-up work aimed at (1) estimating geochemical thresholds for these elements based on “near-total” soil, bedrock and sediment heavy metals and (2) determining the genetic relationship between soil and bedrock using rare earth elements (REEs or lanthanides) as tracers. “Near-total” concentration of 34 elements (Al, Ca, Fe, K, Mg, Na, As, Ba, Cd, Cr, Cu, Li, Mn, Ni, P, Pb, Sc, Ti, V, Zn, Y and the rare earth elements Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Yb) were obtained by ICP-MS and ICP-OES. The results show that the soil composition is largely controlled by the soil parent material, though extreme outliers are indicative of contamination at a few sites of parkland and allotments. Cumulative frequency plots show the presence of different data sets for which separate “background” values should be determined. The REE data provide evidence that weathering of the underlying sandstone

was a determinant factor leading to the relatively high heavy metal enrichment found in soil samples and sediments. Reference to UK soil guidelines to decide on possible remediation measures could be very misleading due to the natural high background levels of some elements in the underlying bedrock. Before defining land as “contaminated”, a thorough geochemical investigation is required at local scale in order to produce a more realistic and correct environmental assessment.

**Keywords** Urban soils · Contaminated land · Geochemical threshold · Heavy metals · Rare earth elements · Sediments

## Introduction

### The study area

The city of Bristol is located in the south-west of England. Much of the city is underlain by Carboniferous Limestone of the Pembroke Limestone Group, by the Carboniferous Coal Measures (mudstone, sandstone and coal seams) and by mudstone and sandstone of the Triassic Mercia Mudstone Group. Morainic material, boulder clay and till of the Quaternary Period are not common in this region. In Bristol, the Carboniferous Coal Measures were mined for bituminous coal, and Pb and Zn (from galena and smithsonite) were extracted from the Clifton Down

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Limestone and the Dolomitic Conglomerate (Green 1992). Haematite ( $\text{Fe}_2\text{O}_3$ ) was also extracted from Pennant Sandstone (Barton et al. 2002). Other local activities that depended on coal included pottery and glass industries, the production of brass, lead and lead shot. A detailed description of the geology of the district covered by the geological 1:50,000 Series Sheet 264 Bristol can be found in Green (1992) and Kellaway and Welch (1993).

A simplified bedrock geology of the district and the sampling areas are shown in Online Resource 1. The type of rock samples and GPS coordinates of all sampling locations are listed in Online Resource 2.

As previously described by Giusti (2011), in the Bristol district, poorly draining gleys and gleyed brown earths are found preferentially on sandstone and mudstone, whereas shallow brown earth/rankers are usually present over limestone. Information on the type of soils and underlying bedrock is provided in Online Resource 3.

Bristol is drained by the River Avon. It starts in Gloucestershire (north of Bristol) where it flows over Jurassic Limestone. It runs through Bradford-on-Avon, and the city of Bath. After Bath, it flows over Pennant Sandstone and across Triassic rocks (Mercia Mudstone and Sandstone) in central Bristol before reaching the Clifton gorge incised into Carboniferous Limestone. It joins the Severn Estuary at Avonmouth. The lower reaches of the Bristol Avon River experience a tidal range of about 10 m. Stream sediments in the lower reaches of the River Avon (i.e. from Bristol City Centre to the Bristol Channel) are mostly composed of silt and clay, whereas the stretches of the river east of the city are mostly sandy and often rich in gravel. These sediments and those of tributary streams of the River Avon (i.e. Frome River, Trym River) have been previously analysed in our laboratory (Giusti 2011).

The use of rare earth elements (REEs) in soils as tracers of parent material

The REEs (also referred to as the lanthanides) have been used in a number of studies on the evolution of the Earth's crust and on the genesis of rocks, minerals and sediments (Henderson 1984). More recently, some investigations have used soil REE composition to elucidate weathering and pedogenetic processes (e.g. Kurtz et al. 2000; Laveuf and Cornu 2009). Despite

their increasing use (e.g. in magnets, batteries, lasers, fibre-optic telecommunication cables, computer monitors, televisions, catalysts, fluorescent lamps), the REEs presently found in soil are usually of natural origin and derived mostly from the soil parent material, though atmospheric emissions, fertilisers and various soil amendments may be confounding factors. Sedimentary rocks have quite characteristic REE concentration ranges, with shales normally showing the highest values as a result of the high concentration of REEs in clay minerals. Absolute REE abundances tend to decrease in rocks that have a lower percentage of clay minerals and a higher content of quartz and biogenic carbonate (Haskin et al. 1966). In this study, REE data were used to trace the origin of metals found in the soils of the region and to estimate natural metal enrichment associated with bedrock weathering processes. REE data are usually normalised to the REE abundances in average chondritic meteorites. In this study, the REE results were normalised to the chondritic averages reported by Anders and Ebihara (1982).

Urban soils and contaminated land legislation

In the UK, legislation on contaminated land (e.g. the Environment Act 1995) was stimulated by the need to redevelop land previously affected by mining, smelting, landfilling and a variety of industrial activities, and this resulted in the local authorities' duty to keep a record of contaminated land. Bristol had a long history of coal and metal mining, but all mining activities ceased many decades ago. During the twentieth century, the main industrial activities in Bristol were located in the suburb of Avonmouth, along the Severn Estuary, and included chemical manufacturing companies, energy industries, waste management operators and a large smelter (Environment Agency 2002) that produced Zn, Pb, Cd and sulphuric acid for more than 70 years until closure in 2003. During its operation, large areas of Bristol were affected by atmospheric emissions containing Zn, Pb, Cd,  $\text{SO}_2$  and particulate matter (Environment Agency 2002).

In the UK, land is defined as contaminated only when there is a risk of significant harm to humans, ecosystems, controlled waters, buildings and property, based on the existence of a pathway by which pollutants may impact on these receptors. Soil Guideline Values (SGVs) for a series of contaminants were

derived using the Contaminated Land Exposure Assessment (CLEA) model (DEFRA and Environment Agency 2002a). This model estimates exposures to soil contaminants for those living, working and/or playing on contaminated sites. In 2008, these SGVs were withdrawn by the Environment Agency and new SGVs were published in 2009 for Hg, Ni, Se, As, Cd (EA 2009a, b, c, d, e) and for some organic compounds. SGVs do not represent the threshold levels at which a significant possibility of significant harm (SPOSH) occurs nor do they automatically represent an unacceptable intake by humans but they can be considered a useful starting point for a risk assessment (DEFRA 2008).

Barraclough (2007) used aqua-regia digestion to determine the “ambient background” heavy metal concentrations in UK soils. The heavy metal concentrations published in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland 1992) were derived after aqua-regia digestion according to the procedure of McGrath and Cunliffe (1985).

Geochemical “baseline” or “threshold” values change depending on the geology of a region, and on a more local basis due to overburden and soil pedogenetic processes. Regional geochemical baselines obtained from sediment samples depend on the material analysed, such as bulk samples, sand (<2 mm), mud (<63 µm) or other fine-grained fractions. The British Geological Survey’s geochemical mapping of the UK was initially based on the analysis of the <150-µm fraction of stream sediments and more recently has included also stream water and the <2-mm fraction of soils (Fordyce et al. 2005). At the time of writing, soil geochemical data for the south-west of England were not available from the British Geological Survey G-BASE (Geochemical Baseline Survey of the Environment). However, a number of publications (e.g. McGrath and Loveland 1992; Black et al. 2002; Rieuwerts et al. 2006; Barraclough 2007) provide data on heavy metal levels in soils of this region of the UK, including studies of land contaminated by past mining activities or known to have high natural levels of potentially toxic substances (e.g. Abrahams and Thornton 1987; Davies and Ballinger 1990; Fuge et al. 1991). “Baseline” data for Europe, partly based on soil composition, can be found in the atlas produced by the Forum of European Geological Surveys (FOREGS 2005, 2006).

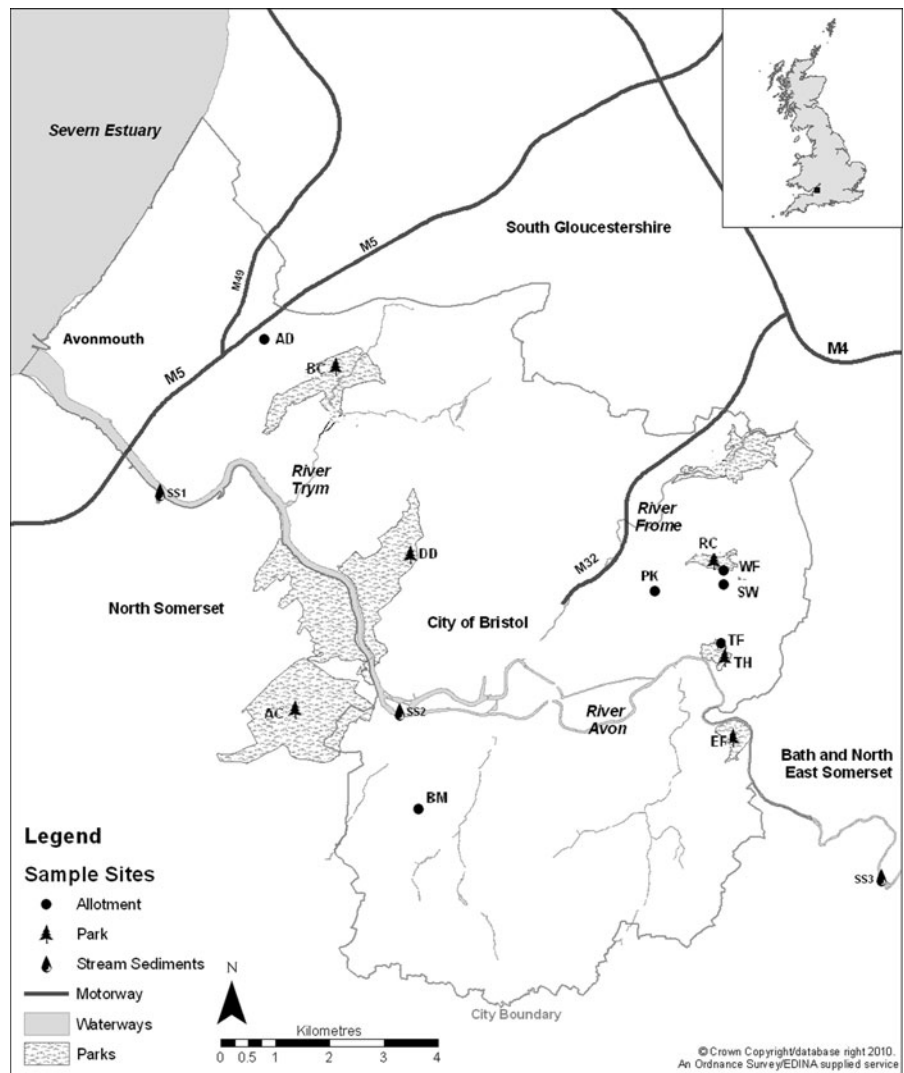
As in other regions of the UK, local authorities have become under increasing pressure from allotment holders worried about the quality of the soil in their allocated plots of land. In the city of Bristol, there are currently 99 allotment sites (Bristol City Council 2006). Within the city boundary, there are also many parks and green areas (Fig. 1), such as Blaise Castle Estate, Clifton and Durdham Downs, Leigh Woods, Ashton Court Estate and Oldbury Court Estate/Snuff Mills. Given the paucity of data on the soil characteristics in the Bristol district, an initial survey of pH, organic matter content, texture and “pseudo-total” (aqua-regia extracted) heavy metal composition of the topsoil (15 cm) of the main parks and of selected allotments of the city of Bristol was completed. The results are described in detail in a separate publication (Giusti 2011). This work focuses on the “near-total” concentration of 34 elements in the same soil samples, as explained below. This information was used (1) to identify sites that could be classified as “contaminated” on the basis of existing UK Soil Guideline Values (SGVs), (2) to define heavy metal “inspection levels” after estimating geochemical thresholds based on local soil and bedrock near-total composition and (3) to determine the genetic relationship between soil and bedrock by comparing the rare earth elements (REEs) composition of both media. Stream sediment data were also obtained to aid the overall interpretation of the geochemistry of the catchment area.

## Materials and methods

### Sampling and analytical methods

The “near-total” composition of soils was obtained during this stage of the investigation. The term “near-total” refers to the fact that a sample digestion in very strong acids does not necessarily dissolve refractory minerals. In order to reduce the number of analyses, aliquots of composite samples were processed. During the first stage of this investigation (Giusti 2011), 216 soil samples were collected from allotments and green areas in Bristol. At each sampling location, three samples were taken from the corners of an equilateral triangle of 3-m sides. After drying at 40 °C and sieving through a 2-mm stainless steel mesh, aliquots of the 3 individual samples collected at each site were

**Fig. 1** Map of the study area showing the boundaries of the city of Bristol, the location of the parks, green areas and allotment sites investigated in this study, in addition to the sediment sampling sites along the River Avon. Parks and green areas: AC, Ashton Court; BC, Blaise Castle Estate; DD, Durdham Downs; RC, Ridgeway and Coombe Brook Valley; TH, Troopers Hill. Allotment sites: AD, Atwood Drive; PK, Packers; WF, Whitefield; TF, The Farm. Sediments: SS1, Pill; SS2, Hotwells; SS3, Keynsham



separated and analysed by ICP-OES after aqua-regia digestion. Organic matter content and pH were determined at this stage. The remaining soil material was thoroughly mixed in order to produce a composite sample for each site. These composite aliquots were used for the determination of soil texture and of the near-total heavy metal concentrations reported here for each site. More specifically, the soil samples from 5 parks or green areas (Ashton Court, Blaise Castle, Durdham Downs, Ridgeway and Coombe Brook Valley, Troopers Hill) and 4 allotments (Atwood Drive, Packers, Whitefield, the Farm) were ground to a fine powder and digested using a “total” decomposition method (HF–HNO<sub>3</sub>–HCl–HClO<sub>4</sub>) to determine the concentration of Al, Ca, Fe, K, Mg, Na,

As, Ba, Cd, Cr, Cu, Li, Mn, Ni, P, Pb, Sc, Ti, V, Zn, Y and the rare earth elements Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Yb) by ICP-MS (X Series II, Thermo Electron, USA) and/or by ICP-OES (Vista-PRO, Varian Inc.), as appropriate. Overall, 84 soil samples were analysed (42 from allotments and 42 from parks/green areas). Microwave-assisted digestion of 0.500 ± 0.001 g sample aliquots was carried out in high-purity reagents (5.0 mL HNO<sub>3</sub>, 10 mL HF and 2.0 mL HClO<sub>4</sub>), followed by evaporation and further addition of 8 mL aqua regia as described by Lin et al. (2007). Aliquots for ICP-MS analysis were diluted 1,000 times with 0.25 M HNO<sub>3</sub>. Aliquots to be used for ICP-OES analysis were diluted 25 times with 0.25 M HNO<sub>3</sub>.

Rock samples were obtained from 14 outcrops (6 of limestone and 8 of sandstone) in the 7 areas of Bristol shown in Online Resource 1. After crushing, about 500 g of unweathered fragments was milled to a very fine powder and quartered, and aliquots digested using the HF–HNO<sub>3</sub>–HCl–HClO<sub>4</sub> method described above.

Sediment samples were collected at 3 sites (SS1, SS2 and SS3) along the Avon River (SS1 at Pill near the estuary, SS2 at Hotwells near the City Centre and SS3 at Keynsham, east of the city of Bristol). At each site, 3 separate grab samples (of approximately 2 kg each, wet weight) were collected at 15–20 m distance from each other. They were wet sieved through a 2-mm stainless steel mesh to produce “bulk” samples that were dried at 40 °C in a drying cabinet. After milling to a fine powder, aliquots of quartered samples were digested using the same HF–HNO<sub>3</sub>–HCl–HClO<sub>4</sub> digestion method described for soil and rock samples.

The results obtained for Al, Ca, K, Mg, Na and Fe are reported here as percentage oxides in order to facilitate comparisons with published information.

#### Quality control

Soil reference standards (GSS1, GSS2, GSS3 and GSS8), sediment reference standards (river sediment GBW08301, marine sediment GBW07313) and a rock standard (Moroccan phosphate rock BCR 32) were analysed for quality control purposes. The standard reference materials GSS1, GSS2, GSS3 and GSS8 (National Research Center for Geoanalysis, Chinese Academy of Geological Sciences of China) comprise different types of soil material: GSS1 is a dark brown podzolic soil from Yichun (Heilongjiang), in a district known for its Pb and Zn mineralisation; GSS2 is a composite soil from various sites in the arid region of Beinaimiao (Inner Mongolia); GSS3 is a yellow–brown soil from Shandong; and GSS8 is a loess soil from Luochuan (Shaaxi). GBW08301 (National Research Center for Certified Reference Materials, Beijing, China) is a river sediment collected from the Xiangjiang River in the Hunan Province, and GBW07313 (Institute of Marine Geology, Qingdao) was collected in the central part of the Pacific Ocean. The Moroccan phosphate rock BCR 32 (Community Bureau of Reference, EU, Brussels, Belgium) was included because the high concentration of elements such as Ca, P and F in the matrix of this material is a source of interferences when determining trace elements.

Element recovery in all certified standards was in the range of 92–110 % of the certified concentration. Certified standards and aliquots of selected samples were routinely reanalysed to assess reproducibility. Replicate analyses showed variation coefficients of <10 % for all trace metals and <5 % for the major metals. Blank values were negligible. The detection limit ( $3SD \times$  total procedure blank) was in the range of 0.05–0.1 % for the macroelements, 0.1 mg/kg for the REEs (except for Ce and La: about 1 mg/kg), 0.03 mg/kg Cd, 0.7 mg/kg As, 0.8 mg/kg Cu, 1 mg/kg Ni and Pb, 2 mg/kg Zn and Cr, and 10 mg/kg Mn and P.

#### Statistical analysis of the data

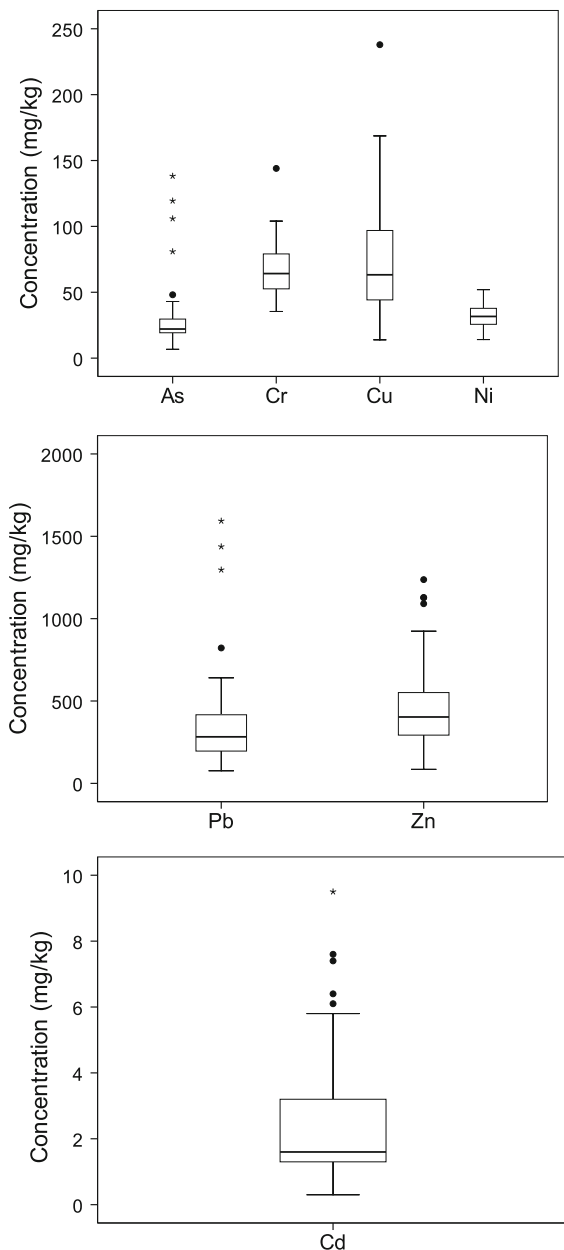
Raw data were analysed with Microsoft Excel and SPSS 17.0 software for basic statistical parameters and for exploratory analysis to test for normality. The distribution pattern of the 84 “near-total” results showed some departure from normality for most elements. Kolmogorov–Smirnov test gave significant values only for CaO, Na<sub>2</sub>O, Cr, Ni and Y. However, departure from normality is caused by a limited number of extreme outliers.

The identification of soil “threshold” values and of “statistically extreme” values were based (1) on the calculation of median “near-total” heavy metal values, (2) on the upper whisker of box-plots (when the % of outliers was less than 10 %) and (3) on the 95th percentile of cumulative probability plots (Reimann et al. 2005). Cumulative plots allowed a quick visualisation of the presence of multiple populations and outliers. The “threshold” values were also compared to data obtained from local bedrock samples.

#### Results

The results are presented in the form of box-plots, cumulative frequency distribution plots and correlation plots. Standard Tukey’s box-plots for near-total As, Cr, Cu, Ni, Pb, Zn and Cd of the 84 soil samples are provided in Fig. 2. These allowed the identification of outliers exceeding  $1.5 \times$  (upper hinge – lower hinge). Box-plots were also produced for each individual park and allotment, for limestones, sandstones and stream sediments (as shown in Online Resource 4). The REE data are discussed in a separate section below.





**Fig. 2** Tukey's box-plots of near-total heavy metals As, Cr, Cu, Ni, Pb, Zn and Cd in Bristol topsoil ( $n = 84$ ). The stars show the far outliers (i.e. those that exceed the value of the upper hinge plus 3 times the hinge width). The solid circles are the outliers that exceed  $1.5 \times$  (upper hinge – lower hinge) but that are less than the upper hinge plus 3 times the hinge width

The Tukey's box-plots of Fig. 2 indicate the presence of very few outliers, the most notable being for Pb (1,296–1,593 mg/kg) and Zn (1,091–1,237 mg/kg) in soils samples from the park of Durdham Downs,

and for Cd at Blaise Castle park (9.5 mg/kg) and Atwood Drive allotments (6.1–7.6 mg/kg). The four As “far outliers” are from Packers allotments, and the remaining As outlier is a soil from Durdham Downs. One Cr outlier is from Whitefield allotments, and the only Cu outlier is from Troopers Hill.

The soils of parks and green areas were found (Giusti 2011) to be more acidic (median pH range, 4.2–6.6) than allotment soils (median pH range, 6.5–6.8), probably due to the soil amendments applied to the latter. The lowest pH values (as low as 3.5) were recorded for the sandy clay soils of Troopers Hill. The organic matter content was generally high, ranging 9–30 %.

As far as the macroelements are concerned, most of the soils from parks and allotments fall within a relatively narrow compositional range, that is, 6–12 %  $\text{Al}_2\text{O}_3$ , 4–6 %  $\text{Fe}_2\text{O}_3$ , 1–4 % CaO, 1–2 %  $\text{K}_2\text{O}$ , up to about 1 % MgO, 0.2–0.4 %  $\text{Na}_2\text{O}$ , 0.15–0.40 % Ti and less than 0.15 % Ba. The most notable exceptions are the soils of Atwood Drive allotments, with 12–14 %  $\text{Al}_2\text{O}_3$ , 3.5–4.4 %  $\text{K}_2\text{O}$ , 3–4 % MgO and 0.4–0.5 %  $\text{Na}_2\text{O}$ . These allotment soils also have significantly higher Cd (4.8–7.6 mg/kg). The most abundant trace elements are Pb and Zn, especially in the park soils of Durdham Downs (up to 1,593 mg/kg Pb and 1,237 mg/kg Zn). Three allotments (Parkers, Whitefield and the Farm) stand out for higher P (>2,000 mg/kg) and Cu (up to 238 mg/kg). High Cu was also found at Troopers Hill Nature Reserve (up to 169 mg/kg).

Table 1 lists the “near-total” concentration of heavy metals extracted from limestone, sandstone and sediments. These are also compared to some examples of “total” heavy metal levels reported in the literature for the continental crust.

The REE composition of soils, rocks and sediments is reported in Online Resource 5. Figure 3 shows the normalised REE composition of (a) limestone and (b) sandstone/mudstone typical of the local bedrock and (c) the REE compositional variations in sediments from the Avon River. The REE trends found for the soils of parks and allotments are so similar that only two representative examples (the soils of Blaise Castle park and Atwood Drive allotments) are shown in Fig. 3d, e. The REEs include the elements with atomic number 57–71, that is, from lanthanum to lutetium. Based on their atomic weight, they are conventionally divided into light REEs (LREEs) and heavy REEs

**Table 1** “Near-total” heavy metals (values in mg/kg, except for Fe shown as % Fe<sub>2</sub>O<sub>3</sub>) in rocks of and sediments of the study area, and comparison with average crustal material

Near-totals	As	Cd	Cr	Cu	Zn	Pb	Ni	Mn	Fe <sub>2</sub> O <sub>3</sub> (%)
Limestone ( <i>n</i> = 6)									
Mean	5.1	0.5	16.3	2.5	19.0	8.0	7.5	173.2	0.5
Median	3.8	0.5	15.4	2.0	12.5	5.0	6.3	86.5	0.3
SD	3.9	0.1	7.4	1.4	14.3	5.9	2.8	158.0	0.6
Sandstone ( <i>n</i> = 7)									
Mean	5.8	0.7	213.9	8.6	47.3	13.9	22.9	168.1	2.3
Median	5.0	0.1	197.9	5.1	41.0	13.0	21.0	99.0	2.4
SD	2.8	1.6	63.2	6.5	28.5	8.9	10.1	133.0	1.1
Ironstone ( <i>n</i> = 1)	49.0	0.7	114.5	3.6	1,157	132.0	89.7	275.0	54.7
Sediments									
Mean SS1 ( <i>n</i> = 3)	11.8	0.3	96.1	36.5	258.0	85.0	40.3	940.3	5.7
SD SS1	0.3	0	2.9	0.3	1.7	3.6	0.2	11.0	0.1
Mean SS2 ( <i>n</i> = 3)	13.9	0.3	93.5	32.6	239.3	76.3	38.7	912.0	5.5
SD SS2	0.7	0	0.5	1.9	11.1	3.5	2.5	9.5	0.1
Mean SS3 ( <i>n</i> = 3)	13.4	0.4	25.3	15.7	106.7	33.0	10.8	325.7	1.8
SD SS3	0.4	0.1	1.8	0.9	3.8	2.0	0.8	12.3	0.1
Crustal material									
Limestone <sup>a</sup>	1	0.04	10	4	25	8	12	1,100	0.5
Shale <sup>a</sup>	15	0.3	100	50	100	20	70	850	6.7
Sandstone <sup>b</sup>	1	0.05	35	30	30	10	9	460	0.38 <sup>c</sup>

<sup>a</sup> Turekian and Wedepohl (1961); Levinson (1974)

<sup>b</sup> Alloway (1990)

<sup>c</sup> Pettijohn et al. (1987)

(HREEs), the former comprising the REEs from lanthanum (La) to gadolinium Gd), and the latter including those from terbium (Tb) to lutetium (Lu). An overall summary of the HREE and LREE characteristics of soils, bedrock and sediments is provided in Online Resources 6.

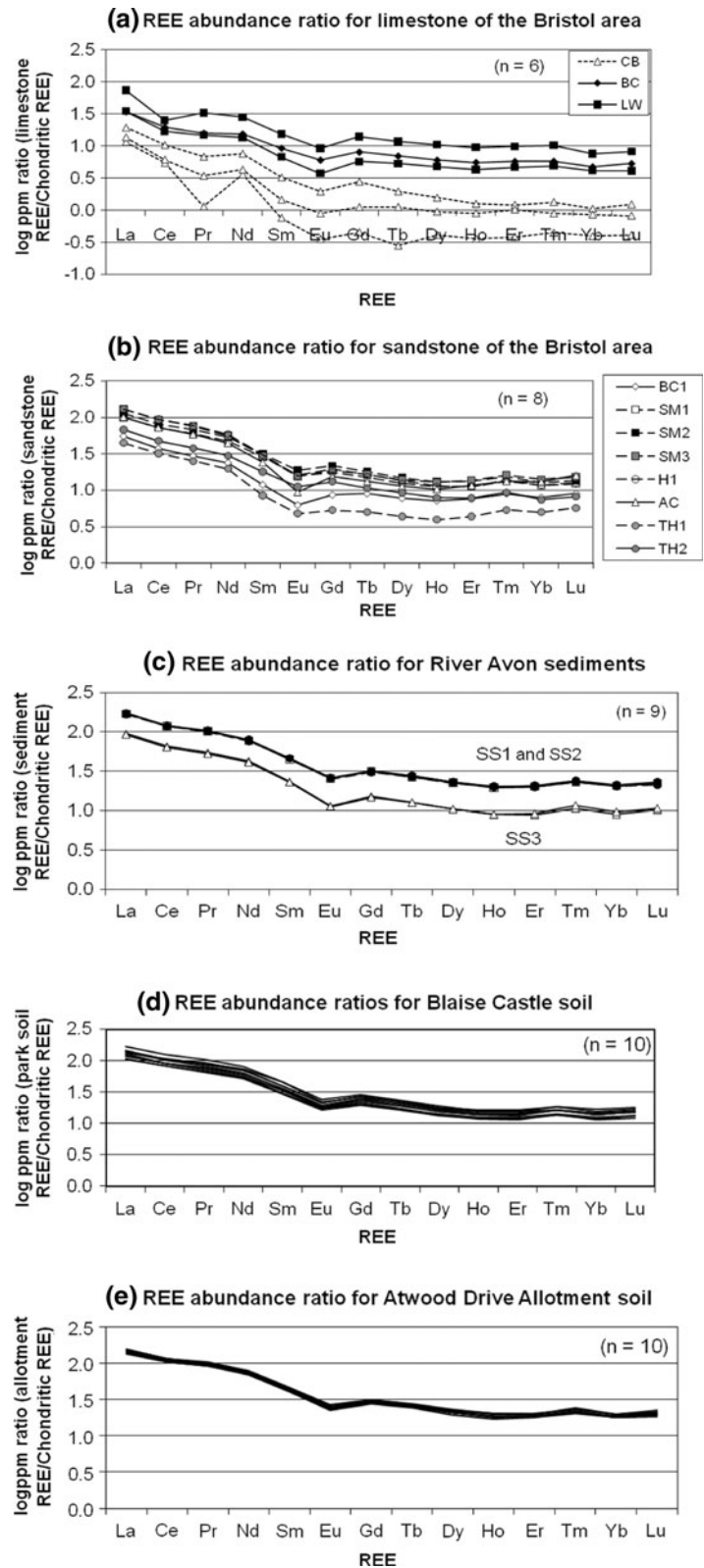
## Discussion

Except for Cd, heavy metals in sandstone are present in concentrations that are significantly higher than those found in limestone. In limestone, the elements As, Cd and Cr are more enriched than in typical crustal limestone (e.g. Turekian and Wedepohl 1961). Also, the sandstone from Bristol is enriched in Cr, Ni, Zn, Cd and As compared to the sandstone analysed by Pettijohn et al. (1987), though visible evidence of mineralisation in sandstone from Bristol was noticed only in one sample that can be classified as ironstone

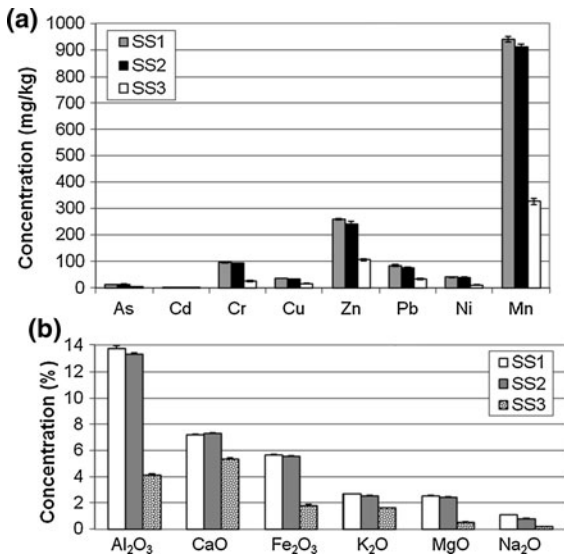
(about 55 % Fe<sub>2</sub>O<sub>3</sub>). Though both sandstone and limestone bedrocks were found to have relatively high levels of heavy metals, their enrichment is not as pronounced as in the Carboniferous Limestone from the Mendip Hills region of north Somerset (UK) analysed by Fuge et al. (1991). Only one sample of sandstone was found to be strongly enriched in Fe, As, Zn, Pb, Ni and Mn. Unfortunately, the mudstone bedrock of the Bristol area was not studied sufficiently in our work to enable an assessment of its potential contribution to the soil heavy metal composition. In rock samples, the main associations between macroelements and trace heavy metals were found for sandstone (*n* = 7), namely: Zn versus Fe<sub>2</sub>O<sub>3</sub> ( $r^2 = 0.8751$ ), Ni versus Al<sub>2</sub>O<sub>3</sub>, ( $r^2 = 0.8772$ ), Ni versus MgO ( $r^2 = 0.9018$ ) and Ni versus K<sub>2</sub>O ( $r^2 = 0.9048$ ).

Bulk sediments show heavy metal enrichment (especially Mn, Zn, Pb, Cr, Ni, As) at sites closer to the Avon River estuary (Fig. 4a), and the main cations (Al, Ca, Fe, K, Mg, Na) follow a similar trend

**Fig. 3** REEs in **a** limestone and **b** sandstone from the Bristol district, and **c** in bulk sediments from the Bristol Avon River, and in Bristol soils from **d** Blaise Castle and **e** Atwood Drive allotments. All REE data are normalised to the chondritic averages of Anders and Ebihara (1982). *CB*, Clifton and Durdham Downs; *BC*, Blaise Castle Estate; *LW*, Lee Woods (North Somerset); *SM*, Snuff Mills; *H*, Hanham; *AC*, Ashton Court; *TH*, Troopers Hill. *SS1*, Pill; *SS2*, Hotwells; *SS3*, Keynsham







**Fig. 4** **a** Near-total heavy metals, and **b** oxides of macroelements in bulk sediment of the Bristol Avon River. SS1, Pill; SS2, Hotwells; SS3, Keynsham

(Fig. 4b). The sediments (SS1) collected near the estuary were very rich in clay- and silt-sized particles (<63 μm), together accounting for more than 90 % of the total weight (after the removal of particles larger than 2 mm). The mud fraction was about 85 % by weight in the samples collected in the city centre (SS2). The sediments from Keynsham (SS3) were mostly sand and pebbles, with sand accounting for about 70 % of the <2-mm fraction.

The determination of geochemical baselines for a catchment area and the assessment of contamination have often been based on a regression technique that establishes a mathematical relationship between the “total” concentration of heavy metals in stream sediments and the “total” concentration of a conservative element (e.g. Al, Li, Sc, Fe) thought to be of natural origin (Loring and Rantala 1992). The assumption is that the conservative element varies with grain size due to its association with minerals such as micas or clays, and thus it can be used to “normalise” the data, that is, to compensate for grain size variations. A similar approach has been applied by various authors (e.g. Horckmans et al. 2005; Zhang et al. 2007) to the study of contamination in soil. Regression calculations for the entire Bristol soil data set show very significant (at least  $p < 0.01$ ) linear correlations between pairs of the elements Al, Li, Sc, Cr, Ni, Ti, V and the REEs. For some of these

elements, even stronger correlations were found for subpopulations such as the soils underlain by sandstone (i.e. all allotments and the two green areas of Troopers Hill and Ridgeway and Coombe Brook Valley). The weakest correlations are typical of the soils of the 3 parks (Ashton Court, Blaise Castle and Durdham Downs) underlain by limestone and dolomitic conglomerate. This is due to the presence of outliers and to different trends for each individual park. Online Resource 7 illustrates the trends for Al<sub>2</sub>O<sub>3</sub> versus Li. It is useful to note the similar trends shown by sandstone bedrock and soils underlain by sandstone bedrock. Similar associations were found for other parameters (e.g. Al<sub>2</sub>O<sub>3</sub> vs. Sc, Al<sub>2</sub>O<sub>3</sub> vs. Li, Al<sub>2</sub>O<sub>3</sub> vs. Ti, Al<sub>2</sub>O<sub>3</sub> vs. Cr, Al<sub>2</sub>O<sub>3</sub> vs. V, Ti vs. V, Sc vs. Cr, Sc vs. Ni, Sc vs. Ti, Sc vs. V, Sc vs. Li, Li vs. Cr). These trends are strongly indicative of a natural origin of all these elements, including Cr and Ni. Theoretically, any of these elements could be used as a normaliser to calculate the pristine values of other heavy metals. Unfortunately, scatter-plots of most heavy metals and any of the normaliser elements have too many outliers, and the choice of a regression line would be quite subjective. This is likely to be due to the lack of a linear relationship between the normaliser concentration and the percentage of fine-grained particles (either the clay fraction or the mud fraction) in the soil. Exceptions include specific allotment and park soils, such as most (8 out of 10) of the soils of Blaise Castle analysed that give a significant Sc versus Zn correlation ( $r^2 = 0.905$ ). The two outliers had 318 mg/kg and 537 mg/kg excess Zn.

With the exception of Ca (up to 52.1 % CaO), the percentage of the main metals (Al, Fe, K, Na and Mg) in limestone is quite small compared to those found in stream sediments and soil (Online Resource 4). The range of Al<sub>2</sub>O<sub>3</sub> in soil is similar to the range found in sediments (about 4–14 %) and in sandstone (about 2–12 %). Atwood Drive allotment soils stand out for higher K<sub>2</sub>O (around 4 %) and MgO (also around 4 %). Based on their texture, the Atwood Drive soils can be classified as clay (41–58 % clay) and the clay minerals are likely to account for much of the soil composition. There is more Na<sub>2</sub>O in sediments (median = 0.8 %) and sandstone (0.6 %) than in soils (median = 0.3 %). Some of the Na in sediments is due to sea salt carried upstream during tidal periods. Fe<sub>2</sub>O<sub>3</sub> in soils (median = 5 %) and estuarine sediments (median = 5.6 %) is enriched compared to sandstone

(median = 2.4 %) and limestone (0.3 %). Soils and sediments also show median Mn levels that are 4–5 times those found in sandstone and limestone (median = 99.0 and 86.5 mg/kg, respectively). The increase in heavy metal levels during weathering, soil formation and diagenetic processes is reflected in the comparable metal range found in soils and sediments.

Strong associations between Zn and Cd ( $r^2 = 0.9585$ ), Pb and Cd ( $r^2 = 0.8928$ ), and Pb and Zn ( $r^2 = 0.8159$ ) were found for the soils of Atwood Drive allotments, and between Zn and Cd ( $r^2 = 0.7756$ ) in Blaise Castle park soils. The number of soil samples from Durdham Downs is insufficient to draw a conclusion. The association between P and Cd ( $r^2 = 0.9301$ ;  $n = 9$ ) at Troopers Hill Nature Reserve could be due to the high % of clay (36–43 %).

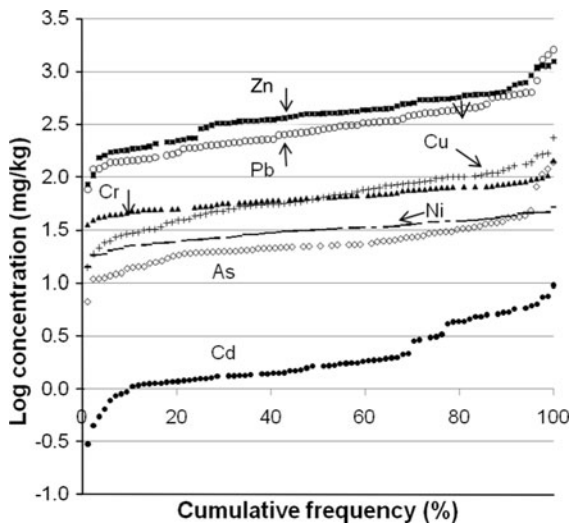
Most trace elements in soil are enriched compared to their abundance in their respective unweathered bedrock material (Online Resource 8). In the case of park soils on limestone terrain (two examples are shown in Online Resource 8), enrichment is greater for Ba, K, Ti, Pb, Al, Fe, P, Zn, Li, Na, Cu, Mn (10 × to 100 ×), whereas Ca would appear to be the only element depleted during weathering. In the case of allotment sites on sandstone (two examples are also shown in Online Resource 8), the elements Pb, Zn, Cu, Cd, As, P and Ca are typically enriched. Depletion of K, Mg and Na seems typical of soils on sandstone bedrock. Atwood Drive is the only exception, showing only depletion of Na (among the macroelements) during weathering. Surprisingly, some Cr also seems to have been lost as a result of the weathering of sandstone. Normally, Cr is considered to be one of the least mobile elements during weathering, though there is evidence of significant Cr mobilisation during lateritic weathering (McFarlane et al. 1994). Elements such as Ca, P and Cd may have been added to the allotment soils via fertiliser applications. Assuming that the soils presently overlaying limestone terrain derived mostly from sandstone (the last two examples in Online Resource 8 refer to Ashton Court and Blaise Castle), the estimates of relative element enrichment or depletion become very similar for the entire district.

Definition of “inspection levels” of heavy metals in soil

Cumulative frequency distribution curves and Tukey’s box-plots were used to try and define “inspection

levels” of heavy metals in soil that may be referred to by local authorities during a preliminary screening process. The presence of inflection points in the cumulative frequency distribution curves of Fig. 5 provides statistical evidence that different subpopulations of data are present among the soil results, particularly in the case of Zn and Cd. This in turn means that the choice of a single-value inspection level for this district is inappropriate. However, the definition of an indicative “upper limit” or “threshold level” based on the 95th percentile and/or on the upper Tukey’s box-plot whisker may be justified as a preliminary inspection recommendation. These values are listed in Table 2, together with the median “ambient background” values for England published in the soil survey carried out by Barraclough (2007), and the median and threshold range previously estimated by Giusti (2011) with pseudo-total data. The As threshold range (22–45 mg/kg) may appear quite high. However, as clearly shown by the As map of Europe published by FOREGS (2005, 2006), similar As values are common in the south-west of England due to the presence of relatively old and fine-grained soils less affected by glaciations than other regions of northern Europe (Reimann et al. 2009). The adoption of a screening value equivalent to the median As concentration (22 mg/kg) would cause serious concern in the Bristol region where most soils have higher As content. In this respect, the present UK SGVs for As in allotment soils (43 mg/kg) and in soils for residential use (32 mg/kg) are similar to the As upper threshold range obtained by statistical calculations. All Ni values in soil are well below the UK SGVs of 230 and 130 mg/kg for the two types of land use, respectively. No other relevant SGVs were available at the time of writing. Table 3 lists the median and upper background levels of heavy metals in sandstone and limestone defined using box-plots of near-total heavy metals in local bedrock.

During the past centuries, diffuse sources of trace elements (such as domestic and industrial coal combustion, metal smelting and traffic) must have contributed a fraction of the heavy metals present in Bristol soils and thus increased their background concentrations. The statistical methods used here to arrive at a range of “threshold levels” are useful for the identification of sites of significant local pollution. Identifying contamination from diffuse pollution is more complicated, and for some trace elements, this



**Fig. 5** Cumulative frequency distribution curves of log-transformed near-total As, Cd, Cu, Cr, Ni, Pb and Zn concentrations in 84 samples of Bristol soil

source may have left a signature only in specific phases (e.g. litter, organic matter, clay minerals, Al-, Fe- and Mn-(hydr)oxides of the top few centimetres of soil.

Assessment of potential risks to human health

The assessment of health risks associated with contaminated land requires the identification of a contaminant source, a pathway that can expose a receptor to the contaminant and a receptor. As defined by Part 2a of the Environmental Protection Act 1990, land can only be designated as contaminated where it

**Table 3** Median and background levels (mg/kg) defined on the basis of box-plots of near-total heavy metals in local bedrock

	Median, sandstone (n = 7)	Median, limestone (n = 6)	Upper box-plot whisker (sandstone)	Upper box-plot whisker (limestone)
As	5.0	3.8	13.7	4.6
Cd	0.1	0.45	0.32	0.98
Cr	197.9	15.4	313.3	33.3
Cu	5.1	2.0	20.3	5.0
Pb	41.0	12.5	36.3	31.5
Ni	13.0	5.0	58.1	19.1
Zn	21.0	6.3	117.3	76.5

is causing an unacceptable risk to human health or other specific receptors.

The procedure for investigating a potentially contaminated site should meet the criteria outlined in the Contaminated land Report CRL11 on Model Procedures for the Management of Land Contamination (DEFRA and Environment Agency 2002b). If the need for an investigation is identified, the site must enter a tiered risk assessment process that includes a Phase I (a preliminary risk assessment via a desk study), a Phase II (a generic quantitative risk assessment and, if necessary, a detailed quantitative risk assessment) and a Phase III (remediation strategy). After Phase I, a preliminary conceptual model linking source, pathway and receptor can be produced.

The work presented here provides background information for a Phase I desk study (preliminary risk assessment) and can be useful when deciding on site-

**Table 2** Suggested threshold ranges based on Tukey’s upper box-plot whisker and 95th percentile

	English “ambient soil background” (Barraclough 2007)	Median (pseudo-totals) (Giusti 2011)	Median (near-totals)	95th percentile	Upper box-plot whisker	Threshold range (pseudo-totals) (Giusti 2011)	Threshold range (near-totals)
As	8.32	21.7	22.1	74.3	45.3	41–56	45–74
Cd	0.31	1.1	1.6	6.1	6.0	4.7–4.9	6
Cr	29.5	23.1	64.2	96.3	119.8	36–47	96–120
Cu	17.4	60.1	63.3	154.5	176.8	120–135	155–177
Pb	40.7	210.1	282.5	640.0	738.1	504–558	640–738
Ni	16.4	21.0	31.7	45.9	55.4	32–33	46–55
Zn	79.5	272.6	401.4	1,065.8	936.2	560–567	936–1,066

Median and 95th percentiles of near-total heavy metals (mg/kg) were obtained assuming that all 84 soil samples are part of the same population. Median and threshold ranges previously obtained from pseudo-total data and English “ambient soil background” are also provided for comparison

specific risk assessment criteria (Phase III). Based on the soil heavy metal levels found in this work, the soils that would require more scrutiny after a Phase I desk study are some of the soils of Durdham Downs park due to their Pb and Zn enrichment, the allotment soils of Atwood Drive due to their high Cd content and Packers allotment soils in view of their As concentration. Also, some of the land in the Troopers Hill area has soils showing relatively high levels of As and Cu.

In case of allotment soils, the main exposure pathways include consumption of site-grown produce, direct ingestion of soil (especially in the case of children), skin contact with soil and inhalation of soil-derived dust. The main exposure pathways in the parks and green areas are soil ingestion (mostly by children) and the occasional consumption of wild berries and mushrooms; at Durdham Downs, the land showing high Pb levels is rarely used for sports or other recreational activities and so exposure via skin contact with soil or dust inhalation is likely to be minimum.

A preliminary analysis of produce from Atwood Drive (Giusti, unpublished data) has indicated that produce grown on the plots of this allotment is not a major accumulator and that the concentration of Cd and other heavy metals in produce is very small and not exceeding guidelines. Similar conclusions (S. Clampin, pers.comm., April 19, 2012) were reached for the levels of As at Packers allotments after an investigation commissioned by Bristol City Council. Therefore, consumption of locally grown produce would not be a major risk to human health. The total amount of heavy metals in soil is not a useful guide to their uptake by plants and to the bioavailable and bioaccessible fractions once plants or soil particles are ingested. The potential risk associated with direct ingestion of soil can be estimated using a bioaccessibility test (e.g. Ruby et al. 1996; Cave et al. 2003; Roussel et al. 2010). This work is in progress and will be published elsewhere.

#### The REEs as tracers of parent material

The trends defined by the soil REEs on the chondrite-normalised plots of Fig. 3 are very similar for both sandstone and limestone, with typical fractionation of the LREEs from the HREEs, and a negative Eu anomaly. However, there are large differences in absolute concentrations of REEs, especially in the case of limestone from different outcrops (Fig. 3a). The

REE concentration in sandstone is typically 2–5 times the concentration in limestone. The variations found in sandstone are likely to be due to the different texture of the sediment from which sandstone originated. Limestone from the Clifton area of Bristol (near the Avon gorge) is less enriched in REEs than limestone from Lee Woods in North Somerset. This difference can be related to the lower concentration of Al, Fe and P in Clifton limestone. Small amounts of phosphates, amorphous or crystalline Fe oxides or Fe nodules and silicate minerals can affect the REE characteristics of limestone.

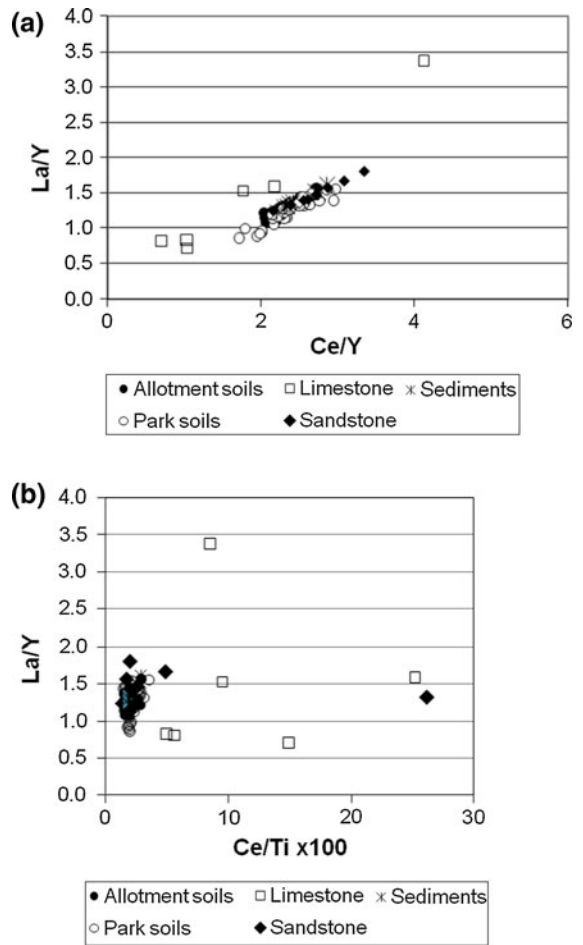
The REE patterns for the soil samples provide evidence of a similar fingerprint between local soils and sandstone. The ratio of normalised REEs in soils to normalised REEs in sandstone ranges between 1.0 and 1.8, showing very little or moderate enrichment in soil REEs during soil formation. The highest ratios are typical of Atwood Drive and Whitefield allotments, and of the parks of Ashton Court, Blaise Castle and Durdham Downs. By contrast, assuming that limestone is the parent rock of the overlying park soils (i.e. assuming that these are residual soils, as opposed to transported soils) would lead to higher soil/limestone REE ratios (3.6–7.4). This cannot be excluded and would indicate that a larger volume of limestone was weathered compared to the volume of sandstone removed by weathering. However, the REE concentrations and REE pattern (especially of the HREEs) found in some of the limestone samples from Lee Woods and Blaise Castle show similarities to those found in sandstone and in most of the soils, the main difference being a high Ce ratio (3.5–4.1) due to a Ce anomaly in limestone. Mass balance calculations would be required to interpret the LREE/HREE enrichment during rock weathering. The limestone sampled in the Clifton area of Bristol shows a praseodymium anomaly. This may be due to a different biogenic carbonate content of some of the limestone formations of this area. Some of the limestone outcrops in the Bristol district are often very rich in fossilised remains of marine organisms (e.g. crinoids, corals and brachiopods). The soil REEs show highly significant positive correlation with Y, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Li, Ti, Sc, Cr, V. More importantly, most soil samples with high REE levels also show the highest concentration of Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Fe<sub>2</sub>O and Mn, indicating a likely association with clay minerals, and Al-, Fe- and Mn-(hydr)oxides. This points to the fact

that, in addition to the preferential leaching of HREEs over LREEs during weathering (Ma et al. 2002), soil processes (chemical weathering, adsorption, redox and pH condition) affected the absolute value of soil REEs via incorporation into secondary minerals. The preferential association of REEs with fine-grained particles can also be seen in sediment samples from the Avon River (Fig. 3c). The bulk samples from SS3 (Keynsham) are more coarse grained (mostly sand), and their normalised REE pattern shows lower REE concentrations than in the more fine-grained sediment from sites SS1 and SS2 located along the lower stretches of the Avon River. Regression calculations indicated a close association between soil composition and sandstone bedrock material. The REE patterns confirm a close similarity between REEs in sandstone and REEs in all soils of the Bristol district, as shown also by the median values of  $\sum$ LREEs and  $\sum$ HREEs for all soils, limestone, sandstone and bulk sediments (Online Resource 6). It is also apparent that most of these soils are enriched in both LREEs and HREEs compared to sandstone, indicating that other factors need to be considered. The most important of these are pedogenetic factors and the presence of a relatively high concentration of clay-sized particles.

Assuming (1) that the local bedrock material is the only soil parent material and (2) that elements such as Ce, Y, La and Ti are relatively immobile during weathering (Kabata-Pendias and Pendias 1984), the ratio of immobile trace elements in soil and bedrock should be quite similar. Figure 6a, b show that the clusters of soil samples ( $n = 82$ ), sediment samples ( $n = 9$ ) and sandstone samples ( $n = 8$ ) overlap (only one sandstone outlier in Fig. 6b), indicating a similar origin of the relatively immobile elements in most of these samples. Given the scatter of limestone samples in Fig. 6, soils are unlikely to have originated from this material and its influence has been of secondary importance.

### Conclusions

Bedrock composition and weathering processes were an important factor leading to the natural enrichment in heavy metals of many soils of this district. Extreme heavy metal values indicative of contamination (either natural or anthropogenic) are mostly confined to the parks of Durdham Downs (Pb and Zn), to Atwood



**Fig. 6** Comparison of less mobile elements in allotment soils ( $n = 83$ ), limestone ( $n = 6$ ), sandstone ( $n = 8$ ) and sediments ( $n = 9$ ) using **a** La/Y versus Ce/Y ratios and **b** La/Y versus Ce/Ti ratios. Assuming that these elements are relatively immobile under oxidising conditions, these ratios should remain unchanged for bedrock and soils during weathering processes. Nearly all samples of soil, sandstone and sediment form a cluster in the same region of the diagram, confirming that the assumptions are correct. All limestone samples are outliers

Drive allotments (Cd) and to Packers allotments (As). There is also evidence of Cu enrichment at Troopers Hill Nature Reserve. The clay-rich soils of Atwood Drive allotments and one sample (a sandy clay loam) from Blaise Castle show levels of Cd that exceed present UK soil guidelines. Given the location of these sites close to past anthropogenic sources of Zn, Pb and Cd (i.e. the Avonmouth smelter), the possibility that a fraction of these metals might have derived from atmospheric deposition cannot be ruled out. However, the high linear correlation between Zn, Pb and Cd in



the soils of Atwood Drive and the lack of outliers points to a natural origin of these metals. The Pb and Zn enrichment of the soils of Durdham Downs park can be explained by contamination due to past quarrying and metal extraction. Given the absence of natural sources of Cu in the Bristol district, the Cu anomaly at Troopers Hill allotments must be a legacy of past copper and brass production with ore imported from other regions of the UK. Some of the plots of land of Packers allotments and Troopers Hill have soils that exceed the present UK soil guideline values for As.

Published As and Cd “ambient background” for English soil do not appear to be applicable to the Bristol area given the fact that these values are already exceeded in the local bedrock. Regional-scale geochemical baselines are inappropriate at local scale level, especially in urban environments with a combination of natural and anthropogenic sources of heavy metals.

The REE composition and fractionation patterns found in soil, in bedrock and in sediments are very useful geochemical tools for the identification of soil parent material and lead to the conclusion that sandstone was the parent material of much of the soil cover of this region.

Near-total soil digestion extracted much more Cr, Cd, Pb, Ni and Zn than aqua-regia digestion, leading to higher estimated threshold level ranges. Thresholds derived from both data sets (pseudo-totals and near-totals) may be used at a preliminary screening stage, after which a study of the bioaccessibility of the heavy metals should give a more realistic assessment of the potential risk to humans due to exposure to the soils of the Bristol district.

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