GSUE: Urban geochemical mapping in Great Britain

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ABSTRACT:

The British Geological Survey is responsible for the national strategic geochemical survey of Great Britain. As part of this programme, the Geochemical Surveys of Urban Environments (GSUE) project was initiated in 1992 and to date, 21 cities have been mapped. Urban sampling is based upon the collection of top (0.05 to 0.20 m) and deeper (0.35 to 0.50 m) soil samples on a 500 m grid across the built environment (1 sample per 0.25 km^2). Samples are analysed for *c.* 46 total element concentrations by X-ray Fluorescence Spectrometry (XRFS), pH and loss on ignition (LOI) as an indicator of organic matter content. The data provide an overview of the urban geochemical signature and because they are collected as part of a national baseline programme, can be readily compared with soils in the rural hinterland to assess the extent of urban contamination. The data are of direct relevance to current UK land use planning, urban regeneration and contaminated land legislative regimes. An overview of the project and applications of the data to human health risk assessment, water quality protection and contaminant source identification are presented.

KEYWORDS:

Urban geochemical mapping; soil; contaminants; land quality; potentially harmful elements

INTRODUCTION

The British Geological Survey (BGS) is responsible for carrying out the national strategic geochemical survey of Great Britain and Northern Ireland, the Geochemical Baseline Survey of the Environment (G-BASE) programme. The programme began in the late 1960s in the north of the country and, working southwards, is due to complete coverage by 2020. The programme is based primarily on the collection of stream sediment samples at a density of 1 per 1.5 km^2, however, rural soil samples (at a sample density of 1 per 2 km^2) and a greater range of determinands in stream waters have been incorporated into the programme in more recent years (see Johnson *et al.* this volume). Historically, the programme avoided sampling in urban areas so that the rural geochemical baseline could be established.

However, at the start of the 1990s, United Kingdom (UK) government targets to build 60% of new homes (4.4 million) on brownfield sites by 2016 and city regeneration programmes lead to an increased interest in the quality of urban land (DETR 1998). In response to growing concerns about potentially harmful elements (PHE) in the urban environment and new statutory requirements for UK local authorities to manage contaminated land (Environmental Protection Act Part IIa 1990), urban geochemical mapping commenced in 1992.

The Geochemical Surveys of Urban Environments (GSUE) project, developed from preliminary studies carried out in collaboration with Imperial College, London in Wolverhampton and Richmond-on-Thames (Kelly *et al*. 1996; Bridge *et al.* 1997; Kelly 1997) and to date, 21 urban centres have been sampled (McMillan *et al.* 2001 and Fig. 1).

The concentrations of many PHE are enhanced in the urban environment as a result of atmospheric and terrestrial contamination and the nature of urban ground,

which is often disturbed and in-filled and bears little relation to the soils, bedrock and superficial cover of the surrounding rural hinterland (Thornton *et al.* 1985; Wong 1996; Birke & Rauch 2000; Mielke *et al.* 2000; Sanchez-Martin *et al.* 2000; Tijhuis *et al.* 2002; Imperato *et al*. 2003; Peltola & Astrom 2003). Even in completely undisturbed urban areas such as parks, many PHE signatures are elevated relative to the rural background due to atmospheric contamination, littering, urban surface run-off and other factors (Chronopoulos *et al.* 1997; Ander *et al.* 2001). Hence it is necessary to establish the overall urban signature so that areas of concern within a city can be highlighted and detailed site investigation and contamination studies can be assessed in terms of the urban geochemical profile in addition to the rural background. It should be noted that systematic urban surveys do not replace the need for site-specific contaminated land investigations; rather the data provide the citywide framework and context to more detailed assessments.

METHODS

Urban surveying is based upon the collection of soil samples on a systematic grid. Soils are sampled at a density of 4 per km^2 across the built-up area whereby each UK National Grid kilometre square as defined from 1: 25 000 scale topographic maps (Ordnance Survey®) is split into four 500 m x 500 m sub-cells. Samples are collected from open ground as close as possible to the centre of each 500 m cell. Typical locations for sampling include gardens, parks, sports fields, road verges, allotments, open spaces, schoolyards and waste ground. Whilst attempts are made to select the least disturbed area of open ground as close as possible to the centre of the 500 m cell, contamination is not purposefully avoided as the aim of the survey is to provide an overview of the urban geochemistry and not to establish a 'near natural' geochemical

baseline. Although the aim is a systematic survey, the regularity of the sampling grid is often constrained by the amount of surface sealing and accessibility of soils in the city environment (see Johnson *et al.* this volume).

A standard depth rather than horizon-based sampling strategy is adopted to be consistent with rural G-BASE soils (see Johnson *et al*. this volume) and because soil profiles in the urban environment are often poorly developed and disturbed. Surface (0.05 to 0.20 m) and profile (0.35 to 0.50 m) samples are collected using a handheld Dutch auger. Each sample is a composite of five sub-samples collected from the corners and centre of a 20 x 20 m square in accordance with standard G-BASE (Johnson *et al.* 2003) and international (Salminen *et al.* 1998) methods (Fig. 2). This sampling strategy provides information on the chemistry of near-surface soils, which may be influenced by atmospheric contamination, and of deeper soils, which should more closely represent substrate materials at each site. The sub-samples are homogenised at site to form one surface sample and one deeper sample from each location.

Observations of soil colour, depth and clast lithology and abundance are recorded at site, and the samples are classified into five textural groups (sand, sand-silt, silt, silt-clay and clay). Information on the location, geology, contamination, land use and other features required for data interpretation are also entered on a computer-compatible data-card in a standard G-BASE/GSUE format (see Johnson *et al.* this volume).

Following collection, the soils are air- and then freeze-dried at < 30 °C to prevent the volatilsation of Se and Hg. During the 1990s the surface soil samples were sieved to < 2 mm, the environmental standard whereas deeper soil samples were sieved to < 150 µm to be compatible with the rural stream sediment and soil data

collected under the G-BASE programme. However, since 2000 both surface and deeper soil samples have been sieved to < 2 mm to allow better down-profile comparisons. The samples are then homogenised, coned and quartered and a 30 g sub-sample ground in an agate planetary ball mill until 95 % is < 53 µm. The pulverised material is further sub-sampled to obtain portions for analysis. The number of determinands has increased from 18 in the early 1990s to the current suite of 46 total element concentrations by X-ray Fluorescence Spectrometry (XRFS) (Ingham & Vrebos 1994; Johnson *et al.* this volume). These include elements of concern in terms of contaminated land such as As, Cd, Cr, Ni, and Pb (Table 1). However, the major element composition (for example, CaO, K_2O, Fe_2O_3 and MnO), soil pH and loss on ignition (LOI), as an indicator of organic matter content, are also analysed as these factors can influence the mobility of PHE in soils. Soil pH is determined by adding 10 g of < 2 mm sample to 25 ml of 0.01M $CaCl_2.2H_2O$ (calcium chloride). The mixture is shaken to form a slurry prior to analysis by pH electrode. This method of pH determination generally gives lower results (0.5 pH units) than water based methods (Rowell 1994). LOI is determined on 2 g of < 2 mm material heated in a furnace and kept at 450 °C for a minimum of 4 hours.

Once preparation is completed, sample residue materials are stored in the GSUE sample archive where they form part of the BGS National Geoscience Data Centre collection (Johnson *et al.* this volume).

The analytical results undergo the rigorous quality assurance procedures followed by the G-BASE programme (Johnson *et al*. this volume). Systematic error in field sampling and analysis is monitored using a method based on randomised sample site numbers (Plant 1973). Field-based procedures at each stage of the sampling process are designed to minimise error (Johnson *et al.* 2003). Six percent of the

samples analysed are controls comprising field duplicate, analytical replicate and primary and secondary reference materials. Long-term analytical drift between batches of samples is monitored using time versus concentration plots for each of the reference samples. Tolerance limits are arbitrarily set at mean $\pm 2\sigma$ to assess data quality. Simple arithmetic correlations are applied to normalise the data for systematic drift. Values below the lower limit of detection are assigned to a value of one half of the detection limit and all field duplicate sample results removed prior to statistical treatment (for example BGS 2000).

Sampling and analytical precision are calculated using a procedure based on analysis of variance (ANOVA). Plots of cumulative frequency versus concentration for each element in the soils are examined to assess the degree to which the elements conform to a Gaussian distribution; in most cases elements are log-transformed before undergoing ANOVA, to improve their conformity to the model distribution (Plant *et al.* 1975).

A random nested model of ANOVA is used because all the analyses are part of a single randomised dataset (Snedecor & Cochran 1989). The NESTED procedure from the SAS™ statistical software package is used to perform the ANOVA (SAS Institute Inc. 1989). Residual variance (representing inter-alia inhomogeneities introduced in sample preparation and sub-sampling, and errors in chemical analysis), between-sample variance (representing within-site variability as well as any variability introduced by the process of sample collection) and between-site variance (representing the distribution of the elements in the soils) are calculated.

However, it should be noted that because the frequency distribution of most elements is multi-modal and none fit the Gaussian model perfectly, there is an unquantifiable overstatement of the between-site variance a problem that is inherent

in using ANOVA on geochemical data. Statistical F-tests are not quoted because the data do not satisfy this and other assumptions required for formal ANOVA. Rather the data are described in terms of percentiles of the data distribution and 'average' values are based on the median concentration.

The percentage of variance attributable to between-site, between-sample and residual variance of duplicate and replicate surface soil pairs from 11 urban centres (Cardiff, Swansea, Stoke-on-Trent, Telford, York, Kingston-upon-Hull (Hull), Doncaster, Mansfield, Scunthorpe, Lincoln and Sheffield) are given in Table 2, and provide a general indication of the reliability of the geochemical data. In most cases over 90 % of the variability can be attributed to between-site variance demonstrating the robustness of the field sampling method. ANOVA results for Cu, Cd, Sn and U fall below the 90 % between-site-variance level largely as a result of the inhomogeneous nature of urban soils. Sample preparation and analytical variability (residual variance) is very low (< 1.6 % for most elements) indicating the reliability of the analytical techniques. Results for Cd, Sb, Sn and U probably reflect the fact that concentrations of these elements in soils are close to the limit of detection (Lister 2002).

Once error controlled and spatially registered, the urban geochemical data are stored digitally in the corporate BGS Geochemistry Database and are available to users under licence (Johnson *et al.* this volume; Coats & Harris 1995).

DATA PRESENTATION

Geochemical data can be presented in a number of formats; the standard method for rural G-BASE data is as interpolated maps in the BGS series of geochemical atlases (for example, BGS 1997; BGS 2000). These maps comprise computer-generated

surface grids for each element produced by interpolation of the real data using Inverse Distance Weighting (IDW) (Johnson *et al.* this volume). An example of a gridded urban soil geochemical map is given in Figure 3 and shows the concentrations of Pb in deeper (0.50 m) soils derived from a survey of 285 urban sites in the city of Wolverhampton in the English West Midlands undertaken in 1992-1993. The surrounding rural data are derived from the G-BASE regional survey completed as part of the Welsh and West-Central England geochemical atlas area (BGS 2000). Whilst the interpolated maps are a robust presentation method for rural geochemical data where element distributions tend to form regional patterns, urban soils are highly heterogeneous and variable over small distances and there is concern that urban data presented in this way could be misinterpreted if not accompanied by validation information to give an estimate of the likely level of error in the interpolation. ANOVA investigations of field duplicate data indicate that the urban sampling methodology is valid, namely samples collected from the same site are more similar than samples from different sites (Lister 2002). However, further studies into the spatial variability of urban data using nested sampling, variogram and cross-validation techniques (Fordyce & Ander 2003; Rawlins & Brown 2003) and geostatistical assessments of various gridding algorithms (Nathanial *et al.* 1997) demonstrate a large nugget effect of a range of PHE, namely that differences between concentrations over very short distances are similar to those at increasing distance. Hence commonly used interpolation techniques are likely to be of limited use. Indeed due to dilation effects caused by the programme algorithms, interpolated maps do not provide a suitable method for presenting urban data. At the close scale of interrogation necessary in urban areas, interpolations can give misleading results, as the spatial extent of high element values can be over-emphasised.

As a result, methods of presenting urban geochemical data as graduated symbol maps using ArcView®/ArcGIS® geographic information system (GIS) software packages have been adopted (Fig. 4). Figure 4 shows the concentrations of As in surface soils collected from 747 sites over an area of 195 km^2 from the urban area of Stoke-on-Trent in the English Midlands during 1993. Although the geochemical patterns are not as readily identified as they are on interpolated maps, presentation of the data as graduated symbol maps avoids uncertain extrapolation between sampling points. Interpolated maps are still used with caution by the GSUE project to assess rural-urban soil comparisons and multi-element associations.

Once, plotted the GSUE data are presented as a series of BGS urban geochemistry reports (for example, Morley & Ferguson 2001; Brown 2003; Fordyce & Ander 2003; Rawlins & Brown 2003; Freestone *et al.* 2004; O'Donnell 2004).

DATA APPLICATIONS

Urban geochemical data have a number of applications to current UK land quality legislation and urban planning needs as follows:

Legislative drivers

The distribution of chemical elements in the environment is of concern because although many are essential to life, at least 26 of the naturally occurring elements are potentially harmful to plants and animals in high doses (Mertz 1986; Fergusson 1990; WHO 1996; Fordyce & Ander 2003). Many UK city environments have a long history of urbanisation resulting in elevated concentrations of PHE such as As, Cd, Cr, Cu, Ni, Pb, V and Zn derived from industrial and mineral processing and the atmospheric deposition of Pb and other toxins from traffic fumes and power

generation (Thornton *et al.* 1985; Moir & Thornton 1989; Farago *et al.* 1996; Paterson *et al.* 1996; Wang *et al.* 1997; Farmer *et al.* 1999). Whether or not these substances constitute a hazard depends on a variety of factors. These include their chemical form, concentration, mobility and behaviour in the environment, the extent to which they are taken up by living organisms (bioavailability), the properties of the substrate in which they occur such as the acidity of waters or soils, the soil texture and mineral composition, the level of exposure and the dose received (Farmer *et al.* 1989; Thornton *et al.* 1994; Mielke *et al.* 1997; Rieuwerts *et al.* 1998; DEFRA-EA 2002a; DEFRA-EA 2002b; Hough *et al.* 2004).

In UK urban areas, the major pathways via which PHE can enter the human body are through the inhalation of dusts and gases; direct contact with and ingestion of contaminated soil in gardens, play areas and allotments etc. Soil ingestion can be inadvertent for example from vegetables grown in the urban environment or from hand to mouth contact, especially in children. Deliberate eating of soils is also common among children. Water is unlikely to pose a risk to human health due to the high standard of public water quality in UK and the minimal use of private wells in city areas; however, the protection of water resources is a major issue in the urban environment (DEFRA-EA 2002a; DEFRA-EA 2002b).

Prompted by concerns about land and water quality, national governments and international agencies are developing policies to limit the amount and impacts of PHE in the environment. Although links between long term human health effects and PHE are often difficult to prove, the majority of regulatory authorities adopt a precautionary principal approach to legislate against high environmental concentrations. In the UK, the Environmental Protection Act, Part IIa (1990) places the responsibility for the identification, assessment, remediation and monitoring of

contaminated land with local authorities and is based on a 'suitable for use' approach. Land is categorised as contaminated only if the current or intended use of a site has the potential to cause 'significant harm' to four receptors namely humans, ecosystems, water resources and buildings and operates a 'polluter pays' principle in terms of remediation. However, it is important to point out that Part IIa only applies to a sub-set of land that is chemically contaminated. The identification of contaminated land relies on the concept of risk assessment, based on a pollutant linkage whereby the presence or source of contamination has the potential to impact on a receptor by means of a pathway (Fig. 5). This approach requires that land be assessed for redevelopment on a site-specific basis (DETR 2000).

Threats to water quality are not only addressed under the UK Environmental Protection Act but are directly linked to the European Union (EU) Water Framework Directive, which requires the protection of all surface and groundwater bodies (CEC 1998; EA 2002).

Soil guideline values and human risk assessment

In terms of human risk assessment, in 2002 the UK government launched the Contaminated Land Exposure Assessment (CLEA) model (DEFRA-EA 2002c). The model adopts an ecotoxicological approach and considers the exposure to contaminants from the direct and indirect ingestion and inhalation of soils (DEFRA-EA 2002a). To date, generic soil guideline values (SGV) for As, Cd, Cr, Pb, Hg, Ni and Se have been defined (DEFRA-EA 2003b) (Table 3). The GSUE project provides information for all these elements with the exception of Hg, which due to budgetary constraints is not analysed routinely. Summary statistics for these PHE in surface soils from 14 urban centres are presented for the first time in Table 3. It is anticipated that

data for the remaining 7 urban centres surveyed will be available by 2005. Table 3 represents the most comprehensive dataset on contaminant concentrations in UK urban soils since the work of Thornton *et al.* (1985).

Although the standard way to plot geochemical maps is using a full range of percentiles to describe the data distribution (Fig. 4), the data can also be presented to show where the SGV are exceeded thus highlighting areas for further investigation and follow-up. Figure 6 shows locations in the Stoke-on-Trent urban area where As concentrations in surface soils are above the SGV of 20 mg/kg for residential use (DEFRA-EA 2002d). The large number of sites reflects the general dispersion of As in the environment around Stoke-on-Trent due to the presence and exploitation of coal-bearing strata in the area; the dispersal of coal waste products as fill materials across the urban environment and the long industrial history of the city. However, the large number of sites is also a consequence of the low SGV for this element relative to natural abundances (Fordyce & Ander 2003). Indeed further examination of As concentrations in surface soils from 13 of the cities surveyed by the GSUE project demonstrates that more than 50 % of the soils sampled in Swansea, Manchester, Scunthorpe, Sheffield and Hull are above the SGV of 20 mg/kg, which again is not only a measure of the industrial heritage of these cities but of the relatively low guideline value for this element compared to its natural distribution (Fig. 7). Although the SGV is exceeded, it is essential to point out that this is not an indication of actual risk, rather that further assessments should be carried out (DEFRA-EA 2002d). The BGS is working with a number of authorities to follow up areas highlighted by the GSUE survey for more detailed investigation.

For example, a geochemical survey of 389 soils from 97 km^2 carried out in 2000 in the urban area of Coventry in the English Midlands, highlighted allotments

with soil Cd concentrations in excess of the 1 mg/kg at soil pH 6 SGV for areas where plants are grown. The mean pH of soils in the allotments was 6.1. Since the CLEA model assumes that 99 % of the exposure to Cd may be through the consumption of homegrown vegetables (DEFRA-EA 2002e) there was potential concern of a source-pathway-receptor linkage and risk to human health. Results of a follow-up soil and vegetation survey carried out in conjunction with the city authority demonstrate that the high Cd (> 1 mg/kg) and low pH (< 6) values are not spatially extensive. The levels of Cd in vegetables are all below the European Union (EU) regulatory limit of 0.2 mg/kg fresh weight (FW) for leafy and 0.1 mg/kg FW for stem and root vegetables (CEC 2001). The average daily exposure to Cd in soil estimated using the CLEA model indicates no significant toxicological risk for gardeners working at the allotments (Rawlins & Brown 2003; Palumbo *et al*. 2004).

The GSUE data have also been used to develop risk assessment methods to determine Cd, Cu, Ni, Pb and Zn exposure for populations living on and growing food in urban locations (Hough *et al.* 2004). The study showed that element concentrations in homegrown vegetables predicted from the GSUE soil data for Wolverhampton were satisfactory with the exception of Pb. This is probably because plant Pb uptake via the root system is limited and the main source of Pb contamination in vegetables is via atmospheric deposition (Dalenberg & Van Driel 1990). The study also demonstrated that the majority of the population were at low risk of health effects from vegetables grown on urban soils but highlighted particular areas associated with road junctions, railways and canals that may be inappropriate for residential use.

The UK SGV are based upon the assumption that 100 % of the elements in soil are bioavailable (DEFRA-EA 2002b), and one of the further steps in a source-pathway-receptor risk assessment is to investigate the likely bioavailability of

potential contaminants in soil. In addition to studies of plant uptake, data from the GSUE project are being used to develop quantitative analytical methods to assess the human bioaccessibility of PHE in soils that are directly consumed. These are known as physiologically based extraction tests (PBET) and are designed to mimic conditions in the stomach during soil ingestion giving a more accurate assessment of exposure. The tests originated in the United States and to date have been validated against animal models for As and Pb (Ruby *et al.* 1996). The methods have been adapted for use in the UK and for example, when applied to surface soils from Cardiff, demonstrate that although total As concentrations of up to 150 mg/kg are recorded, the bioaccessibility ranges from only 6 to 15% (Cave *et al.* 2003). The range in values highlights the site-specific nature of bioaccessibility, particularly in heterogeneous urban environments. This information is being used by the UK Environment Agency (EA) to direct its policy on the use of bioaccessibility data for ingested As in risk assessments.

Threats to water quality

The potential threats to groundwater from contaminants leaching down-profile from surface soils have been assessed using the GSUE data for Stoke-on-Trent (Fordyce & Ander 2003). The method utilised the Blume & Brummer (1991) and Boden (1994) groundwater vulnerability-leaching model, which requires the input of parameters that control the attenuation of specified contaminants in soils such as pH, organic matter, clay and sesquioxide contents. Soil pH and organic matter (LOI %) are measured as part of the GSUE survey and could be incorporated directly into the model. Clay and sesquioxide contents are not determined routinely but a simple system to derive this

information from GSUE soil texture and colour data was developed (Fordyce & Ander 2003).

The results demonstrate that due to the calcareous nature of the Coal Measures bedrock in Stoke-on-Trent and the base-rich character of the made ground underlying the city, soil pH values are circum-neutral over much of the area. As a result, the majority of soils have a high attenuation capacity and the leaching potential of the 11 contaminants examined (Cd, Mn, Ni, Co, Zn, Al, Cu, Cr Pb, Hg and Fe) is generally low. Although the model does not require soil PHE data, the benefit of the GSUE survey is that the element concentrations are known and can be evaluated in conjunction with the leaching potential results. Comparisons show that the regions of high element concentrations in the city centre correspond to soils with poor leaching potential therefore the risks of pollutant migration to groundwater are less. Potential leaching risks over the Triassic sandstones on the southeast of the urban periphery are of greater concern because of the poorer attenuation capacities of these soils and the importance of the Triassic sandstone aquifer for drinking water abstraction. However, comparisons with the GSUE data show that the majority of PHE in soils are found in low concentration over this lithology (Fig. 8).

Whilst it is possible to draw these very generalised conclusions about groundwater vulnerability using the GSUE data it should be noted that the hydrogeology of urban areas is normally extremely complex and further assessments of potential threats to groundwater quality are hampered due to the lack of net infiltration and depth to groundwater information. Although groundwater vulnerability maps produced by the EA in conjunction with the BGS and the National Soil Survey are available for England and Wales, urban areas are not characterised

because of the unknown properties of urban fill materials (EA 1998; Palmer & Lewis 1998).

Rural - urban comparisons

To provide an overview of the increased levels of PHE in urban environments relative to rural background, median values for urban areas can be compared to results for national datasets. National soil geochemical data generated by the Soil Survey of England and Wales National Inventory comprise surface soil total element concentrations (< 2 mm fraction) based on collection at a sample density of 1 per 25 km^2 (McGrath & Loveland 1992) (Table 3). However, it should be noted that although the sampling depth (0.15 m) is similar to the GSUE surface soils, the analysis of the national samples is based on an extraction rather than a total technique (aqua-regia 4:1 $HCl:HNO_3$ vol/vol followed by inductively coupled plasma atomic emission spectrometry). This is likely to lead to some bias in the results when comparing one dataset to the other. None the less, comparisons of the median values demonstrate that in general Cd, Cr and Ni concentrations are elevated up to 2.5 to 3 times and Pb up to 5 times national levels in most of the 14 cities presented in Table 3 giving an indication of the degree of contamination in the urban environment. Whilst these comparisons are interesting, they do not take account of natural variations in the rural baseline around individual cities.

The benefits of a systematic urban (GSUE) and regional (G-BASE) geochemical survey are that direct comparisons between urban and rural environments are possible. For example, Figure 3 shows the concentration of Pb in deeper (0.50 m) soils in the environment around Wolverhampton. Enhanced concentrations of the element in the urban environment are very evident relative to the

rural hinterland. On a regional scale, Figure 9 shows information for Cu from seven of the urban centres in the Humber-Trent region of England in relation to the surrounding G-BASE rural soils data. Between 1994 and 1996, 6 500 soil samples were collected by the G-BASE programme throughout this part of rural eastern England covering a total area of around 13 000 km^2. The rural-urban comparisons demonstrate that Hull and Sheffield, show greatest enhancement of Cu relative to rural baseline conditions.

Rural-urban relationships have been investigated in more detail in Stoke-on-Trent. Table 4 outlines the data ranges for selected total element concentrations in G-BASE rural and GSUE urban soils for the area. The rural soil samples were collected as part of the Northwest England and North Wales and Wales and West-Central England geochemical atlas areas (BGS 1997; BGS 2000). For the purposes of the rural-urban comparisons, a sub-set of the rural data was selected from an area underlain by the same lithological units as the city over a 10 km radius around Stoke-on-Trent. On the basis of median values for deeper soils, the urban area contains *c.* 1.2 times the average Cr, Ni, Sn, Pb and Zn of the rural hinterland, whereas As shows little elevation in the urban soils relative to rural background (Fordyce & Ander 2003). Using GIS technology, it is now possible to readily select sub-sets of the geochemical data based on particular areas of interest. This is extremely useful to examine the relationships between rural and urban soils over particular stratigraphic units and parent materials in more detail (Fig. 10). Stoke is primarily underlain by Westphalian age sandstones, mudstones and coals and the Triassic age Sherwood Sandstone and Mercia Mudstone Groups (Wilson *et al.* 1992). Concentrations of V, Fe$_2$O$_3$, Co, Ni, Cu and Zn in soils are highest over the Westphalian rocks relative to other the stratigraphic units as expected due to the presence of coals (Fig. 10).

However, these 'natural' geochemical variations are small compared to the contrast between rural and urban environments. Figure 10 shows that in almost all cases, element concentrations are enhanced in the urban relative to the rural environment for each stratigraphic unit. As a further comparison, the ratios of element median values in the urban versus rural deeper soils for each parent material type are shown in Table 5. Soils over river terrace deposits show some of the greatest increases in element concentrations between rural and urban environments (for example, MnO x2.7, Zn x2.9, Pb x2.4 and Sn x2.8). This may indicate that these deposits act as sinks for contaminants in cities and may also reflect the historical preference for locating industrial activity on the banks of drainage systems (Fordyce & Ander 2003).

Inter-city comparisons

One of the benefits of a national systematic urban survey is that the results from different cities can be compared directly. For example, Figure 11 shows the median concentration of selected elements in Stoke-on-Trent, Cardiff, Telford and Swansea surface soils. These cities are all underlain by Westphalian Coal Measures and have a long history of industrialisation. Interestingly, the results are rather similar with the exception of Swansea where the import of ores and metal smelting contributes significantly to the soil contaminant load (Morley & Ferguson 2001). Equally, Table 3 demonstrates that median concentrations of Cr are highest in Glasgow and Sheffield surface soils, two cities renowned throughout the world for their ore processing and steel making histories. In contrast, median concentrations of As, Cr, Ni and Pb in Lincoln and Mansfield are relatively low compared to other cities as these are small less industrialised urban centres (Table 3). Similarly, concentrations of Cu in Lincoln surface soils are similar to the rural baseline (Fig. 9). These comparisons are useful to

establish 'typical' urban geochemical signatures and highlight exceptions that can be attributed to different current and historic land uses.

Contaminant sources in the environment

Rural-urban and inter-city comparisons are also important in the context of identifying possible contaminant sources in the environment.

Under the UK contaminated land regime, local authorities are required to identify and develop a strategy for managing contaminated land and the guidance to achieve this is based largely on current and historical land use. The likely types of contaminants associated with particular industrial activities are considered (DOE 1994; DOE 1995). However, the advantage of geochemical information is that the actual levels of contamination in the environment can be assessed independent of assumptions related to land use.

A broad-scale example is that in the highly industrialised city of Wolverhampton, highest soil Pb concentrations were associated with the industrial corridor to the east of the city centre as expected based on land use (Fig. 3). In contrast, sampling in the largely residential green suburban area of Richmond-on-Thames, London revealed high soil Pb concentrations proximal to the road network. However, concentrations of Pb in surface soils from Richmond-on-Thames were higher on average (median 185 mg/kg) than Wolverhampton (median 101 mg/kg), an outcome that would not be predicted from the historical land use records of the two urban areas alone (Kelly *et al.* 1996; Kelly 1997).

On-going work in the Humber-Trent region of Eastern England is a further example of the application of GSUE data to contaminant source identification in the context of rural and urban comparisons. During the summer of 1996, a soil

geochemical survey was undertaken in the City of Hull, comprising 411 individual sampling locations across 160 square kilometres. Based on a subset of the surrounding G-BASE Humber-Trent rural survey data and the urban data from Hull, a preliminary surface soil geochemical map was generated for Sn over the region (Fig. 12). The map highlights a series of anomalously high Sn concentrations around the site of the former Capper Pass tin smelter, which was operational between 1937 and 1991. There is a clear trend of decreasing Sn concentrations at increasing distances from the smelter site, consistent with the dominant prevailing wind direction (from the southwest). Further work is currently being undertaken in conjunction with local agencies to assess the nature, magnitude and extent of aerial metal deposition related to the former operation of the smelter.

The relationships between element concentrations and different land types have been examined in more detail in Stoke-on-Trent (Fordyce & Ander 2003). Stoke is an interesting urban environment as the presence of coal, ironstone and clay in the area resulted in rapid growth during the Industrial Revolution (*c.* 1760 onwards) and the city became a world-leading centre for coal, iron and steel and pottery manufacture. As a result of this long industrial heritage, the majority of Stoke-on-Trent is built on urban fill and made ground material, much of which derived historically from industrial wastes. The types of made ground underlying the city had been mapped previously by the BGS (Wilson *et al.* 1992) allowing spatial comparisons with the soil geochemical information. Investigations were carried out using a combination of GIS spatial query function to select sub-sets of the geochemical data over different types of made ground and data within 250 m of the road and rail network followed by presentation as box and whisker plots (see for example Fig. 13); three-component maps of multi-element distributions (Breward *et*

al. 1992); Spearman Rank correlation matrices and principle component analysis (Fordyce & Ander 2003). The main element associations evident from these studies are outlined in Table 6.

Interestingly no overt geochemical signature with the road and rail network in Stoke-on-Trent was apparent. Due to falling levels of traffic-derived Pb in urban environments as a result of the widespread use of lead-free petrol in recent years, Monaci & Bargagli (1997) and Monaci *et al.* (1999) have suggested that Ba is a good indicator of traffic fume contamination as it is added to diesel to reduce soot emissions (for example, Petkov *et al.* (1999). Elements such as Zn (used in tyres) are also enhanced in the urban environment as a result of road vehicle usage. However, none of these elements (Pb, Ba and Zn) showed an association with the road network in Stoke-on-Trent. Undoubtedly traffic fumes do contribute to the metal loadings of soils in the city but the geochemical signature, as determined by the studies carried out to date, is not distinct because of the many other sources of these elements in this complex urban environment and naturally enhanced concentrations of elements such as Ba in the local bedrock (Fordyce & Ander 2003).

In general, the main control on element distributions in soils from Stoke-on-Trent is the presence of made ground. The majority of elements, with the exception of SiO_2 and MgO, are elevated over made ground compared to the rural periphery. Within the urban area, multi-element anomalies are associated with different industrial land uses and made ground types aiding the identification of possible contaminant sources. For example, As is enhanced in profile soils developed over domestic and industrial waste and ironworks slag (Fig. 13). In general, soils developed over coal spoil and coal ash waste are high in Fe_2O_3, CaO, MgO, K_2O, Al_2O_3, SiO_2, As, Hg, V, Ni, Cr, Zn, Cu, Cd, Ba and Pb whereas domestic waste soils

although containing high trace metal concentrations, have lower major element (Al_2O_3, K_2O, SiO_2 TiO_2) contents. Soils developed over ironworks slag and former steel works sites have a distinctive geochemical signature, which is not only high in trace metals (Fe_2O_3, Ni, Cr, Sn, Mo, Cd, V, Cu and Zn), but in base metals such as CaO, MgO and P_2O_5 reflecting the use of these products in the steel making process. The use of pigments containing Cd, Cr, Cu, Co, Fe, Mn, Ni, U and V and ceramic glazes containing SiO_2, Al_2O_3, CaO, SnO_2 PbO and $FeTiO_2$ in the potteries industry in Stoke-on-Trent account for localised anomalies due to historic factory emissions and dumping of ceramic waste.

Investigations into element associations also demonstrate that the concentrations of Al_2O_3, SiO_2, TiO_2, MgO and Ba in Stoke-on-Trent soils are largely controlled by geological processes whereas CaO, P_2O_5, Pb, Cd, Cu, Co, Cd, Sn, Hg, Mo, MnO, Sb, Zn reflect industrial activity and Cr, As, Ni, V, Fe_2O_3, K_2O distributions are partly controlled by the underlying geology and partly by anthropogenic inputs (Fordyce & Ander 2003).

These results highlight the importance of a multi-element survey, which determines the major as well as the trace element components of soil as an aid to contaminant source identification.

CONCLUSIONS

1. The quality of urban land is of increasing concern in the UK and many other countries as the need to reuse brownfield sites and regenerate city environments grows. However, information on the chemical and physical properties of urban soils is often limited as historically these areas were avoided by soil surveys.

2. Systematic multi-element urban geochemical surveys generate valuable information on the concentration, distribution, sources and likely mobility of potentially harmful elements in city environments providing an overview and framework to more detailed site investigations and can highlight areas for further follow-up in terms of contaminated land.

3. To date, geochemical datasets for up to 48 parameters in urban soils have been generated for 21 cities in the UK by the GSUE project. These data are of direct relevance to a number of legislative drivers including the assessment of sources; pathways and risks to human receptors under the UK contaminated land regulations. The data also have application to the protection of water resources required by the EU Water Framework Directive and to soil quality soon to be addressed by the proposed EU Soils Framework Directive.

4. The BGS is increasingly working with local authorities and environmental protection agencies to develop the applications of the urban geochemical datasets. Major gaps in information include data for Hg and organic contaminants in the urban environment. It is anticipated that these will be addressed via end-user partnership arrangements in the future.

(analysis) and the many geochemists and students who have worked for BGS on the

GSUE project over the past 12 years ensuring a well-founded systematic survey.

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Table 1 *List of parameters currently determined in urban soils by the GSUE project*

Analytical Method	List of Determinands
XRFS	Ag, Al_2O_3, As, Ba, Bi, Br, CaO, Cd, Ce, Co, Cr, Cs, Cu, Fe_2O_3, Ga, Ge, Hf, I, K_2O, La, MgO, MnO, Mo, Na_2O, Nb, Ni, P_2O_5, Pb, Rb, Sb, Sc, Se, SiO_2, Sn, Sr, Ta, Te, Th, TiO_2, Tl, U, V, W, Y, Zn, Zr
$CaCl_2.2H_2O$ Slurry	pH
Heating at 450 °C	Loss on Ignition

Table 2 *Percentage of variance in surface soil samples (0.20 m) from 11 urban centres attributable to between-site, between-sample and residual variance*

	Between site (%)	Between sample (%)	Residual (%)
TiO_2	97.44	2.17	0.39
MnO	93.87	6.05	0.07
Fe_2O_3	89.81	10.10	0.08
V	97.67	2.29	0.03
Cr	94.94	3.53	1.51
Co	99.31	0.31	0.37
Ni	98.46	1.37	0.16
Cu	80.93	18.50	0.56
Zn	98.38	1.61	0.01
As	98.79	1.14	0.06
Mo	98.12	1.70	0.17
Ba	98.15	1.39	0.45
Pb	97.67	1.99	0.33
U	80.16	2.7	17.09
Cd	47.88	6.7	45.34
Sn	83.10	5.54	11.35
Sb	89.20	6.22	4.57

ANOVA based on 37 replicate pairs except Cd (27); Mo (33); Sb (16)
All data log transformed

Table 3 *Summary statistics for selected total element concentrations in surface soils (0.20 m) in 14 UK urban areas*

City	Count	As (mg/kg) Min	Max	Median	Cd (mg/kg) Min	Max	Median	Cr (mg/kg) Min	Max	Median	Ni (mg/kg) Min	Max	Median	Pb (mg/kg) Min	Max	Median	Hg (mg/kg) Min	Max	Median	Se (mg/kg) Min	Max	Median
Cardiff	508	6	150	16	0.50	82	1	1	2426	72	9	476	26	14	7575	76	Nd	Nd	Nd	Nd	Nd	Nd
Doncaster	279	2	74	13	0.50	7	1.0	21	499	64	5	163	19	18	1100	78	Nd	Nd	Nd	Nd	Nd	Nd
Glasgow	1381	1	283	9	0.25	16	0.3	38	4286	108	6	1038	47	13	5001	127	Nd	Nd	Nd	0.20	14.5	0.9
Hull	411	3	205	20	0.35	5	0.4	22	1809	83	6	1123	39	10	2900	116	Nd	Nd	Nd	Nd	Nd	Nd
Lincoln	216	4	65	11	0.45	5	0.4	19	260	43	2	101	14	15	1400	55	Nd	Nd	Nd	Nd	Nd	Nd
Manchester	300	2	1001	20	0.25	80	0.9	30	1238	76	4	148	29	20	2758	218	Nd	Nd	Nd	0.05	3.2	0.4
Mansfield	257	3	71	11	0.35	9	1.0	18	250	54	4	102	16	1	1319	76	Nd	Nd	Nd	Nd	Nd	Nd
Scunthorpe	196	3	190	19	0.45	28	1.0	7	1108	55	1	202	15	9	3300	45	Nd	Nd	Nd	Nd	Nd	Nd
Sheffield	575	4	239	22	0.35	8	1.0	43	1251	102	8	473	32	19	4300	164	Nd	Nd	Nd	Nd	Nd	Nd
Stoke~	747	2	136	14	0.40	43	2.0	22	441	73	5	124	23	10	4208	93	0.005	7.22	0.14	Nd	Nd	Nd
Swansea	373	8	2047	53	1.00	61	2.0	20	565	74	8	349	37	20	14714	225	Nd	Nd	Nd	Nd	Nd	Nd
Telford	294	5	54	10	0.50	30	1.0	25	164	65	7	153	28	20	1236	92	Nd	Nd	Nd	Nd	Nd	Nd
Wolverhampton	285	4	157	17	0.00	70	1.0	39	1297	95	12	264	33	27	2853	158	Nd	Nd	Nd	0.00	4.0	1.0
York	191	3	93	10	0.35	9	1.0	27	639	59	6	84	19	24	2400	106	Nd	Nd	Nd	Nd	Nd	Nd
National*	5692			Nd			0.7			39			22			40			Nd			Nd

UK 'Typical' Soil Guideline Values (SGV) in dry weight soil (mg/kg)#

	As	Cd	Cr	Ni	Pb	Hg	Se
Residential with plant uptake	20	1 (pH 6) 2 (pH 7) 8 (pH 8)	130	50	450	8	35
Residential no plant uptake	20	30	200	75	450	15	260
Allotments	20	1 (pH 6) 2 (pH 7) 8 (pH 8)	130	50	450	8	35
Commercial/Industrial	500	1400	5000	5000	750	480	8000

* National Soil Inventory of England and Wales (McGrath & Loveland 1992) aqua regia digest (0.15 m) Nd = No data
~ Hg is not routinely analysed in the GSUE survey but determinations in surface soils from Stoke were carried out by digestion of 1 g of milled sample in aqua-regia and analysis by cold vapour atomic absorption spectrometry (Fordyce & Ander 2003)
# DEFRA-EA (2002b) Typical soil guideline values (SGV) derived from the UK CLEA contaminated land assessment model

Table 4 *Summary statistics for selected total element concentrations in rural and urban soils from Stoke-on-Trent*

Statistics	Soil Type	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Sn (mg/kg)	Zn (mg/kg)
Minimum	Urban A	2	0.4	22.0	5.0	10	1	6
	Urban S	4	0.4	41.0	6.0	15	2	20
	Rural S	4	1.0	23.0	5.0	9	1	13
Maximum	Urban A	136	43.0	441.0	124.0	4208	662	2589
	Urban S	167	408.0	574.0	250.0	4207	657	7408
	Rural S	47	6.0	116.0	86.0	301	72	1032
Mean	Urban A	16	1.7	76.3	27.1	176	17	156
	Urban S	18	1.4	94.9	34.6	164	14	170
	Rural S	14	1.1	72.1	23.9	57	5	93
Median	Urban A	14	2.0	73.0	23.0	93	7	108
	Urban S	14	0.4	92.0	30.0	61	6	90
	Rural S	13	1.0	72.0	23.0	47	5	80

Urban = GSUE urban soils for Stoke-on-Trent (n = 747)   Rural = G-BASE rural soils around Stoke-on-Trent (n = 368)
A = Surface (0.20 m) Soils (< 2 mm)   S = Deeper (0.50 m) Soils (< 150 µm)

Table 5 *Ratio of urban/rural median element concentrations in deeper soils (0.50 m) over each 1: 625 000 scale superficial deposit and 1: 250 000 scale solid geology unit in the Stoke-on-Trent area*

Parent Material	MnO	Fe_2O_3	V	Cr	Co	Ba	Ni	Cu	Zn	As	Mo	Pb	U	Sn	Sb	MgO	P_2O_5	K_2O	CaO
Alluvium	2.0	1.8	1.4	1.5	1.7	1.1	1.9	1.8	1.6	0.9	1.9	1.6	1.0	1.4	1.0	0.8	0.8	0.9	1.0
Boulder Clay	1.6	1.3	1.3	1.2	1.3	1.1	1.2	1.5	1.0	1.2	2.6	1.4	1.1	1.3	1.0	0.7	0.9	0.6	0.5
Glacial Sand and Gravel	1.0	1.9	1.4	1.4	1.4	1.4	1.5	3.0	1.3	1.6	8.5	2.3	0.8	1.5	2.5	0.6	0.8	0.9	0.7
River Terrace	2.7	1.8	1.5	1.2	1.8	1.5	1.4	2.5	2.9	1.5	1.6	2.4	1.0	2.8	1.0	0.2	0.8	0.5	1.1
Mercia Mudstone	1.4	1.2	1.1	1.1	1.2	1.0	1.1	1.2	1.1	1.1	2.3	1.2	1.0	1.2	1.0	0.5	0.7	0.8	0.4
Sherwood Sandstone	1.3	0.9	0.9	1.0	1.0	1.0	1.0	1.4	1.2	0.8	1.2	1.0	1.0	1.2	1.0	0.7	0.8	0.8	0.3
Salop Formation	1.5	1.3	1.0	1.1	1.2	1.0	1.0	1.3	1.1	1.1	2.3	1.4	1.0	1.5	1.0	0.7	1.2	1.0	0.4
Westphalian	1.2	1.2	1.1	1.2	1.2	1.2	1.2	1.2	1.1	1.1	1.4	1.1	1.0	1.2	1.0	0.7	1.0	0.9	0.6
Millstone Grit	0.9	1.0	1.3	1.3	1.0	0.8	1.1	0.7	0.7	Nd	2.0	0.7	Nd	0.9	Nd	0.7	Nd	0.9	4.0

Nd = No data

Table 6 *Element associations indicative of various made ground types and major controls on elements in soils from Stoke-on-Trent*

Source	Element Association
Coal Measures	As, V, Mo, Ni, Cu, Zn, Pb, CaO
Coal spoil/ coal ash waste	Fe_2O_3, CaO, MgO, K_2O, Al_2O_3, SiO_2, As, Hg, V, Ni, Cr, Zn, Cu, Cd, Ba, Pb
Ironworks slag/ former steel works	Fe_2O_3, Ni, Cr, Sn, Mo, Cd, V, Cu, Zn, MgO, P_2O_5 CaO,
Pigments/ ceramic glazes	Cd, Cr, Cu, Co, Fe, Mn, Ni, U, V, SiO_2, Al_2O_3, CaO, Sn, Pb

Control	Element
Geological processes	Al_2O_3, SiO_2, TiO_2, MgO
Anthropogenic processes	CaO, P_2O_5, Pb, Cd, Cu, Co, Cd, Sn, Hg, Mo, MnO, Sb, Zn
Geological and anthropogenic processes	Cr, As, Ni, V, Fe_2O_3, K_2O

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Figure 1 *Locations of the 21 UK urban centres sampled to date by the GSUE project*

Urban Soil Geochemistry 21 Cities Sampled to Date

1   Cardiff
2   Corby
3   Coventry
4   Derby
5   Doncaster
6   Glasgow
7   Hull
8   Leicester
9   Lincoln
10   Mansfield
11   Northampton
12   Nottingham
13   Peterborough
14   Scunthorpe
15   Sheffield
16   Swansea
17   Stoke-on-Trent
18   Telford
19   Wolverhampton
20   York
21   Manchester
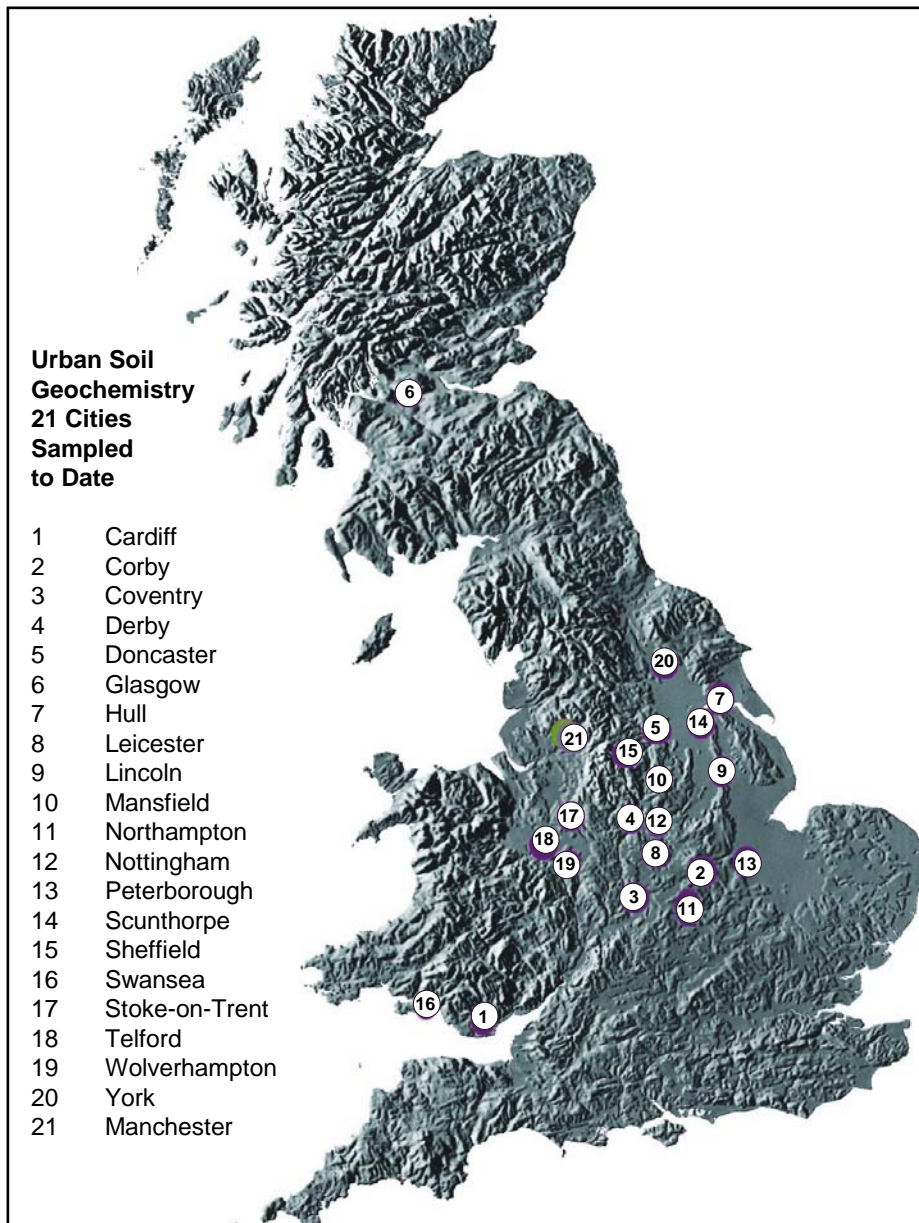
Figure 2 *Diagram of the GSUE composite soil sampling strategy*
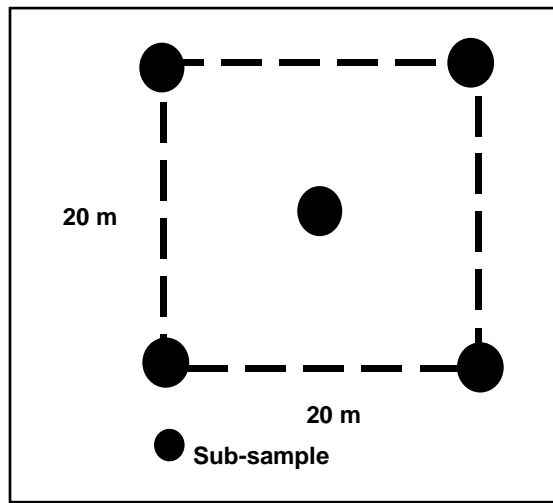
Figure 3 *Interpolated map of total Pb in deeper soils (0.50 m) from the Wolverhampton region*
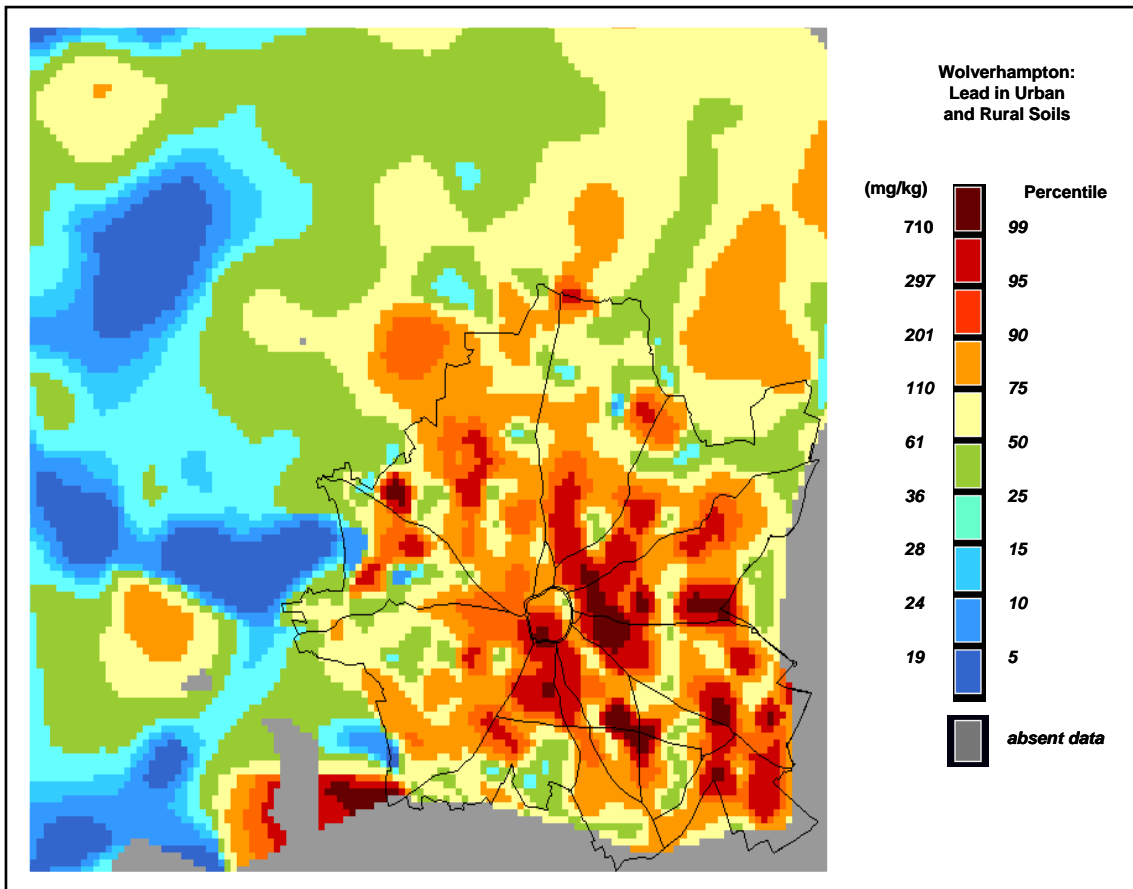
Figure 4 *Graduated symbol map of total As in 747 surface soils (0.20 m) from Stoke-on-Trent*
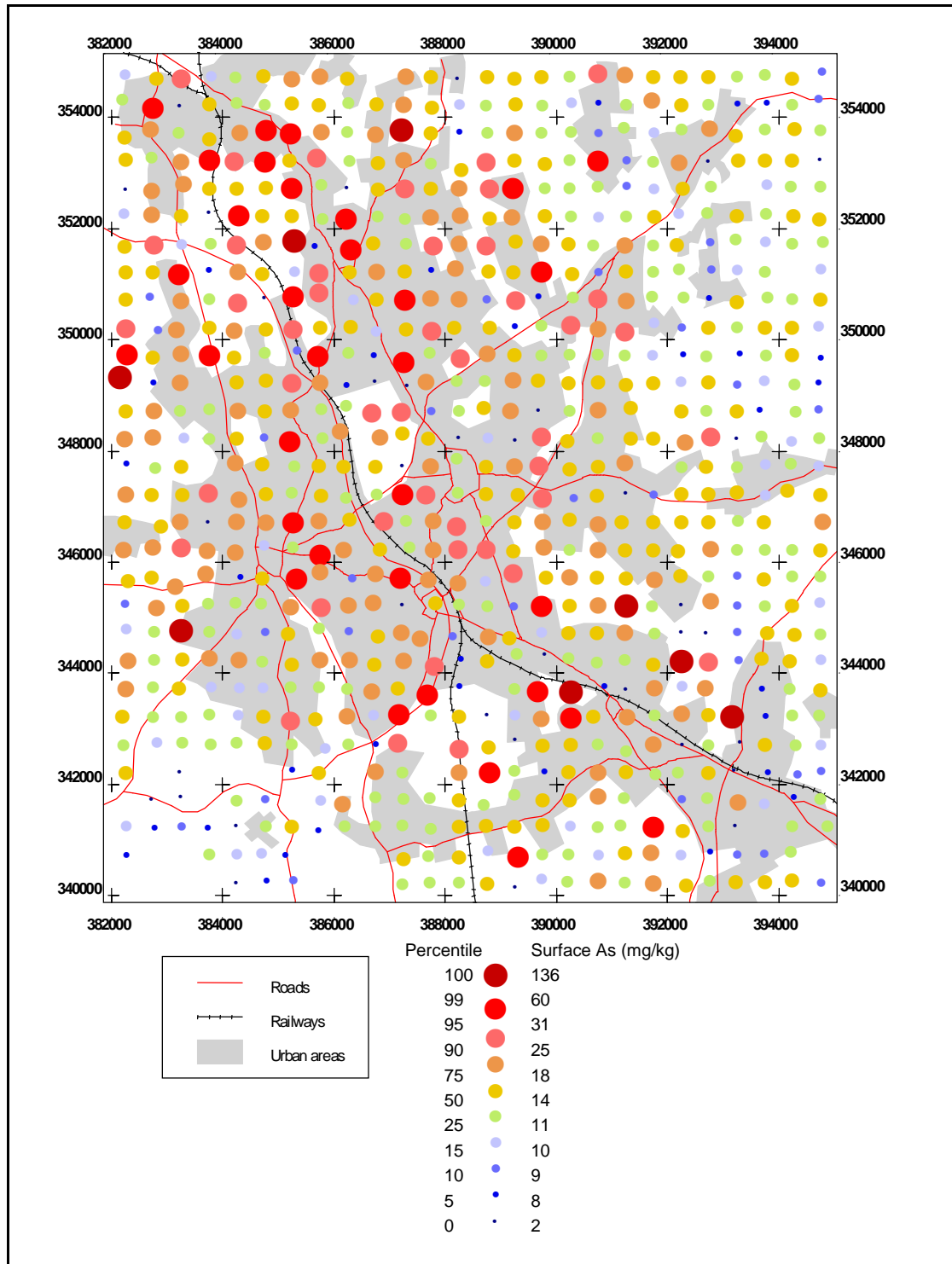
Figure 5 *Concept of source, pathway and receptor in the assessment of contaminated land*
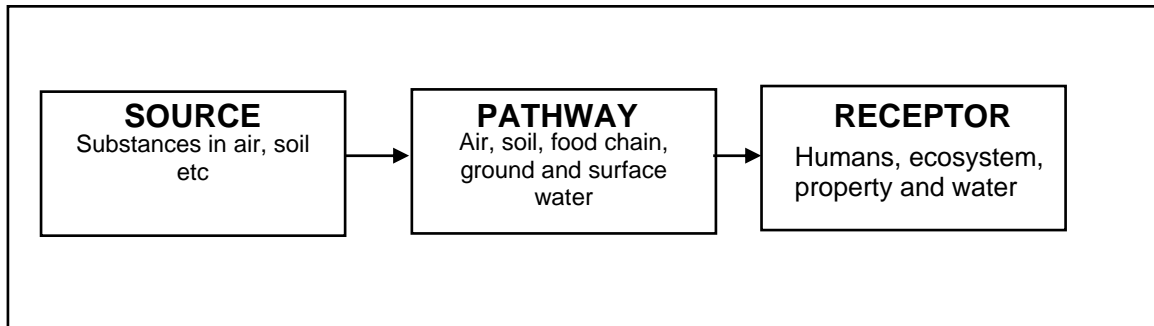
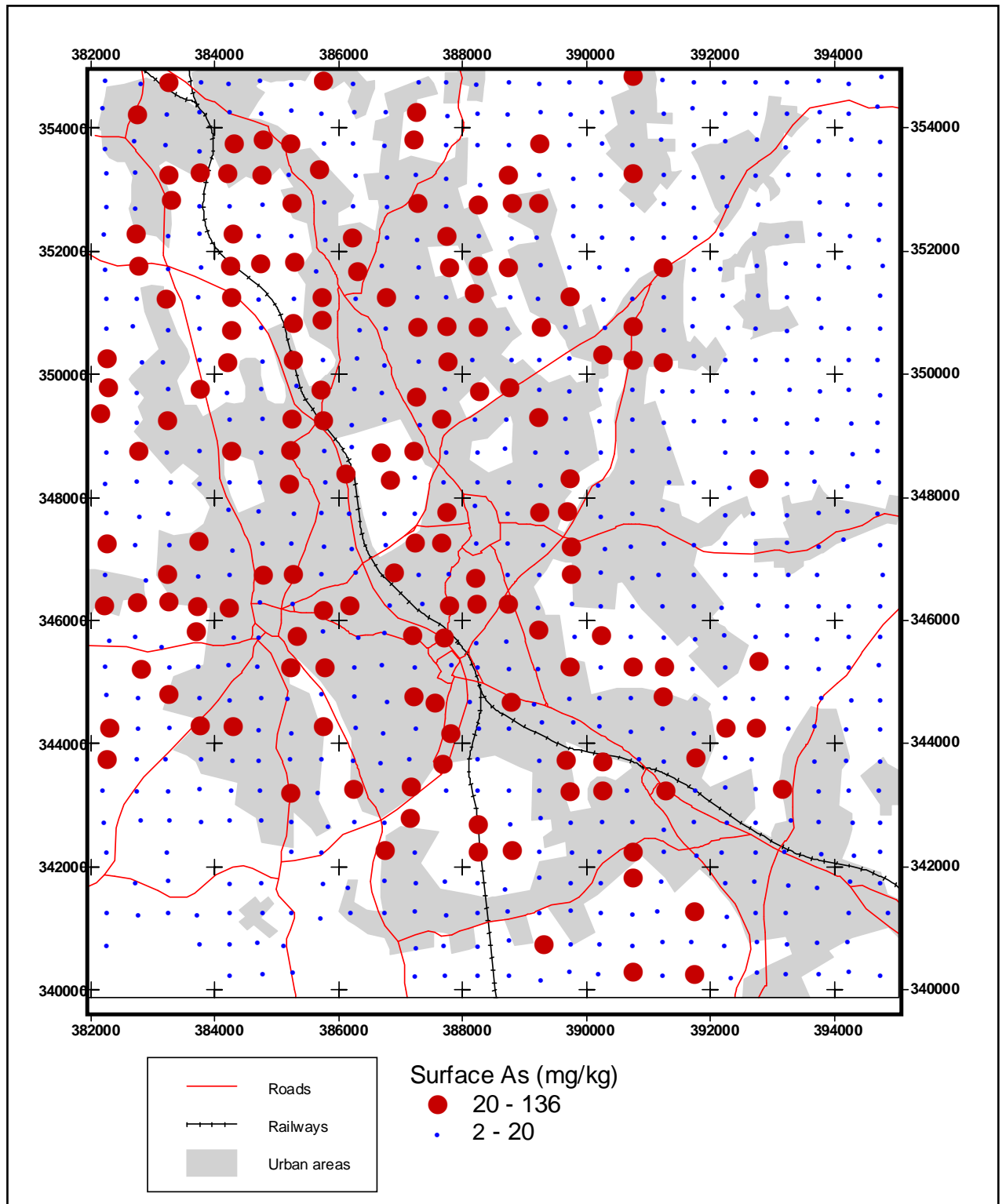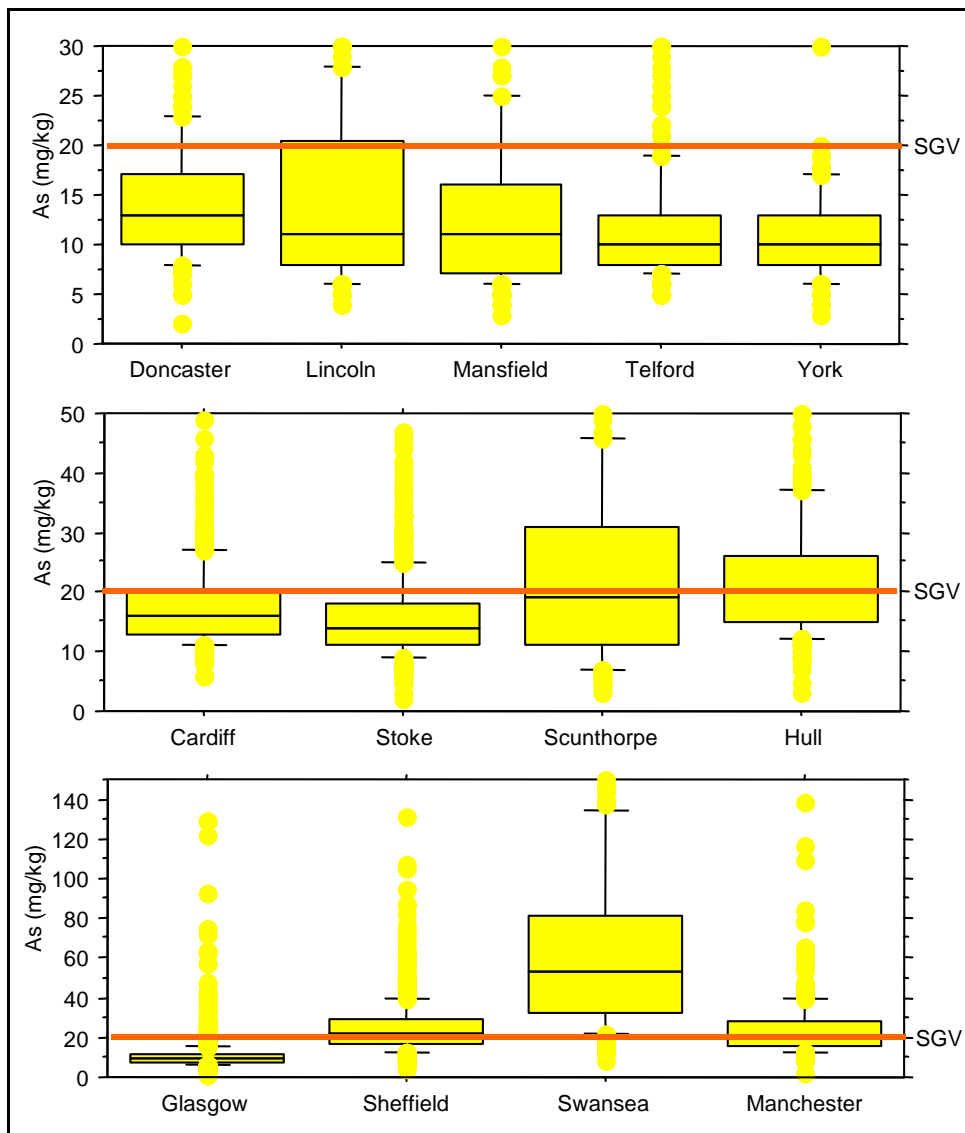**Figure 6** *Locations where total As in 747 surface soils (0.20 m) exceed the 20 mg/kg CLEA SGV in Stoke-on-Trent*

Figure 7 *Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of total As concentrations in surface soils (0.20 m) from 13 UK cities*

Line and SGV = CLEA soil guideline value for As in soils in residential areas 20 mg/kg (DEFRA-EA 2002d)
The plots are maximised to display up to the 90th percentile of the distribution therefore some highly anomalous values
are not shown   For numbers of samples see Table 3

Figure 8 *(a) Total concentrations of Cd in deeper (0.50 m) soils and (b) Cd soil attenuation capacity across Stoke-on-Trent.*
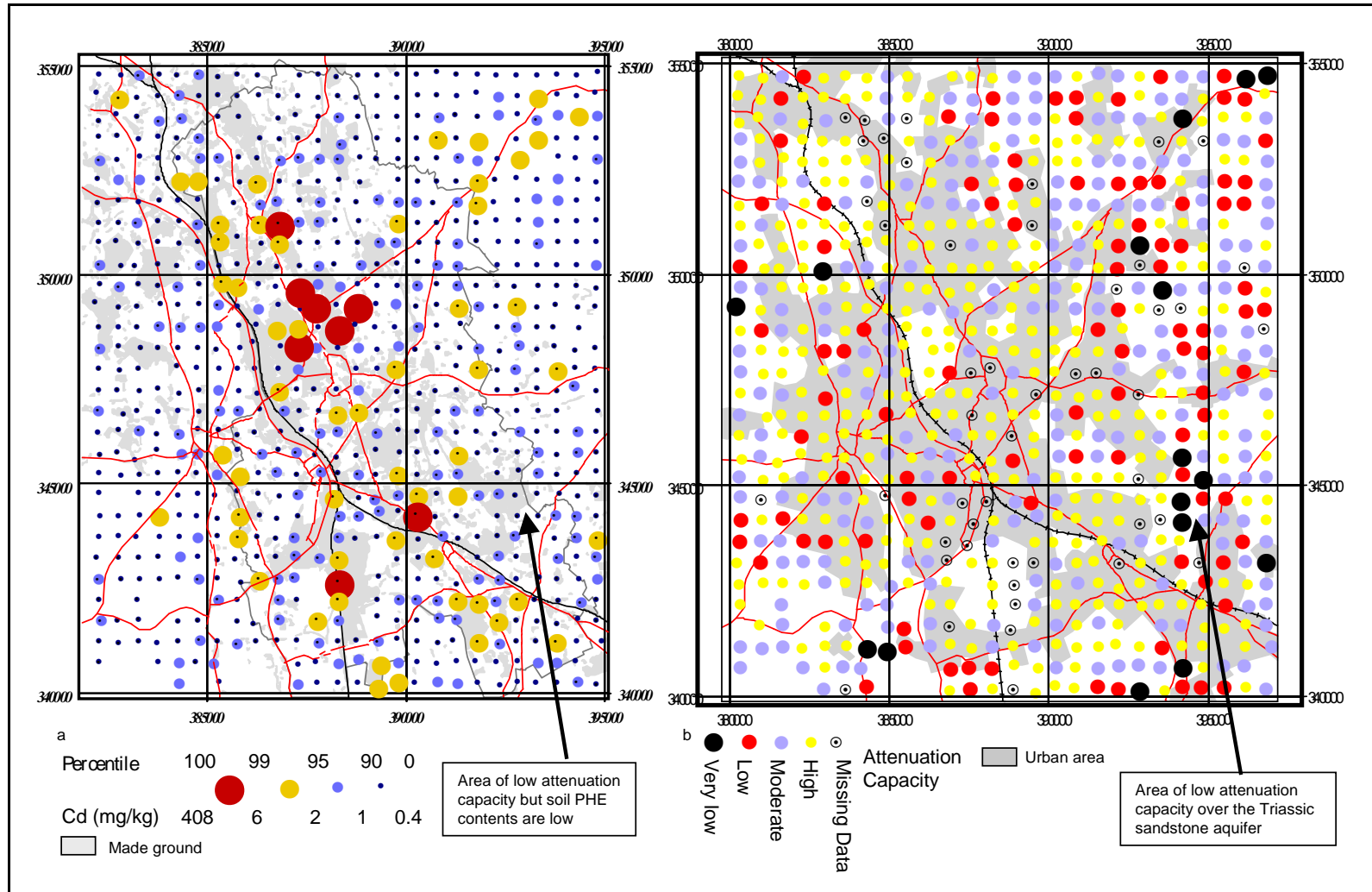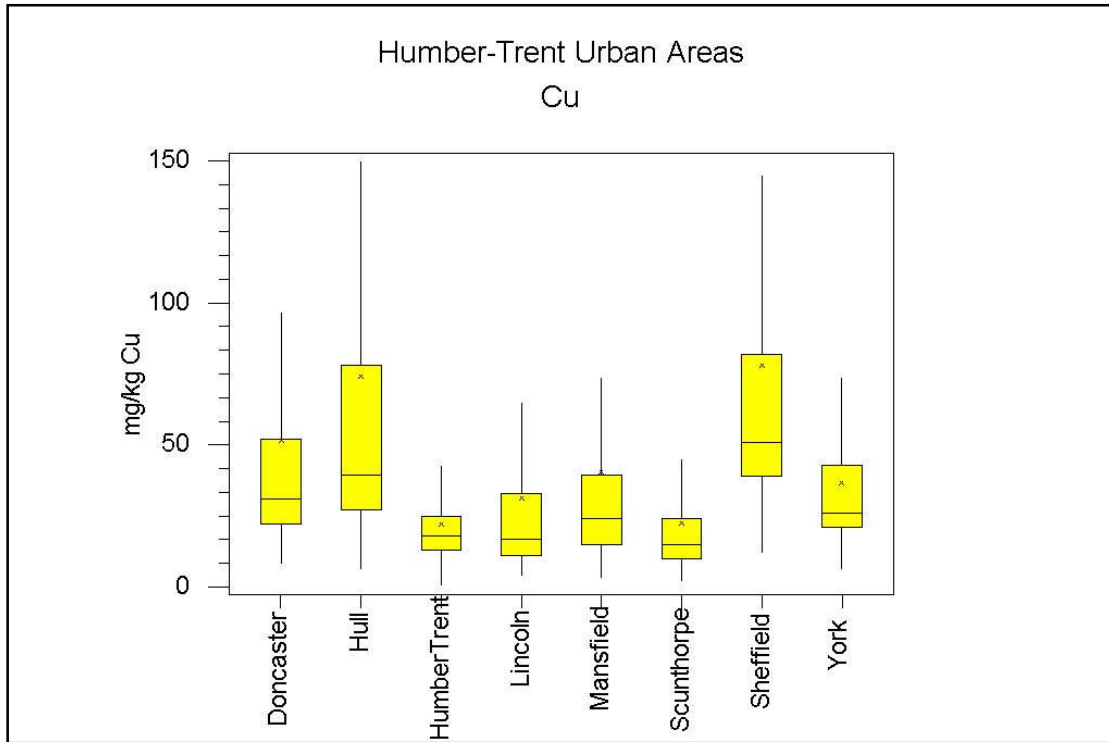
Figure 9 *Box and whisker plots of the 5th, 25th, 50th, 75th and 95th percentiles of total Cu concentrations in surface soils (0.20 m) from 7 urban areas and surrounding rural soils of the Humber-Trent region*

x = mean value

Figure 10 *Total concentrations of selected elements in deeper (0.50 m) soils over different rock types in the rural and urban environment of Stoke-on-Trent*
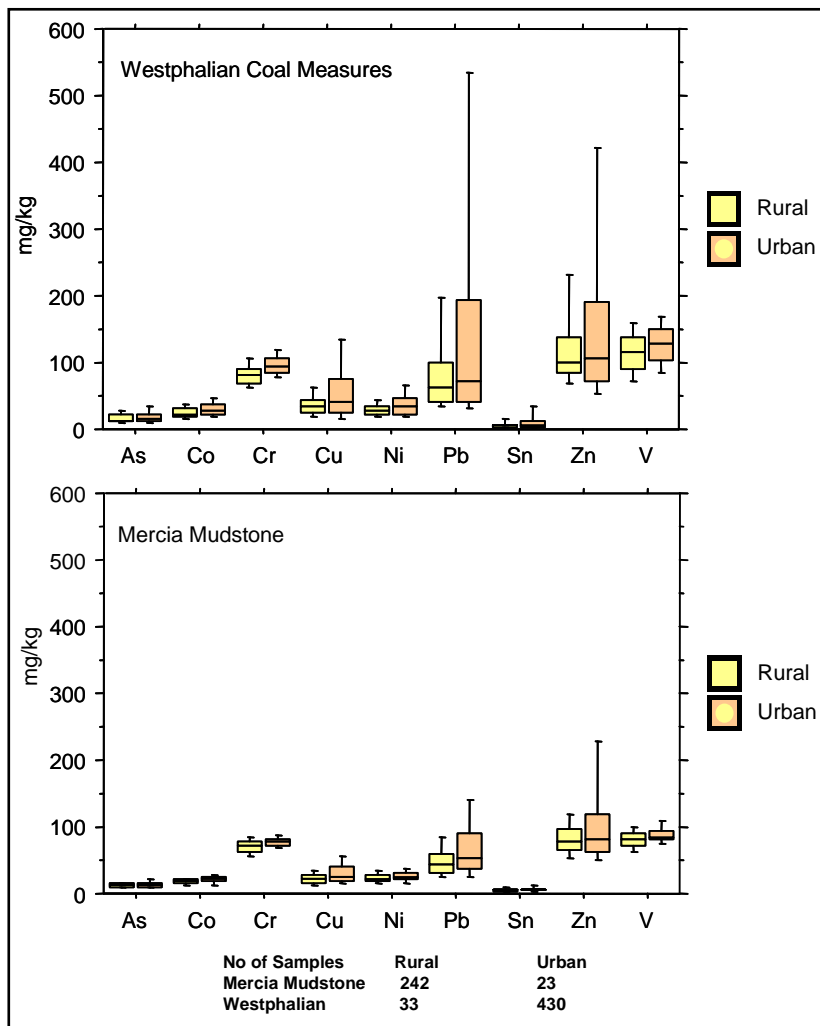
Figure 11 *Bar chart showing the median of total concentrations of selected elements in surface soils (0.20 m) from Stoke-on-Trent, Swansea, Cardiff and Telford urban centres*
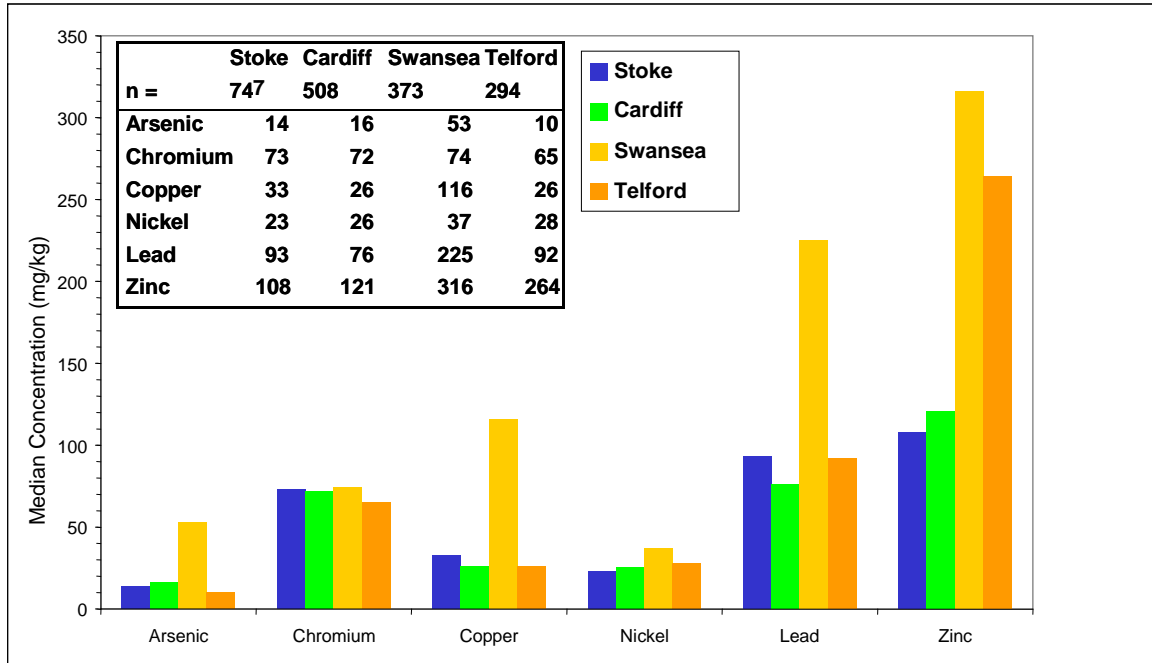

	Stoke	Cardiff	Swansea	Telford
n =	747	508	373	294
Arsenic	14	16	53	10
Chromium	73	72	74	65
Copper	33	26	116	26
Nickel	23	26	37	28
Lead	93	76	225	92
Zinc	108	121	316	264

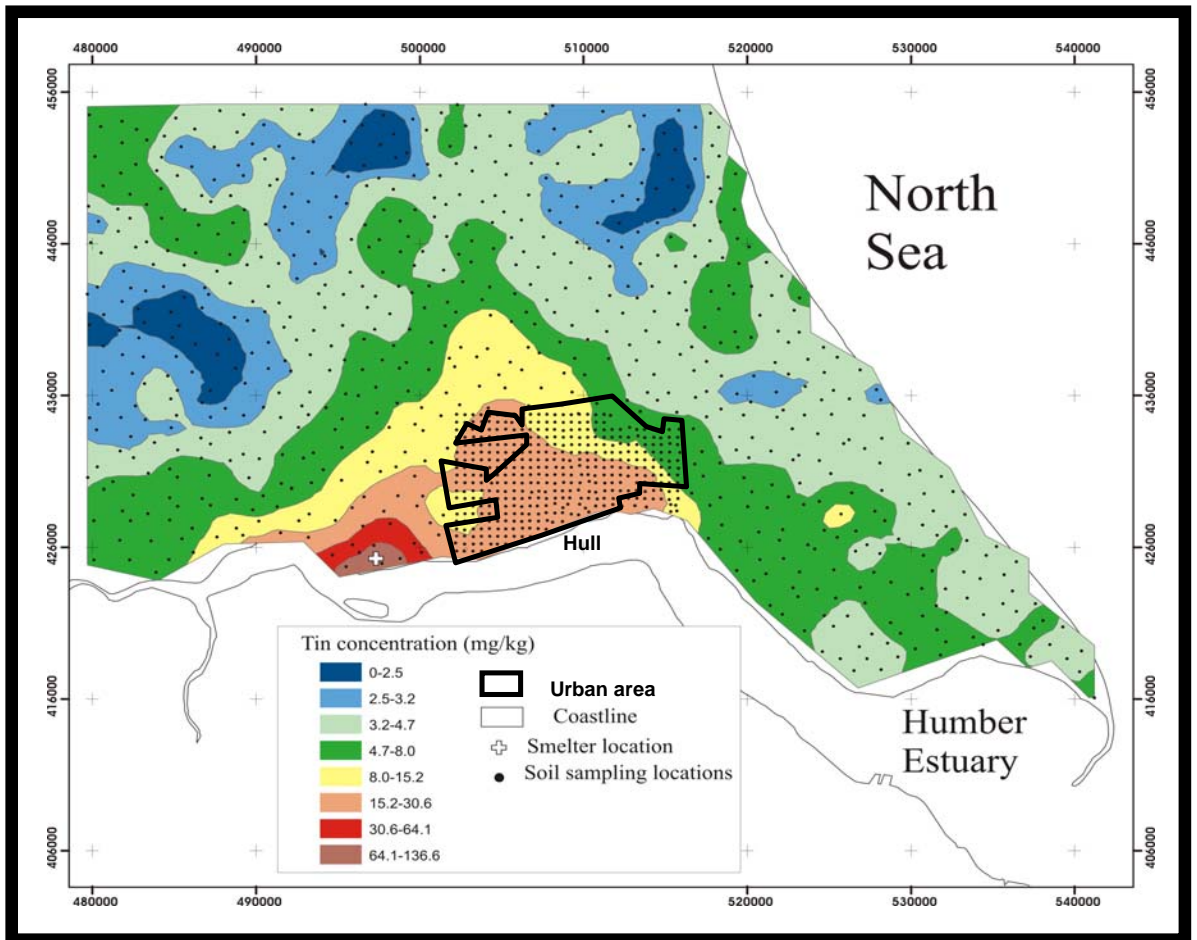**Figure 12** *Total Sn concentrations in surface soils (0.20 m) from the Hull region*

Figure 13 *Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of total As distribution in deeper (0.50 m) soils from Stoke-on-Trent categorised on the basis of underlying made ground type*