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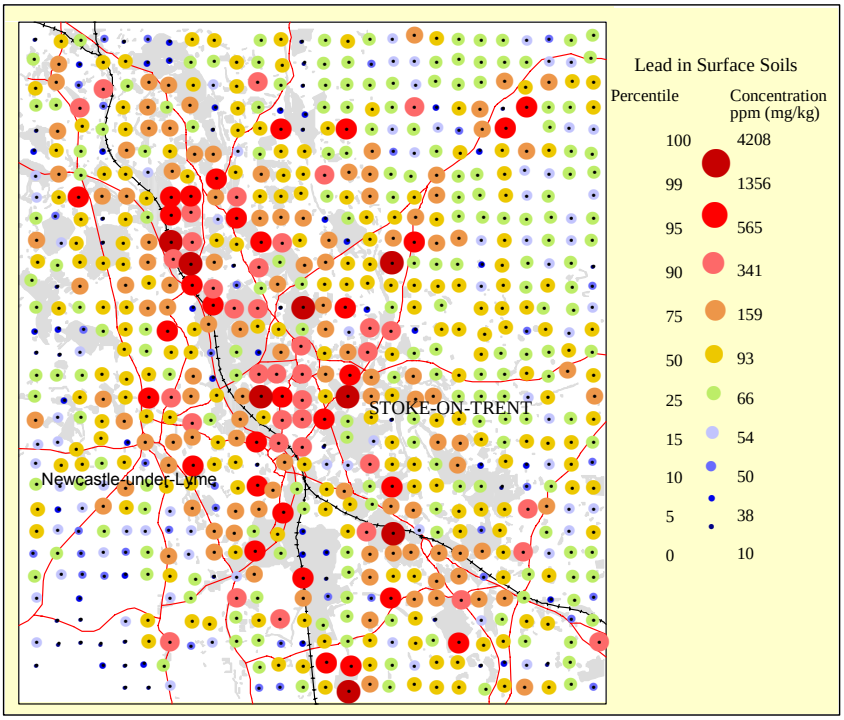
Urban Soils Geochemistry and GIS-aided Interpretation – A Case Study from Stoke-on-Trent

Urban Geoscience & Geological Hazards Programme
Research Report IR/01/35R



BRITISH GEOLOGICAL SURVEY

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RESEARCH REPORT IR/01/35R

Urban Soils Geochemistry and GIS-aided Interpretation – A Case Study from Stoke-on-Trent

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Front cover

Proportional symbol map of total lead concentrations in Stoke-on-Trent surface soils.

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Tables and Figures

Glossary

AAS	Atomic Absorption Spectrometry
BGS	British Geological Survey
CBRE	Centre for the Built Environment
CEC	Commission of the European Community
CLEA	Contaminated Land Exposure Assessment
DC-ARC-ES	Direct Reading Arc Emission Spectrometry
DETR	Department of the Environment, Transport and the Regions
DTLR	Department of Transport, Local Government and the Regions
DTM	Digital Terrain Model
EA	Environment Agency
ESRC	Economic and Social Research Council
G-BASE	Geochemical Baseline Survey of the Environment
GDI	Geoscience Data Index
GIS	Geographic Information System
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
ICRCL	Interdepartmental Committee on the Redevelopment of Contaminated Land
IDEA	Improvement and Development Agency
IDW	Inverse Distance Weighting
JISC	Joint Information Systems Committee
LA	Local Authority
LLD	Lower Limit of Detection
LLR	Lower Limit of Reporting
LOI	Loss on Ignition
MAC	Maximum Admissible Concentration
ME	Mean Error
NGDC	National Geoscience Data Centre
NLUD	National Land Use Database
NGR	National Grid Reference
OS	Ordnance Survey
PAH	Polynuclear Aromatic Hydrocarbons
PBET	Physiologically Based Extraction Tests
PCB	Polychlorinated Biphenols
PHE	Potentially Harmful Element
PHS	Potentially Harmful Substance
PPM	Parts Per Million
RSS	Residual Sum of Squares
SOBI	Single Onshore Boreholes Index
SPZ	Source Protection Zone
SSSI	Site of Special Scientific Interest
URL	Upper Reporting Limit
US-EPA	United States Environmental Protection Agency
WFD	Water Framework Directive
WHO	World Health Organisation
XRF	X-ray Fluorescence Spectrometry

Foreword

The primary purpose of this report is to assess methods for analysing and presenting urban soil geochemical data collected by the British Geological Survey (BGS) Geochemical Surveys of Urban Environments (GSUE) project. The intended audience for this report is BGS staff working on urban geochemical surveys, or using the data from such surveys.

This report presents the results of a case study carried out between 2000 – 2002 using data from Stoke-on-Trent and makes recommendations for future practices in other urban areas under investigation by the GSUE project and for the corresponding survey in rural areas, the Geochemical Baseline Survey of the Environment (G-BASE) programme.

This report pre-dates some recent changes to the UK government guidelines on contaminated land (DETR, 2000), which are relevant to the applications of urban soil geochemical data and should be read in this context.

Executive Summary

The systematic geochemical mapping of urban soils has been undertaken by the British Geological Survey (BGS) Geochemical Surveys of Urban Environments (GSUE) project since 1992 and to date 21 urban centres have been sampled. The city of Stoke-on-Trent was chosen for a review of GSUE methods as the area contained sufficient sample numbers (approximately 750) and additional information such as geology and land use to allow an assessment of sampling techniques, data presentation and the applicability of geochemical data to wider environmental problems.

Separate chapters in this report address:

- The presentation of urban geochemical data, both within the urban area and in relation to rural geochemical data
- The possible controls on soil geochemistry and distributions of chemical elements in the area
- The application of geochemical data to risk-based human exposure and groundwater vulnerability assessments in relation to chemical elements in urban soils

The results demonstrate that the geochemistry of soils in Stoke-on-Trent primarily reflects that of the soil parent material. In areas underlain directly by natural bedrock and drift deposits, these play an influential role in soil chemistry, despite the increased incidence of diffuse pollution in urban compared to rural areas. In contrast, element distributions in soils developed over made ground show that this substrate has a major, often detrimental effect on soil quality. However, it should be noted that much of the waste material used as fill (prior to modern regulatory systems) in Stoke-on-Trent is very base-rich providing buffering against acid soil conditions. Therefore, the mobility of many potential harmful metal and other trace elements is likely to be restricted in the neutral to alkaline soils of the area than may otherwise be the case in ‘natural’ soils.

This study has generated a series of recommendations to inform future geochemical surveying strategies ranging from the inclusion of additional analyses, to the application of the data for further risk assessment studies.

Synopsis and Recommendations

OVERVIEW

The British Geological Survey (BGS) is responsible for the national strategic geochemical survey known as the Geochemical Baseline Survey of the Environment (G-BASE) programme, which provides information on the chemical composition of the UK surface environment. As part of this programme, the Geochemical Surveys of Urban Environments (GSUE) project was initiated in the early 1990s to generate information on chemical element distributions in city environments. The urban survey was developed in light of growing interest in city regeneration within the context of new government legislation on contaminated land (Environmental Protection Act Part IIa, 1990). Many elements such as arsenic, cadmium, lead, zinc, copper and mercury are of concern because, if present in high concentrations, they are potentially harmful to ecosystems and humans, and government regulations are in place to limit the dispersion of these substances in the environment.

As part of the GSUE project, an urban geochemical survey of the Stoke-on-Trent area was completed during 1993. The study area of 195 km^2 extends from UK national grid reference 382000E, 340000N to 395000E, 355000N in the Midlands of central England. Geologically the area comprises a sequence of tilted Carboniferous and Permo-Triassic sedimentary rocks, which increase in age from the southwest to the northeast. The built-up area is primarily underlain by Westphalian rocks comprising the Coal Measures and overlying Barren Measures whereas Namurian Millstone Grit and Triassic Sherwood Sandstone cropout on the urban periphery. Superficial deposits in the region comprise glacial till (boulder clay) and river alluvium. The presence of coal, ironstone and clay resulted in rapid growth during the Industrial Revolution (c. 1760 onwards) and the area became a world-leading centre for coal, iron and steel and pottery manufacture. The legacy of these heavy industries is evident in the area today and the city remains a major centre for ceramics, engineering, light industry and merchandising. 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 geochemical survey was based upon the collection of approximately 747 surface (0.15 m depth) and profile (0.45 m depth) soil samples on a grid pattern at a sampling density of 4 per km^2 across the urban area. Following air-drying, surface soil samples were sieved to < 2mm and profile soils to < 150µm before analysis by X-ray Fluorescence Spectrometry (XRF) for total concentrations of approximately 25 elements. Mercury, pH and loss-on-ignition (LOI) (as a measure of organic matter content) were also determined in surface soils. The resultant geochemical data are available in geo-registered digital format for the urban area.

Whilst the local geochemistry presented in this report is specific to Stoke-on-Trent, approaches used in this case study form the basis of recommendations for the wider GSUE and G-BASE projects in the following broad areas:

- Sample preparation and analyte selection
- Data presentation methods appropriate for urban areas
- The development of an urban geochemistry geographic information system (GIS) based on the ArcView® software package
- Integration of geochemical data with other environmental datasets for land quality determinations

- The development of risk assessment applications for two of the key receptors identified under the Part IIa (1990) contaminated land legislation, groundwater and humans

CONCULSIONS AND RECOMMMENDATIONS

1. Urban Geochemical Survey Methods

The investigation of possible sources of elements in soils, relationships with natural and man-made parent materials and assessments of likely threats to groundwater and humans from soils outlined in the present study are only possible because of the determination of key parameters. These are pH, LOI and the major element chemistry. For example, the geochemical signatures associated with foundry waste were identified in Stoke-on-Trent because CaO, MgO and P_2O_5 were analysed in addition to the trace metals. These parameters had not previously been determined for urban soils.

- ***It is recommended that the full range of parameters determined in this study should be incorporated into all urban surveys in the future***

Surface and profile soils can provide a useful indication of likely element sources in the urban environment. For example, elements such as Fe_2O_3, Ni, Cu, As, Cr and CaO present in higher concentrations in profile soils can indicate contamination by industrial and metal processing, made ground and fill materials. Alternatively, elements deposited from atmospheric fall out, such as Pb and Cd related to road vehicle usage, tend to be concentrated in surface soils. Comparisons between surface and profile soil results for Sn, Cd and Pb from Stoke-on-Trent suggest enhancement in the surface relative to profile soils indicating the greater influence of diffuse pollution sources such as litter and traffic on these element distributions.

It should be noted, however, that investigations into the relationships between surface and profile soils were complicated during the present study by the GSUE sampling strategy whereby surface soils are sieved to a coarser (< 2 mm) fraction than profile soils (< 150 µm). Although this strategy was established with a sound scientific basis in the early 1990s (profile soils which more closely represent soil parent materials were compatible with < 150 µm regional stream sediment data), it is now recognised that soil studies are of prime environmental importance and a consistent sieved size fraction is desirable.

- ***It is recommended that both surface and profile soils are sieved to the environmental standard < 2 mm size fraction***

In the Stoke area, and many other urban centres covered by the GSUE project to date, sampling was carried out beyond the extent of the built-up environment into the urban periphery. The experience in Stoke-on-Trent is that this complicates the definition of the truly urban versus rural geochemical signatures.

- ***It is recommended that in future, the GSUE project focuses on soil collection in the urban built environment whereas urban periphery and rural coverage be provided by the G-BASE programme to clearly distinguish the built urban versus non-built rural geochemical signatures***

The purpose of systematic urban geochemical mapping is to provide an overview of soil quality in the urban environment as a framework to planning and management. Surveys at the citywide scale are not designed to examine specific problems or locations and do not replace the need for detailed site investigation reports. None-the-less, this study has shown that the data provide a useful insight into the likely controls on element distributions in the urban environment and general relationships with land use, ground types and possible sources of contamination, highlighting areas for further investigation.

- ***It is recommended that urban geochemical signatures are established for other cities in the UK in order to determine element sources in soils and provide a framework to more detailed site investigations because systematic variations in chemistry were observed compared to soils over equivalent lithologies in the rural environment during the present study***

2. Urban Geochemical Data Presentation and GIS Development

In recent years, GISs have become useful tools for the display and interrogation of spatial information and are increasingly used by the BGS, local authorities and other professional institutions for urban management and planning. One of the main aims of the present study was to devise methods of presenting geochemical data in an ArcView® format suitable for urban planning and contaminated land assessments.

The standard method of presenting geochemical data as interpolated maps involving extrapolation of information into areas where the actual nature of soils is unknown is highly effective for rural surveys where soils display regional compositional trends. However, variogram analysis applied to the present study demonstrated that there was little spatial connectivity between soils at the 500 x 500 m sampling interval adopted for the Stoke-on-Trent survey. Therefore, the preparation of interpolated maps was not valid due to the heterogeneous nature of urban soils and could lead to mis-interpretation in terms of contaminated land assessments. As an alternative, a method of presenting urban geochemical data as proportional symbol maps was developed in ArcView® for Stoke-on-Trent because these maps provide an indication of geochemical trends whilst retaining the spatial representivity of the data. Despite the inherent problems associated with interpolated maps of urban areas, with careful interpretation they can provide useful overviews of rural-urban relationships and multi-element associations. Therefore interpolated maps generated using the ArcView®-based G-BASE 'in house' algorithm called the Gridder programme were incorporated into the present report for information only. However, it should be noted that the Gridder programme requires further development as data classification and histogram generation have to be carried out manually at the present time.

- ***It is recommended that ArcView® proportional symbol maps be adopted as the standard geochemical data presentation method for all urban areas. However, it should be noted that spatial variability in urban soils is under further investigation by the GSUE project in Coventry, and these follow-on studies are likely to inform urban data presentation methods in the future***

- ***It is recommended that interpolated rural-urban and three component maps are included in urban studies where appropriate as they provide useful overview information. However, these maps should appear in report format only and should not be distributed digitally outside the BGS due to the potential for mis-interpretation of the results***

- ***It is recommended that real rather than interpolated percentiles are used to classify interpolated maps generated by the G-BASE 'in-house' Gridder programme, as these are more representative of the data distribution***

Within the GIS, data are stored as an ArcView® 'project' file organised into a series of views displaying surface soil geochemistry, profile soil geochemistry, background information layers, groundwater vulnerability and human risk assessments. The GIS facilitates the ready display and interrogation of individual or combinations of data layers allowing relationships to be more easily resolved.

Difficulties were encountered during the present using ArcView® files across the BGS computer network between office sites and transferring files across storage devices. Future GIS must be designed to avoid these issues.

- ***It is recommended that urban geochemistry GIS need to be in a format suitable for easy distribution. To achieve this, all data layers including interpolated grid files must be stored as ArcView® shape files and all legends for all layers must be saved as ArcView® legend files. All shape and legend files must be stored in the same or subordinate file directories to allow the ArcView® 'project' file to be transferred across drives or servers***

3. Digital Environmental Datasets

In addition to the geochemical maps, a variety of datasets were available for the Stoke-on-Trent area, many resulting from a previous environmental geology investigation carried out by the BGS during the early 1990s (Wilson et al. 1992). These included solid and drift geology and the nature and extent of artificial deposits. Given the long history of mineral extraction and industrialisation in the Stoke-on-Trent area, these datasets provided extremely useful background information to aid the interpretation of the geochemical data and were digitised and incorporated into the GIS for the present study. However, such detailed made ground information may not be available for other urban centres and the BGS is currently investigating methods of mapping artificial deposits. Other key environmental datasets included groundwater vulnerability and present and historic land use. It is recognised that all Local Authorities in the UK are collecting related potentially useful information under the Environmental Protection Act, Part IIa (1990), and in England, information is also acquired under the National Land Use Database (NLUD, 2000) all of which could aid future urban assessments.

- ***It is recommended that made ground type, solid and drift geology, historic and current land use, groundwater vulnerability and abstraction zones are key environmental datasets that should be digitally captured and incorporated into future urban geoscience GIS wherever possible***

4. Land Quality and the Nature of Made Ground

During the present study, direct comparisons between the urban data from Stoke-on-Trent with rural soils on the city periphery, from the Humber-Trent region and from other UK cities underlain by Coal Measure geology were possible due to the systematic methods adopted by the BGS G-BASE and GSUE projects in rural and urban environments respectively. These comparisons indicate that the majority of metal and metalloid elements are elevated in Stoke-on-Trent soils by 1.2 – 2 times local rural soil averages. Comparisons with the Soil Survey of England and Wales national soil inventory data also indicate that most elements are 1.5 – 4 times above national soil average contents although these results should be treated with caution due to differences in the survey methods between the two datasets. Although the concentrations of potentially harmful substances are enhanced in the Stoke

urban area relative to rural backgrounds, they are similar to other UK cities underlain by the Coal Measures such as Cardiff, Telford and Swansea indicating that Stoke is not unusual.

These general comparisons are useful to indicate the level of element enhancement in urban versus rural areas, however, they do not take account of the influence of natural soil parent materials on the geochemistry. The Coal Measures, which underlie the city, are naturally elevated in many metal and metalloid elements such as As, V, Mo, Cu, Ni, Zn, Pb and CaO and account, in part, for the high concentrations of these elements in Stoke-on-Trent soils relative to national averages. It should be noted however, that given the long and extensive history of industrialisation of the Coal Measures in the UK, it is difficult to establish a truly natural baseline for this rock type. In contrast, many trace elements are present in much lower concentrations over the quartz-rich Namurian Millstone Grit and Triassic Sherwood Sandstones of the Stoke urban periphery reflecting natural lithochemistry and the lack of major industrial development associated with these strata. Superficial deposits mainly comprise boulder clay, which due to its heterogeneous nature in the Stoke-on-Trent area shows no clear geochemical signature. Soils developed over alluvial sediments contain high concentrations of several metals including Pb. This probably indicates the tendency for drainage systems to act as contaminant sinks in the environment and the historical development of industry and transport routes along waterways in the Stoke-on-Trent area. These results have implications for the remobilisation of contaminants from alluvial soils during flood events and potential impact on drainage water quality.

However, by far the greatest controls on soil geochemistry in Stoke are the presence of made ground, urbanisation and industrialisation whereby geochemical signatures reflect the long history of coal and iron extraction and metal and pottery industries the area. The majority of elements, with the exception of SiO_2 and MgO, are elevated in the made ground urban-built environment compared to the rural periphery regardless of the underlying natural parent material. 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. Soils developed over coal spoil and coal ash waste, materials which have been widely dispersed in Stoke-on-Trent historically, 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 may account for localised anomalies due to historic factory emissions and dumping of ceramic waste. Although no distinctive geochemical signature was found with the road and rail network in Stoke-on-Trent, anomalous metal contents along the Caldon Canal indicate possible contamination associated with the transportation of industrial products and canal dredging. Multi-element anomalies are also associated with a former sewage treatment works to the south of Stoke-on-Trent. Interestingly, concentrations of potentially harmful substances are low in surface soils collected from flower beds in the city centre indicating the presence of ‘clean topsoil’ imported for landscaping following urban regeneration programmes. Whilst such soils are important for assessing human risk via contact with the surface environment, the levels may not be representative of those in the surrounding locale and soils at depth.

This study has shown 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.

The linkages between different soil element associations and made ground types are interesting because this study had the opportunity to assess whether geochemical survey data could be used to aid made ground mapping.

- ***It is recommended that geochemical signatures could be used to assist the identification and classification of made ground types and more detailed geochemical mapping could prove useful in defining the spatial boundaries of artificial deposit units in urban areas***

- ***It is recommended that if more detailed land quality studies are required these should be carried out as follow-up projects to the GSUE survey in close collaboration with the Local Authorities concerned since much of the key information, including past and present day land use and development history, is held by Local Authorities in the UK***

5. Groundwater Vulnerability and Human Risk Assessment

Two of the main issues of concern addressed under the recent contaminated land legislation (Environmental Protection Act, Part IIa, 1990), are the migration of potentially harmful substances through the environment to groundwater and humans. The legislation 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 (groundwater or humans) by means of a pathway (air, soil, surface deposits, solid geology, man-made structures, water, food, inhalation, contact and ingestion etc.). Thus contamination is only considered a problem if a pathway to a receptor is demonstrated. Groundwater and human health risk assessments were undertaken as part of the present study to assess the potential application of systematic geochemical data to these issues.

The ISO (2001) groundwater vulnerability contaminant-leaching model was tested on the Stoke-on-Trent study area. The model requires 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%) were measured as part of the GSUE survey and were directly incorporated into the model. Clay and sesquioxide contents were not determined routinely but a simple system to derive this information from GSUE soil texture and colour data was developed during the present study and can be used for other areas in the future.

Results show that due to the calcareous nature of the Coal Measures bedrock in Stoke-on-Trent and the base-rich character of much of the made ground material such as foundry and ceramic waste, soil pH values are circum-neutral over much of the built up area. As a result, the majority of soils have a high attenuation capacity and the leaching potential of the 11 contaminants examined in this study is generally low. Although the ISO (2001) model does not require data on element distributions in soils, the benefit of the GSUE survey is that the element concentrations are known and can be evaluated with the leaching potential results. Comparisons show that the regions of high element concentrations associated with the built-up area correspond to soils with poor leaching potential therefore the risks of pollutant migration to groundwater are less. Potential leaching risks over the Triassic and Namurian sandstones 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 potentially harmful elements in soils are found in low concentration over these lithologies.

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, for example. As such, this type of generic model should be used for guidance only. Although groundwater vulnerability maps produced by the Environment Agency in conjunction with the BGS and the Soil Survey are available for England and Wales, urban areas are not characterised because of the unknown properties of urban fill materials.

- ***The lack of information on the disruption of natural lithological and pedological sequences in urban areas restricts the assessment of groundwater vulnerability It is recommended that the BGS continue to address this very important issue***

- ***It is recommended that the wider application of the ISO (2001) leaching potential model to the G-BASE and GSUE surveys is tested using regional geochemical data in areas where more hydrogeological information is available***

In terms of human health risks associated with contaminants in the environment, the government sets guideline or trigger values for potentially harmful substances in soils (ICRCL 1987) and has just released a Contaminated Land Exposure Assessment (CLEA) model. Since the CLEA model was not available at the time of the present study, a human risk assessment scheme was tested for Stoke-on-Trent based on the ICRCL (1987) guidelines.

In the scheme, all surface soils that exceed the guideline values for any of the following elements: As, Cd, Cu, Pb, Ni, Hg, Pb and Zn were identified first providing a basic level risk assessment. The likely pathway for these substances to humans was then taken into account by selecting ground likely to provide contact with the local population such as gardens, allotments, play areas and parks. In the final level of the risk assessment the likely mobility and bioavailability of potentially harmful substances in these soils was qualitatively considered on the basis that low soil pH (< 7), clay (< 10 wt% Al_2O_3) and organic matter (< 10 % LOI) content equates to high mobility, therefore greater risk and high soil pH (> 7), clay (> 10 wt% Al_2O_3) and organic matter (> 10% LOI) content equates to low mobility, therefore less risk.

Results for the Stoke-on-Trent area show that although As concentrations over much of the city exceed the ICRCL (1987) guideline level, due to the circum neutral pH of the urban soils, there are only three locations where readily bioavailable potentially harmful substances occur in soils on sensitive land use types such as gardens and allotments and these areas should form the focus of further investigation.

Examination of the relationships between potentially harmful substances in soils and land use were carried out using Landline® data provided to the BGS by the City of Stoke-on-Trent Council for the duration of the project. However, at the time this study was carried out, these data were not polygonised and assessments of land use were carried out by individual examination, as it was not possible to select all areas of a particular land use within the city using GIS methods.

The BGS is developing quantitative analytical methods to assess the bioavailability and bioaccessibility of potentially harmful substances in soils. 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. Methods such as these could be used in the future to examine human risk in selected areas in more detail.

- ***It is recommended that current and historical land use datasets, are crucial for the risk interpretation of urban geochemical data and should be provided in digital polygonised format for Stoke and other urban areas in future assessments***

- ***It is recommended that future human risk assessments involve the new CLEA model, as the ICRCL (1987) guidelines are now considered obsolete by the UK government***

- ***It is recommended that follow-up studies into human risks in the Stoke-on-Trent area should also consider the application of physiologically based extraction tests (PBET) to assess the bioaccessibility of potentially harmful substances in soils***

- ***It is recommended that methods to provide systematic urban data and risk assessments could form a useful component of existing Environmental Protection Act, Part IIa investigations and the proposed new contaminated land planning regulations (DTLR, 2002)***

1. Introduction

By F M Fordyce

This report describes the results of a case study based on the city of Stoke-on-Trent carried out in 2000-2002, as part of the Geochemical Surveys of Urban Environments (GSUE) project. The study investigated the applications of systematic geochemical data to urban planning with the following main aims:

(i) Examine methods of presenting geochemical data in urban environments suitable for contaminated land investigations

(ii) Develop risk assessment applications of the data in the context of the recent UK Government Environmental Protection Legislation (Environmental Protection Act Part IIa, 1990) with particular emphasis on Local Authority (LA) contaminated land management strategies.

Geochemical data presentation and the risk assessment methods were based on a digital geographical information system (GIS), which provides a useful platform to display and interrogate spatial environmental data. GISs are increasingly utilised by LAs for urban management. The urban geochemistry of Stoke-on-Trent and the development of the risk assessment GIS with particular reference to protected waters and to humans are outlined in this report. Recommendations for future progress in urban GIS and geochemical mapping are also summarised.

1.1 GEOCHEMISTRY AND ENVIRONMENTAL CONCERNS

The 92 naturally occurring elements on Earth that form the different rocks, soils, waters and gases that are the building blocks of the planet are not distributed evenly across the globe. Concentrations at any location are often controlled by factors such as geology, vegetation, soil forming processes and climate. In addition to natural sources of these elements, environmental concentrations can be enhanced by anthropogenic activities such as mining, industrialisation, urbanisation and waste disposal. The distribution of the elements 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 (Table 1.1). The toxicity and mobility of these potentially harmful substances are often controlled by the amount of other elements present so it is important to understand as fully as possible, the chemical composition of the environment.

TABLE 1.1 POTENTIALLY HARMFUL ELEMENTS FOR HUMAN, ANIMAL AND PLANT HEALTH (FROM APPLETON, 1995)

Chemical Symbol	Element Name	Chemical Symbol	Element Name
Al	Aluminium	Mn	Manganese
As	Arsenic	Mo	Molybdenum
B	Boron	Ni	Nickel
Bi	Bismuth	Pb	Lead
Cd	Cadmium	Sb	Antimony
Cl	Chlorine	Se	Selenium
Co	Cobalt	Sn	Tin
Cr	Chromium	Te	Tellurium
Cu	Copper	Th	Thorium
F	Fluorine	Tl	Thallium
Fe	Iron	U	Uranium
Hg	Mercury	V	Vanadium
I	Iodine	Zn	Zinc

Although potentially harmful in excess, the majority of elements are essential to health in small doses. Elements listed in blue have no/limited biological function and are generally toxic to most organisms

Also of concern are the quantities of potentially harmful organic compounds of man-made origin many of which are detrimental to health. These include the polynuclear aromatic hydrocarbons (PAHs), which have been linked to cancer, the polychlorinated biphenols (PCBs), and the endocrine system disrupting chemicals that affect metabolic activity control. Whilst these substances were not measured as part of the current study, other parameters such as soil pH, organic matter content and major element chemistry could be used to predict their likely mobility in future investigations.

Many UK city environments have a long history of urbanisation resulting in elevated concentrations of potentially harmful substances (PHSs) including organic contaminants (PAHs, PCBs etc.), radioactive materials and potentially harmful elements (PHEs) 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. 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 (for example, the acidity of waters or soils and the soil texture and mineral composition), the level of exposure and the dose received.

In UK urban areas, the major pathways via which PHSs can enter the human body are through inhalation of dusts and gases and contact with 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 the 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.

1.2 UK LEGISLATIVE FRAMEWORK

Prompted by concerns about land and water quality, national governments and international agencies are developing policies to limit the amount and impacts of PHSs in the environment. Although links between long term human health effects and PHSs are often difficult to prove, the majority of regulatory authorities adopt a precautionary principal approach to legislate against high environmental concentrations of PHSs.

In the UK, one of the main legislative drivers relating to PHSs are the Government's targets for sustainable development, which focus on the re-use of Brownfield sites for 60% of new residential homes. Whilst this policy protects green belts around urban environments, Brownfield sites include land that may or may not be contaminated with PHSs.

The Environmental Protection Act, Part IIa (1990) was implemented on 1st April 2000 in England, 14th July 2000 in Scotland and 1st July 2001 in Wales. The Act places the responsibility for the identification, assessment, remediation and monitoring of contaminated land with LAs as follows:

Environmental Protection Act, Part IIa (1990)
Definitions:

Contaminated land is defined as:
"any land which appears to the local authority in whose area it is situated to be in such a condition by reason of substances in, on or under the land that:

Significant harm is being caused or there is a significant possibility of such harm being caused or
Pollution of controlled water is being or likely to be caused"

Harm is defined as:
"harm to the health of living organisms, or other interference with the ecological systems of which they form a part, and in the case of man, harm to his property"

The Act addresses the pollution of waters and threats to ecosystems and buildings in addition to human health risks 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 (Figure 1.1). If the linkage does not exist then, in terms of the Act, the land is not contaminated. Thus, for example, an area of ground could contain high concentrations of As but if this is not affecting water resources, property, living organisms or ecosystems then it will not be classified as contaminated.

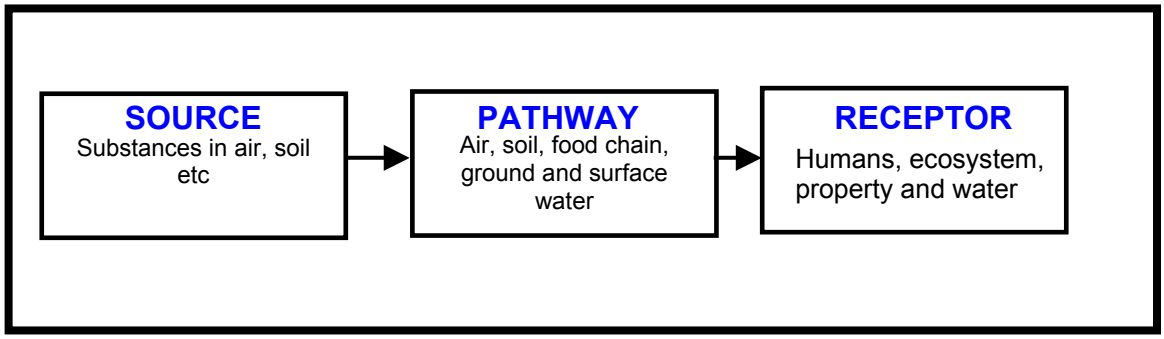


Figure 1.1 Concept of source, pathway and receptor in the assessment of contaminated land

The statutory duties of the LAs under Part IIa include:

- Inspection of LA area to identify potential contaminated land
- Determine contaminated land
- Establish whether sites should be designated as 'special sites' and thus become the responsibility of the Environment Agency (EA)
- Serve remediation notices where necessary
- Undertake assessment of the best practical remediation option -and tests for reasonableness
- Consult other parties including the EA
- Compile and maintain contaminated land registers
- Consult the EA on pollution of controlled waters

As a first stage, the Act requires LAs to adopt and implement a strategy for identifying and prioritising contaminated land, which will involve the collation of current and historical information on the distribution of potential receptors, the movement of contaminants in the environment and on contaminant sources.

Several guidelines exist to aid the identification, assessment and management of contaminated land. In terms of water quality, the World Health Organisation (WHO) defines maximum admissible concentrations (MACs) of PHEs in drinking water (WHO, 1996). The European Union Water Quality Framework Directive (CEC, 1998) incorporates many of the WHO values and is the legislative basis for water suppliers and regulatory authorities in the UK.

Similarly, many governments devise standards for soil quality. The UK Government Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL, 1987) guidelines provide maximum recommended thresholds or trigger values for contaminants in soil depending on the land use (Table 1.2).

The Government is currently developing a new risk assessment tool for human exposure known as the Contaminated Land Exposure Assessment (CLEA) model. Initially conceived by Nottingham University, the model is now being developed by the EA and will include risk assessment information for As, Cd, Cr, cyanide, Pb, Hg, Ni, phenol, PAHs, and Se.*

The Government does not prescribe any particular risk assessment model for contaminated land investigations and other software packages currently available include Risk Assistant® (Hampshire Research Institute, 1996) from the USA. In terms of water, groundwater vulnerability based on generic assumptions about the underlying geology has been mapped in England and Wales (EA, 1998) whereas new vulnerability assessments, which are PHE specific, have been developed by Blume and Brummer (1991). All these models require input of the physio-chemical parameters that control the movement of and the exposure to a given contaminant by a receptor.

To aid the identification and assessment of contaminated land, the BGS is providing systematic information on the concentration of PHSs and related physio-chemical parameters across UK city environments as follows.

TABLE 1.2 EXAMPLES OF THE ICRCL (1987) TRIGGER VALUES FOR PHSS IN SOILS

Element	ICRCL Trigger Value mg/kg (ppm)		
	Domestic Gardens and Allotments	Parks, Playing-fields and Open Spaces	Anywhere Plants are to be Grown
As	10	40	
Cd	3	15	
Cr	600	1000	
Cr^{6+}	25		
Pb	500	2000	
Hg	1	20	
Se	3	6	
B*			3
Cu*			130
Ni*			70
Zn*			300

Guidelines are based on total element concentrations in < 2-mm soils
* Elements that are rarely hazardous to human health but are phytotoxic (injurious to plants)

* Note: - since this study was undertaken, the CLEA guidelines are now available

1.3 GEOCHEMICAL SURVEYS OF URBAN ENVIRONMENTS (GSUE)

The BGS is responsible for carrying out the national strategic geochemical survey, known as the Geochemical Baseline Survey of the Environment (G-BASE), which defines the spatial distribution of chemical element concentrations across the UK surface environment. The programme began in the late 1960s in the north of Scotland and working southwards, will eventually provide information for the whole country (BGS, 2000). Initially, the programme focussed on rural areas, but in response to concerns about PHEs in the urban environment and the new statutory requirements on LAs (Environmental Protection Act Part IIa, 1990), urban 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, 1997, Kelly and Thornton, 1996, Bridge et al., 1997) and to date, 21 urban centres have been sampled (Fordyce et al, 2001).

Urban surveying is based upon the collection of surface (0.15 m) and profile (0.45 m) soil samples at a sampling density of 4 per km^2 and is designed to give an overview of the city's geochemical signature. The soils are analysed for a range of total element concentrations including elements that are of concern in terms of contaminated land such as Pb, As and Cd. In addition, the GSUE project includes analysis of parameters such as 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 as these factors can influence the mobility of PHEs in soils. The concentrations of many substances 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 bedrock/superficial cover of the surrounding rural hinterland. Even in completely undisturbed urban areas, many PHEs signatures are enhanced relative to the rural background due to atmospheric contamination, littering, urban surface run-off and other factors. 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 urban systematic 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.

The BGS is the only organisation providing systematic geochemical information on urban environments in the UK. The rigorous standards and quality control procedures adopted by the GSUE and G-BASE projects allow direct comparison of data from different urban centres and with rural soil data (Kelly and Thornton, 1996; Bridge et al., 1997; Fordyce et al., 2001).

1.4 URBAN GEOGRAPHIC INFORMATION SYSTEMS

The GSUE geochemical data are stored digitally allowing ready incorporation into a geographic information system (GIS). A GIS is a computer system for capturing, storing, checking, integrating, manipulating, analysing and displaying spatial data. Maps are the most common type of spatial data and show the distribution of features and the locational relationships between objects. A GIS is based upon a database that allows spatial information such as grid references or postcodes, which can only be visualised by plotting on a map, to be linked to attribute data. Attribute data provide other information about points in space such as the type of a building or road, or the height of a hill. A GIS digitally integrates databases and maps to produce a very powerful tool for environmental analysis. One of the main benefits of a GIS is the ready ability to store different information as separate data layers, which can be superimposed and interrogated simultaneously. GISs were developed to make cartography and data analysis easier and as such allow the storage of large amounts of data in a systematic format and the easy output of information as maps and reports. Due to their versatility, GISs are used increasingly by LAs to aid urban planning.

The importance of geoscience information and GISs to urban planning have been outlined by Ellison et al. (1998) and Hooker et al. (2000) and the BGS is currently developing urban GIS procedures for LAs. These combine geoscience information generated by the BGS with other spatial databases such as topography and land use (Brown and Marchant, 2000). Future GIS developments involving geochemical data are likely to take place within the broader context of the urban planning and contaminated land prioritisation GISs currently under construction in the BGS.

In combination with other datasets (such as geology, groundwater resources, land use etc.) digital geochemical data provide a useful tool to aid the identification and management of contaminated land. Following initial work in Wolverhampton (Bridge et al., 1997), the Stoke-on-Trent study provides the first opportunity within the BGS to examine the incorporation of systematic data into an urban GIS. A number of GIS software packages are commercially available and the ArcView® software was selected for the present study, as it is the BGS corporate standard and is the system most commonly used by LAs.

1.5 OBJECTIVES OF THE PRESENT STUDY

Throughout the development of the urban geochemistry GIS the objectives of the study were to:

1. Document the urban geochemical survey of Stoke-on-Trent
2. Recommend methods of presenting systematic geochemical data in a format suitable for contaminated land assessments
3. Examine the applications of geochemical data to contaminant source and contaminated land identification
4. Develop a risk assessment GIS to address two of the key receptors identified in the Environmental Protection Act, Part IIa (1990): protected waters and humans

2. Environmental Information

By A Marchant, B Hope and F M Fordyce

This chapter provides a background to the study area outlining the environmental data layers available for incorporation into the Stoke-on-Trent GIS and assesses the availability of similar data nationally. The spatial information incorporated into the GIS was derived from a variety of sources, however, many of the geoscience layers result from a detailed investigation carried out in the Stoke-on-Trent area during the early 1990's to provide the geological background to assist urban planning (Wilson et al., 1992). A detailed account of the environment and of the development of Stoke-on-Trent is provided by Wilson et al. (1992), although, a summary of the information pertinent to the present study is presented here.

2.1 THE STOKE-ON-TRENT STUDY AREA

The study area comprises 195 km^2 extending from UK National Grid Reference (NGR) 382000E, 340000N to 395000E, 355000N around the City of Stoke-on-Trent, situated to the south-west of the Pennines on the eastern edge of the Cheshire plain in the Midlands of central England (Figure 2.1). It includes the built-up areas of Stoke-on-Trent, Newcastle-under-Lyme and the satellite towns of the Potteries conurbation. The area lies predominantly within the remit of the City of Stoke-on-Trent Council with the remainder administered by Newcastle-under-Lyme Borough and Staffordshire District Council. Although Newcastle-under-Lyme is a market town with a history dating back to the 12th century, the adjacent six villages to the east experienced rapid growth during the Industrial Revolution to form the current Borough of Stoke-on-Trent. The development of the area was almost entirely based on mineral extraction related to the local geology. The numerous and easily accessible coal and ironstone seams of the Coal Measures provided the fuel and raw materials to support a thriving pottery and iron centre.

Ironstone workings in the area date back to the 13th century and were active during the 17th century at Red Street, Apedale and Tunstall (Figure 2.1). However, during the 19th century, the advent of the blast furnace heralded the rapid growth of the industry at Shelton, Apedale, Silverdale, Norton, Chatterley, Kidsgrove, Goldendale and Longton (Figure 2.1). Although the industry went into decline during the 20th century due to international competition, the Shelton Steelworks (Figure 2.1) remained in operation from 1839 to 1978.

Pottery making began in the area in the late 1600s based on the clays of the Etruria Formation and, by the late 18th century, Stoke-on-Trent was the heart of a world-leading ceramic industry. Although the local clays continued to be used for roofing tiles and bricks, for pot making they were increasingly abandoned in favour of materials brought in from elsewhere including kaolin, feldspar, quartz, flint, ball clay and bone ash. Currently the industry in Stoke-on-Trent produces sanitary ware, ceramic insulators, tiles, pottery and china.

The Potteries coalfield has 60 recorded mined horizons, 52 coal seams and 8 ironstone bands. Many of the earliest workings are within the Hanley, Burslem, Tunstall and Longton areas of the city (Figure 2.1). Opencast mining has been carried out since the mid 20th century mainly in the west of the area around Red Street (Figure 2.1). The extensive mining activity in the area has generated surface colliery spoil or minestone tips containing mudstone, siltstone, sandstone, ironstone and coal (Table 2.1). Furnace slag from ironworks has been used as a source of hardcore and the tips at Apedale have been extensively quarried away over the latter part of the 20th century. The largest slagheaps in the area are

at the former Shelton Steelworks and have been partially landscaped and built over. Furnace slag tips are also found at the former Goldendale and Hollybush works (Figure 2.1).

A number of the quarries excavated over the past 200 years have been filled subsequently with a combination of pottery waste (unwanted till, mudstone and sandstone from the clay extraction and faulty tiles bricks and ash) and domestic and other industrial waste. Quarries used for domestic waste disposal include Blurton, Crackley and Apedale Road, Chesterton. The former Metallic Tilery Company Quarry at Chesterton was licensed for industrial waste disposal until the mid 1980s (Figure 2.1).

During the latter years of the 20th century, the long history of mineral extraction and industrialisation left a legacy of derelict land in Stoke-on-Trent which has subsequently been the subject of grant schemes from the Department of the Environment Transport and the Regions (DETR). As a result, many of these derelict areas have undergone remediation and regeneration (Table 2.1).

TABLE 2.1 SOME EXAMPLES OF FORMER DERELICT LAND REDEVELOPMENTS IN THE STOKE-ON-TRENT AREA (FROM WILSON ET AL., 1992).

Location	Former Use	Redevelopment Use
Northwood	Colliery Tip	Playing Fields
Wolstanton	Colliery Tip	Playing Fields
Chell	Railway Cutting	Colliery infill converted to Parkland
Sneyd Hill Park	Central Forest Park	Community Land
Shelton	Colliery Tip/Ironworks	Industrial Estate
Fenton	Colliery Tip	Industrial Estate
Parkhouse	Colliery Tip	Industrial Estate
Birchenwood	Colliery Tip	Industrial Estate
Tunstall	Clay Pit	Industrial Estate
Cobridge	Clay Pit	Industrial Estate
Rowhurst	Clay Pit	Industrial Estate
Lightwood	Quarry	Housing
Chell	Quarry	Athletics Stadium
Red Street	Opencast coal	Housing
Apedale	Mine/ Ironworks	Country Park
Silverdale	Colliery Tip	Pasture

Locations are shown on Figure 2.1

To support the booming Potteries industry during the Industrial Revolution, the Trent-and-Mersey Canal was constructed through the centre of Stoke-on-Trent from 1766, followed by the Caldon Canal (Figure 2.1). The railway network supplemented the canals during the 19th century. During the latter half of the 20th century improvements to the road network have included the building of the M6 motorway to the southwest of Stoke-on-Trent and more recent upgrading of the A500 motorway link road and the A34 through Stoke-on-Trent city centre. With these excellent transport networks, Stoke-on-Trent today remains a major ceramic industry centre and is a focus for engineering, tyre manufacture, light industry and merchandising.

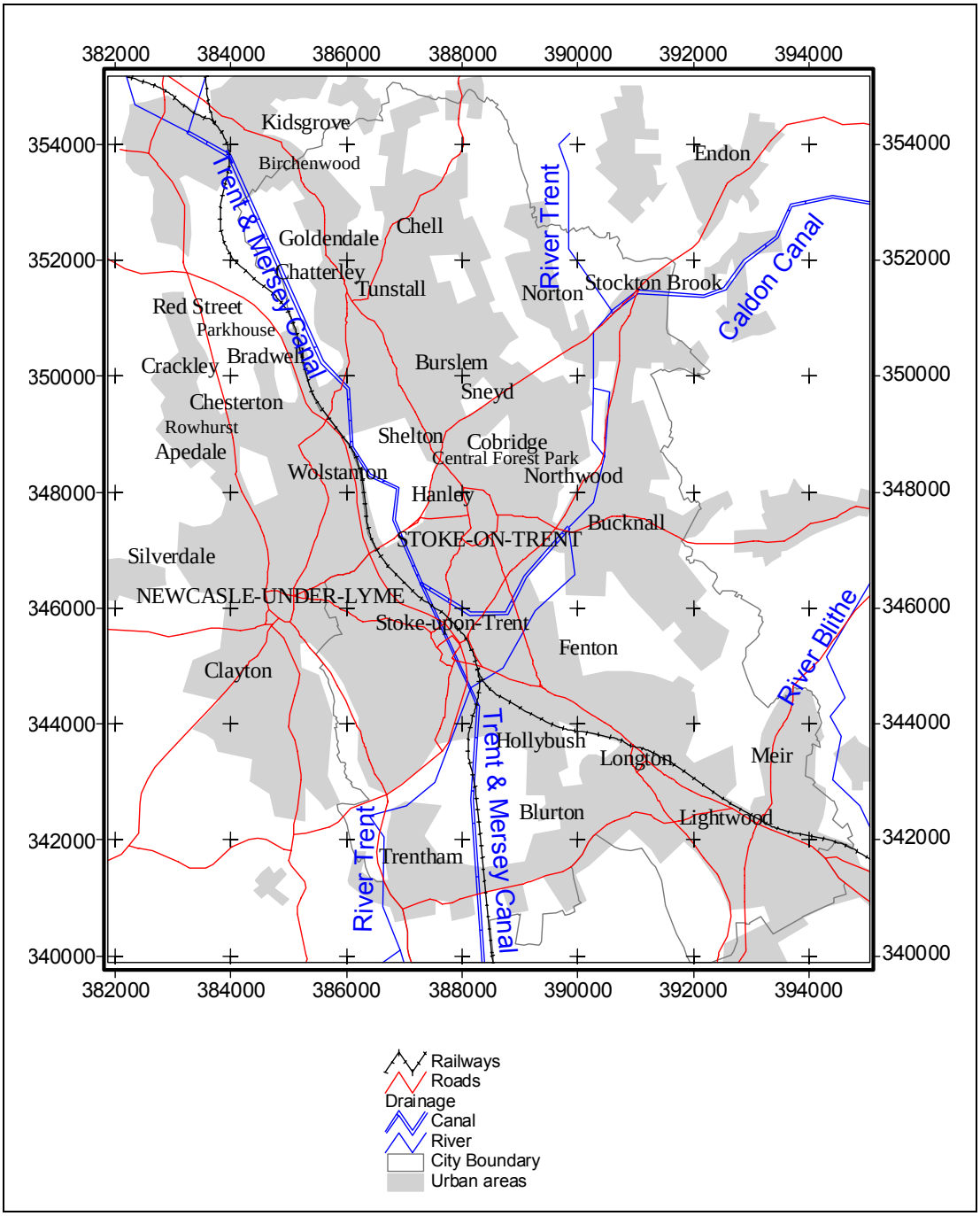


Figure 2.1 Map of the Stoke-on-Trent geochemical study area showing selected areas of the city associated with former colliery, iron and pottery industry activity.

2.2 ENVIRONMENTAL DATA FOR STOKE-ON-TRENT AND OTHER AREAS

As background to the present study, environmental data for Stoke-on-Trent were incorporated into an ArcView® GIS for the urban area (Table 2.2). The following sections briefly describe these data, restrictions on their usage and likely availability of the various data types in future geochemical investigations of other urban centres.

TABLE 2.2. LIST OF DIGITAL ENVIRONMENTAL DATASETS INCORPORATED INTO THE STOKE-ON-TRENT URBAN GIS

FILE NAME	DESCRIPTION	SOURCE
Grndvul	Groundwater vulnerability map	Joint BGS/EA/Soil Survey maps
Waterabs_point	Water abstraction sites	Environment Agency
Spzsrc	Source Protection Zone sources	Environment Agency
Spz	Source Protection Zones	Environment Agency
Railways	Railways	OS Meridian dataset
Roads	Main Roads	OS Meridian dataset
Boreholes	Boreholes	SOBI boreholes, BGS GDI
Water wells	Water Wells	BGS, Wallingford
Boundary	Boundary of Stoke-on-Trent City local authority	OS Meridian dataset
Study area	Study area covering all geochemistry sample points	Created from map of geochemistry sample points
Meridian	OS Meridian data from north 1: 50 000 topographic sheet	OS
Meridian2	OS Meridian data from south 1: 50 000 topographic sheet	OS
Dtm	Digital terrain model	Derived from OS Landform Panorama contours
Made ground	Made ground dataset	Identified by Wilson et al. (1992)
Sssi	SSSI's	English Nature
Monuments	Historic Monuments	English Heritage
Stoke_pop_region	Population Map	1991, Census, Crown Copyright
Stoke_quarry_ugm_region	Quarries	BGS
Sj84.tif	OS colour 1: 50 000 topographic raster image	OS
Landline	OS 1: 10 000 Landline® data	City of Stoke-on-Trent Council
Petrol stations	Petrol Stations	The Data Consultancy
Rural_soil_data	Rural soil data sample sites	BGS
Surface/profile locations	Urban soil data sample sites	BGS
Rural_and_urban_soil_data	Rural and Urban soil data sample sites	BGS
Solid250k	1: 250 000 Solid Geology	BGS GDI
Drift625k	1: 625 000 Superficial Deposits	BGS GDI
Stoke_study_artif	1: 50 000 Artificial Deposits	BGS
Stoke_study_mass	1: 50 000 Mass Movement	BGS
Stoke_study_drift	1: 50 000 Superficial Deposits	BGS
Clipped solid	1: 50 000 Solid Geology	BGS

OS = Ordnance Survey GDI = Geoscience Data Index
SOBI = Single Onshore Boreholes Index

2.2.1 Ordnance Survey Topographic Information

All data derived from the Ordnance Survey (OS) are covered by the corporate BGS licence, which allows use of the data for internal non-commercial projects only. Figure 2.2 shows the digital 1: 50 000 scale OS raster map of Stoke and Figure 2.3 the Meridian data line-work derived from the OS 1: 50 000 topographic maps. Although the Meridian line-work is currently colour-coded such that distinctions are made between roads, rivers and railways etc., these data have yet to be classified into different data types. The OS 1: 50 000 topographic maps provide useful locational information and an overview of land use and surface water resources in the study area, and are incorporated into the GIS to provide a geographic reference to the other datasets for Stoke-on-Trent. These data are available for most city

areas and could be incorporated into urban GIS as a standard background information layer in the future.

2.2.2 Land Use Information

Current and historical land use data are key to assessing contaminated land and urban planning in any city centre. Detailed (1: 10 000 scale) digital Landline® land use data were made available to the BGS by the City of Stoke-on-Trent LA for the duration of the project under the Stoke-on-Trent Service Level Agreement with the OS. These data are only available for work carried out by the BGS on behalf of Stoke-on-Trent City Council and cannot be used commercially or shown to a third party without permission. The Landline® data consist of attributed line-work defining different land uses. Therefore it is possible to identify particular land use types of interest to contaminated land studies such as schools, gardens, industrial units and open spaces etc. (Figure 2.4). However, the current spatial query functionality of the data is limited as the data are not in the form of attributed polygons. As a result, it is not yet possible to select all ground within Stoke-on-Trent associated with schools, for example. The availability of polygonised Landline® and other OS-derived data is currently under review by the BGS and it is likely that these datasets may be obtainable in the future. In the urban geochemistry GIS, the data are held as a series of tiles covering the Stoke-on-Trent area. In order to display these tiles, a library is created within ArcView® that stores the tiles separately and allows only the tiles relevant to the area of interest to be displayed on the GIS screen at any time. Whilst the Landline® data are vital for detailed investigations, their use in terms of producing a report-size (A4 page) overview of land use in the Stoke-on-Trent area are limited due to the difficulties of displaying the data for the whole area. Creating one large file combining all the tiles greatly reduces the efficiency of the GIS. Furthermore, at the current time in BGS it is not possible to store the ArcView® libraries on shared network areas thus access to the Landline® data is restricted to individual computers.

Digital land use information for England is being collated by the National Land Use Database (NLUD) project, which is a partnership between DETR, English Partnerships, the Improvement and Development Agency (IDea) (representing the interests of local government) and the OS (http://www.nlud.org.uk). This project aims to standardise land use information from LAs around the country and is under on-going development but as yet, information for Stoke-on-Trent is unavailable. The BGS is currently in consultation with NLUD to standardise BGS-held land use information to the NLUD system.

The BGS has recently acquired raster format historical land use maps for the whole country under an agreement with SiteScope™. At the present time, these maps have not been geo-registered but could prove a potentially useful source of information in the future to assess relationships between geochemistry and previous contaminative land uses. Many of the historical land use maps and records held by LAs are in paper format and the BGS is actively involved in digitising this information into urban planning GIS systems. Historical land use information is likely to be available for Stoke-on-Trent in the future as part of an on-going urban GIS development programme with the BGS.

In terms of land use, Stoke-on-Trent developed as a series of small towns based on mineral processing and industrial development. Thus former and present industrial land use is located throughout the built up area and is not concentrated in particular zones of the city. This is in contrast with previous urban centres investigated by the GSUE project such as Wolverhampton, which had a clearly defined industrialised corridor (Bridge et al., 1997). In general terms, the land between Hanley and Tunstall eastwards to the main railway line (Figure 2.1) was highly industrialised. The Pottery industry was based from Longton in the south of the city to Tunstall in the north, whilst coal and iron workings extended to the east (historically) and more recently to the west of the city. This pervasive range of industrial activity makes it difficult to separate industrial from non-industrial sectors of the built environment. This will not necessarily be the case for other cities investigated under the GSUE project, and for other centres it may be possible to generate overview land use maps showing different sectors of the city to aid geochemical and contaminated land investigations.

Road and rail line-work derived from the 1: 50 000 OS Meridian data provide useful locational markers for the study area (Figure 2.1) and highlight areas at possible risk from transport-derived pollution. These data are in vector format, therefore relationships between the geochemical data and possible sources of contamination can be examined using the buffer zone function of ArcView® for example, to

select all data within a certain distance of major roads. These data should be readily available for all urban areas in the UK and routinely incorporated in future urban GIS.

Other land use datasets of relevance to urban planning and contaminant assessment include the location of historical monuments requiring protection (Figure 2.5) derived from English Heritage data and sites designated by English Nature to be of special scientific interest (SSSIs) (Figure 2.6). These data are available for the whole country and are routinely incorporated into urban GIS systems. There are five SSSIs in the Stoke-on-Trent area, all on the periphery of the built-up area with the largest to the west of the City at Wetley Moor.

Also of interest from the contaminant source perspective are the locations of petrol stations in the urban area (Figure 2.5). These are derived from a national dataset under licence to BGS from 'The Data Consultancy'. At the local scale the data accuracy is questionable, but they do give an overview of petrol station locations in the urban area.

2.2.3 Digital Terrain Model

A digital terrain model (DTM) for the study area has been derived from the OS Platform Dataset and is covered by the normal OS restrictions on usage (Figure 2.7). The model can be used to locate the likely water table in an area by assessing the locations of rivers and springs and therefore aids the assessment of threats to water resources in the urban environment.

2.2.4 Solid Geology and Superficial Deposits

Although digital 1: 50 000 solid geology line-work is not yet available for all parts of the country, the BGS is in the process of creating national digital cover. Therefore these datasets should be available for urban study areas in the future. Included with the solid geology digital line-work is basic information on the extent of made and worked ground and mass movement deposits. The 1: 625 000 digital superficial deposits line-work is available in the BGS for the whole country and should be included as a standard dataset in urban GIS until more detailed line-work becomes available.

The 1: 50 000 and 1: 250 000 solid geology (Figure 2.8) and 1: 50 000 and 1: 625 000 superficial deposits line-work (Figure 2.9) for the study area have been incorporated into the GIS from the BGS geoscience data index (GDI). The study area is underlain by sequence of tilted sedimentary rocks of Carboniferous and Permo-Triassic age (340 – 220 million years ago), younging from the northeast to the southwest. The oldest rocks in the area are the Namurian Millstone Grits in the northeast, which comprise a sequence of mudstones and sandstones with coarser sandstones originally laid down in a river delta. These are overlain by the Westphalian Coal Measures Group, which is a sequence of mudstones and siltstones with some sandstones, numerous seatearth horizons (ancient soils) and coal seams. The upper parts of the sequence contain thin layers of ironstone comprising clayband (siderite – iron carbonate) and blackband (carbonaceous ironstone) types. The Coal Measures are overlain by mudstones and red sandstones of the Etruria Formation, which were formed in a well-drained alluvial environment. These constituent lithologies are easily weathered and tend to form valleys in the study area. Overlying the Etruria Formation are the grey sandstones, siltstones, mudstones and inpersistent limestones of the Halesowen Formation. Although the conditions of deposition were similar to those during Coal Measures times and this sequence also contains coal seams, they are generally too thin to be workable. The succeeding Salop Formation consists of a cyclic sequence of reddish brown mudstones and siltstones with purple-grey sandstones. For the purposes of this report, these latter three formations combined are known as the Barren Measures due to the lack of workable coals in these horizons. At the end of the Carboniferous period major earth movements resulted in faulting and folding along a predominately north or north-westerly trend and the rocks were subsequently eroded during the Permian period. During the Triassic, the climate was more arid and wind-blown reddish brown sandstones were deposited first followed by a thick sequence of fluviatile sandstone deposits, which together form the Sherwood Sandstone Group. The youngest rocks of the sequence are mudstones and siltstones of the Mercia Mudstone Group (Figure 2.8).

The most extensive superficial deposits over the study area comprise glacial tills, which are thickest in the northwest of the area and cover the rock formations to the south and east of Stoke-on-Trent (Figure

2.9). Under the new BGS classification scheme these deposits are now labelled as diamicton, however, boulder clay is referred to throughout this report to be consistent with the information provided in Wilson et al., (1992) and maintain familiar terminology for non-specialists. Melting ice was also responsible for the deposits of sand and gravel in the northwest of the area which were laid down as outwash approximately 15 000 years ago as the climate ameliorated. River alluvium forms the substrate in the Trent and former Fowlea Brook (now the route of the Trent-and-Mersey Canal) valleys.

2.2.5 Made Ground and Quarries

The BGS is in the process of reviewing methods to categorise made ground in cities, as this is a key issue for environmental planning. Urban geochemical data may aid these studies by characterising the geochemical signature of different waste types. In contrast to the restricted availability of information on made ground, the known locations of quarries across the UK are held by the BGS in digital format and can be readily incorporated into urban GISs.

As part of the urban planning study carried out by Wilson et al. (1992), an attempt was made to categorise the nature of made ground in the Stoke-on-Trent urban area based on field surveys, borehole records and archive data. Maps of comparable detail to Stoke-on-Trent are currently not available for most urban areas. For Stoke-on-Trent, the made ground maps were held in paper format only, although for the purposes of the present study the maps were digitised and incorporated into the urban geochemistry GIS. In many cases, the nature of the ground could not be determined or was so mixed that it could not be classified. The map of made ground types (Figure 2.10) gives a best estimate of the conditions but the composition of any given type cannot be guaranteed. One of the easiest classes of made ground to identify is colliery waste, which forms the most extensive type identified in Stoke-on-Trent covering large areas around the Hollybush, Lightwood, Northwood, Norton and Red Street sectors of the city (Figures 2.1 and 2.10). Ironworks-slag is largely associated with the former Shelton Steelworks site to the west of the city centre, whereas ceramic and brick industry waste is found in smaller tips throughout the city from Longton in the south to Kidsgrove in the north.

The distribution of quarries shown on Figure 2.11 reflects the development of Stoke-on-Trent, with workings for coal and ironstone in the Upper Coal Measures, and clay pits in the Etruria Formation throughout the centre of the Stoke-Newcastle conurbation. Many of these quarries have been filled with waste from the ceramic industry, or with domestic waste (see section 2.1 of this report).

2.2.6 Borehole Records

Figure 2.12 shows the location of boreholes held in the BGS SOBI database for the study area. These data are available for the whole country and are routinely incorporated in urban GIS for planning and development. In addition to providing information on ground conditions, individual logs can contain data that are essential to the determination of groundwater contamination risks such as the physical properties of superficial deposits and depth to the water table. However, many of the borehole records are held in paper format at the present time and locating the relevant information can be time consuming and laborious. The data are incomplete and of variable quality and age making the study of important parameters such as depth to groundwater difficult. The BGS is in the process of digitising the borehole record holdings, which should aid the assessment of these data in the future.

2.2.7 Water Source Protection Zones and Groundwater Vulnerability

The EA provides locational information on water abstraction sites and aquifer sources subject to protection policy in England and Wales. In terms of source protection zones, Inner Zone 1 is defined by a 50-day travel time from any point below the water table to the source and, additionally, as a minimum 50-m radius from the source. It is based principally on biological decay criteria and is designed to protect against the transmission of toxic chemicals and water-borne disease. Outer Zone 2 is defined by the 400-day travel time or 25% of the source catchment area, whichever is larger. The travel time is derived from consideration of the minimum time required to provide delay, dilution and attenuation of slowly degrading pollutants. Source Catchment Zone 3 is defined as the area needed to support the protected yield from long-term groundwater recharge (effective rainfall). In areas where the aquifer is

confined beneath impermeable strata, this source catchment may be located some distance from the abstraction. In addition to the source protection zone information, the EA, in conjunction with the BGS and the Soil Survey, has prepared a set of groundwater vulnerability maps for the UK. These maps assess the thickness and permeability of surface cover materials such as soils and superficial deposits and the nature of underlying bedrock in terms of permeability and fractures etc. with respect to the location and importance of groundwater resources to assess the risk of groundwater contamination. All urban areas in the scheme are classified as high vulnerability reflecting the inadequate occurrence and integrity of soils and surficial deposits in city environments. These types of water resource data are available for most of the country and are important to the assessment of contaminative threats to protected water resources (see Chapter 7 of this report).

Data relating to the locations of water wells and abstraction sites, source protection zones and groundwater vulnerability for Stoke were incorporated into the GIS for the present study and are shown in Figures 2.13, 2.14 and 2.15 respectively. Although there are several points of water abstraction, it is in the east of the study area that groundwater resources within the Sherwood Sandstone Group have been extensively utilised for public water supply at three boreholes, Meir, Sheepswash and Wallmyres (Figure 2.14) and are subject to aquifer protection policy by the EA. In the Stoke-on-Trent area, the major aquifer with high vulnerability occurs in the Sherwood Sandstone in the south of the area (Figure 2.15). The built-up area is underlain by minor aquifers (sandstones in the Coal Measures, Etruria and Halesowen Formations) that are also classed as highly vulnerable due to the limited superficial deposit cover and transmissible nature of overlying urban soils.

2.2.8 Population Density

Figure 2.16 shows the population density across the Stoke-on-Trent area based on the number of persons per 200-m cells and provides useful background information to the assessment of risk from contamination to the human population (see Chapter 8 of this report). This information is drawn from the Surpop web site with the proviso that the following source is acknowledged: The 1991 Census, Crown Copyright, ESRC/JISC purchase. The data were generated by David Martin, Ian Bracken and Nick Tate and obtained by Manchester Computing. If BGS wishes to use this data routinely in the future for commercial work, a licence to use the data will require investigation.

2.2.9 Summary

In summary, with increasing digitisation of data, there is a wealth of environmental information available to incorporate into urban geochemistry GIS to aid the assessment of urban planning and contaminated land. With the exception of key information on made ground and land use, which will vary between cities, the majority of the other background datasets are available for most parts of the country. The relationships between these types of data and urban geochemical information for the Stoke-on-Trent study area will be examined in the following chapters of this report.

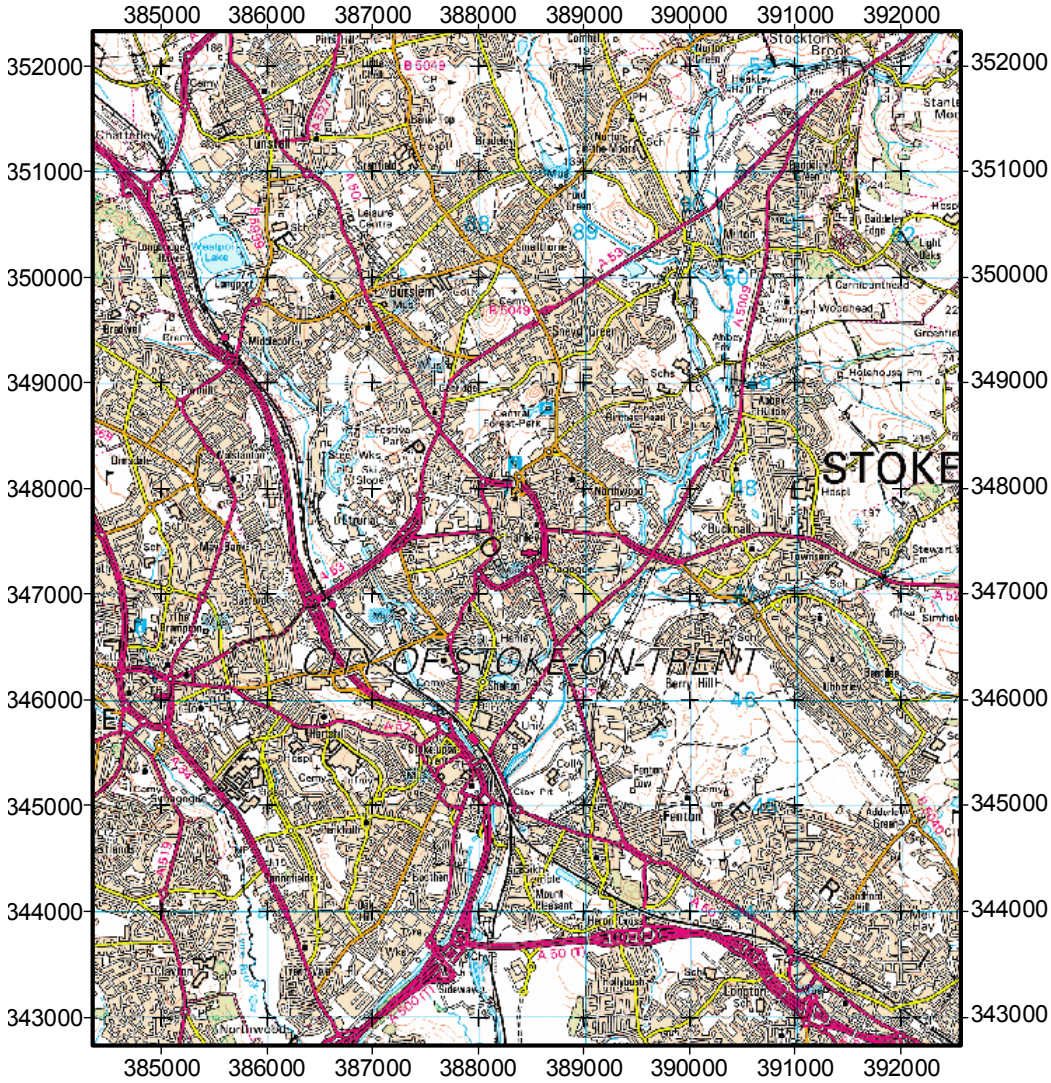


Figure 2.2 Raster image of the 1:50 000 OS topographic map for Stoke-on-Trent

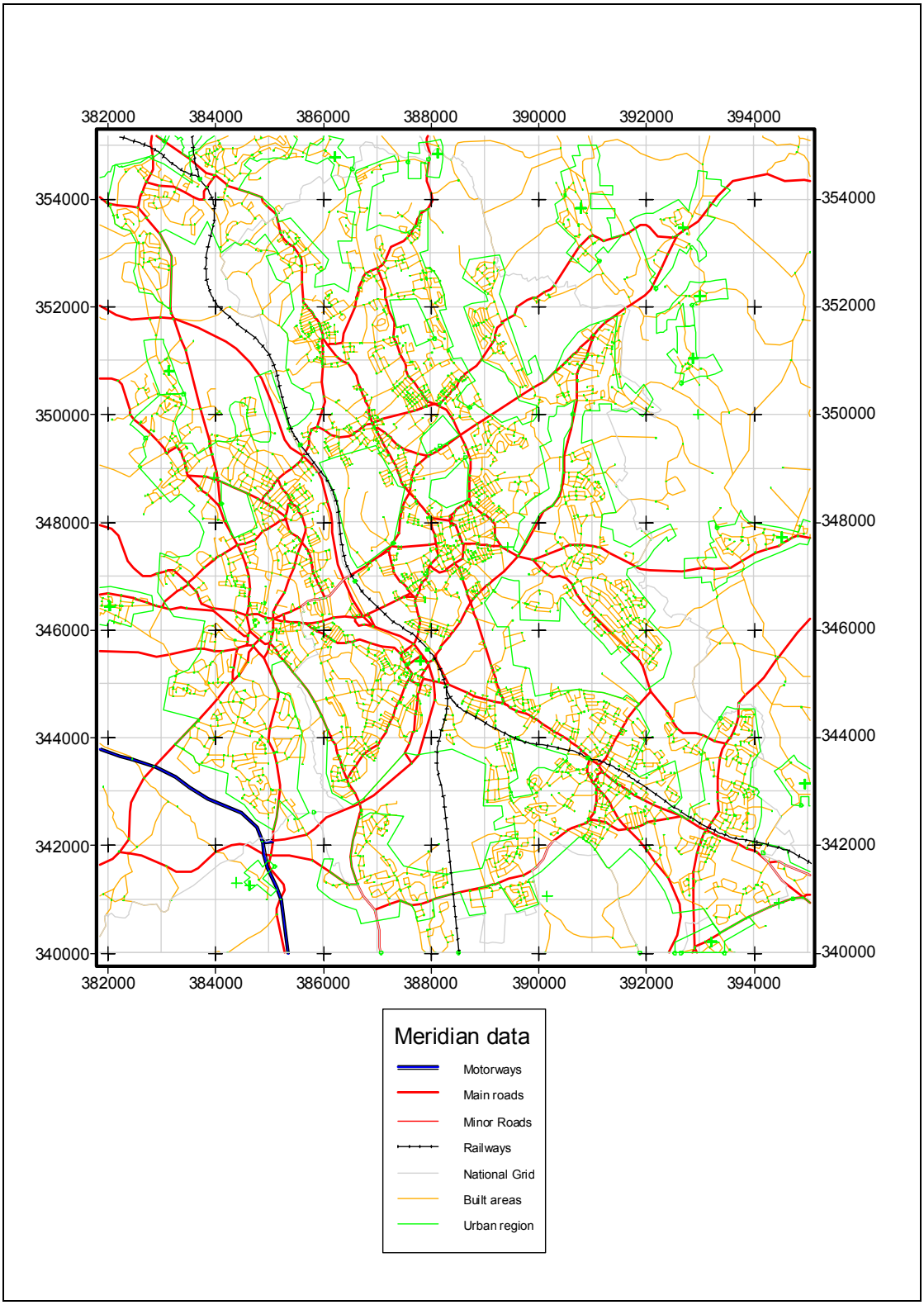


Figure 2.3 Meridian line data derived from the OS 1: 50 000 topographic maps for the Stoke-on-Trent geochemical study area

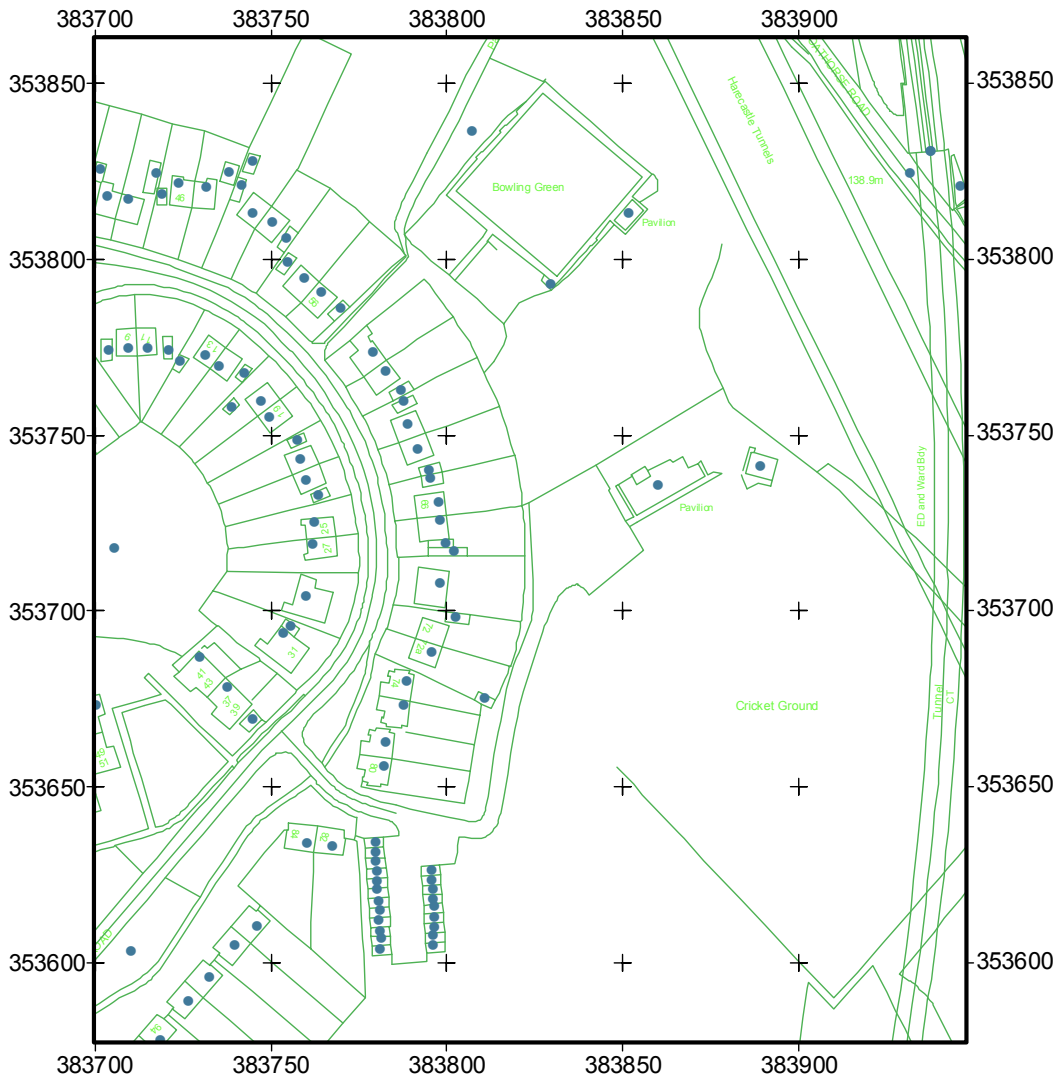


Figure 2.4 Example of the 1: 10 000 scale Landline® data for an area Stoke-on-Trent showing land uses such as residential homes with gardens and playing fields.

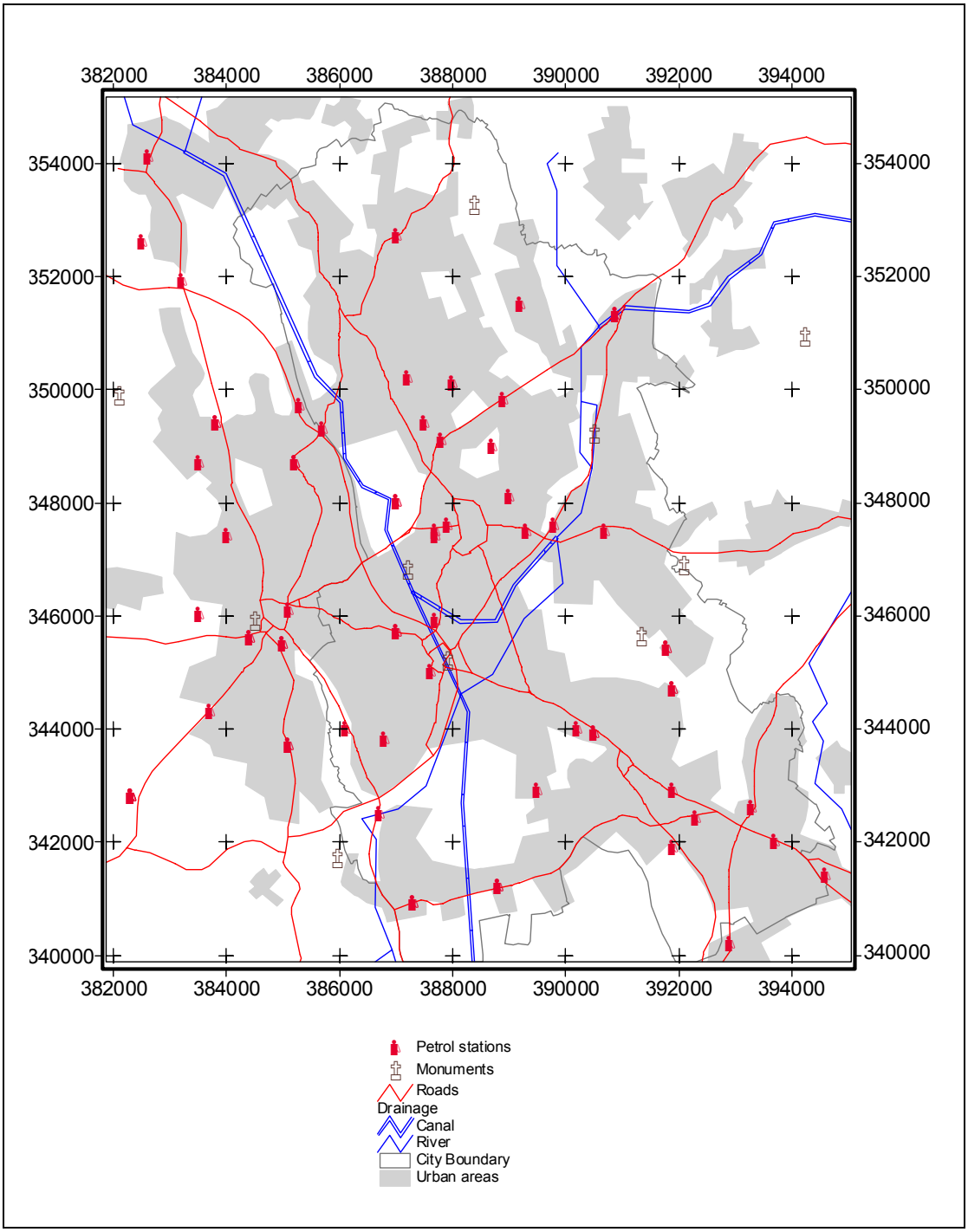


Figure 2.5 Map showing the location of petrol stations (from The Data Consultancy licence) and historical monuments (from English Nature) in the Stoke-on-Trent geochemical study area.

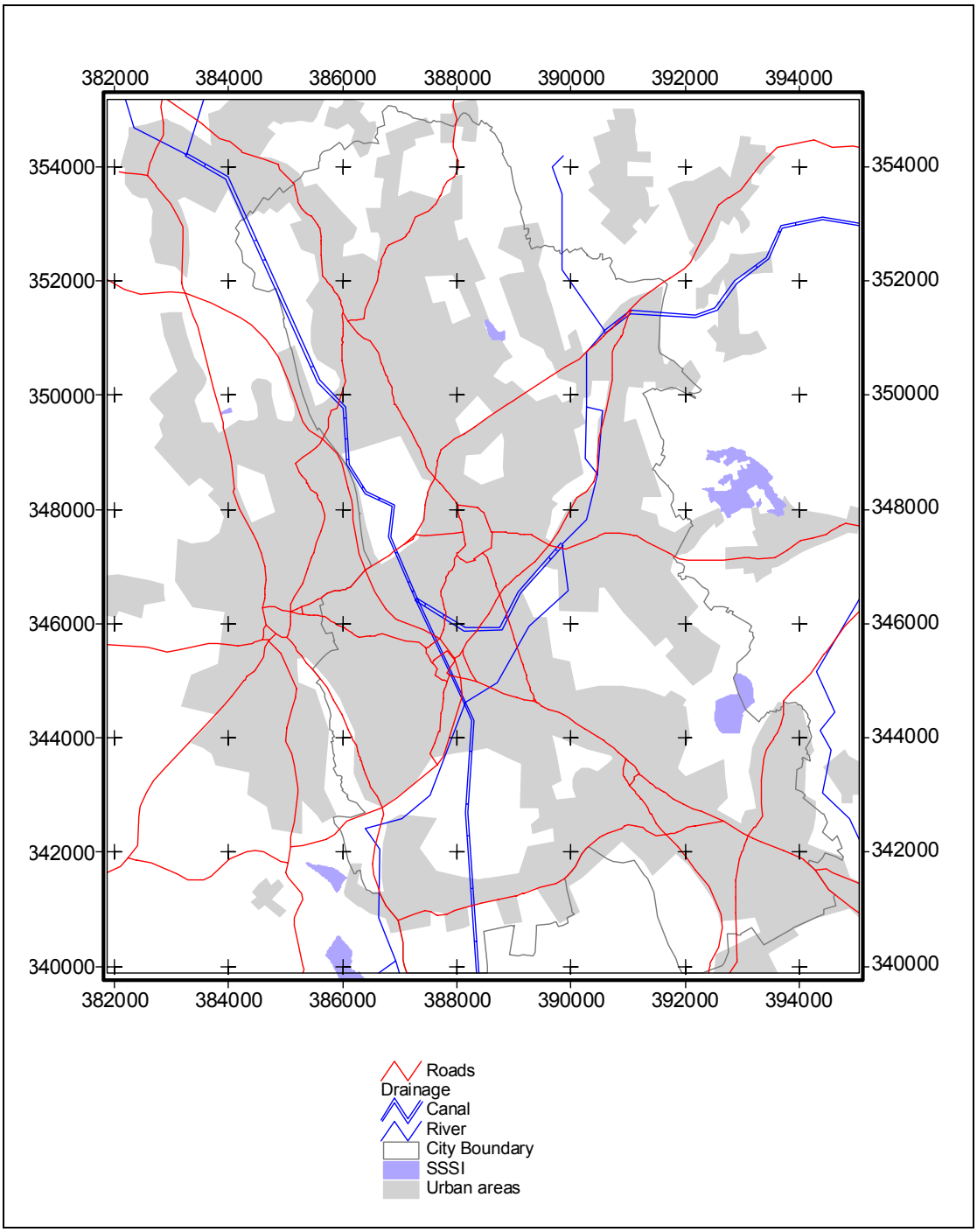


Figure 2.6 Map showing the location of Sites of Special Scientific Interest (SSSI) in the Stoke-on-Trent geochemical study area, derived from English Nature data.

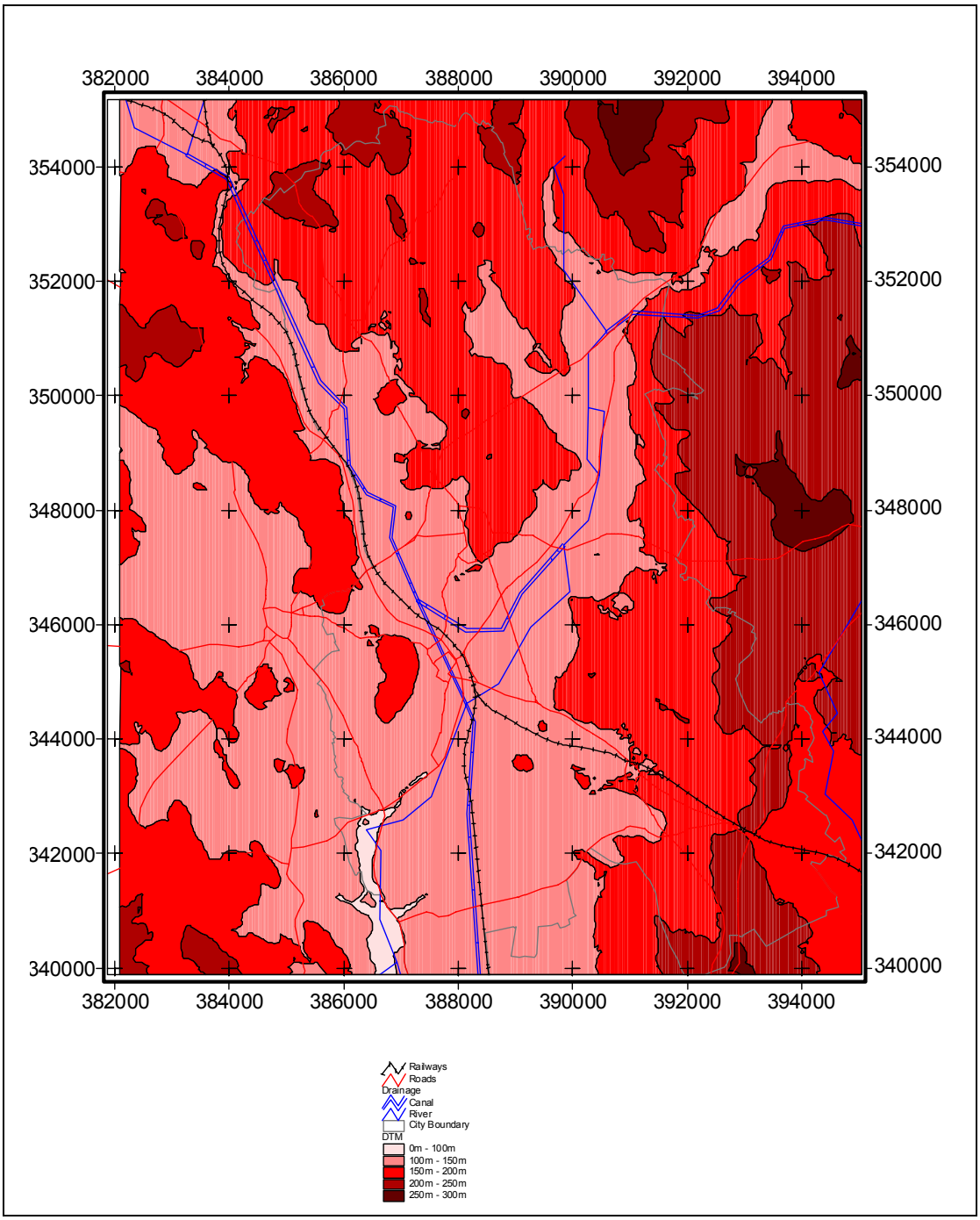


Figure 2.7 Map showing a digital terrain model (DTM) (m above sea level) of the Stoke-on-Trent geochemical study area derived from the OS Platform dataset.

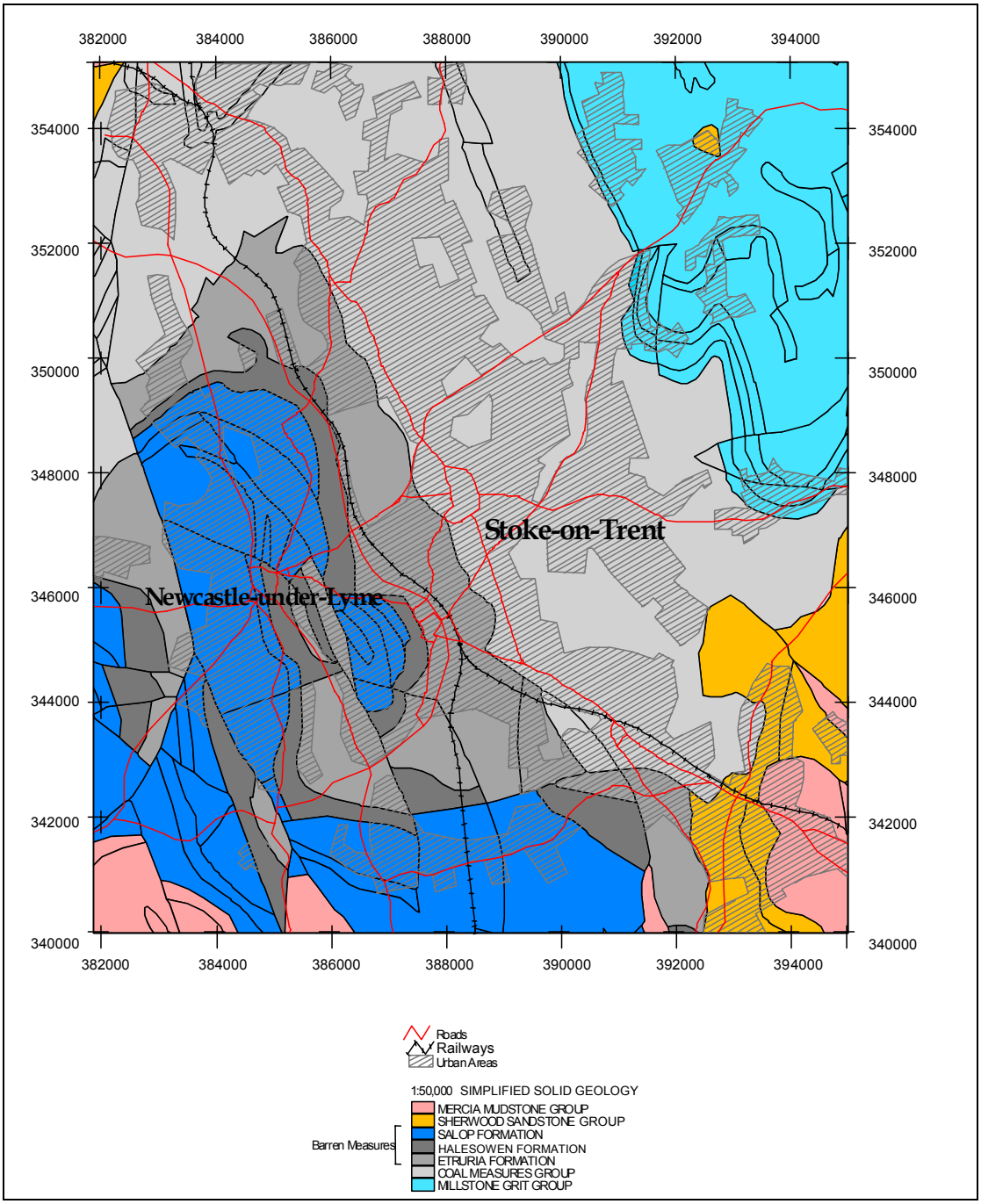


Figure 2.8 Simplified bedrock geology map (1: 50 000 scale) of the Stoke-on-Trent geochemical study area derived from BGS data.

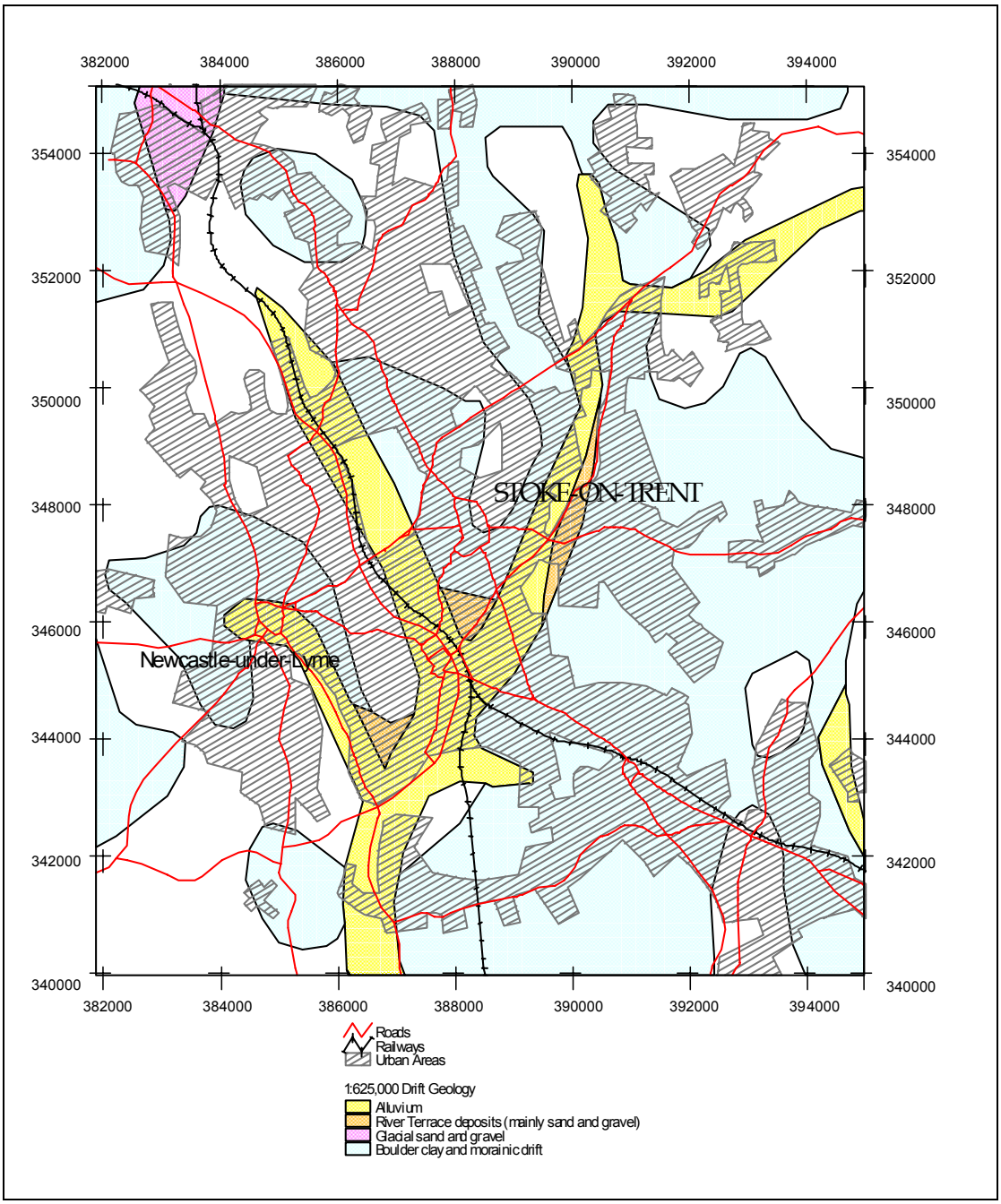


Figure 2.9 Simplified superficial deposits (drift) map (1: 625 000 scale) of the Stoke-on-Trent geochemical study area derived from BGS data.

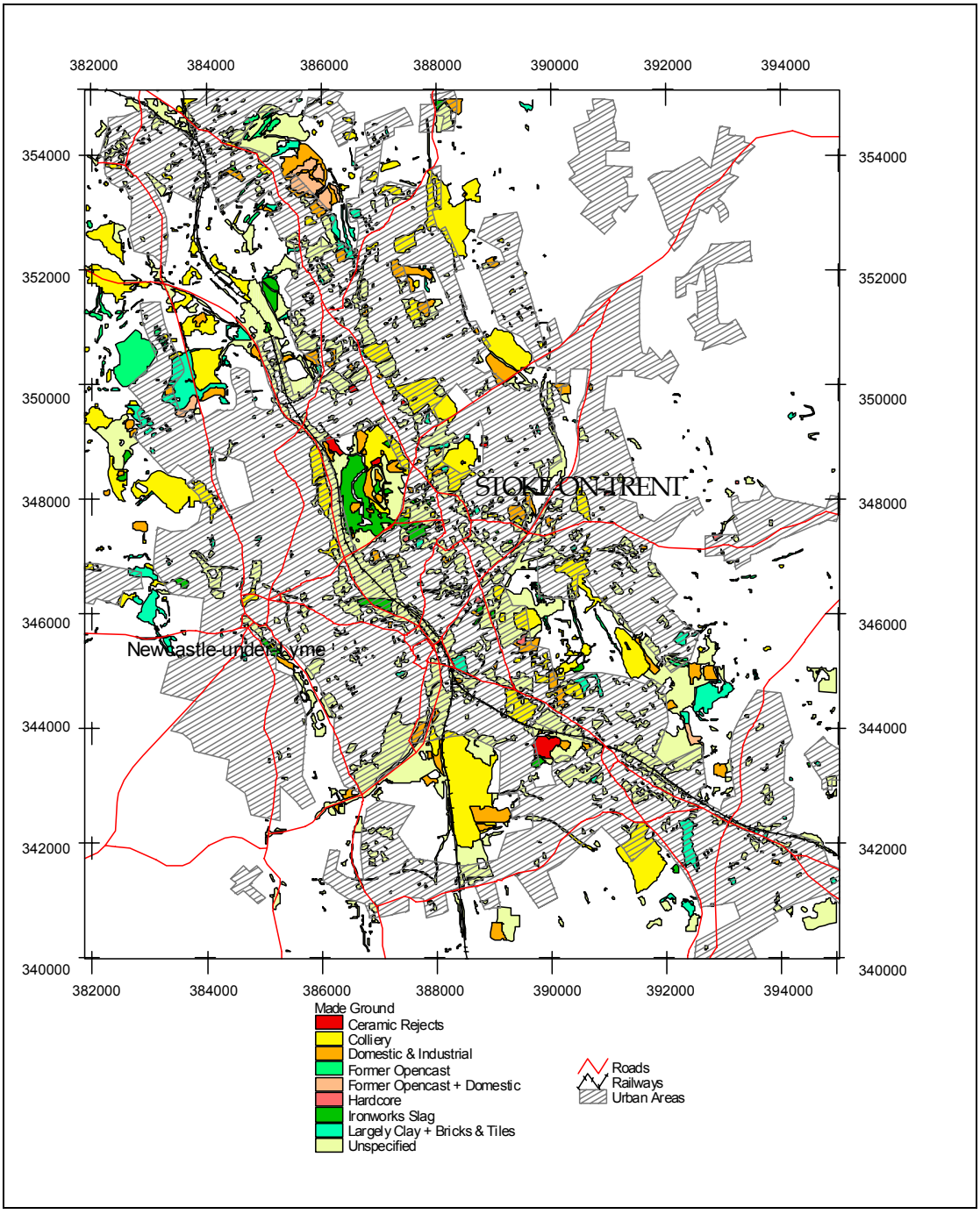


Figure 2.10 Map of made ground types in the Stoke-on-Trent geochemical study area digitised from Wilson et al. (1992).

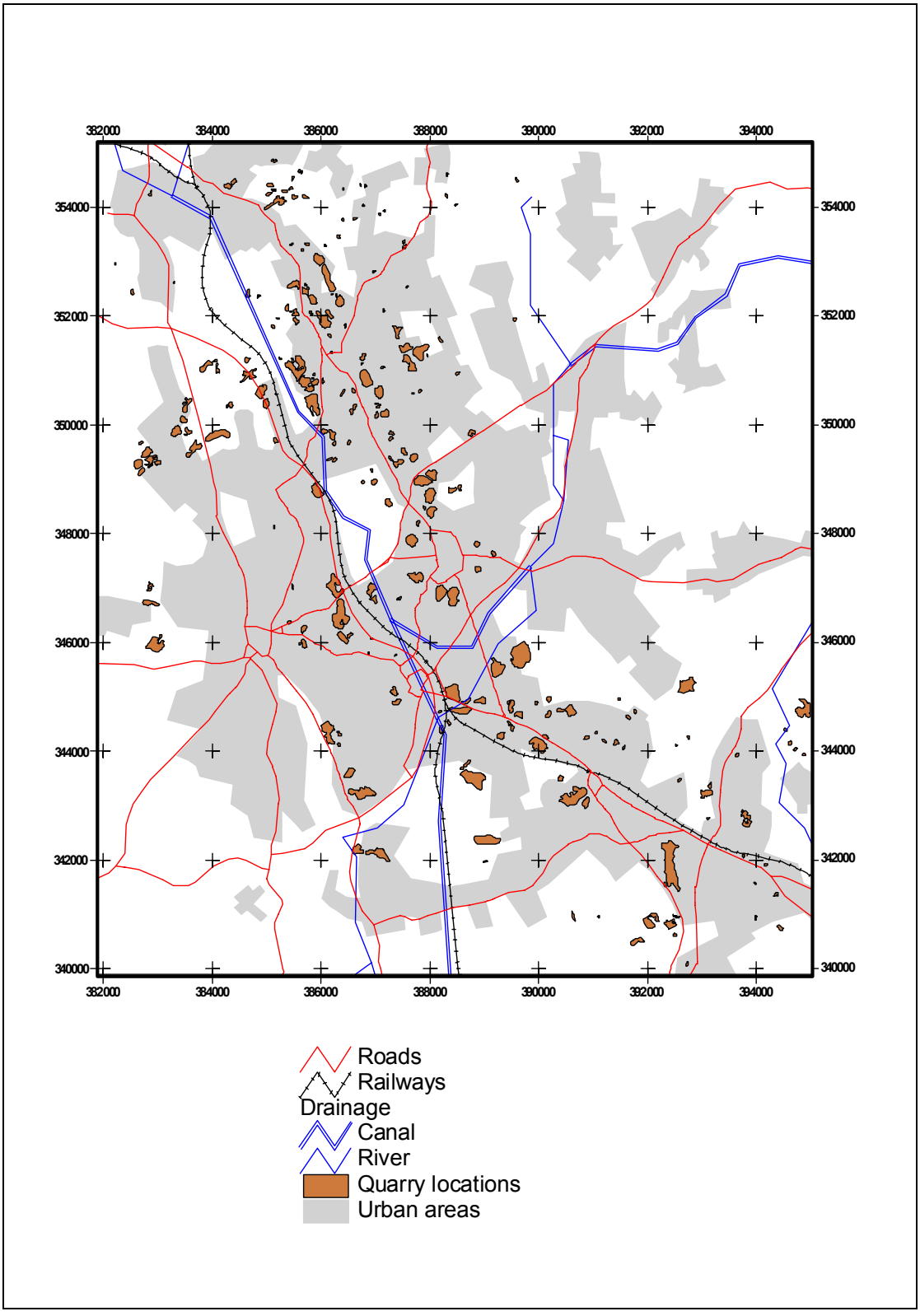


Figure 2.11 Map showing the location of known quarries in the Stoke-on-Trent geochemical study area derived from BGS data.

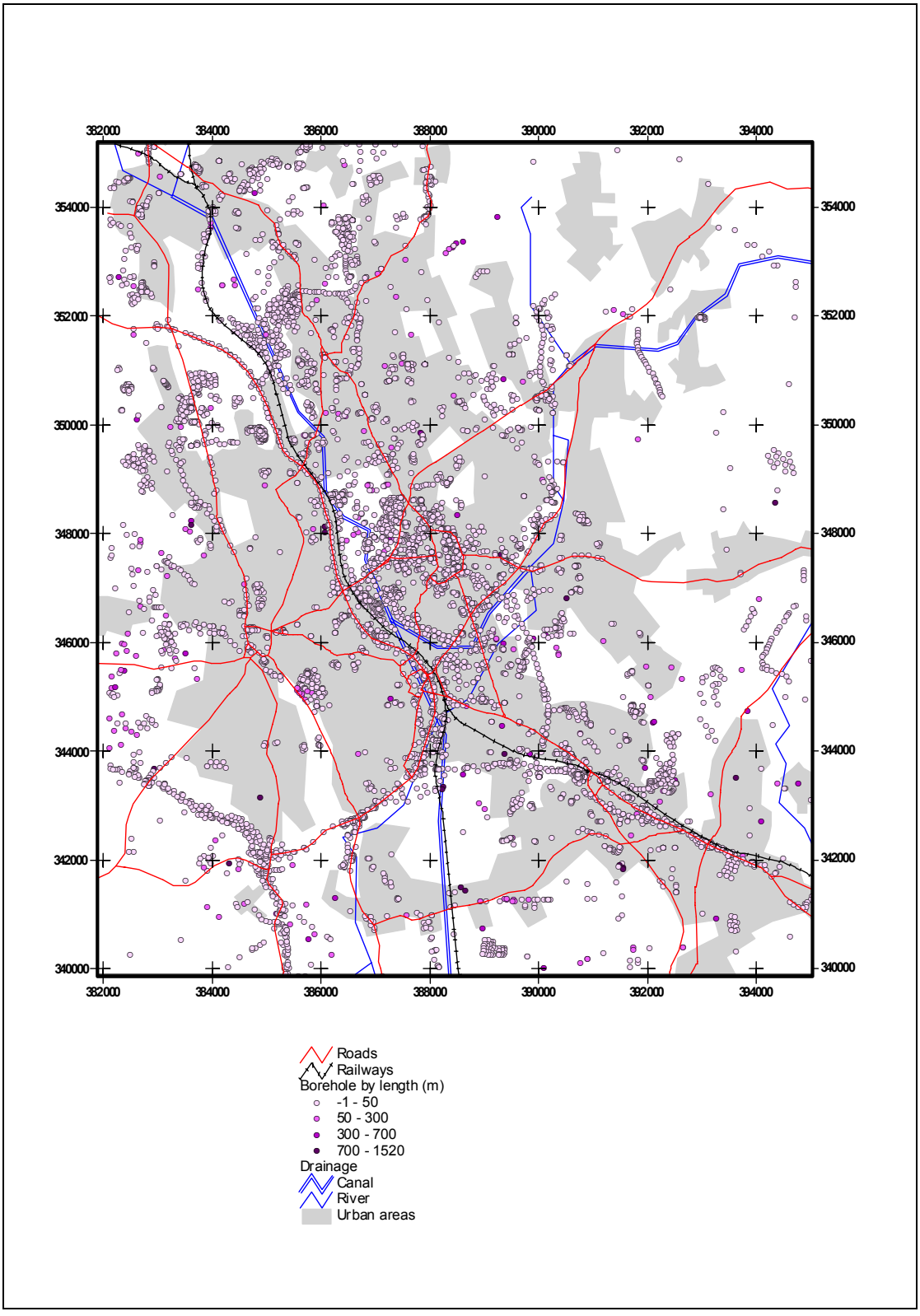


Figure 2.12 Map showing the location of borehole records in the Stoke-on-Trent geochemical study area held by the BGS on the SOBI database.

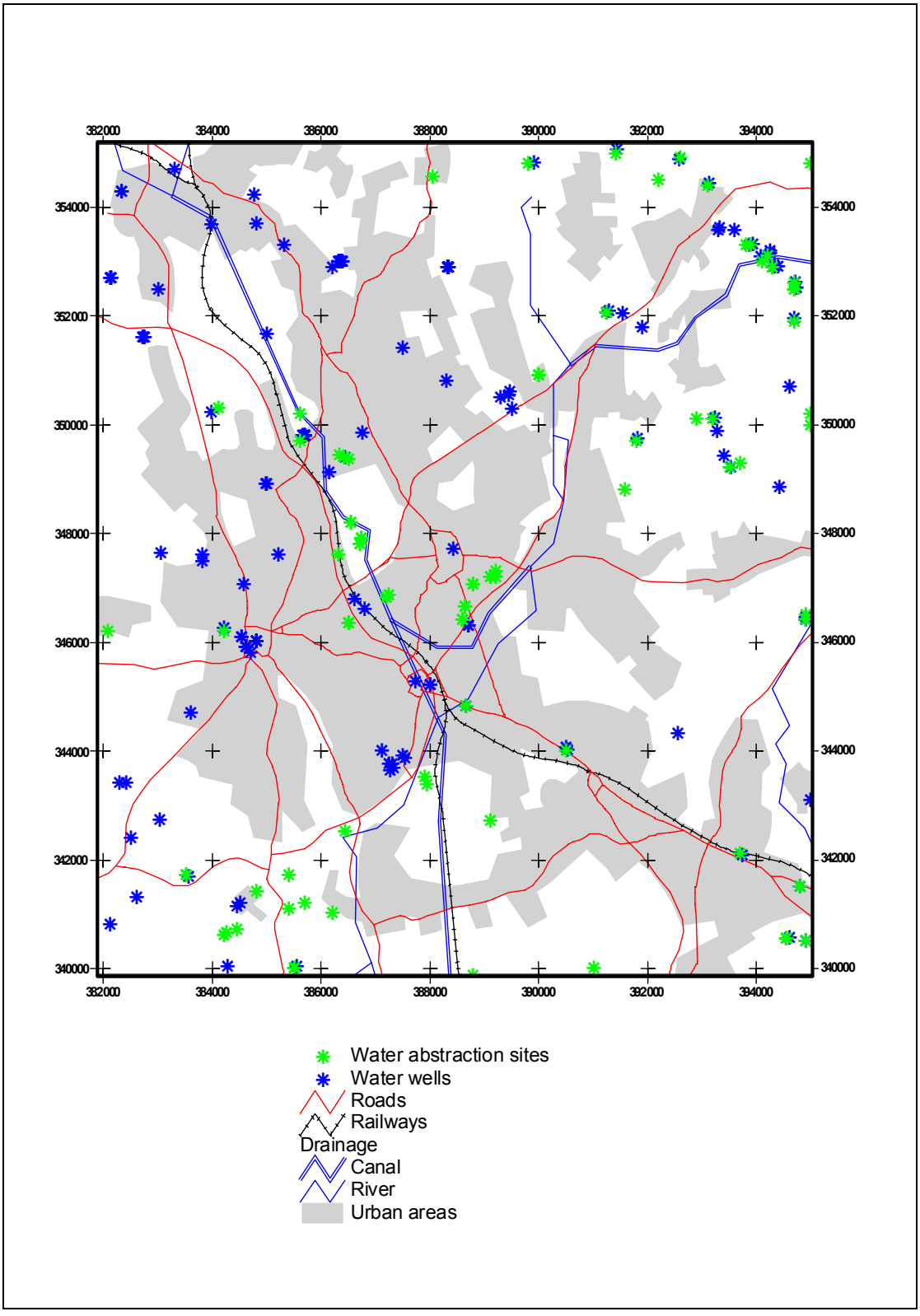


Figure 2.13 Map showing the location of water wells and abstraction sites in the Stoke-on-Trent geochemical study area derived from BGS and EA data.

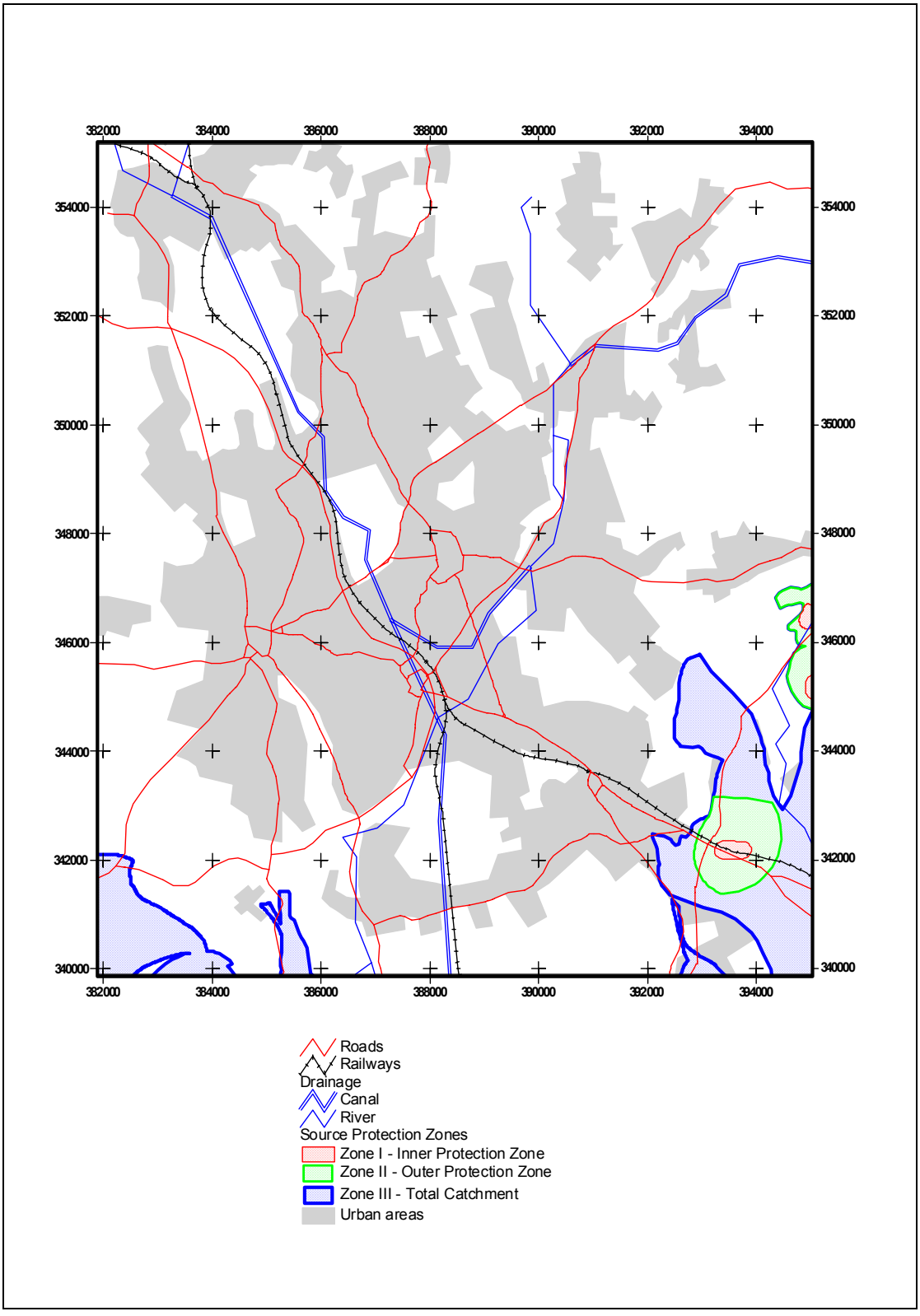
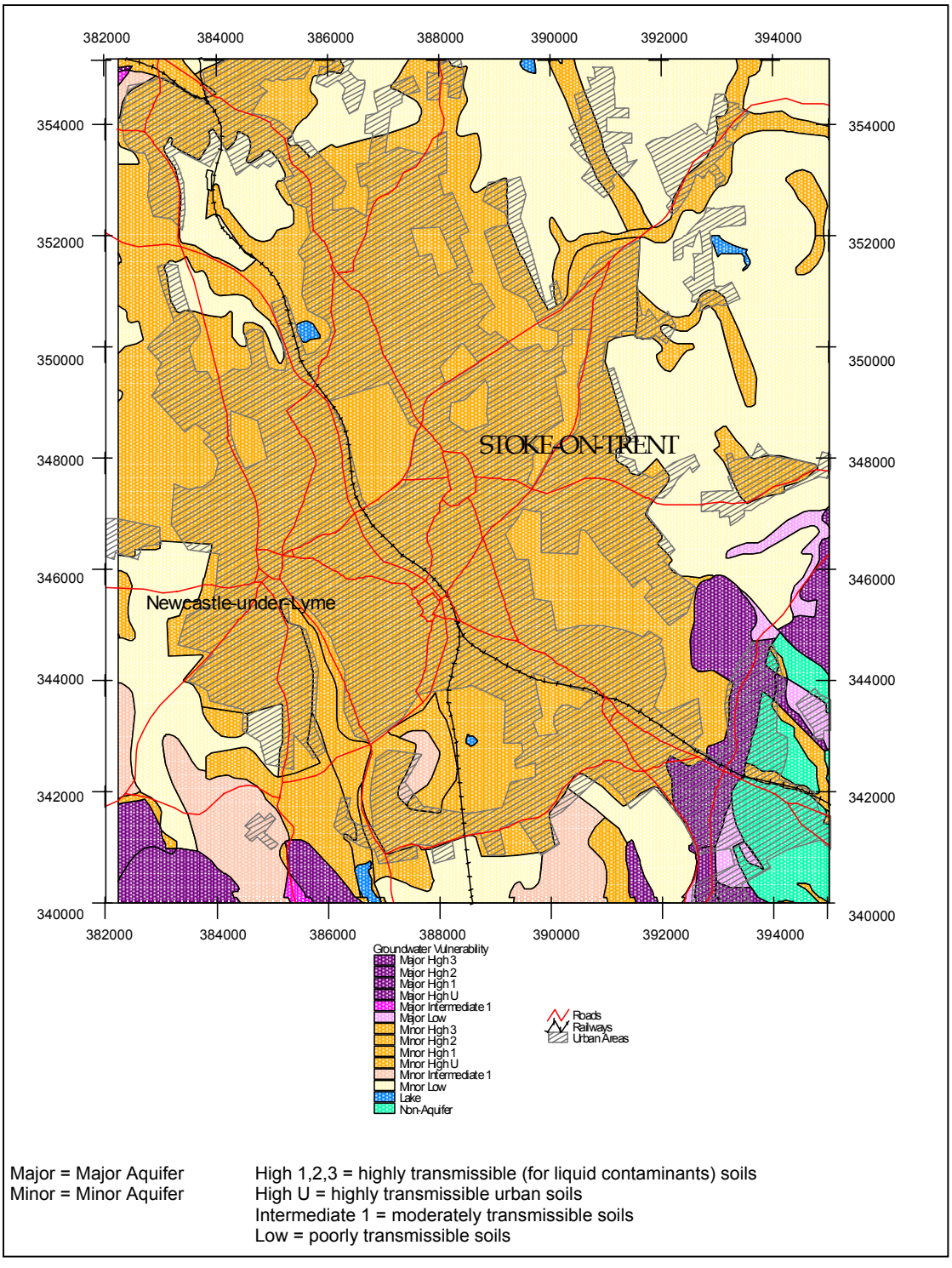


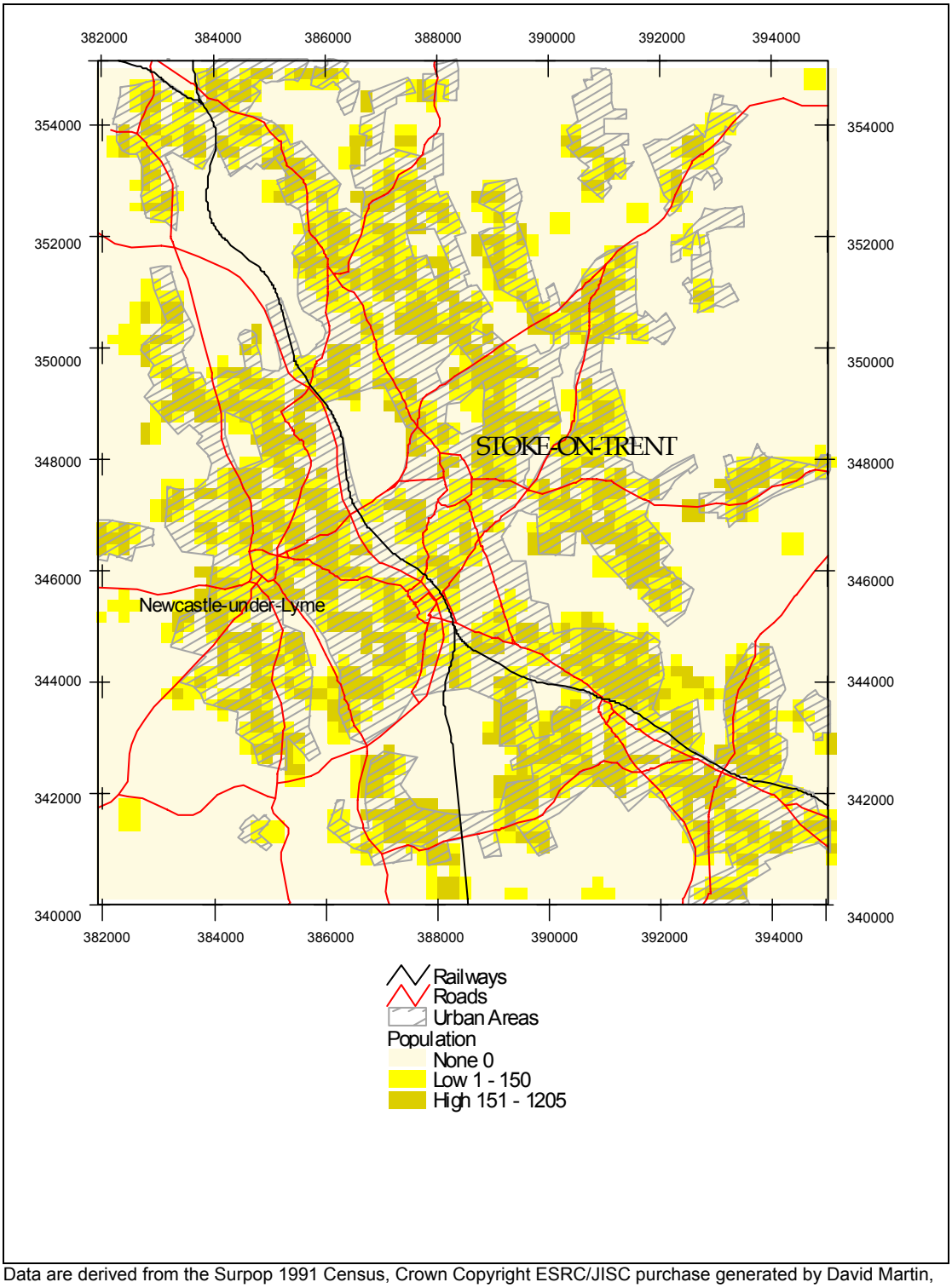
Figure 2.14 Map showing water Source Protection Zones (SPZ) in the Stoke-on-Trent geochemical study area derived from EA data.



Major = Major Aquifer
Minor = Minor Aquifer

High 1,2,3 = highly transmissible (for liquid contaminants) soils
High U = highly transmissible urban soils
Intermediate 1 = moderately transmissible soils
Low = poorly transmissible soils

Figure 2.15 Groundwater vulnerability map of the Stoke-on-Trent geochemical study area derived from BGS/EA/Soil Survey data.



Data are derived from the Surpop 1991 Census, Crown Copyright ESRC/JISC purchase generated by David Martin, Ian Bracken and Nick Tate obtained from Manchester Computing.

Figure 2.16 Map of population density based on number of persons per 200 x 200 m (data classified by quartiles) in the Stoke-on-Trent geochemical study area.

3. Urban Geochemical Survey Methods

By M Strutt, T R Lister and S E Brown

3.1 INTRODUCTION

Geochemical surveys rely on carefully devised sampling, error control, analytical standards, and protocols to ensure data quality and consistency and to provide the best possible estimate of likely element concentrations in the surface environment (Fordyce et al., 2001). In the urban environment, ground investigation reports frequently contain analytical data on the chemical composition of different sites. However, in order to compare data from different surveys it is important to know the sampling and analytical methods used so that the likely effects, if any, of the survey procedures on the analytical outcome can be assessed. For example, many metals are concentrated in the fine clay material in soils; therefore if the fine fraction (< 100 µm) of the soil is analysed, this will invariably return much higher metal concentrations than an analysis of the coarse fraction (< 2 mm) of the same soil. This chapter outlines the standardised methods used to generate data in the geochemical survey of Stoke-on-Trent.

3.2 SAMPLE COLLECTION

Following the sampling methodology developed during earlier orientation studies in Wolverhampton, approximately 747 soil samples were collected at a density of 4 per km^2 in Stoke-on-Trent during 1993 (Figure 3.1). Sampling was carried out by a team of three university students led by a BGS staff member. The team worked in pairs but were interchanged daily to reduce the possibility of sampling bias being introduced by the use of individual procedures. Within the sampled area, each 1 kilometre national grid-square on 1: 25 000 scale OS maps was subdivided into four sub-squares with 500 m x 500 m dimensions. A soil sample was collected as close as possible to the centre point of each 500 m square accepting access and ground characteristic limitations. Common sites for collection included gardens, parks, road verges, allotments, open spaces, school yards and waste ground.

At each site, two separate composite soil samples (a surface and a profile soil sample) each of approximately 250 g of unsieved material were recovered from a 2 x 2 m square using a hand auger. 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 top few centimetres of surface vegetation was discarded and nine surface soil sub-samples were collected from a standard depth of 0 – 0.15 m at positions one metre apart in the 2 x 2m square (Figure 3.2). At the same location, three profile soil sub-samples (0.40 – 0.50 m) were collected along the diagonal of the same 2 x 2m square (Figure 3.2) using the same holes created by the surface sampling. The sub-samples were homogenised to form one surface sample and one profile sample from each site. Observations of soil colour, depth and clast lithology and abundance were recorded at site, and the samples were classified into five textural groups (sand, sand-silt, silt, silt-clay and clay).

At each sample site, information on the location, site, geology, contamination, land use and other features required for data interpretation were entered on a computer-compatible data-card in a standard BGS format. Locations were also plotted on master copies of the 1: 25 000 OS maps.

During the early 1990s the G-BASE and GSUE projects were in the process of constructing the corporate BGS Geochemistry Database. Initially it was advised that surface and profile urban soil samples should be given separate numbers, as different sample types could not have the same number

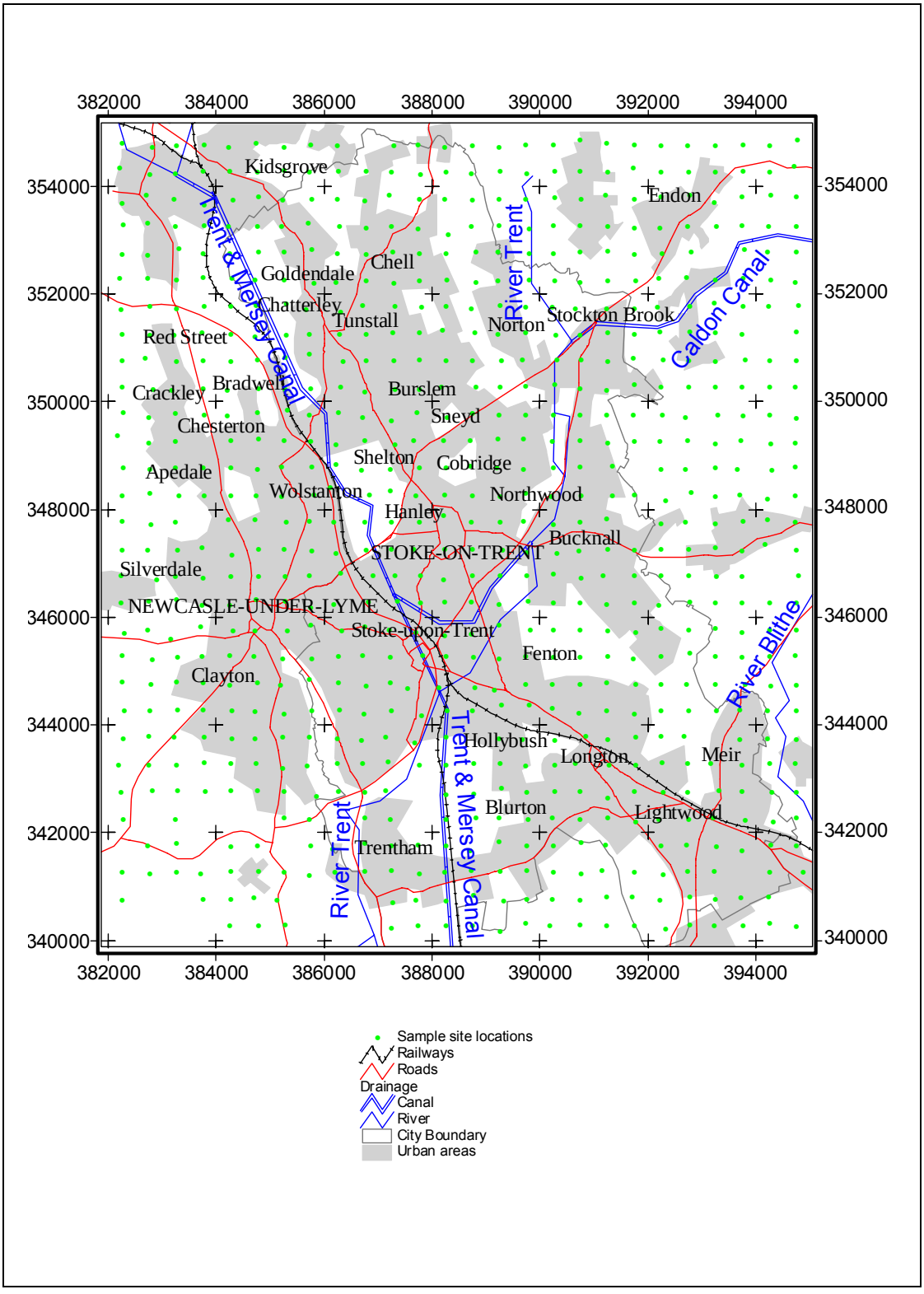


Figure 3.1 Location of soil geochemical sampling sites across the Stoke-on-Trent urban area

in the Geochemistry Database. Therefore soil samples collected from the same location in Stoke-on-Trent were assigned two different numbers, one for surface and one for profile soils. The Stoke-on-Trent samples were given the prefix code 38 and comprise sample numbers 388001 - 389622. The samples were labelled S to indicate a surface soil and SD to indicate a profile soil. This did not correspond to the labelling system employed by G-BASE for the collection of rural soils, which were labelled A for surface soils and S for profile soils. For the purposes of database consistency and to avoid confusion, the Stoke-on-Trent samples have been relabelled as A and S in the Geochemistry Database and will be referred to as A and S samples throughout this report. It should be noted, however, that the field data-cards and sample archive containers from Stoke-on-Trent are still labelled with the original S (surface) and SD (profile) codes.

Within each batch of 100 samples, a set of field duplicate samples was collected within 2 m of the original samples using identical methodology.

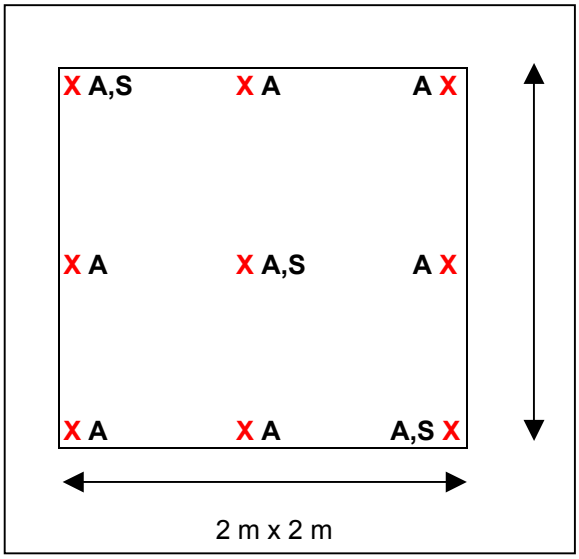


Figure 3.2 Pattern of sub-sampling composite surface (A) and profile (S) soils in Stoke-on-Trent

3.3 SAMPLE ANALYSIS

Urban soil samples were air dried prior to sieving to < 2 mm for surface soils, the environmental standard soil fraction, and < 150 µm for profile soils to be compatible with G-BASE regional stream sediment and soil data. All samples were coned and quartered and a 30 g sub-sample ground in an agate planetary ball mill until 95% was < 53 µm. The pulverised material was further sub-sampled to obtain portions for analysis.

Following preparation, sample residue materials were stored in the BGS National Geoscience Data Centre (NGDC) GSUE sample archive. Table 3.1 outlines the sample archive material available for the Stoke-on-Trent study area.

TABLE 3.1 SOIL SAMPLE RESIDUE MATERIAL AVAILABLE IN THE BGS NGDC SAMPLE ARCHIVE FOR STOKE-ON-TRENT.

Surface Soils	
< 2mm material for all samples Ground excess material for approximately half the samples XRF pellets for all samples	
Profile Soils	
< 150-µm material for approximately two thirds of the samples Ground excess material for the remaining third of samples XRF pellets for all samples	
Missing Samples	
Surface Soils	Profile Soils
388535	388359
388884	388454
389579	388533
	388793
	389309
	389396
	389468

Total major and trace element concentrations in soil samples were determined at the BGS by Wavelength Dispersive X-ray Fluorescence Spectrometry (XRF) (Ingham & Vrebos 1994). XRF pellets were prepared by grinding 12 g of milled sample and 3 g of Elvacite 2013 binder (n-butyl methacrylate copolymer, Dupont & Co) in an agate planetary ball mill for 30 minutes. The mixture was then pressed under a 25-ton load into 40 mm diameter pellets.

Three sequential XRF spectrometers were used: a Philips model PW1480 and two Philips model PW2400. The PW1480 spectrometer was fitted with a 216-position sample changer and a 3-kW/100 kV tungsten anode x-ray tube and was used to determine Cd, Sn and Sb.

Both PW2400 spectrometers had 102 position sample changers and were fitted with 3 kW/60 kV rhodium anode x-ray tubes and were used to determine MgO, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Al_2O_3, SiO_2, V, Cr, Co, and Ba as one suite and Ni, Cu, Zn, As, Mo, Pb, and U as another.

Lower limits of detection (LLD) and upper and lower reporting limits (URL and LLR) are shown in Table 3.2 and the determinants in each soil sample type are listed in Table 3.3. The quoted LLDs are theoretical values for the concentration equivalent to three standard deviations above the background count rate for the analyte in a silica matrix. High instrumental stability results in practical values for these materials approaching the theoretical.

Mercury determinations in surface soil samples were carried out by Bondar Clegg Laboratories, Canada by digestion of 1 g of milled sample in aqua-regia and analysis by cold vapour atomic absorption spectrometry (AAS).

Soil pH was measured in surface soils by adding 25 g of each sample to 25 ml of 0.01M $CaCl_2.2H_2O$. The mixture was shaken to form a slurry prior to analysis by pH electrode (Rowell, 1994). This method of soil pH determination generally gives lower results (0.5 pH units) than water based methods.

Loss on ignition (LOI) was determined for surface soil samples on 2 g of < 2 mm material heated in a furnace and kept at 450 °C for a minimum of 4 hours. Moisture and any organic matter are burnt off at this temperature and the LOI (difference in weight of the sample prior to and after heating at 450 °C) can be used as an indicator of soil organic matter content. Rowell (1994) reports that LOI is similar to organic matter content in sandy soils but may be up to twice the organic matter content in heavy textured soils because clays and sesquioxides lose 'structural' water between temperatures of 100 – 500 °C.

TABLE 3.2 LOWER LIMITS OF DETECTION AND UPPER AND LOWER REPORTING LIMITS FOR XRF AND AAS ANALYSIS IN STOKE-ON-TRENT SOILS.

Analyte	LLD (mg/kg)	LLR (%)	URL (mg/kg)	URL (%)
MgO	-	0.1	-	50.0
P_2O_5	-	0.05	-	1.5
K_2O	-	0.05	-	15.0
CaO	-	0.05	-	60.0
TiO_2	-	0.010	-	100.0
MnO	-	0.010	-	10.0
Fe_2O_3	-	0.01	-	100.0
Al_2O_3	-	0.1	-	60.00
SiO_2	-	0.1	-	100.0
V	2	-	20000	-
Cr	3	-	250000	-
Co	2	-	10000	-
Ni	1	-	4000	-
Cu	1	-	6500	-
Zn	1	-	10000	-
As	1	-	10000	-
Mo	1	-	1000	-
Cd	1	-	500	-
Sn	1	-	10000	-
Sb	1	-	10000	-
Ba	3	-	600000	-
Pb	1	-	10000	-
U	1	-	650	-
Hg* P	0.04	-	-	-
Hg * R	0.01	-	-	-

LLD = Lower Limit of Detection
LLR = Lower Limit of Reporting
ULR = Upper Limit of Reporting
*AAS analysis by Bondar Clegg Laboratories
P = practical LLD R = reported LLD

TABLE 3.3 LIST OF DETERMINANTS IN STOKE-ON-TRENT SURFACE AND PROFILE SOILS.

Surface Soils < 2mm	**Profile Soils < 150 µm**	**Name**
TiO_2		Titanium
MnO	MnO	Manganese
Fe_2O_3	Fe_2O_3	Iron
SiO_2	SiO_2	Silicon
P_2O_5	P_2O_5	Phosphorous
K_2O	K_2O	Potassium
CaO	CaO	Calcium
MgO	MgO	Magnesium
Al_2O_3	Al_2O_3	Aluminium
V	V	Vanadium
Cr	Cr	Chromium
Co	Co	Cobalt
Ni	Ni	Nickel
Cu	Cu	Copper
Zn	Zn	Zinc
As	As	Arsenic
Mo	Mo	Molybdenum
Ba	Ba	Barium
Pb	Pb	Lead
U	U	Uranium
Cd	Cd	Cadmium
Sn	Sn	Tin
Sb	Sb	Antimony
Hg		Mercury
LOI		Loss on Ignition
pH		pH

3.4 ERROR CONTROL AND DATA QUALITY

3.4.1 Field and Laboratory

Systematic error in field sampling and analysis was monitored using a method based on randomised sample site numbers (Plant, 1973). Rigorous field-based error control procedures at each stage of the sampling process are designed to minimise error (Flight and Lister, 2000). Long-term analytical drift between batches of samples was monitored using a series of standards representing a range of concentration for each element. The standards included several bulk soil samples collected over representative rock types in the study area, two of which were analysed in every batch of 100 samples. Time versus concentration plots for each of these reference samples were prepared. Tolerance limits arbitrarily set at the mean $\pm 2\sigma$ were used to assess data quality. Simple arithmetic correlations were applied to normalise the data for systematic drift (Jones et al., 2000a).

3.4.2 Analysis of Variance

Sampling and analytical precision were calculated using a procedure based on analysis of variance (ANOVA). Duplicate surface soil samples were collected at 15 sites and duplicate profile soils at 14 sites, representing approximately one site in 50; the sites were chosen using random number lists. The number of duplicate samples collected was not sufficient to perform a nested ANOVA therefore samples from 11 urban areas (Cardiff, Swansea, Stoke-on-Trent, Telford, York, Hull, Doncaster, Mansfield, Scunthorpe, Lincoln and Sheffield) were included in the same statistical appraisal. Major elements such as (SiO_2, Al_2O_3 P_2O_5, CaO and MgO) have not been routinely analysed in urban areas therefore the dataset from Stoke-on-Trent is too small to carry out ANOVA tests for these elements.

Each duplicate sample was dried and split into two portions, producing a total of four replicates from each site for chemical analysis. As a check against mis-labelling or other errors, the analyses of the two portions were plotted against each other, for selected elements of differing chemical properties, to assess whether any sample pairs were consistently out-lying. The pairs of samples were averaged, and routine and duplicate sample pairs were examined in a similar manner. No errors were found.

One set of duplicate profile samples from Cardiff (Sample Numbers 600876/600886 and 600881/600878) containing 28% Fe_2O_3 were removed from the dataset prior to the ANOVA calculation as anomalous values of all metals were also present. This is probably due to metal contamination from manufactured materials in the soil, which contained slag, ash and coal clasts as well as cement and glass fragments. These samples were considered incompatible with the majority of the dataset, and consequently liable to distort the statistical analysis.

Plots of cumulative frequency versus concentration for each element in the soils were examined to assess the degree to which the distribution of the element conformed to the Gaussian distribution; as a result, the concentrations of all trace and major elements were log-transformed before undergoing ANOVA, to improve their conformity to the model distribution (Plant et al., 1975).

A random nested model of ANOVA was selected because all the analyses were part of a single randomised dataset (Snedecor and Cochran, 1989). The NESTED procedure from the SAS™ statistical software package was 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 natural distribution of the elements in the soils) were calculated.

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 have not been quoted because the data do not satisfy this and other assumptions required for formal analysis of variance.

The percentage of variance attributable to between-site, between-sample and residual variance are given in Tables 3.4 and 3.5, 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 Cd and Sn fall below the 90% between site variance level largely as a result of the inhomogeneous nature of the soil. 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 probably reflect the fact that concentrations of this element in soils are close to the limit of detection. Residual variance for U indicates that the analytical method for this element is not as reliable as it is for the other elements. A full discussion of ANOVA methods for GSUE data is given in Lister (2002).

TABLE 3.4 PERCENTAGE OF VARIANCE IN URBAN SURFACE SOIL SAMPLES 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

All data log transformed

TABLE 3.5 PERCENTAGE OF VARIANCE IN URBAN PROFILE SOIL SAMPLES ATTRIBUTABLE TO BETWEEN-SITE, BETWEEN-SAMPLE AND RESIDUAL VARIANCE.

	Between site %	**Between sample %**	**Residual %**
MnO	95.05	4.91	0.03
Fe_2O_3	96.61	3.38	0.01
V	95.05	4.91	0.03
Cr	95.66	3.95	0.39
Co	96.79	3.13	0.08
Ni	95.73	4.22	0.04
Cu	98.36	1.62	0.01
Zn	93.14	6.84	0.01
As	95.93	4.05	0.03
Mo	96.26	3.65	0.08
Ba	91.70	8.27	0.02
Pb	92.80	7.18	0.00
U	74.67	12.63	12.70
Cd	68.90	0.00	31.06
Sn	94.47	5.52	0.00
Sb	90.34	8.90	0.76

All data log transformed

Once full error control and data quality procedures were completed, the Stoke-on-Trent geochemical and locational data were merged and loaded into the BGS Corporate Oracle® Database (Harris and Coats, 1992) where they can be retrieved by means of a database front-end.

4. Urban Geochemical Data Presentation

By M Di Bonito, B G Rawlins, T R Lister, A Mackenzie, E L Ander, N Breward, A J Ferguson and F M Fordyce

4.1 STANDARD METHODS OF GEOCHEMICAL DATA PRESENTATION

Geochemical data can be presented in a number of formats; the standard method for regional G-BASE data is as interpolated maps in the BGS series of geochemical atlases (for example, BGS, 2000). These maps comprise computer-generated surfaces whereby grids for each element are produced by interpolation of the real data using the method of Inverse Distance Weighting (IDW). The standard grid cell (pixel) size adopted for G-BASE regional data represents 250 x 250 m on the ground. IDW assigns a calculated value derived from the real data and nearby sample sites to each grid cell. The standard G-BASE calculation, which is based on ArcInfo® GIS software, uses all sample sites within 1500 m weighted in accordance with distance from the site r such that the weighting is proportional to r^2.

The maps are then colour coded according to percentile classes of the interpolated data distribution. For the majority of elements, the maps are classified by the 5^{th}, 10^{th}, 25^{th}, 50^{th}, 75^{th}, 90^{th}, 95^{th}, 99^{th} and 100^{th} percentiles. For some elements, large proportions of the sample concentrations fall below the detection limit and these are classified into fewer percentile intervals. Missing data are set to null (no value) prior to the classification.

Interpolated-surface maps provide an estimate of element concentrations across the whole area of interest and have the advantage that spatial trends in the data are easy to recognise. This presentation method has proved extremely effective for regional geochemical data and has been adopted by many countries around the world. However, it should be noted that by its very nature, interpolation requires the extrapolation of data values into areas where no real data have been collected and care must be exercised when assessing these maps, particularly in the identification of contaminated land (see for example Appleton, 1995).

Another advantage of interpolated-surface maps is the ability to combine geochemical maps for three different elements together as a colour-addition image allowing the concentrations of different groups or combinations of elements to be clearly displayed elucidating spatial relationships and enhancing data interpretation. This method of data presentation has been used successfully with regional geochemical data (see for example 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 areas. Methods for presenting urban geochemical data have therefore been reviewed as part of the Stoke-on-Trent case study. This review forms part of a wider investigation into GIS methods of geochemical data presentation, which aims to move away from the ArcInfo® system to the BGS corporate standard GIS software package ArcView®.

4.2 BOX AND WHISKER PLOTS

In addition to interpolated maps, simple statistical analyses are used to enhance the quantitative description of geochemical data. These include summarising element ranges as box and whisker plots which show the 10th, 25^{th}, 50^{th}, 75^{th} and 90^{th} percentiles or the 5^{th}, 25^{th}, 50^{th}, 75^{th} and 95^{th} percentiles (depending on the computer package used to generate the plots, Statview® and Minitab® respectively)

of the data distribution (Figure 4.1). For the purposes of this report, the outlier values, sometimes plotted as asterisks, have been omitted from some diagrams because they compress the scale.

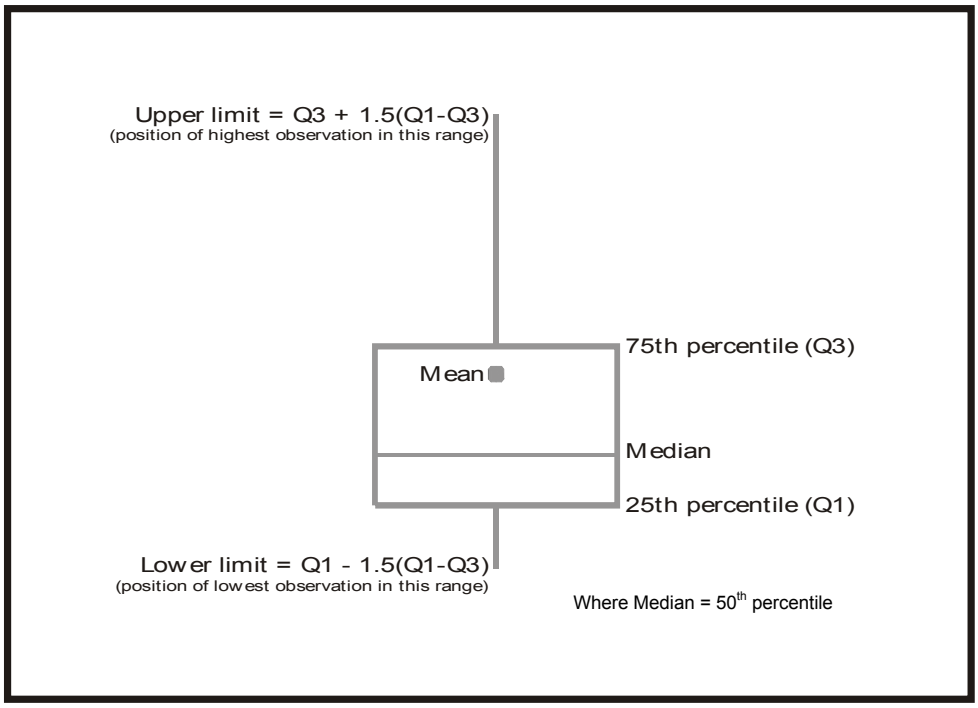


Figure 4.1 Explanation of box and whisker plots used to show geochemical data distributions.

4.3 PRESENTATION METHODS FOR THE STOKE-ON-TRENT URBAN AREA

Methods of presenting the Stoke-on-Trent urban data were investigated initially using the MapInfo® GIS software package during 1996-1999, however, following the BGS decision to adopt ArcView® GIS software as the corporate standard, more recent developments have been based on this platform.

4.3.1 Interpolated Maps of the Stoke-on-Trent Urban Area

The generation of interpolated maps using the MapInfo® GIS software package Vertical Mapper v.2 was tested by Di Bonito (1997 and 1999). IDW interpolation was used to generate gridded surfaces from the geochemical data for Stoke-on-Trent based on a cell size of 100 m, a distance r of 1000 m and maximum selection of 8 nearest neighbour samples.

Due to dilation effects caused by the programme algorithms, interpolated maps do not provide a suitable method for presenting the Stoke-on-Trent 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. Figure 4.2 shows an interpolated map of total Pb concentrations in surface soils from Stoke-on-Trent overlain on made ground types from Wilson et al. (1992). The dilation effect of the interpolation procedure is clearly demonstrated around high Pb values and interpretation of the distribution of soil Pb in the context of made ground types is hampered as a result.

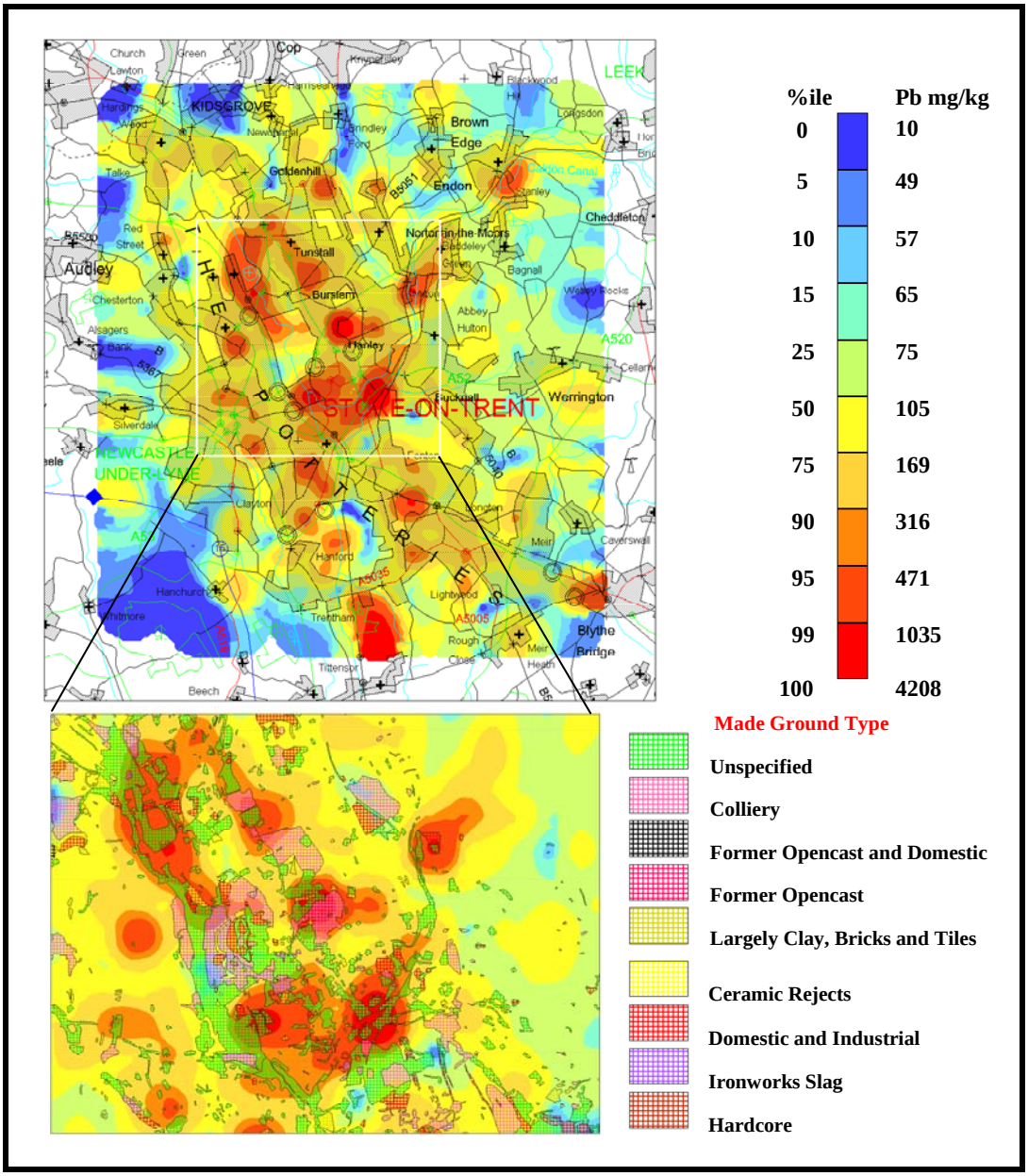


Figure 4.2 MapInfo® interpolated map of total Pb concentrations (classified by interpolated data percentiles) in surface soils in the Stoke-on-Trent geochemical study area (UK NGR 382000E, 340000N – 395000E, 355000N) overlain by made ground type defined by Wilson et al. (1992).

4.3.2 Un-interpolated Grid Maps of the Stoke-on-Trent Urban Area

As an alternative to interpolated maps, the presentation of data as un-interpolated block-grid maps was investigated using MapInfo® GIS software. Maps were prepared by assigning each element sample value to the 500 x 500 m square in which it was collected (Di Bonito, 1999). Although this presentation method avoids issues related to dilation effects, it produces maps that are difficult to interpret and may not represent true conditions on the ground, giving a misleading impression of the extent of contaminated land. The method relies on the assumption that the element concentration determined at the sampling site is representative of the 500 x 500 m square (Figure 4.3).

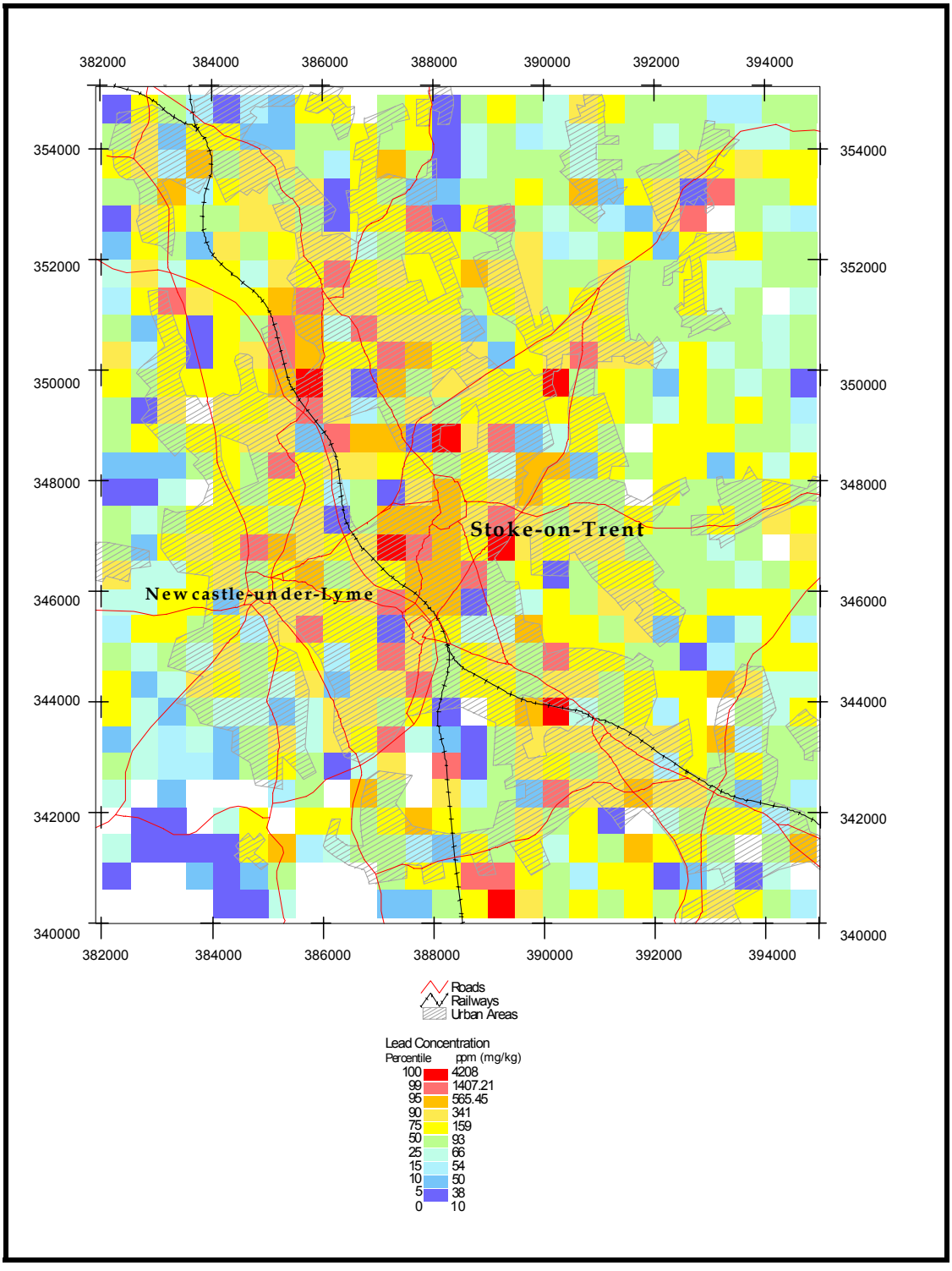


Figure 4.3 Example of an un-interpolated grid-block map of total Pb concentrations in surface soils (classified by real data percentiles) in the Stoke-on-Trent geochemical study. Lead concentrations for each sample site are assigned to each 500 x 500 m survey gird-square.

4.3.3 Spatial Variability of the Stoke-on-Trent Geochemical Data

Analysis of variance investigations of field duplicate data showed that the urban sampling methodology was robust, namely samples collected from the same site were more similar than samples from different sites (Chapter 3). However, the heterogeneous nature of urban soils and the issue of how to present urban geochemical data for contaminated land studies required further investigation.

The spatial variability of GSUE data was assessed previously for Wolverhampton by the Centre for the Built Environment (CBRE) at Nottingham Trent University (Nathanial et al., 1997). During orientation studies carried out by BGS and Imperial College in 1993, soil samples in Wolverhampton were collected at two resolutions; 4 samples per km^2 across the entire urban area and 25 samples per km^2 in the southwest of the city. Geostatistical techniques were used to assess a range of interpolation methods. The study concluded that due to the large nugget effect of a range of PHEs (i.e. that differences between concentrations over very short distances were similar to those at increasing distance), commonly used interpolation techniques were likely to be of limited use. This was despite the collection of some samples at a high resolution (25 per km^2), which according to regionalised variable theory and other published studies (Webster and Oliver, 1990) should lead to smaller nugget variances.

There was some concern that the presentation of data using interpolation techniques could be misinterpreted if not accompanied by validation data to give an estimate of the likely level of error in the interpolation. Therefore, surface soil geochemical data from Stoke-on-Trent were subject to geostatistical analysis to assess the validity of using interpolation techniques for the presentation of urban geochemical data.

The IDW standard interpolation method adopted by the G-BASE rural programme can only be effective for data where points which are closer together have more similar values than those further apart. This is the same basis upon which variograms are produced to determine the spatial continuity of a dataset. The variogram is a good first approximation for understanding whether any interpolation technique is likely to be effective. A flat variogram (where the nugget variance is large – see Figure 4.4a) shows that there is no spatial continuity in a dataset and indicates that standard interpolation techniques are not appropriate. Where the nugget variance is sufficiently small (for example, Figure 4.4b) and the variogram can be modelled adequately, interpolation techniques, may be appropriate.

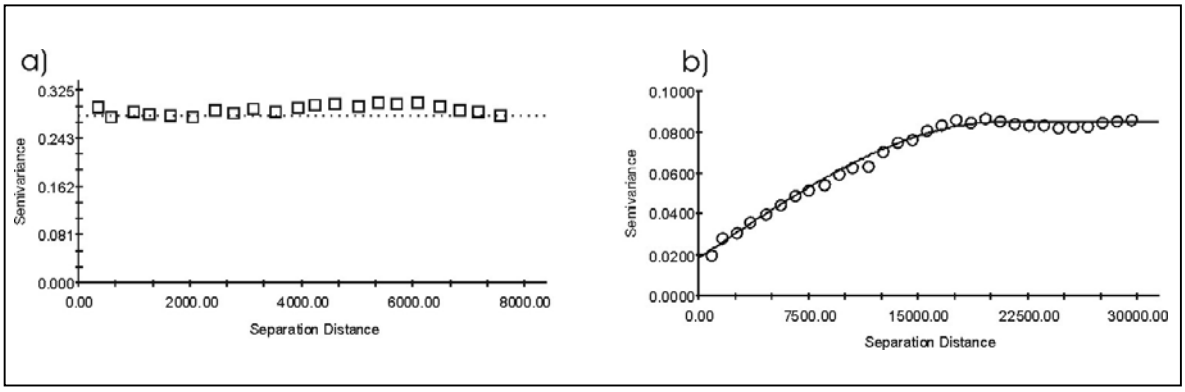


Figure 4.4 Examples of isotropic variograms with a) large, and b) small, nugget variances

Another way of assessing the effectiveness of interpolation is to perform a cross validation exercise. Davis, (1987) outlines methods for this type of investigation. One simple method is to allow each point in the dataset to be removed individually and to run the interpolation to predict the concentration of the element at that point. The average percentage error and the goodness of fit (R^2) between the actual and estimated values can then be calculated.

Exploratory data analysis was used to determine whether the data distribution of each element was more normal with or without log transformation. Isotropic variograms (Figures 4.5 and 4.6) and their parameters were calculated for 20 of the elements determined in surface soils from Stoke-on-Trent (see Table 4.1) using the computer programme GS+ (a geostatistical analysis package). Mathematical functions were fitted to the models by residual sum of squares (RSS) and the regression coefficient (R^2) calculated to indicate the accuracy of the model fit (Table 4.1).

The data were interpolated using two methods:

i) by IDW (assuming a weighting power of 2 and a search radius of 1500 m)
ii) by kriging using the function fitted to the sample variograms

A cross validation exercise was performed using both methods whereby each point was removed from the dataset and its value interpolated, repeating this for each value in the dataset. The mean error (ME) and the regression (R^2) of the best fit through the data were calculated. In addition, the average percentage error prediction for each of the interpolated sample points was calculated for the inverse distance weighted interpolation (Table 4.2).

TABLE 4.1 PARAMETERS OF THE ISOTROPIC VARIOGRAMS SHOWN IN FIGURES 4.5 AND 4.6 FOR SELECTED ELEMENTS IN STOKE-ON-TRENT SURFACE SOILS.

	TiO_2	MnO	Fe_2O_3	V	Cr	Co	Ni	Cu	Zn
transformation	none	log	log	log	log	log	log	log	log
model*	exp	exp	exp	exp	exp	exp	exp	exp	exp
lag interval (m)	370	370	500	370	370	370	370	400	400
lag distance (m)	4000	12000	12000	4000	4000	4000	4000	8000	8000
nugget	0.009	0.249	0.16	0.055	0.011	0.135	0.06	0.23	0.186
sill	0.03	0.661	0.32	0.116	0.084	0.271	0.21	0.59	0.374
Range (m)	1893	24460	16000	880	446	3690	1752	7980	18000
% correlation	71	62.3	50	52	86.6	50	72	60.4	50
R^2	0.992	0.992	0.966	0.987	0.968	0.785	0.91	0.971	0.781
RSS	1.60E-06	5.90E-04	4.80E-04	3.50E-05	4.40E-05	1.33E-03	7.50E-04	2.45E-03	1.83E-03

	As	Mo	Ba	Pb	U	Cd	Sn	Sb	K_2O
transformation	log	log	log	log	none	log	log	log	log
Model*	exp	exp	exp	exp	exp	n/a	exp	exp	exp
lag interval (m)	370	400	400	370	370	n/a	400	400	350
lag distance (m)	3700	8000	8000	3700	4000	n/a	8000	8000	3500
nugget	0.16	0.22	0.075	0.256	0.338	n/a	0.31	0.14	0.006
sill	0.322	0.44	0.15	0.645	0.677	n/a	0.62	0.28	0.057
range	8110	14000	9440	741	9110	n/a	19350	20410	1311
% correlation	50.2	50	50	60	50	n/a	50	50	89
R^2	0.619	0.906	0.524	0.952	0.6	n/a	0.881	0.457	0.961
RSS	1.02E-03	1.50E-03	2.50E-03	3.20E-03	4.30E-03	n/a	2.30E-03	3.60E-03	2.60E-05

* exp refers to the exponential isotropic function fitted to the variograms

TABLE 4.2 RESULTS OF THE CROSS VALIDATION EXERCISE FOR IDW AND KRIGING INTERPOLATIONS OF SELECTED ELEMENTS IN STOKE-ON-TRENT SURFACE SOILS.

	TiO_2	MnO	Fe_2O_3	V	Cr	Co	Ni	Cu	Zn
Std Error (IDW)	0.063	0.073	0.072	0.06	0.086	0.074	0.07	0.083	0.082
R^2 (IDW)	0.245	0.17	0.163	0.278	0.132	0.156	0.186	0.148	0.136
Mean error IDW (%)	20.8	44.1	31.5	22.2	19.9	35.7	35.8	54.7	42.8
Std Error (kriging)	0.058	0.077	0.076	0.057	0.069	0.077	0.076	0.087	0.092
R^2 (kriging)	0.245	0.188	0.17	0.282	0.133	0.167	0.166	0.158	0.13

	As	Mo	Ba	Pb	U	Cd	Sn	Sb	K_2O
Std Error (IDW)	0.126	0.107	0.115	0.154	0.083	0.313	0.098	0.160	0.072
R^2 (IDW)	0.035	0.06	0.066	0.102	0.082	0.001	0.114	0.027	0.187
Mean error IDW (%)	37	43.4	23.7	70.8	34.6	53	110	32.2	16.7
Std Error (kriging)	0.139	0.115	0.126	0.147	0.093	0.368	0.111	0.186	0.064
R^2 (kriging)	0.037	0.065	0.05	0.099	0.08	0.001	0.121	0.023	0.181

The isotropic variograms in Figures 4.5 and 4.6 show there are large nugget variances for the majority of elements. In those cases where simple models could not be fitted to variograms over short distances (< 4 km), they were fitted over greater distances (8 –12 km). The typical pattern for the latter is of a gradual reduction in semi-variance at shorter lag intervals, suggesting that most of the spatial variation occurs at distances of between 0 and 500 m. For the variograms where models were fitted over short distances (for example, log Ni, log Pb), the majority of the spatial correlation occurs at distances of less than 500 m. However, as relatively few pairs of sample points were collected at short separation distances (only 6 below 350 m), there was insufficient data at smaller distances upon which to model the variogram and hence produce accurate estimates.

Table 4.2 shows the results of the cross validation exercise in which the accuracy of both IDW and kriging interpolation were assessed. Both interpolation methods give poor estimates of the actual values for almost all of the elements, with the exception of Ba, K_2O and V. The regression coefficient values (R^2) below 0.2 indicate that the estimated values are not providing good estimates of the actual values, whilst those below 0.1 suggest that the estimates are very poor. The highest R^2 values were for TiO_2 (0.245), V (0.278) and K_2O (0.187) indicating more accurate estimates.

Using the IDW interpolation estimates, negative differences between actual and estimated values were converted to positive values and the mean calculated (Table 4.2). The mean error values are generally large (30-70%) indicating that the IDW interpolation estimates are relatively inaccurate. The smallest mean errors were for TiO_2 (21%), V (22%) and K_2O (17%). Figure 4.7 shows the distribution of the errors, highlighting that more than 25% of the errors in many cases are greater than 50% of the actual value (e.g. Cd, Cu, MnO, Pb, Sn, and Zn).

For comparison, the error distribution from the cross validation of some interpolated G-BASE rural profile soil MgO data was plotted (Figure 4.7). With the exception of K_2O and Ba in the urban dataset, the error values are generally much lower for the rural data. The median error (the line across the box) is around 15%, with only a quarter of the error values above 25%.

This study has shown that the errors associated with the interpolation of urban geochemical data for Stoke-on-Trent are considerable. The question then arises: are the errors so large that interpolated images are misleading? The answer is dependent on the purpose for which the maps are intended. If the maps are simply used as a guide to indicate the broad distribution of an element across the urban area, then the presentation of interpolated data may be appropriate. However, for many elements they are not suitable for use in a quantitative way; for example to determine what proportion of the urban area contains element soil concentrations above a regulatory threshold value. If interpolated images are produced for this purpose, they should be accompanied by some form of cross validation data to provide the user with a measure of the uncertainty associated with the interpolation.

If interpolated urban data are to be utilised for detailed assessments in the future, information could be improved by the incorporation of a nested sampling design in the GSUE project. Although the CBRE study (Nathanial et al., 1997) reported large nugget variances when sampling was carried out at short distances (25 samples per km^2), other surveys of contaminated soil have shown that a nested sampling design can provide sufficient information on small-scale variability to accurately model the variogram (Atteia et al., 1994). A nested design is one in which samples are collected at arithmetically increasing distances from a node (Figure 4.8) using about a fifth of the grid points as nodes. The benefit of this approach over that adopted by Nathanial et al. (1997) is that the design is more representative of the entire area. In addition, as the element concentrations at the nodes are already known for the urban centres sampled thus far, nodes could be selected which are likely to be representative of the whole city. The BGS is currently investigating the results of a nested sampling survey of Coventry to assess whether it is possible to model accurately the sample variogram over short distances, and hence improve interpolation techniques in the future.

4.3.4 Discussion

The results of the MapInfo® investigations into data presentation methods and spatial variogram analysis suggest that although interpolated geochemical maps for Stoke-on-Trent may be useful to show broad trends in the geochemical data at large scales, they are not an appropriate presentation method for detailed investigations into urban geochemical data.

Whilst soils from other urban centres may show better spatial correlation than Stoke-on-Trent at the 500 x 500 m sampling scale, it is likely that most city soils will be highly heterogeneous due to the long history of urbanisation and industrialisation in the UK. It is recommended that spatial variogram analysis is carried out routinely on urban geochemical datasets in the future as a measure of variability and to determine the validity of data interpolation. Increasing the sample density in UK urban areas would be desirable, providing higher resolution spatial data. However, this would have serious cost and time-scale implications on the survey programme. It should also be noted that under the new guidelines (DETR, 2000), no matter how detailed the sampling density, systematic city-wide surveys do not replace the need for site-specific contaminated land investigations. The purpose of the systematic surveys is to provide an overview of the urban geochemical profile and highlight areas for detailed investigation, not to provide specific information on contaminated sites.

Taking the results of the data presentation investigations into account, a strategy to develop ArcView® based proportional symbol maps for urban areas and interpolation methods for overview rural/urban comparison maps and three-component maps has been developed for Stoke-on-Trent and is likely to form the model for other urban areas as follows.

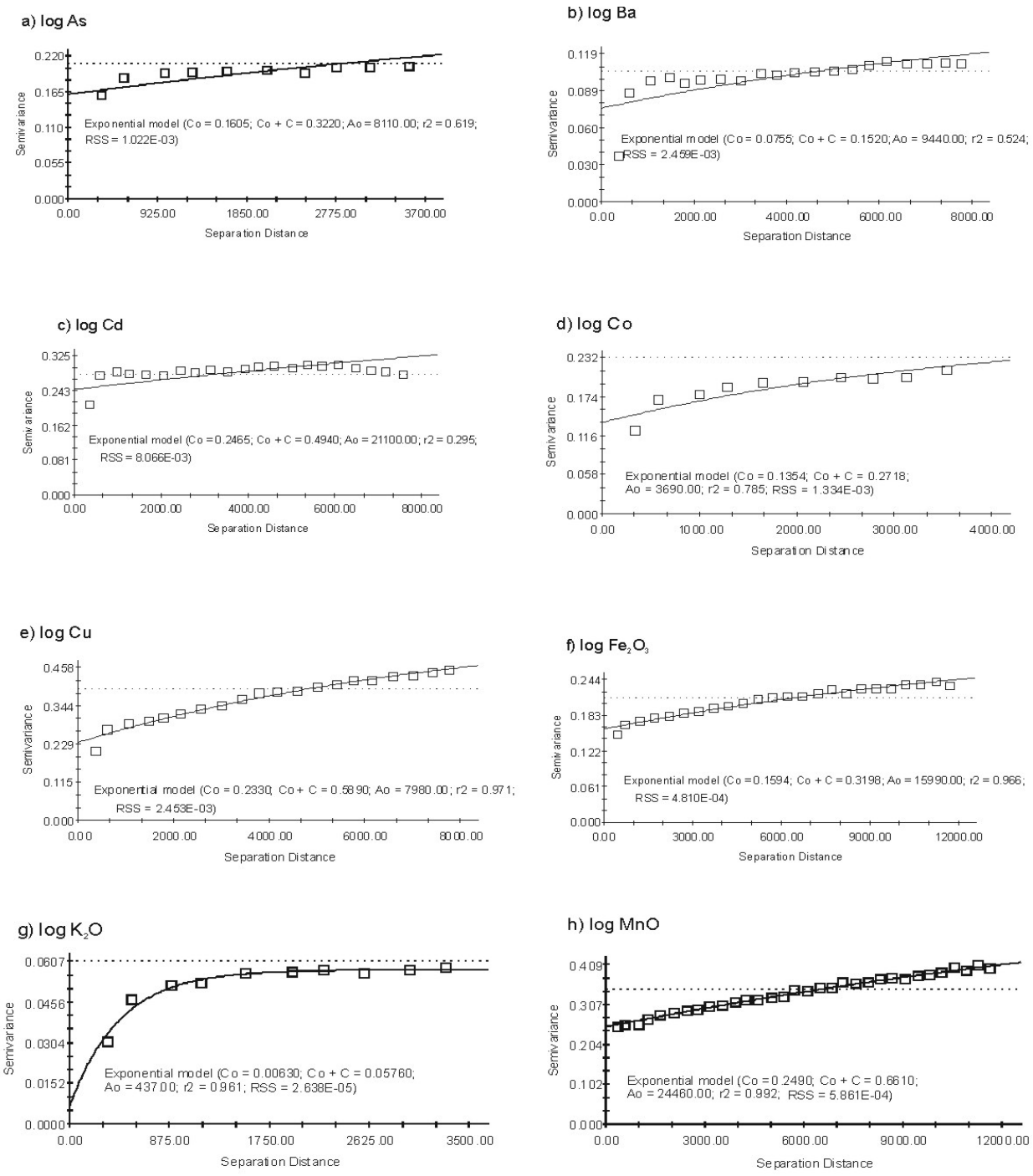


Figure 4.5 Isotropic variograms of surface soils from Stoke: a) log As, b) log Ba, c) log Cd, d) log Co, e) log Cu, f) log Fe_2O_3, g) log K_2O and h) log MnO. The separation distance is in metres.

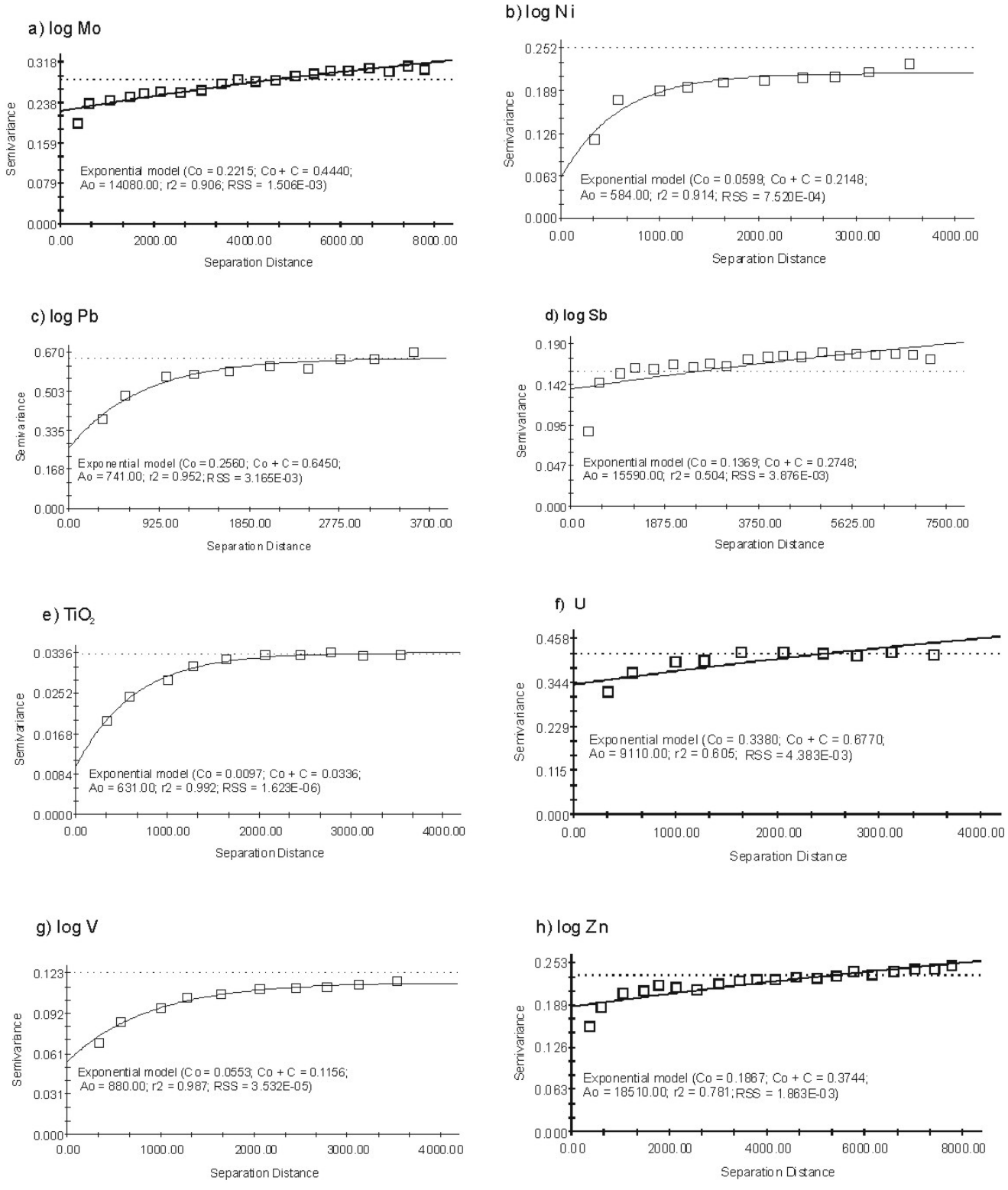


Figure 4.6 Isotropic variograms of surface soils from Stoke: a) log Mo, b) log Ni, c) log Pb, d) log Sb, e) TiO_2, f) U, g) log V and h) log Zn. The separation distance is in meters.

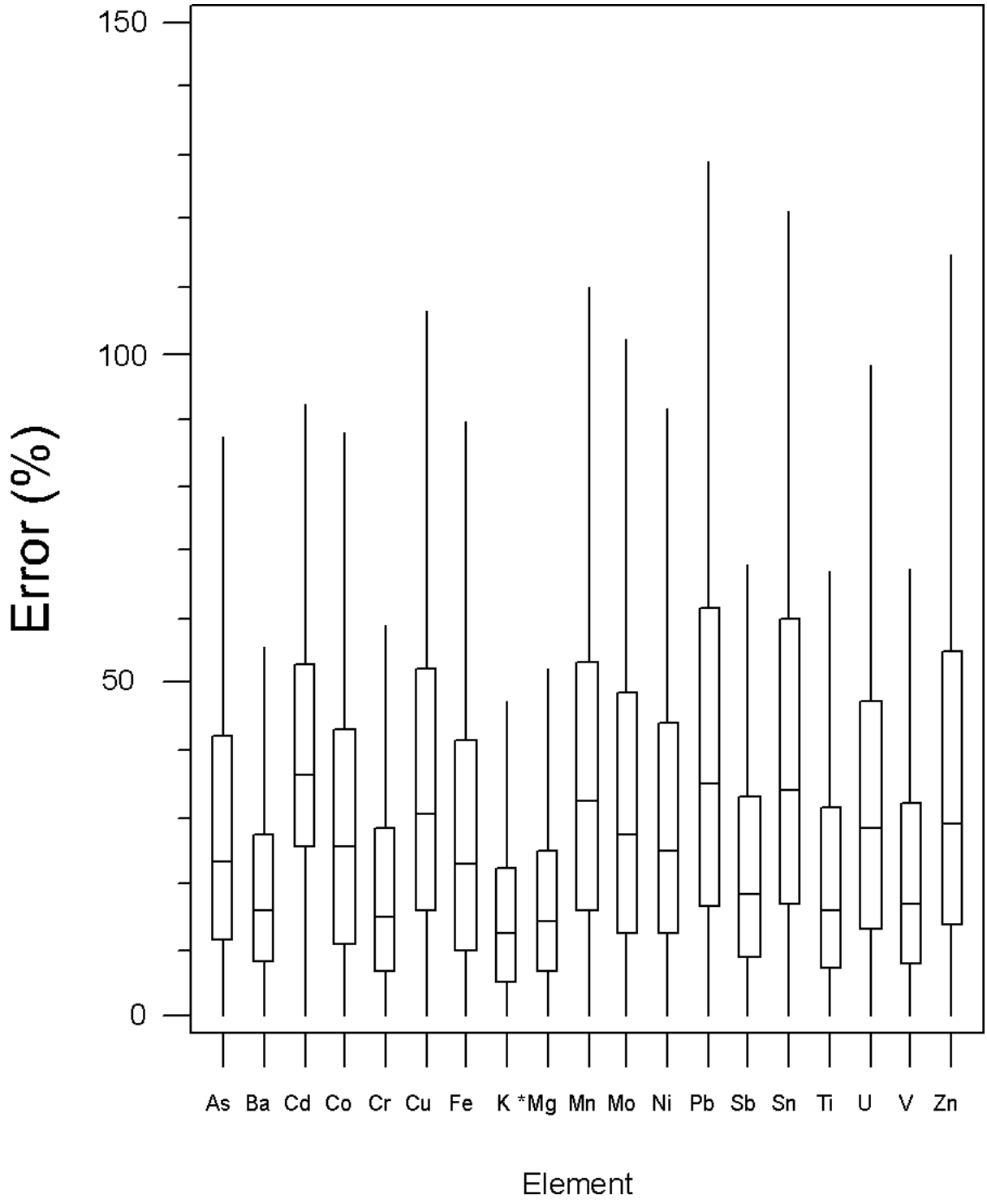


Figure 4.7 Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of IDW estimation error values for Stoke-on-Trent urban surface soil data and an example of rural profile soil data.

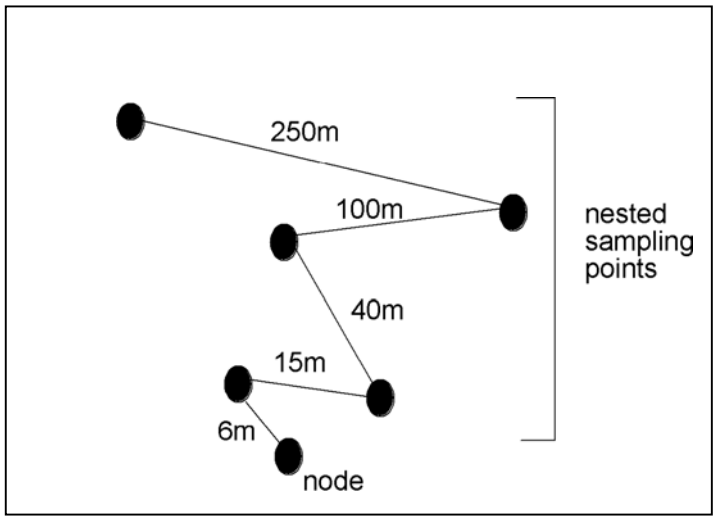


Figure 4.8 Example of a spatial configuration for a nested sampling design

4.3.5 Proportional Symbol Maps of the Stoke-on-Trent Urban Area

Presentation of the Stoke-on-Trent geochemical data as proportional symbol maps avoids uncertain extrapolation between sampling points (as portrayed in interpolated-surface maps) and displays the data in a form that more truly indicates the spatial representivity of urban samples. Maps of element concentrations in surface and profile soils for the Stoke-on-Trent urban study were generated using the ArcView® GIS proportional symbol function. Elements were classified according to the 5^{th}, 10^{th} , 25^{th}, 50^{th}, 75^{th}, 90^{th}, 95^{th} and 99^{th} percentiles of the real data distribution whereby circle symbol-size and colour correspond to the data percentile class. Although, geochemical patterns are not as readily identified as they are on interpolated maps, the proportional symbol method allows easy interpretation of the data and gives a better indication of the sampling locations (Annex 1). These maps were incorporated into the Stoke-on-Trent urban geochemistry GIS where they can be interpreted and assessed in the context of other environmental information for contaminated land and urban planning purposes.

It should be noted that for data close to the analytical detection limit the results are rounded up to the nearest integer and this may lead to several percentile classes in the data distribution with the same element concentration. Whilst this is a true reflection of the data and prevents “over-interpretation” of the data to decimal points which are not significant, it leads to the absence of several percentile classes on the proportional symbol maps for some elements such as Cd, MgO, Sb and Sn.

4.3.6 Interpolated Maps of the Stoke-on-Trent Rural and Urban Area

Whilst not appropriate for detailed investigations in urban areas, interpolated geochemical maps provide a useful overview for comparisons between rural-background to urban geochemistry. A method of presenting combined G-BASE rural soil data and the urban soil datasets is under development. Whilst interpolated rural-urban comparison maps are presented in this report (Annex 2), these maps will not be available in digital format to users outside the BGS due to the care required when interpreting these images in the context of contaminated land.

The ArcView® interpolation method is based on an IDW algorithm and as with other software packages, the interpolation determines grid-cell values using a linearly weighted combination of known data points. The weight is a function of inverse distance r but relies on the assumption that nearer points are more closely related than points further away. The influence of the known data points on the interpolated grid-cell values is controlled by changing the power-function of r. A larger power will

result in less influence from distant points, i.e., nearby data will have the most influence. The power is a positive, real number and the most commonly used value is 2 (namely r^2).

The characteristics of the interpolated surface can also be controlled by limiting the number of known data points used to calculate each interpolated grid-cell value. The known data input can be limited by the number of nearest neighbour points (specified as a variable Radius Object), or by a standard radius (specified as a Fixed Radius Object), within which all data points are to be used in the calculation of the interpolated grid-cell values. The Radius Object to be used is identified through the "aRadius"argument in ArcView®. The output interpolated value for a grid-cell using IDW is restricted to the range of known data points used to carry out the interpolation, this is because the IDW is a weighted distance average and the average cannot be greater than the highest or less than the lowest known data points. Therefore, it cannot create ridges or valleys if these extremes have not already been sampled (Watson and Philip, 1985).

Interpolation into areas where no data exists can be limited by the "aBarrierFTab" argument in ArcView®, which is used to specify the location of linear features known to interrupt the surface continuity. Barriers restrict the known data points used to interpolate grid-cell values to only those points on the same side of the barrier as the grid-cell. Input data points that lie exactly on the barrier-line are included in the calculations for both sides of the barrier. It should be noted, however that when barriers are specified, the processing time is significantly extended.

For the purposes of the present study, a combined dataset of rural and urban profile soil data was created (see Chapter 5). A series of single element interpolated maps using an IDW of r^2, a search radius of 1500 m and a grid-cell size of 125 m were generated using a customised gridded-map generation ArcView® algorithm, developed under the G-BASE programme known as the 'Gridder' algorithm. Unlike the interpolation packages used in the past, the ArcView® programme allows the gridded data to be classified according to the real data percentiles rather than the interpolated percentiles. This method of data presentation has proved successful for regional geochemical data from the Humber-Trent area of the UK. However, the application of this presentation method to the urban-rural area of Stoke-on-Trent has highlighted issues related to the calculation of percentile classes and the spatial distribution of the data.

Figure 4.9 shows an interpolated image for the combined rural and urban soil data for MgO classified by real data percentile values. Due to the difference in sampling density between the two datasets (1 per 0.25 km^2 in urban areas and 1 per 2 km^2 in rural areas), the areal extent of the high (> 90^{th} percentile) values in the rural dataset is emphasised relative to the urban area., reflecting the greater proportion of MgO in natural rural versus urban soils. In contrast, an interpolated map of the same data classified by the gridded data percentiles (the traditional G-BASE method of classification) whilst highlighting the same geochemical patterns, does not show the same spatial coverage of the higher (> 90^{th}) percentile classes (Figure 4.10). This is because the latter method effectively classifies the data according to the percentage cover of the map for a given percentile. For example, using the gridded percentile classification, the colour classifications below and up to the 25^{th} percentile will correspond to approximately ¼ of the map area as the classification is based on the gridded data surface for the whole area. In contrast, the real data classification corresponds to the 25^{th} percentile of the actual data and this may not correspond to ¼ of the interpolated surface, especially where there is a marked difference in the distribution of the sample points.

It is concluded, however, that classifying the interpolated maps by the real data method is truer to the actual data distribution therefore, urban-rural interpolated maps were generated by this method for the present study (Annex 2). It should be noted, however, that the scale bar classification and data histogram generation were carried out manually for report presentation purposes therefore the values shown in hard copy may differ from the values given in the ArcView® Gridder versions of the maps. Methods of standardised automated interpolated map presentation in the ArcView® Gridder programme require further development.

Improvement of the ArcView® interpolation methods and investigations into the effects of uneven sample distribution on the generation of gridded maps are on-going as part of the regional G-BASE programme. Watson and Philip, (1985) note, for example, that the best results from IDW are obtained when sampling is sufficiently dense with regard to the local variation being simulated. If the sampling of known data points is sparse or very uneven, the results may not sufficiently represent the desired

surface. The results of these further studies are likely to influence the presentation of rural and urban datasets in the future.

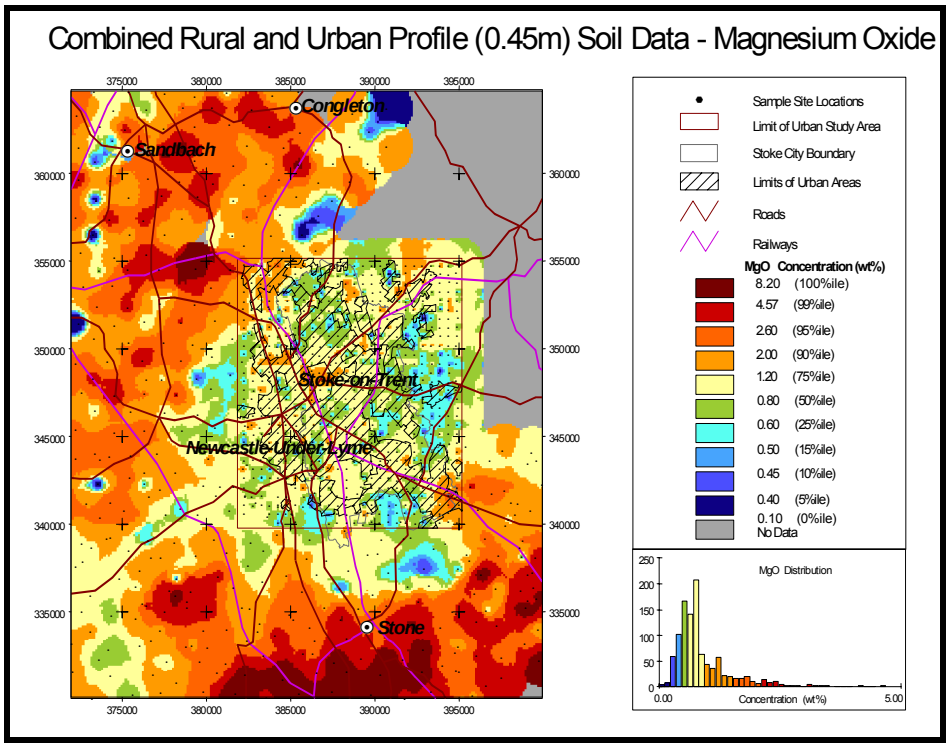


Figure 4.9 Interpolated map of total MgO concentrations in rural and urban profile soils from the Stoke-on-Trent area classified by real data percentiles.

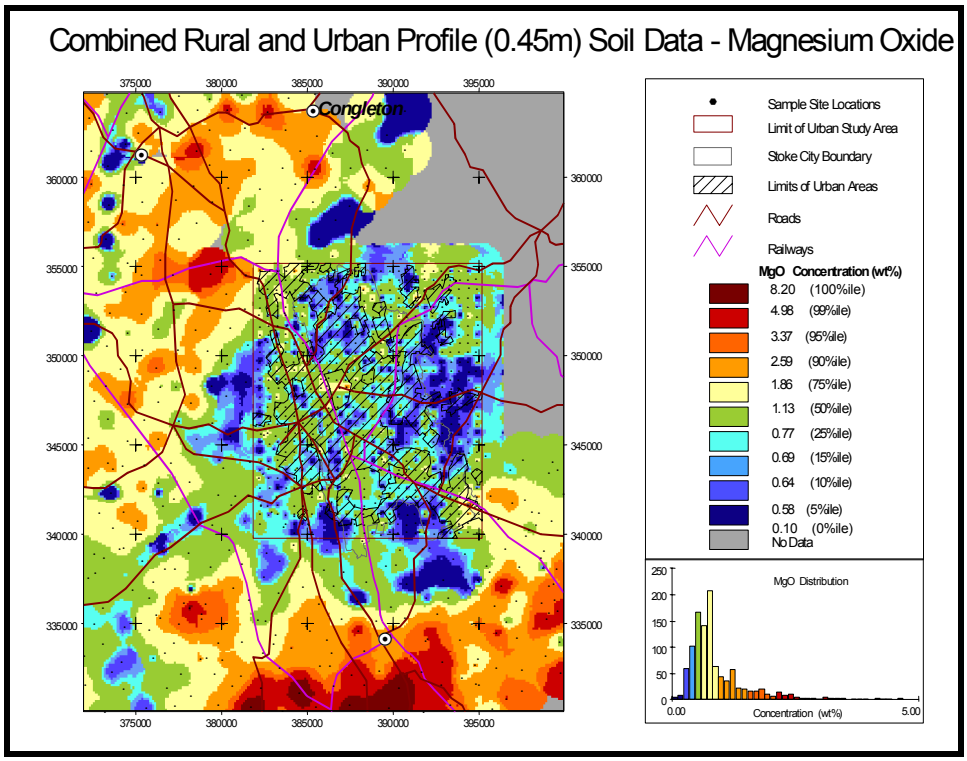


Figure 4.10 Interpolated map of total MgO concentrations in rural and urban profile soils from the Stoke-on-Trent area classified by gridded data percentiles.

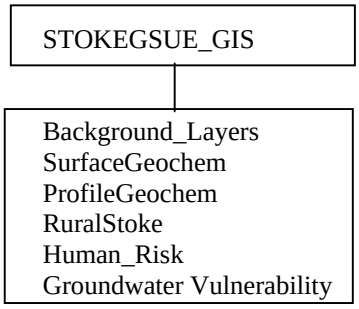
4.3.7 Interpolated Three Component Urban Geochemical Maps

Although interpolated geochemical maps are not recommended as the standard method of urban soil data presentation for the reasons outlined above, the use of these maps to display selected overview three-component maps of urban soils is none-the-less helpful as an aid to data interpretation. Therefore, three component interpolated maps of urban soil data are presented in this report (see Chapter 6) but will not be available in digital format to users outside the BGS due to the care required when interpreting these images in the context of contaminated land.

Methods to generate three-component geochemical maps in ArcView® are currently under development as part of the G-BASE programme. For the present study, these maps were created using NIH-Image® and Adobe Photoshop® software as follows. Individual interpolated grids were produced for each of three elements categorised into 10 percentile classes. Each grid was assigned a primary colour, red, green or blue such that element concentrations were shown in scaled monochrome intensity whereby the highest values were represented by a high intensity of colour and the lowest values by the lowest intensity. For example, a three component map of Cu, Pb and Zn may comprise three interpolated grids of Cu – shown in shades of red, Pb – shown in shades of green and Zn – shown in shades of blue. The composite three component map was made by combining the individual scaled monochrome red, green and blue geochemical grids according to primary-colour addition logic such that red+green=yellow, red+blue=magenta, blue+green=cyan and red+green+blue=white (at full intensity). With up to 10 levels of intensity for each individual primary colour, a wide range of hues and shades were produced and with careful interpretation, the technique allows the concentrations of different groups or combinations of elements to be clearly displayed. The raster images produced by this method were incorporated into ArcView® and spatially co-registered with other data layers in the GIS.

4.4 PRESENTING DATA IN THE GIS

The urban geochemistry GIS for Stoke-on-Trent comprises an ArcView® 'project' (.apr) file, which contains a series of layers or ArcView® shape files (.shp) of background information such as the road network and solid geology as outlined in Chapter 2 of this report. The GIS also contains a full suite of surface and profile soil proportional symbol geochemical maps of the urban area. Under the current system, the proportional symbol legends are created individually for each element in ArcView® and in order for the GIS to be transferred onto CD-ROM etc, it is recommended that each element legend is saved as an ArcView® legend file (.avl) at the time of creation. In addition, interpolated grid maps must be saved as ArcView® shape files rather than as grids in order to be moveable. Indeed in order to transfer the Stoke GIS and future urban GIS between locations it is necessary that all layers are stored as ArcView® shape files and all legends for all layers including background information are saved as legend files. To ensure that ArcView® can locate all the layers contained in the GIS 'project', the shape files and legend files are contained within the same work area or folder with a series of sub-folders for each of the data types as follows:



Once all the data are stored in the same or sub-ordinate directories, it is then possible using BGS in-house ArcView® scripts to save the project file with relative pathnames so that it is transferable.

Groups of layers (or shape files) for each of these data types are shown together as a series of view windows in the GIS and any combination of data layers can be shown together to aid the data interpretation.

5. Rural-Urban Geochemistry of Stoke-on-Trent

By F M Fordyce, T R Lister and B Hope

5.1 INTRODUCTION

As outlined in Chapter 1 of this report, many natural and man-made factors can affect the geochemistry of soils. In rural areas, the solid geology, nature of superficial deposits, climate and topography all influence soils, hence the rural or regional background concentrations of elements can be highly variable depending on conditions in the natural environment. In order to assess the nature and extent of contamination associated with urban environments, in the first instance it is necessary to consider the urban area in the context of the rural or regional hinterland. For example, a city located in a naturally mineralised area will have an elevated regional background for many metalliferous elements such as Cu, Zn and Pb. Urban soil metal contents will reflect these naturally elevated values as well as any contamination due to anthropogenic activities in the city environment. A comparison of rural and urban soil geochemistry can aid the assessment of anthropogenic contamination and indicate the non-urban geochemical baseline for the area providing a benchmark for remediation. Without an understanding of the rural baseline, clean-up strategies could be implemented which reduce the concentrations of PHS's to below the levels naturally present in the immediate rural environment. As indicated in Chapter 1, it is not possible to establish the 'natural' baseline within the urban environment because even areas of undisturbed ground within the city will be subject to diffuse pollution such as atmospheric deposition (especially from traffic fumes), littering and urban surface run-off.

In the Stoke-on-Trent area, rural soils were collected by the BGS G-BASE programme using sampling and analytical procedures identical to those employed in urban areas, with the exception that rural soils were collected at a sample density of 1 per 2 km^2 rather than 1 per 0.25 km^2. The consistency between rural and urban surveying allows direct comparison between soils from the two environments as discussed in this chapter.

5.2 SPATIAL COMPARISONS BETWEEN RURAL G-BASE AND URBAN GSUE DATA FOR STOKE-ON-TRENT

5.2.1 Data Selection

Surface and profile soils were collected from the rural hinterland of Stoke-on-Trent as part of the West-Central England and Wales regional geochemical atlas areas (BGS, 2000). Rural soil surveying was designed to complement the main programme of regional stream sediment collection to avoid gaps in sample coverage in areas of poor drainage development over the Sherwood Sandstone and Mercia Mudstone Groups of the Cheshire Basin to the west and south of Stoke-on-Trent (Figure 5.1).

To date, total element concentrations have been determined in the rural profile soils (< 150 µm fraction) by Direct Reader Arc Emission Spectrometry (DC-ARC-ES) (BGS, 1997) to the northwest of Stoke-on-Trent, and by XRF to the south. Table 5.1 indicates the analyses available for both urban and rural areas. The different analytical techniques correspond to an upgrade in BGS analytical facilities to XRF technology at the time of sampling. A controlled change-over between the different analytical methods ensured that data consistency was maintained for the West-Central England and Wales atlas

areas. It should be noted, however, that rural data for As, Cd, P_2O_5, Sb, and U were not determined by DC-ARC-ES; therefore information for these elements is lacking for the area to the northwest of Stoke-on-Trent.

TABLE 5.1 LIST OF DETERMINANTS IN G-BASE RURAL PROFILE SOILS (< 150 µM FRACTION) AROUND STOKE-ON-TRENT, WHICH HAVE BEEN DETERMINED IN GSUE SOILS IN THE STOKE-ON-TRENT URBAN AREA.

DC-ARC-ES	XRF
	Sb
	As
Ba	Ba
	Cd
CaO	CaO
Cr	Cr
Co	Co
Cu	Cu
Fe_2O_3	Fe_2O_3
Pb	Pb
MgO	MgO
MnO	MnO
Mo	Mo
Ni	Ni
	P_2O_5
K_2O	K_2O
Sn	Sn
	U
V	V
Zn	Zn

A sub-set of the rural profile soil data was combined with the urban profile data for Stoke-on-Trent to produce one dataset from which a series of interpolated rural-urban geochemical maps were generated (Annex 2). The spatial limits of the rural area were constrained by the availability of rural soil analyses to the north and east of Stoke-on-Trent and to a distance of 10 km to the west and south (limits of the rural area are UK NGR 372130E, 330310N – 399780E, 364600N). This distance was selected to place Stoke-on-Trent in the context of the surrounding environment but limit the extent of the rural comparison to a local area underlain by similar lithological units. The interpolated rural-urban maps provide an overview of geochemical trends for Stoke-on-Trent as follows.

5.2.2 Geochemical Interpretation

Many of the metal and metalloid elements such as Sb, As, Ba, CaO, Cr, Co, Cu, Fe_2O_3, Pb, MnO, Mo, Ni, Sn, V and Zn are generally elevated in the urban area soils relative to the rural background as expected (Annex 2). In contrast, the majority of Cd values are below the detection limit in the rural area with sporadic anomalous (> 90^{th} percentile) values indicating localised contamination in the urban environment. The distribution of P_2O_5 between the rural and urban environments indicates some contamination in the urban area, but most of the high contents occur in the rural area, which may reflect bedrock geochemistry or agricultural inputs to the soils. Anomalous U values are sporadic, occurring in both rural and urban soils probably indicating very localised contamination or bedrock geochemistry (presence of uraniferous nodules and minerals). Magnesium and K_2O contents are low in the urban environment relative to the rural hinterland indicating that geology is the dominant control on these elements, which are higher over the Mercia Mudstone and Sherwood Sandstone soil parent lithologies than on urban fill materials or the Westphalian Coal and Barren Measures.

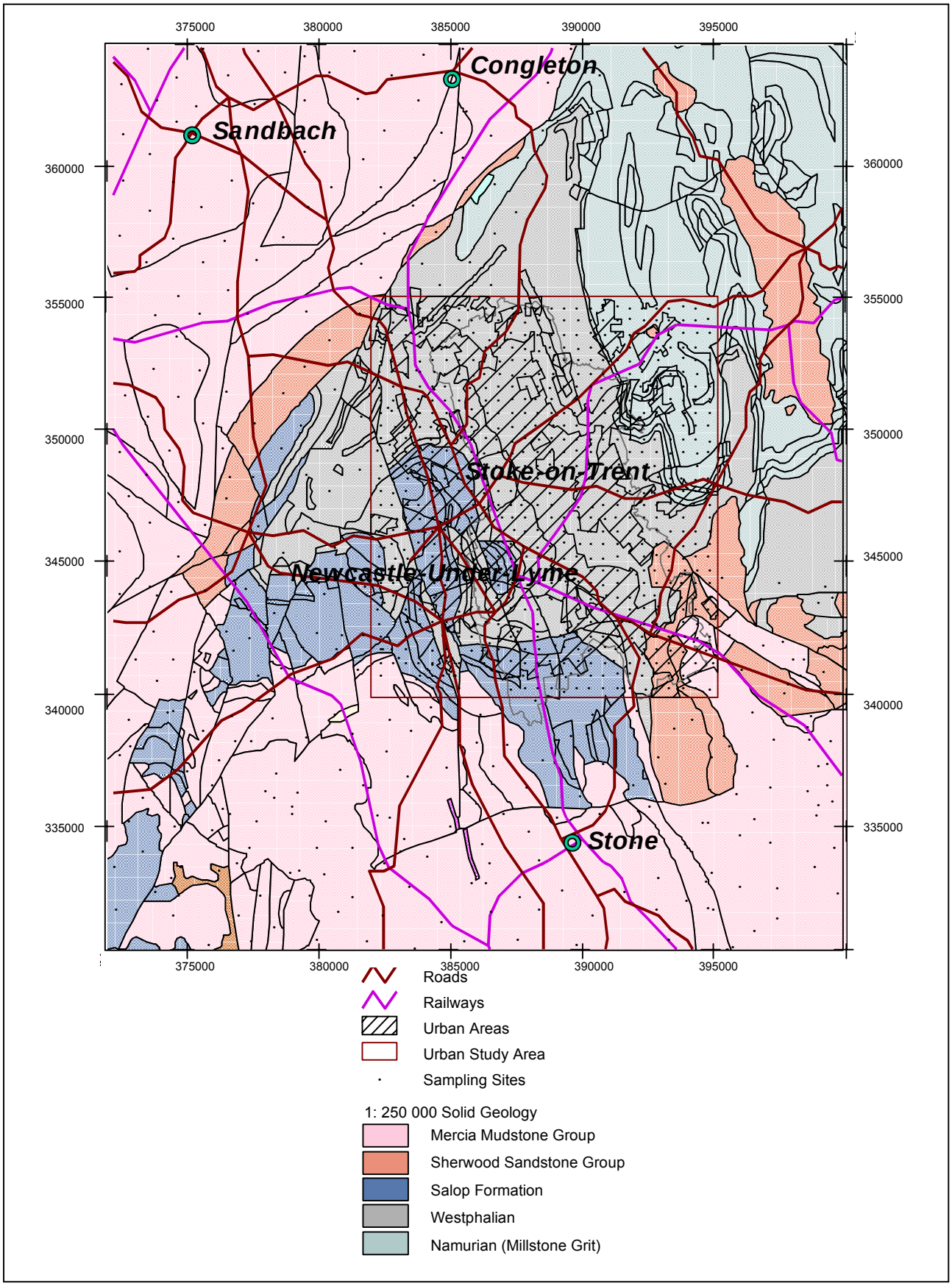


Figure 5.1 Rural and urban profile soil sampling sites overlain on simplified 1: 250 000 scale solid geology map for the area around Stoke-on-Trent

Stoke-on-Trent is underlain by Westphalian age rocks including the Coal Measures, hence several of the metal and metalloid elements could be naturally enhanced in urban soils because coals often contain relatively high concentrations of these substances. The outcrop of the Westphalian extends beyond the built up area of Stoke-on-Trent, to the north of the study area and to the west of Newcastle-under-Lyme (Figure 5.1) providing an opportunity to examine the differences in soil chemistry over the same lithology but within and outside the urban area. For example, the distributions of high (> 90th percentile) Sb, Ni, Co values are coincident with the city boundary but do not extend into the rural areas to the north and west of Stoke-on-Trent underlain by the Westphalian. This suggests that the urban environment is the dominant control on high concentrations of these elements. In contrast, concentrations of As, Cu, Cr, Fe_2O_3, MnO, Mo, Sn, Zn, V, Ni, are high to the north and/or west of the study area as well as in the built-up centre. However, the distributions of anomalous values outside the urban area do not extend over the entire rural outcrop of the Westphalian but are limited to areas of disturbed or mined ground on the urban periphery. Therefore Westphalian bedrock geochemistry is responsible for higher concentrations of these elements in soils but only in areas where the ground has been disturbed.

Over the rural outcrop of the Westphalian to the north of Stoke-on-Trent, between Kidsgrove and Congleton (Figure 5.1 and Annex 2), the majority of metal and metalloid elements show low concentrations in soils relative to the urban area.

By far the greatest control on the elevated element concentrations in the urban environment is the distribution of made ground (Figure 2.10). The majority of high element concentrations (As, CaO, Ba, Sb, Cu, Co, Cr, MnO, Fe_2O_3, V, Zn, Pb, Mo, Ni and P_2O_5) show a strong spatial correlation with made ground (Annex 2). The high concentrations of CaO, P_2O_5 and Ba probably reflect foundry and ceramic industry waste materials in the urban fill, whereas metal and metalloid concentrations may be elevated in these and in colliery slag materials. The distribution of high Pb values is also closely related to the built-up area, but interestingly shows dispersion along some of the major road and rail networks to the south and south-east of Stoke-on-Trent.

It should be noted, that the combined rural-urban dataset maps in Annex 2 only provide an overview of the rural background *relative* to the urban environment. For example, in the context of the rural data alone, it is likely that the background concentrations of metal and metalloid elements are higher over the Westphalian compared with some of the other local lithologies such as the Millstone Grit or Mercia Mudstone, although, these relationships are obscured by the very high concentrations present in the urban environment. These issues are examined in more detail in the following chapters of this report. Another possible way to present the rural background data might be to develop ArcView®-based interpolation methods that allow the rural and urban data to be classified according to the rural percentiles rather than percentiles based on the rural and urban combined dataset. In this way, the distribution of the rural background would be represented in a manner which is independent of the urban environment and, for the majority of elements, the urban environment would plot in the highest percentile classes indicating the levels of contamination in relation to rural concentration ranges.

In conclusion, however, it is clear that by whatever method the data are presented, within the urban environment studied here, geological influences are of secondary importance to the nature and extent of made ground in determining most soil element concentrations.

5.3 STATISTICAL COMPARISONS BETWEEN RURAL AND URBAN DATASETS

Statistical comparisons between rural and urban data can be used to examine the level of contamination relative to rural background in the urban environment. Table 5.2 outlines the data ranges for total element concentrations in G-BASE rural and GSUE urban soils. It should be noted, however, that comparisons between urban surface soils (< 2 mm) and rural profile soils (< 150 µm) should be treated with caution due to the different size fractions analysed. As a general overview, the maximum concentrations of As, Ba, Cd, Cr, Co, Cu, Pb, Fe_2O_3, Mo, MnO, Ni, P_2O_5, Sn and Zn are elevated in the urban environment relative to the rural dataset. Median values give a general indication of the levels of element enhancement in the urban area versus the rural background and on this basis, urban profile soils contain approximately 1.2 – 2 times the average Cr, Co, Cu, Fe_2O_3, MnO, Ni, Sn, Mo, V, Pb and Zn contents of rural profile soils, whereas As and Sb show little elevation in the urban soils relative to rural background.

Whilst these comparisons give a general indication of the overall levels of contamination relative to local rural baselines, further investigations into the relationships with rural geochemical profiles were carried out in terms of the solid geology and superficial deposit cover. One of the developments in data manipulation as a result of GIS technology is the ready ability to select sub-sets of the geochemical data based on particular areas of interest such as individual stratigraphic units. This type of data manipulation has been carried out for rural and urban profile soils in the Stoke-on-Trent area on the basis of 1:250 000 scale solid geology units and 1: 625 000 superficial deposit units. In addition to sub-sampling based on lithological units, the data were further categorised into rural or urban datasets allowing statistical comparisons between the rural and urban soils over the same geological/ superficial deposit unit (Figure 5.2).

The box and whisker plots (Figure 5.3 – 5.6) and summary statistics table (Table 5.3) demonstrate that in rural soils, concentrations of V, Fe_2O_3, Co, Ni, Cu and Zn are highest over the Westphalian rocks relative to other the stratigraphic units as expected due to the presence of coals whereas Ba is highest over the Namurian age Millstone Grit Group, probably reflecting natural barite mineralisation in the Pennines to the northeast of the study area. MgO in soils is highest over the Mercia Mudstone Group and K_2O is also highest over this Group and the Sherwood Sandstone Group relative to other units. The majority of other elements show similar concentrations in soils across the different solid-geology stratigraphic divisions in rural areas. In terms of superficial cover, in rural areas, MgO soil contents are higher over river terrace deposits than on other deposit types and K_2O contents are lower over alluvial deposits. Soil trace element contents show little variation across the different superficial deposit units in the rural area with the exception that Pb is higher over alluvium probably reflecting diffuse pollution in rural fluvial systems.

However, the magnitude of difference in soil element concentrations between stratigraphic units in the rural environment is much less than that between the rural and urban environments. Figures 5.3 – 5.6 show that in almost all cases, trace element concentrations are enhanced in the urban relative to the rural environment for each stratigraphic unit. As a further comparison, the ratios of soil element median values in the urban versus rural environments were calculated for each stratigraphic unit. Table 5.4 shows that soils over river terrace deposits show some of the greatest increases in concentration between rural and urban median values (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 contamination in the urban environment and may also reflect the historical preference for locating industrial activity on the banks of drainage systems. Mo and Cu medians are noticeably enhanced in urban relative to rural soils (x8.5 and x3.0 respectively) over glacial sand and gravel deposits. These elements are generally of very low abundance in natural glacial sands and gravels and their enhancement in the urban environment possibly reflects their use in pottery glazes etc. The majority of other trace element medians are 1.2 – 2 times higher in urban relative to rural soils (Table 5.4). It is interesting to note that the level of enhancement in the urban versus rural environment over the Westphalian is similar to that of the other stratigraphic units, indicating the effects of urbanisation regardless of parent material.

When considering these rural-urban comparisons it is important to note the representivity of the rural baseline data. Stoke-on-Trent is underlain in the main by Westphalian rocks and 430 of the geochemical sampling sites were collected over this parent material in the urban area. In contrast, information on rural element concentrations over the Westphalian is limited by the extent of the regional G-BASE programme at that time (33 sites). Similarly, rural data for only 19 sites over the Sherwood Sandstone and 6 sites over the Namurian age Millstone Grit are available. Whilst the Westphalian and Sherwood Sandstone data may provide some representative indication of rural background, the results for Millstone Grit should be treated with caution due to the small size of the sample-set. The G-BASE rural programme currently collects rural soil samples systematically across the country and not just in areas of poor drainage density hence these issues should not affect urban areas sampled in more recent years. However, due to the very close link between the outcrop of the Westphalian and the extent of major built-up areas in the UK, establishing the rural baseline for the Westphalian may prove difficult around urban centres and comparisons with wider rural datasets are outlined in Chapter 6 of this report. The definition of rural and urban used in these comparisons is based upon the rural G-BASE and urban GSUE datasets. However, the urban sampling programme of Stoke-on-Trent extended beyond the boundary of the built-up area into the rural environment immediate to the city (Figure 5.1). These urban periphery samples may skew the element concentration ranges in the urban soil dataset to lower values than present in the actual built environment. As such, it is recommended that future GSUE surveys cover only the built environment whereas G-BASE rural

surveys provide data on the non-built urban periphery. Relationships between samples in the built environment and the immediate rural hinterland within the urban dataset are examined in Chapter 6.

5.4 SUMMARY

In summary, comparisons between rural and urban soil datasets are useful to examine the level of contamination in the urban environment against natural background. It is not possible to establish the natural background within the city area due to the effects of diffuse pollution even in areas of undisturbed ground. Rural-urban comparisons rely on consistency in methodology between urban and regional sampling campaigns and the availability of comparative datasets over the different lithologies present in the urban environment and rural hinterland. Whilst data for Millstone Grit in the rural area around Stoke-on-Trent are limited in extent due to protocols adopted at the time of surveying, the current G-BASE rural sampling strategy should provide adequate data for rural-urban comparisons in the future. Investigations in Stoke-on-Trent have shown that on average (median values) urban soil metal and metalloid element concentrations are 1.2 – 2 times local rural soil averages. Although concentrations of V, Fe_2O_3, Co, Ni, Cu and Zn are highest over Westphalian rocks relative to other stratigraphic units due to the presence of coals, by far the biggest control on metal and metalloid element concentrations in soils in the urban environment is the distribution of made ground. Urban river terrace deposits show up to 3 times the rural concentrations of several metal elements probably reflecting the fact that these deposits act as sinks for contamination in the urban environment.

TABLE 5.2 SUMMARY STATISTICS OF ELEMENT DISTRIBUTIONS IN STOKE-ON-TRENT RURAL AND URBAN SOILS.

Statistics ppm = mg/kg	Soil Type	Al_2O_3 (wt %)	Sb (mg/kg)	As (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	CaO (wt %)	Cr (mg/kg)	Co (mg/kg)	Cu (mg/kg)	Fe_2O_3 (wt %)	Pb (mg/kg)	MgO (wt %)	pH
Minimum	Urban A	3.4	0.5	2	175	0.4	0.03	22.0	4.0	7	0.6	10	0.1	2.9
	Urban S	1.6	0.5	4	146	0.4	0.03	41.0	1.0	7	1.7	15	0.1	nd
	Rural S	nd	0.5	4	253	1.0	0.08	23.0	2.0	4	0.6	9	0.1	nd
Maximum	Urban A	23.0	43.0	136	3590	43.0	10.92	441.0	452.0	1729	32.3	4208	3.0	8.0
	Urban S	27.2	71.0	167	4269	408.0	17.80	574.0	133.0	1260	43.7	4207	3.7	nd
	Rural S	nd	7.0	47	2348	6.0	29.54	116.0	75.0	335	16.9	301	8.2	nd
Mean	Urban A	12.2	2.0	16	512	1.7	0.99	76.3	24.7	51	5.7	176	0.7	5.5
	Urban S	15.4	2.3	18	579	1.4	1.07	94.9	28.1	56	6.9	164	0.8	nd
	Rural S	nd	1.3	14	516	1.1	0.78	72.1	19.3	26	4.7	57	1.6	nd
Median	Urban A	11.9	1.0	14	454	2.0	0.57	73.0	22.0	33	5.2	93	0.6	5.4
	Urban S	15.1	1.0	14	496	0.4	0.44	92.0	26.0	33	6.5	61	0.7	nd
	Rural S	nd	1.0	13	462	1.0	0.54	72.0	19.0	23	4.5	47	1.3	nd

Statistics	Soil Type	MnO (wt %)	Hg (mg/kg)	Mo (mg/kg)	Ni (mg/kg)	P_2O_5 (wt %)	K_2O (wt %)	SiO_2 (wt %)	Sn (mg/kg)	TiO_2 (wt %)	U (mg/kg)	V (mg/kg)	Zn (mg/kg)	LOI (wt %)
Minimum	Urban A	0.03	0.005	0.6	5.0	0.06	0.53	20.6	1	0.096	0.3	23	6	0.6
	Urban S	0.02	nd	0.2	6.0	0.03	0.42	12.6	2	nd	0.3	41	20	nd
	Rural S	0.01	nd	0.2	5.0	0.03	0.79	nd	1	0.350	0.5	11	13	nd
Maximum	Urban A	0.67	7.220	25.8	124.0	3.74	3.60	78.1	662	1.393	4.9	241	2589	73.3
	Urban S	1.07	nd	69.1	250.0	1.42	4.20	76.9	657	nd	7.0	296	7408	nd
	Rural S	0.96	nd	5.5	86.0	0.83	5.74	nd	72	1.281	44.5	226	1032	nd
Mean	Urban A	0.15	0.254	2.9	27.1	0.34	1.57	60.0	17	0.622	1.5	95	156	12.6
	Urban S	0.16	nd	4.1	34.6	0.24	1.95	58.2	14	nd	2.4	114	170	nd
	Rural S	0.10	nd	1.5	23.9	0.25	2.57	nd	5	0.749	2.7	87	93	nd
Median	Urban A	0.13	0.143	2.4	23.0	0.29	1.52	60.9	7	0.617	1.5	89	108	11.7
	Urban S	0.14	nd	2.7	30.0	0.19	1.85	59.3	6	nd	2.4	108	90	nd
	Rural S	0.09	nd	1.4	23.0	0.22	2.53	nd	5	0.748	2.4	83	80	nd

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

LOI = Loss on Ignition nd = No data

TABLE 5.3 SUMMARY STATISTICS OF TOTAL ELEMENT CONCENTRATIONS IN RURAL AND URBAN SOILS FROM THE STOKE-ON-TRENT AREA OVER A) 1: 250 000 SOLID GEOLOGY UNITS AND B) 1: 650 000 SUPERFICIAL DEPOSIT UNITS

(All concentrations in ppm (mg/kg) except MnO, Fe_2O_3, MgO, P_2O_5, K_2O and CaO in weight %)

a) Solid Geology Units

Mercia Mudstone	Urban																			
	MnO	Fe_2O_3	V	Cr	Co	Ba	Ni	Cu	Zn	As	Mo	Pb	U	Cd	Sn	Sb	MgO	P_2O_5	K_2O	CaO
Count	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23
Minimum	0.03	2.28	64.00	60.00	10.00	363.00	13.00	11.00	29.00	8.00	1.10	25.00	1.50	0.40	4.00	0.50	0.60	0.11	1.72	0.06
Maximum	0.61	8.25	117.00	92.00	35.00	649.00	47.00	75.00	260.00	26.00	4.80	161.00	3.00	2.00	21.00	3.00	3.70	0.49	3.58	4.39
Mean	0.14	5.10	88.04	77.70	20.91	462.65	25.74	30.78	106.00	14.22	2.40	69.13	2.30	0.62	7.48	1.39	1.23	0.21	2.38	0.87
Median	0.12	4.94	85.00	79.00	21.00	446.00	24.00	26.00	82.00	13.00	2.30	53.00	2.40	0.40	6.00	1.00	1.00	0.17	2.38	0.38
Mercia Mudstone	Rural																			
	MnO	Fe_2O_3	V	Cr	Co	Ba	Ni	Cu	Zn	As	Mo	Pb	U	Cd	Sn	Sb	MgO	P_2O_5	K_2O	CaO
Count	242	242	242	242	242	242	242	242	242	156	242	242	156	156	242	156	242	156	242	242
Minimum	0.01	1.00	24.00	23.00	2.00	354.00	5.00	4.00	13.00	4.00	0.20	9.00	0.50	1.00	1.00	0.50	0.10	0.03	2.00	0.08
Maximum	0.29	10.00	149.00	103.00	33.00	1169.00	44.00	81.00	193.00	25.00	6.00	175.00	7.20	2.00	17.00	3.00	8.00	0.82	4.00	13.00
Mean	0.09	4.17	80.79	69.93	17.73	496.48	22.90	23.51	83.30	12.53	1.52	49.95	2.42	1.04	4.88	1.24	2.03	0.27	2.74	0.78
Median	0.08	4.00	80.00	71.00	18.00	462.00	22.00	21.00	77.00	12.00	1.00	43.00	2.40	1.00	5.00	1.00	2.00	0.23	3.00	1.00

TABLE 5.4 RATIO OF SOIL ELEMENT URBAN-MEDIAN/RURAL-MEDIAN CONCENTRATIONS FOR EACH 1: 625 000 SCALE SUPERFICIAL DEPOSIT AND 1: 250 000 SCALE GEOLOGY UNIT IN THE STOKE-ON-TRENT STUDY AREA.

	MnO	Fe_2O_3	V	Cr	Co	Ba	Ni	Cu	Zn	As	Mo	Pb	U	Cd	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	0.4	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	0.4	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	0.4	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	0.4	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	0.4	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	0.4	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	0.4	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	0.4	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		2.0	0.7	nd	nd	0.9	nd	0.7	nd	0.9	4.0

Note: Cd and Sb comparisons are hampered by proximity of values to the limit of detection nd = No data

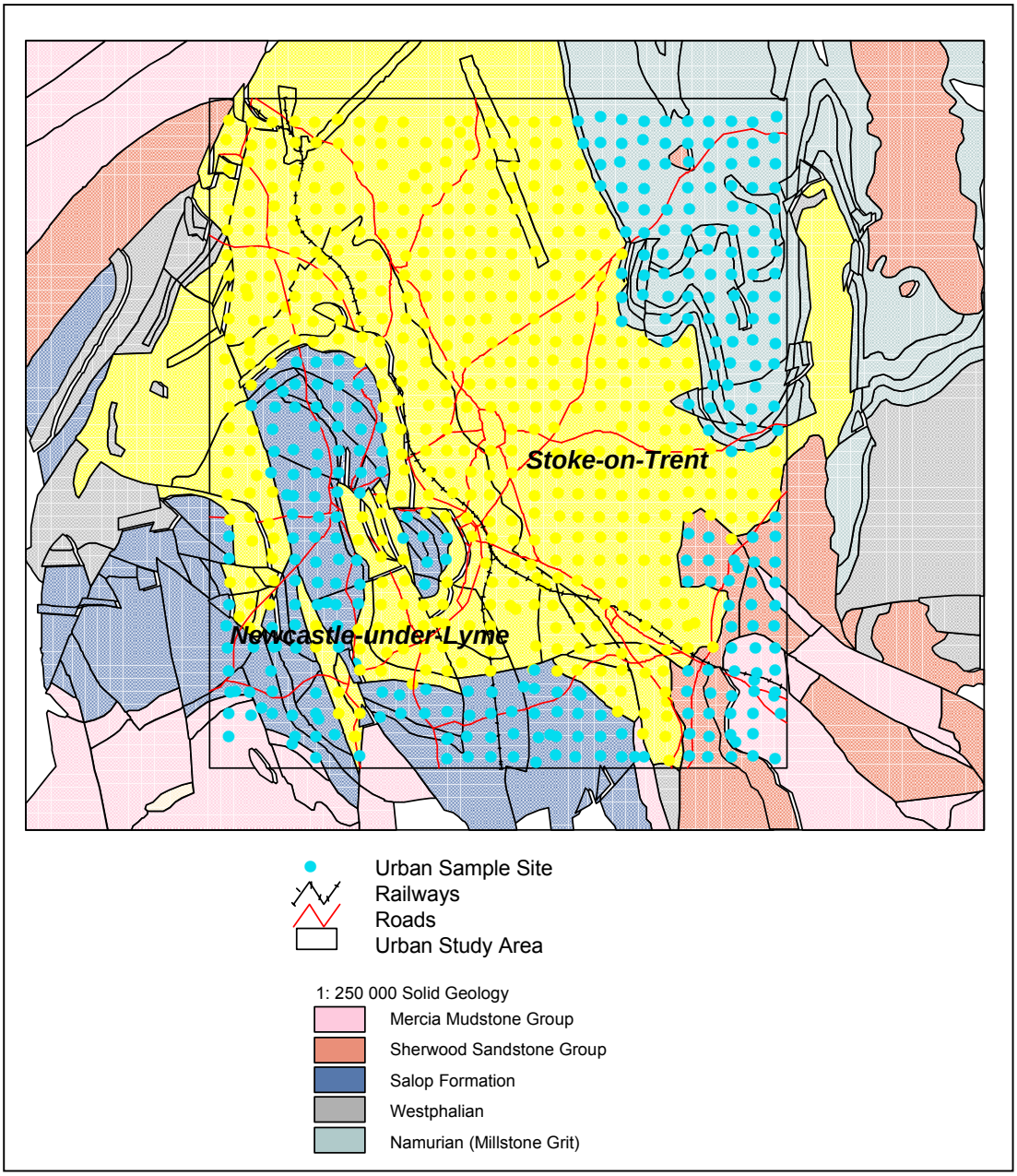
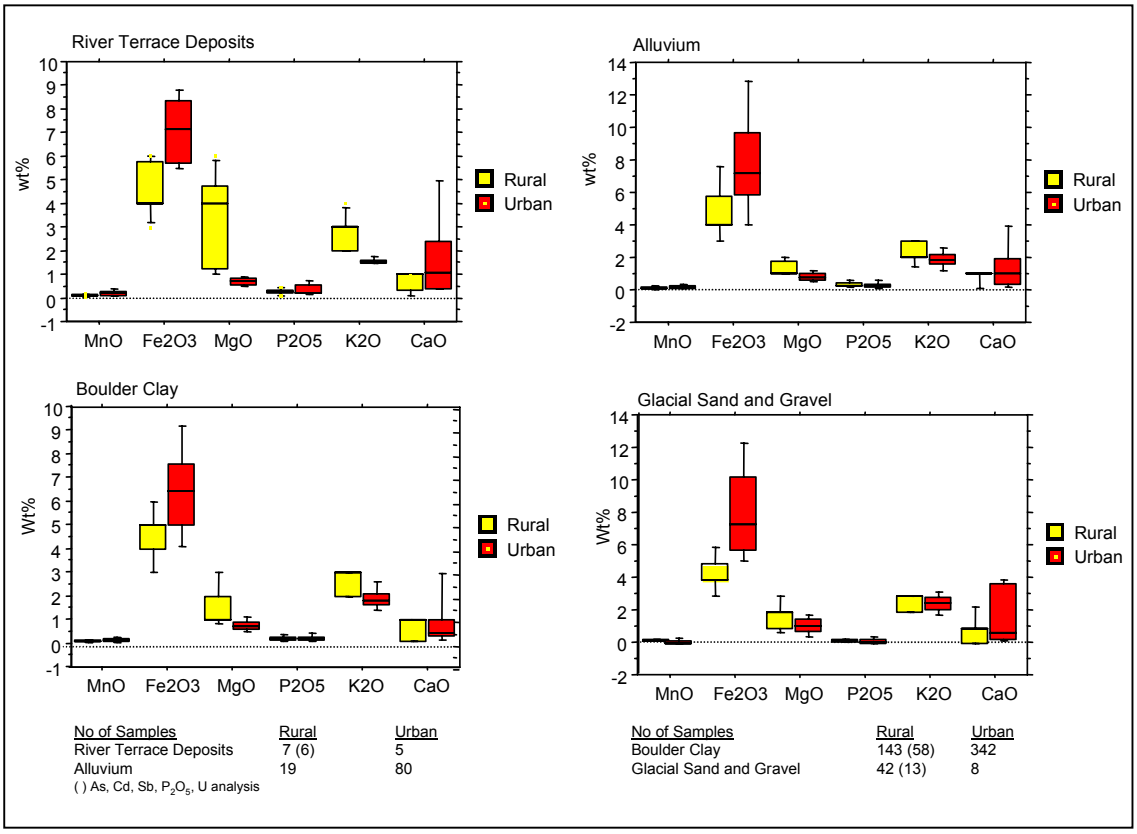


Figure 5.2 Stoke-on-Trent urban profile soil sample sites overlain on the simplified 1: 250 000 scale solid geology map.

Profile soils underlain by Westphalian age rocks have been selected using the region of interest tool in ArcView® (shown in yellow points and polygon) allowing statistical processing of soil geochemical data for individual rock units.



No of Samples	Rural	Urban
River Terrace Deposits	7 (6)	5
Alluvium	19	80
Boulder Clay	143 (58)	342
Glacial Sand and Gravel	42 (13)	8

( ) As, Cd, Sb, P_2O_5, U analysis

Figure 5.3 Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of major element distributions in rural and urban profile soils from the Stoke-on-Trent area (UK NGR 372130E, 330310N – 399780E, 364600N) categorised by 1: 625 000 scale superficial deposit units.

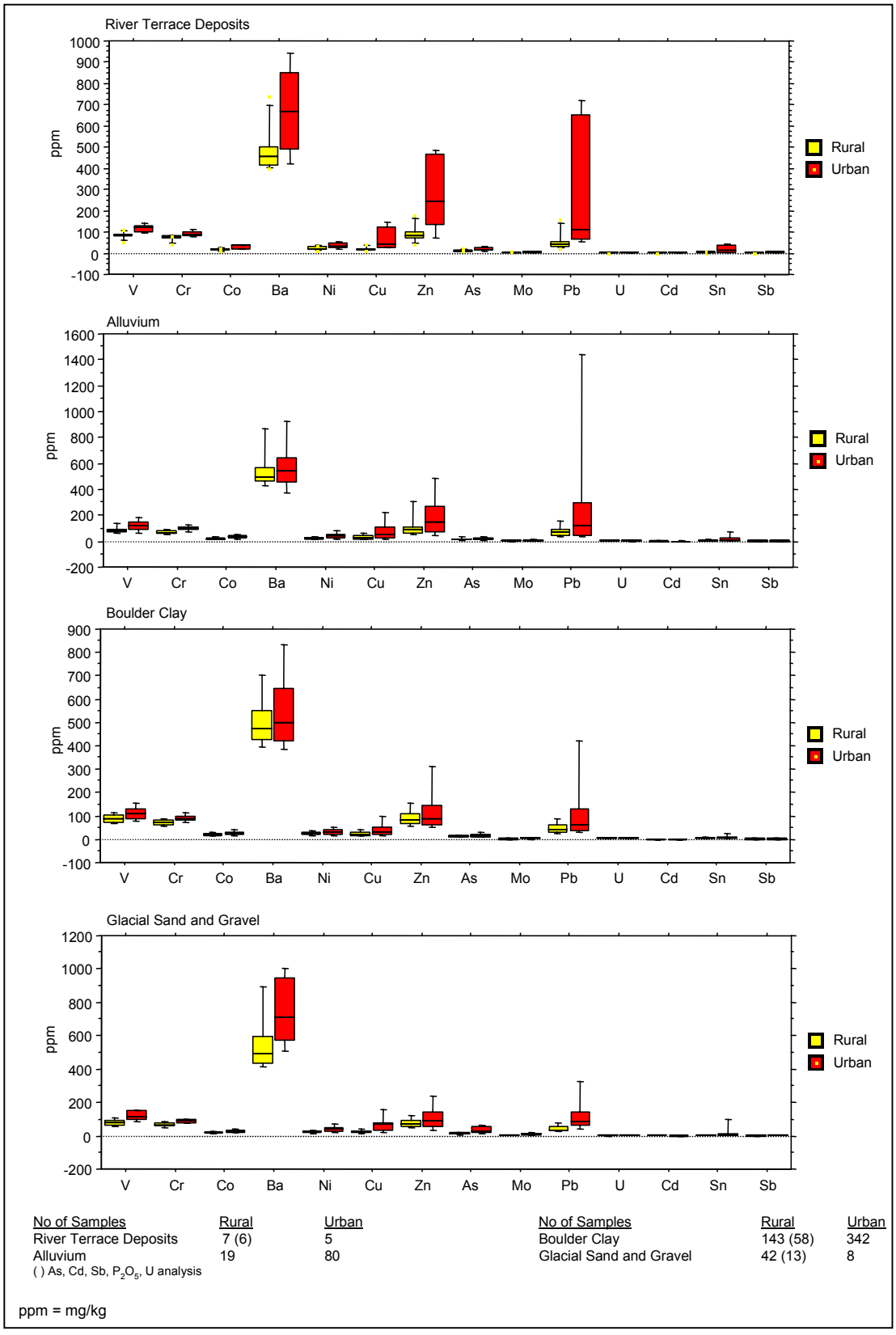


Figure 5.4 Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of trace element distributions in rural and urban profile soils from the Stoke-on-Trent area (UK NGR 372130E, 330310N – 399780E, 364600N) categorised by 1: 625 000 scale superficial deposit units.

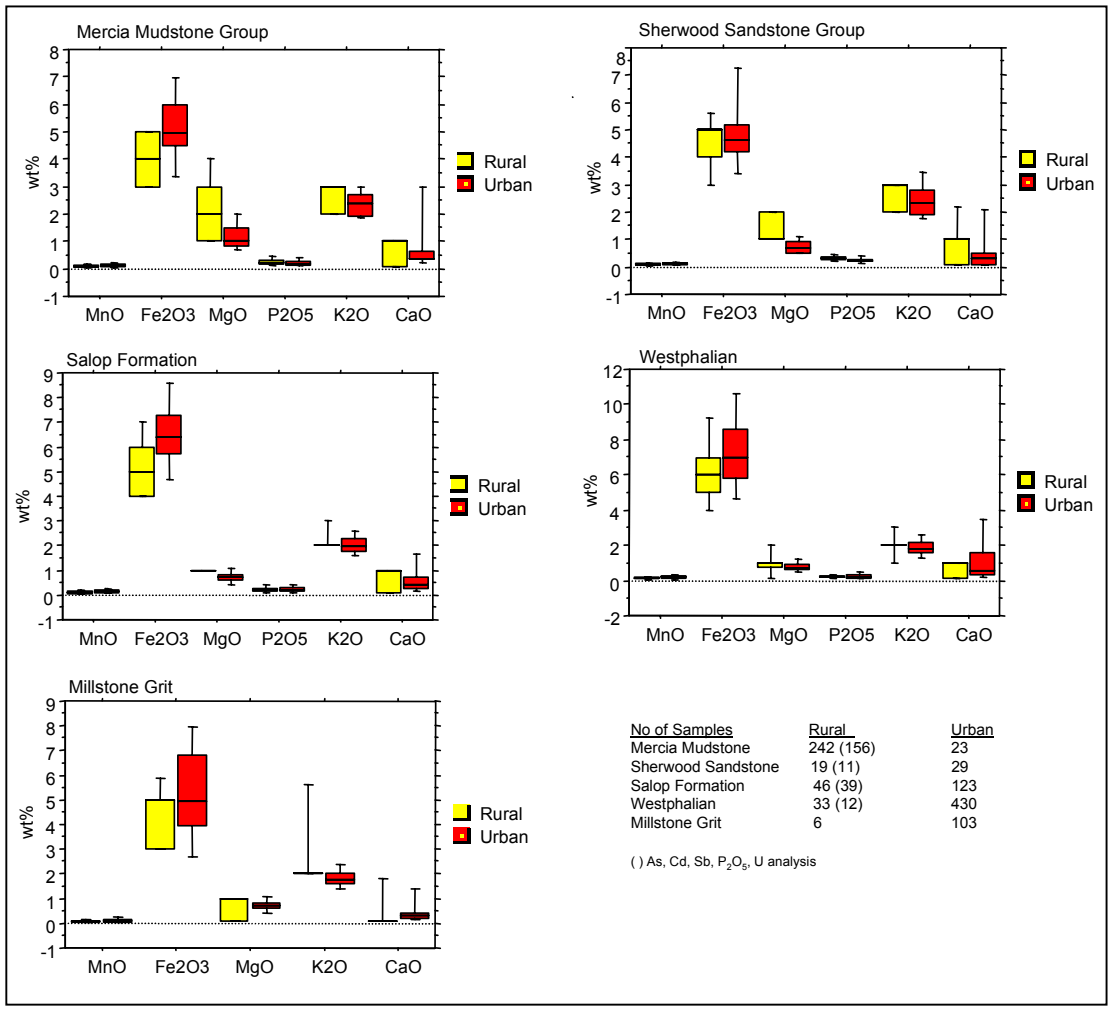
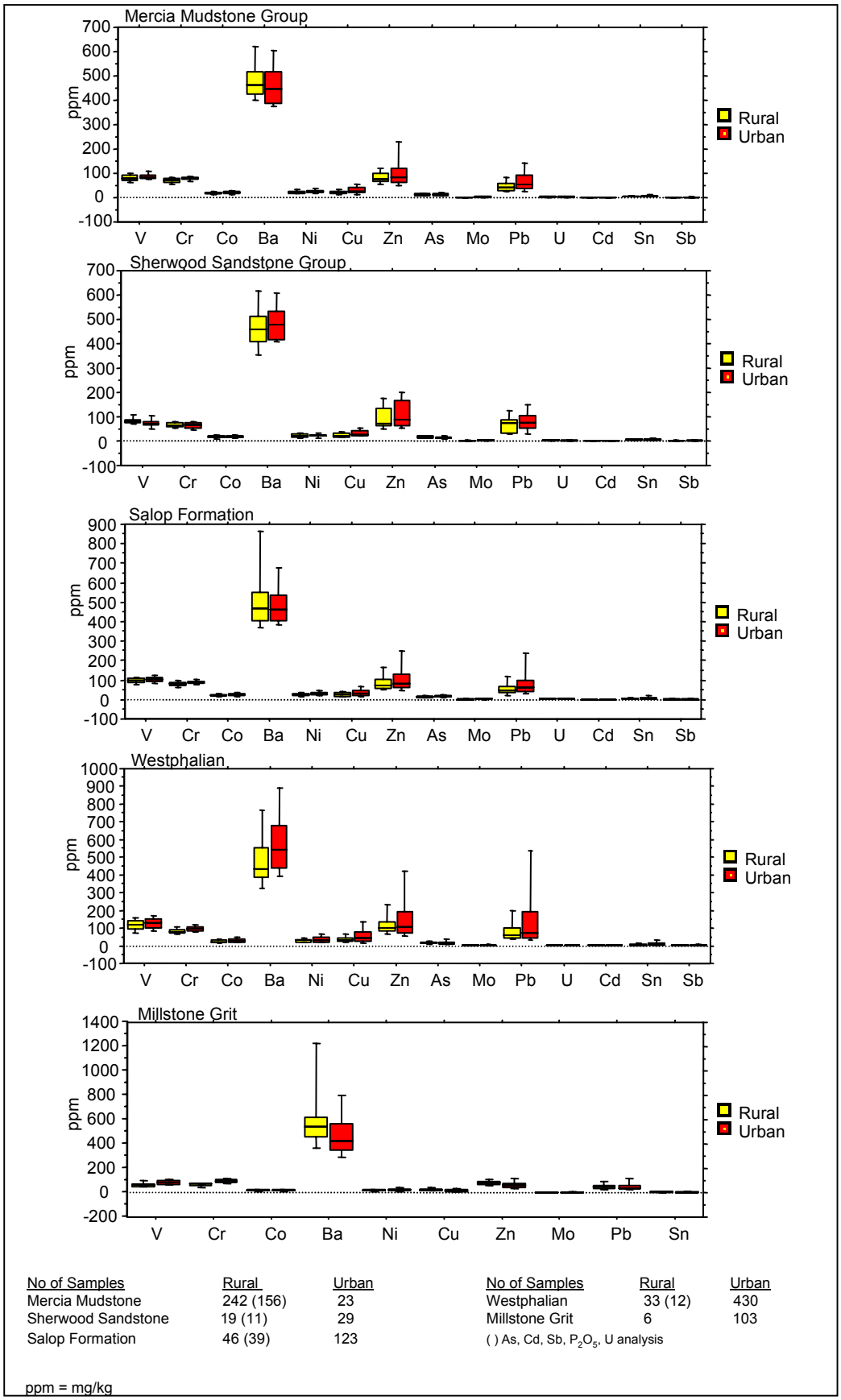


Figure 5.5 Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of major element distributions in rural and urban profile soils from the Stoke-on-Trent area (NGR 372130E, 330310N – 399780E, 364600N) categorised by 1: 250 000 scale solid geology units.



No of Samples	Rural	Urban	No of Samples	Rural	Urban
Mercia Mudstone	242 (156)	23	Westphalian	33 (12)	430
Sherwood Sandstone	19 (11)	29	Millstone Grit	6	103
Salop Formation	46 (39)	123			

( ) As, Cd, Sb, P_2O_5, U analysis

ppm = mg/kg

Figure 5.6 Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of trace element distributions in rural and urban profile soils from the Stoke-on-Trent area (NGR 372130E, 330310N – 399780E, 364600N) categorised by 1: 250 000 scale solid geology unit

6. Urban Geochemistry of Stoke-on-Trent

By E L Ander, N Breward, F M Fordyce, B G Rawlins, S E Brown and A J Ferguson

This chapter discusses some of the likely causes for variations in soil element concentrations across the study area, outlining the factors that most strongly influence the soil geochemistry.

6.1 POTENTIAL SOURCES OF CONTAMINATION IN THE URBAN ENVIRONMENT

The likely sources of contaminants in urban environments have been well documented in the literature and useful synopses are provided by Fergusson (1990); Bridge et al. (1997); Appleton (1995), Hooker et al., (2000) and Ander et al. (2001). Possible sources include building, waste disposal, transport, industrial and manufacturing activities and the use of fossil fuels. The types of contaminants commonly associated with these activities are summarised as follows.

6.1.1 Buildings, Households and Waste Disposal

Metal accumulation in household gardens is well documented and is often associated with the disposal of fossil fuel residues (ash and soot), household refuse, bonfires, fragments of Pb-containing paint and the application of phosphate fertilizers (P_2O_5 and Cd). Gardens are also affected by atmospheric contamination from the burning of fossil fuels, vehicle emissions and industrial processes. Although the majority of building materials are relatively inert, the demolition of properties, particularly older buildings may lead to contamination of soils with metals such as Pb from paint. Metal contaminants are often present in variable concentrations in domestic and industrial wastes. Over 90% of refuse in the UK is now deposited in landfill sites from which there is usually little dispersion of metals into the neighbouring environment, however, the disposal of waste materials was often undocumented and uncontrolled in the past. In addition to solid refuse, waste-waters from a host of urban activities such as food processing, laundries and breweries often contain high concentrations of metal and metalloid elements; As is present in household detergents, for example.

6.1.2 Urban Surface Run-off and Transport

Urban surface run-off waters often contain high concentrations of Pb, Zn and Cu derived from road traffic and industrial sources. Until recently, traffic fumes have also been a major source of Pb in surface soils and, for example, Kelly et al. (1996), Davies (1995) and Ward (1990) have demonstrated the effects of proximity to roads on urban soil geochemistry. Although there is evidence to suggest that Pb levels in urban environments are falling due to removal of this element from petrol, studies have shown a coincident increase in Pt concentrations as a result of usage in catalytic converters (Farago et al., 1996). Due to the fall in Pb levels, Monaci and 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. In addition to road transport, areas of railway land often contain scrap metal, oil and debris from rolling stock in the soil whereas canal sediments are commonly contaminated with spillage from cargo, motor fuel and paint.

6.1.3 Metal Smelting

Metal smelting activities can result in the contamination of land and drainage via stack and fugitive emissions, liquid effluent and the dumping and erosion of slag materials and the transport and spillage of

metal concentrates. Historically, atmospheric emissions were large but today depend on the technology employed in the plant, the composition of the raw materials and the pollution control system. Elevated levels of Ni, Cu, Zn, Cd, As, Sb Ag, Se, Hg and Pb are often recorded in the vicinity of smelters and other elements such as F, Mo, Tl, Sn, W, Au and Bi may also be enhanced in the local environment depending on the type of smelter.

6.1.4 Extraction and Combustion of Fossil Fuels

Coal mining and the waste products derived from it (ash and slag) can contain elevated concentrations of PHEs. Drainage waters from old coal mines and leachates and run-off from coal and waste piles may be extremely acid due to the oxidation of sulphides. These fluids can contain high levels of Fe, Mn, Cu, Ni and Zn and appreciable amounts of other elements such as As and Pb which can contaminate soils. Sites of disused and demolished power stations often contain soluble salts such as B, residues of coal and pulverised fuel ash (which is highly alkaline pH 11 – 12). Atmospheric contaminants associated with power stations include Cu, Zn, Ag, Cd, Sb, Se, Hg and Pb and soils around coal power stations can be enhanced in Ti, Fe, Co, Cr, Ni, Cu, Zn, Cd and Hg. Fly ash from power stations, which was often used historically to condition land, contains concentrated levels of B, Be, V, Ni, Mn, Cu, Zn, Cd, Mo, As, Se, Sb and Te and may result in soil contamination if application to soils is not regulated correctly.

6.1.5 Manufacturing Industries

Many industrial processes can give rise to contamination, as a general rule, the older the industry, the more likely it is to have produced substantial contamination of nearby soil and drainage systems. Chemical works, gas works and oil refineries give rise to a wide range of contaminants in air, soil and waters. Potential pollutants from chemical works include Cr, Cu, Zn, Cd, Sn, Hg and Pb. Agricultural-chemical and fertiliser industries may be associated with a wide range of contaminants (trace metals, metalloid elements, phosphorous and nitrogen) whilst explosive works residues may contain Cu, As, Hg and Pb. Oil refineries and the manufacture of oil- based products are potential sources of Cr, Ni, V, Co, Cu, Zn, Cd, Mo, As and Pb whereas petroleum cracking catalysts have been traced as the source of light rare-earth element anomalies. Old gas works may be contaminated with coal and coal residues, spent iron oxides, cyanides, sulphates and a range of organic compounds.

Many metals may be present in high concentrations around steelworks, foundries, electroplating and finishing works. The cleaning and etching of bare metal surfaces in metal finishing and plating processes are major sources of Cr, Ni, Cu, Zn and Cd in drainage systems. Battery manufacture may generate waste rich in Ni, Cd, Zn, Sb, Hg and Pb. The processing of scrap metals results in site contamination with metal and metalloid elements in addition to organic substances. Waste-waters derived from paint and dye-stuff producers often contain elevated levels of Cr, Cu, Cd, Se, Hg and Pb from the pigments and raw materials of these industries. Electrical and electronic industry waste can contain Cd, Zn, Se, Cu and Pb whereas Zn, Sn, Pb and Cd are used in the manufacture of synthetic rubber and plastics as stabilisers and pigments. The leather and textile industries use chromates and dichromates to condition cloth, which can be sources of Cr enhancement in drainage systems. Finally the glass and ceramic industries use Cr, Pb, Co, Se, Cu, Mo, Ti and Fe among other elements as pigments, glazes and conditioning agents.

In summary, an extensive array of activities in urban environments forms potential sources of contamination. Under current UK legislation, establishing contaminant sources is of major importance to the ‘polluter pays’ principle of remediation. The following sections describe the geochemistry of soils from Stoke-on-Trent in terms of likely natural and man-made controls on the element distributions.

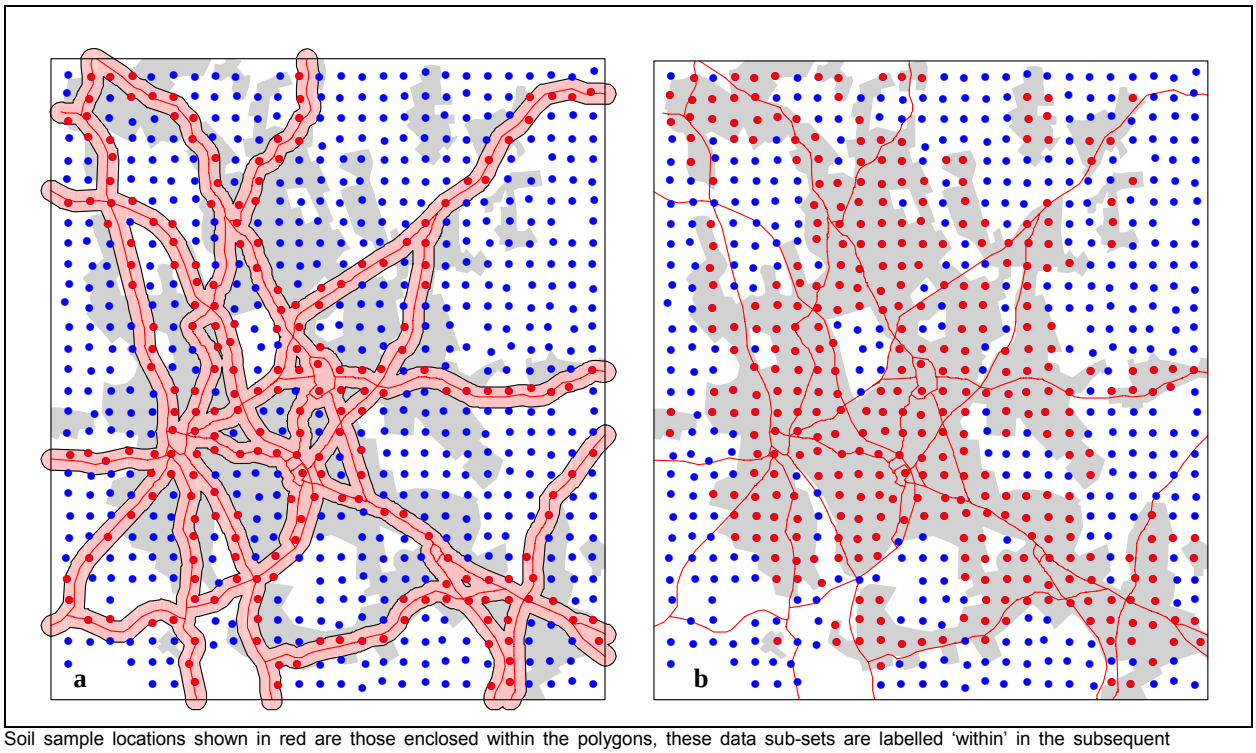
6.2 URBAN SOIL DATA IN RELATION TO PARENT MATERIAL AND LAND USE

Chapter 5 of this report outlined the general relationships between the urban and surrounding rural G-BASE soil datasets for Stoke-on-Trent. In this chapter, the urban dataset alone is considered more closely. The chemical compositions of surface and profile soils in the urban area of Stoke-on-Trent are shown in the proportional symbol maps presented in Annex 1. In addition to descriptions of these maps, and consideration of the dataset as a whole, the following sections of this chapter describe the relationships between various

sub-sets of the data and likely controls on soil chemistry. As indicated in Chapter 5, the data interpretation is significantly enhanced by the ready ability using GIS technology to select and classify soils in terms of spatial parameters that may influence the composition at a given location such as the underlying geology or land use. The GIS spatial query function was used to examine relationships between the soil geochemistry and parent material, the built environment and transport networks as follows.

Parent material (whether natural or man-made) exerts a fundamental control on soil geochemistry and the soils were first categorised by superimposing the extent of made ground (Figure 2.10), Quaternary drift cover (Figure 2.9) and solid geology (Figure 2.8) over the geochemical data in the GIS. Where a soil sample location intersected a made-ground polygon, this was taken as the soil parent material. In the absence of made ground, and intersection with a drift polygon, the drift type was selected as the soil parent material. Where neither made ground or drift polygons were intersected, the solid geology was taken as the soil parent material. However, it should be noted that this approach relies upon the accuracy of the made ground and drift deposit maps.

In addition to the presence of made-ground, the influence of human activity and land use on the soil geochemistry was examined further by consideration of the extent of urbanisation and location of transport networks. As indicated in Chapter 5, the urban soils were collected from within and outside the built environment of Stoke-on-Trent and differences between the strictly 'urban' and non-built environments were examined by superimposing the map of the urban areas over the soil data points and categorising each point according to whether it intersected the urban polygons or lay outside them. An example of this type of spatial query is shown in Figure 6.1.



Soil sample locations shown in red are those enclosed within the polygons, these data sub-sets are labelled 'within' in the subsequent statistical analyses. Sample locations shown in blue are outside the polygons and these data sub-sets are labelled 'outside' in the subsequent statistical analyses

Figure 6.1 Examples of the GIS spatial query function to select soil sample locations within a) a 250 m buffer zone around roads b) the urban built-up area polygons.

Road and rail networks are another possible source of contamination in the urban environment that may influence soil geochemistry. This is not only in terms of the ground disturbance caused by construction of these routes but also includes the transport of potentially contaminating materials, vehicle emissions and the tendency for these networks to act as vectors along which much industrial development does, and would historically, have occurred. Soils located in close proximity to the road and rail networks were examined to

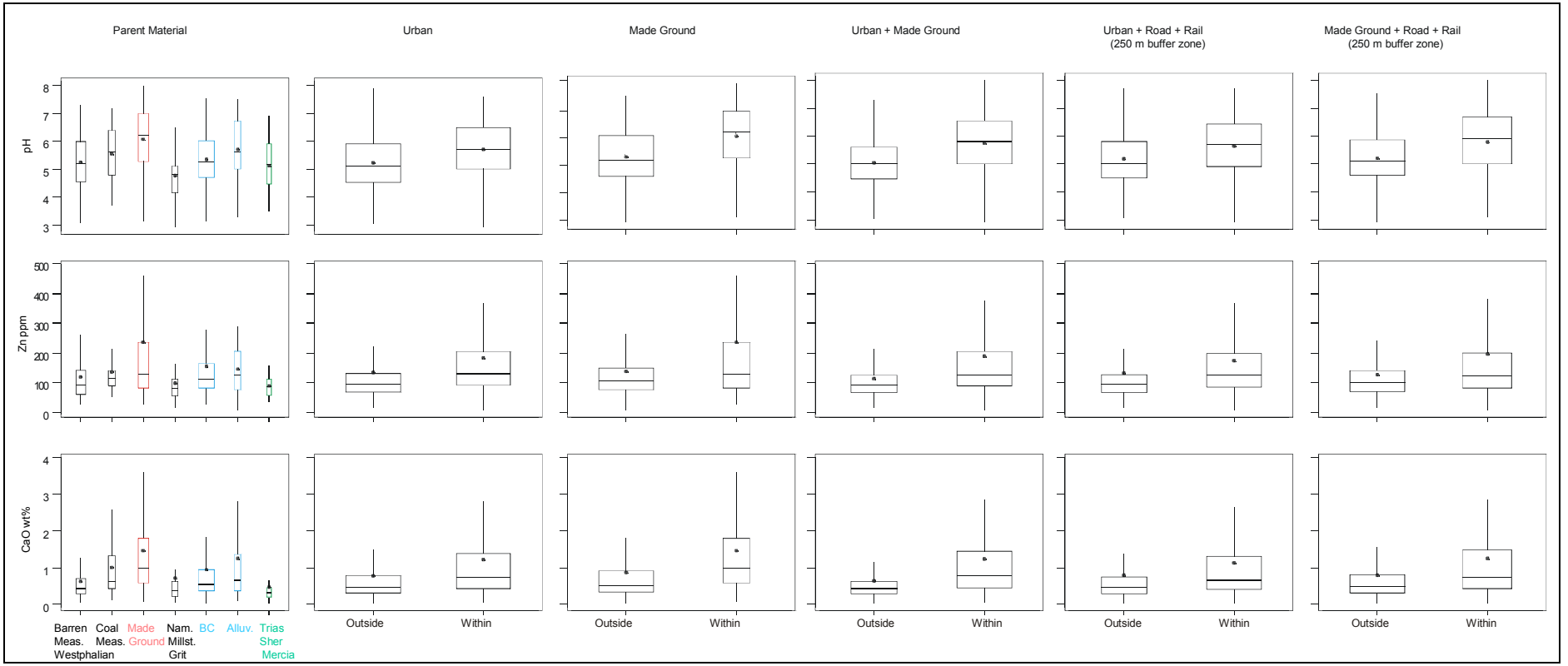
assess whether or not a geochemical signature related to transport pollution could be identified. Using the spatial query function of the GIS, buffer zones of 250 m were established around roads and railways and the soils labelled as to whether they occurred within or outside these zones. An example of this type of buffer zone query is shown in Figure 6.1.

For the purposes of this study, the presence of the urban built up and made ground polygons were taken as indicators of the intensity of human activity and soil samples categorised as occurring within these polygons were studied separately and in combination using an "AND" logic operation in the GIS. The transport route buffer zones were combined with made ground or urban polygons in a logical "AND" operation to assess whether element concentrations in these soils were different from those in the urban or made ground areas.

Once categorised according to spatial features in the GIS, the soil geochemistry was readily presented for interpretation as box and whisker plots (see for example Figure 6.2) and summary tables.

The results of the spatial queries indicate that there are markedly higher element concentrations in soils located in urban and made-ground versus non-built environments but element levels are not further enhanced by proximity to the transport networks (see for example Figure 6.2). Therefore, the urban geochemistry is considered further in this chapter in terms of soil parent material and location within or outside the urban built environment only.

The lack of overt geochemical enhancement of any of the trace elements associated with traffic Pb, Zn and Ba compared to the general urban environmental signature is interesting. Undoubtedly traffic fumes do contribute to the metal loading of urban soils in Stoke-on-Trent as in many other cities. As indicated later in this chapter traffic may contribute to the higher levels of Pb in surface than profile soils in the area but the geochemical signature is not distinct because of the many other sources of these elements in the urban environment of Stoke, a city with such a long history of industrial development and naturally enhanced concentrations of elements such as Ba in the local bedrock.



Parent Materials

BC =	Boulder Clay and Glacial Drift
Alluv. =	Alluvium
Trias. Sher Mercia =	Triassic Age Sherwood Sandstone and Mercia Mudstone
Barren Meas. =	Westphalian Age Barren Measures
Coal Meas. =	Westphalian Age Coal Measures
Nam. Millst. Grit =	Namurian Age Millstone Grit

Land Use

Urban = location of soils within our outside the urban built up area
Made Ground = location of soils within or outside areas of made ground
Road + Rail = location of soils within or outside 250 m of the road and rail network

ppm = mg/kg

Figure 6.2 Box and whisker plots of the 5th, 25th, 50th, 75th and 95th percentiles of pH, Zn and Ca distributions in urban surface soils from the Stoke-on-Trent urban area (UK NGR 382000E, 340000N – 395000E, 355000N) categorised using the GIS spatial query function in terms of location relative to natural and man-made influences on soil geochemistry.

6.3 SURFACE SOIL GEOCHEMISTRY

6.3.1 Contextual Data – Soil pH, Organic Matter and Texture

Soil pH, organic matter content and texture exert fundamental controls on soil processes affecting the distribution and mobility of many chemical elements. The organic matter content is a key factor determining the available exchange sites in a soil (Sposito, 1989), and soil texture influences the ability of the soil to trap and retain certain elements in the soil structure. Therefore, clay and organic-rich soils generally contain higher concentrations of metal and metalloid elements than sandy or organic-poor soils (see section 6.4). Soil pH controls the potential mobility and bioaccessibility of mineral phases and soil solution ions (McBride 1994 and Sposito 1989) and can range from acid (< 5.5) to neutral (6 – 7.5) through to alkaline (> 7.5). Many metal and metalloid elements (for example, As, Cu, Cr, Ni, Pb, Zn, Hg) are more mobile in acid than in alkaline soils. Hence, information on these important physio-chemical soil parameters aids the understanding and interpretation of the soil geochemistry.

The proportional symbol map (Annex 1) shows the distribution of surface soil pH values across the study area and the box and whisker plots (Figure 6.3) show pH categorised by parent material and urban-built versus non-built land use. The majority (70%) of the pH values in surface soils are in the range 4.7 (25^{th} percentile) to 7.2 (95^{th} percentile) (mean 5.5, median 5.4 respectively) and pH values rarely exceed 7 across the urban area. The lower pH values are associated with the Namurian Millstone Grit arenaceous (quartz-rich) facies occurring to the north and east of Stoke-on-Trent, which is low in base (alkali) cations. The proportional symbol map (Annex 1) shows that the majority of values above pH 7 are associated with the urban/industrial area of the central Stoke valley, an observation confirmed by the higher mean and median pH values for soils developed over made ground or those occurring within, rather than outside, the urban built-up area (Figure 6.3). The probable cause of these higher pH values in the built-area soils is the disposal of alkali-rich waste from historically important industrial processes such as coal mining, steel and pottery manufacture. Weathering of these waste products releases base cations to the surface environment maintaining higher pH conditions. Without these industrial inputs, it is likely that soils developed in the central Stoke valley would be weakly acid in nature as they are largely formed on glacial and alluvial deposits. Although these types of deposits are commonly of low pH, in the Stoke area they overlie Westphalian Coal Measures, rocks that are relatively base-rich. The presence of the Coal Measures is likely to account for the circum-neutral pH (6-7) values observed in soils over much of the area (Annex 1). From the contaminated land perspective, this is of benefit as it means that PHEs such as As, Cu, Cr, Hg, Ni, Pb and Zn will be less mobile in these soils than under more acid conditions (see Chapter 7 of this report).

Surface soil organic matter content (as shown by % LOI) varies little across the urban study area, with a small inter-quartile range from 9.2% (25^{th} percentile) to 14.7% (75^{th} percentile) (Figure 6.3) and lack of systematic spatial variation (proportional symbol map, Annex 1). Figure 6.3 shows that only the soils collected over the Westphalian Barren Measures and Triassic Sherwood Sandstone/Mercia Mudstone parent materials have lower median and mean values than the other parent materials. The lack of distinction in organic matter content between samples collected in the built-up/made ground versus non-built environments may indicate the widespread dispersion of organic-rich soil clasts derived naturally from the Coal Measures and anthropogenically from coal spoil across the region. These are likely to be less abundant in soils formed over the non coal-bearing Triassic and Barren Measure lithologies. Spearman Rank correlation results indicate that none of the metal/metalloid elements show strong correlations with pH in surface soils but As, Mo and V strongly correlate (> 0.500) with organic matter content (LOI), which may also reflect the influence of coal bearing strata on soil chemistry (Table 6.1).

Soil texture and soil colour were recorded at the time of sampling. However, it should be noted that the GSUE sampling teams have only limited training in the acquisition of these data and a basic colour coding scheme (Table 6.2) is adopted compared to the more complex Munsell Colour Chart classifications used by the Soil Survey of England and Wales. Similarly, a simplified soil texture classification scheme is used (Figure 6.4 and Table 6.3) compared to those adopted by the Soil Survey (Figure 6.5). Therefore, it is unlikely that the data will be suitable for purely quantitative work. Despite the simplified recording scheme, confidence in the use of this information is demonstrated by the relationships between soil texture and parent material type over Stoke-on-Trent, which follow expected trends (Figure 6.6). For example, the greatest proportion of clay and silty-clay soil texture classifications occur over argillaceous (clay-rich) lithologies.

These data are used in the qualitative assessment of the potential leaching of soil contaminants to groundwater (Chapter 7), and will not be described further here.

As outlined at the start of this section, sandy soils containing a high proportion of quartz grains tend to have lower metal/metalloid element contents than clay-rich soils. In addition to a physical description of the soil texture, the soil chemistry can be taken as a broad guide to the textural composition using silicon as an indicator of quartz (SiO_2) content and aluminium as an estimate of the clay fraction (alumino-silicates). In Stoke-on-Trent surface soils, Spearman Rank correlation coefficient results show that the majority of metal and metalloid elements are significantly (95% confidence level) correlated with each other. These elements are negatively (95% confidence level) correlated with SiO_2 but show strong correlations with Al_2O_3. Surface soils are sieved to < 2mm and are likely to contain a significant proportion of quartz grains as well as finer clay minerals. The correlation of the metal and metalloid elements with Al_2O_3 indicates that, as would be expected, they are associated with the finer clay fraction of the soils rather than the coarser quartz-dominated fraction. Relationships between soil texture and composition are examined in more detail in section 6.4.

TABLE 6.1 SPEARMAN RANK MATRIX OF SIGNIFICANT (95% CONFIDENCE LEVEL) CORRELATIONS BETWEEN ELEMENT CONCENTRATIONS IN STOKE-ON-TRENT SURFACE SOILS

	MNO	FE2O3	V	CR	CO	BA	NI	CU	ZN	AS	MO	PB	U	CD	SN	SB	MGO	AL2O3	SIO2	P2O5	K2O	CAO	LOI
MNO																							
FE2O3	0.76																						
V	0.65	0.86																					
CR	0.44	0.66	0.79																				
CO	0.79	0.88	0.85	0.65																			
BA	0.49	0.60	0.55	0.42	0.64																		
NI	0.66	0.81	0.79	0.63	0.88	0.74																	
CU	0.54	0.67	0.61	0.47	0.70	0.69	0.80																
ZN	0.61	0.64	0.53	0.44	0.69	0.67	0.73	0.77															
AS	0.49	0.72	0.64	0.49	0.63	0.52	0.60	0.63	0.61														
MO	0.61	0.77	0.65	0.55	0.72	0.64	0.74	0.78	0.72	0.78													
PB	0.34	0.42	0.29	0.22	0.43	0.52	0.46	0.68	0.75	0.58	0.65												
U	0.42	0.54	0.66	0.61	0.51	0.33	0.47	0.23	0.24	0.36	0.35												
CD						0.09		0.14	0.22	0.09	0.08	0.27	-0.11										
SN	0.32	0.41	0.30	0.27	0.40	0.44	0.45	0.66	0.70	0.58	0.62	0.82		0.22									
SB	0.09	0.13	0.06	0.06	0.14	0.27	0.20	0.41	0.43	0.35	0.38	0.60	-0.16	0.21	0.59								
MGO	0.22	0.24	0.30	0.29	0.31	0.36	0.48	0.29	0.31	0.10	0.19	0.07	0.27		0.09								
AL2O3	0.50	0.68	0.85	0.71	0.68	0.40	0.63	0.36	0.30	0.40	0.38		0.68	-0.09	0.08	-0.15	0.33						
SIO2	-0.60	-0.79	-0.81	-0.70	-0.77	-0.66	-0.79	-0.69	-0.65	-0.67	-0.74	-0.47	-0.48		-0.44	-0.24	-0.31	-0.64					
P2O5	0.29	0.21	0.09	0.13	0.22	0.24	0.19	0.41	0.56	0.40	0.45	0.62	-0.10	0.20	0.58	0.43	-0.08	-0.09	-0.29				
K2O			0.06		0.08	0.27	0.22	0.08		-0.07	-0.06	-0.16	0.10		-0.12		0.55	0.23	-0.09	-0.24			
CAO	0.38	0.31	0.32	0.26	0.40	0.53	0.54	0.57	0.62	0.25	0.47	0.45	0.15	0.18	0.39	0.26	0.40	0.13	-0.50	0.35	0.11		
LOI	0.26	0.46	0.51	0.49	0.43	0.37	0.37	0.40	0.46	0.65	0.55	0.49	0.28	0.15	0.48	0.32		0.31	-0.66	0.43	-0.23	0.22	
pH	0.28	0.14	0.14	0.09	0.25	0.34	0.39	0.34	0.35		0.18	0.12	0.08	0.08	0.09		0.42	0.07	-0.23		0.24	0.82	

n = 750, r95% = 0.06 (Koch and Link, 1970)

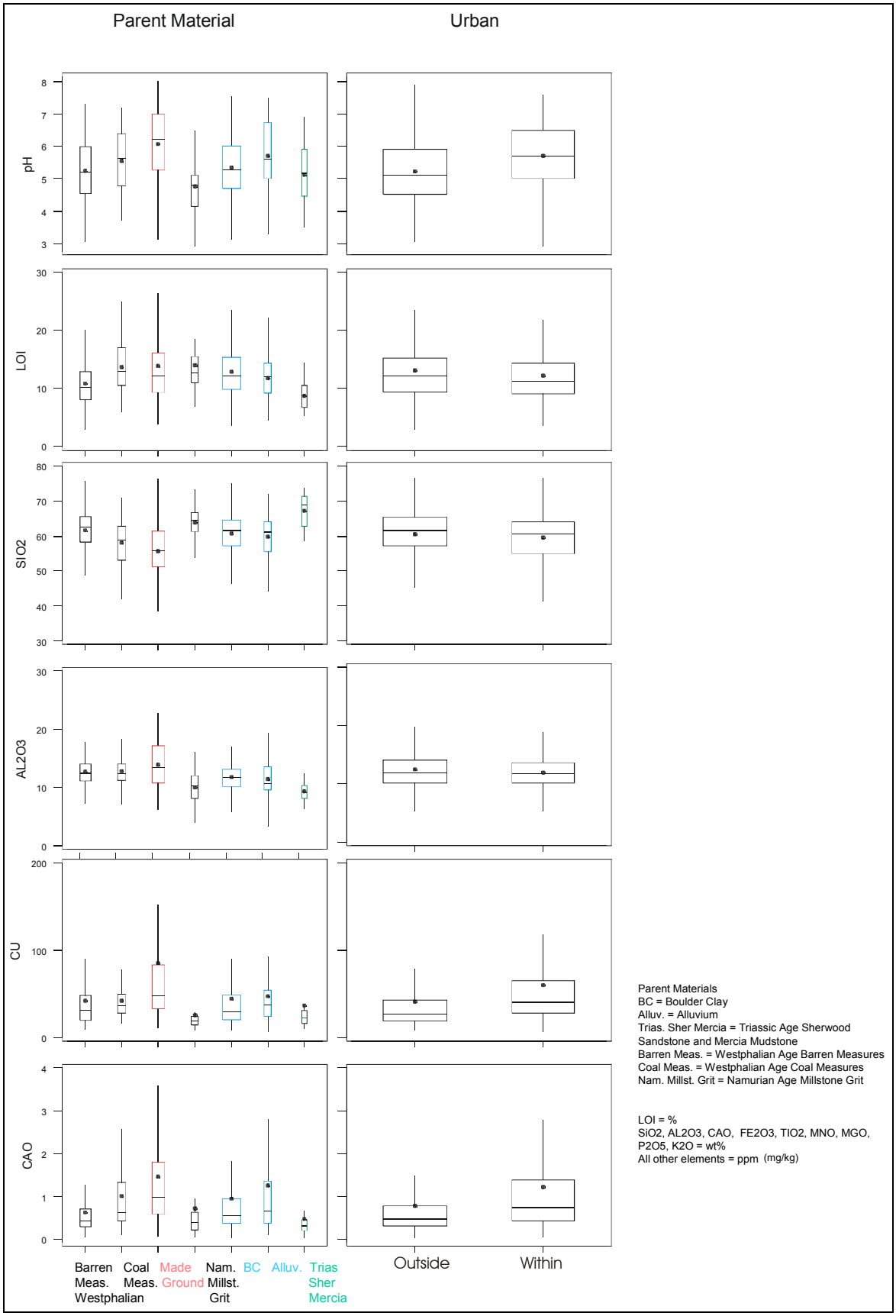


Figure 6.3 Box and whisker plots of the 5th, 25th, 50th, 75th and 95th percentiles of element distributions in Stoke-on-Trent urban surface soils categorised according to parent material and location within or outside the urban built environment.

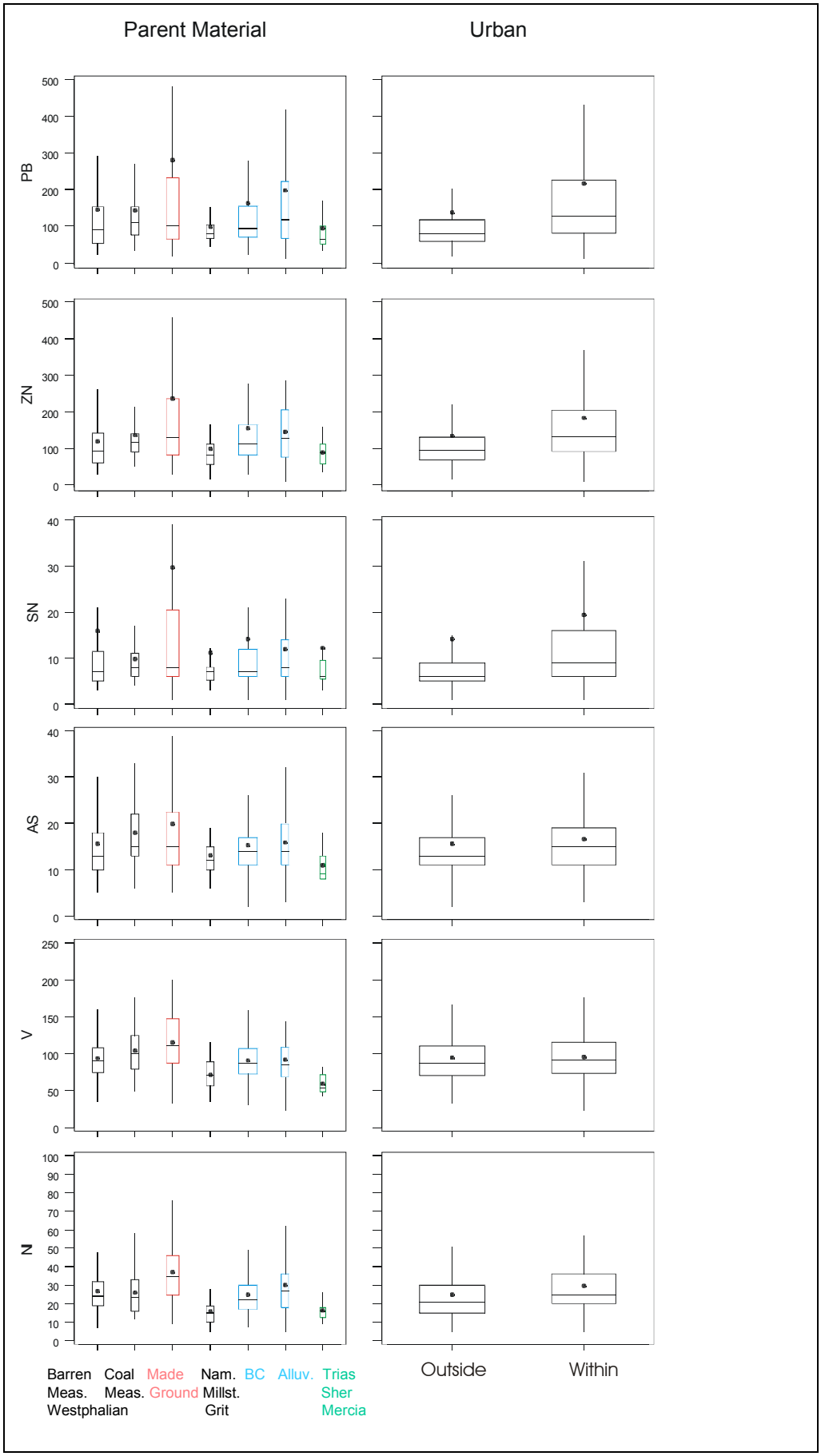
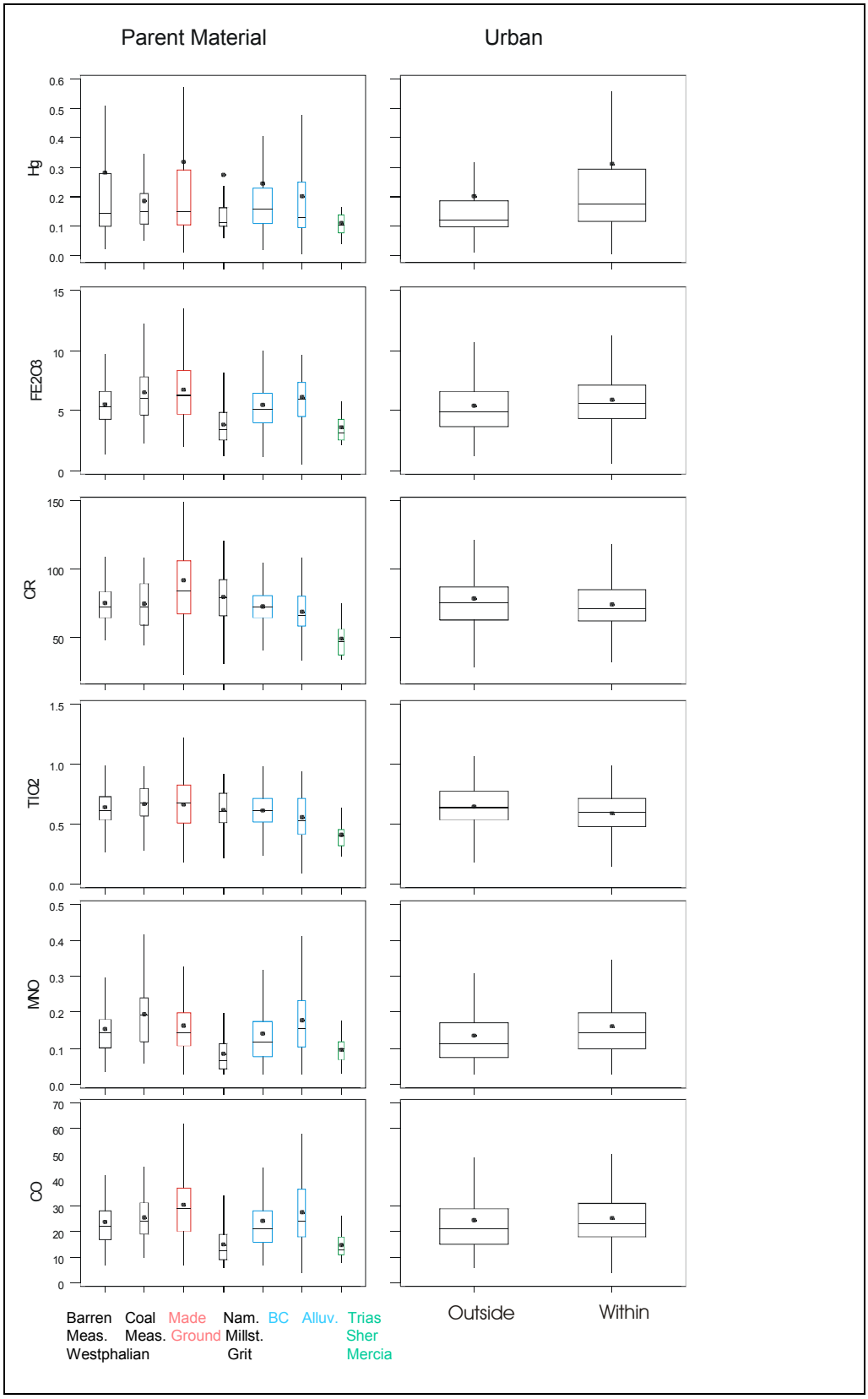


Figure 6.3 cont.



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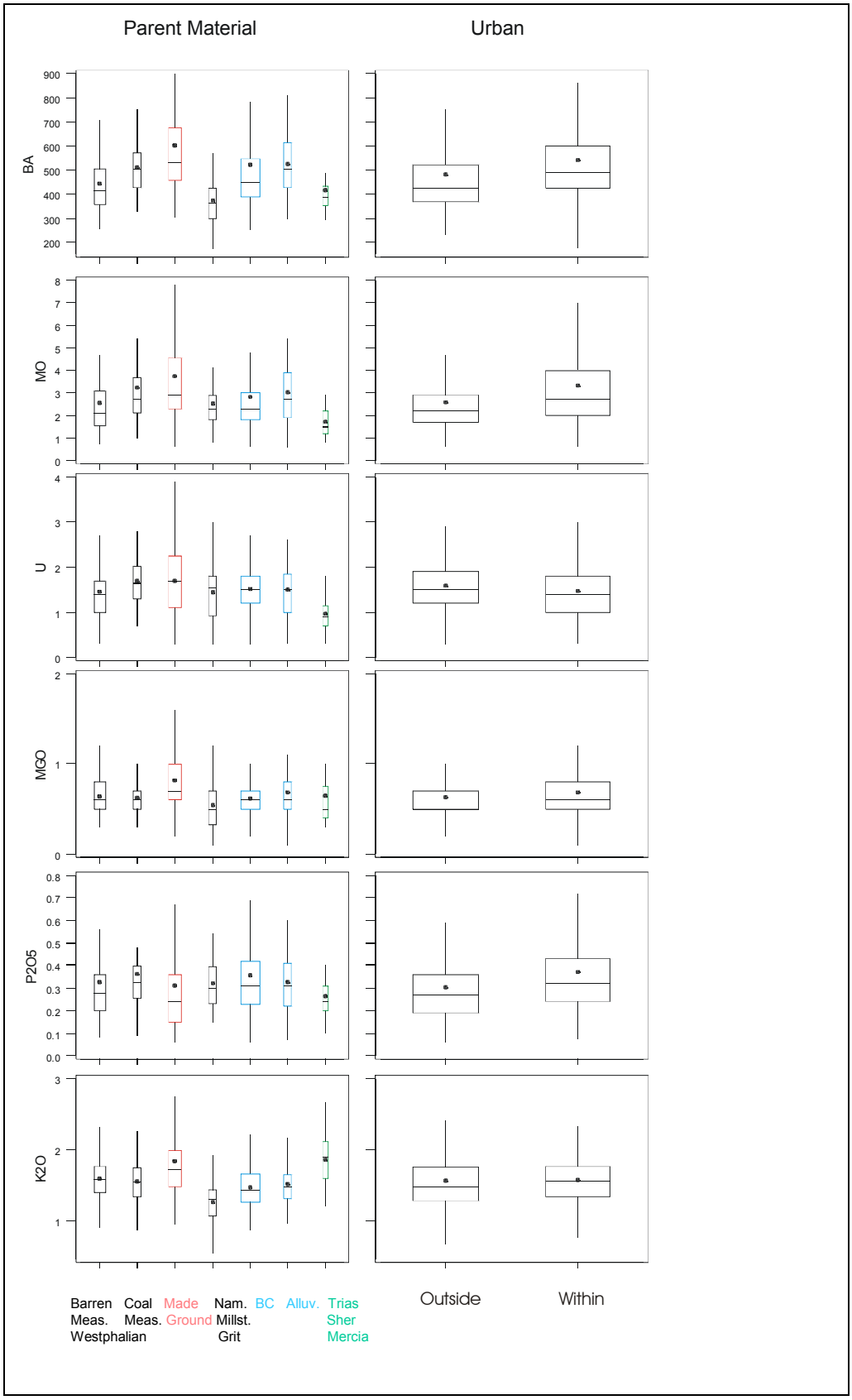


Figure 6.3 cont.

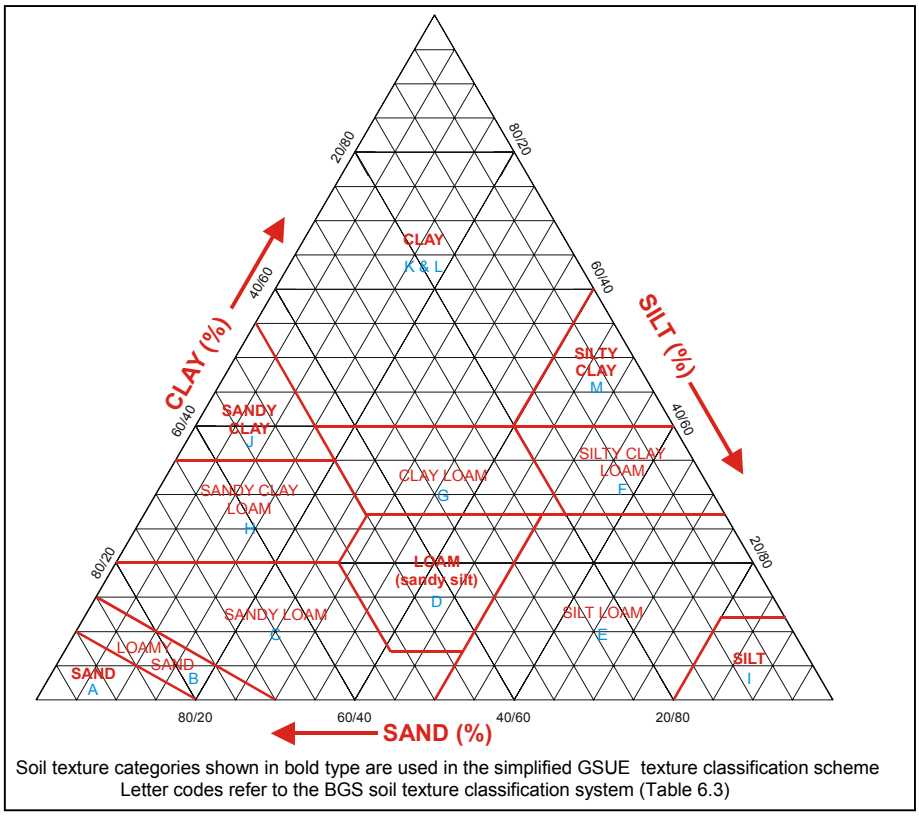


Figure 6.4 Soil texture diagram showing the categories used in the BGS and GSUE classifications

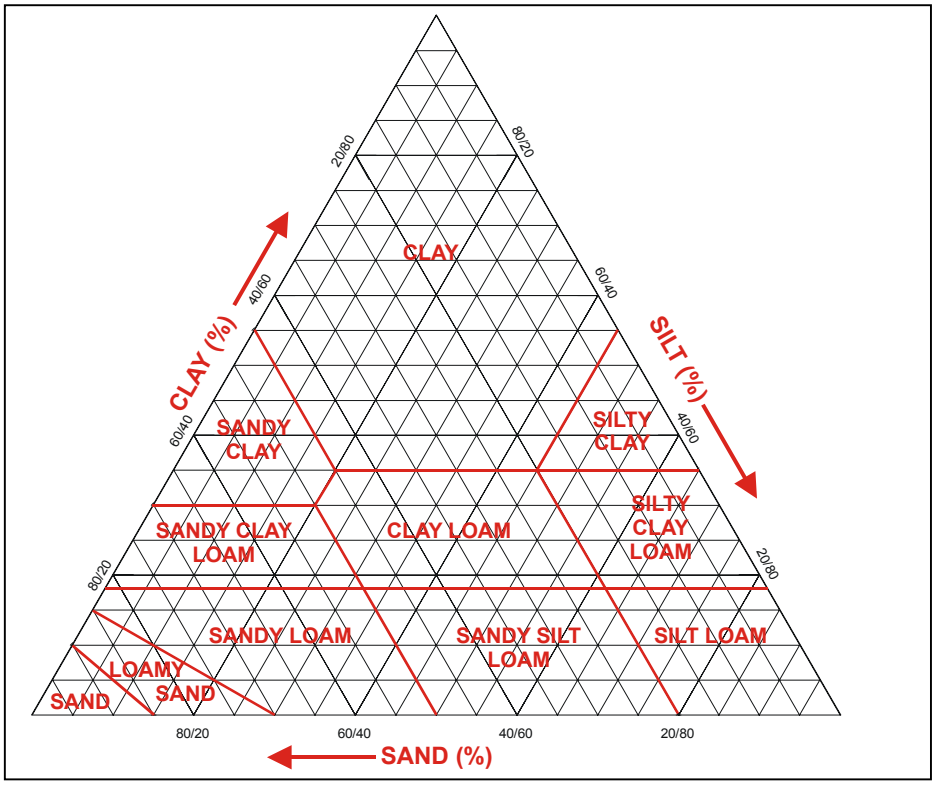


Figure 6.5 Soil texture diagram showing the categories used in the Soil Survey of England and Wales classification (Soil Survey of England and Wales, 1976).

TABLE 6.2 THE GSUE SIMPLIFIED SOIL COLOUR CLASSIFICATION SCHEME

Field Code	Colour
BL	Black
DB	Dark brown
LB	Light brown
RE	Red
OR	Orange
YE	Yellow
GR	Green
GY	Grey

TABLE 6.3 SOIL TEXTURE CLASSIFICATIONS USED IN THE BGS

Soil Texture Class	BGS Texture Code (Harris et al., 1993)*	GSUE Field Code
Sand	A	SAND
Loamy Sand	B	-
Sandy Loam	C	-
Loam (Sandy Silt)	D	SASI
Silt Loam	E	-
Silty Clay Loam	F	-
Clay Loam	G	-
Sandy Clay Loam	H	-
Silt	I	SILT
Sandy Clay	J	SACL
Clay	K & L	CLAY
Silty Clay	M	SICL

* The compositional definitions of these texture codes are shown on Figure 6.4

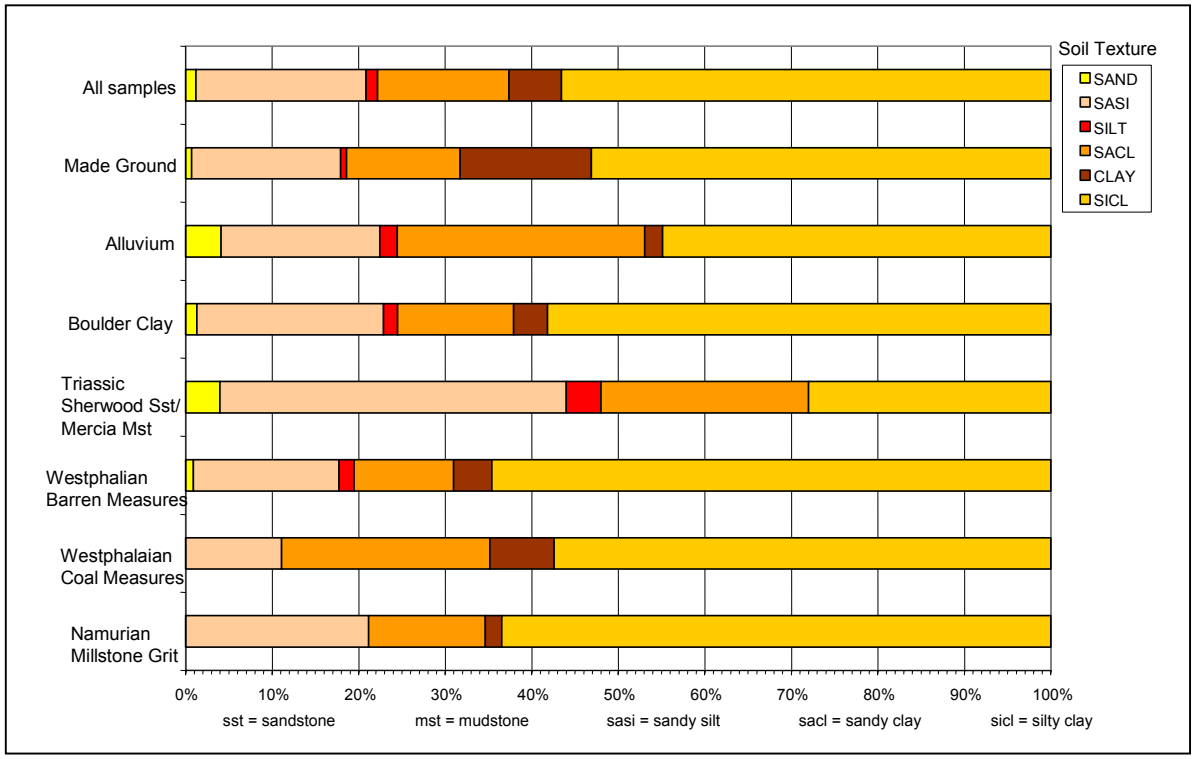


Figure 6.6 Distribution of soil texture classes recorded in Stoke-on-Trent urban surface soils across different parent materials

6.3.2 Element Distributions in Surface Soils

Silicon (SiO_2) concentrations in surface soils are generally lower in the central built-up area of Stoke-on-Trent and higher over the predominantly arenaceous (quartz-rich) lithologies of the Namurian Millstone Grit sediments and Triassic Sherwood Sandstone Group of the urban periphery. The lower concentrations in areas underlain by the Westphalian Coal and Barren Measures are likely to result from the more argillaceous (clay-rich) composition of these parent materials, the presence of boulder clay over large parts of the central Stoke valley (Figure 2.9) and dilution of the natural soil composition by physical contaminants, such as pottery and steel works waste. Box and whisker plots of the soil geochemistry categorised by location within or outside the built-up urban and made ground areas and by soil parent material show that the soils most affected by human activity have lowest SiO_2 concentrations. Those developed directly over solid or drift strata or in sparsely populated areas have the highest SiO_2 concentration (Figure 6.3).

Aluminium (Al_2O_3) and **potassium** (K_2O) concentrations in surface soils also suggest a strong lithological control, however, the spatial distributions of these elements are the opposite to those of SiO_2, namely higher over the central Stoke area and lower over the Namurian Millstone Grit facies on the urban periphery (Annex 1 and Figure 6.3). This is to be expected as the Millstone Grit sediments are clean coarse quartz arenites, which weather to form relatively sandy soils with low alumino-silicate (clay mineral) contents. Al_2O_3 and K_2O soil contents are greater over the more clay rich sediments of the Westphalian and boulder clay deposits underlying central Stoke and are relatively elevated over made ground (Figure 6.3). Highest concentrations of soil Al_2O_3 and K_2O in areas underlain by made ground are associated with colliery spoil.

Magnesium (MgO) surface soil concentrations are generally lower in the urban area than in the surrounding environment (see Chapter 5). However, lithology still exerts a fundamental control on MgO distribution within the urban dataset. Soils developed over the Mercia Mudstone Group (Figure 2.8) have higher MgO contents than the Sherwood Sandstone Group, reflecting differences in bedrock MgO composition (Figure 6.3). Soils developed over glacial boulder clay and morainic drift deposits derived from the nearby Mercia Mudstone outcrop of the Cheshire Basin in the north west of the study area are similarly higher in MgO than surrounding soils (Annex 1). Highest MgO concentrations in soils occurring in the urban-built and made ground environments are related to colliery, furnace and other industrial wastes.

Calcium (CaO) concentrations are highest in soils developed over the central urban area reflecting naturally high concentrations in limestones and calcareous sandstones of the Westphalian Coal and Barren Measures. However, CaO concentrations in the urban environment are also influenced by the presence of alkali-rich waste products from the steel works and ceramics industries as demonstrated by the high values for soils developed over made ground (Annex 1 and Figure 6.3). This observation is corroborated by Spearman Rank results, which show that CaO is strongly correlated with many of the metal elements in surface soils an element association that may indicate the dumping of calcareous material in metal foundry waste (Table 6.1).

Iron (Fe_2O_3) concentrations show some relationship with the solid geology being lowest over the quartz-rich Millstone Grit and Sherwood Sandstone lithologies as expected (Figure 6.3). However, soil Fe_2O_3 contents are largely controlled by past industrial activity and are elevated in the urban-built/ made ground environment compared to the surrounding urban periphery (Appendix 1 and Figure 6.3). The industrial processes likely to have contributed Fe_2O_3 to the urban environment include coal and iron mining and steel works with associated waste.

Phosphorous (P_2O_5) is also used in the steel making process and in pottery production, which may account for the higher values in the central urban area of Stoke (Appendix 1) and in soils developed in the urban-built rather than surrounding urban periphery environment (Figure 6.3).

Manganese (MnO) concentrations are lowest over the quartz-rich sediments of the Millstone Grit and Sherwood Sandstone lithologies (Figure 6.3) demonstrating some relationship with underlying geology. However, areas of enhanced concentrations in the urban area are associated with shallow coal and clay workings in the Goldenhill (UK NGR 385E, 352N) to Standfield (UK NGR 387E, 351N) area; coal spoil in the Silverdale (UK NGR 382E, 346N) area and general industrial activity coincident with alluvial deposits in Sideway (UK NGR 387E 342N).

Barium (Ba) concentrations are generally lowest in soils developed over the quartz-rich facies of the Millstone Grit and Sherwood Sandstone (Figure 6.3 and Annex 1). Soils over the Coal Measures have a

higher range of concentrations than those over the Barren Measures, which is consistent with differences in bedrock chemistry. Anomalously high concentrations in the Werrington-Baddeley Edge district (UK NGR 392E, 348N) are probably due to barite ($BaSO_4$) cementation in a thick Lower Coal Measures sandstone unit. Barite mineralisation may also be a geologically plausible explanation for elevated soil Ba contents in the Trentham Golf Course area (UK NGR 385E, 341N) as these are proximal to the Apedale Fault. Highest concentrations of Ba in surface soil occur over made ground, for which no definitive source can be identified.

Zinc (Zn) concentrations are not markedly elevated in the urban-built environment (median 130 ppm (mg/kg)) compared to the non-built environment (median 108 ppm (mg/kg)) (Figure 6.3 and Annex 1). However, sporadic high values indicative of contamination occur over made ground, which raise the mean of the geochemical distribution close to the 75th percentile of the dataset (Figure 6.3) and demonstrate the strong influence of anthropogenic activities on Zn dispersion in soils.

Tin (Sn) concentrations in most natural soils are low and this is reflected in the median concentrations shown in Figure 6.3 for most of the parent material types in the Stoke area. However, isolated high concentrations due to contamination have the effect of skewing the data distribution so that the mean values are higher than the median for all parent material types (Figure 6.3). The effect is most noticeable over made ground where the mean value is approximately 4 times higher than the median and 1.5 times the 75th percentile (Figure 6.3). The effects of anthropogenic tin contamination tend to remain very localised as the element is poorly mobile in the soil environment and not readily chemically dispersed.

Lead (Pb) may be naturally elevated in soils developed over the Coal Measures compared to other parent materials due to the presence of galena (PbS) mineralisation (non-economic) in the area. However, Pb soil concentrations are strongly influenced by anthropogenic activity and are elevated in the urban and made ground areas relative to the urban periphery (Annex 1 and Figure 6.3). As with Sn, the high mean relative to median values for soils developed over all parent types are indicative of the presence of anomalously high values caused by contamination. Pb levels in soils developed over alluvium are relatively high compared to other parent materials probably reflecting the fact that river systems act as a sink for Pb in the environment. The strong influence of urban and industrial activity on Pb distributions is demonstrated by markedly higher median value (128 ppm (mg/kg)) in the urban-built, versus non-built (93 ppm (mg/kg)) environment.

Copper (Cu) concentrations show enrichment in the urban-built versus non-built environments in the same way as lead and tin with a median of 41 ppm (mg/kg) and elevated mean value equivalent to the 75th percentile of the data indicating the presence of anomalous high values due to contamination (Figure 6.3 and Annex 1). There is no expected source of geogenic enrichment in the study area.

The majority of **antimony** (Sb) results fall below the analytical detection limit (< 1 ppm (mg/kg)) reflecting the low abundance of this element in soils. Anomalous values are consistent with anthropogenic sources and relate to industrialisation (Annex 1).

Arsenic (As) concentrations are lower in soils developed over the quartz-rich Millstone Grit and Sherwood Sandstone facies as expected (Annex 1 and Figure 6.3) and are higher over Coal Measure than Barren Measure lithologies, probably because As is enhanced locally in association with pyrite (FeS_2) in the coals. Arsenic concentrations in coal and mining wastes are elevated for the same reason. This factor may account for the similar distribution of As in soils developed over the Coal Measures and those over made ground (Figure 6.3).

Only 5% of the data values for **cadmium** (Cd) are above the analytical limit of detection reflecting the naturally low distribution of this element in the environment. Isolated anomalies (> 2 ppm (mg/kg)) throughout the area are likely to be associated with industrial activity (Annex 1).

Chromium (Cr) concentrations in soils developed over the Millstone Grit facies are elevated relative to soils over other parent materials reflecting natural lithochemistry as these rocks contain a minor Cr-bearing heavy mineral component in magnetite and chrome-spinel phases. Cr concentrations in soils developed over the Coal and Barren Measures are higher than over other parent materials for the same reason. In contrast, Cr concentrations over the Sherwood Sandstone facies are low (Figure 6.3 and Annex 1). As a result of these strong geogenic controls, Cr concentrations in soils within and outside the urban-built environment are similar. However, concentrations in soils developed over made ground are higher than over natural parent materials reflecting localised contamination associated with industrial and urban processes.

Cobalt (Co) concentrations are low in soils over Millstone Grit and Triassic Sherwood Sandstone and Mercia Mudstone lithologies reflecting natural bedrock geochemistry (Figure 6.3 and Annex 1). Higher concentrations are found over Coal Measure and made ground parent materials, however, variation between the urban-built and non-built environments is less distinct than for some of the other metal elements.

With the exception of the Triassic Sherwood Sandstone and Mercia Mudstone facies, which are naturally low in **mercury** (Hg), the element shows an interesting spatial distribution in that soils developed over all parent materials have higher mean (which generally equates to the 75th percentile) than median values indicative of sporadic anomalies (Figure 6.3 and Annex 1). This suggests localised but widespread Hg contamination in the study area. Natural sources of Hg include the Coal Measures hence coal spoil is also enriched in the element and coal burning is also likely to cause Hg volatilisation and subsequent aerial deposition. Many industries formerly used Hg in electrical switch-gear and this may be another source of the element in the Stoke area.

Molybdenum (Mo) concentrations are similar in soils developed over all parent materials including the Millstone Grit although the widest range in results is recorded over made ground. As with most of the other metal/metalloid elements, concentrations are enhanced in the urban-built versus non-built environment and high concentrations are associated with local multi-element anomalies (Annex 1 and Figure 6.3).

Nickel (Ni) concentrations in soils over the Triassic and Namurian Millstone Grit sediments are lower than over other parent materials reflecting natural lithochemistry (Figure 6.3 and Annex 1). Although there is little contrast between soils collected within and outside the urban-built versus non-built environment, soils developed over made ground have markedly higher Ni contents reflecting the specific association of this element with industrial sources such as wastes from the steel, engineering, ceramic colouring and glazing industries, rather than urbanisation in general.

Titanium (TiO_2) surface soil concentrations reflect strong geogenic controls and are lower over Triassic sediments than the other parent materials (Figure 6.3 and Annex 1). The area of generally elevated values around Red Street (UK NGR 383E, 350N) to Silverdale (382E, 346N) may reflect residual heavy mineral (for example ilmenite) solifluction products derived from Coal Measure sandstones over the steep topography of the central Stoke valley.

Uranium (U) shows a very narrow range of concentrations in surface soils over the study area and has a similar distribution over all parent materials (Figure 6.3 and Annex 1). Highest values of uranium in soils probably reflect natural localised geogenic sources of the element.

Vanadium (V) concentrations in soils are likely to reflect both natural and anthropogenic sources in this region. As expected, values are lower over the Namurian Millstone Grit and Triassic sediments than other parent materials. Higher concentrations in soils over the Coal Measures may reflect the natural affinity of the element for the kerogenic fraction of coals. As a consequence of this association, coal spoil and coal-ash are also enriched in vanadium and other industrial sources in the area may include vanadium-steel alloy material and pigments used in the ceramic industry.

6.3.3 Multi-element Relationships in Surface Soils

In addition to consideration of individual element distributions, relationships between elements in surface soils were examined to elucidate the main controls on soil geochemistry in the study area. As a means to examine the likely sources of elements in Stoke-on-Trent surface soils, principal component analysis (PCA) was carried out. PCA is a multivariate statistical method that is commonly applied in geochemical studies to distinguish trends in large and complex datasets. The method finds the principal axes of a multi-dimensional configuration and determines the co-ordinates of each sample value relative to these. This is equivalent to rotating the geochemical data distribution to new axes. The relationships between the variables in the context of the first two principal axes can then be displayed. By examining the latent vectors for those variables that load heavily, it is sometimes possible to give the axes a physical interpretation. The analysis depends on the variances of the geochemical data being approximately equal. This can be achieved by transforming the values to standard normal variates (z) using the following formula:

$$z_{ji} = \left(x_{ji} - \bar{x}_j\right) / \sigma_j$$

where $\bar{x}_j$ and σ_j are the mean and standard deviation of element distribution *j*, respectively.

The element geochemistry data, soil pH and LOI (%) for the 23 variables of the 747 surface soil samples from Stoke-on-Trent were transformed in this way and a PCA was performed. The initial analysis using the entire dataset showed that soil pH and organic matter content (LOI) had low vector loadings in the first and second components. Hence, they were removed from the subsequent principal component analysis (Tables 6.4 and 6.5).

TABLE 6.4. LATENT ROOTS OF THE PCA CORRELATION MATRIX FOR STOKE-ON-TRENT SURFACE SOILS

Component	1	2	3	4	5	6
Root	8.60	3.78	1.73	1.62	1.00	0.84
Proportion of variance (%)	37	17	8	7	4	4
Cumulative (%)	37	54	61	68	73	76

TABLE 6.5. VECTORS OF THE FIRST TWO COMPONENTS (SURFACE SOIL SAMPLES)

Variable	TiO_2	MnO	Fe_2O_3	V	Cr	Co	Ni	Cu	Zn	As	Mo	Ba
PC1	-0.17	-0.218	-0.276	-0.271	-0.218	-0.236	-0.309	-0.186	-0.23	-0.214	-0.258	-0.213
PC2	-0.325	-0.093	-0.137	-0.265	-0.075	0.127	-0.048	0.163	0.223	-0.075	0.037	0.078

Variable	Pb	U	Cd	Sn	Sb	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO
PC1	-0.197	-0.167	-0.127	-0.177	-0.181	-0.083	-0.195	0.294	-0.167	-0.05	-0.148
PC2	0.311	-0.336	0.279	0.276	0.258	-0.083	-0.336	0.099	0.286	-0.151	0.139

Results show that the first two components account for more than 50% of the variance in the entire dataset. The variates that are heavily weighted in the first component (Al_2O_3, SiO_2, TiO_2 and Fe_2O_3) and account for 37% of the total variance are those that reflect the natural geological controls on soil geochemistry. For example, Al_2O_3 and SiO_2 and reflect the distribution of aluminosilicate mineral assemblages, TiO_2 and Fe_2O_3 are associated with many major rock forming minerals and V is often associated with Fe_2O_3 (Figure 6.7). The variates that are heavily weighted in the second component (17% of the variance) reflect various forms of metalliferous (Cu, Cd, Sb, and Pb) and ceramic sources (CaO and P_2O_5) derived from anthropogenic activity (Figure 6.7).

Given the industrial history of Stoke-on-Trent and the widespread presence of made ground including large quantities of pottery waste, furnace slag and ash, these weightings are entirely consistent with field observations. Ceramic waste, especially of the 'bone china' variety, is rich in CaO and P_2O_5, while both plain and, in particular coloured, glazes may be rich in heavy metals such as Pb, Sn, Cd, Cu and Co. Furnace and iron foundry waste is also often rich in CaO and P_2O_5, whilst engineering, colliery and gasworks wastes are also common sources of Sb, Pb, Cu, Cd and other metals. A number of the other variates (Cr, As, Ni) have vector loadings with intermediate values for the first and second components, which suggests that their distributions are controlled to some extent by both natural geological controls and anthropogenic contamination. The results of the PCA confirm the observations noted from descriptions of the individual element distributions in soils from the study region.

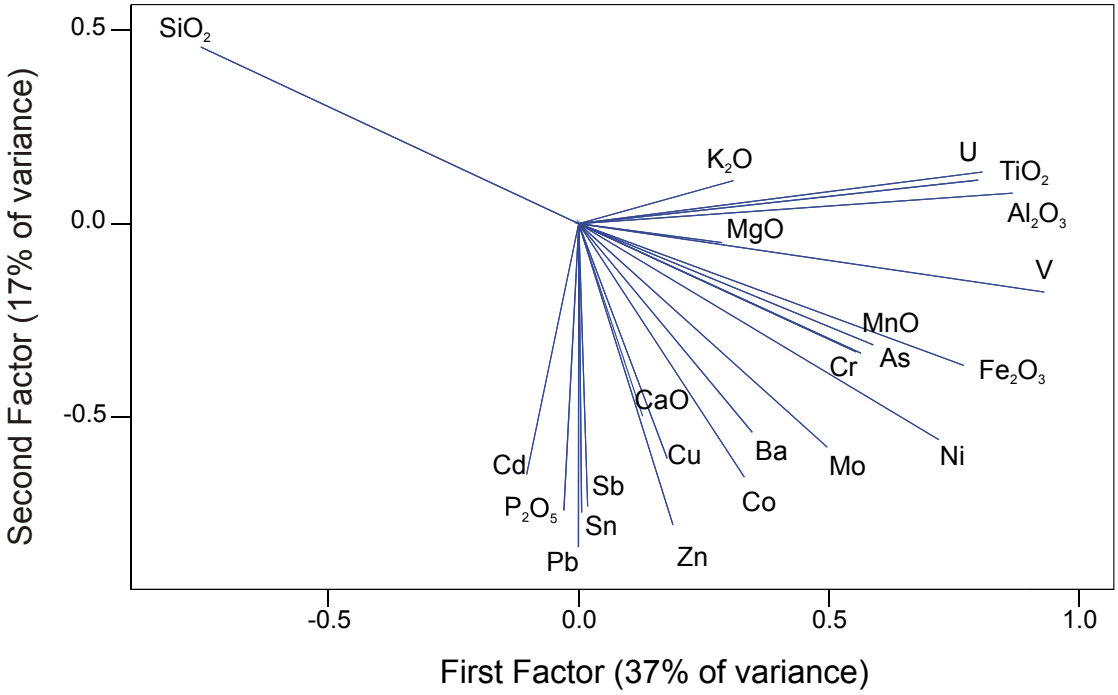


Figure 6.7. Varimax rotation of the vectors projected on components 1 and 2 (surface soil samples)

Some of these relationships were examined visually using the three-component mapping techniques described in Chapter 4 of this report. Three-component interpolated grid maps were prepared for 9 elements in surface soils from Stoke-on-Trent grouped as follows: Cu-Pb-Zn; Mo-Ni-V and CaO-Fe-P_2O_5. The choice of elements and element groupings was made on the basis of similarities and contrasts in natural geochemical behaviour so as to maximise anthropogenic geochemical signatures as it is highly unlikely that natural metallogenic processes could simultaneously produce very high levels of such a disparate range of elements. Three-component maps were prepared by combining individual red, green and blue element maps and a colour key is shown in Figure 6.8 to aid map interpretation.

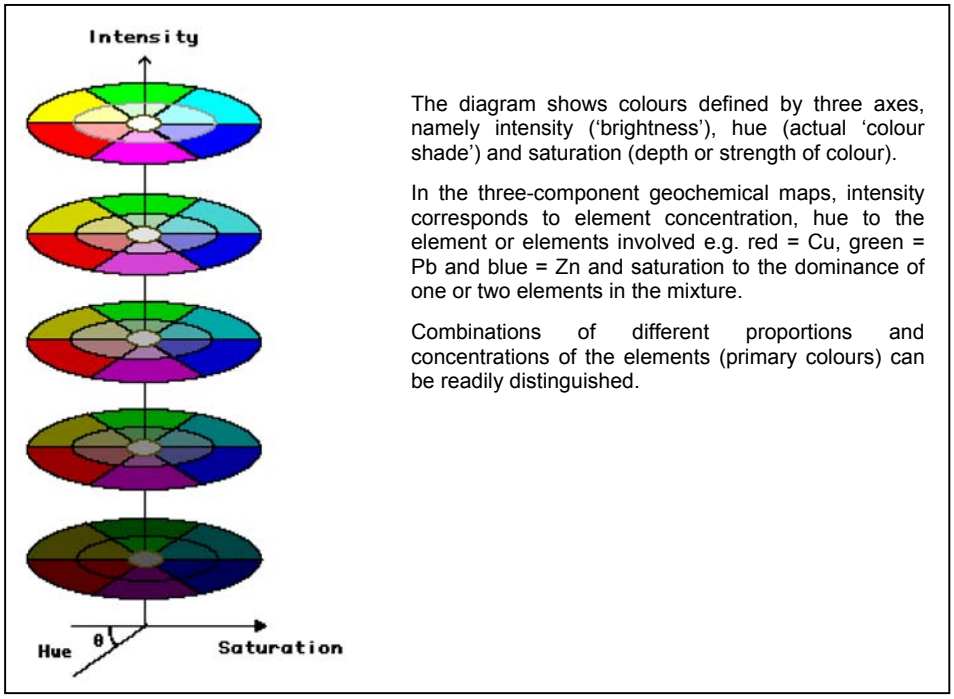


Figure 6.8 Colour-wheel key to three-component geochemical maps.

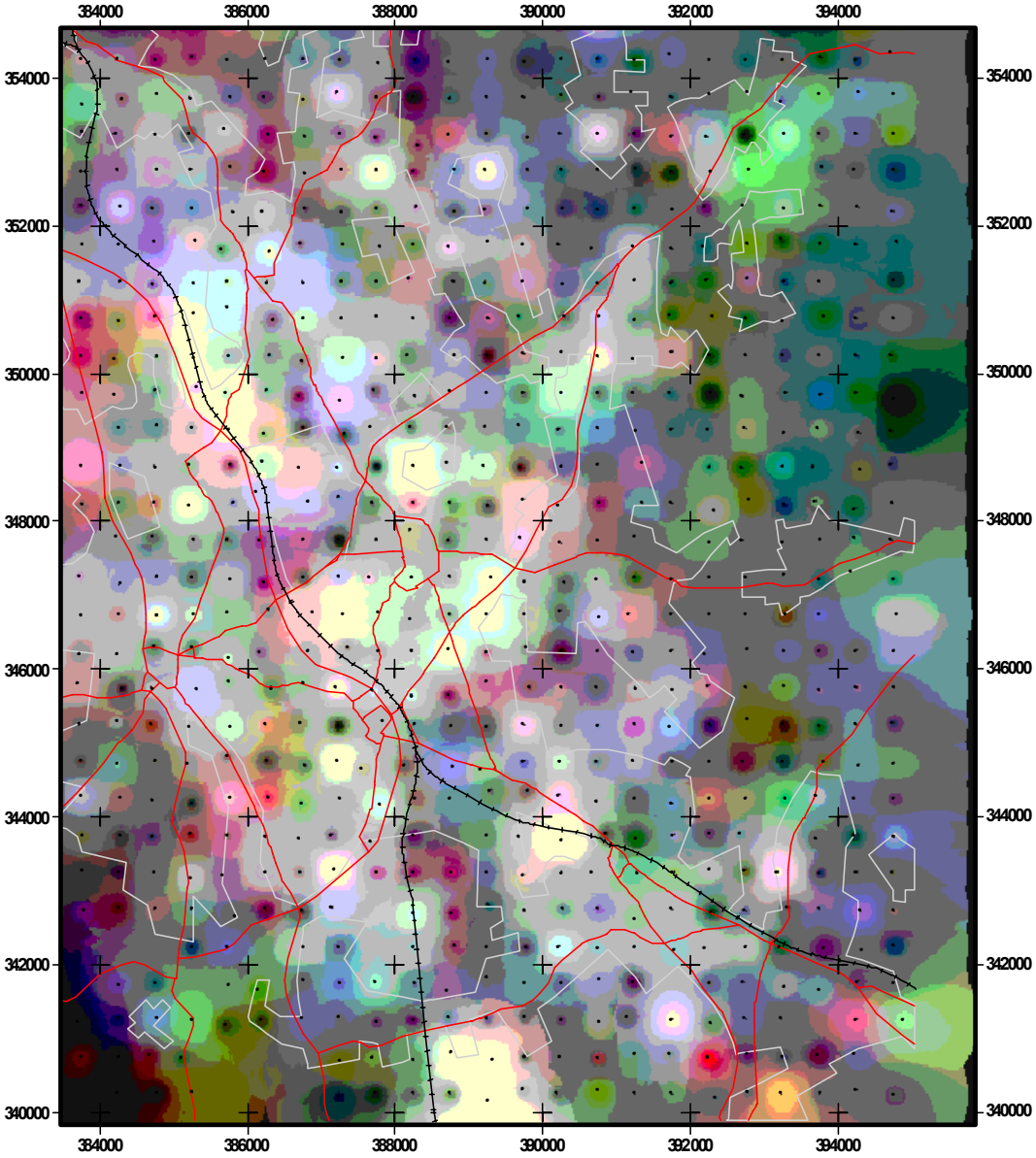


Figure 6.9 Three-component interpolated map showing copper (red), lead (green) and zinc (blue) in Stoke-on-Trent surface soils.

Copper, lead and zinc are three of the most common heavy metals, and although high levels of each may be produced by naturally occurring mineralisation, combinations of all three at moderately high concentrations are more typical of urban-industrial contamination. Thus in the Stoke region there is a fairly tight spatial association of the white, light grey and pastel shades, indicating high levels of all three metals, with the area of urbanisation. More localised anomalies shown by white spots are closely associated with the historic industrial areas. The contrast between the urban area and the low metal levels (dark greys and dull colours) of the surrounding rural environment is also well marked (Figure 6.9).

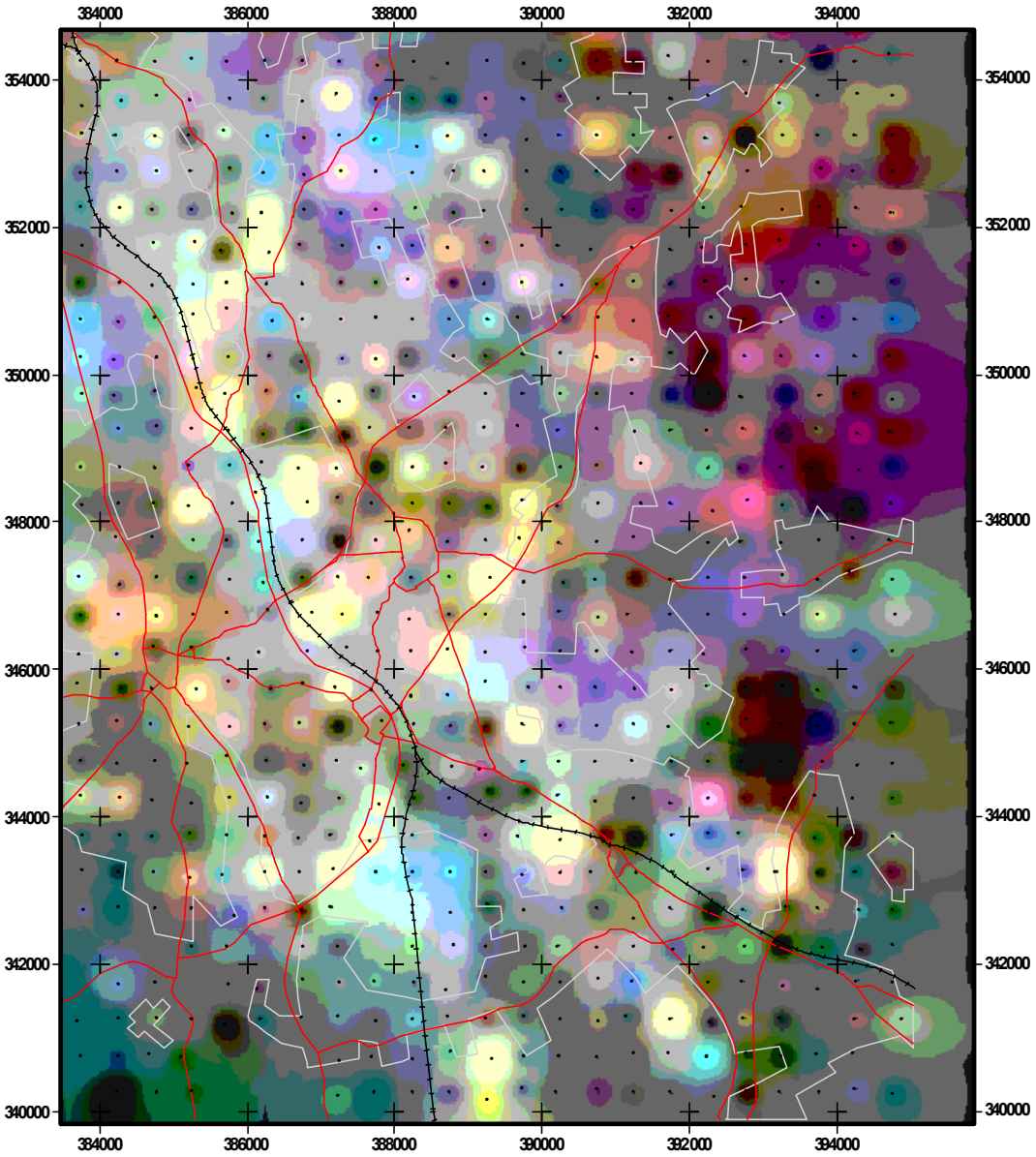


Figure 6.10 Three-component interpolated map showing molybdenum (red), nickel (green) and vanadium (blue) in Stoke-on-Trent surface soils.

Although background levels of the rarer metals Mo, Ni and V may be elevated by natural geological associations in the Stoke area, notably of Ni and V with the Coal Measures, industrial sources include the wastes associated with coal-burning and gas production and the steel industry where they are used as alloying materials to produce special steels for tools and other uses in engineering. Smaller amounts of Ni and V are used in ceramic colour and special glazes by the pottery industry. As with Cu, Pb and Zn, there is a strong spatial association between Mo, Ni and V and the urbanised area, which has substantially higher levels than the surroundings. In addition there are a number of 'white spot' anomalies, which are closely linked with the former steel-making area of Shelton Bar and a number of other industrial sites (Figure 6.10).

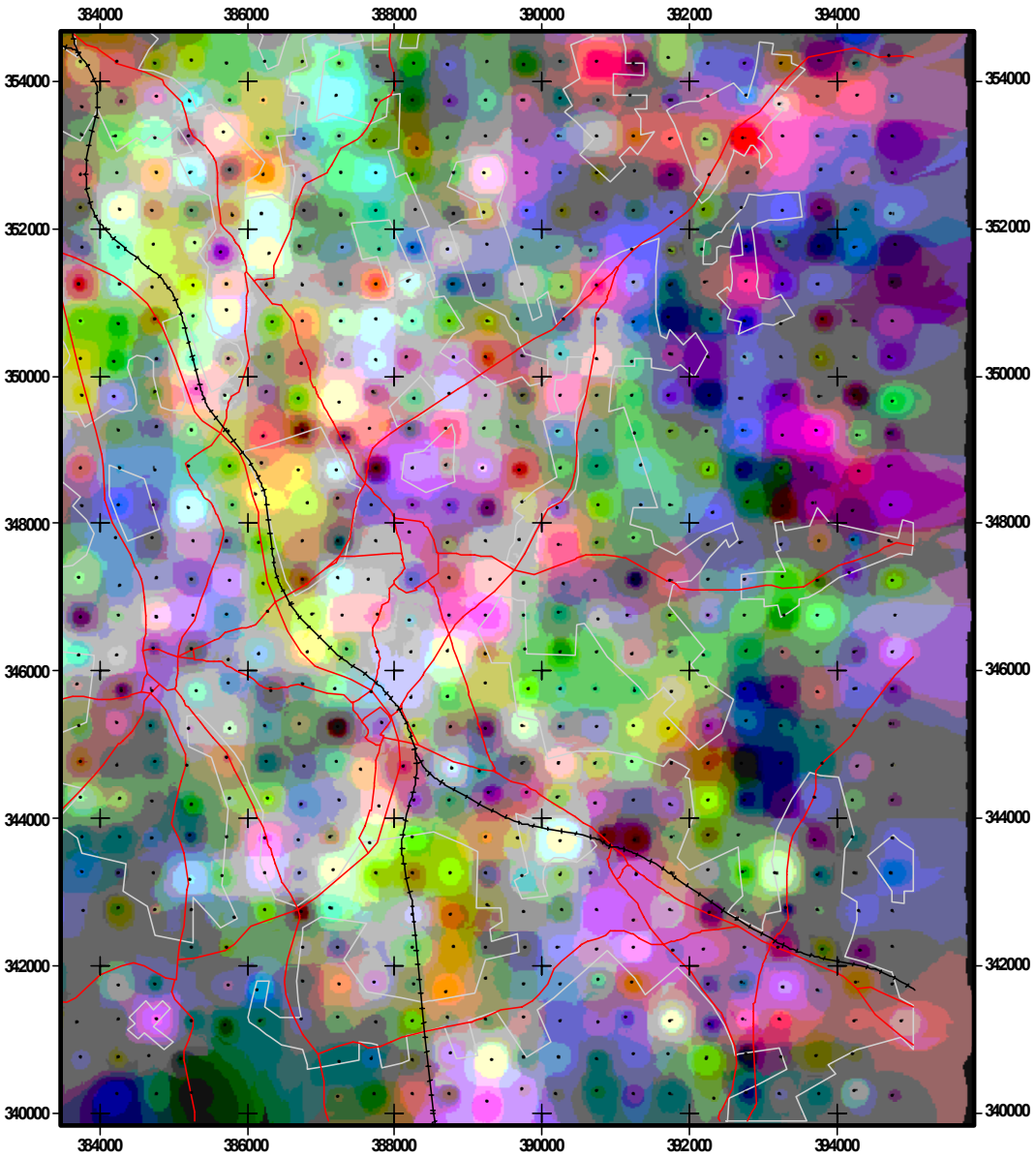


Figure 6.11 Three-component interpolated map showing calcium (red), iron (green) and phosphorus (blue) in Stoke-on-Trent surface soils.

In this area, CaO, Fe_2O_3 and P_2O_5 may occur independently, or together at high levels in some ironstones, such as those present at various horizons within the North Staffordshire Coalfield, but are most prominently associated in the slags produced by iron and steel works, where limestone is used to remove phosphate from the iron ore during the smelting process in blast furnaces. Such furnace slag is widespread and readily recognised in made ground in Stoke, being derived both from small-scale iron workings (notably in parts of Fenton) and larger-scale operations such as Shelton Bar. 'Basic slag' from these sources was also widely used as a soil conditioner and fertiliser (on account of its high CaO and P_2O_5 content) well away from the industrial areas. Hence the map shows a broader spread of high levels of these elements, while stronger colours also show a weaker association between the three elements, indicating independent sources, especially of iron, which shows contrasting greens against a purple (CaO+ P_2O_5) background in several areas (Figure 6.11).

6.4 SURFACE AND PROFILE SOIL COMPARISON

Whilst it is possible to examine the distribution of element concentrations in surface versus profile soils shown in Annex 1, these relationships, must be treated with caution due to the differences in sample preparation method. As described in Chapter 3, surface soils were sieved to the environmental standard < 2 mm (2000 µm) size fraction whereas profile soils were sieved to < 150 µm to be consistent with regional stream sediment and soil data. This section will briefly discuss the likely effects of these methodological differences, on the soil geochemistry of Stoke-on-Trent.

The effect of the different size fractions on the soil geochemistry can be further understood with reference to Figure 6.12a. This shows that sand (60-2000 µm) can be the dominant particle size fraction in some soils, therefore removal of the 150-2000 µm material during sieving will result in a relative increase in the proportion of silt (2 - 60 µm) and clay (<2 µm). In most soils, the majority of the sand fraction comprises quartz and some detrital primary materials (Figure 6.12b), which generally have a low surface area and number of surface exchange sites per unit surface area (McBride, 1994). The high unit surface area and large number of exchange sites of the clay size fraction (predominantly secondary silicate and sesquioxide minerals) means that trace and minor elements tend to be associated with the fine size fractions in soils. Thus the increase in the relative proportion of these particles caused by sieving the profile soils to <150 µm, not only effectively changes the soil texture towards the clay-silt types (Figure 6.13), but is likely to increase the abundance of trace elements relative to the < 2mm fraction of the same soil. Sieving to < 150 µm is likely to have the same affect on the soil organic carbon, which has a close affinity with clay minerals and can have a strong control on surface charge and sorption in soils.

Therefore, comparisons between surface and profile soils sieved to different size fractions are difficult. Unequivocally distinguishing differences due to geochemical processes in the weathering environment from those that are artefacts of the sample preparation process is not possible. Although the urban soil sample preparation strategy was devised to maintain consistency between rural and urban soils, it is recommended that in future both surface and profile soils are sieved to the environmental standard < 2 mm size fraction. The following comparisons of surface and profile soil geochemistry attempt to take account of soil size fraction issues.

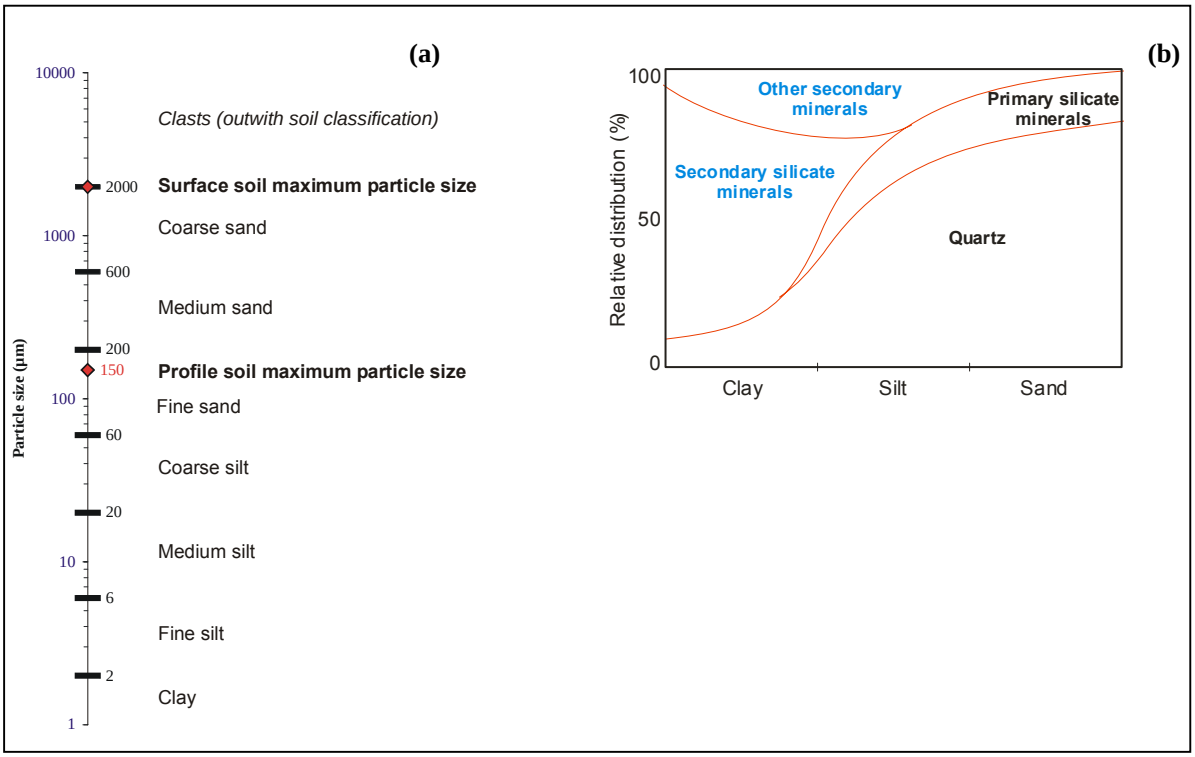
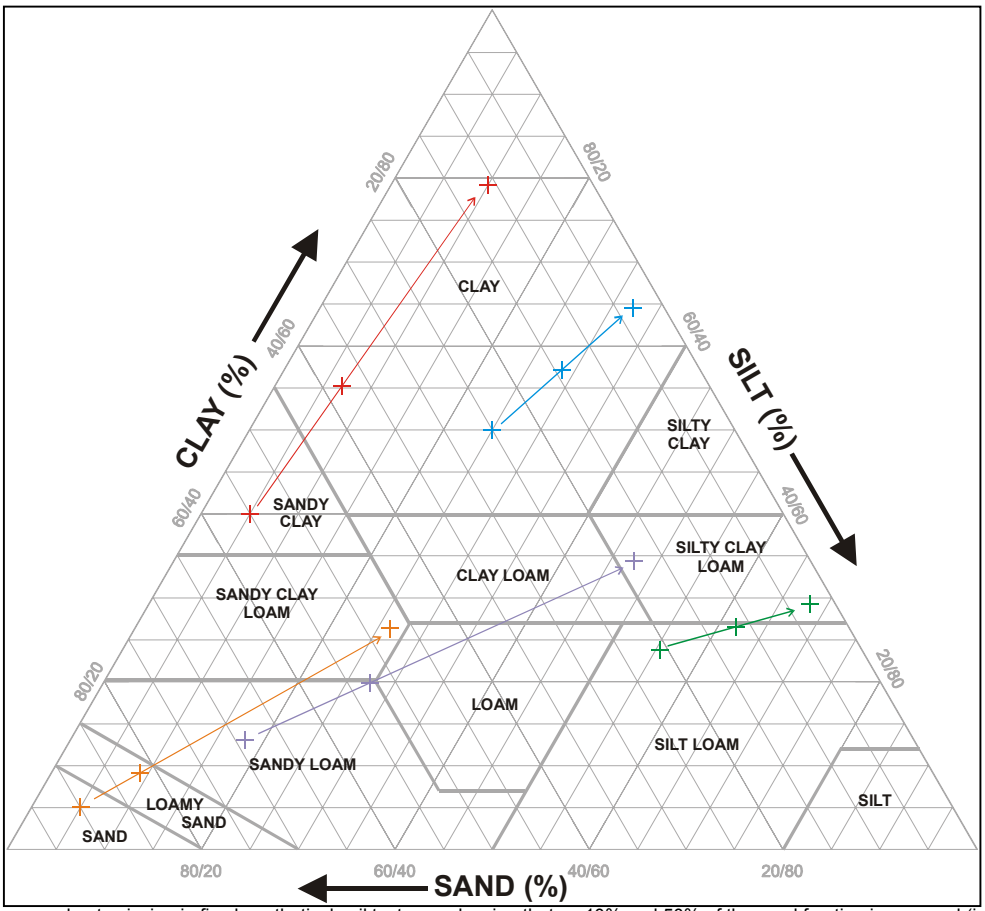


Figure 6.12 Soil particle size classification showing a) GSUE sieve fractions compared to standard particle size classes and b) the general composition of particles in different soil size fractions.



Changes due to sieving in five hypothetical soil textures, showing that as 10% and 50% of the sand fraction is removed (in the direction of the arrow towards 50% removal), the silt and clay components of the soil may become dominant

Figure 6.13 Potential alterations in soil texture due to sieving to < 150 µm.

6.5 PROFILE SOIL GEOCHEMISTRY

Plots of the surface versus profile soil element distributions across the Stoke-on-Trent urban area are show in Annex 3 and in the box and whisker diagrams in Figure 6.14. Many of the elements display similar spatial (Annex 1) and statistical (Annex 3 and Figure 6.14) distributions in surface and profile soils and these elements are not discussed further here. Notable differences between surface and profile soils are as follows.

In general, Annex 3 demonstrates that as would be expected, the major elements (Al_2O_3, MgO, K_2O and SiO_2) show much better correlation between surface and profile soils than the trace elements due to the strong geological (rather than man-made) control on these distributions.

However, the results for **silicon** (SiO_2) demonstrate the effect of the sample size fraction on soil composition. At low concentrations SiO_2 values are highly variable in both surface and profile soils, but high concentrations are predominately found in surface soils due to the greater quartz content of this coarser sieved fraction (Annex 3 and Figure 6.14). As expected, high silicon concentrations in profile soils show a slightly stronger spatial (Annex 1) and statistical (Figure 6.14) association with quartz-rich parent materials of the Namurian Grit and Triassic Sherwood Sandstone than surface soils.

Similarly, **phosphorous** (P_2O_5) contents in surface soils show a greater range than in profile soils (Figure 6.14, Annex 3 and Annex 1). Whilst it cannot be ruled out that this may be due to the exclusion of sand-size particles containing phosphate minerals (primary apatites) or phosphate-containing wastes in the profile soils during sieving, these results could also reflect the very insoluble nature of phosphate in many soils. The phosphorous present in surface soils may originate from natural sources, from fertiliser use in the urban area or from steel and pottery wastes but translocation down profile to deeper soil horizons may be prohibited by the precipitation of Ca, Mg and Fe phosphates in the surface zone.

In contrast to silicon and phosphorous, **aluminium** (Al_2O_3) and **potassium** (K_2O) concentrations are generally elevated in profile with respect to surface soils throughout the study area. These differences are reasonably systematic at 0.5% and 3% respectively, suggesting that all the variation could be due to grain size changes resulting from the sample preparation process, namely the greater concentration of clay minerals in the < 150 µm profile soil material (Annex 3, Figure 6.14 and Annex 1). Although the overall K_2O concentrations are lower in surface than in profile soils, more of the high K_2O values in surface soils are associated with made ground, especially colliery spoil than in profile soils (Annex 1).

Calcium (CaO) and **barium** (Ba) also show a greater range of high values in the profile soils (Annex 1, Annex 3 and Figure 6.14). Since these elements are not likely to be enhanced in the finer soil fraction but are present in foundry and ceramic industry wastes and highest values occur over made ground parent materials, it is likely the profile soil chemistry of these elements is affected by contamination. As with surface soils, calcium shows strong correlations (95% confidence level) with many of the metal elements in profile soils (Table 6.6), which also suggests the dumping of calcareous material in metal foundry waste as a source of the element in Stoke-on-Trent.

Spearman Rank results show that as with surface soils, the majority of trace metal and metalloid elements are significantly (95% confidence level) correlated with each other in profile soils (Table 6.6). However, most of these elements including **cobalt** (Co) **chromium** (Cr), **arsenic** (As), **manganese** (MnO), **iron** (Fe_2O_3), **copper** (Cu), **molybdenum** (Mo), **nickel** (Ni) and **zinc** (Zn) show a greater range of high values in profile versus surface soils (Annex 3 and Figure 6.14). Whilst these results could simply indicate elevated metal contents in the finer < 150 µm profile soils, they may also result from natural processes such as the accumulation and sorption of metals in the profile soils following mobilisation from the surface during weathering. Comparison of the results for Mo, Cu and Ni from outside the made ground area (Figure 6.14) show marginally elevated median profile versus surface soil values, which could be indicative of these processes. However, the contrast between surface and profile soil metal concentrations is much greater in soils developed over made ground suggesting that profile soils are more prone to metal contamination over parent materials such as colliery spoil, foundry and ceramic waste than surface soils. Whilst this may be a genuine observation, it should be noted that the apparently lower metal contents of surface soils may reflect the common practice of importing 'clean' topsoil layers during Brownfield site remediation, as much remediation has been carried out in the Stoke urban area.

The spatial distribution of **antimony** (Sb) is locally highly variable and shows a more pronounced urban "clustering" in the profile soils than the surface soils (Annex 1). The isolated anomalies (> 95^{th} percentile values) in the surface soils do not always correspond to high concentrations in the profile soils, and *vice versa*. Potential sources of Sb include colliery spoil and many industrial materials, such as batteries, lead shot and solders. However, the very marked differences in the surface and profile soil concentrations at individual sites are difficult to explain in general terms and probably relate to localised contamination.

Unlike the other trace metals**, vanadium** (V) concentrations are similar in surface and profile soils probably reflecting the influences of Coal Measure parent material and the wide-spread dispersal of colliery waste on both surface and profile soil compositions (Annex 3).

In contrast to the majority of trace metals, **tin** (Sn), **cadmium** (Cd), and **lead** (Pb) concentrations have a broad range in both surface and profile soils and are marginally elevated (median values) in surface compared to profile soils suggesting the greater influence of diffuse and atmospheric pollution sources such as litter and traffic on these element distributions (Annex 3 and Figure 6.14). In the case of tin, the profile soil results very much reflect the low mobility of the element in the soil environment. Outside the made ground area, concentrations are close to natural background values even where anomalies occur in surface soils because the element is not readily leached down the soil profile. It is only within the made ground environment in areas of intense industrial activity that high concentrations of tin are found in profile soils (Annex 1).

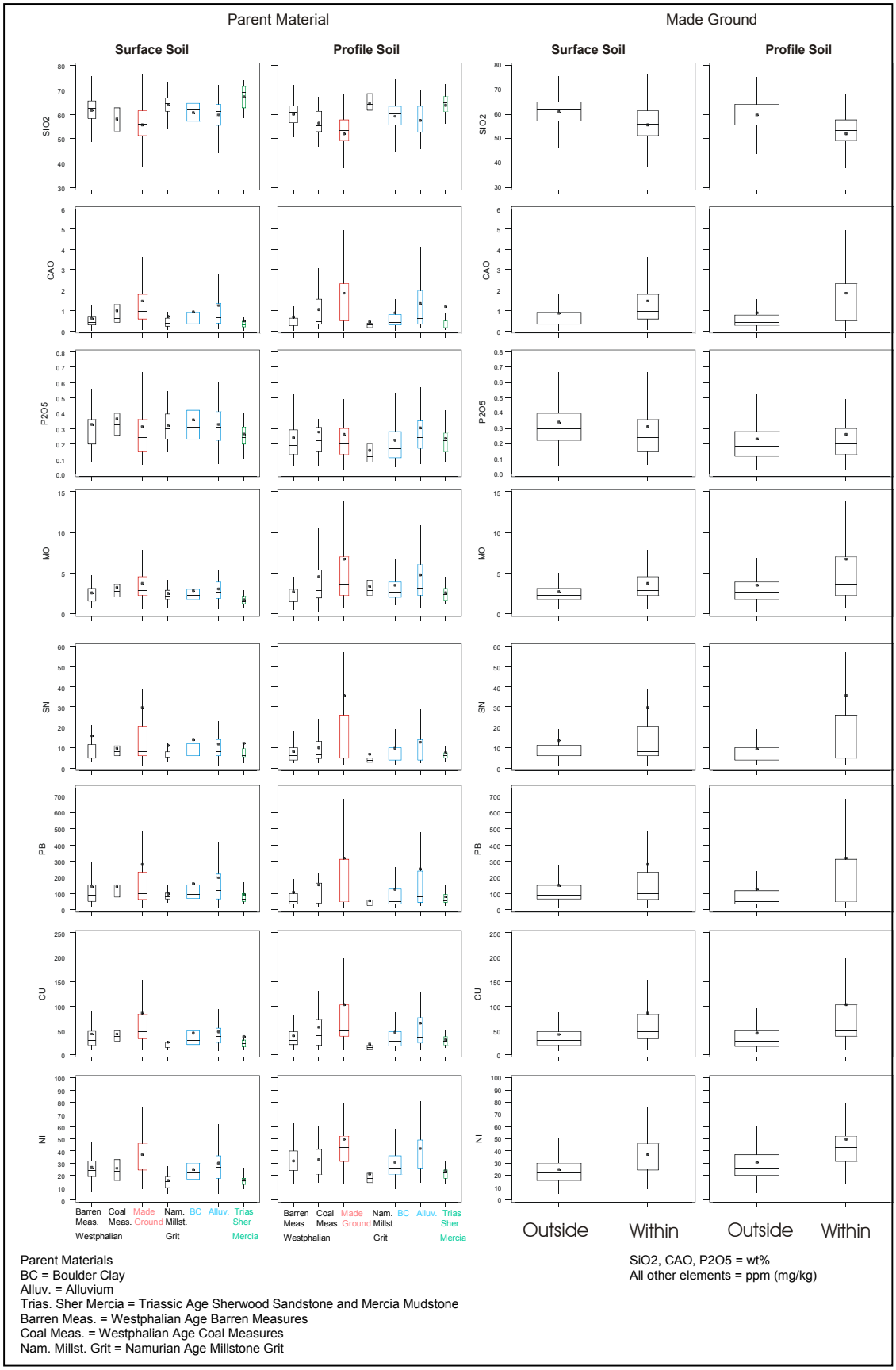


Figure 6.14. Box and whisker plots of the 5th, 25th, 50th, 75th and 95th percentiles of selected element distributions in urban profile soils from Stoke-on-Trent classified by parent material type.

TABLE 6.6 SPEARMAN RANK MATRIX OF SIGNIFICANT (95% CONFIDENCE LEVEL) CORRELATIONS BETWEEN ELEMENT CONCENTRATIONS IN STOKE-ON-TRENT PROFILE SOILS

	MNO	FE2O3	V	CR	CO	BA	NI	CU	ZN	AS	MO	PB	U	CD	SN	SB	MGO	AL2O3	SIO2	P2O5	K2O
MNO																					
FE2O3	0.57																				
V	0.40	0.73																			
CR	0.13	0.50	0.67																		
CO	0.71	0.74	0.71	0.46																	
BA	0.42	0.38	0.38	0.15	0.54																
NI	0.54	0.68	0.72	0.51	0.84	0.67															
CU	0.53	0.60	0.62	0.30	0.72	0.65	0.81														
ZN	0.59	0.52	0.44	0.18	0.69	0.67	0.75	0.80													
AS	0.43	0.56	0.42	0.22	0.56	0.57	0.62	0.74	0.69												
MO	0.38	0.41	0.28	0.18	0.43	0.54	0.49	0.64	0.63	0.72											
PB	0.46	0.37	0.28	0.04	0.51	0.63	0.55	0.76	0.82	0.73	0.73										
U	0.08	0.28	0.45	0.46	0.23	0.08	0.24														
CD	0.20	0.11	0.08		0.21	0.26	0.19	0.25	0.29	0.24	0.30	0.34									
SN	0.42	0.34	0.28	0.08	0.46	0.58	0.56	0.70	0.76	0.66	0.61	0.82		0.30							
SB	0.23	0.15	0.10		0.27	0.49	0.38	0.53	0.55	0.53	0.55	0.65		0.26	0.67						
MGO		0.13	0.22	0.29	0.24	0.25	0.46	0.22	0.25	0.17		0.07	0.24		0.14						
AL2O3		0.33	0.69	0.55	0.34		0.36	0.16					0.54				0.26				
SIO2																					
P2O5	0.55	0.26	0.11		0.37	0.47	0.37	0.59	0.69	0.60	0.63	0.79		0.30	0.71	0.53					
K2O						0.24	0.12										0.47	0.27			
CAO	0.42	0.42	0.43	0.18	0.54	0.62	0.68	0.73	0.71	0.61	0.59	0.67	0.03	0.26	0.62	0.48	0.31			0.52	

n = 750, r95% = 0.06 (Koch and Link, 1970)

6.6 SURFACE AND PROFILE SOILS IN RELATION TO MADE GROUND

One of the key issues in urban environments is how to characterise different types of made ground as surface exposure is frequently limited and it is often difficult to determine the composition and likely source of fill materials. The different geochemical signatures associated with certain fill products may be a tool that can aid made ground classification. The Stoke-on-Trent study had the opportunity to examine relationships between urban soil geochemistry and fill types due to the detailed made ground mapping carried out by Wilson et al (1992). Using the same method described in previous sections of this report, comparisons were made using the spatial query function of the ArcView® GIS whereby the map of made ground types (Figure 2.10) was superimposed on surface and profile soil sample points and the geochemical data categorised according to location within each made ground polygon. Once classified according to made ground type, the geochemical distributions were displayed in box and whisker plot format (Figure 6.15). This approach relies on the accuracy of the made ground mapping, which as already indicated, is not a straightforward task. Indeed, the majority of made ground in the Stoke-on-Trent area is classified as 'unspecified' (Figure 2.10). Furthermore, it should be noted that the standard GSUE geochemical survey is not specifically designed to investigate made ground types. Therefore, although sampling is carried out at a much greater density in urban areas (4 per km^2) than in rural areas (1 per 2 km^2), it is none-the-less a rather coarse sampling grid with respect to the limited spatial extent of some made ground types in the urban environment. As a consequence, some made ground types in Stoke-on-Trent have very few soil samples collected over them, for example, ceramic rejects (1 sample), ironworks slag (2 samples), former opencast and domestic waste (3 samples) and former opencast waste (4 samples) and these results must be treated with caution as they may not be very representative. Despite these issues, the following broad relationships are evident.

Many of the elements show very little variance in median values across the different made ground types including As, Fe_2O_3 and Mo in surface soils, Cu and MgO in profile soils and Ba, Cd, Co, Sb, U, Al_2O_3, K_2O and P_2O_5 in both top and profile soils. For many elements the broadest range in high concentrations is associated with the '**unspecified**' made ground type including As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, U, V, Zn, CaO, Fe_2O_3 in surface and profile soils and SiO_2 in profile soils (Figure 6.15). As expected, soils developed over **colliery waste** are relatively enhanced in a wide range of elements including As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V, Zn, Fe_2O_3, MgO and K_2O and P_2O_5 commensurate with coal geochemistry. **Domestic and industrial waste** soils also contain relatively high metal and metalloid element concentrations as expected including highest As, Ba, P_2O_5, Mo, Sb, Sn and Zn values and elevated CaO, Cd, Co, Cr, Cu, Ni, Pb, V, MgO and Fe_2O_3 contents. However, soils over this waste type are characterised by low Al_2O_3, K_2O, SiO_2 and TiO_2 values, which probably reflect the lesser geological and greater man-made composition of this parent material (Figure 6.15).

Soils over **former opencast waste** contain higher Al_2O_3, K_2O, SiO_2, TiO_2, V and CaO contents relative to other types an element suite indicative of clay, sandstone, coal and limestone waste products and similar relationships are seen for soils over a mixture of **former opencast and domestic waste.** However, most metal and metalloid elements are enhanced over the latter waste type relative to 'former opencast waste' indicating the influence of the domestic component on soil geochemistry, the exception is CaO (Figure 6.15). Former opencast and domestic waste soils have the highest U, MnO and TiO_2 contents, MnO and TiO_2 may indicate a high clay content in this parent material but U may be related to man-made waste.

Clay, bricks and tiles waste soils are generally low in metal and metalloid elements including As, Ba, Cd, Co, Cr (with the exception of one very high value which may be due to sporadic metal contamination), Cu, Sb, Sn, U, Mo Ni, Pb, V, Zn and K_2O and contain highest SiO_2 contents reflecting the inert nature of these waste products compared to other waste types in the area (Figure 6.15).

The two most interesting soil geochemical signatures relate to **ceramic waste** and **ironworks slag**. Although only one or two samples were collected over these waste types, the element associations are quite distinctive. The **ceramic waste** soil is characterised by high Sb, Sn, Zn, CaO, SiO_2, MgO, MnO and P_2O_5 values and contains highest Co and Pb levels relative to median values for other waste types. CaO and P_2O_5 are added to ceramics to produce bone china whereas Si, Sn, and Pb are used in glazes. The oxides of elements such as Co, Zn and Sb are used as ceramic pigments and the high levels of Co in soils over this waste type are particularly interesting in light of the volume of cobalt-blue pottery produced in Stoke-on-Trent for which the area is world famous. However, it is emphasised again that these results should be treated with caution as they refer to one soil sample and may not be representative of soils over this waste type as a whole. Indeed ranges for Co in Stoke surface soils are similar to those reported for Swansea (Morley and Ferguson, 1991).

Soils developed over **ironworks slag** contain highest median values for As, Cd, Cr, Cu, Mo, Ni, V, Fe and Mg and are also high in Pb, Co, Zn, MnO, Al_2O_3, P_2O_5, CaO, K_2O and TiO_2 but low in SiO_2 relative to other waste types. These multi-trace-metal element anomalies coupled with high CaO, MgO and P_2O_5 values are indicative of this type of waste. The likely impacts of these waste products on soil geochemistry are discussed on more detail in section 6.8.

In terms of using geochemistry as a tool to aid the mapping of made ground, these results show that there are specific soil element assemblages associated with different types of made ground. However, on the scale of urban geochemical surveying (4 samples per km^2) it may not be possible to use the geochemical data to accurately delineate the spatial extent of different made ground types, this would require more detailed sampling, which may be dependent on access to soils in the urban environment. None-the-less, this study has demonstrated that on a city-wide basis, combining geochemical element assemblage information, such as the Spearman Rank correlations, PCA and three component maps outlined in previous sections of this report, with made ground mapping, historical and land use information soil geochemistry can be used to aid the classification of likely fill materials and may prove useful in other urban centres where made ground mapping is a priority.

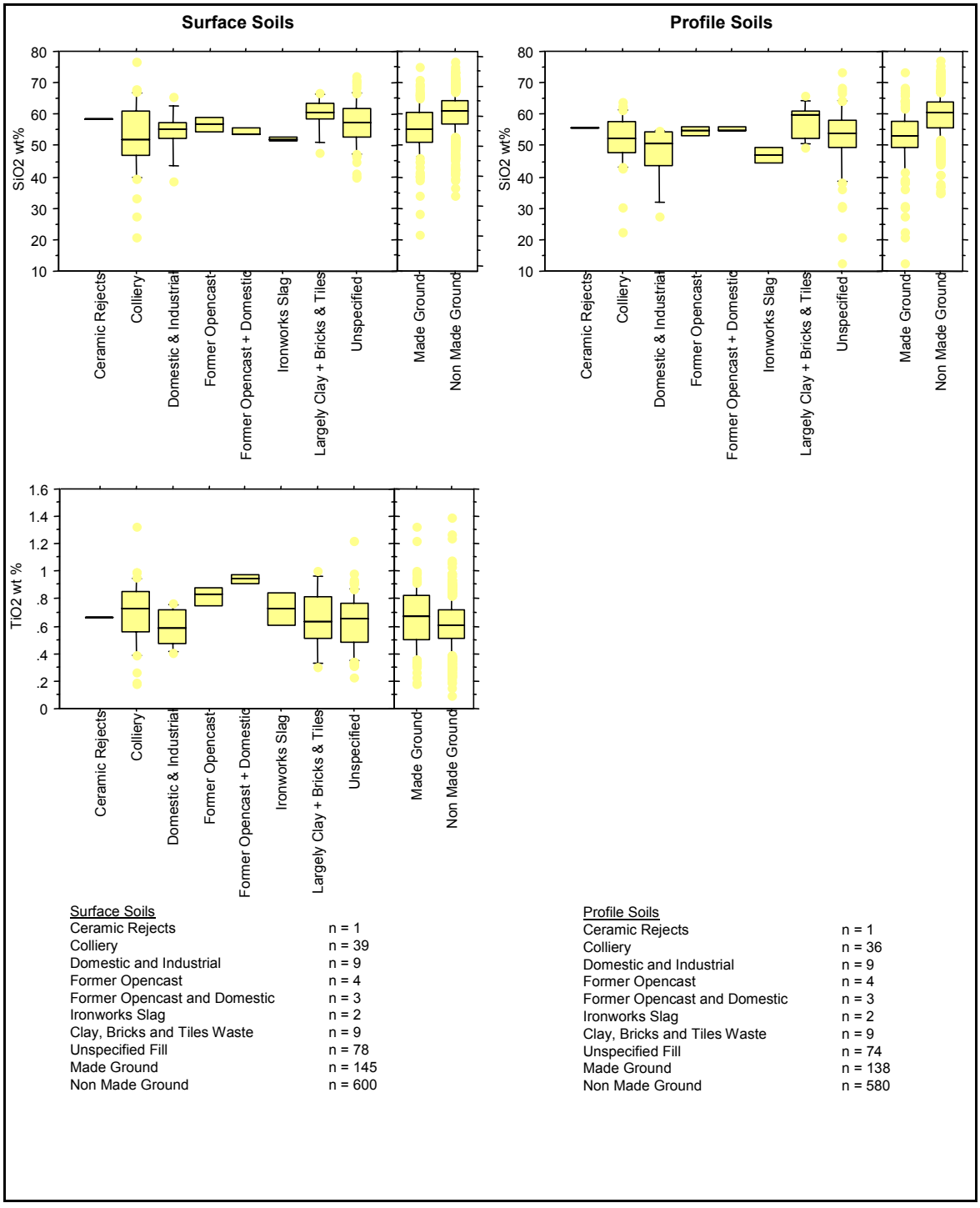
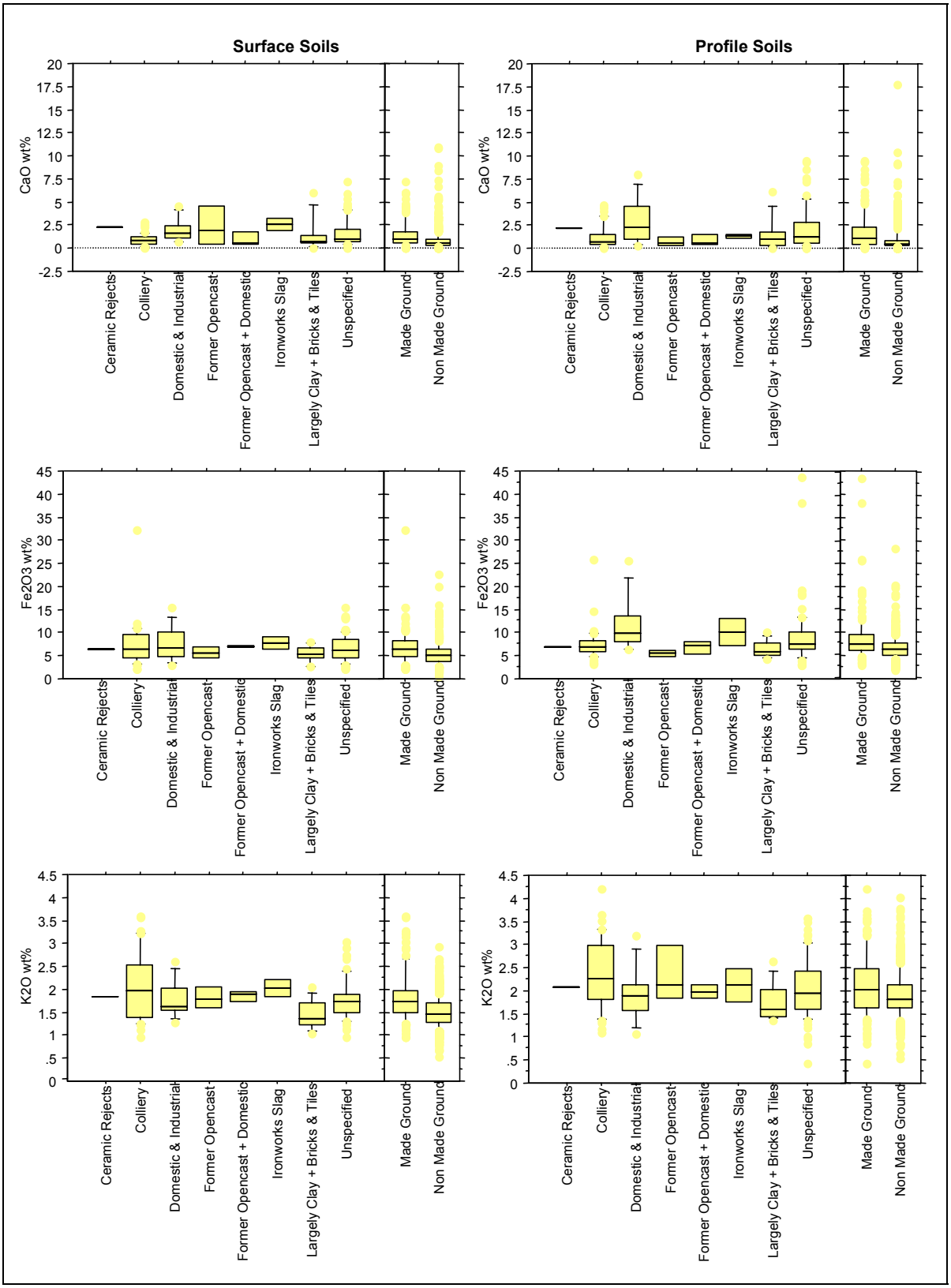


Figure 6.15. Box and whisker plots of the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in surface and profile soils from Stoke-on-Trent classified by made ground type.



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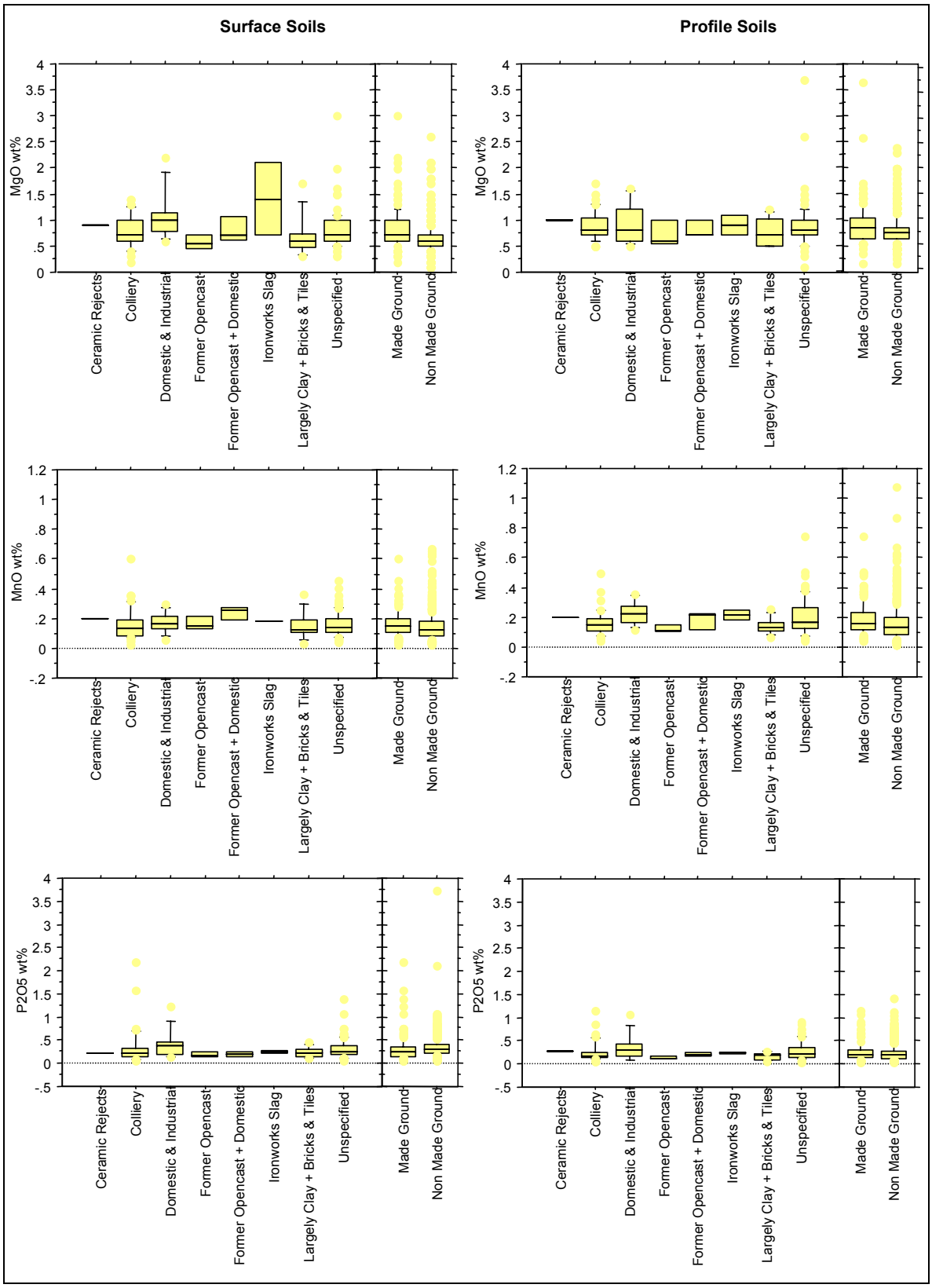

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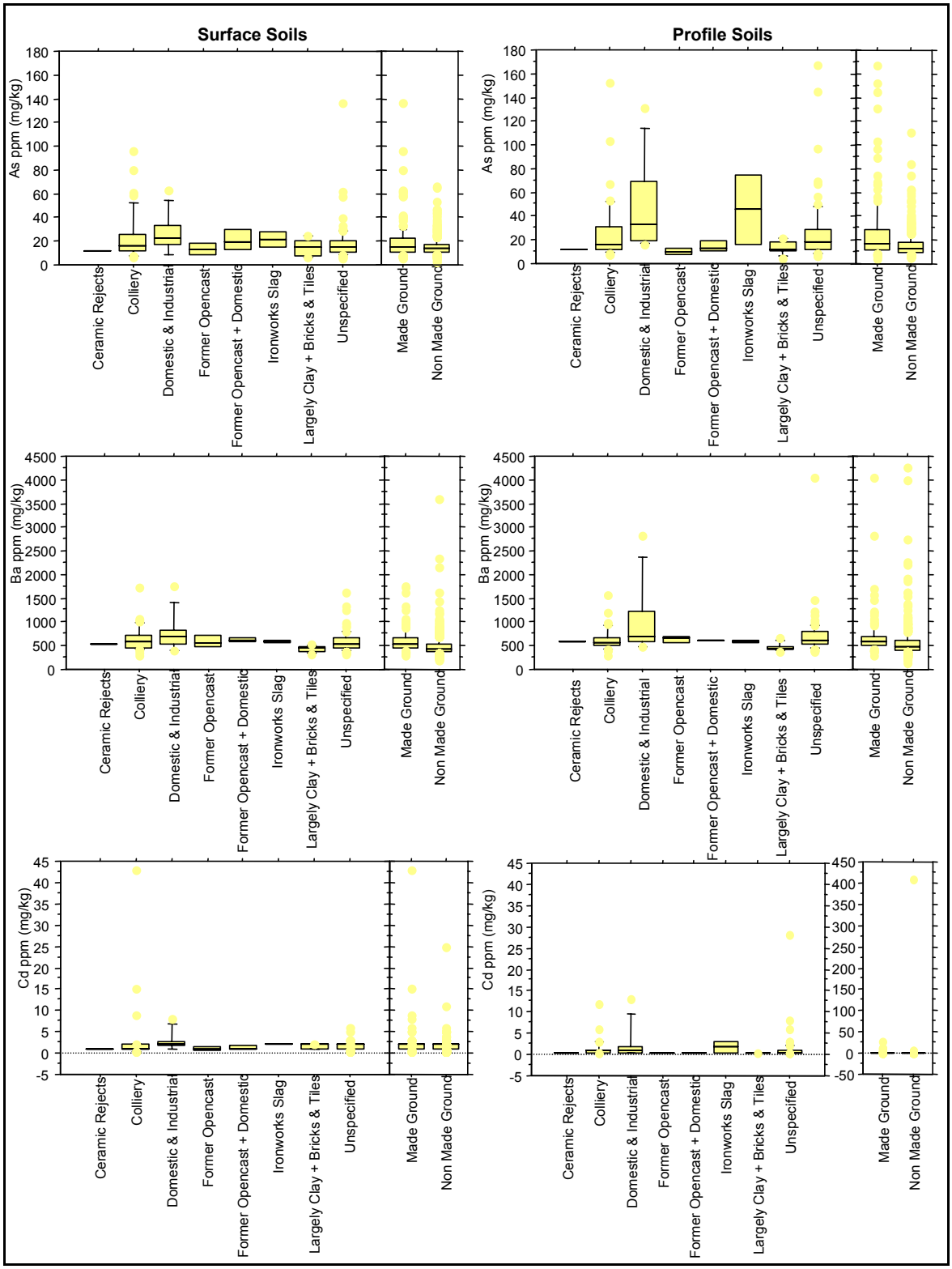

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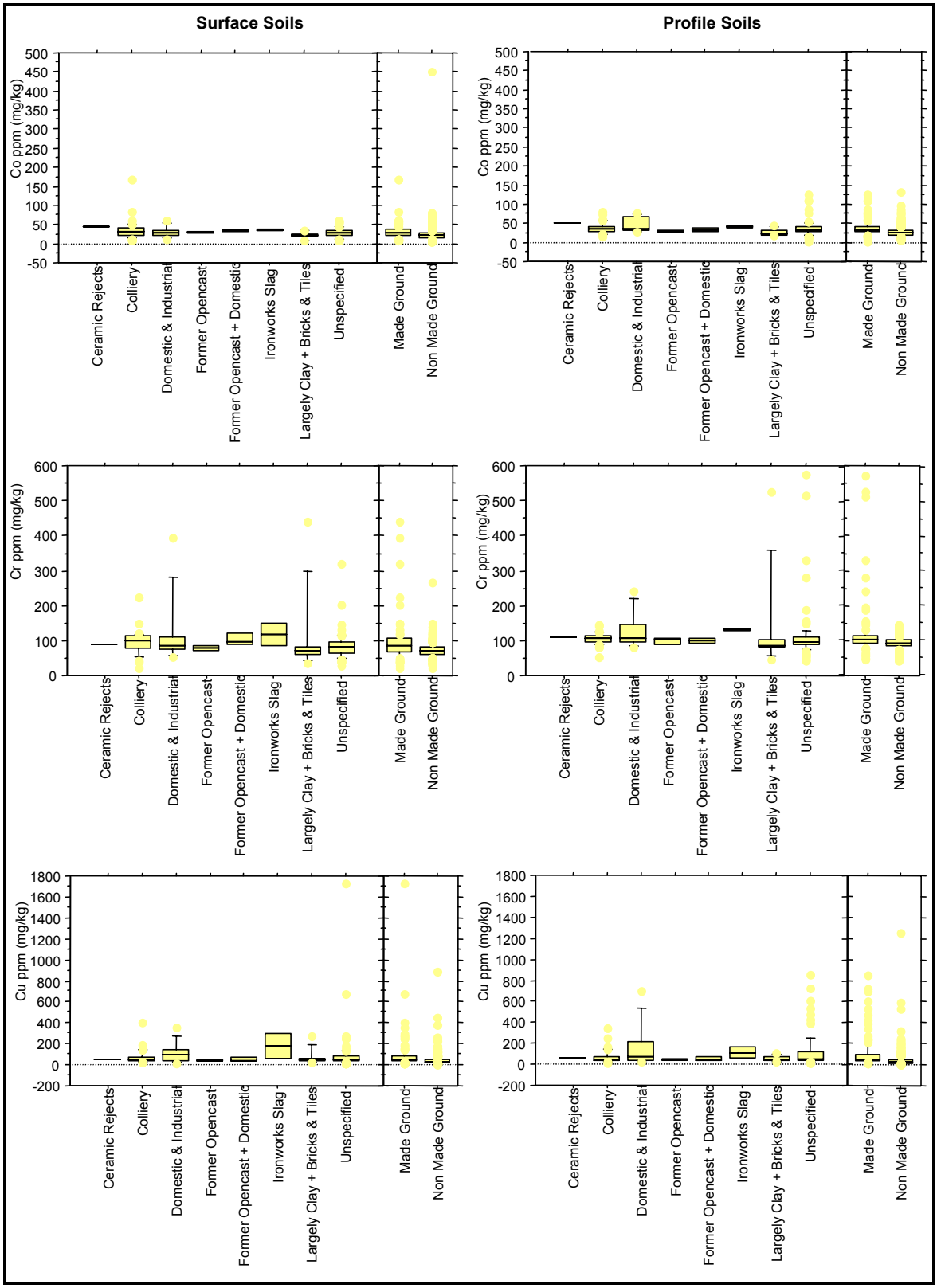

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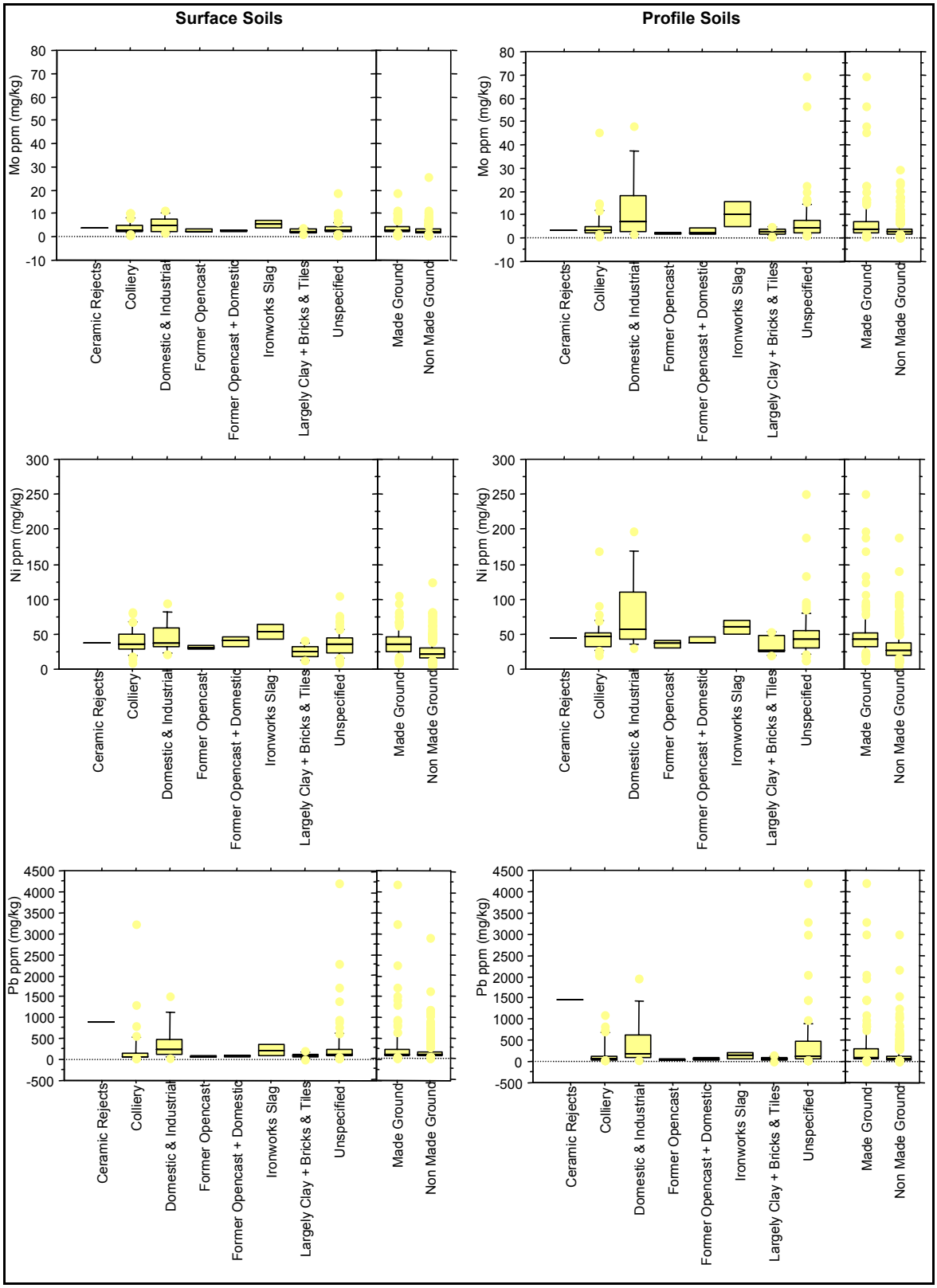

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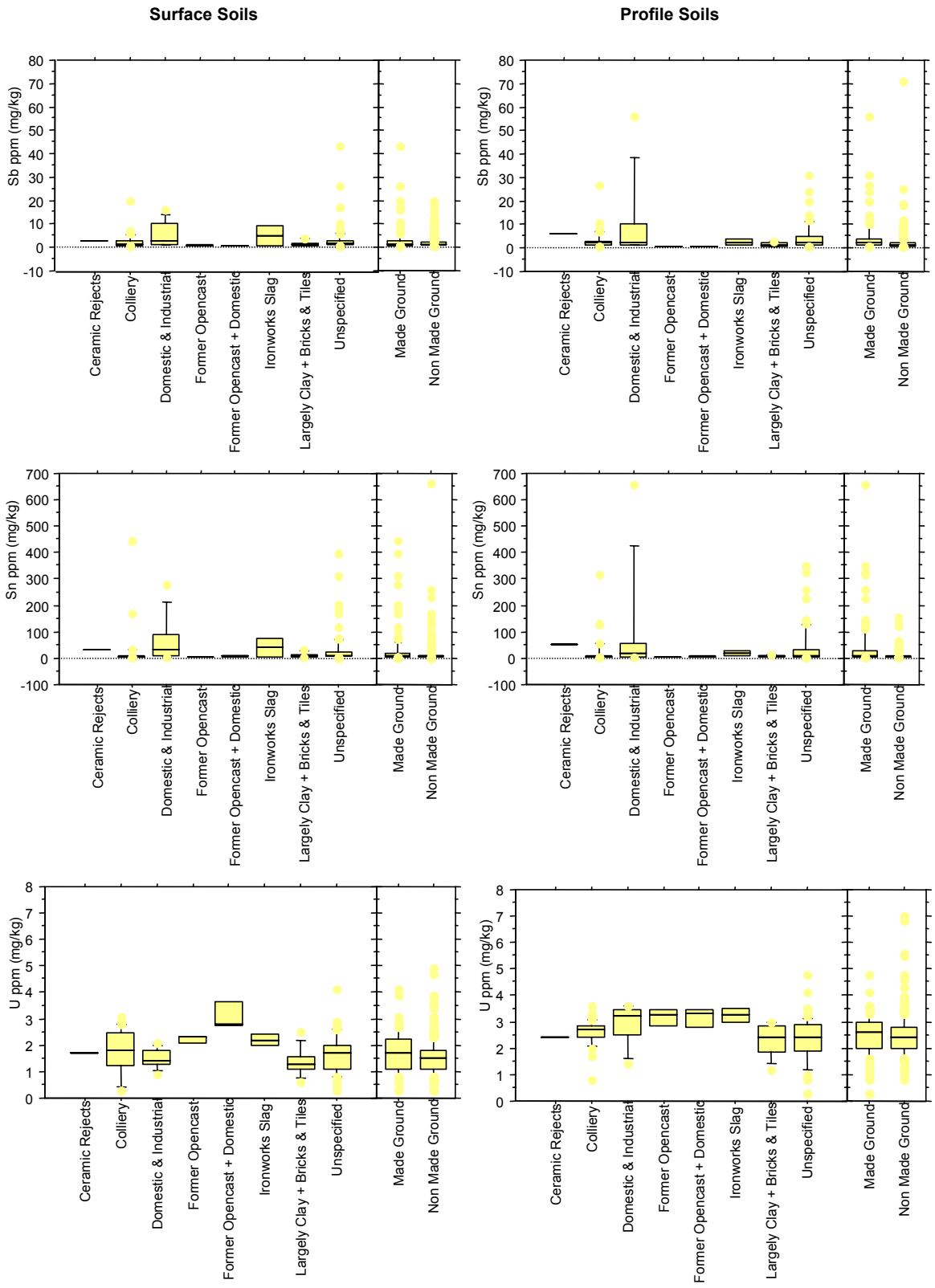

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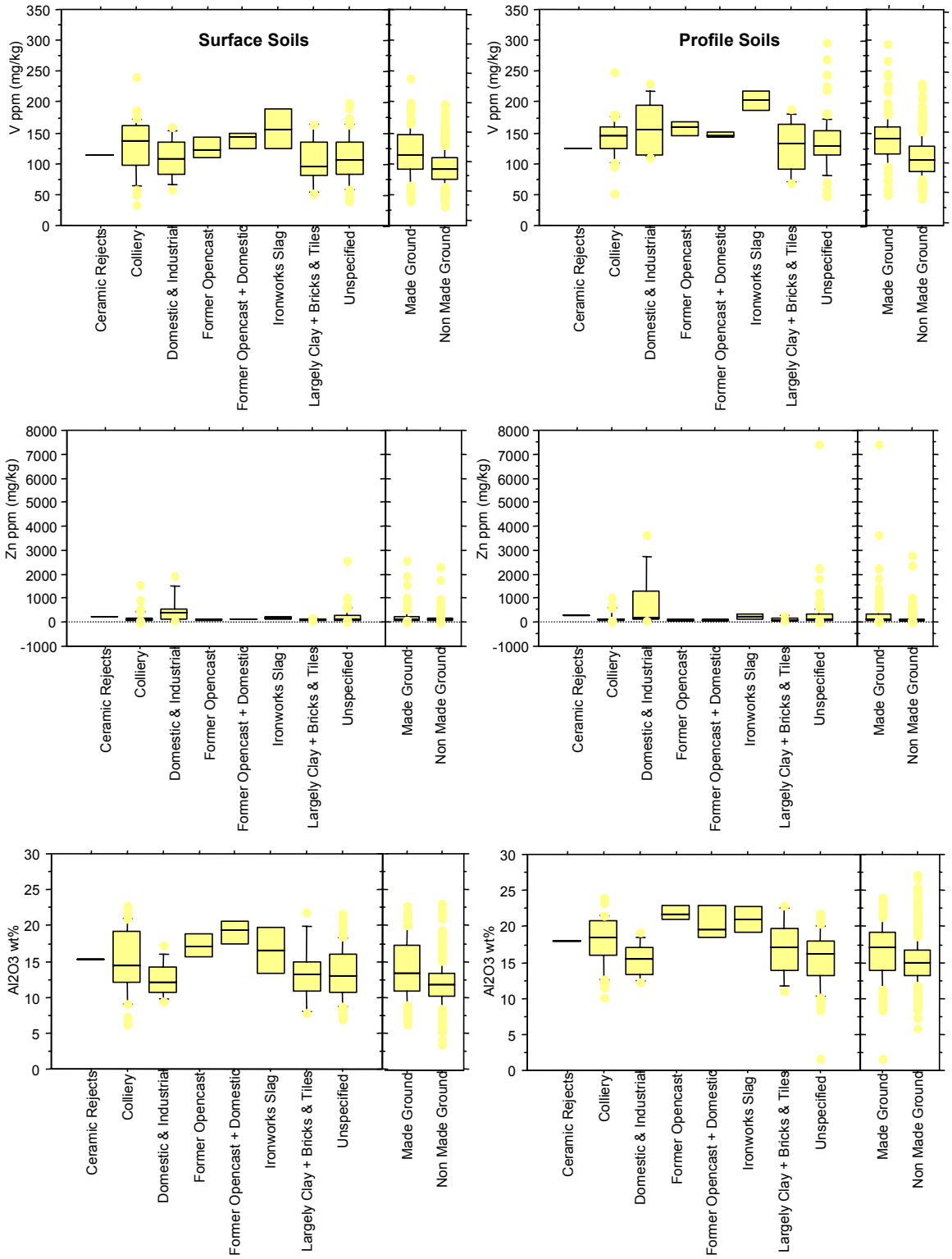


Figure 6.15 cont.

6.7 COMPARISONS WITH OTHER REGIONS

In addition to the comparisons between the urban soils and the immediate rural hinterland described in Chapter 5 of this report, the results were compared with regional and national soil data and urban areas elsewhere to assess the geochemistry of Stoke-on-Trent in the wider context. Several datasets were available for comparison with Stoke-on-Trent soils including rural surface soil data collected at a sample density of 1 per 2 km^2 over the Humber-Trent region by the BGS G-BASE programme (British Geological Survey, In Prep); urban surface soil data collected at a sample density of 4 per km^2 in other UK urban centres by the BGS GSUE project (Brown, In Prep, Brown 2003 and Morley and Ferguson 2001) and national top soil data generated by the Soil Survey of England and Wales Soil Inventory (McGrath and Loveland, 1992). Comparisons with G-BASE regional and data can be made directly as the sampling and analytical methods are the same as Stoke-on-Trent. Data from the national inventory provide an overview of surface soil total element concentrations (< 2 mm fraction) for England and Wales based on collection at a sample density of 1 per 25 km^2. However, it should be noted that although the sampling depth (0.15 m) was the same as that of G-BASE/GSUE surface soils, the analysis of the national samples was carried out by an extraction (aqua-regia 4:1 $HCl:HNO_3$ vol/vol followed by inductively coupled plasma atomic emission spectrometry (ICP-AES)) rather than a total technique. This is likely to lead to some bias in the results when comparing one dataset to the other.

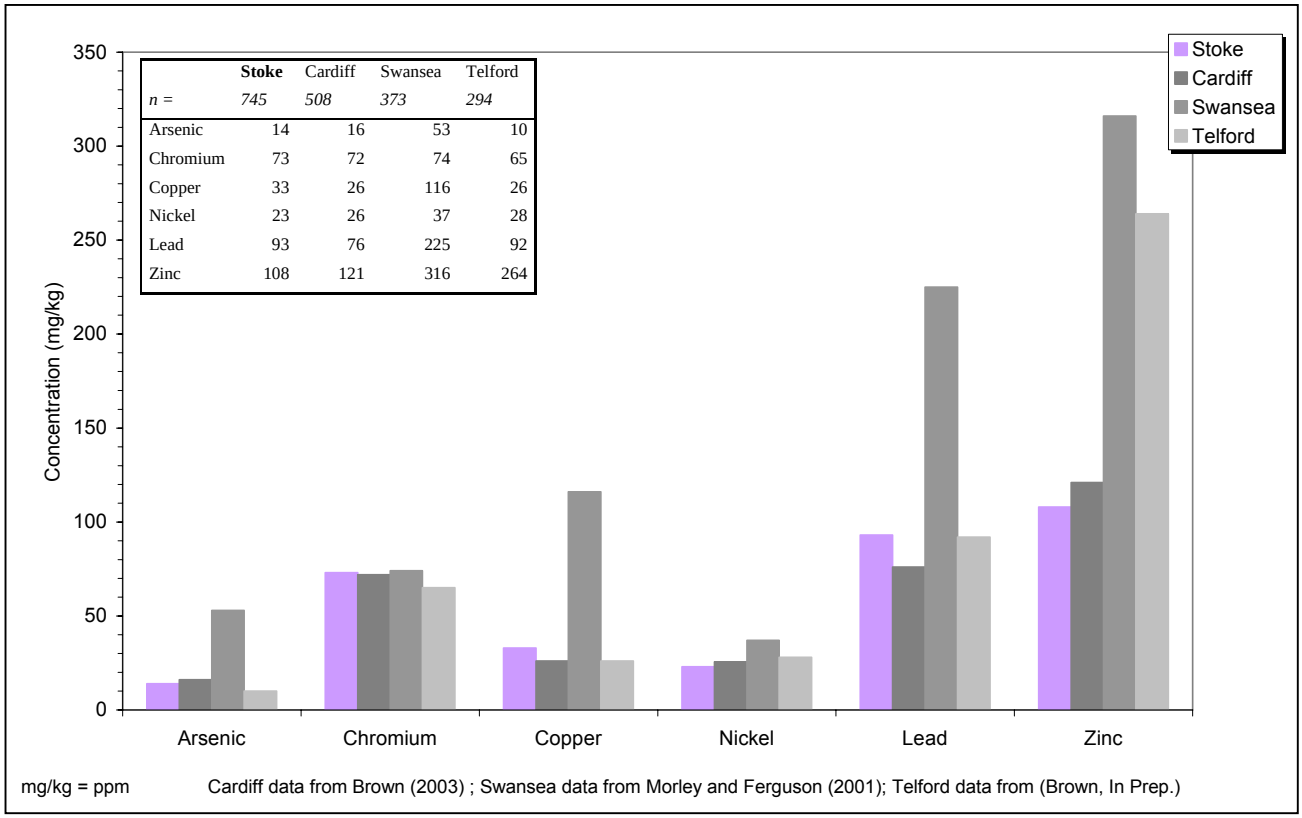
Summary statistics of the results for Stoke-on-Trent, G-BASE Humber-Trent regional surface soils (British Geological Survey, In Prep) and national topsoil data (McGrath and Loveland, 1992) are shown in Table 6.7. Median values for Ni and MgO are comparable between the urban-built and urban non-built Stoke surface soils and the Humber-Trent and national datasets. However, Ba and K_2O concentrations in the Stoke-on-Trent area are generally enhanced (x4 and x3 respectively) relative to national soil averages. Average (median) Al_2O_3, Fe_2O_3, P_2O_5, MnO, Cd, Cr, Co and Pb contents in urban soils are twice the national median value, (with the exception of Cd and P_2O_5 in profile soils) whereas CaO, Cu and Zn contents in surface soils are 1.5 times the national average. In general, metal and metalloid elements are elevated by 1.2 – 2 times the national average contents in the Stoke-on-Trent urban soils although no national baseline data are available for As, Sb, Sn, V, Hg, Mo and U (Environment Agency, 2002a) Highest values for Ba, Cd, P_2O_5, K_2O (surface and profile) and Co, Cu (surface only) and Fe_2O_3, Zn (profile only) in urban soils exceed the maximum concentrations of the national dataset. Whilst these comparisons with national averages are interesting, they do not take account of likely local background concentrations in the Stoke-on-Trent area.

Since Stoke-on-Trent is underlain primarily by Westphalian age Coal Measures, the G-BASE Humber-Trent dataset was sub-sampled to give a more extensive indication (958 samples) of regional background element concentrations in soils developed over this lithology than the immediate rural data around Stoke-on-Trent described in Chapter 5 of this report. Interestingly, median values reported for the Coal Measures sub-set and the whole Humber-Trent region are similar for the majority of elements (TiO_2 is an exception and is higher over the Coal Measures) reflecting the significant influence of this lithology on the regional averages as it underlies 15% of the Humber-Trent area. Median values for many elements (Al_2O_3, Sb, As, Ba, Cd, Ca, Cr, Co, Cu, Fe_2O_3, Pb, MgO, MnO, Hg, Mo, Ni, P_2O_5 and Zn) in the Stoke-on-Trent, Humber-Trent Coal Measures and Humber-Trent soils are similar and are all elevated compared to the national dataset (Table 6.7). This suggests that because of the presence of the Coal Measures, the rural background of the Stoke region is significantly higher than the national average as the national data are collected over a very large range of parent materials many of which contain low concentrations of metal and metalloid elements. It should be noted, however, that because of the very close relationship between the outcrop of the Coal Measures and industrialisation in the UK it is difficult to distinguish a truly natural geochemical baseline for this lithology and even over the large rural area of Humber-Trent the Coal Measure soils may demonstrate a mixed natural and man-made geochemical signal. None-the-less, for some elements, elevated concentrations over the Coal Measures are likely to be naturally rather than anthropogenically controlled. For example, results for Ba in Stoke-on-Trent soils compared to national averages suggested a four-fold increase in concentration, which might be interpreted as contamination. However, the Ba contents of urban soils are similar to those of the Humber-Trent Coal Measures probably due to the presence of minerals such as barite ($BaSO_4$). Thus the soils in Stoke-on-Trent are not enriched in Ba beyond natural levels. On the other hand, some element median concentrations are elevated in the urban environment over and above the Humber-Trent Coal Measure values indicating the additional influence of anthropogenic activity on the soil composition (for example Cu, Pb, Hg, Sn and Zn, Table 6.7). In the case of Pb, greater enhancement in the surface soils is probably indicative of atmospheric traffic pollution and historical use of lead-bearing paint etc in the urban area.

In order to compare the geochemical environment of Stoke-on-Trent and other urban areas surveyed by the GSUE project underlain by the Coal Measures, the distributions of selected elements (As, Cr, Cu, Ni, Pb and Zn) in surface soils are shown in Figure 6.16 and of Pb and Cr in Figure 6.17. Stoke-on-Trent median values are similar to those reported in both Telford (Brown, In Prep.) and Cardiff (Brown, 2003) but are lower than those in Swansea (Morley and Fergusson, 2001). Hence it can be concluded that Stoke-on-Trent soils show a significant urban industrial geochemical signature for several metal elements relative to rural background, however, the concentrations of these pollutants are similar to those of other urban centres and are lower than levels in Swansea, where metal smelting contributes significantly to the soil contaminant load.

Urban studies elsewhere have demonstrated similar enhancements of specific contaminants associated with urban and industrial activities including relationships between urban and rural background, for example in Edinburgh (Purves and Mackenzie, 1969), Richmond-on-Thames (Kelly et al., 1996) and Aberdeen (Paterson et al., 1996). However, many of the published studies on urban soil geochemistry in Britain are for restricted analytical suites of elements limiting comparisons with the GSUE data.

Similar systematic urban soil geochemical sampling has been carried out in Norway based on the collection of the top 2 – 3 cm of the soil profile at a sample density of 1km rather than 500 m across the urban area (Tijhuis et al., 2002). Soils were analysed by a pseudo total nitric acid ICP-AES technique and results presented as proportional symbol maps analogous to those for Stoke-on-Trent. Although the results are not directly comparable due to the differences in analytical techniques, with the exception of Zn, median metal concentrations in Stoke-on-Trent surface soils are 2 – 4 times those reported for Oslo reflecting the differences in geological setting and industrial history of the two urban areas.



	Stoke	Cardiff	Swansea	Telford
n =	*745*	*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 6.16 Bar chart showing the median concentrations of selected elements in Stoke-on-Trent surface soils compared to data from Swansea, Cardiff and Telford urban centres.

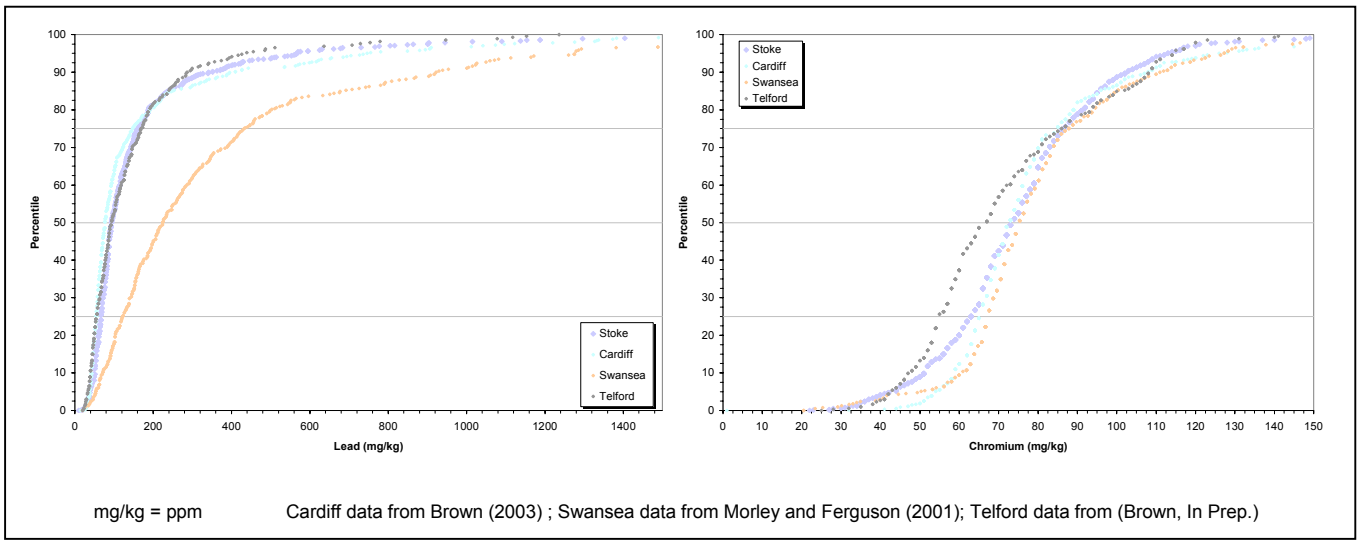


Figure 6.17 Percentile graphs of Cr and Pb concentrations in Stoke-on-Trent surface soils compared to data from Swansea, Cardiff and Telford urban centres.

6.8 SUMMARY

The main factors controlling the composition of soils in Stoke-on-Trent can be summarised as follows:

6.8.1 Geology

The Namurian age Millstone Grit sediments to the east of the region comprise fluvio-deltaic sandstones and mudstones. The quartz-rich quartz-cemented sandstones are generally resistant to weathering with low concentrations of other minerals and as a result form predominately sandy soils with low trace element concentrations and high SiO_2 values. Whilst the mudstones would weather to form more clay and silt rich soils with higher trace element concentrations, the high SiO_2 geochemical signature from the Stoke-on-Trent region indicates that the quartz-rich facies dominate this area.

The Westphalian age Coal Measures comprise intercalated sandstone, mudstone, limestone and coal horizons, which vary in proportion and thickness across the area. Soils over this lithology are generally rich in base metals (for example, CaO and MgO) and enhanced in many trace elements relative to other strata, particularly elements found in sulphide minerals (for example, Ni and Zn) and organic matter (for example V and Cu). However, it is very difficult to distinguish the truly natural background of soils developed over this rock type from the modern geochemical signature due to the extensive industrial and urban development associated with these strata since the Industrial Revolution (c. 1760 onwards) and resultant widespread point source and diffuse pollution.

The Westphalian age Barren Measures are compositionally similar to the Coal Measures in all aspects except for the lack of workable coals. In contrast, the extraction of clays for brick and tile manufacture was an important economic resource but these are generally much lower in trace element content than the coals. However, many coal mines were located on the outcrop of the Barren Measures working the concealed Coal Measures below giving rise to widespread colliery waste at the surface over this lithology. As a result, the soil geochemical composition over the Barren Measures is very similar to that of the Coal Measures.

The continental facies sandstones and conglomerates of the Triassic age Sherwood Sandstone Group, like the Namurian, weather to form sandy soils with low trace element concentrations with the exception that soils developed over the Sherwood Sandstone have higher zirconium (Zr) values indicating the presence of resistate minerals such as zircon. In addition to the naturally low concentrations of many trace metals in these sandstones and in the Namurian, neither of these groups of rocks were subject to the developmental pressures of industry and urbanisation to the extent of the other geological units in the study area due to their lower economic value. Hence the levels of man-made disturbance and diffuse pollution in soils over these strata are lower than for other soils in the area.

Boulder Clay deposits comprise highly heterogeneous sediments that may be derived locally or transported considerable distances prior to deposition. These factors may contribute to the indistinct geochemical character of soils developed over boulder clay in the Stoke region.

Soils developed over alluvium can be variable in their geochemical composition depending on the geology of the upstream catchment and the river flow. Coarse sandy alluvial material is generally low in trace elements whereas clay-rich alluvium can contain higher concentrations. However, in the Stoke-on-Trent area the flat topography characteristic of alluvial deposits has been the focus of development for the main transport routes and industry for over 200 years, especially along the River Trent, Lyme Brook and Fowlea Brook valleys, and the natural geochemical signature has been modified by the deposition of contaminants which can be widely dispersed downstream of source. The potential effects of contaminated floodplain soils on surface water quality have not been considered during this study, because stream and river waters do not form part of the GSUE project. However, it can be surmised that flooding events could lead to the remobilisation of contaminants from such soils as well as the deposition of more pollutants from riverbed sediments onto soils. Indeed, soil and sediment resources can contain considerable quantities of contaminants (Hudson-Edwards, 1999) and evidence in rural areas suggests that soils are a source term that may need to be included in a tiered risk screening approach for contamination of surface waters (DETR, 2000). It is well established that the erosion of flood plain materials is a source of sediment to natural rivers and whilst the complexity of highly engineered urban water courses would need to be assessed, in the Stoke area the Trent-Lyme-Fowlea river system is known to actively erode coal spoil tips and this material is one of the main sources of sediment and alluvial material in the area.

6.8.2 Urban and Industrial Activity

The mining of coal and iron generates spoil heaps of waste materials that generally resemble the source lithologies in their trace element composition although local enhancements can occur. However, the extensive use of coal for power and local industry results in large quantities of coal ash waste, which is generally enriched in many refractory elements. In Stoke-on-Trent, the widespread use of this material for urban fill accounts for the high concentrations of Fe_2O_3, CaO, MgO, Al_2O_3, SiO_2, V, Ni and Cr and multi-element anomalies in soils at various locations throughout the study area.

Waste slag derived from steel manufacturing is often rich in base metals (CaO and MgO) and phosphates as well as in metals such as Fe and Ni and trace elements such as V and Cr, which are used in the production of alloys. Environmental contamination can occur in association with these wastes, from the raw materials used in the production process and from the use of steel products in local engineering industries. Several of the multi-element soil anomalies in Stoke-on-Trent are associated with the extensive history of steel manufacture in the area.

The pottery and ceramics industries generate waste that is base-rich due to the incorporation of calcined bone (calcium phosphate) with kaolinite clay to produce ‘bone china’. Other metals such as Ba, Ti or Fe are added to alter the properties of the china for specific uses. In the Stoke-on-Trent area, an important subsidiary of the pottery industry was the supply of ceramic pigments and glazes. This became a specialised branch of industrial chemistry as it relied on materials that could withstand not only the lower temperature earthenware kilns but also the high temperatures required to produce china and porcelain ware. Ceramic pigments usually comprised refractory oxides or silicates of metals such as Cd, Cr, Cu, Co, Fe, Mn, Ni, U, V and Zn whereas glazes contain silica (SiO_2) and alumina (Al_2O_3) with additives such as calcium oxide (lime), Pb, Sn-oxides and other minerals such as ilmenite ($FeTiO_3$).

Although the modern day industry is particularly well regulated in terms of the disposal of such potentially harmful substances and industrial emissions are minimalised, the historical legacy of atmospheric dispersion and dumping of metal oxide materials in landfill and made ground are indicated by localised multi-element anomalies in Stoke-on-Trent soils.

Several urban studies have highlighted the contaminative effect of transport networks on soils (for example Kelly et al., 1996) and although no clear relationship was found between high element values and the major road and rail network in Stoke-on-Trent, soils in the Stockton Brook Gap (UK NGR 3916E, 3520N) located along the Caldon Canal, show systematically elevated element concentrations contrary to the geological signature for the underlying Namurian Millstone Grit. Originally this canal was used for the transport of industrial products to and from Stoke, especially limestone from the Caldon Low quarries (UK NGR 408E, 348N) and this geochemical signature may result from the inadvertent dispersion of such raw materials during transport. The disposal of canal dredgings is recognised as a potential source of contaminants in soils. Dredging is essential for the maintenance of open canal routes (Beckwith et al., 1995), and is used in some cases for the amelioration of both water and sediment quality within a canal system (Bromhead and Beckwith, 1994). Prior to 1988 the disposal of dredgings was not licensed (Beckwith et al., 1995) and may have resulted in the deposition of canal sediments to soil in this study region, which may also explanation the anomaly seen along the Caldon Canal

Multi-element anomalies observed at Newstead (UK NGR 388E, 340N – 389E, 340N) may arise from former sewage farm treatment and disposal processes in the area.

Domestic garden soils can show very varied geochemical signatures depending on the management schemes adopted by local residents. Common practices through time have included the use of coal ash, farm wastes (chicken, horse and pig manures), commercial fertilisers which commonly contain nitrogen, phosphorous and potassium as well as essential plant trace elements such as Zn and Cu, liming (application of CaO) and pesticide use. For example, the Dresden area (UK NGR 391E, 342N) of the city shows evidence of nutrient enrichment in domestic gardens.

Urban regeneration programmes may include the construction of flower beds and landscaping using wholly imported ‘clean’ top soil, which may provide the only sampling location within the 500 x 500 m sampling area of the survey. Sampling of these locations can give rise to anomalously low concentrations of elements in surface soils in relation to the surrounding background. Whilst these values are representative for use in any plant and human risk models, which deal with exposure to topsoils, they may not provide a reasonable estimate of soil contamination in the surrounding environment or at depth.

TABLE 6.7 SUMMARY STATISTICS OF ELEMENT DISTRIBUTIONS IN STOKE-ON-TRENT RURAL AND URBAN SOILS COMPARED TO DATA FROM THE NATIONAL SOIL INVENTORY OF ENGLAND AND WALES AND RURAL G-BASE SOIL DATA FROM THE HUMBER-TRENT REGION

Statistics	Soil Type	Al_2O_3	Sb	As	Ba	Cd	CaO	Cr	Co	Cu	Fe_2O_3	Pb	MgO	pH
ppm = mg/kg		(wt %)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(wt %)	(mg/kg)	(mg/kg)	(mg/kg)	(wt %)	(mg/kg)	(wt %)	
Minimum	Urban A	3.4	0.5	2	175	0.4	0.03	22.0	4.0	7	0.6	10	0.1	2.9
	Urban S	1.6	0.5	4	146	0.4	0.03	41.0	1.0	7	1.7	15	0.1	nd
	Rural S	nd	0.5	4	253	1.0	0.08	23.0	2.0	4	0.6	9	0.1	nd
	National A	0.1	nd	nd	11	<0.2	0.007	0.2	0.2	1	0.06	3	0.007	3.1
Maximum	Urban A	23.0	43.0	136	3590	43.0	10.92	441.0	452.0	1729	32.3	4208	3.0	8.0
	Urban S	27.2	71.0	167	4269	408.0	17.80	574.0	133.0	1260	43.7	4207	3.7	nd
	Rural S	nd	7.0	47	2348	6.0	29.54	116.0	75.0	335	16.9	301	8.2	nd
	National A	15.0	nd	nd	2973	40.9	47.56	838.0	322.0	1508	37.8	16338	10.4	9.2
Mean	Urban A	12.2	2.0	16	512	1.7	0.99	76.3	24.7	51	5.7	176	0.7	5.5
	Urban S	15.4	2.3	18	579	1.4	1.07	94.9	28.1	56	6.9	164	0.8	nd
	Rural S	nd	1.3	14	516	1.1	0.78	72.1	19.3	26	4.7	57	1.6	nd
	National A	5.3	nd	nd	141	0.8	1.94	41.2	10.6	23	4.0	74	0.6	nd
Median	Urban A	11.9	1.0	14	454	2.0	0.57	73.0	22.0	33	5.2	93	0.6	5.4
	Urban S	15.1	1.0	14	496	0.4	0.44	92.0	26.0	33	6.5	61	0.7	nd
	Rural S	nd	1.0	13	462	1.0	0.54	72.0	19.0	23	4.5	47	1.3	nd
	National A	5.3	nd	nd	121	0.7	0.46	39.3	9.8	18	3.8	40	0.5	6.0
	Built A	12.0	2.0	15	490	2.0	0.73	71.0	23.0	41	5.6	128	0.6	5.7
	Non-built A	12.0	1.0	13	425	1.0	0.47	75.0	21.0	26	4.9	80	0.5	5.1
	Humber A	14.0	4.0	17	444	1.0	0.59	84.0	26.0	30	6.6	76	0.8	nd
	Hum Coal A	12.0	1.0	15	504	2.0	0.64	77.0	24.0	38	5.8	104	0.6	5.4

Urban = GSUE soils for Stoke-on-Trent (n = 747)

Rural = G-BASE rural soils around Stoke-on-Trent (n = 368)

National = National Soil Inventory of England and Wales (McGrath and Loveland, 1992) (n = 5692)

Built = Stoke on Trent soils within the urban-built environment (n = 362)

Non-built = Stoke-on-Trent soils outside the urban-built environment (n = 380)

Humber = G=BASE rural soils from the Humber-Trent regional atlas area (British Geological Survey, In Prep) (n = 6575)

Hum Coal = G-BASE rural soils over Coal Measures from the Humber-Trent regional atlas area (British Geological Survey, In Prep) (n = 958)

A = Surface Soils (< 2 mm)

S = Profile Soils (< 150 µm)

LOI = Loss on Ignition

Nd = no data

Table 6.7 cont

Statistics	Soil Type	MnO (wt %)	Hg (mg/kg)	Mo (mg/kg)	Ni (mg/kg)	P_2O_5 (wt %)	K_2O (wt %)	SiO_2 (wt %)	Sn (mg/kg)	TiO_2 (wt %)	U (mg/kg)	V (mg/kg)	Zn (mg/kg)	LOI (wt %)
Minimum	Urban A	0.03	0.005	0.6	5.0	0.06	0.53	20.6	1	0.10	0.3	23	6	0.6
	Urban S	0.02	nd	0.2	6.0	0.03	0.42	12.6	2	nd	0.3	41	20	nd
	Rural S	0.01	nd	0.2	5.0	0.03	0.79	nd	1	0.35	0.5	11	13	nd
	National A	0.0004	nd	nd	0.8	0.008	0.007	nd	nd	nd	nd	nd	5	0.1
Maximum	Urban A	0.67	7.22	25.8	124.0	3.74	3.60	78.1	662	1.39	4.9	241	2589	73.3
	Urban S	1.07	nd	69.1	250.0	1.42	4.20	76.9	657	nd	7.0	296	7408	nd
	Rural S	0.96	nd	5.5	86.0	0.83	5.74	nd	72	1.28	44.5	226	1032	nd
	National A	5.50	nd	nd	440.0	1.25	2.48	nd	nd	nd	nd	nd	3648	65.9
Mean	Urban A	0.15	0.25	2.9	27.1	0.34	1.57	60.0	17	0.62	1.5	95	156	12.6
	Urban S	0.16	nd	4.1	34.6	0.24	1.95	58.2	14	nd	2.4	114	170	nd
	Rural S	0.10	nd	1.5	23.9	0.25	2.57	nd	5	0.75	2.7	87	93	nd
	National A	0.10	nd	nd	24.5	0.17	0.60	nd	nd	nd	nd	nd	97	nd
Median	Urban A	0.13	0.14	2.4	23.0	0.29	1.52	60.9	7	0.62	1.5	89	108	11.7
	Urban S	0.14	nd	2.7	30.0	0.19	1.85	59.3	6	nd	2.4	108	90	nd
	Rural S	0.09	nd	1.4	23.0	0.22	2.53	nd	5	0.75	2.4	83	80	nd
	National A	0.07	nd	nd	22.6	0.15	0.56	nd	nd	nd	nd	nd	82	3.6
	Built A	0.14	0.17	3.0	25.0	0.32	1.55	61.0	9	0.60	1.4	91	130	11
	Non Built A	0.12	0.12	2.0	21.0	0.27	1.48	62.0	6	0.64	1.5	87	92	12
	Humber A	0.15	nd	3.0	24.0	0.27	nd	nd	6	0.90	2.6	102	101	nd
	Hum Coal A	0.14	0.15	3.0	25.0	0.30	1.53	59	8	0.66	1.7	99	115	13

7. Potential Impacts of Soil Geochemistry on Hydrogeological Resources in Stoke-on-Trent

By E L Ander, K Bateman and B Smith

7.1 HYDROGEOLOGY OF STOKE-ON-TRENT

The hydrogeology of the region is not extensively reviewed here, as the major purpose of this chapter is to assess a methodology for the utilisation of soil properties and geochemical data for the assessment of groundwater vulnerability.

In summary, the River Trent and its tributaries dominate the surface water hydrology. Rainfall to the area is around 740 to 860 mm per year, with c.500 mm being lost to evapotranspiration prior to forming aquifer recharge (Rees and Wilson, 1998). Recharge will, however, be affected in its distribution and quality by interactions with the urban environment. “Surface sealing” by impermeable constructed surfaces may focus recharge, and road drainage may focus both recharge and potential diffuse contaminants (Ander et al., 2001); the sources of recharge may also be from subsurface constructions and are complex to assess for an urban area (see for example, Lerner, 2002).

Westphalian Coal and Barren Measures sediments underlie the major part of the area. The groundwater in these strata are generally of poor chemical quality (for example, high chloride and sulphates) (Rees and Wilson, 1998, Wilson et al., 1992) over most of the study area where undermining has taken place (Wilson et al., 1992). Where these strata have not been undermined then the water is generally of high carbonate hardness and reasonable quality (Rees and Wilson, 1998). These strata are not a major source of water supply, due to their generally low yields or high yields but poor quality (Rees and Wilson, 1998). Much greater detail on the physical properties of this aquifer can be obtained from Jones et al. (2000b). The Millstone Grit is a higher yielding aquifer than the Westphalian sediments, with good quality water in general (Rees and Wilson, 1998), although no further data are available on this study region. The Sherwood Sandstone Group has only a small area of outcrop in the study region, but is the second most important aquifer in terms of public water supply in England (Allen et al., 1997). The only source protection zones defined within the study area are for sources in this aquifer (Figure 2.14) and cover the whole outcrop area within the study. The water quality is good, and characteristically soft water, with hardness <200 mg/l as $CaCO_3$ (Rees and Wilson, 1998). This major aquifer along with the Westphalian strata does not have a soil based groundwater vulnerability classification (Figure 2.15) in the study area, due to the urban nature of the region (see below). Quaternary deposits may be associated with higher water tables (for example, along floodplain deposits) or may result in perched water tables (for example glacial sands and gravels within argillaceous boulder clay deposits). The boulder clays can act as protective aquitards over these deposits, but where they are not present the sands and gravels are considered highly vulnerable to the rapid movement of pollutants to the groundwater and subsequent receptors such as surface water (Rees and Wilson, 1998).

Man-made deposits may also act as aquiclude, aquitard or aquifers depending upon the nature of the material. Perched water tables occurring within spoil heaps can cause particular problems with acidity and trace metals where these occur (Wilson et al., 1992). Another generally unquantifiable issue is that urban and industrial construction may lead to the breaching of hitherto impermeable superficial deposits, or thin confining beds, allowing preferential flow to groundwater, including any contaminants of concern. Therefore, the local hydrogeology is likely to be complex, comprised of many compartmentalised, and possibly poorly characterised, aquifer units of varying size. Additionally the classification of groundwater bodies under the newly implemented Water Framework Directive (WFD) (Environment Agency, 2002b) may move away from the concepts of major and minor aquifers as presently defined, in order to meet the requirements of the Directive. For these reasons, although the groundwater vulnerability calculations are related back to the underlying aquifers, the calculations are based solely on soil data, which was collected as part of this study.

7.2 EXISTING GROUNDWATER VULNERABILITY MAPPING METHODS

In most areas the current scheme of groundwater vulnerability mapping is based on the classification of the solid lithology into major, minor or non-aquifers as used by the Environment Agency (Environment Agency, 1998, Palmer and Lewis, 1998). The aquifer classification is based upon the resource usage and potential of the strata of concern, and is augmented by the expected ability of the soil to impart a protective function to the groundwater, by retarding recharge and attenuating potential contaminants. The function of drift deposits cannot be mapped due to the complexities of establishing continuity of less permeable horizons in three dimensions. These classifications are also designed to be used for diffuse pollutant loadings and where point sources exist, or the normal soil/ unsaturated zone sequence has been interrupted, the vulnerability classification must be assessed carefully to see if it is still valid for the site specific conditions encountered (Palmer and Lewis, 1998). Where extensive urban areas occur the suffix U is applied to the minor or major aquifer classes (Figure 2.15 and Environment Agency, 1997), indicating that the soil information cannot be used (as soils have not been systematically mapped in urban areas of England and Wales).

7.3 SOIL GEOCHEMISTRY LEACHING POTENTIAL METHODOLOGY

In order to examine the likely downward movement of contaminants in soils towards groundwater resources, a leaching potential model was tested in the Stoke-on-Trent area. The method used (ISO, 2001) relates the soil pH, organic carbon, clay and sesquioxide contents to the likelihood of 11 elements, for which the method has been calibrated, leaching to underlying groundwater. Further information is required on the net infiltration and depth to groundwater to complete the full methodology. For the reasons discussed above, these data were not acquired in this study, and are likely to be complex for this heavily industrialised and geologically diverse area. Thus, the leaching results are presented pertaining purely to the soil characteristics as follows.

The pH value measured in the soil is compared against a tabulation for each element of interest for each soil of interest. This value of 'binding force' for that element to the soil, is then used to determine the extent of the influence of the soil clay, organic carbon and sesquioxide in sorbing the elements within the soil and thus attenuating their progress to groundwater. This methodology is founded on field and pot experiments (Blume and Brummer, 1991) and is based on the pH-dependant variable surface charges found on clays, iron oxides and organic carbon compounds, which dictate the degree and nature of surface sorption bonds of elements such as Zn and Pb. Standard texts provide more detail on the mechanisms behind these soil, water and mineral interactions (Brady and Weil, 1999 and McBride, 1994).

The soil pH is compared to the binding force threshold pH values shown in Table 7.1. Where the soil pH is greater than or equal to the value in the top row, the binding force listed below for the element(s) of interest is applied to that soil for that element (note that each element must be scored separately for each soil).

TABLE 7.1 BINDING FORCE VALUES FOR PH

pH:	2.5	2.7	3.2	3.7	4.2	4.7	5.2	5.7	6.2	6.7
Cd	0.0	0.5	1.0	1.5	2.0	2.5	3.5	4.0	4.5	5.0
Mn	0.0	1.0	1.5	2.0	2.5	3.0	4.0	4.5	5.0	5.0
Ni	0.0	1.0	1.5	2.0	2.5	3.0	4.0	4.5	5.0	5.0
Co	0.0	1.0	1.5	2.0	2.5	3.0	4.0	4.5	5.0	5.0
Zn	0.0	1.0	1.5	2.0	2.5	3.0	4.0	4.5	5.0	5.0
Al	1.0	1.5	2.0	3.0	3.5	4.5	5.0	5.0	5.0	5.0
Cu	1.0	1.5	2.0	3.0	3.5	4.5	5.0	5.0	5.0	5.0
Cr(III)	1.0	1.5	2.0	3.0	3.5	4.5	5.0	5.0	5.0	5.0
Pb	1.0	2.0	3.0	4.0	5.0	5.0	5.0	5.0	5.0	5.0
Hg	1.0	2.0	3.0	4.0	5.0	5.0	5.0	5.0	5.0	5.0
Fe(III)	1.5	2.5	3.5	5.0	5.0	5.0	5.0	5.0	5.0	5.0

Where the soil pH is less than or equal to the threshold pH shown in Table 7.2, the lookup value for organic carbon, clay and sesquioxide for each element(s) of interest is carried forward to be used in conjunction with the tables below to derive a binding force score for each of these parameters, for each element in each soil being characterised.

TABLE 7.2 LOOKUP VALUES FOR ORGANIC CARBON, CLAY AND SESQUIOXIDES

METAL	Threshold pH	Organic carbon	Clay	Sesquioxide
Cd	6.0	4.0	2.0	3.0
Mn	5.5	2.0	3.0	3.0
Ni	5.5	3.5	2.0	3.0
Co	5.5	3.0	2.0	3.0
Zn	5.5	2.0	3.0	3.0
Al	5.0	5.0	4.0	4.0
Cu	4.5	5.0	3.0	4.0
Cr(III)	4.5	5.0	4.0	5.0
Pb	4.0	5.0	4.0	5.0
Hg	4.0	5.0	4.0	5.0
Fe(III)	3.5	5.0	5.0	5.0

The lookup value (row one, columns 3 to 6 in Table 7.3) for each element in each soil derived from Table 7.2 is used as a matrix with the measured organic carbon content (column 2, Table 7.3) to derive an organic binding force value for each element in each soil tested, and added to the soil pH binding force value derived from Table 7.1.

TABLE 7.3 BINDING FORCE VALUES FOR ORGANIC CARBON

Humic Type	Percent	2.0	3.0	4.0	5.0
sapric	<1	0.0	0.0	0.0	0.0
sapric	1-2	0.0	0.0	0.0	0.5
sapric	2-4	0.0	0.0	0.5	1.0
sapric	4-8	0.0	0.5	0.5	1.0
sapric	8-15	0.5	0.5	1.0	1.5
sapric	>15	0.5	1.0	1.5	2.0
hemic		0.5	0.5	1.0	1.5
fibric		0.0	0.5	0.5	1.0

The lookup value (row one, columns 2 to 5 in Table 7.4) for each element in each soil derived from Table 7.2 is used as a matrix with the measured clay content (column 1,Table 7.4) to derive a clay binding force value for each element in each soil tested, and added to the cumulative soil binding force for each element in each soil.

TABLE 7.4 BINDING FORCE VALUES FOR CLAY

Clay content (%)	2	3	4	5
< 5	0.0	0.0	0.0	0.0
> 5-12	0.0	0.0	0.5	0.5
>12-25	0.0	0.5	0.5	1.0
25-45	0.0	0.5	1.0	1.5
>45	0.5	1.0	1.5	2.0

The lookup value (row one, columns 2 to 4 in Table 7.5) for each element in each soil derived from Table 7.2 is used as a matrix with the observed sesquioxide content (column 1, Table 7.5) to derive a sesquioxide binding force value for each element in each soil tested, and added to the cumulative soil binding force for each element in each soil.

TABLE 7.5 BINDING FORCE VALUES FOR SESQUIOXIDES

Oxide effect	Chroma:Value ratio where Hue ≤7.5		
	0-1	1-1.5	>1.5
3	0.0	0.5	1.0
4	0.0	1.0	1.5
5	0.0	1.5	2.0

The final score is adjusted back to the maximum value of 5 if the cumulative total is greater than 5. This value is compared against the qualitative ranking scheme shown in Table 7.6. This classification is then applied to the final scores, and the data displayed for each element in each soil in Appendix 7.1a and b.

TABLE 7.6 QUALITATIVE RANKING OF LEACHING ATTENUATION POTENTIAL

Soil binding force value	Classification of leaching attenuation potential
-9999	Missing data
0	None
≥1	Very low
≥2	Low
≥3	Moderate
≥4	High
5	Very high

After the application of this score, it is possible in the original method (ISO, 2001) to use effective recharge and depth to groundwater to further assess the vulnerability of the groundwater to contaminants leached from the soil. This has not been attempted here for the reasons discussed above. It can be seen that either a very high attenuation potential or a very deep water table would give a much lower groundwater vulnerability than does low attenuation capacity, or very close proximity of the water table.

7.4 APPLICATION TO THE STOKE-ON-TRENT SOIL GEOCHEMICAL DATA

LOI and pH were determined in Stoke-on-Trent surface soils as part of the systematic survey and these data are directly applicable to the ISO (2001) methodology. However, clay content is not determined routinely by the GSUE project and was derived from field observations on soil texture. The soil clay content was estimated using the horizontal and angled lines shown on the soil texture classification diagram in Figure 7.1. Thus, the ‘clay’ and ‘silty clay’ classifications noted in the field equate to the >45% clay class shown in Table 7.4. The rules governing the conversion of GSUE soil textures to the classes shown in Table 7.4 are shown in Table 7.7. The classification of sesquioxide content required for the ISO method was determined using GSUE soil colour observations. Where a shade of yellow (‘YE’) or red (‘RE’) was recorded, the maximum score was applied and for all other soils the minimum score was applied.

TABLE 7.7 SOIL TEXTURE CONVERSIONS TO CLAY CONTENT

Texture	Clay percentage classification
CLAY	50
SICL	50
SACL	15
SILT	10
SASI	20
SAND	1

The methodology was developed to run as a batch process within a worksheet environment to facilitate the rapid handling of 11 elements per soil for over 700 soils. This method allows the results to be imported into a GIS package for rapid spatial analysis and presentation of the results. The method does not require any geochemical data to be present for the elements of interest, however the Stoke soil geochemical survey has collected data for the 11 elements of interest (Annex 1) and these can be compared with the outputs from the groundwater vulnerability classification.

The results derived from this method provide a potential vulnerability for the specific elements studied, which does not relate to actual concentrations of these elements in soil or groundwater. The results for the 11 elements calibrated by Blume & Brummer (1991) are shown in Appendix 7.1a. It can be seen that the centre of the urban and industrial area is characterised by low leaching potential for most elements tested at most locations. The factor which controls this low leaching potential is the high pH found in these soils, relative to that of the soil pH binding force table values; this shows that most elements in most soils throughout the study area receive a score of around 5 (Table 7.1) in this first calculation, and are therefore insensitive to variations in the other parameters required. An additional facet of the ISO method invokes the clay content of the subsoil; however, the model was found to be wholly insensitive to this factor (Appendix 7.1b).

Comparing the element distribution maps in Annex 1 to the potential vulnerability maps in Appendix 7.1a shows that most high concentrations of elements occur where the groundwater vulnerability due to soil leaching is predicted to be low. This probably represents a circular argument, as the fundamental dichotomy between soil and groundwater vulnerability, is that low mobility towards groundwater indicates that contaminants are retained in surface soils. The soils with low groundwater vulnerability are generally those over the Coal Measures and the Mercia Mudstones. Appendix 7.1a shows that some soils over the Namurian Millstone Grit and Triassic Sherwood Sandstone Group have a higher leaching potential (see maps for Co, Cd, Mn and Zn). Thus, the loading of any of these contaminants onto soils in these areas would be of greater concern, particularly in respect of the fact that the groundwaters from the Triassic sandstones are utilised for public water supply (Figure 2.14).

7.5 APPRAISAL OF THE LEACHING MODEL TECHNIQUE

7.5.1 Value of the Methodology

The methodology has been shown to work well with the data collected in this study. The master variable is pH, which is measured directly, although inferences and classifications have to be made for the clay and sesquioxide contents, based on GSUE field observations. This is because the model is being developed in another European country where soil mapping is undertaken in a slightly different way to the UK (Figure 7.2 and Table 7.8), and because the data used here were collected as part of a systematic geochemical survey rather than for soil unit mapping purposes. These difficulties are not insurmountable, as shown above and since pH is the key parameter, the method would be more sensitive to the absence of these data, rather than any other. A major benefit of the method is that the data required to undertake a vulnerability assessment are readily collectable, require low cost analysis and can then be applied to any element or compound for which the method has been calibrated. This allows a 'tier-one' procedure in a staged risk assessment for hazards to groundwater to be undertaken. One of the key benefits of using data collected in a systematic geochemical survey is the measurement of the concentrations of the elements for which the vulnerability has been calculated, enabling a semi-quantitative assessment of the likelihood of leaching of those elements to underlying groundwater resources. Assessing the wider applicability of the model is recommended using regional soil data, where greater variations in soil pH, in particular, would test whether pH currently carries too great a weighting, resulting in too many soils attaining a maximum score of 5 (a potential problem in the present limited area dataset), which would reduce the usefulness of the method.

7.5.2 Limitations

A significant limitation to applying the method in urban areas is uncertainty in the assumption that the soil and unsaturated zones are present in their entirety and offer a protective function to the underlying groundwater resources. This problem also occurs in the more generalised existing regulatory method for assessing groundwater vulnerability (Figure 2.15 and section 7.2 of this report). The difficulties in approaching these very small scale variations have been discussed with respect to soil chemistry in section 7.3 of this report, and have been addressed by other researchers either at the very large scale (individual dwelling) mapping for groundwater resources or by taking entire urban areas over uniform groundwater body units as single recharge zones (Lerner, 2002). It is beyond the scope of this report to discuss these alternative methods any further.

The other limitation to applying the method on a wider basis in urban areas arises from the fact that like the existing groundwater vulnerability assessment, the method was developed for the application of diffuse pollutants to rural soils. Thus, where individual soil samples are contaminated enough to be considered point sources, careful consideration should be given as to the appropriateness of this technique.

The method can only be used for those substances for which it is calibrated, and there are elements of potential concern (generally, rather than in the current study area) which are currently absent from this calibration, such as As and U.

7.5.3 Potential Applications of the Method

Accepting the above limitations, the method can be used to provide a more region specific guide to groundwater vulnerability and in addition to the 11 inorganic elements has been calibrated for other substances including 47 organic compounds, which can be assessed using the same approach. The method allows geochemical survey data to be incorporated with existing geological and soil mapping information to provide a systematic approach to the risk of leaching of soil components to groundwater and these assessments will be enhanced in areas where it is possible to include information on effective recharge and depth to groundwater. The method could also be used in conjunction with water resource management tools, and may affect, for instance, the degree of water table rebound desirable in an area where the soils are susceptible to leaching substances of concern.

Table 7.8 the soil texture classification nomenclature derived in Germany (Boden, 1994)

Code	Name	Translation
Ss	reiner Sand	pure sand
Su2	schwach schluffiger Sand	lightly silty sand
Sl2	schwach lehmiger Sand	lightly loamy sand
Sl3	mittel lehmiger Sand	moderately loamy sand
St2	schwach toniger Sand	lightly clayey sand
Su3	mittel schluffiger Sand	moderately silty sand
Su4	stark schluffiger Sand	very silty sand
Slu	schluffig-lehmiger Sand	silty loamy sand
Sl4	stark lehmiger Sand	very loamy sand
St3	mittel toniger Sand	moderately clayey sand
Ls2	schwach sandiger Lehm	lightly sandy loam
Ls3	mittel sandiger Lehm	moderately sandy loam
Ls4	stark sandiger Lehm	very sandy loam
Lt2	schwach toniger Lehm	lightly clayey loam
Lts	sandig-toniger Lehm	sandy clayey loam
Ts4	stark sandiger Ton	very sandy clay
Ts3	mittel sandiger Ton	moderately sandy clay
Uu	reiner Schluff	pure silt
Us	sandiger Schluff	sandy silt
Ut2	schwach toniger Schluff	lightly clayey silt
Ut3	mittel toniger Schluff	moderately clayey silt
Uls	sandig-lehmiger Schluff	sandy loamy silt
Ut4	stark toniger Schluff	very clayey silt
Lu	schluffiger Lehm	silty loam
Lt3	stark toniger Schluff	lightly clayey silt
Tu3	mittel schluffiger Ton	moderately silty clay
Tu4	stark schluffiger Ton	lightly silty clay
Ts2	schwach sandiger Ton	lightly sandy clay
Tl	lehmiger Ton	loam clay
Tu2	schwach schluffier Ton	lightly silty clay
Tt	reiner Ton	pure clay

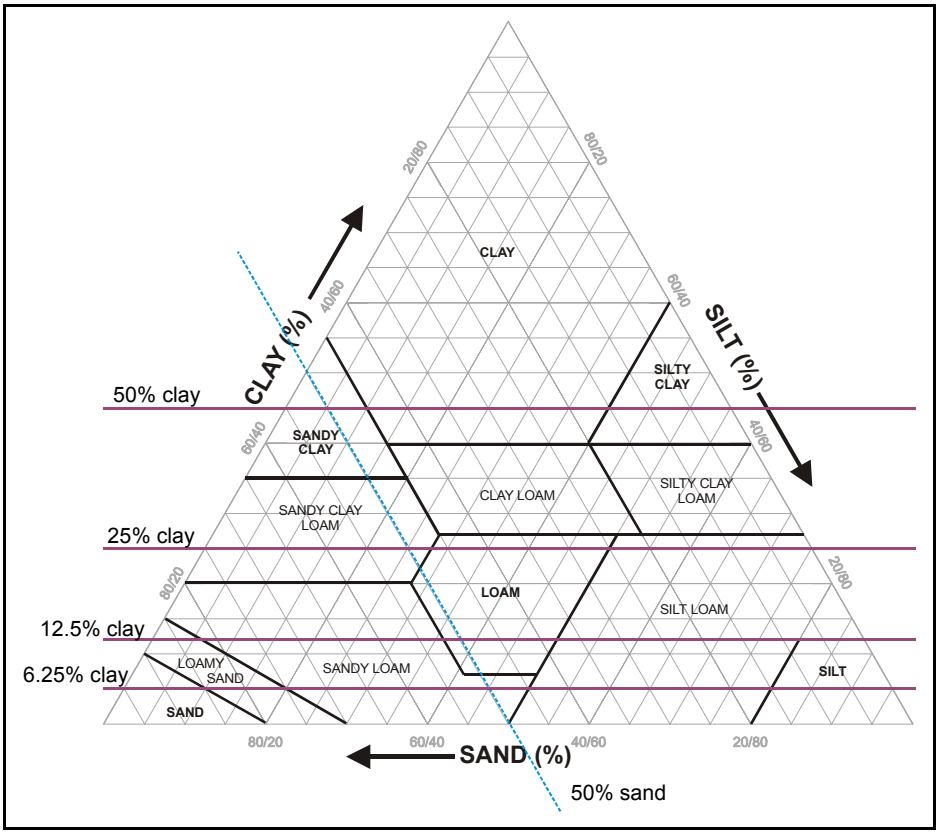


Figure 7.1 Comparison of soil texture data recorded by GSUE with that required for assessing leaching of metals from soil.

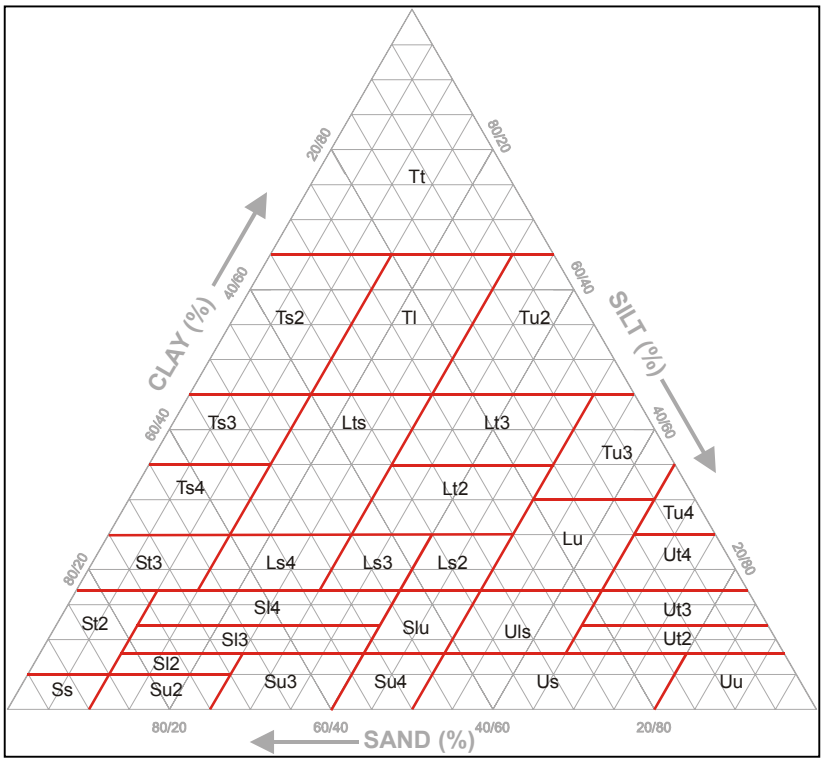


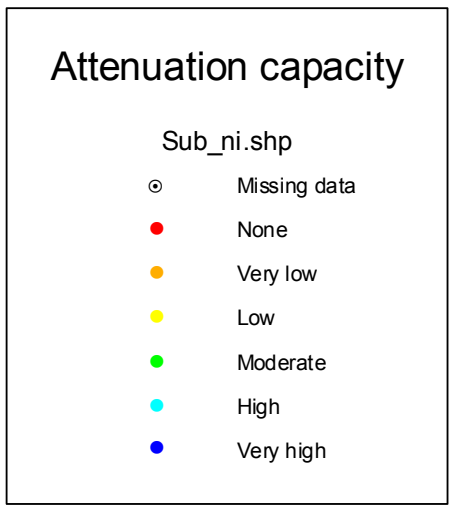
Figure 7.2 The German soil texture classification system (Boden, 1994).

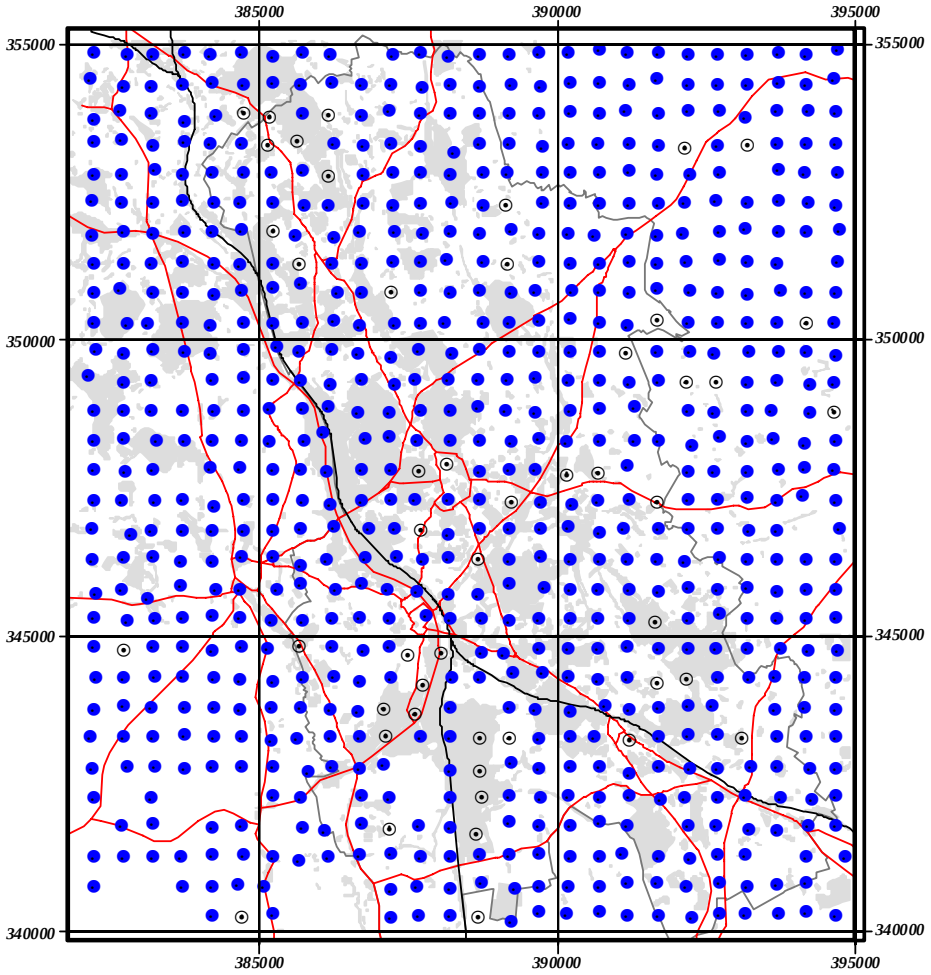
APPENDIX 7.1A BASE MODEL CONFIGURATION TO ASSESS POTENTIAL LEACHING OF INORGANIC SOIL CONTAMINANTS TO GROUNDWATER

Qualitative assessment of potential leaching from soils of inorganic contaminants

Aluminium

"base" model

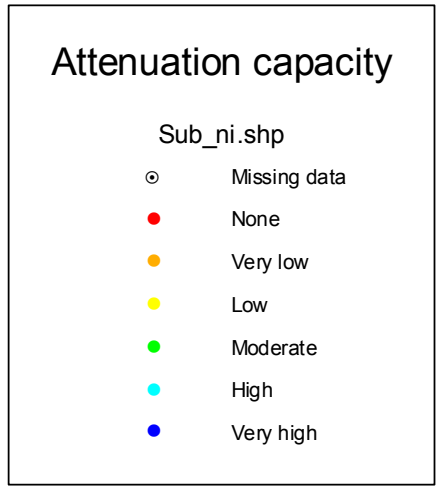


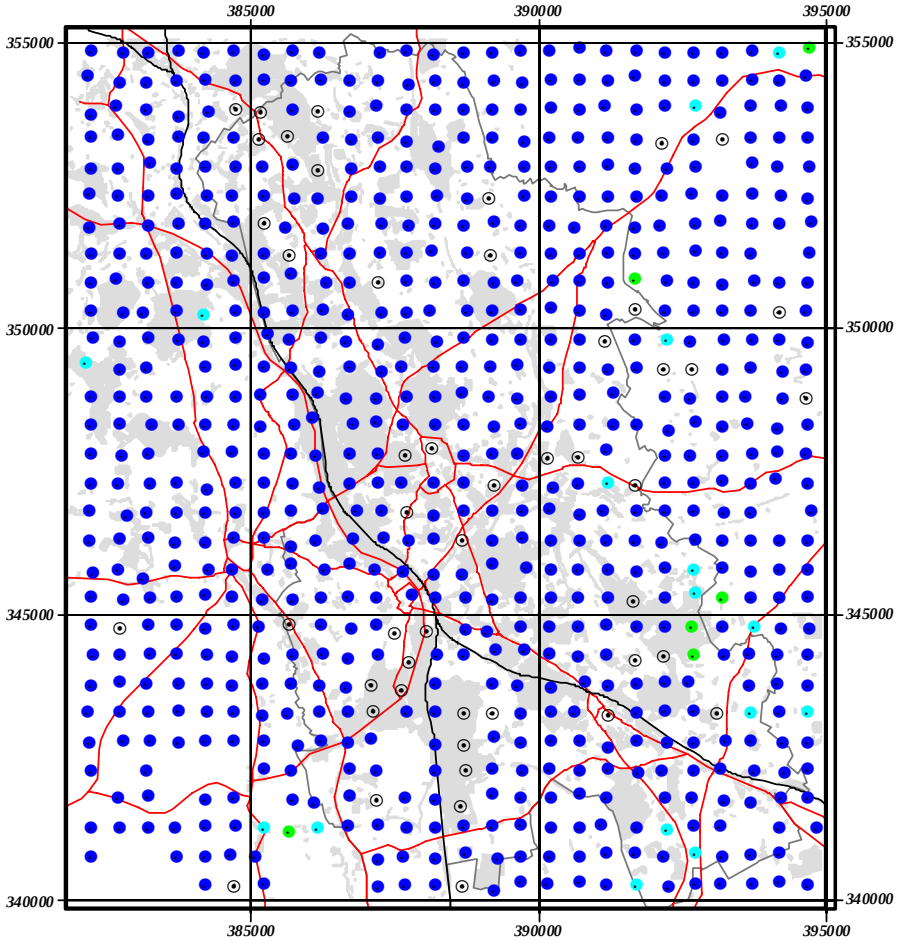


Qualitative assessment of potential leaching from soils of inorganic contaminants

Cadmium

"base" model

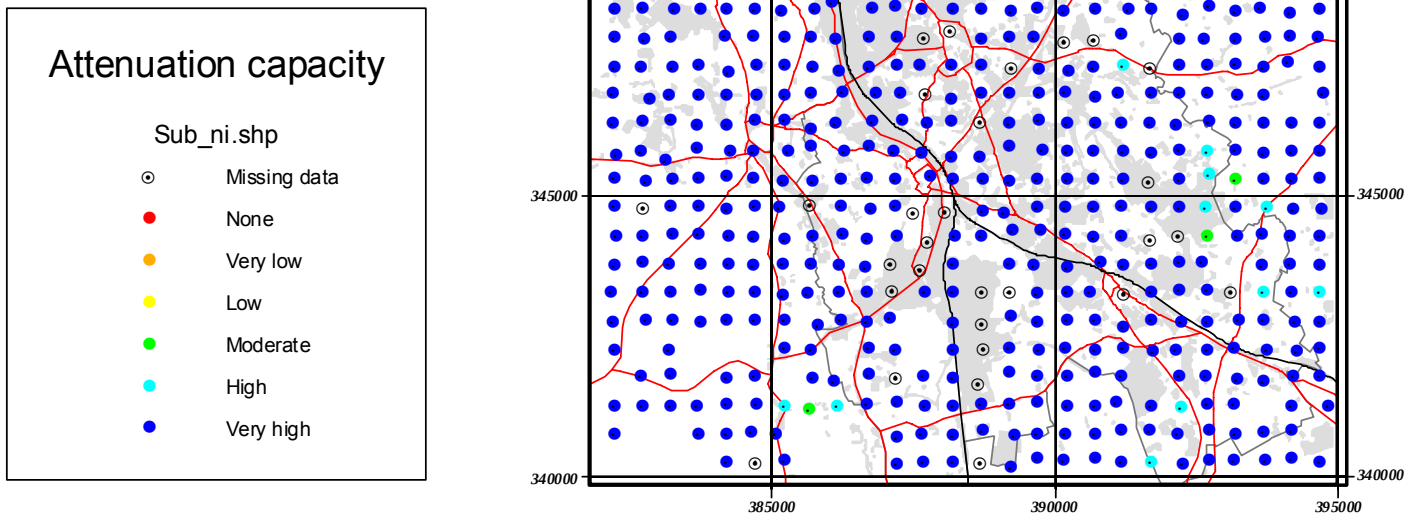




Qualitative assessment of potential leaching from soils of inorganic contaminants

Cobalt

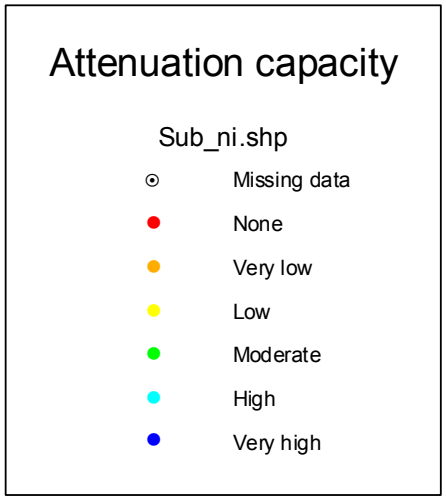
"base" model

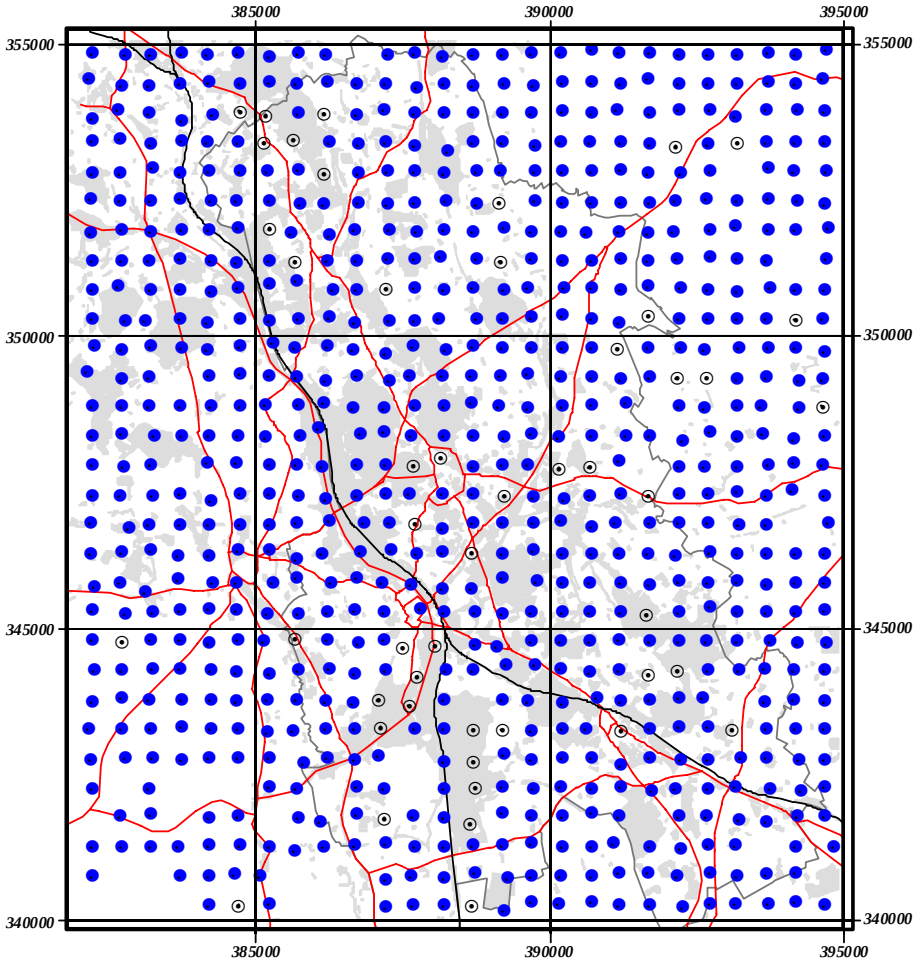


Qualitative assessment of potential leaching from soils of inorganic contaminants

Chromium

"base" model

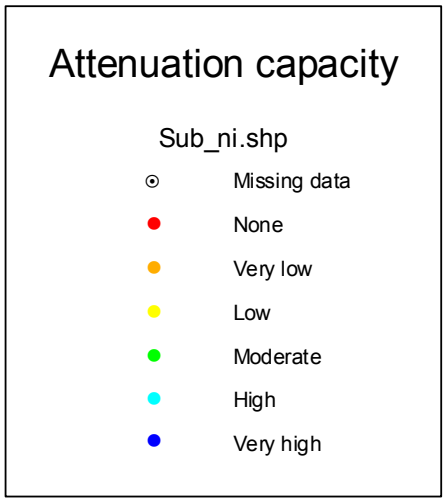


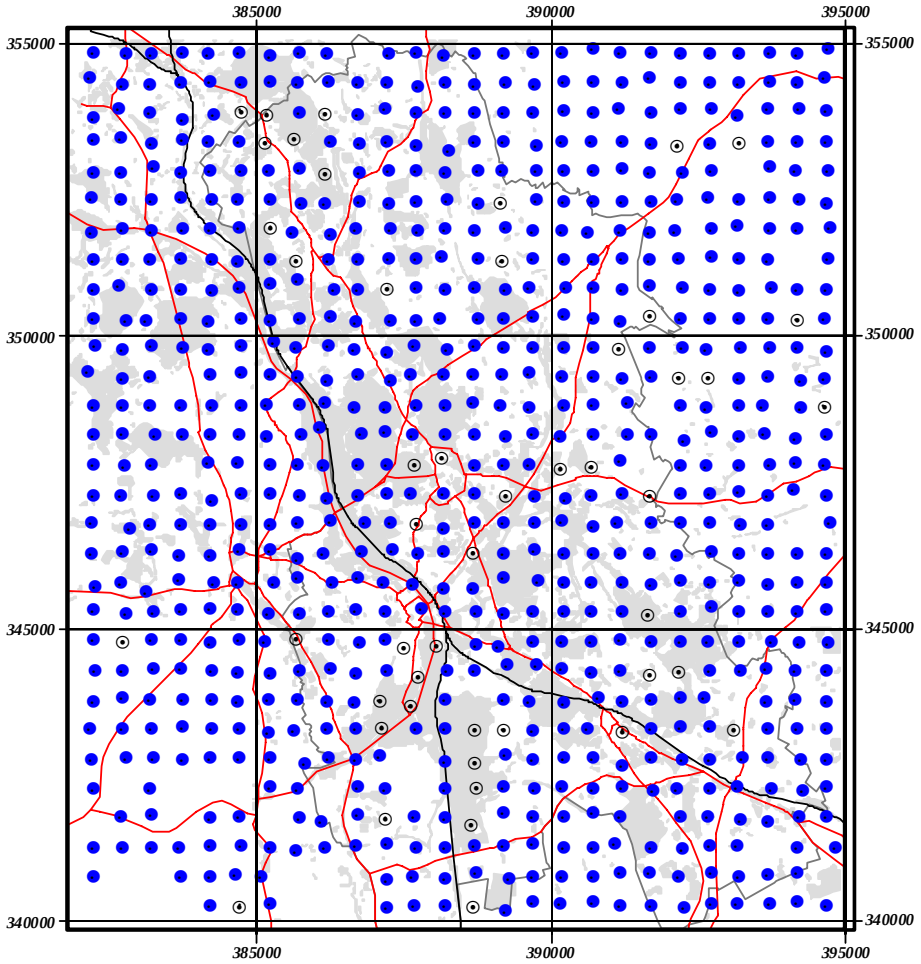


Qualitative assessment of potential leaching from soils of inorganic contaminants

Copper

"base" model

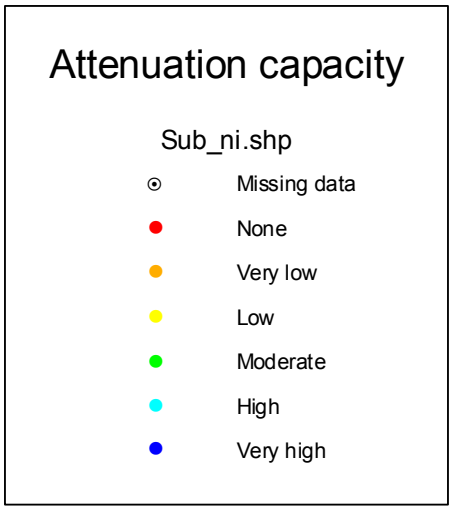


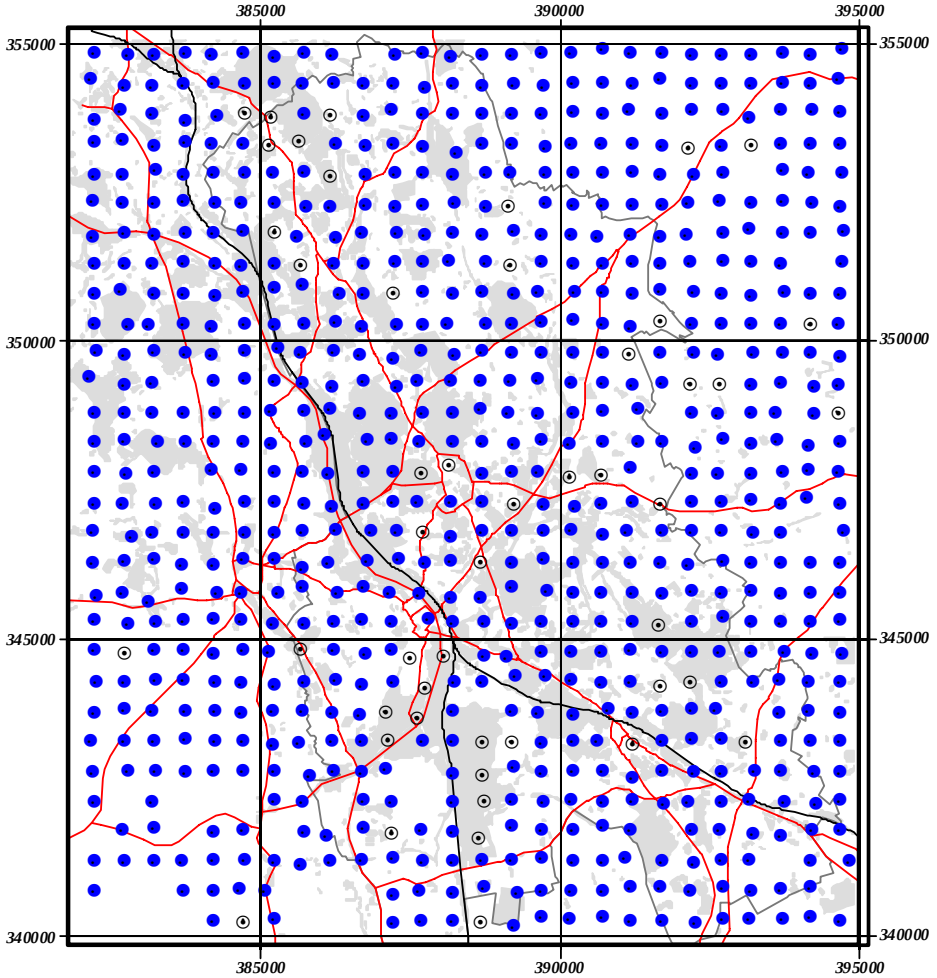


Qualitative assessment of potential leaching from soils of inorganic contaminants

Iron

"base" model

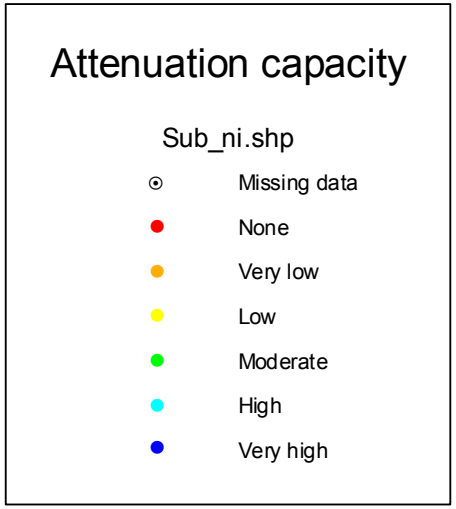


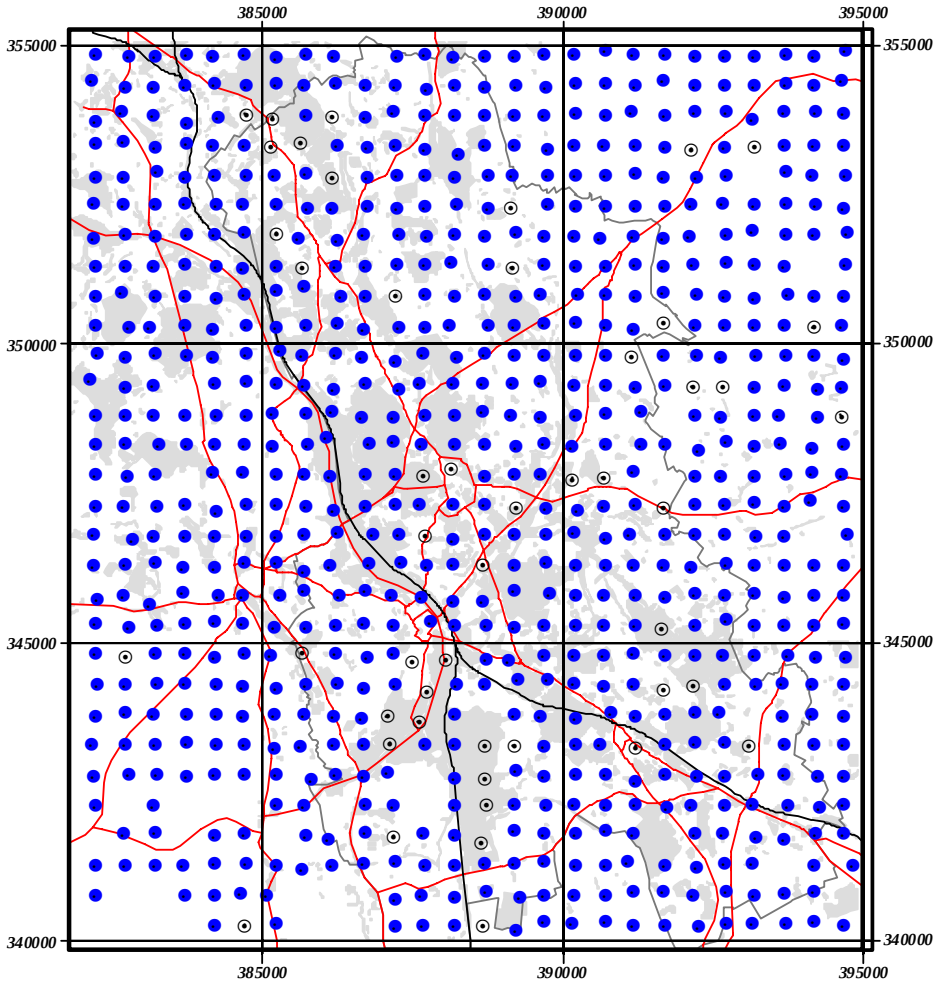


Qualitative assessment of potential leaching from soils of inorganic contaminants

Mercury

"base" model

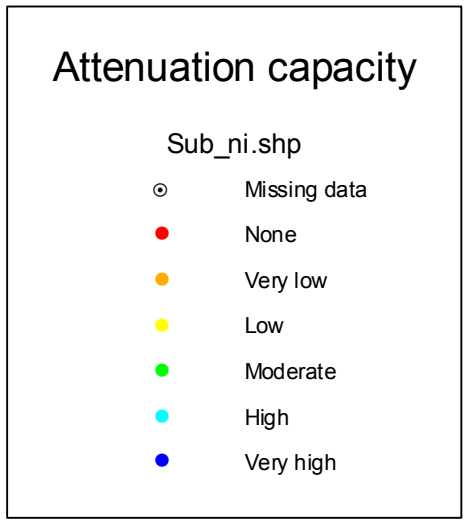


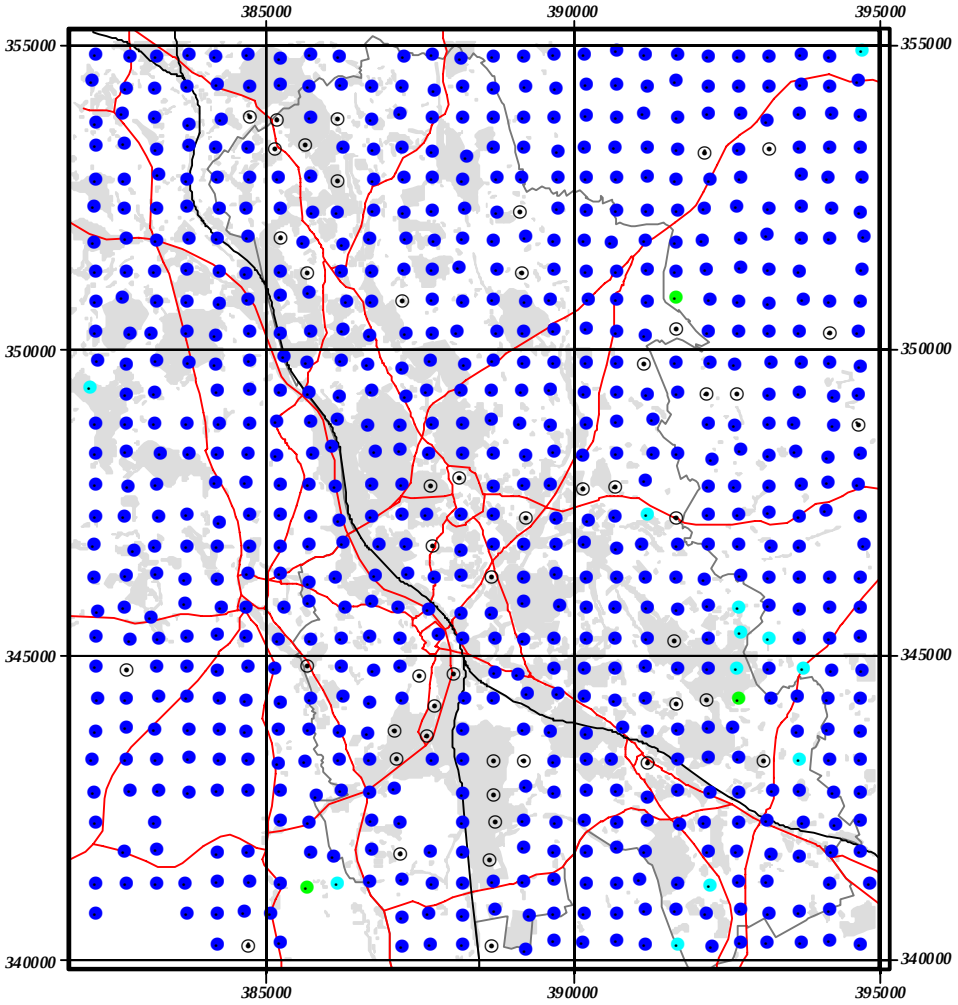


Qualitative assessment of potential leaching from soils of inorganic contaminants

Manganese

"base" model

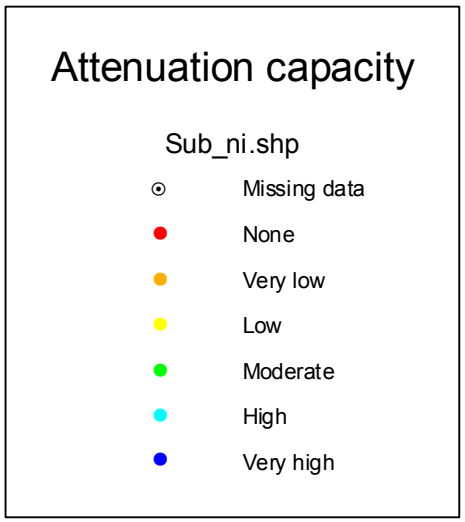


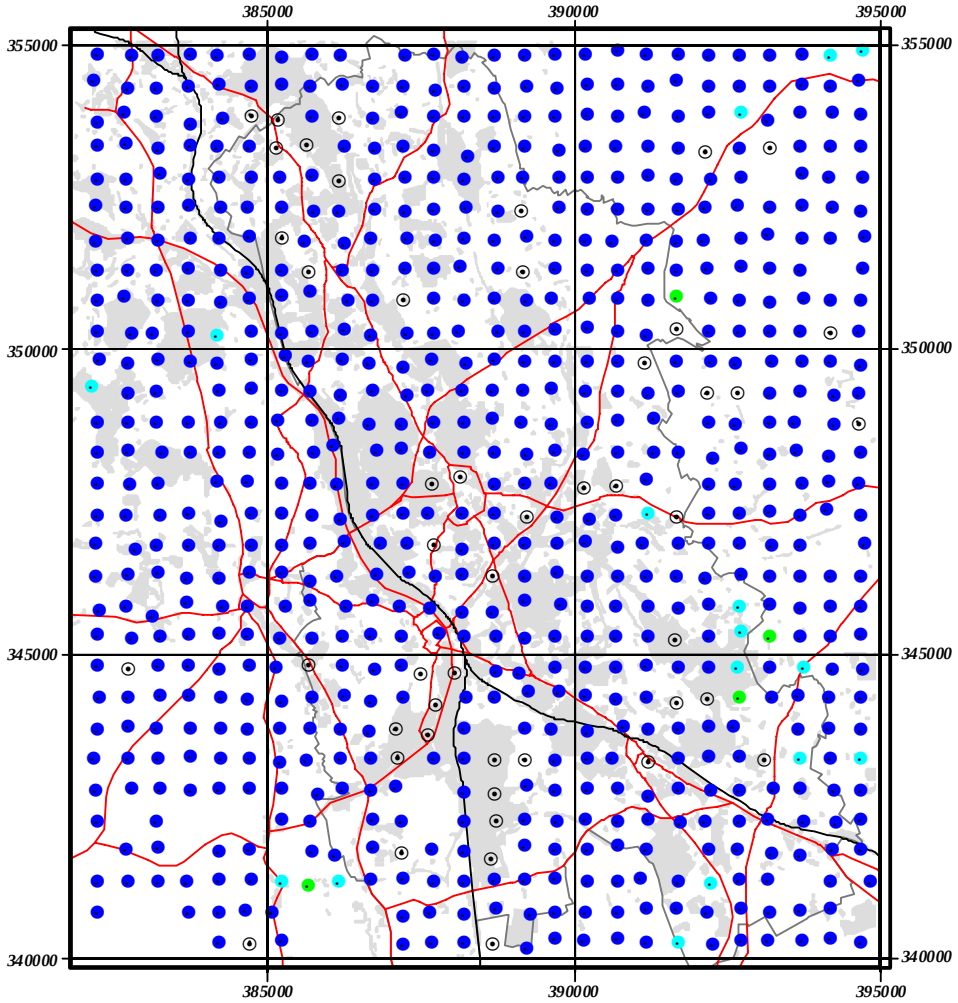


Qualitative assessment of potential leaching from soils of inorganic contaminants

Nickel

"base" model

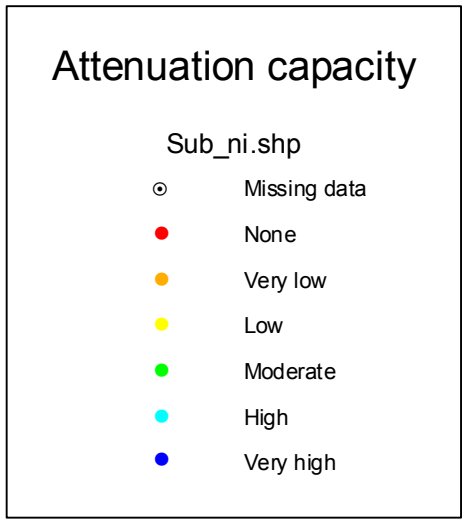


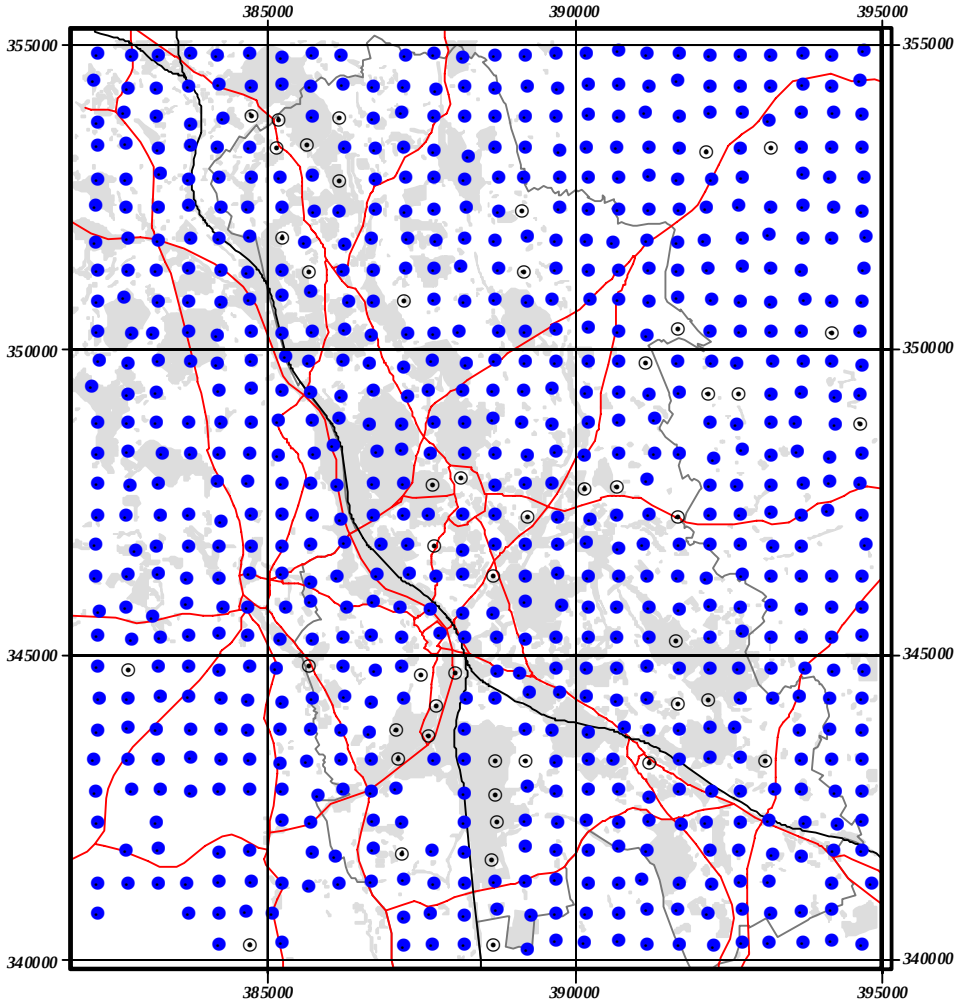


Qualitative assessment of potential leaching from soils of inorganic contaminants

Lead

"base" model

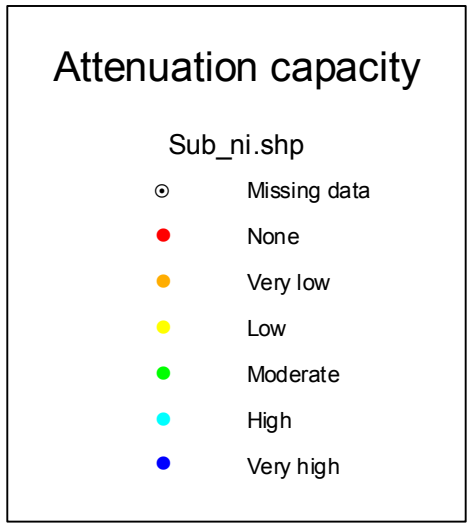


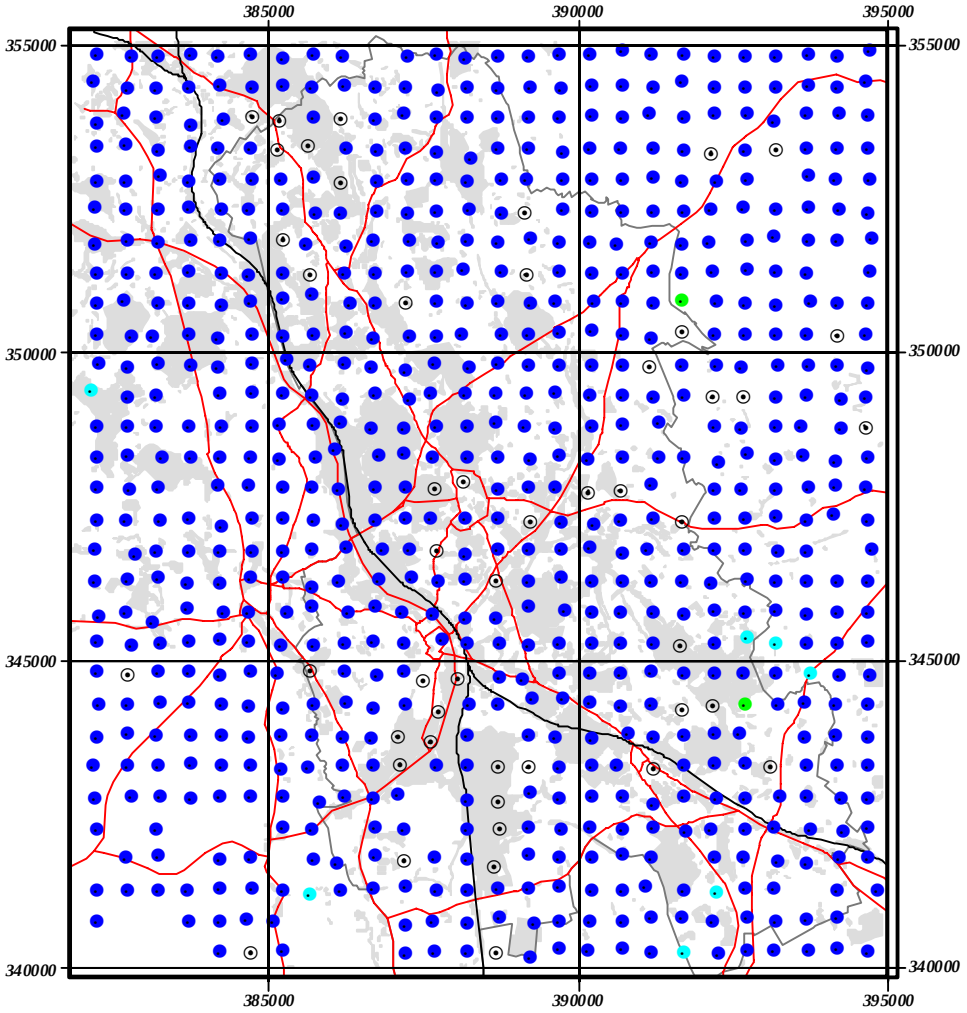


Qualitative assessment of potential leaching from soils of inorganic contaminants

Zinc

"base" model



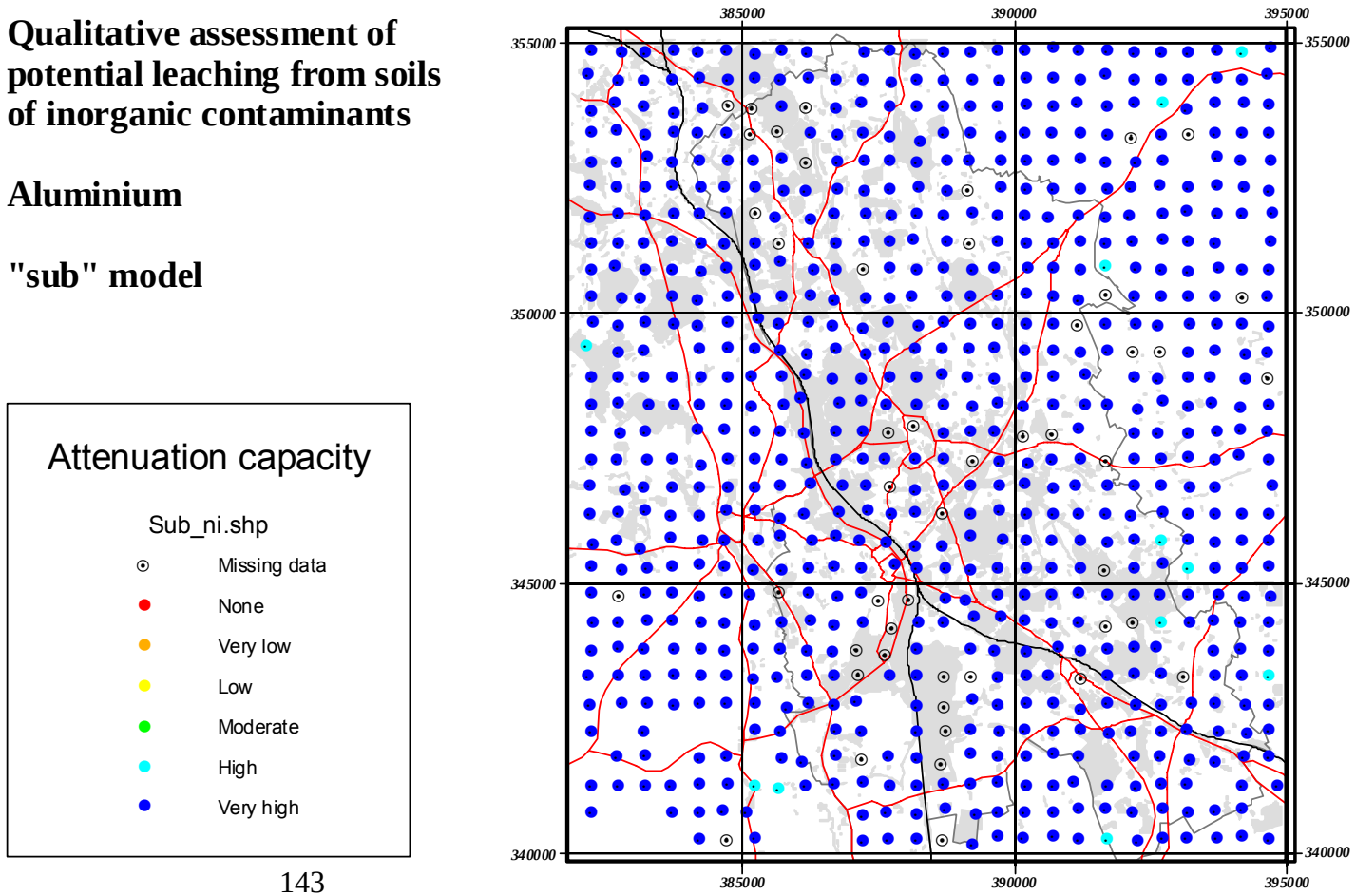


APPENDIX 7.1B 'SUB' MODEL CONFIGURATION TO ASSESS POTENTIAL LEACHING OF INORGANIC SOIL CONTAMINANTS TO GROUNDWATER

Qualitative assessment of potential leaching from soils of inorganic contaminants

Aluminium

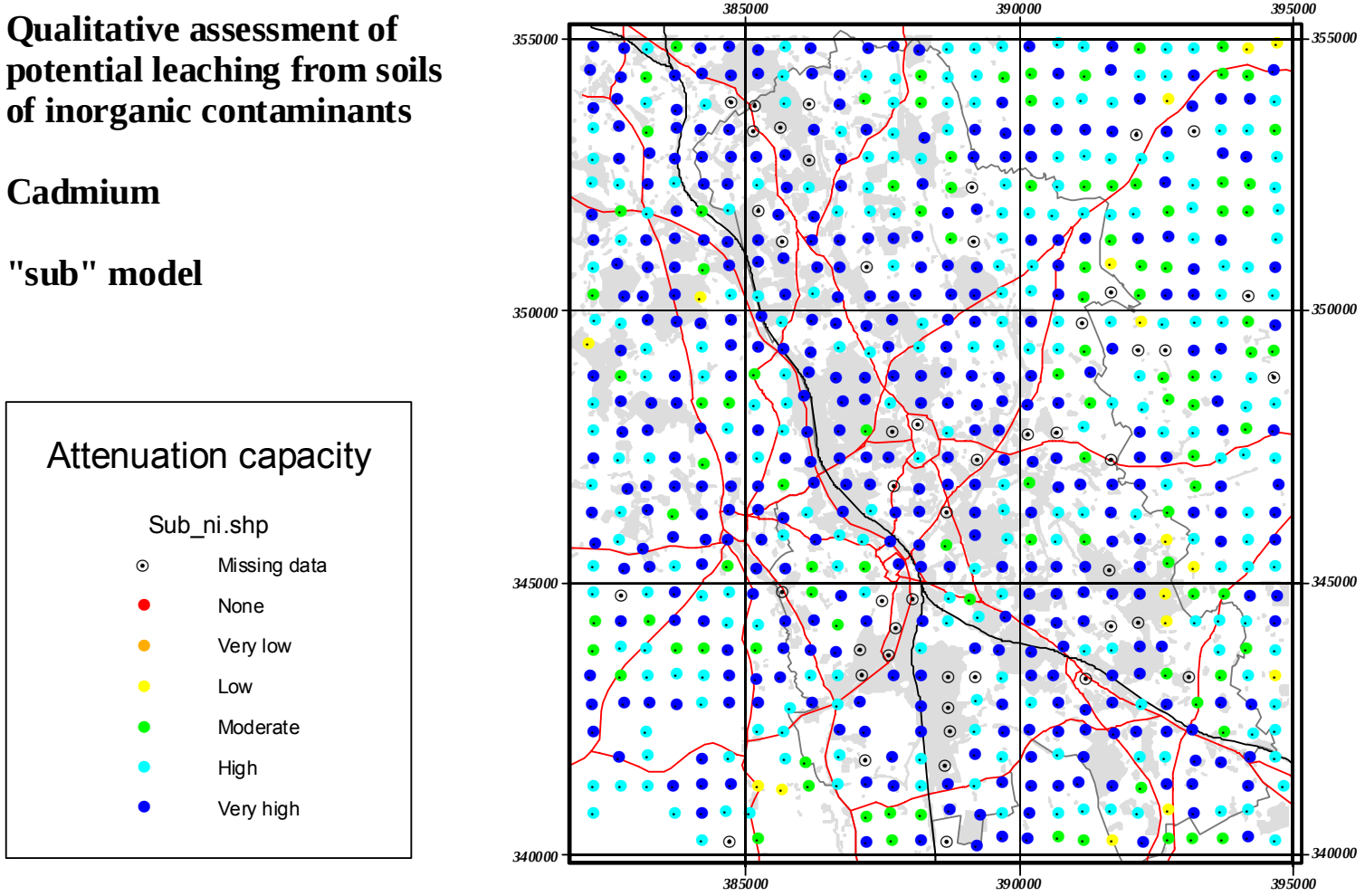
"sub" model



Qualitative assessment of potential leaching from soils of inorganic contaminants

Cadmium

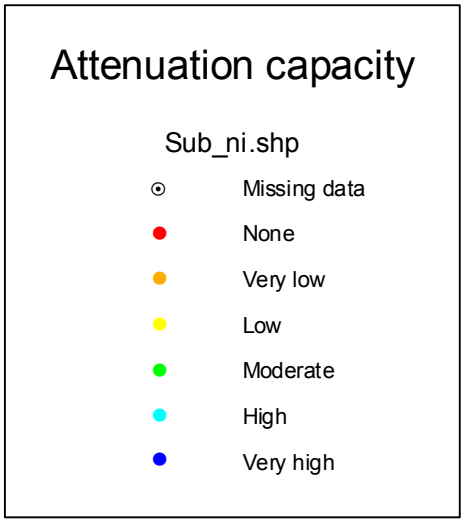
"sub" model

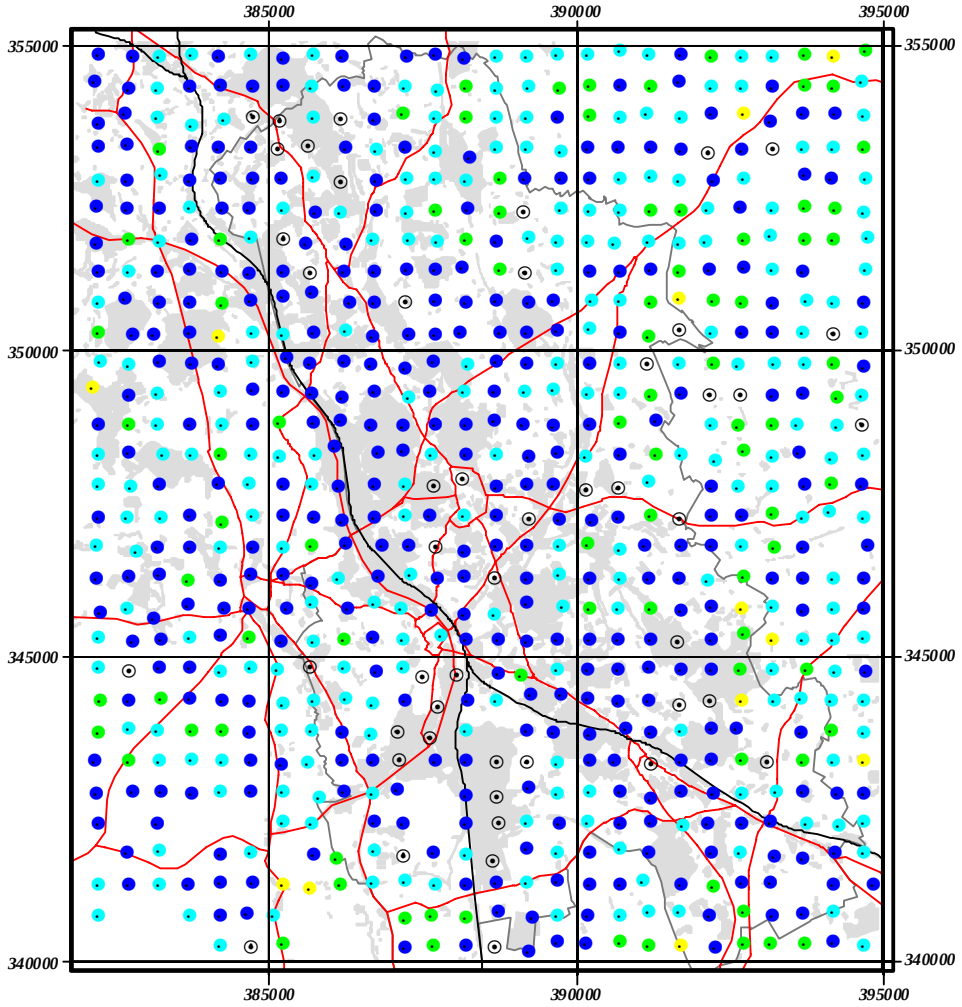


Qualitative assessment of potential leaching from soils of inorganic contaminants

Cobalt

"sub" model

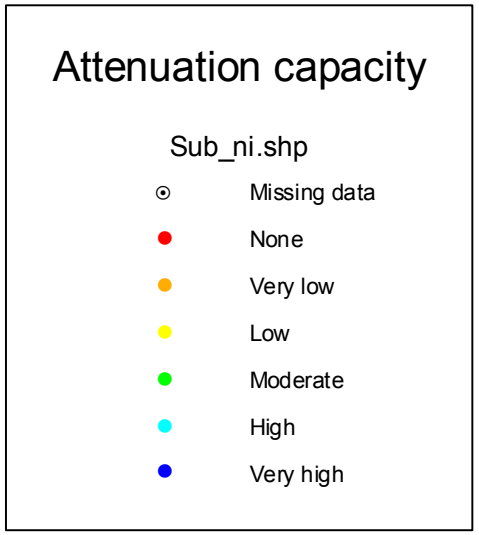


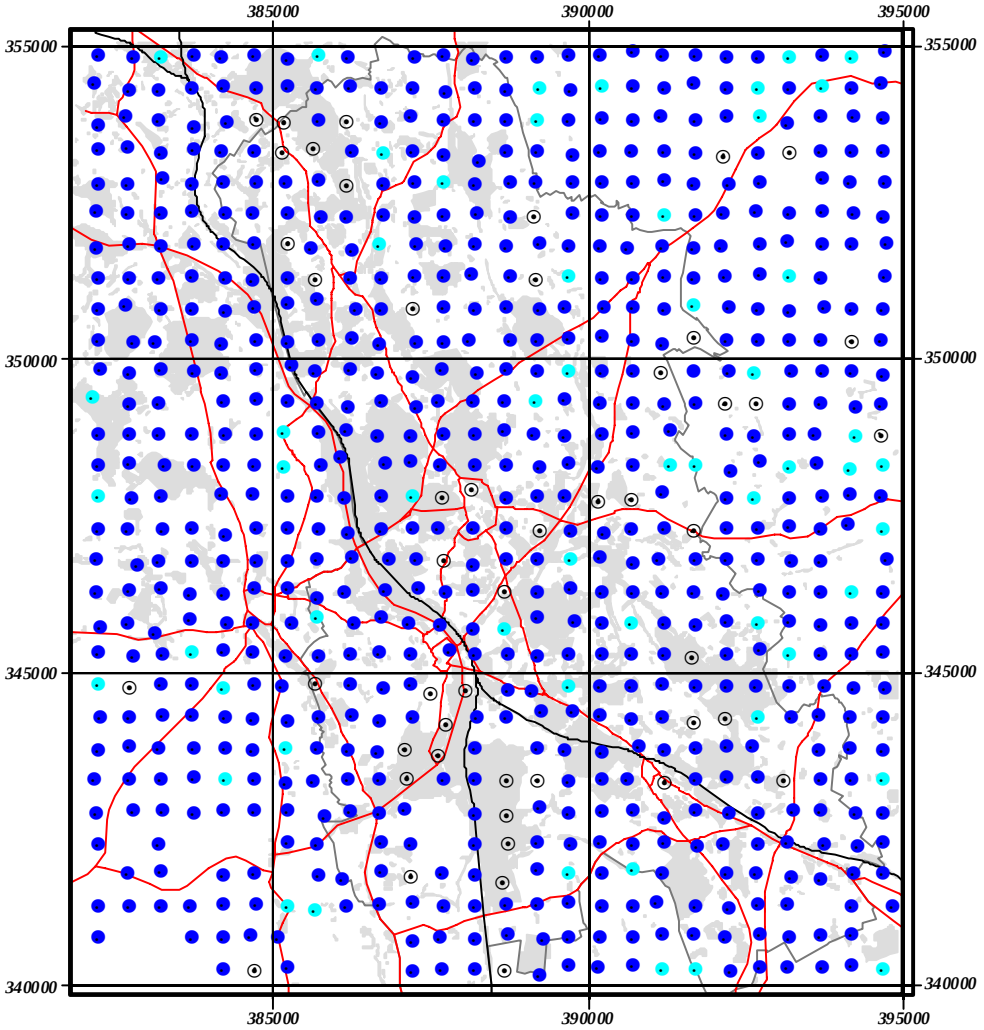


Qualitative assessment of potential leaching from soils of inorganic contaminants

Chromium

"sub" model





Qualitative assessment of potential leaching from soils of inorganic contaminants

Copper

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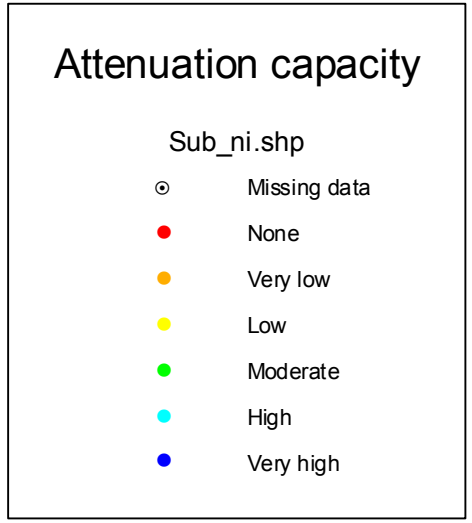

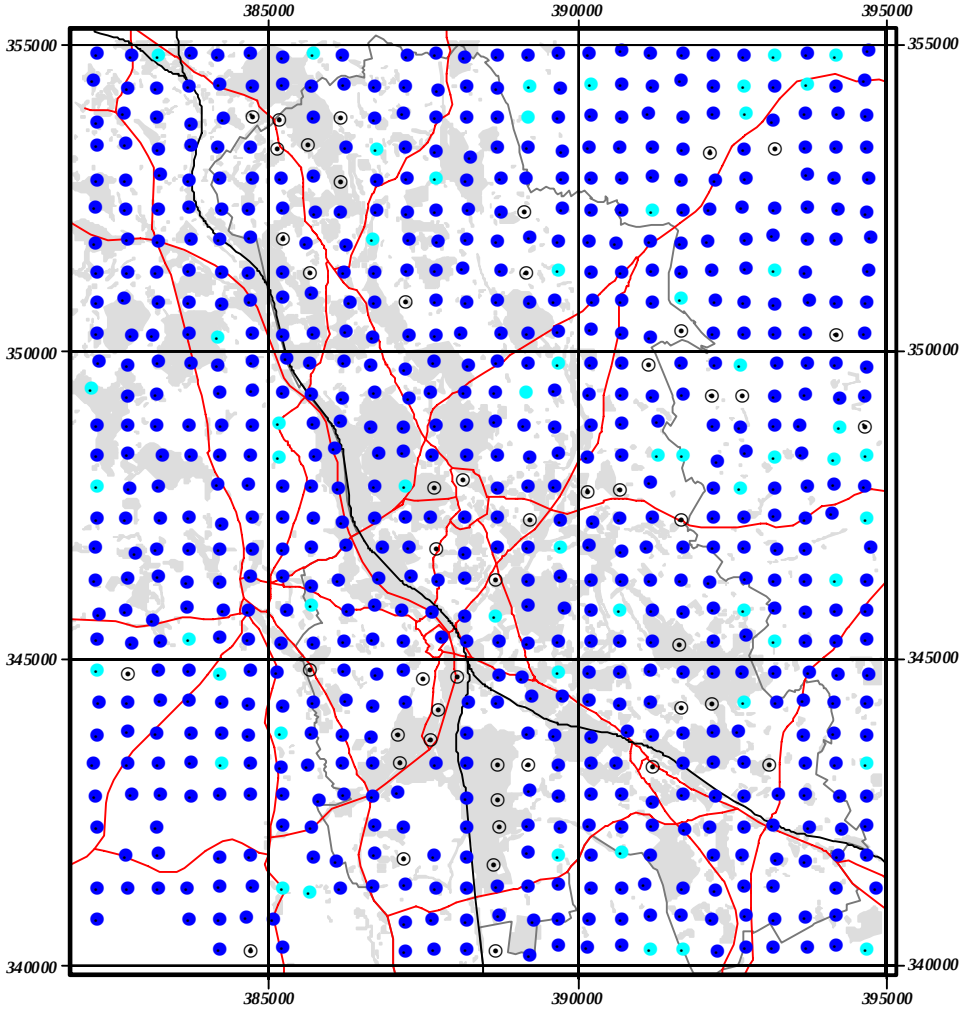

Qualitative assessment of potential leaching from soils of inorganic contaminants

Iron

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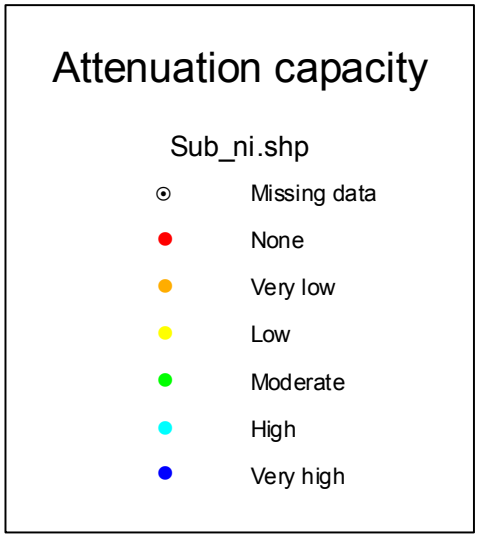
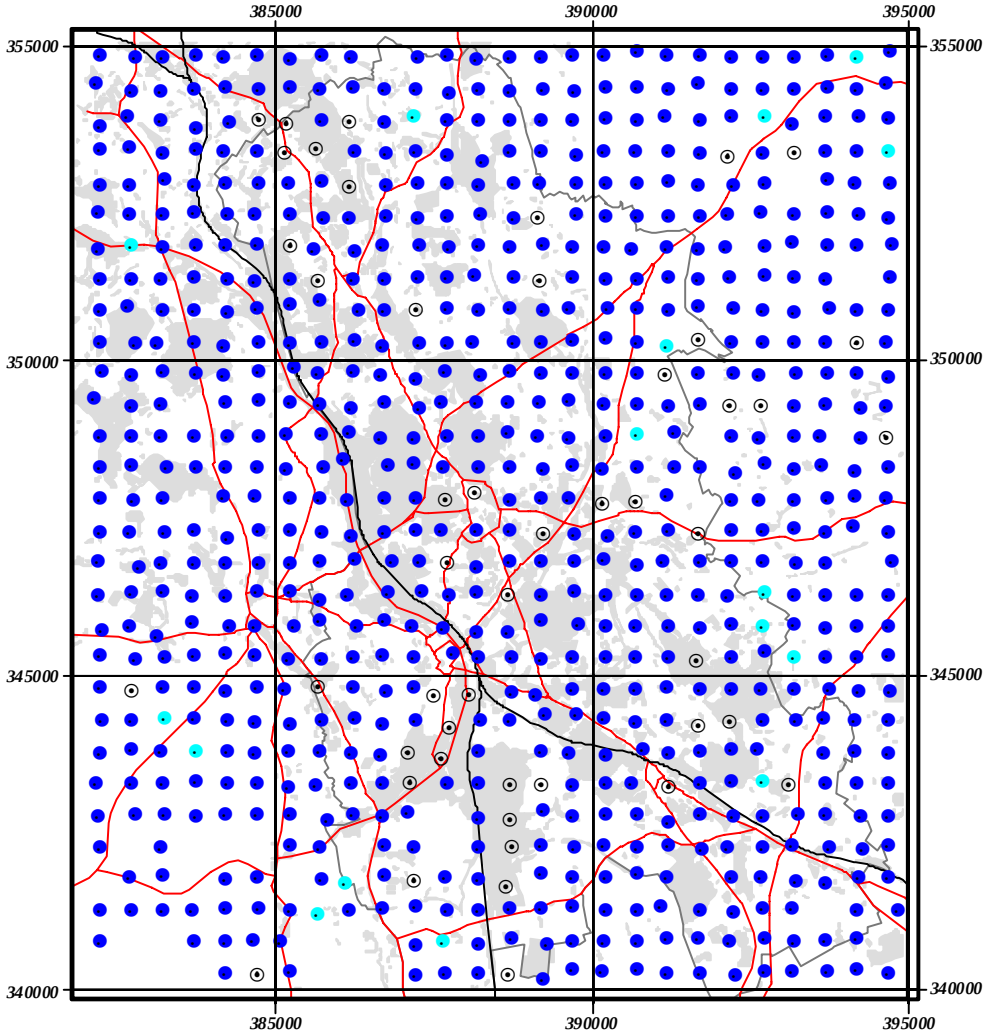
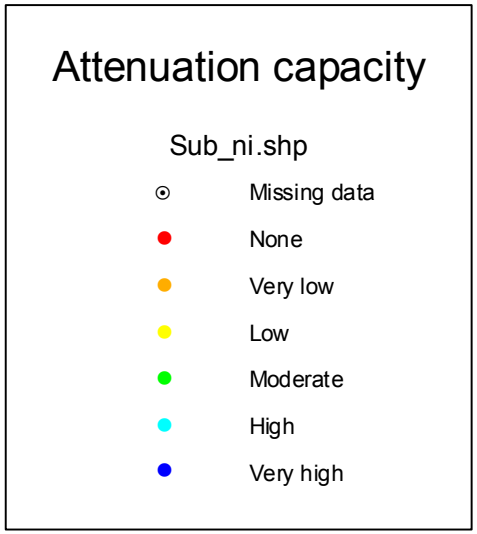


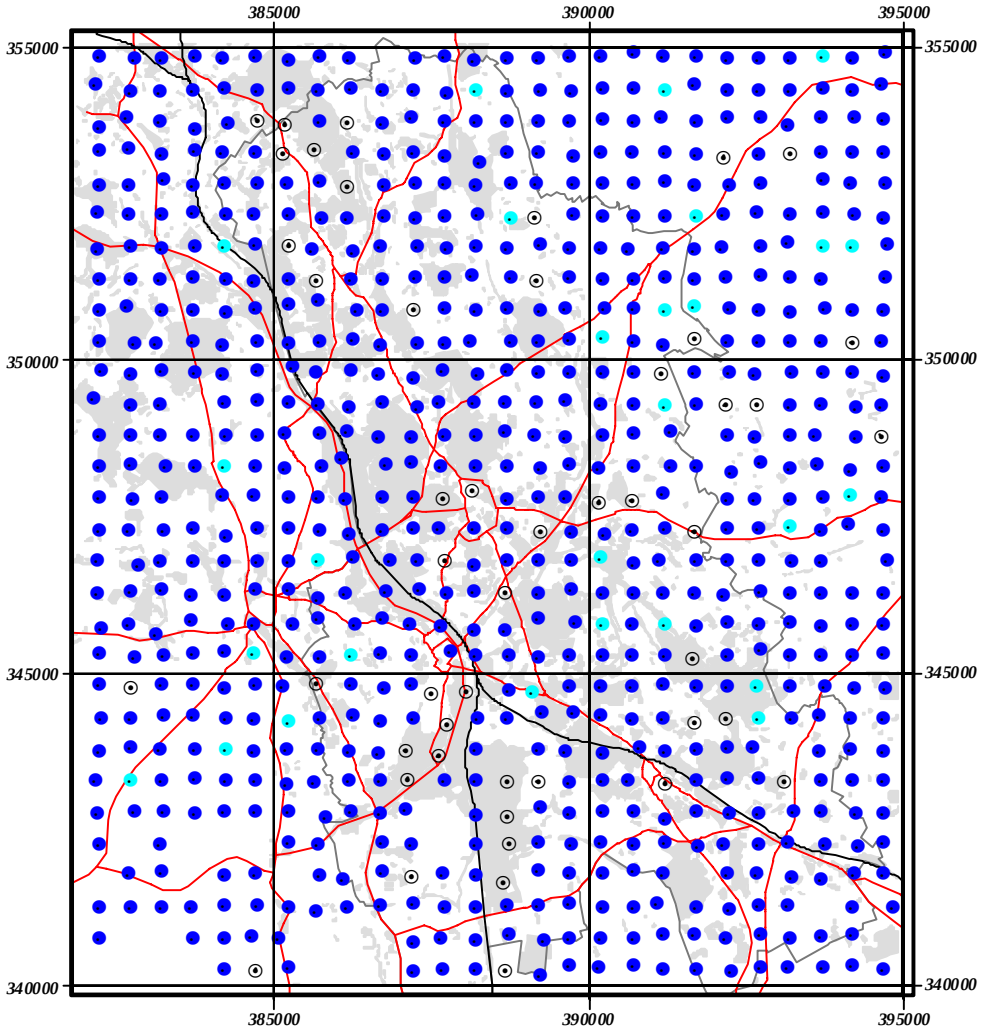


Qualitative assessment of potential leaching from soils of inorganic contaminants

Mercury

"sub" model

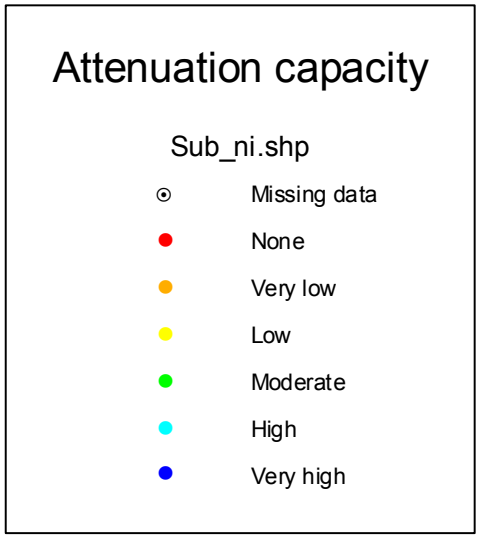


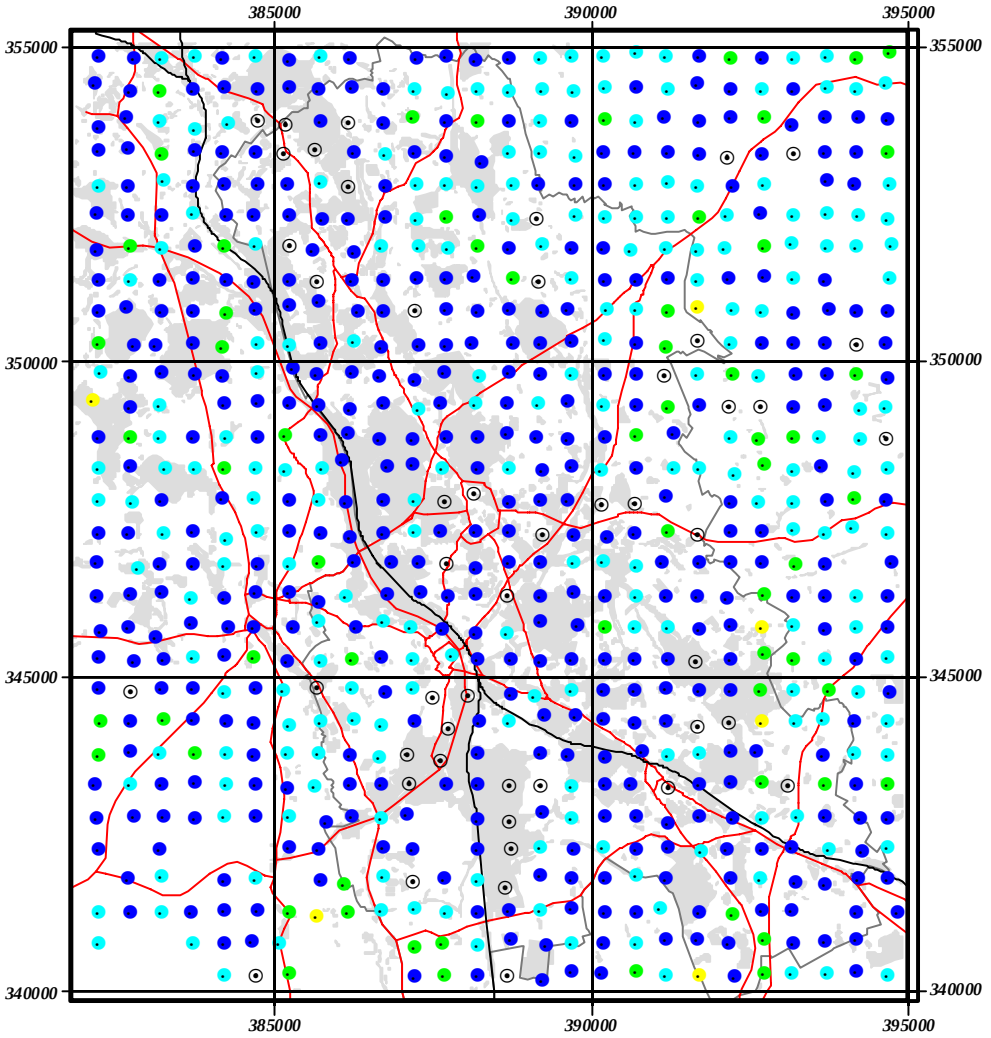


Qualitative assessment of potential leaching from soils of inorganic contaminants

Manganese

"sub" model

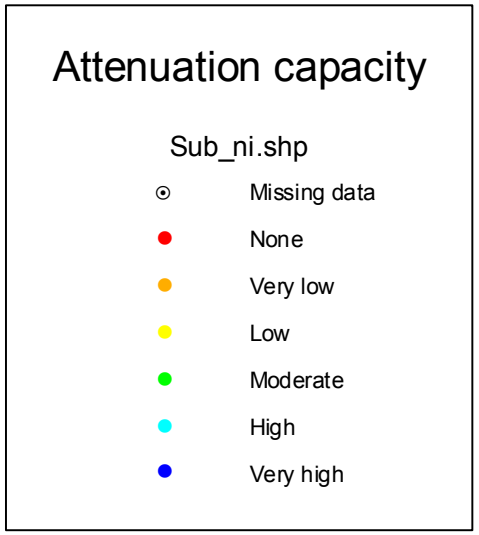


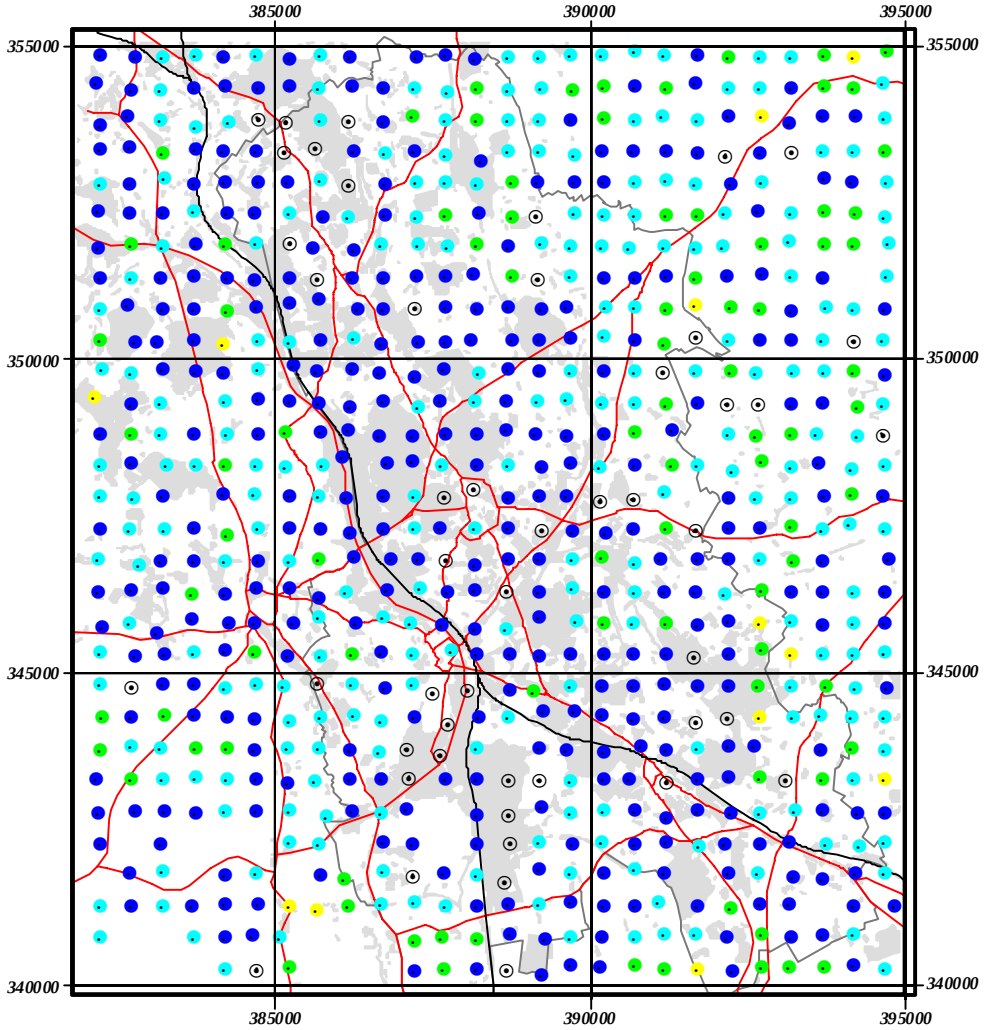


Qualitative assessment of potential leaching from soils of inorganic contaminants

Nickel

"sub" model





Qualitative assessment of potential leaching from soils of inorganic contaminants

Lead

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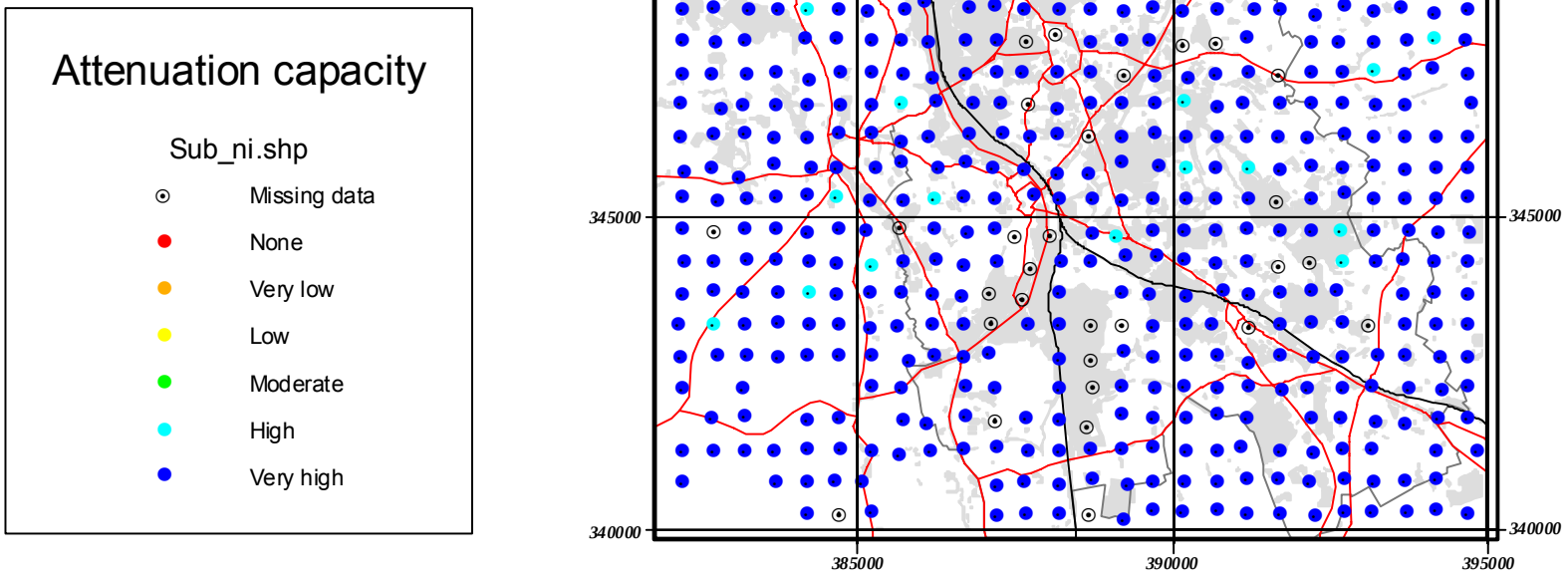

Qualitative assessment of potential leaching from soils of inorganic contaminants

Zinc

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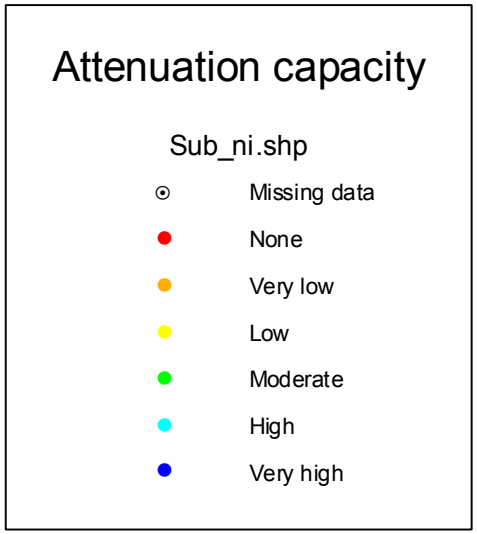
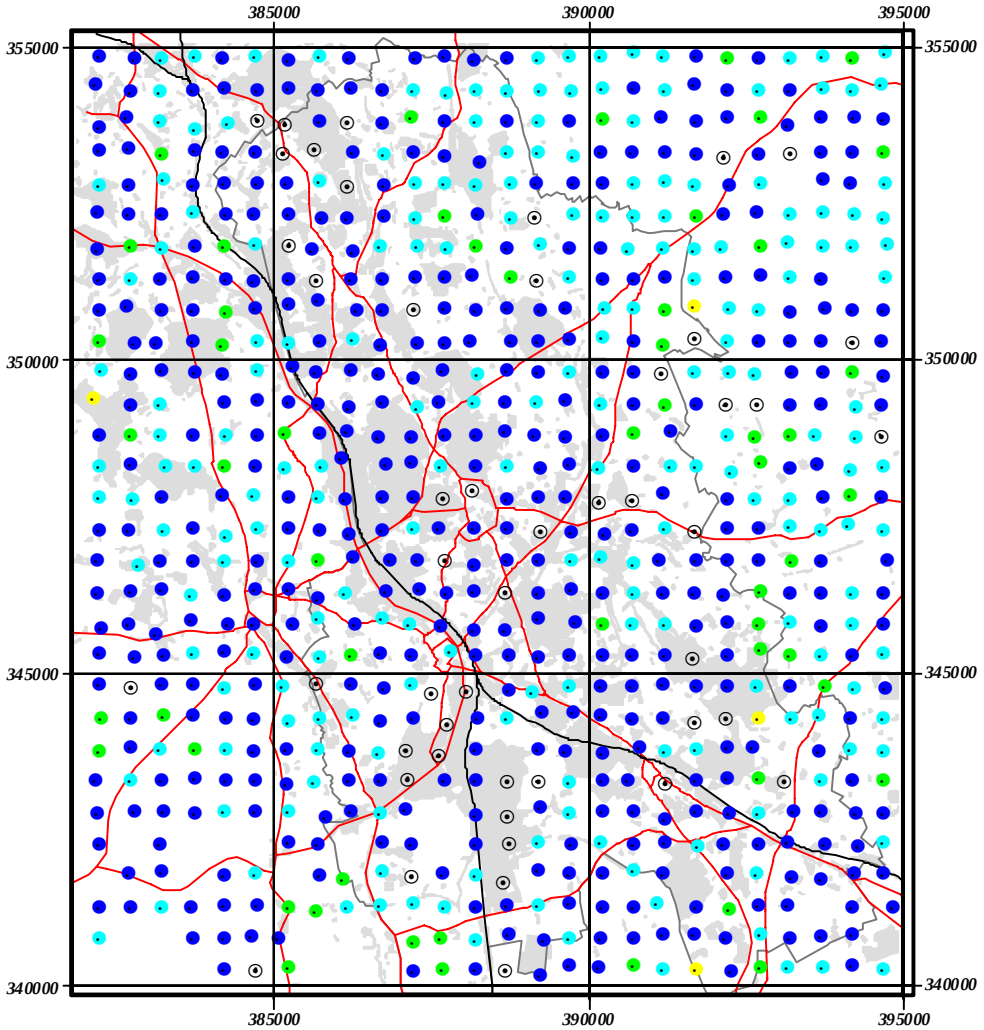




8. Potential Impacts of Soil Geochemistry on Human Receptors in Stoke-on-Trent

By F M Fordyce, B Hope and B Smith

8.1 INTRODUCTION

As outline in Chapter 1, the recent UK legislation on contaminated land considers the sources and pathways of contaminants in the environment and their likely effect on receptors including human beings. As part of the development of the Stoke-on-Trent urban geochemistry GIS, the uses of geochemical data to examine potential impacts on the urban population were investigated so that areas of most concern within the urban environment could be identified. The major exposure routes by which contaminants in soil have the potential to impact upon human health are via the ingestion of soil in gardens, allotments, play areas; from vegetables grown on contaminated land and via the inhalation of soil-derived dusts. The UK government guidelines on human risk assessment from contaminated soils (CLEA) were not available at the time of reporting but will take account of soil element concentrations, bioavailability, human exposure and human toxicology.

The assessment of human exposure risk in urban environments was investigated previously by Nottingham Trent University using the GSUE soil data for Wolverhampton. The outcome of this study was a human health risk map for Pb in residential surface soils. The map was derived on the basis of applying geostatistics and stochastic modelling (conditional simulation) to the Pb data. Variography was used to prove that, unlike Stoke-on-Trent, there was spatial correlation between the sampling points on the 500 m sampling grid and that the interpolation of the Pb concentration values between sample sites was valid. The results of the conditional simulation, using a Monte Carlo method, of the soil Pb concentrations were compared with the ICRCL trigger level of 500 ppm (mg/kg) for domestic gardens and allotments. The resultant health risk map for soil Pb showed the probability of exceeding this guideline value in residential gardens and allotments in Wolverhampton. The chance of a surface soil exceeding this 500-ppm (mg/kg) trigger level varied according to the area chosen, and ranged from essentially zero to around 8% (Nathanial et al., 1997). Although this simulated map gave an indication of likely exceedence of the guideline values across the city, it did not highlight sample sites that on the basis of the GSUE survey where known to exceed the guideline value (i.e. soils known to contain > 500 ppm (mg/kg) Pb).

Work in the USA has shown conclusive links between Pb concentrations in the urban environment and child blood Pb status (Mielke et al., 1997) and is based upon the collection of the top 2.5 cm of the soil horizon as this is considered to be most crucial in terms of child contact. However, the GSUE project is a multi-purpose survey that aims not just to investigate childhood risks but threats from growing vegetables and threats to groundwater, therefore the top 15 cm are sampled. Concentrations of elements like Pb may or may not be lower in these samples than in the very top of the soil profile which is most influenced by atmospheric deposition and the GSUE samples provide a useful first pass assessment of risk.

For the present study, in the absence of the CLEA guidelines, a preliminarily approach to human risk assessment was adopted on the basis of the ICRCL (1987) trigger values in soils as follows.

8.2 STOKE-ON-TRENT GEOCHEMISTRY GIS HUMAN RISK ASSESSMENT

In terms of exposure, surface soils were selected for the Stoke-on-Trent human risk assessment as these are more likely to come into contact with the local population than profile soils and vegetables are grown in the upper soil horizon. Within the GIS environment, the surface soil geochemical data were categorised according to the ICRCL (1987) trigger values for As, Cd, Pb, Hg, Cu, Zn and Ni (Table 1.2). Although the trigger values for areas of open land are higher than for domestic gardens and allotments, this study adopted

the precautionary lower trigger values in the risk assessment. Chromium was not included in the risk assessment due to the unknown proportions of Cr^{3+} and Cr^{6+} in the soil; Cr^{6+} being the toxic form has a much lower trigger value (Table 1.2).

Soil sampling sites where the element contents exceed the trigger values are displayed for each element in map form across the city (Appendix 8.1). This first level assessment indicates sites requiring further investigation. Exceedence of the trigger value for As (10 ppm (mg/kg)) is widespread across the urban study area in built-up and non built-up locations. Whilst this may indicate the general dispersion of As in the environment around Stoke-on-Trent due to the presence and exploitation of coal-bearing strata and industrial contamination, it also reflects the low trigger value for this element relative to natural element abundances. Soil Zn and Pb contents also exceed the trigger values in a number of locations throughout the built-up area, particularly along the old industrial corridor of the Mersey-and-Trent canal and in the Hanley areas of the city. Several of the exceedences are also proximal to the road network. Cu, Ni and Cd show similar patterns to Pb and Zn but far fewer sites exceed the trigger values for these elements. Only a few soils contain levels of Hg above the trigger value in the built-up area between Newcastle-under-Lyme and Stoke-on-Trent. All these elements exceed the trigger values in a cluster to the south of the urban study area, east of the main railway link. These sites correspond to the location of a sewage works described in Chapter 6.

Assessment according to guideline values alone does not take account of the land use at these locations and possible pathways to the human receptor. Using the 1: 10 000 Landline® database provided to the study by Stoke-on-Trent City Council, each location where an element exceedence was noted was investigated further to determine the land use (for example, Figures 8.1 and 8.2). This process was carried out manually within the GIS as at the current time, the Landline® dataset held by BGS is not polygonised therefore it is not possible to select areas on the basis of land type at the city-wide scale. It is recommended that polygonisation of the data is carried out in the future to aid the assessment of geochemistry and land use relationships.

A second suite of element maps was generated in the GIS showing locations where element concentrations exceed the ICRCL trigger values coincident with land use types providing potential pathways to the local population, namely areas of gardens, allotments, playing fields, schoolyards, urban farmland etc. (Appendix 8.1). Sites where As concentrations in soil exceed the trigger value in areas of sensitive land use are widespread throughout the built-up area of Stoke-on-Trent whereas Ni exceedences on sensitive land use types are restricted to 4 locations in the study area. Lead, Zn and the few Cu exceedence values on sensitive land use types are scattered throughout the Stoke-Newcastle built environment whereas Cd exceedences are confined to the south of the study area (Appendix 8.1).

The first and second level risk assessment maps were overlain on the population density map for Stoke-on-Trent as a further indication of risk (Martin et al., 1991). However, there is some difficulty using this basic population data as a risk assessment tool as a high population density does not necessarily mean greater risk. If people are living in flats, for example, the population density is high but the exposure to garden soils etc. may be less than in more sparsely populated areas of the city. Whilst this information provides a guide, it has not been used in the overall risk assessment. It is recommended in the future that more detailed investigations of the population data in conjunction with the Landline® data to determine housing types may provide information for incorporation in human exposure risk assessments.

As a final stage in the risk assessment, the data were combined to form one map of all locations within the urban study area where any of the element concentrations exceed the trigger values on a sensitive land use type. These data were then considered in terms of the likely mobility and availability of the elements in the environment. As outlined in Chapters 1, 6 and 7, many metal and metalloid elements are more mobile and bioavailable in soils that are low in pH, organic matter and clay content. Therefore, the exceedence sites were categorised according to the following scheme. If the soils are acid (pH< 7), with low (< 10 wt%) organic matter content (measured by LOI) and low (< 10 wt%) Al_2O_3 (as a measure of clay content), the site is categorised as high risk. If any of the above factors are low, the site is classed as moderate risk and if none of the factors are low, the site is classed as low risk. The overall risk map for Stoke-on-Trent is shown in Figure 8.3. The majority of sites are categorised as moderate risk and only three sites between Newcastle-under-Lyme and the Wolstanton area of the city are categorised as high risk .

The structure of the risk assessment scheme is outlined in Figure 8.4. At this stage, it has not been possible to write a human risk assessment programme attached to the ArcView® GIS because of the inability to automatically select the land use type from the Landline® data. However, this approach provides an initial

assessment of likely risks from contaminated soil in the Stoke-on-Trent urban area highlighting sites for more detailed follow-up and is an example of the types of assessments that are possible using an urban geochemistry GIS. At this stage, the risk assessment structure is rudimentary and more sophisticated approaches will be possible once the CLEA guidelines are available and the Landline® data for Stoke-on-Trent are polygonised.

Analytical methods that attempt to mimic conditions in the stomach during ingestion and therefore provide a better estimate of the human bioavailability of contaminants in soils have been developed in the USA on behalf of the US Environmental Protection Agency (US-EPA) (Ruby et al., 1996). These techniques, known as physiological based extraction tests (PBET) have been successfully validated against animal experiments for As and Pb. The BGS is the only organisation in the UK developing these tests to give a better estimate of element bioavailability in contaminated land assessments (Kelleher, 1999). Due to the financial constraints on the GSUE project, the PBET do not form part of the routine urban survey at the present time and no data are available for Stoke-on-Trent. It is recommended for future follow-up that PBET information for Stoke-on-Trent would aid the assessment of human risks from contaminated land.

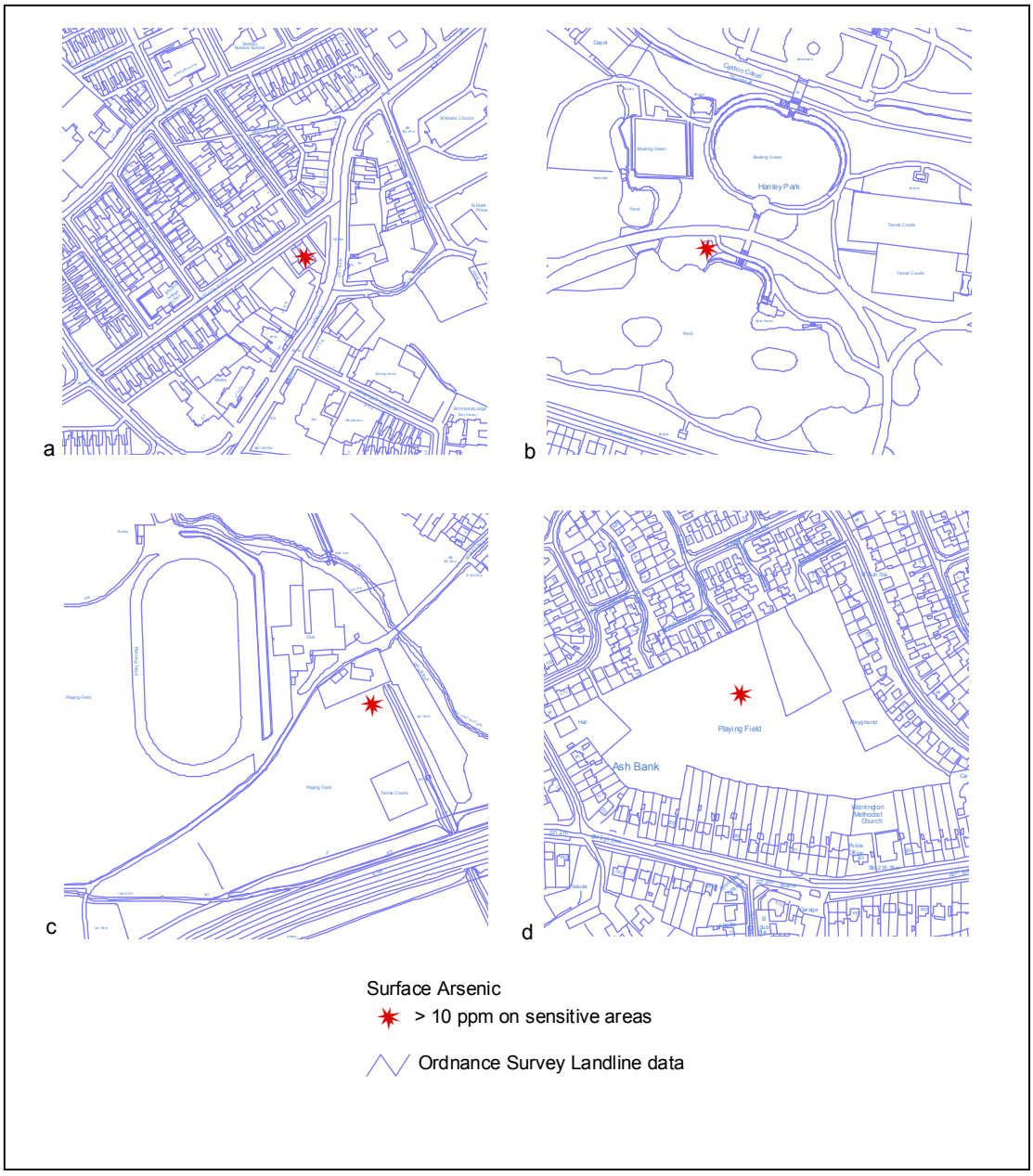


Figure 8.1 Examples of arsenic concentrations in surface soils exceeding the ICRCL (1987) trigger values for domestic gardens and allotments coincident with sensitive land use types indicated by examination of the Landline® dataset for Stoke-on-Trent (a = garden, b = park, c = sports ground, d = playing field)

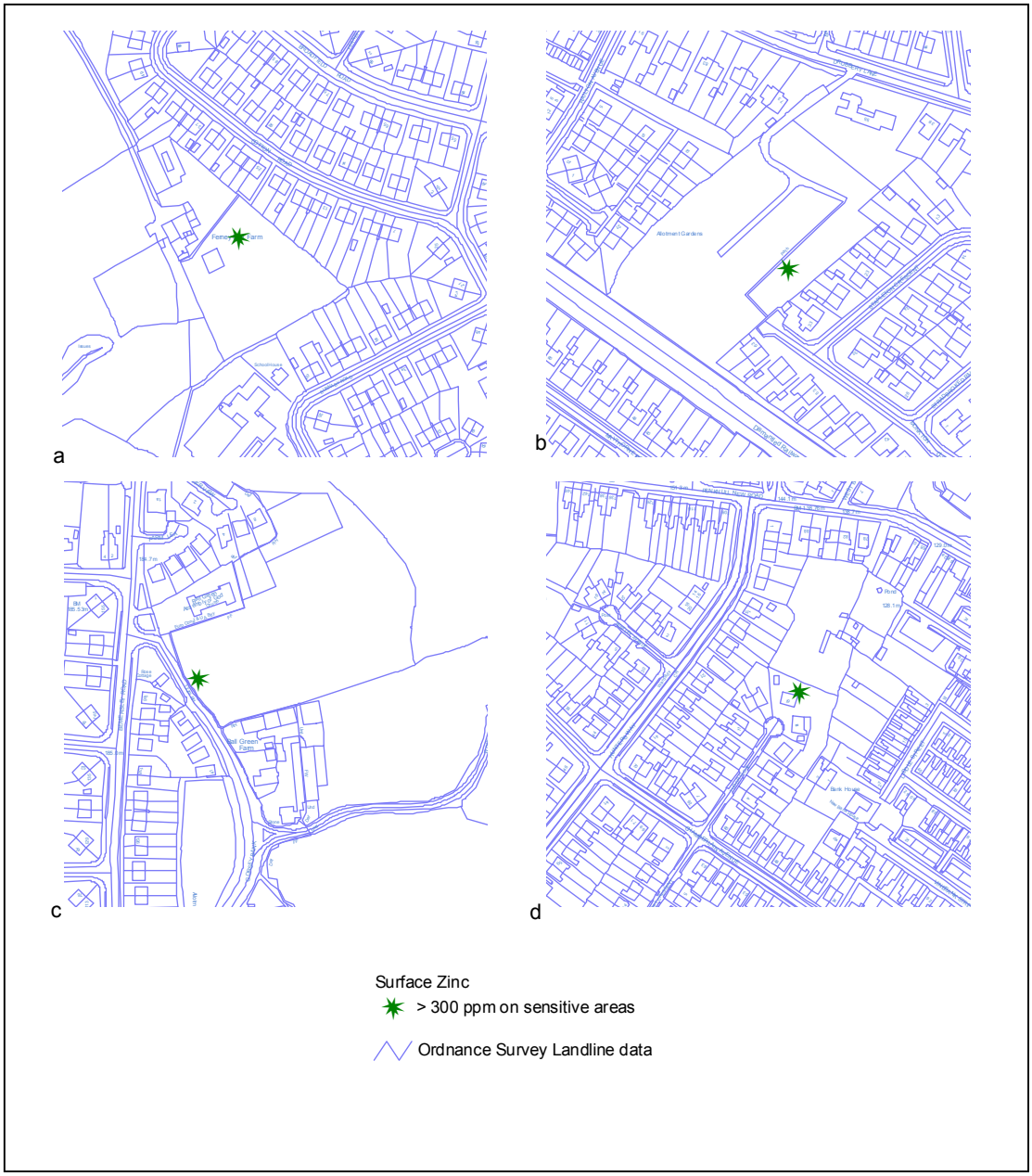


Figure 8.2 Examples of Zn concentrations in surface soils exceeding the ICRCL (1987) trigger values for domestic gardens and allotments coincident with sensitive land use types indicated by examination of the Landline® dataset for Stoke-on-Trent (a = urban farm, b = allotment, c = urban field, d = garden).

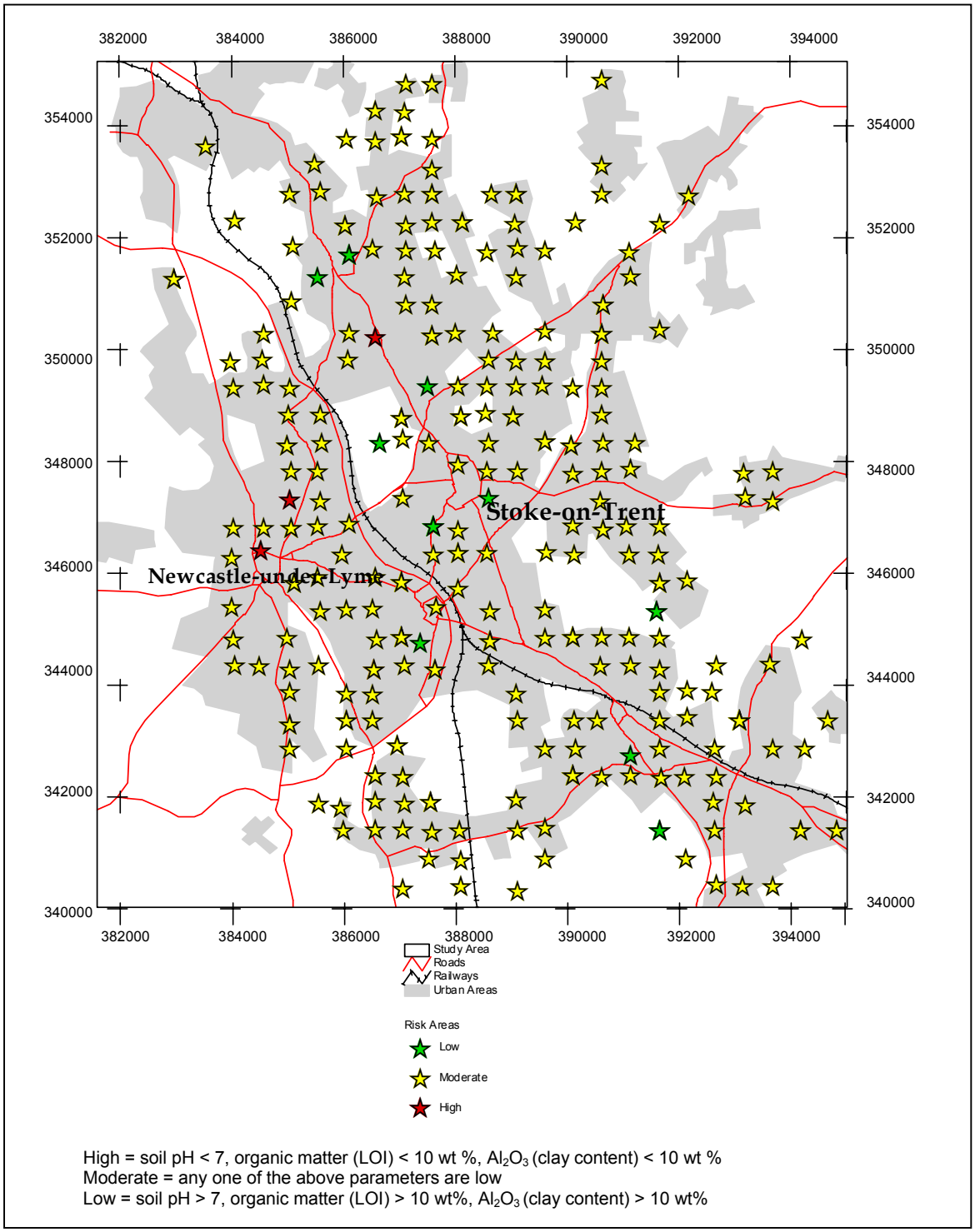


Figure 8.3. Overall human exposure risk assessment map for Stoke-on-Trent based on sites where element (any of As, Cd, Cu, Hg, Ni, Pb and Zn) concentrations exceed the ICRCL (1987) trigger values for domestic gardens and allotments coincident with sensitive land use types (gardens, allotments etc.) characterised by contaminant bioavailability.

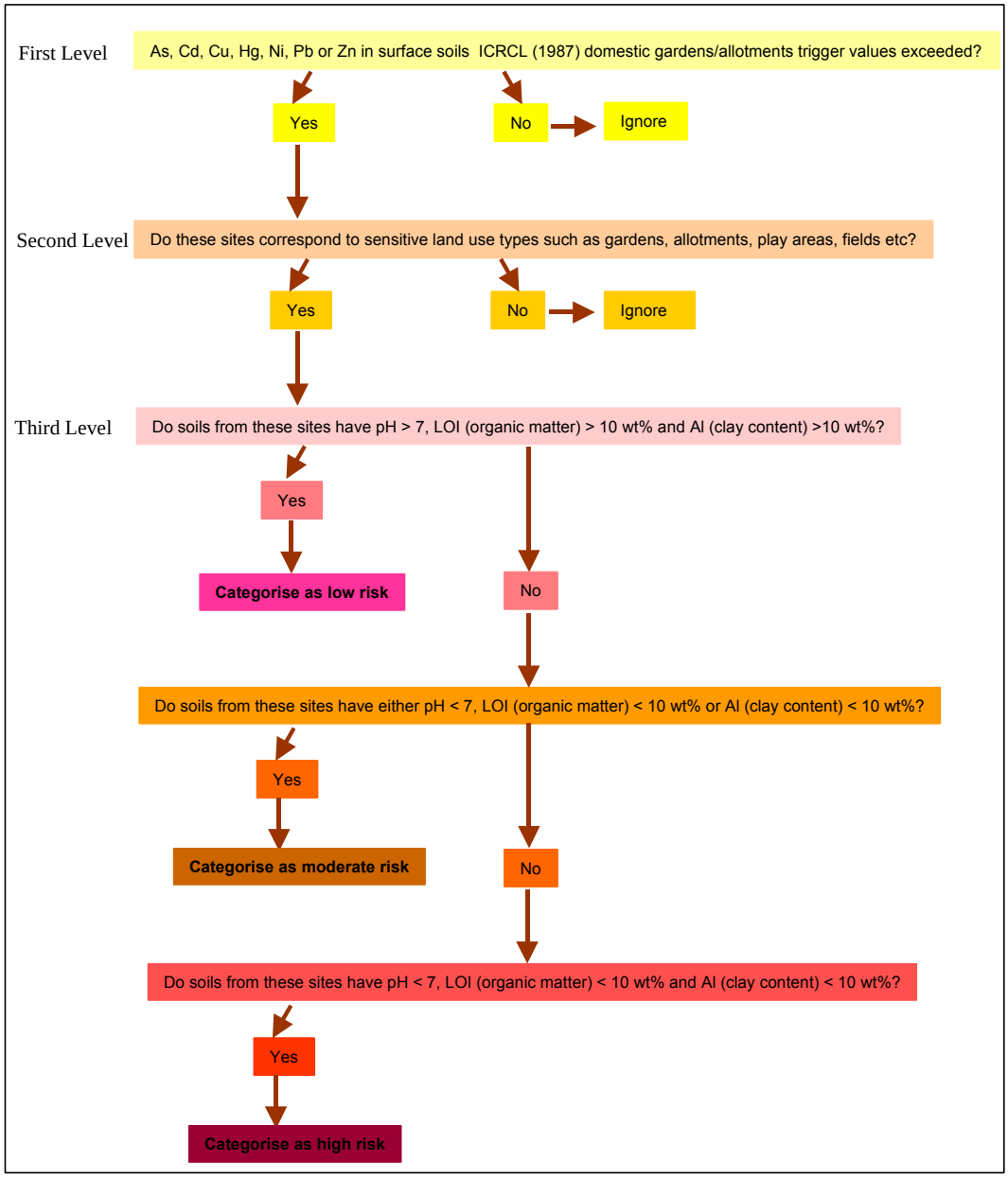
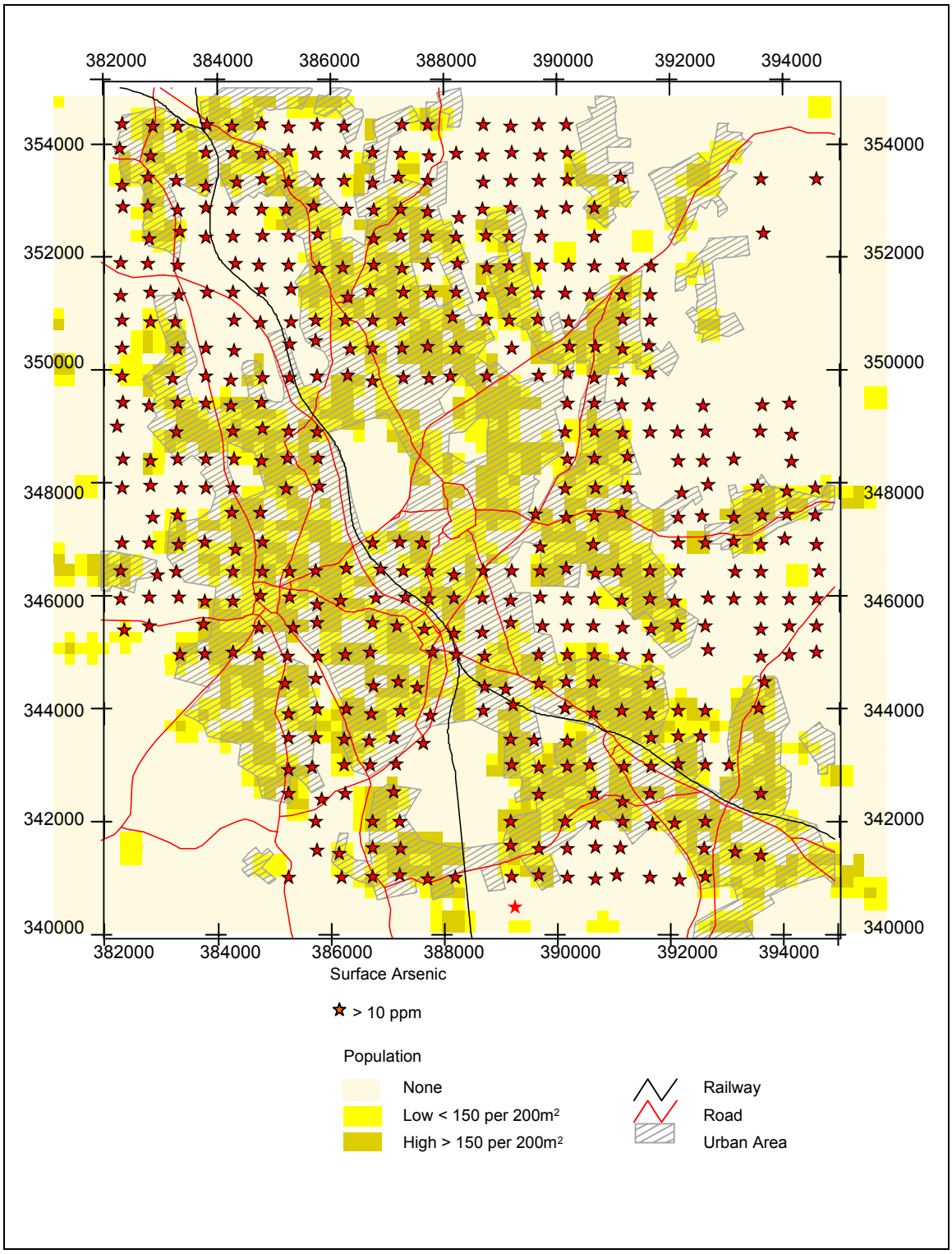


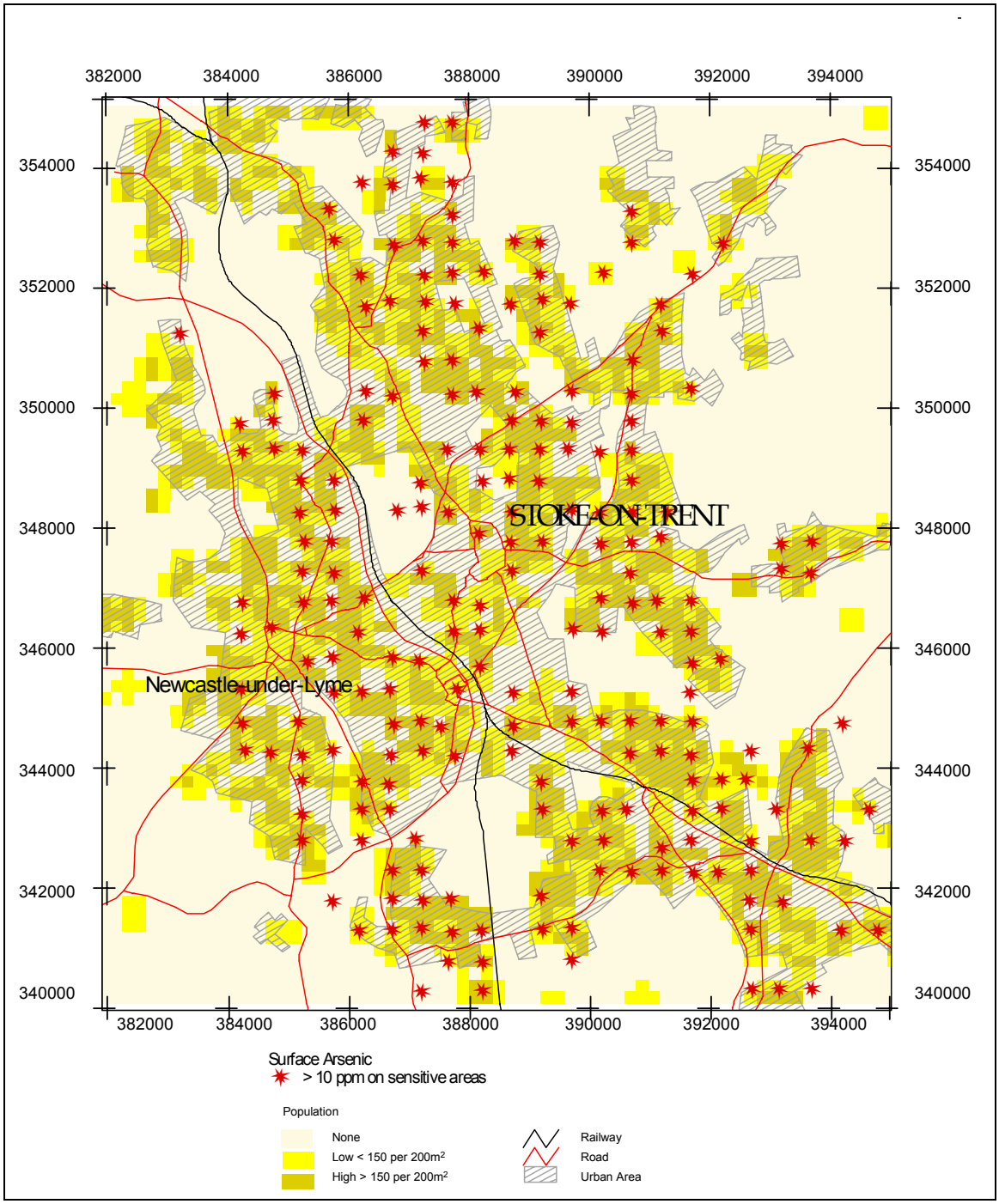
Figure 8.4 Flow diagram of the human exposure risk assessment scheme adopted for Stoke-on-Trent.

APPENDIX 8.1 STOKE-ON-TRENT URBAN GEOCHEMISTRY GIS FIRST AND SECOND LEVEL HUMAN RECEPTOR RISK ASSESSMENT MAPS

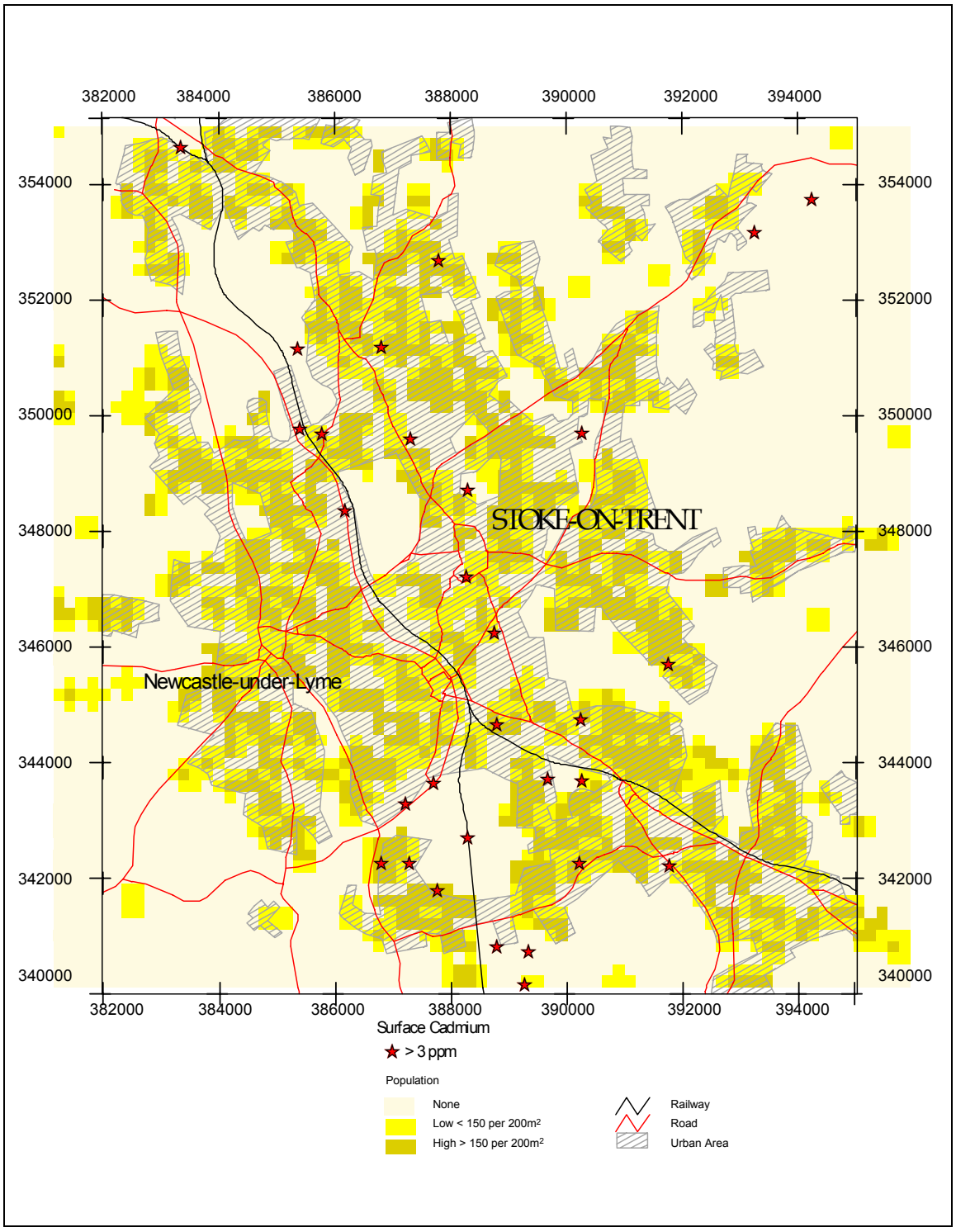
Arsenic concentrations in surface soils exceeding the ICRCL (1987) trigger value (10 ppm (mg/kg)) for domestic gardens and allotments



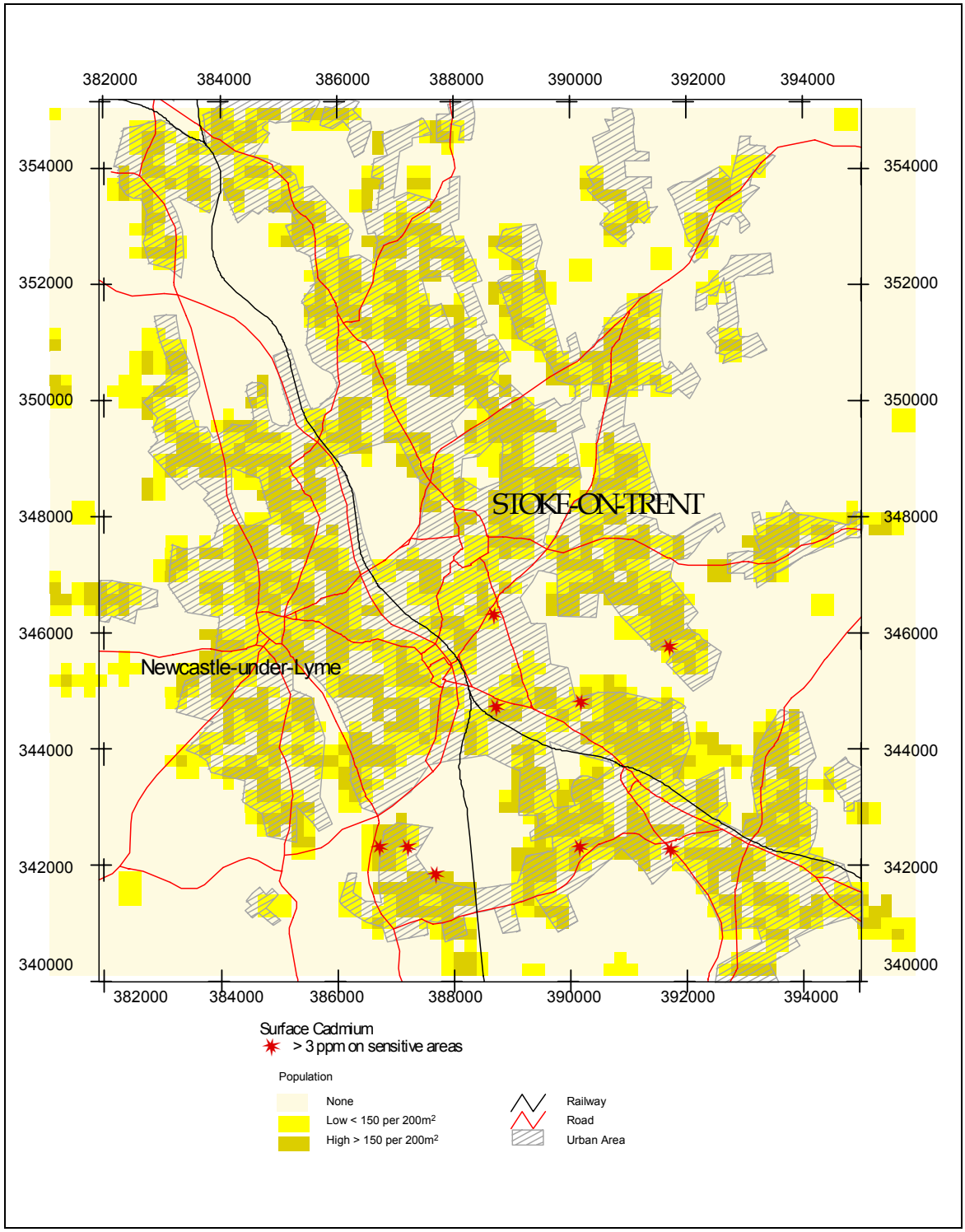
Arsenic concentrations in surface soils exceeding the ICRCL (1987) trigger value (10 ppm (mg/kg)) for domestic gardens and allotments, coincident with sensitive land use types (gardens, allotments, fields, play areas etc.)



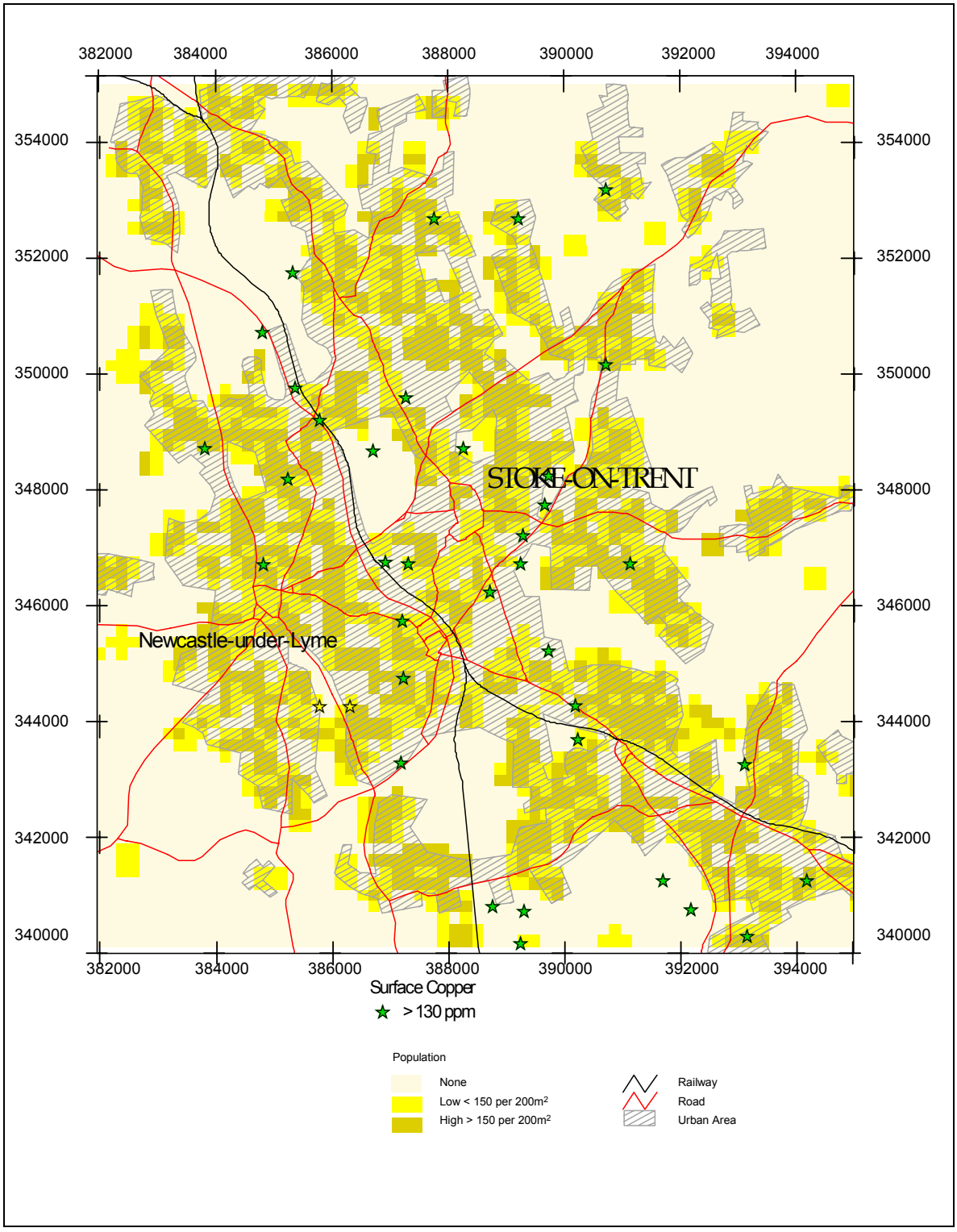
Cadmium concentrations in surface soils exceeding the ICRCL (1987) trigger value (3 ppm (mg/kg)) for domestic gardens and allotments



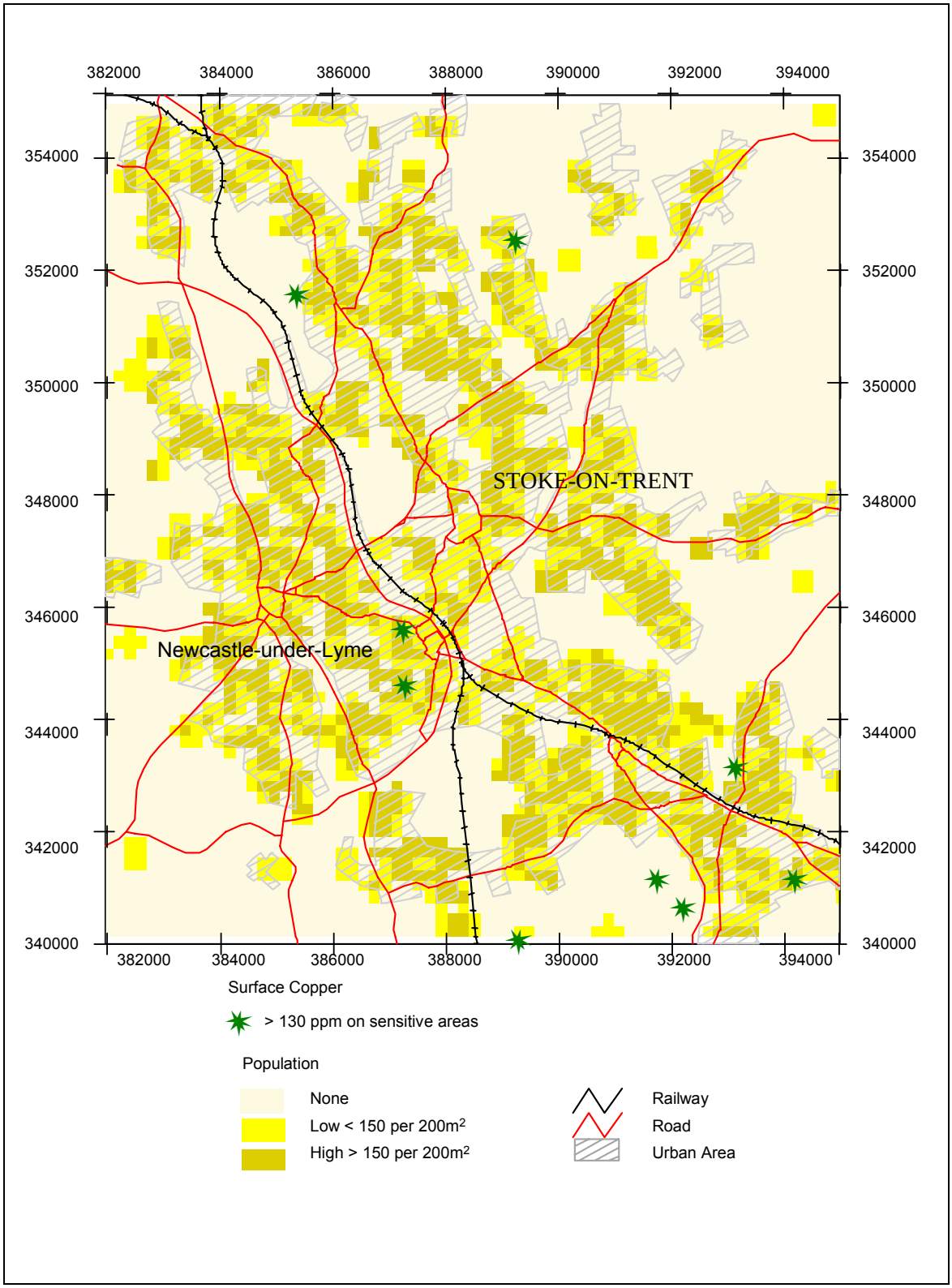
Cadmium concentrations in surface soils exceeding the ICRCL (1987) trigger value (3 ppm (mg/kg)) for domestic gardens and allotments, coincident with sensitive land use types (gardens, allotments, fields, play areas etc.)



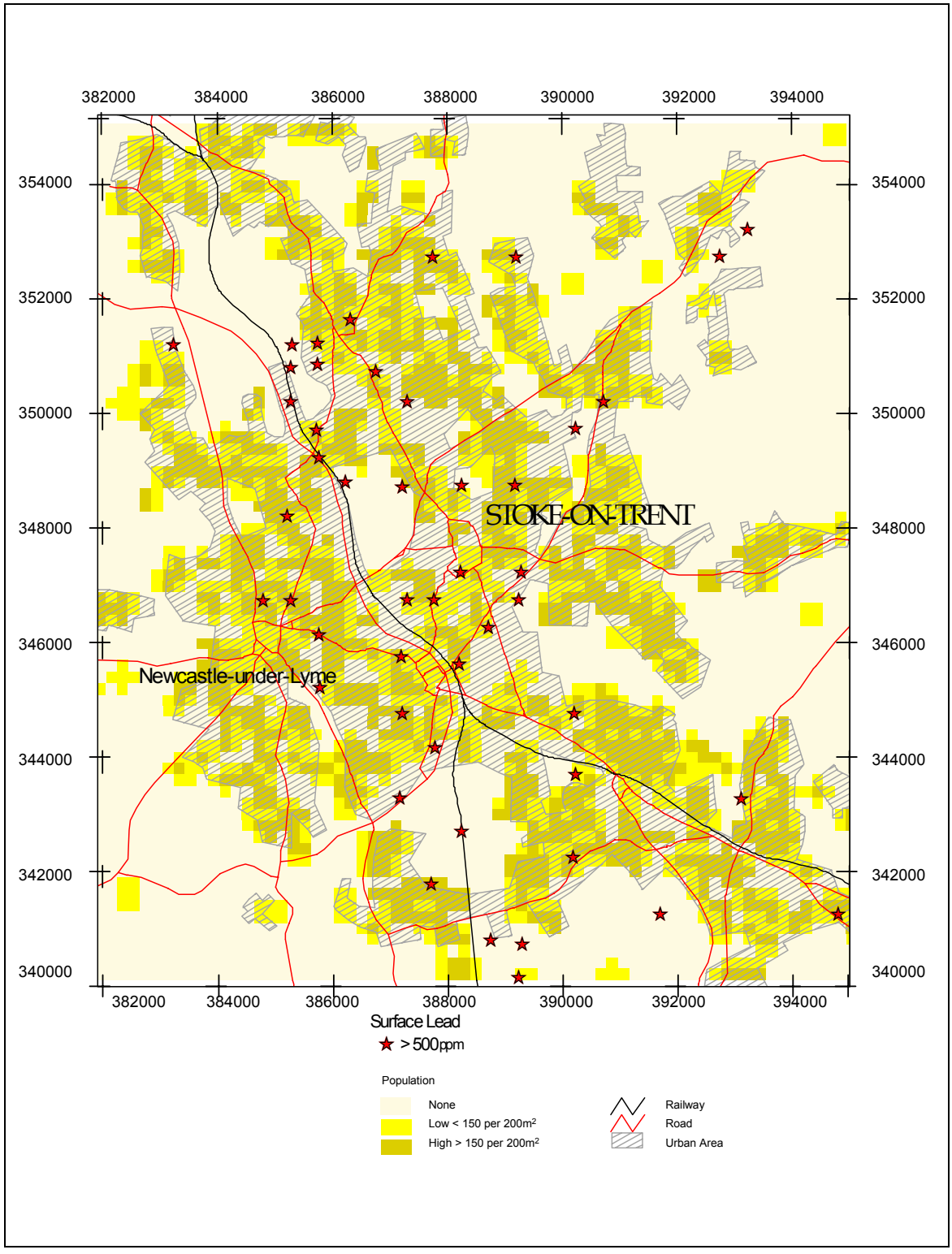
Copper concentrations in surface soils exceeding the ICRCL (1987) trigger value (130 ppm (mg/kg)) for domestic gardens and allotments



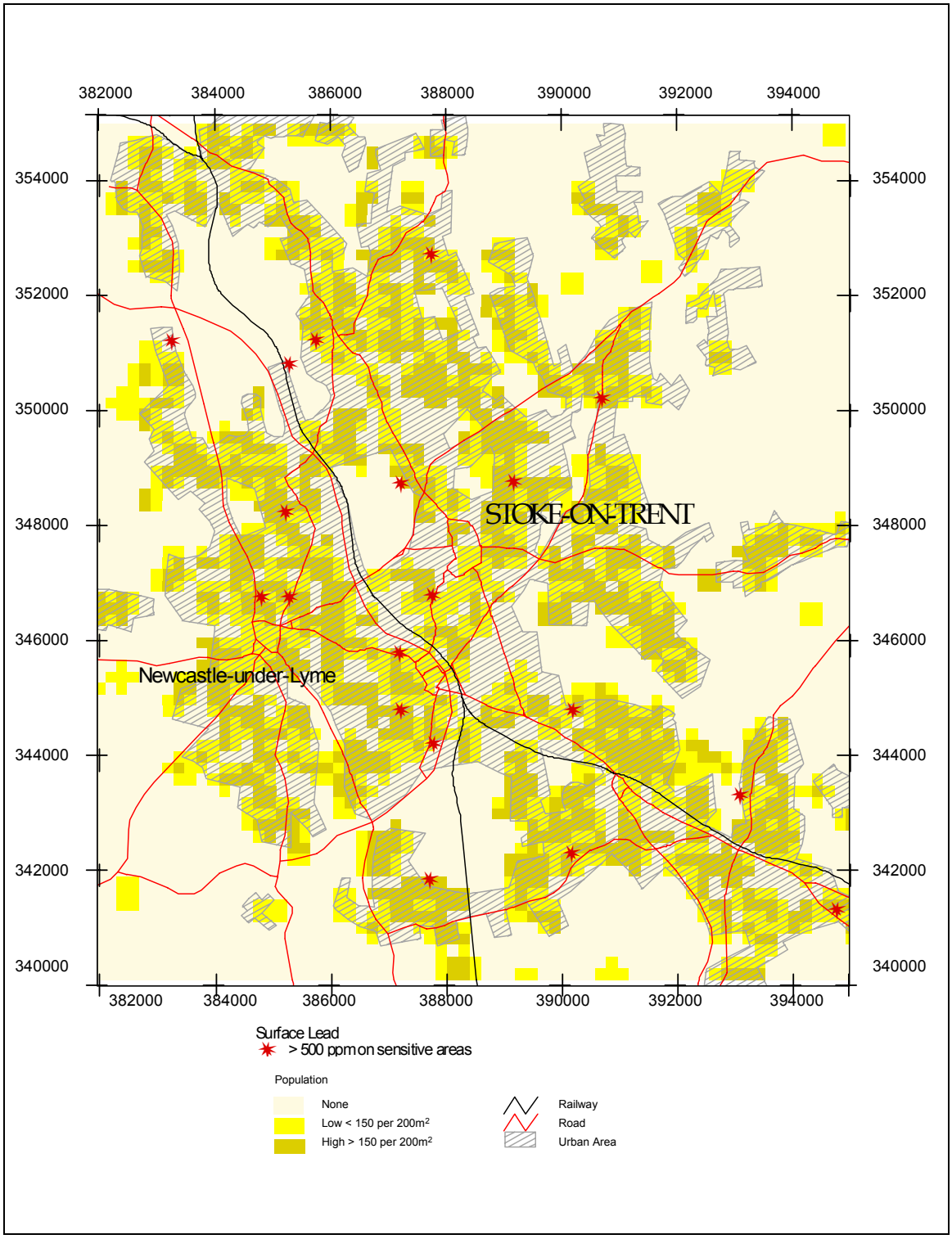
Copper concentrations in surface soils exceeding the ICRCL (1987) trigger value (130 ppm (mg/kg)) for domestic gardens and allotments, coincident with sensitive land use types (gardens, allotments, fields, play areas etc.)



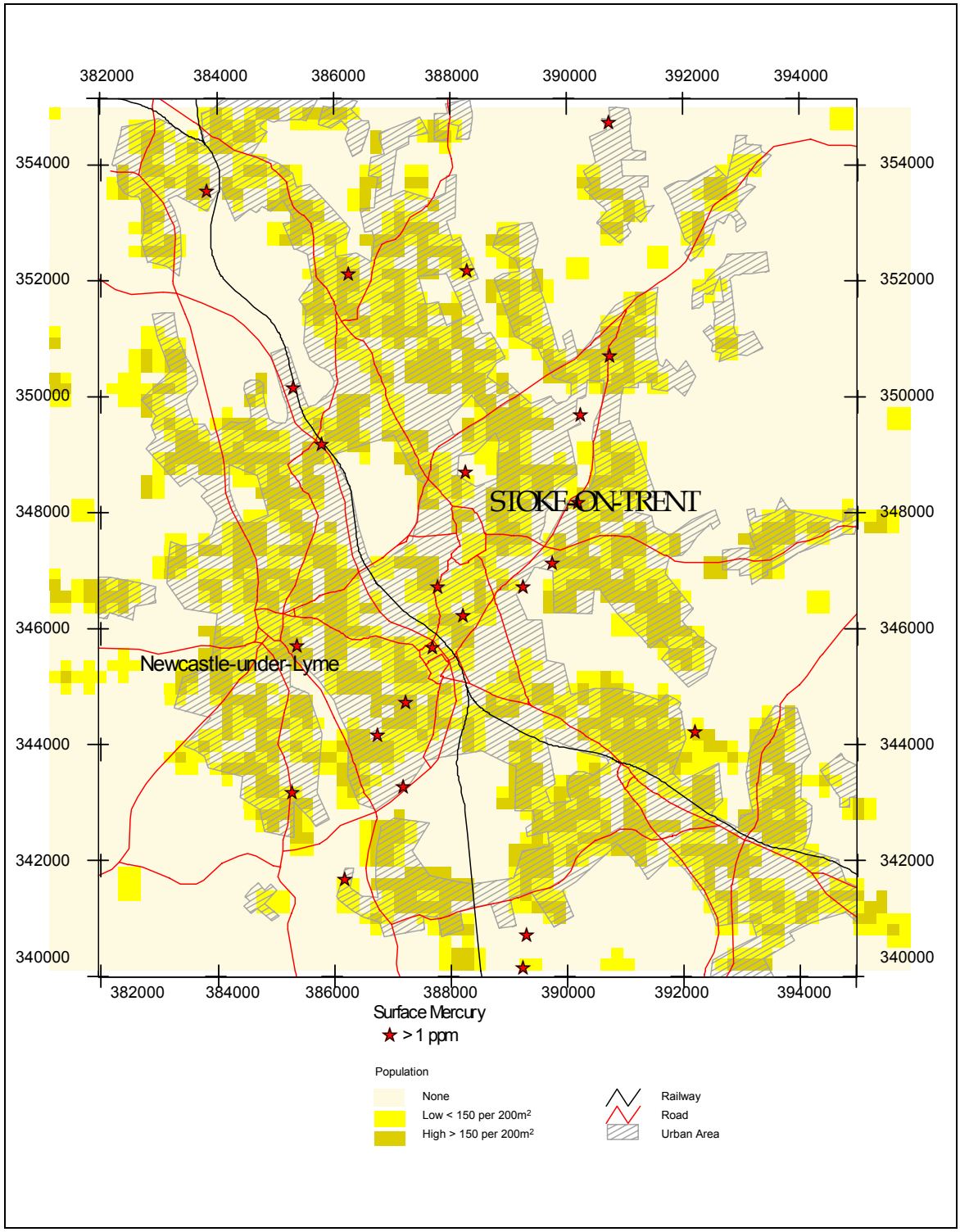
Lead concentrations in surface soils exceeding the ICRCL (1987) trigger value (500 ppm (mg/kg)) for domestic gardens and allotments



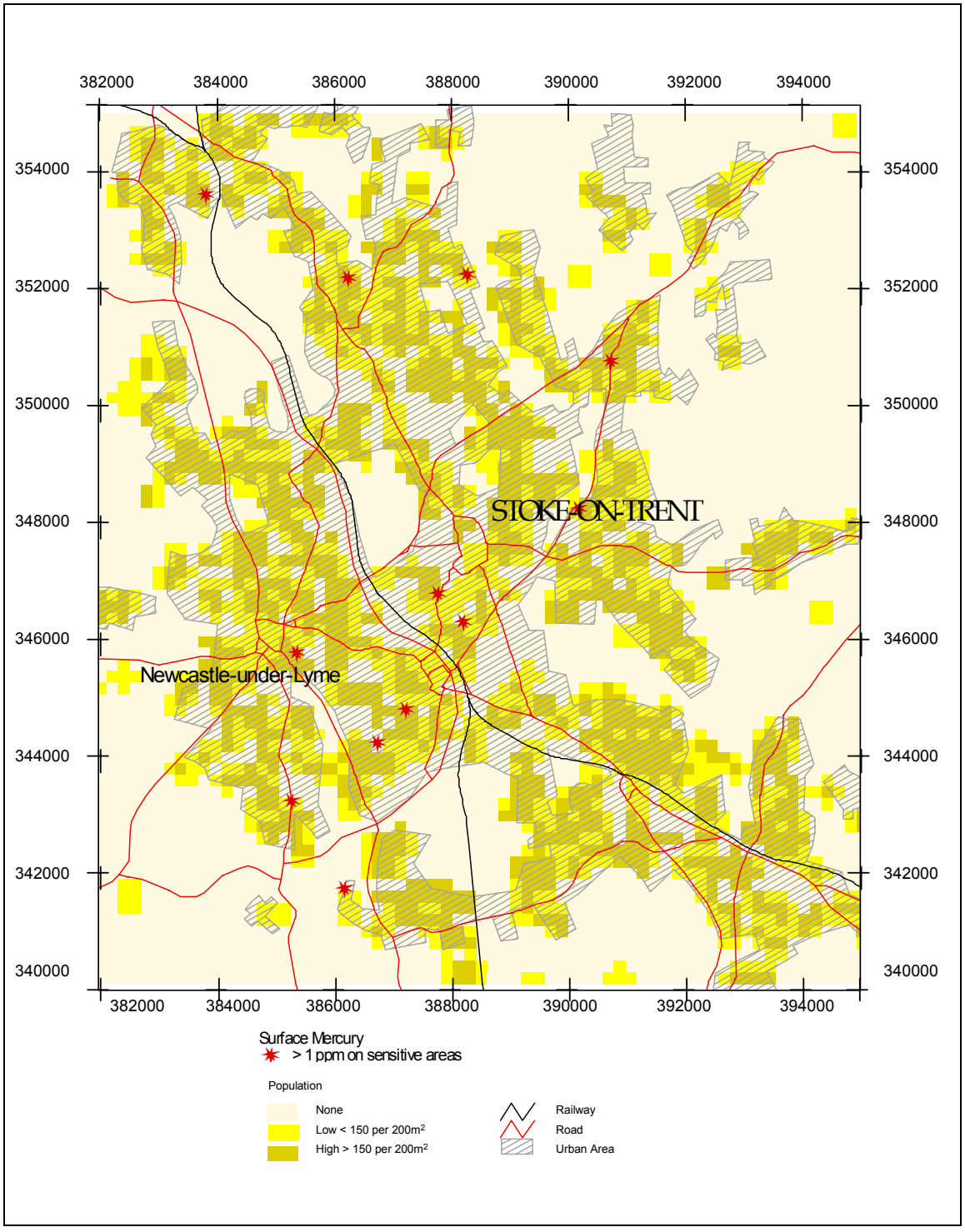
Lead concentrations in surface soils exceeding the ICRCL (1987) trigger value (500 ppm (mg/kg)) for domestic gardens and allotments, coincident with sensitive land use types (gardens, allotments, fields, play areas etc.)



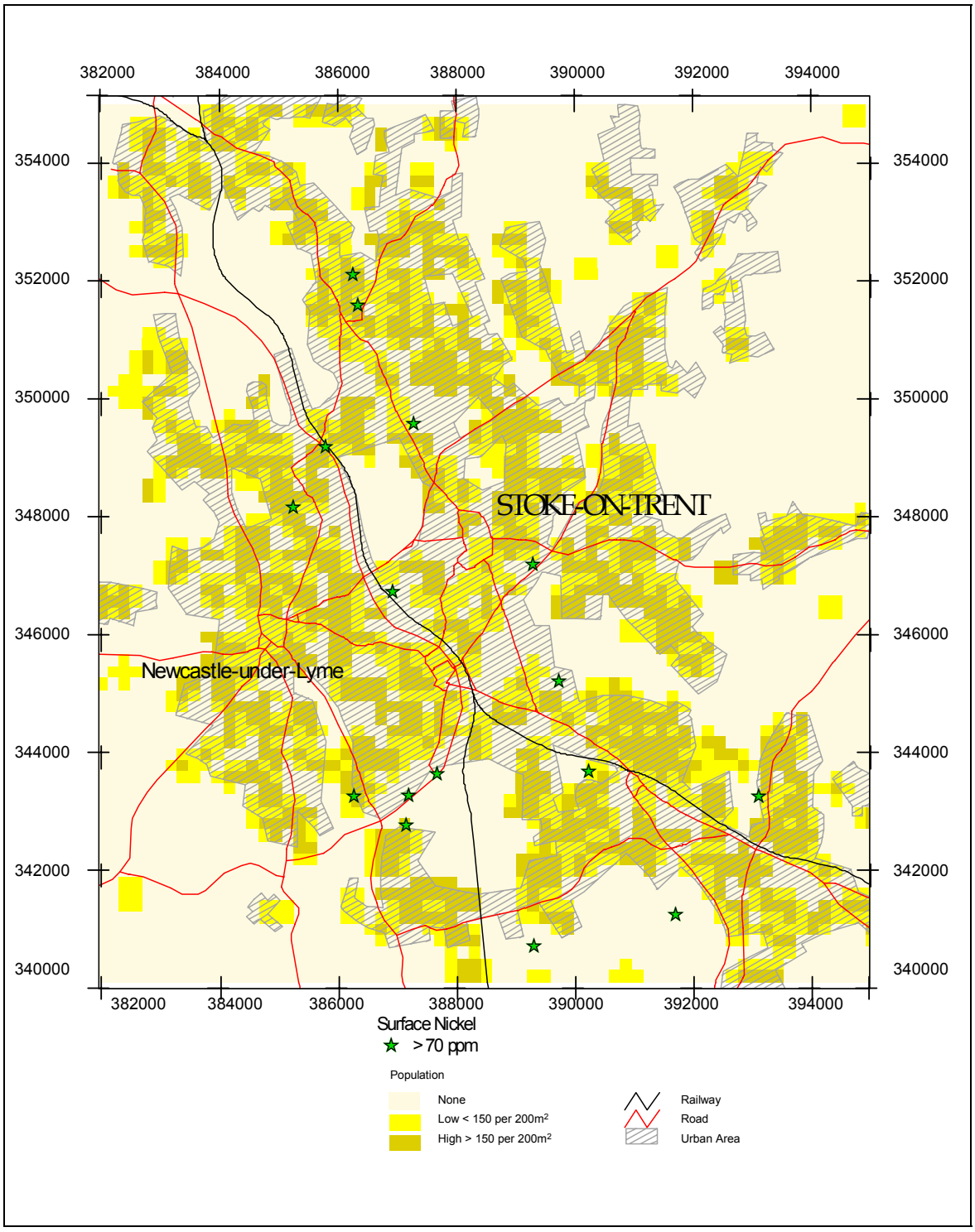
Mercury concentrations in surface soils exceeding the ICRCL (1987) trigger value (1 ppm (mg/kg)) for domestic gardens and allotments



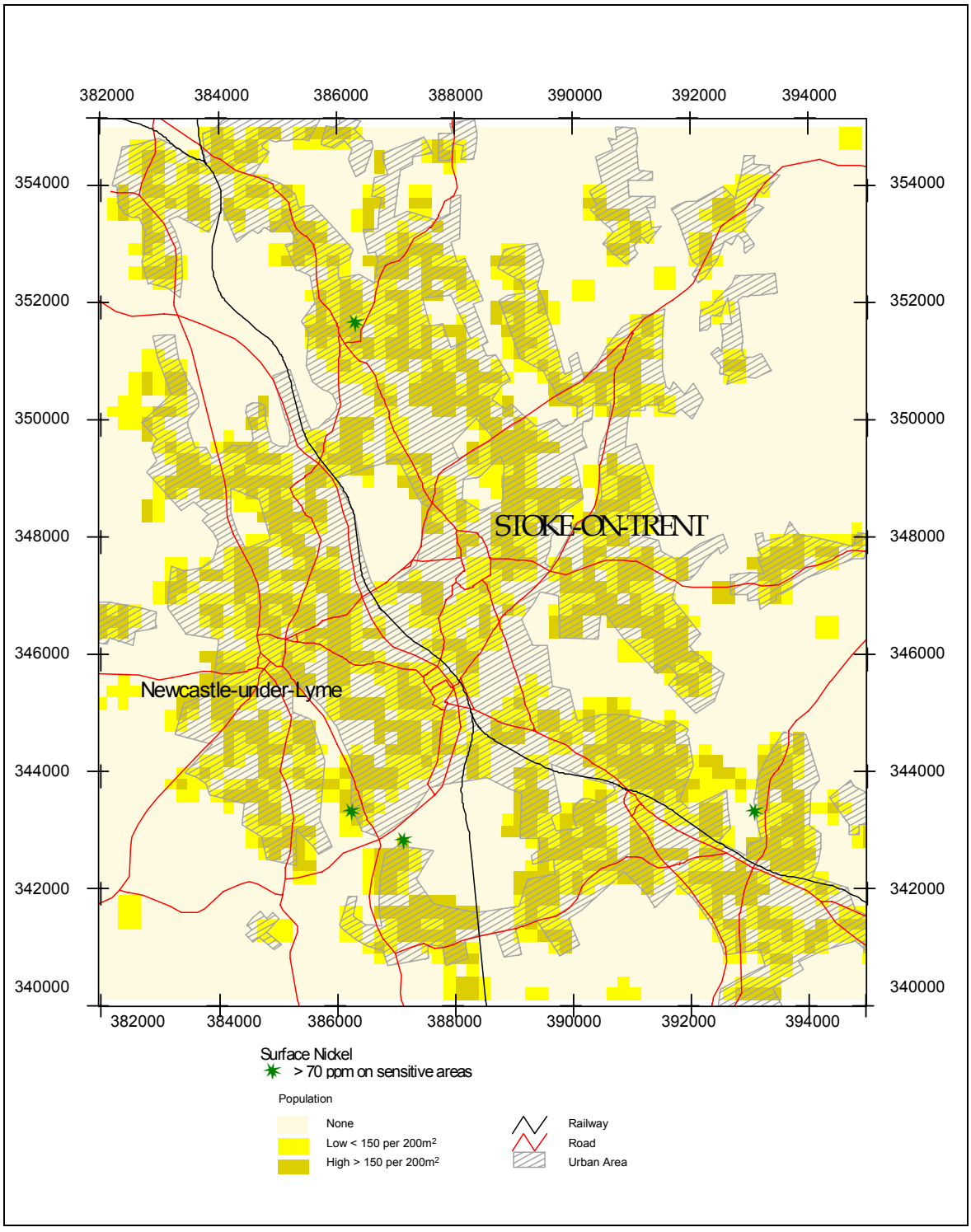
Mercury concentrations in surface soils exceeding the ICRCL (1987) trigger value (1 ppm (mg/kg)) for domestic gardens and allotments, coincident with sensitive land use types (gardens, allotments, fields, play areas etc.)



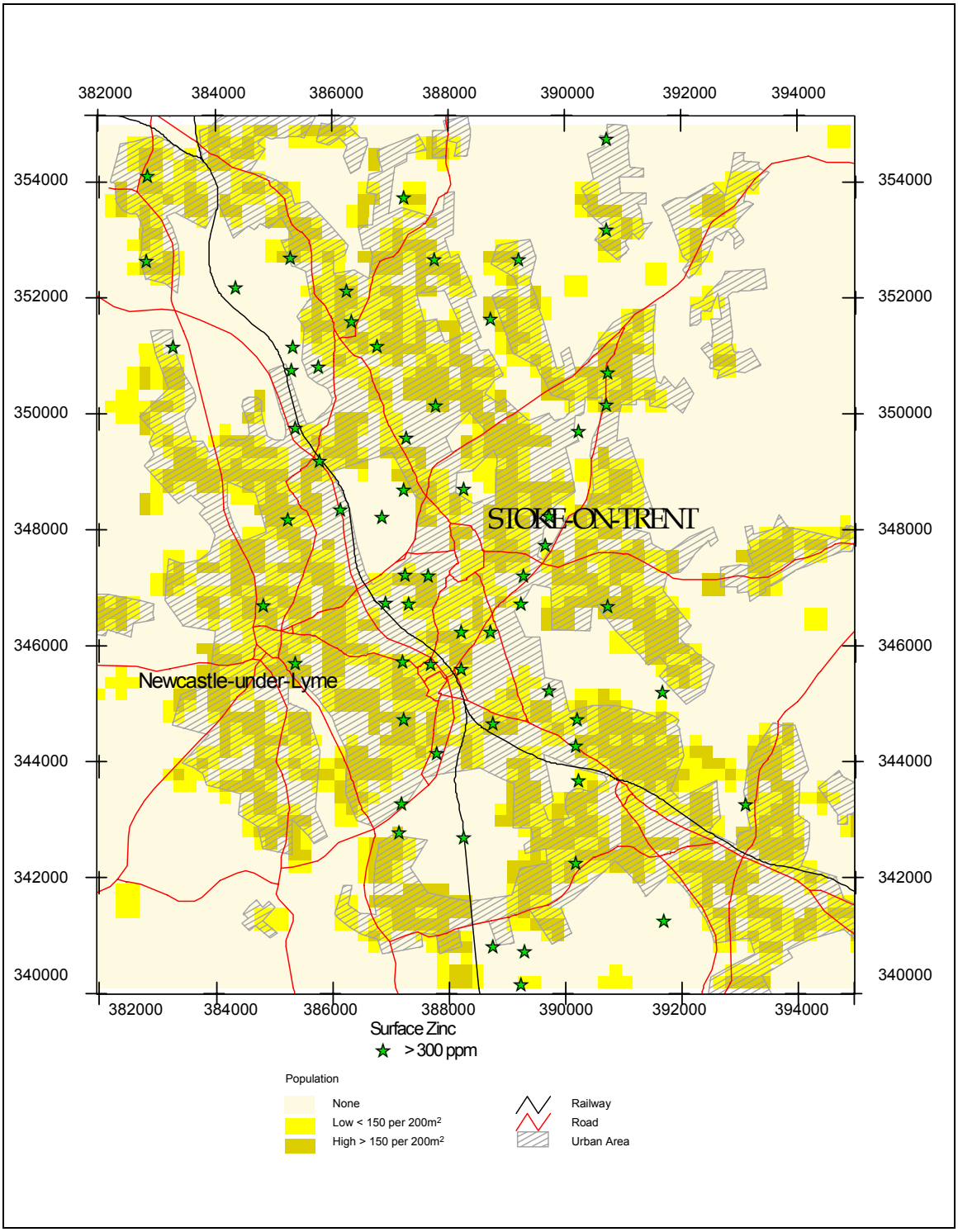
Nickel concentrations in surface soils exceeding the ICRCL (1987) trigger value (70 ppm (mg/kg)) for domestic gardens and allotments



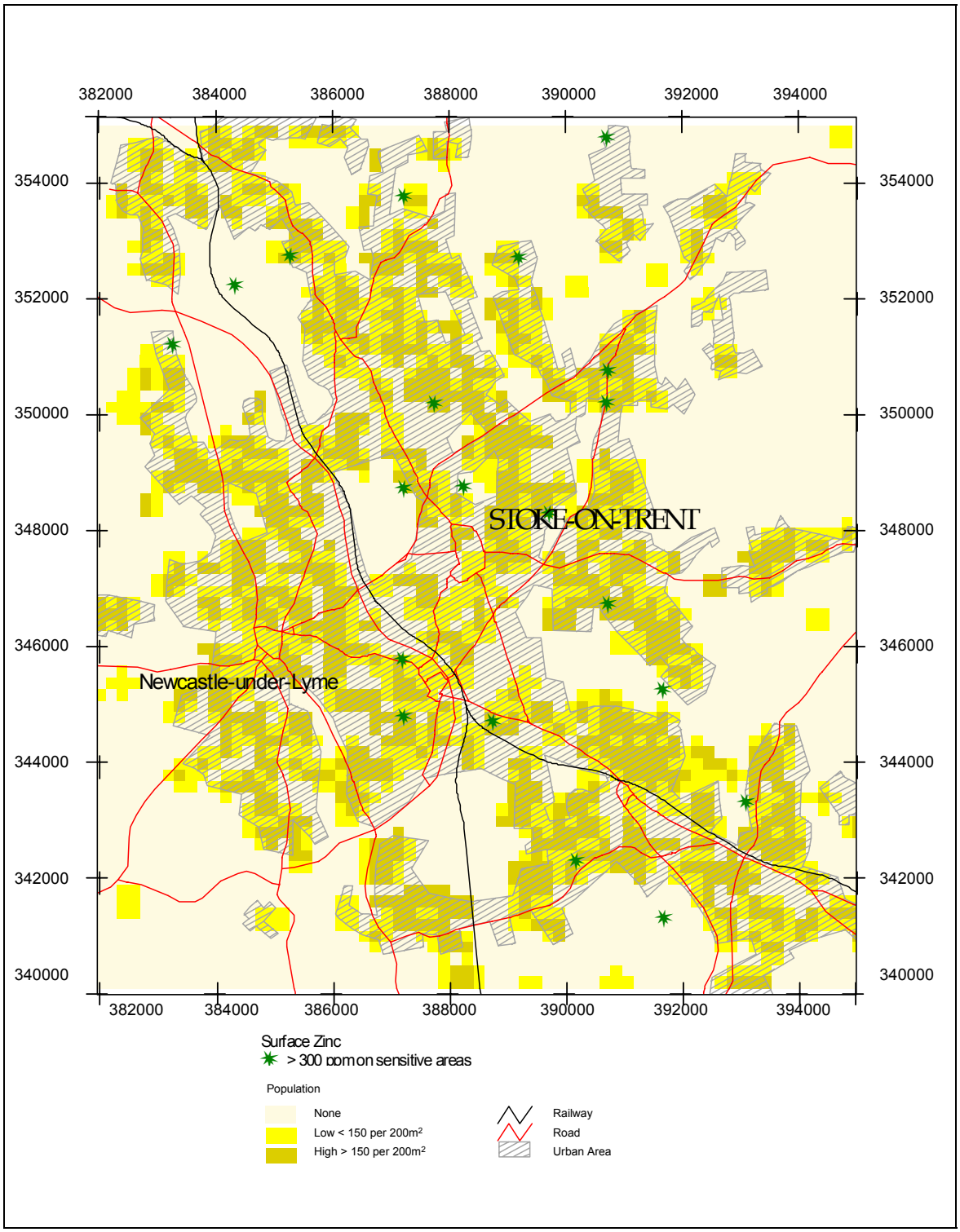
Nickel concentrations in surface soils exceeding the ICRCL (1987) trigger value (70 ppm (mg/kg)) for domestic gardens and allotments, coincident with sensitive land use types (gardens, allotments, fields, play areas etc.)



Zinc concentrations in surface soils exceeding the ICRCL (1987) trigger value (300 ppm (mg/kg)) for domestic gardens and allotments



Zinc concentrations in surface soils exceeding the ICRCL (1987) trigger value (300 ppm (mg/kg)) for domestic gardens and allotments, coincident with sensitive land use types (gardens, allotments, fields, play areas etc.)



9. Conclusions and Future Recommendations

The main conclusions and recommendations of this study on the urban geochemistry of the Stoke-on-Trent and lessons learned in terms of urban geochemical mapping; urban geochemical data presentation; urban geochemistry GIS development and hydrogeological and human health risk assessment are summarised as follows:

9.1 URBAN GEOCHEMICAL SURVEY METHODS

In the past, budgetary constraints resulted in a limited suite of analytes determined in GSUE soils with focus on the PHSs such as As, Cd, Cu, Pb and Zn. The examinations of potential sources of elements in soils, relationships with natural and man-made parent materials and assessments of likely threats to groundwater and humans from soils outlined in the present study are only possible because of the determination of key soil parameters such as the pH, LOI and major element chemistry (for example the geochemical signatures associated with foundry waste are identified because CaO, MgO and P_2O_5 are determined in addition to the trace metals).

- ***It is recommended that the full range of parameters determined in this study should be incorporated in all urban surveys in future.***

Comparisons between surface and profile soils can provide a useful indication of likely element sources in the urban environment. For example, elements such as Fe_2O_3, Ni, Cu, As, Cr and CaO present in higher concentrations in profile soils can indicate contamination by industrial and metal processing, made ground and fill materials. In contrast elements released to the environment via the use of road vehicles such as Pb and Cd concentrated in surface soils, are indicators of atmospheric contamination. Investigations into the relationships between urban surface and profile soils were complicated during the present study by the GSUE sampling strategy whereby surface soils are sieved to a coarser (< 2 mm fraction) than profile soils (< 150 µm). Although this strategy was established with a sound scientific basis in the early 1990s (profile soils which more closely represent soil parent materials were compatible with regional stream sediment data) it is now recognised that soil studies are of prime environmental importance and a consistent survey approach is desirable.

- ***It is recommended that in light of increased interest in environmental studies, both surface and profile soils are sieved to the environmental standard < 2 mm.***

In Stoke-on-Trent and several other cites covered by the GSUE project to date, sampling was carried out beyond the extent of the built-up area into the urban periphery. It is apparent from the present study that this complicates the definition of the truly urban built versus rural non-built geochemical signatures.

- ***It is recommended that in future, the GSUE project focuses on soil collection in the built environment whereas urban periphery and rural coverage be provided by the G-BASE programme to clearly distinguish between the urban built and rural non-built geochemical signatures.***

Within the urban environment, this study had the opportunity to examine the relationships between soil geochemistry and made ground types to assess whether survey data could be used to aid made ground mapping.

- ***It is recommended that geochemical signatures could be used to assist the identification and classification of made ground types and more detailed geochemical mapping could prove useful in defining the spatial boundaries of artificial deposit units in urban areas.***

The purpose of systematic urban geochemical mapping is to provide an overview of soil quality in the urban environment as a framework to planning and management. Surveys at the citywide scale are not designed to examine specific problems or locations and do not replace the need for detailed site investigation reports. None-the-less, the data provide a useful insight into the likely controls on element distributions in the urban environment and general relationships with land use, ground types and possible sources of contamination, highlighting areas for further investigation.

- ***It is recommended that urban geochemical signatures are established for other cities in the UK in order to determine element sources in soils and provide a framework to more detailed site investigations because systematic variations in chemistry were observed compared to soils over equivalent lithologies in the rural environment during the present study.***

- ***It is recommended that since much of the key information necessary for more detailed studies, including past and present day land use and development history, is held by Local Authorities in the UK, these should be carried out as follow-up projects to the GSUE urban survey in close collaboration with the Local Authorities concerned.***

9.2 URBAN GEOCHEMICAL DATA PRESENTATION AND GIS DEVELOPMENT

Geographic information system (GIS) technology makes possible the ready display of geochemical and other environmental data in digital format and the ArcView® GIS software has been adopted as the BGS corporate standard.

Although environmental datasets necessary to aid the interpretation of geochemical data such as the solid geology, superficial cover and nature of made ground are increasingly available in digital format, investigations carried out during the present study were hampered by a lack of digital information on the hydrogeological regime and land use in Stoke-on-Trent.

- ***It is recommended that the BGS examine ways of capturing key datasets such as current and historical land use and ground hydrogeological characteristics in urban environments as a priority.***

Investigations into spatial display methods carried out during the present study show that whereas interpolated geochemical maps are an internationally accepted method of presenting regional geochemical data, they are not appropriate for urban surveys due to the highly heterogeneous nature of urban soils. Although ANOVA results demonstrate that the sampling methodology adopted for urban areas is valid, namely soils collected close together are more similar than soils collected further apart, variogram analysis shows there is little spatial connectivity in the Stoke-on-Trent soils and data interpolation is not valid. As a result, a method of presenting the geochemical data as proportional symbol maps using the ArcView® GIS package was developed during the present study.

- ***It is recommended that ArcView® proportional symbol maps be adopted as standard for all urban areas. It should be noted, however, that spatial relationships in urban soils are being examined further under the GSUE project in Coventry and the results of this study may have further impact on the development of data presentation methods.***

At the broader scale, interpolated geochemical maps can provide useful overviews of rural-urban areas and multi-element linkages via three-component mapping and have therefore been included in this study.

- ***It is recommended that interpolated rural-urban and three component maps are included in urban studies where appropriate as they provide useful overview information. However,***

these maps should not be distributed digitally outside the BGS due to the potential for mis-interpretation of results in terms of contaminated land.

The G-BASE 'in house' method for generating interpolated and three-component maps using ArcView® Gridder requires further development as at the present time, the data categorisation and histogram generation has to be carried out manually for display purposes.

- ***It is recommended that categorising interpolated maps generated in ArcView® Gridder according to the real data percentile distribution is more representative than using interpolated data percentiles.***

Experience of this study has shown that it is important that urban geochemistry GIS are readily transferable between computer systems and output formats such as CD-ROMS.

- ***It is recommended that all data layers including interpolated grid files must be stored as ArcView® shape files and all legends for all layers must be saved as ArcView legend files. All shape and legend files must be stored in the same or subordinate file directories to allow the ArcView 'project' file to be transferred across drives or servers.***

9.3 URBAN GEOCHEMISTRY OF STOKE-ON-TRENT SOILS

Total concentrations for 26 elements in surface (0.15 m depth, < 2mm fraction) and 22 elements in profile (0.45 m depth, < 150 µm fraction) soils collected from 747 sites at a sample density of 4 per km^2 across Stoke-on-Trent provide a systematic soil quality dataset for the urban environment. Direct comparison of these data with rural soils on the periphery of Stoke-on-Trent and from the Humber-Trent region are possible due to the standard methods adopted by the BGS G-BASE programme in rural and GSUE project in urban environments. These comparisons indicate that the majority of metal and metalloid elements are elevated in urban soils by 1.2 – 2 times local rural soil averages. Comparisons also indicate that most elements are elevated 1.5 – 4 times national soil average contents although these results should be treated with caution due to differences in the survey methods between the two datasets. These general comparisons are useful to indicate the level of enhancement in urban versus rural areas, however, they do not take account of the influence of natural soil parent materials on the geochemistry.

With the developments in GIS technology in recent years, it is now possible to readily examine the relationships between soil parent materials and geochemical signatures and investigations carried out in Stoke-on-Trent show some interesting associations. The city is mainly underlain by Westphalian age Coal Measures, rocks which are naturally elevated in many metal elements such as As, V, Mo, Cu, Ni, Zn, Pb and CaO and accounts in part for the high concentrations of these elements in Stoke-on-Trent soils relative to national averages. It should be noted however, that given the long and extensive history of industrialisation of the Coal Measures in the UK, it is difficult to establish a truly natural baseline for this rock type. In contrast, many trace elements are present in much lower concentrations over the quartz-rich Namurian Millstone Grit and Triassic Sherwood Sandstones of the Stoke urban periphery reflecting natural lithochemistry and the lack of major industrial development associated with these strata. Superficial deposits in the Stoke area comprise boulder clay, which due to its heterogeneous nature, shows no clear geochemical signature. Soils developed over alluvial sediments contain high concentrations of several metals including Pb. This probably indicates the tendency for drainage systems to act as contaminant sinks in the environment and the historical development of industry and transport routes along the drainage network in the Stoke-on-Trent area. These results have implications for the remobilisation of contaminants from alluvial soils during flood events and potential impact on drainage water quality.

However, by far the greatest controls on soil geochemistry in the Stoke area are the presence of made ground and urbanisation whereby geochemical signatures reflect the long history of coal and iron extraction and metal and pottery industries the area. The majority of elements, with the exception of SiO_2 and MgO, are elevated in the made ground urban-built environment compared to the rural periphery regardless of the underlying natural parent material. Within the urban area, this study has

shown that multi-element anomalies are associated with different industrial land uses and made ground types aiding the identification of possible contaminant sources. Soils developed over coal spoil and coal ash waste, materials which have been widely dispersed in Stoke-on-Trent historically, 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 may account for localised anomalies due to historic factory emissions and dumping of ceramic waste. Although no distinctive geochemical signature was found with the road and rail network in Stoke-on-Trent, anomalous metal contents along the Caldon Canal indicate possible contamination associated with the transportation of industrial products and canal dredging. Multi-element anomalies are also associated with a former sewage treatment works to the south of Stoke-on-Trent. Interestingly, concentrations of potentially harmful substances are low in surface soils collected from flower beds in the city centre indicating the presence of 'clean topsoil' imported for landscaping following urban regeneration programmes. Whilst such soils are important for assessing human risk via contact with the surface environment, they may not represent PHS levels in the surrounding locale and soils at depth.

Despite the caveats associated with comparisons between surface and profile soils (see below), results for Sn, Cd and Pb suggest enhancement in the surface relative to profile soils indicating the greater influence of diffuse pollution sources such as traffic on these element distributions.

In summary, 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. Although the concentrations of potentially harmful substances are enhanced in the Stoke urban area relative to rural backgrounds, they are similar to other UK cities underlain by the Coal Measures such as Cardiff, Telford and Swansea indicating that Stoke is not unusual given the long history of urbanisation and industrialisation of many UK cities.

9.4 HYDROGEOLOGICAL RISK ASSESSMENT

Under the new government Environmental Protection Act Part IIa contaminated land legislation, the protection of groundwater resources is a priority. Contaminated land is a potential source of pollutants, which can migrate through the soil profile to the groundwater below. To assess the application of GSUE urban data to groundwater vulnerability evaluations the ISO (2001) contaminant-leaching model was tested on Stoke-on-Trent soils. The model requires input of parameters that control the attenuation of 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 are directly incorporated 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 during the present study and can be used for other areas.

Results show that due to the calcareous nature of the Coal Measures bedrock in Stoke-on-Trent and the base-rich character of much of the made ground material such as foundry and ceramic waste, soil pH values are circum-neutral over much of the built up area. As a result, the majority of soils have a high attenuation capacity and the leaching potential of the 11 contaminants examined in this study is low over much of the study area. Although the ISO (2001) model does not require data on element distributions in soils, the benefit of the GSUE survey is that the element concentrations are known and can be evaluated with the leaching potential results. Comparisons show that the regions of high element concentrations associated with the built-up area correspond to soils with poor leaching potential, therefore the probability of pollutant migration to groundwater from soils is less. Potential leaching risks over the Triassic and Namurian sandstones 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 element data show that the majority of trace elements studied in soils are found in low concentration over these lithologies.

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, depth to groundwater and ground disturbance information.

- ***It is recommended that the wider application of the ISO (2001) leaching potential model to the G-BASE and GSUE surveys is tested using regional geochemical data in areas where more hydrogeological information is available.***

9.5 HUMAN RISK ASSESSMENT

Under the new government Part IIa contaminated land legislation, the assessment of risks to human health is a priority. Humans come into contact with potentially harmful substances (PHSs) in soil via ingestion, cultivation of vegetables, dermal contact and inhalation of soil-derived dusts. In order to assess the potential risks to human health of contaminants in the environment, the government sets guideline or trigger values for PHSs in soils (ICRCL 1987) and has just released a Contaminated Land Exposure Assessment (CLEA) model. Since the CLEA model was not available at the time of the present study, a human risk assessment scheme was tested for Stoke-on-Trent based on the ICRCL (1987) guidelines.

The scheme identifies all surface soils that exceed the guideline values for any of the following elements: As, Cd, Cu, Pb, Ni, Hg, Pb and Zn providing a first level risk assessment. The likely pathway for PHSs to humans is then taken into account by selecting ground likely to provide contact with the local population such as gardens, allotments, play areas and parks. In the final level of the risk assessment the likely mobility and bioavailability of PHSs in these soils is qualitatively considered on the basis that low soil pH, clay and organic matter content equates to high mobility, therefore greater risk and high soil pH, clay and organic matter content equates to low mobility, therefore less risk.

Results for the Stoke-on-Trent area show that although As concentrations over much of the city exceed the ICRCL (1987) guideline level, due to the circum neutral pH of the urban soils there are only three locations where readily bioavailable PHSs occur in soils on sensitive land use types such as gardens and allotments and these areas should form the focus of further investigation.

Examination of the relationships between PHSs in soils and land use were hampered during the present study due to the lack of polygonised land use information for Stoke-on-Trent and it is recommended that these data are provided for Stoke and other urban areas in future assessments.

- ***It is recommended that current and historical land use datasets, are crucial for the risk interpretation of urban geochemical data and should be provided in digital polygonised format for Stoke and other urban areas in future assessments.***

- ***It is recommended that future human risk assessments involve the new CLEA model, as the ICRCL (1987) guidelines are now considered obsolete by the UK government.***

- ***It is recommended that follow-up studies into human risks in the Stoke-on-Trent area should also consider the application of physiologically based extraction tests (PBET) to assess the bioaccessibility of potentially harmful substances in soils.***

- ***It is recommended that methods to provide systematic urban data and risk assessments could form a useful component of existing Environmental Protection Act, Part IIa investigations and the proposed new contaminated land planning regulations (DTLR, 2002).***

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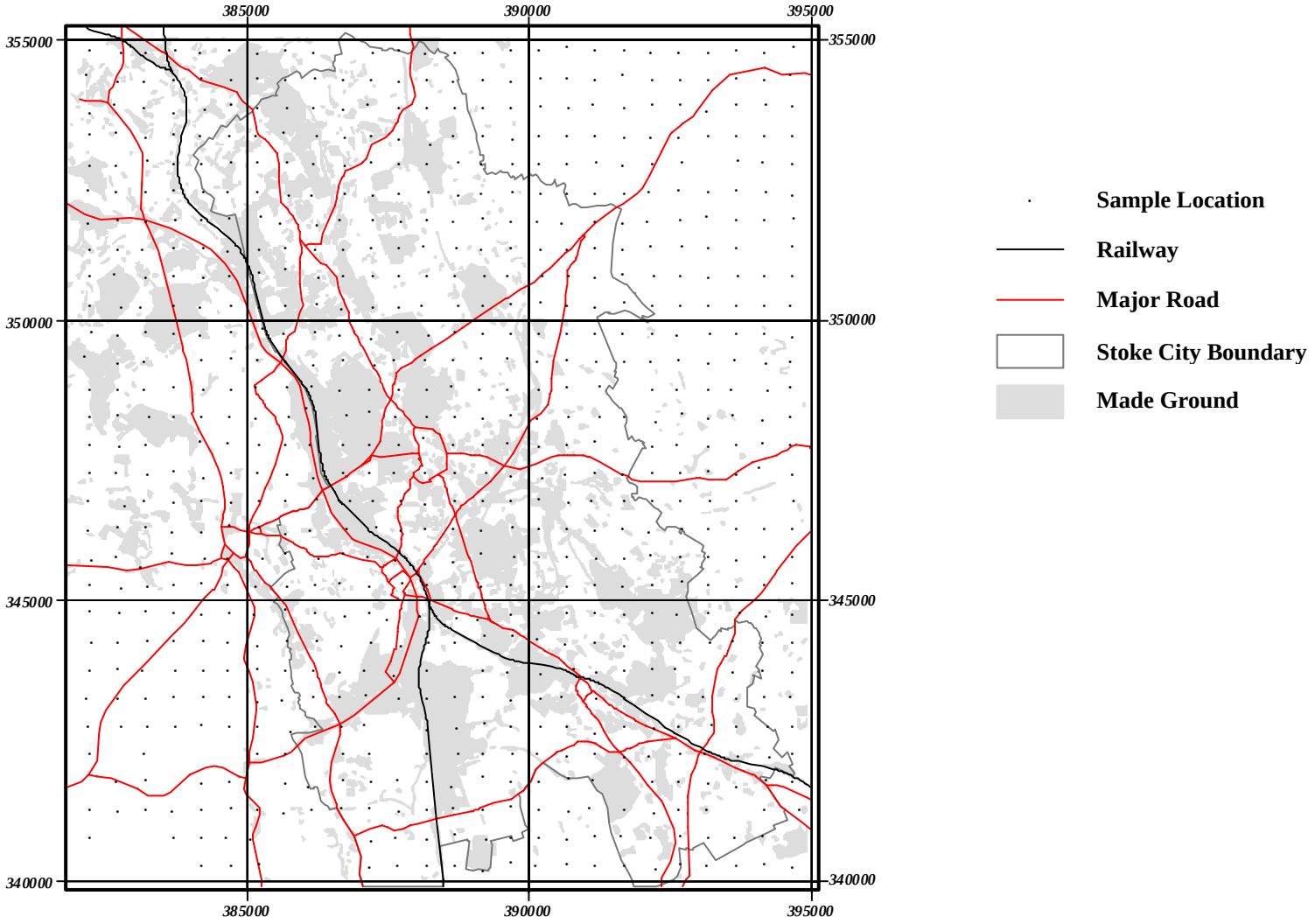
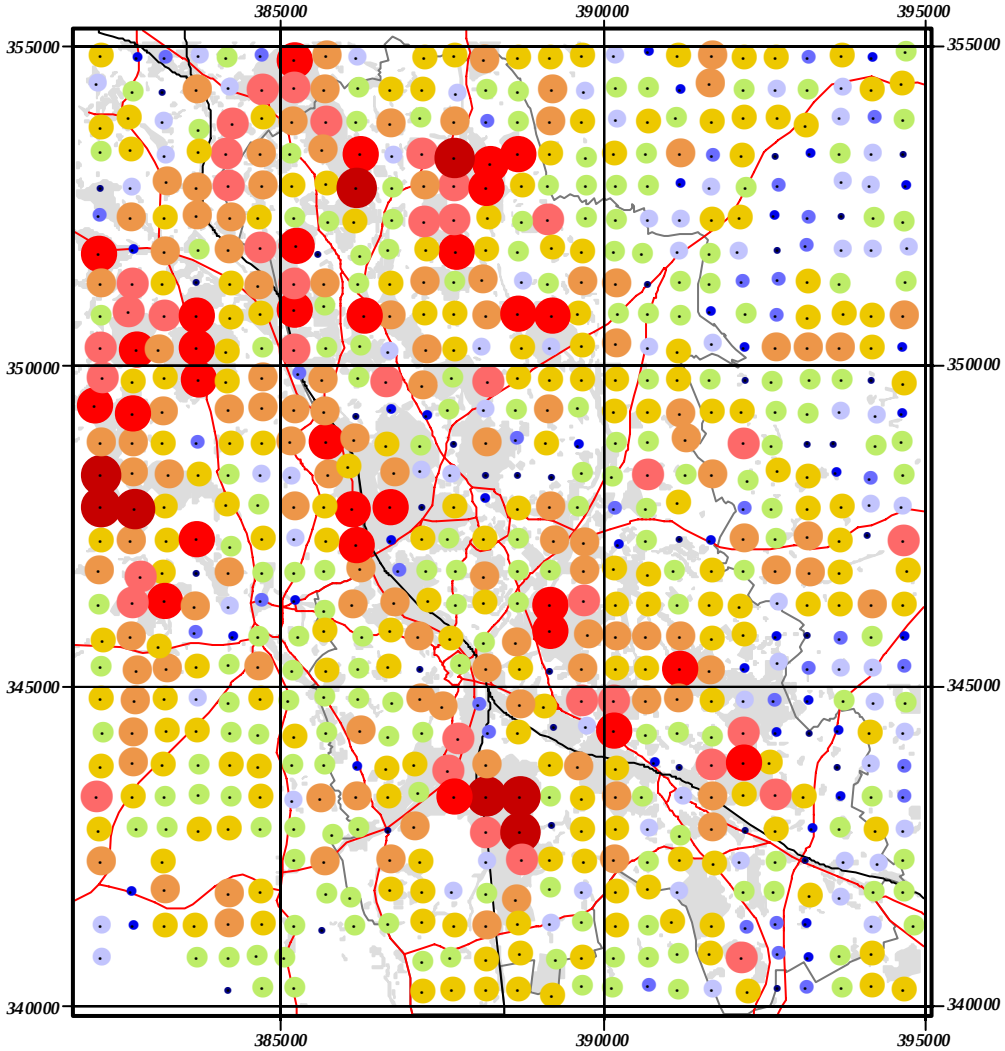
ANNEX 1. Proportional Symbol Geochemical Maps of Stoke-on-Trent Soils

Key to Background Layers

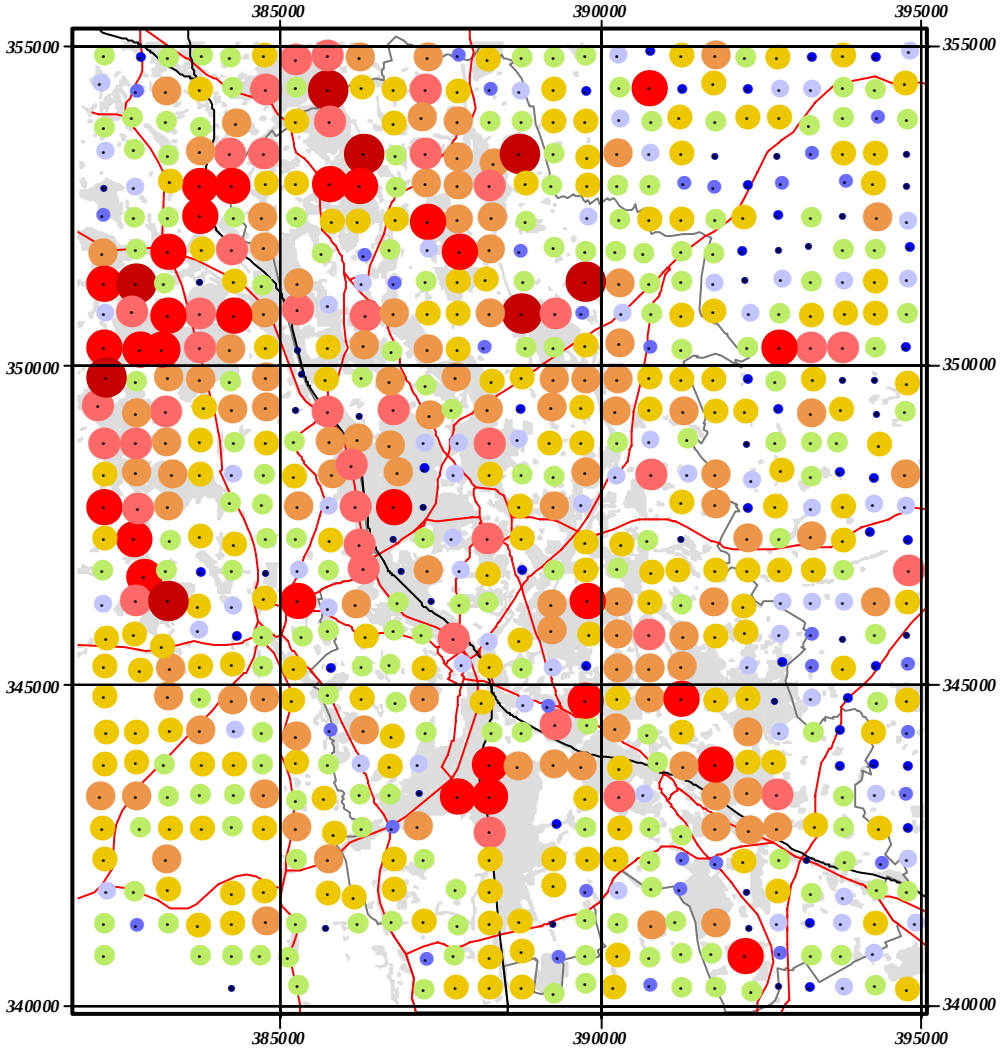


Aluminium in Surface Soils



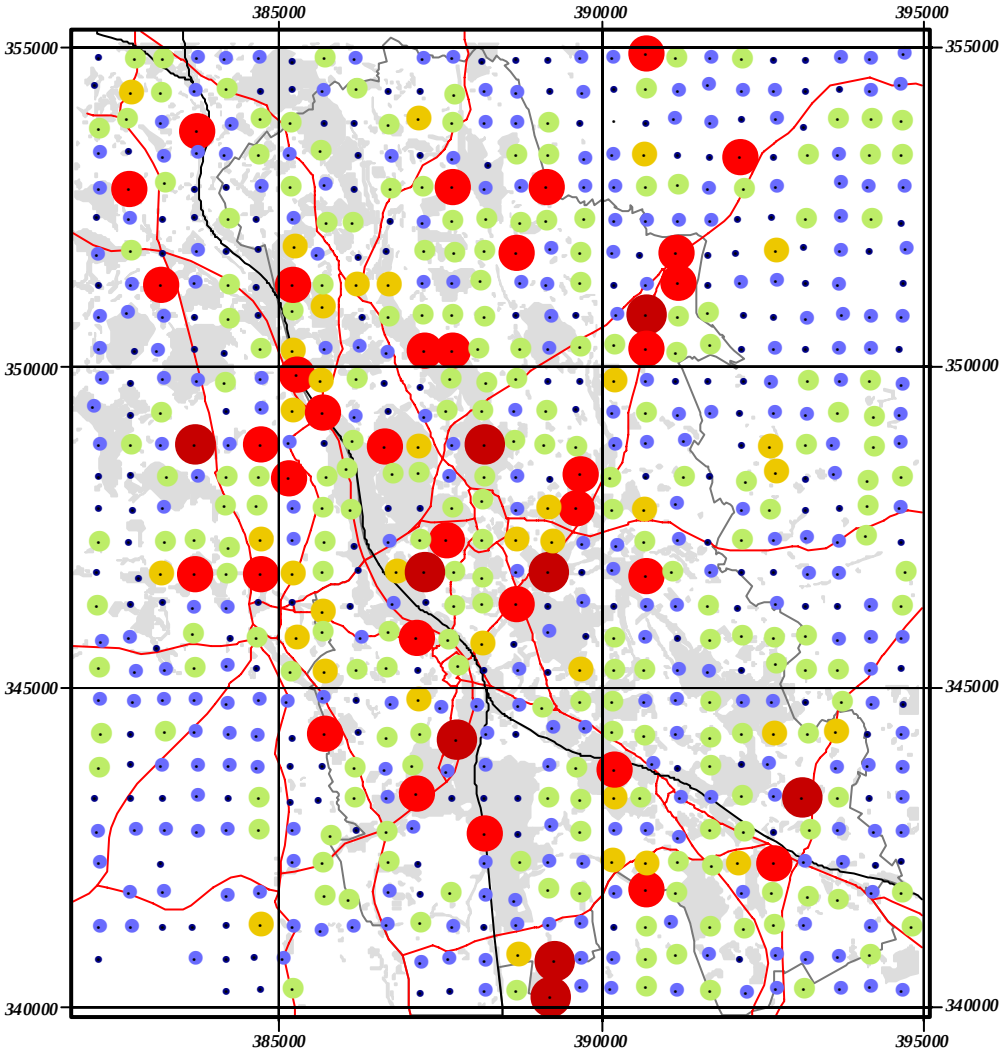
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	23.0	21.7	18.4	16.3	13.8	11.8	10.2	9.2	8.5	7.5	3.4

Aluminium in Profile Soils



Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	27.2	24.0	21.3	19.5	17.3	15.1	13.3	12.6	11.9	10.6	1.6

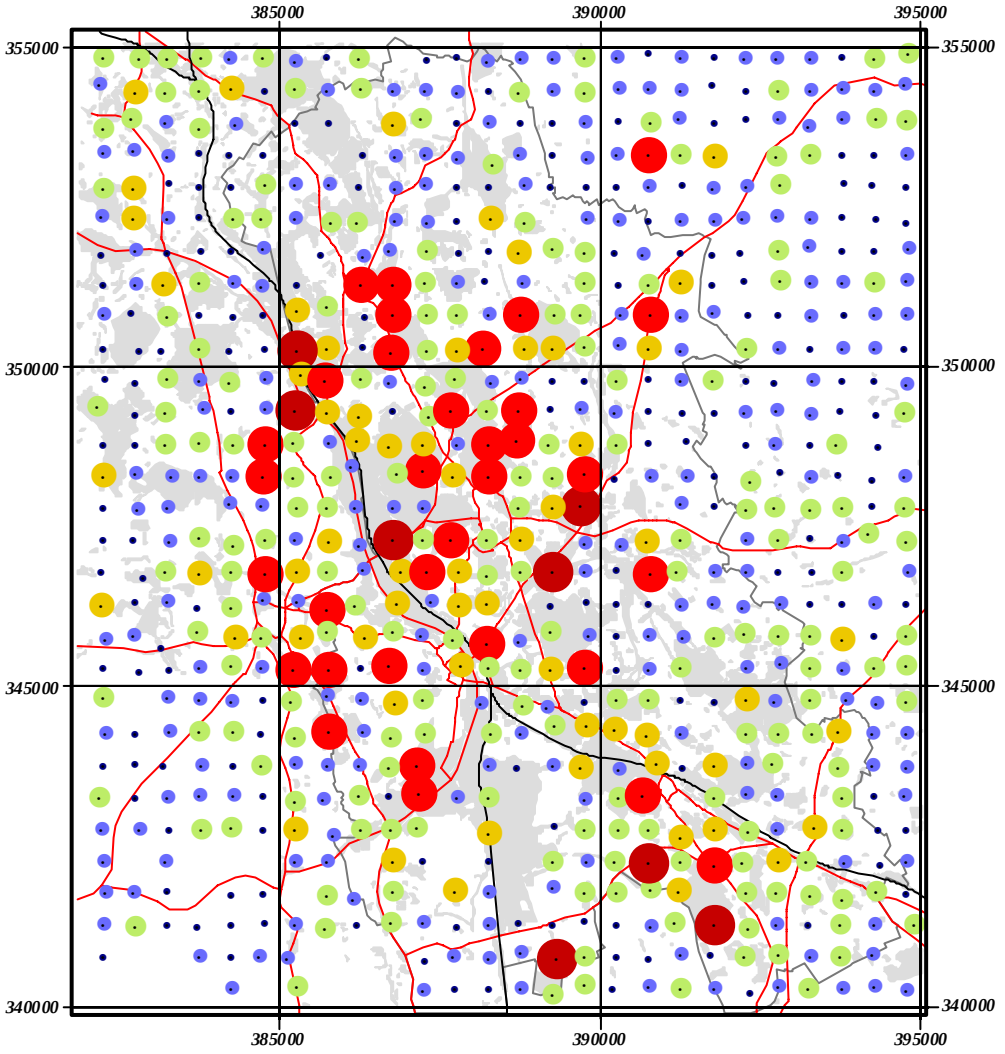
Antimony in Surface Soils



Percentile 100 99 95 90 75 50 0

Concentration (ppm) 43 17 6 4 2 1 0.5 mg/kg

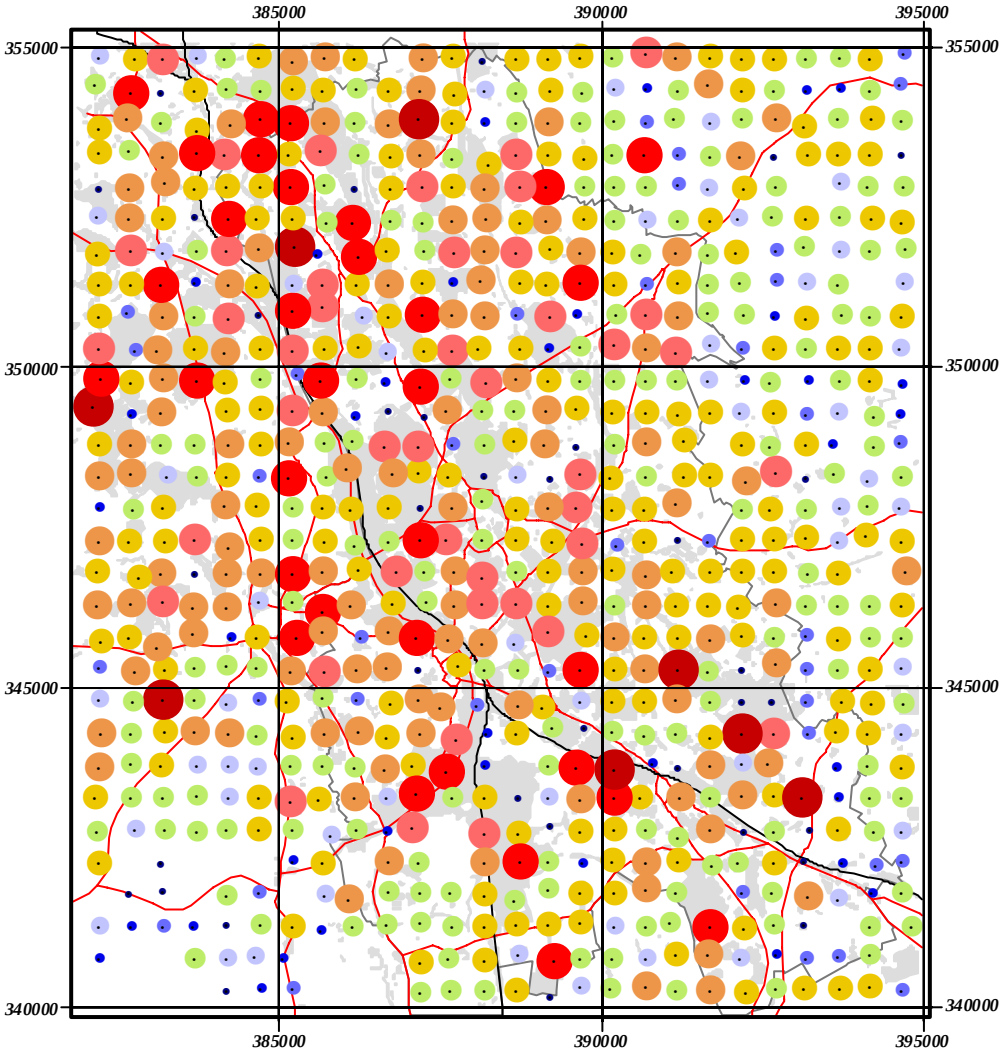
Antimony in Profile Soils



Percentile 100 99 95 90 75 50 0

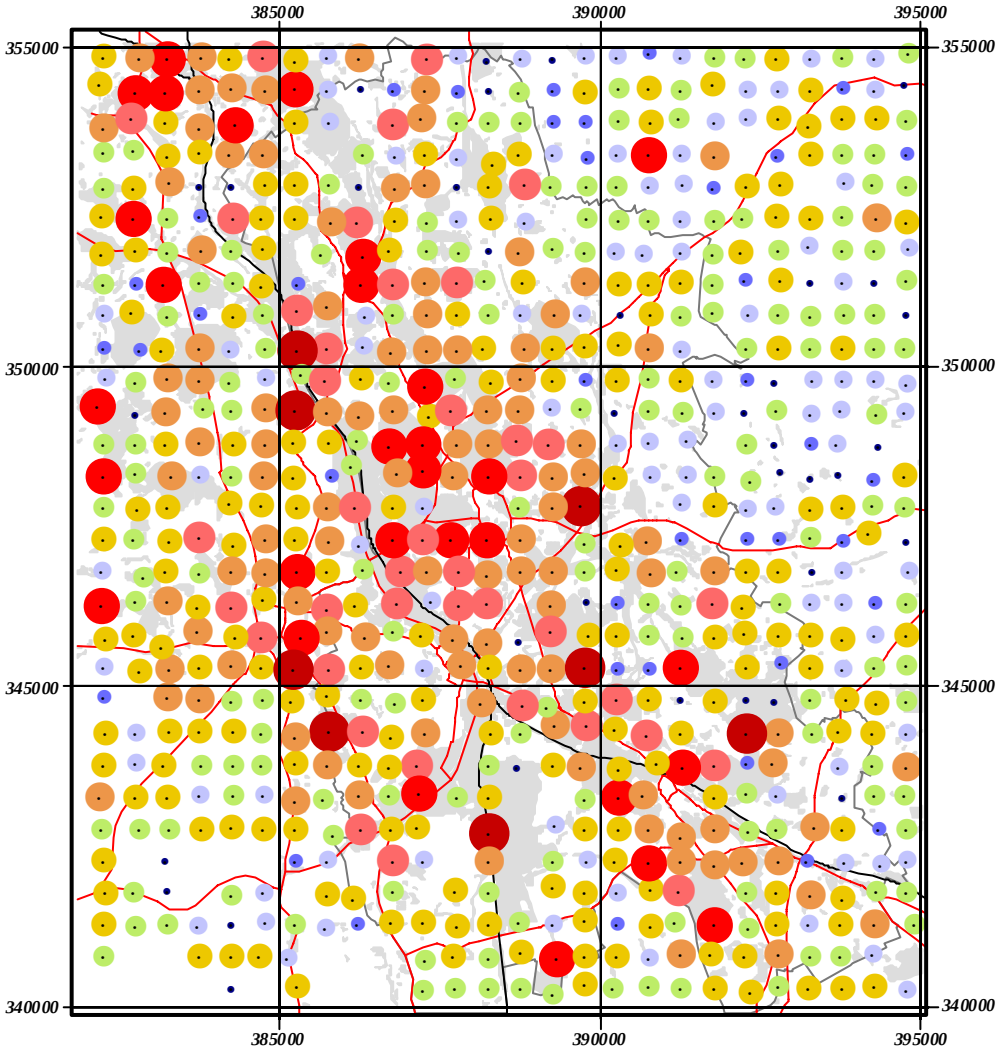
Concentration (ppm) 71 20 7 4 2 1 0.5 mg/kg

Arsenic in Surface Soils



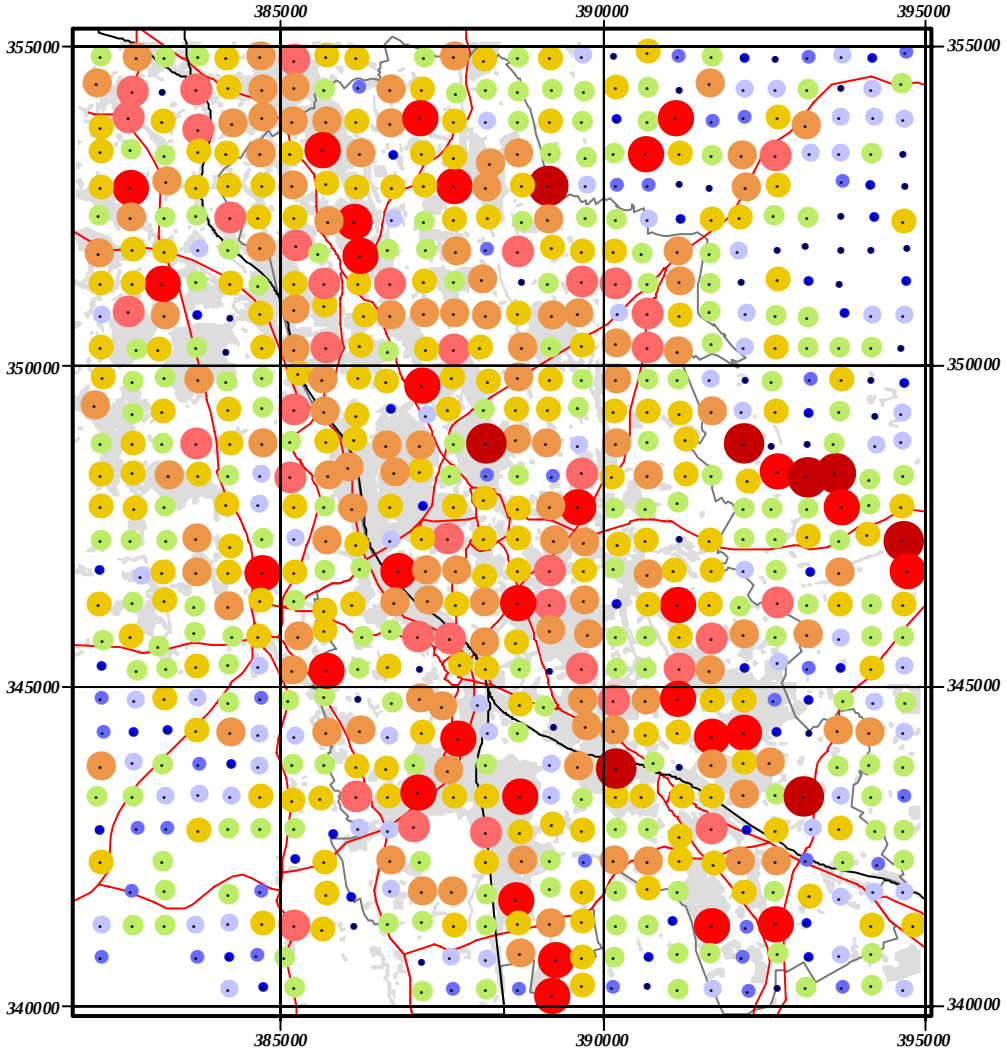
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	136	60	31	25	18	14	11	10	9	8	2

Arsenic in Profile Soils



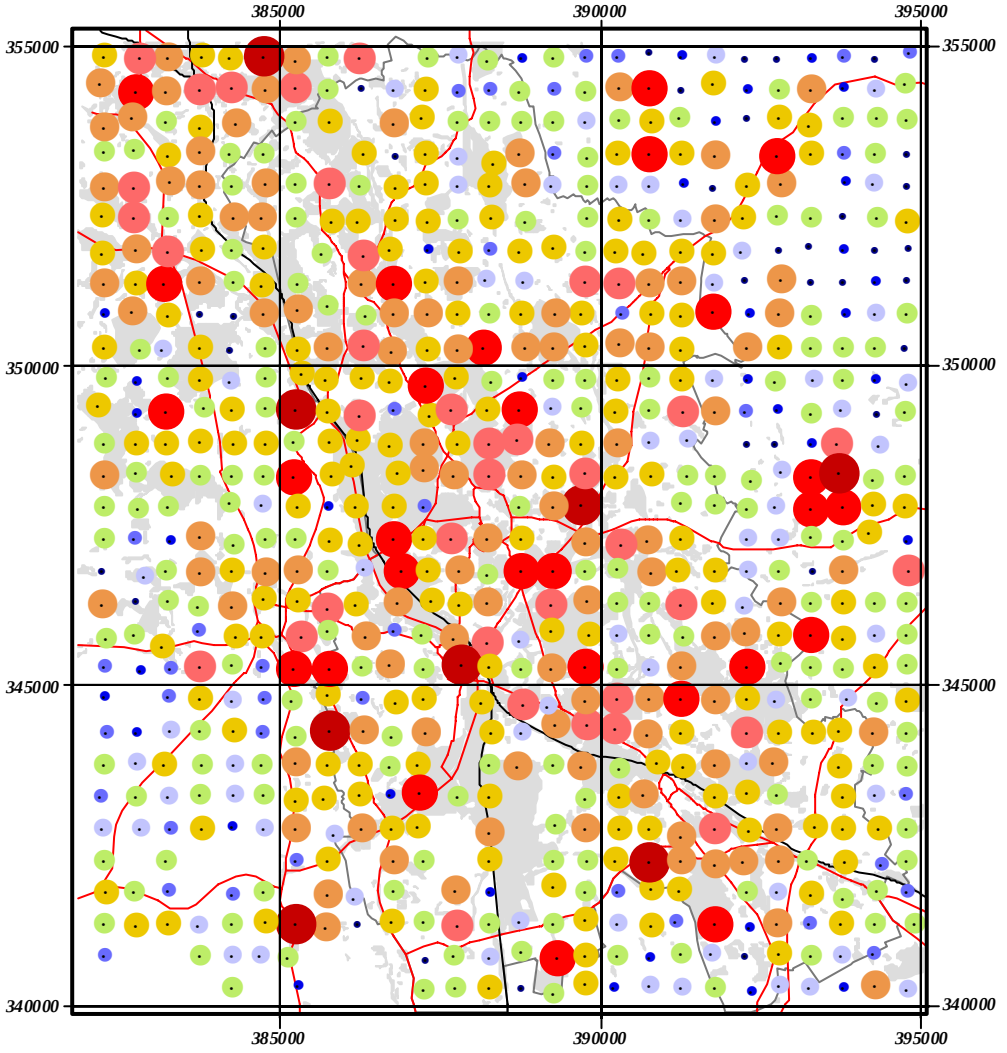
Percentile	100	99	95	90	75	50	25	15	10	0
Concentration (ppm) mg/kg	167	88	41	30	20	14	11	9	8	4

Barium in Surface Soils



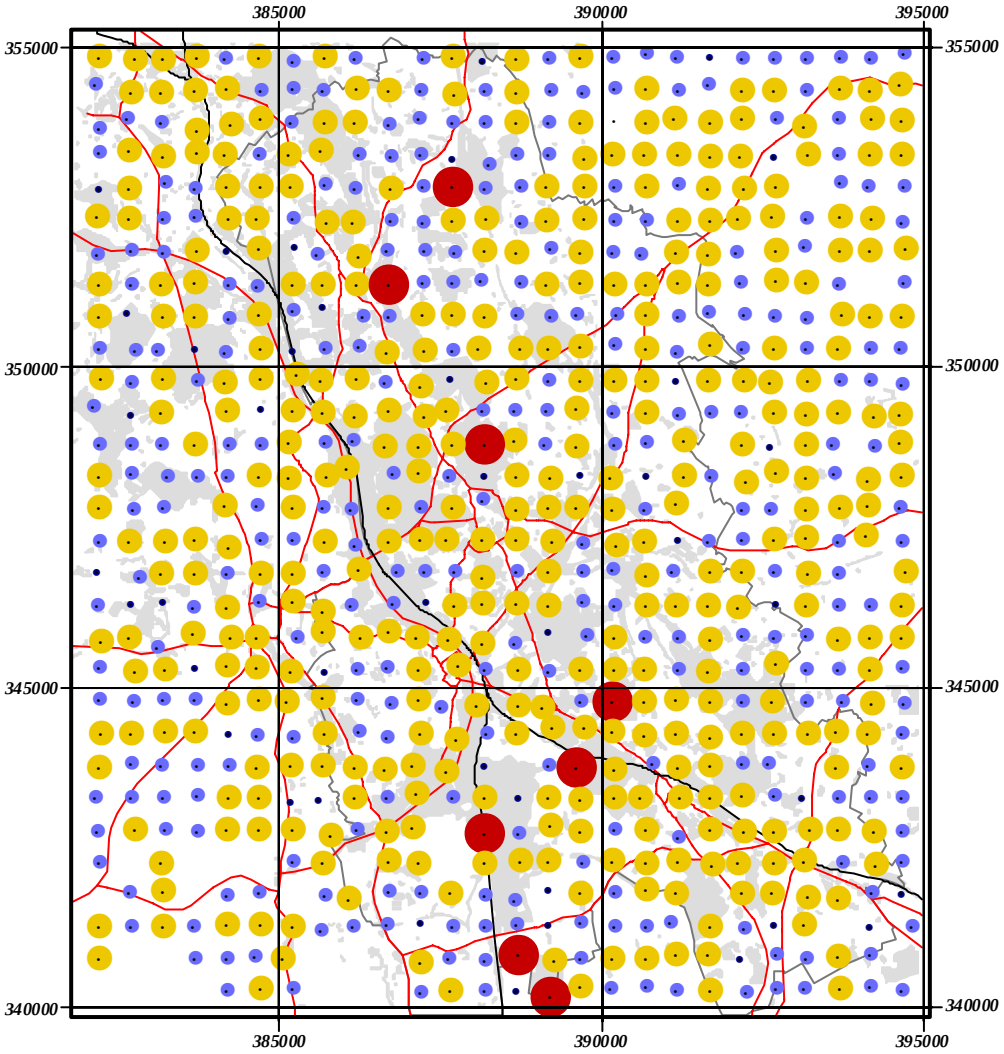
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	3590	1395	862	718	567	453	386	360	347	320	175

Barium in Profile Soils



Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	4269	1914	977	822	631	496	418	395	377	336	146

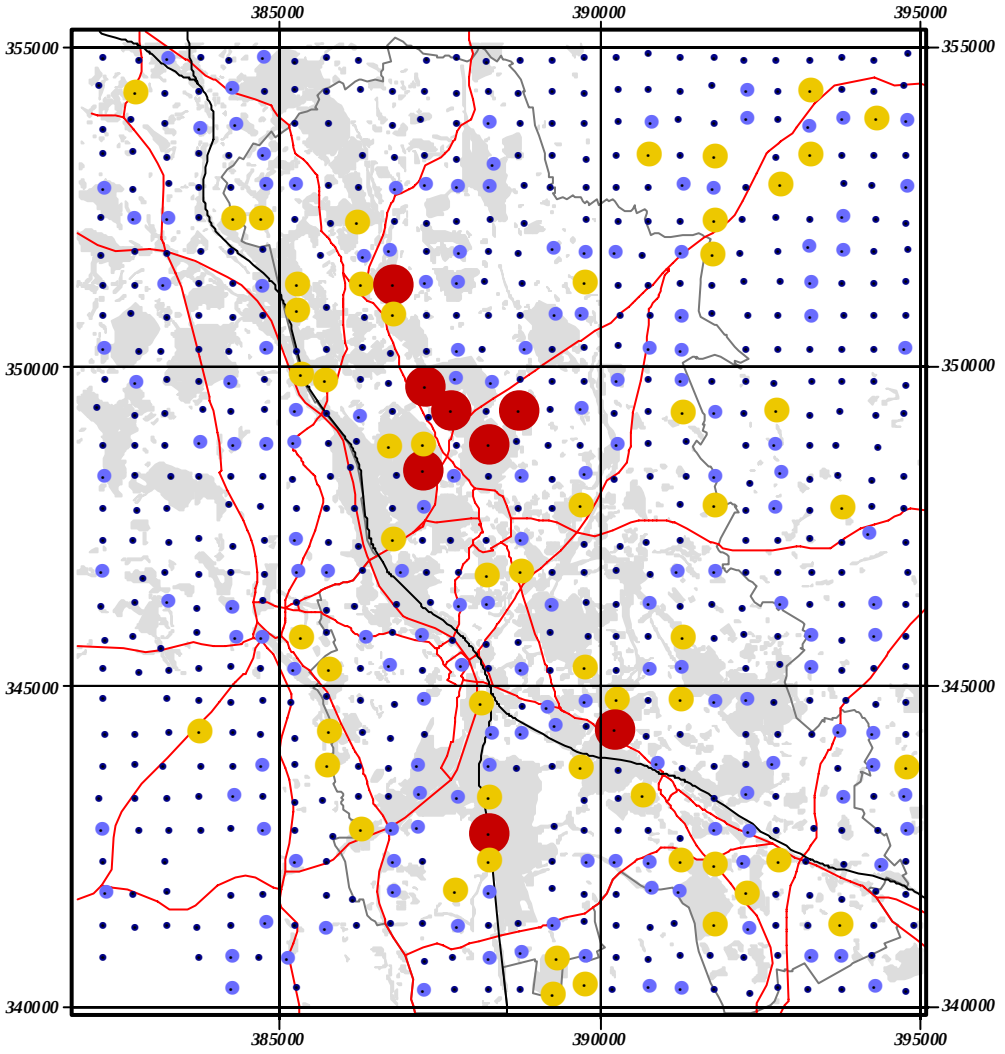
Cadmium in Surface Soils



Percentile 100 99 95 25 0

Concentration (ppm) 43 6 2 1 0.4 mg/kg

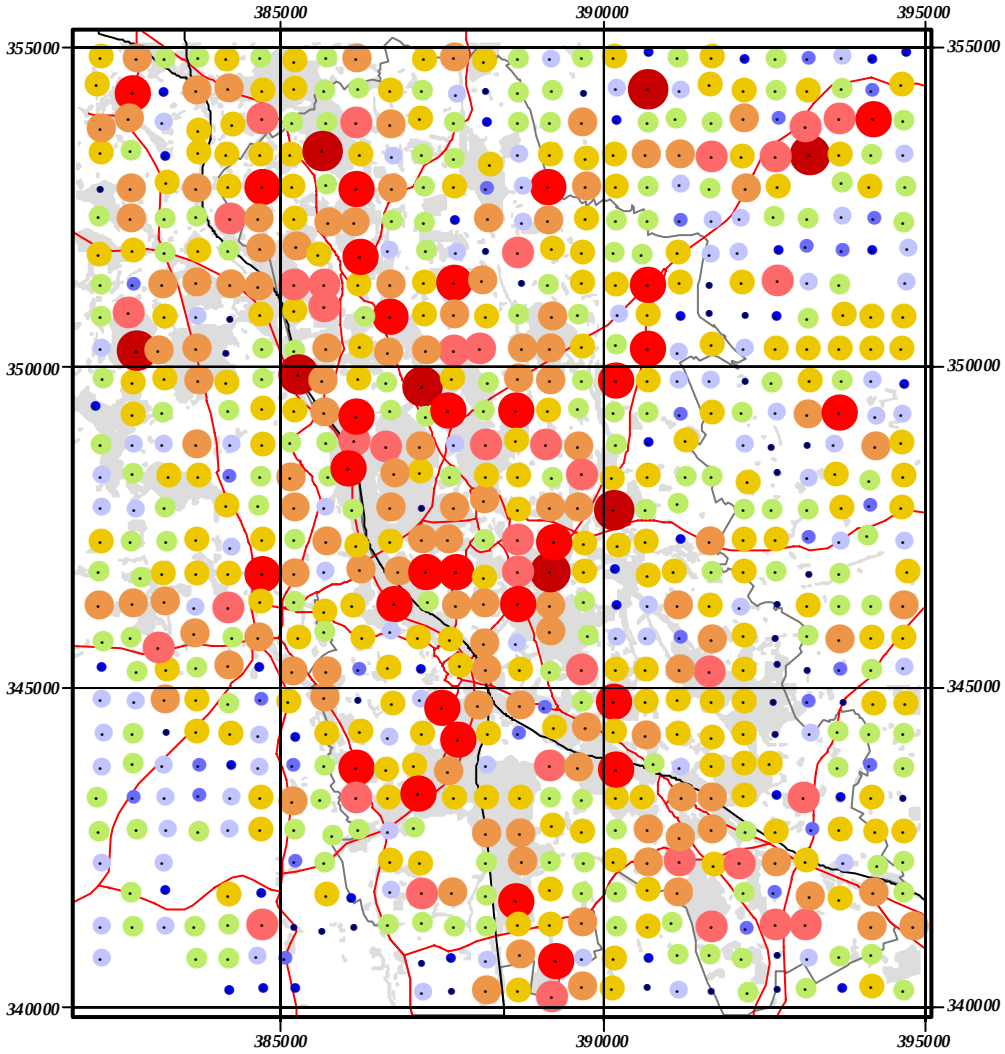
Cadmium in Profile Soils



Percentile 100 99 95 90 0

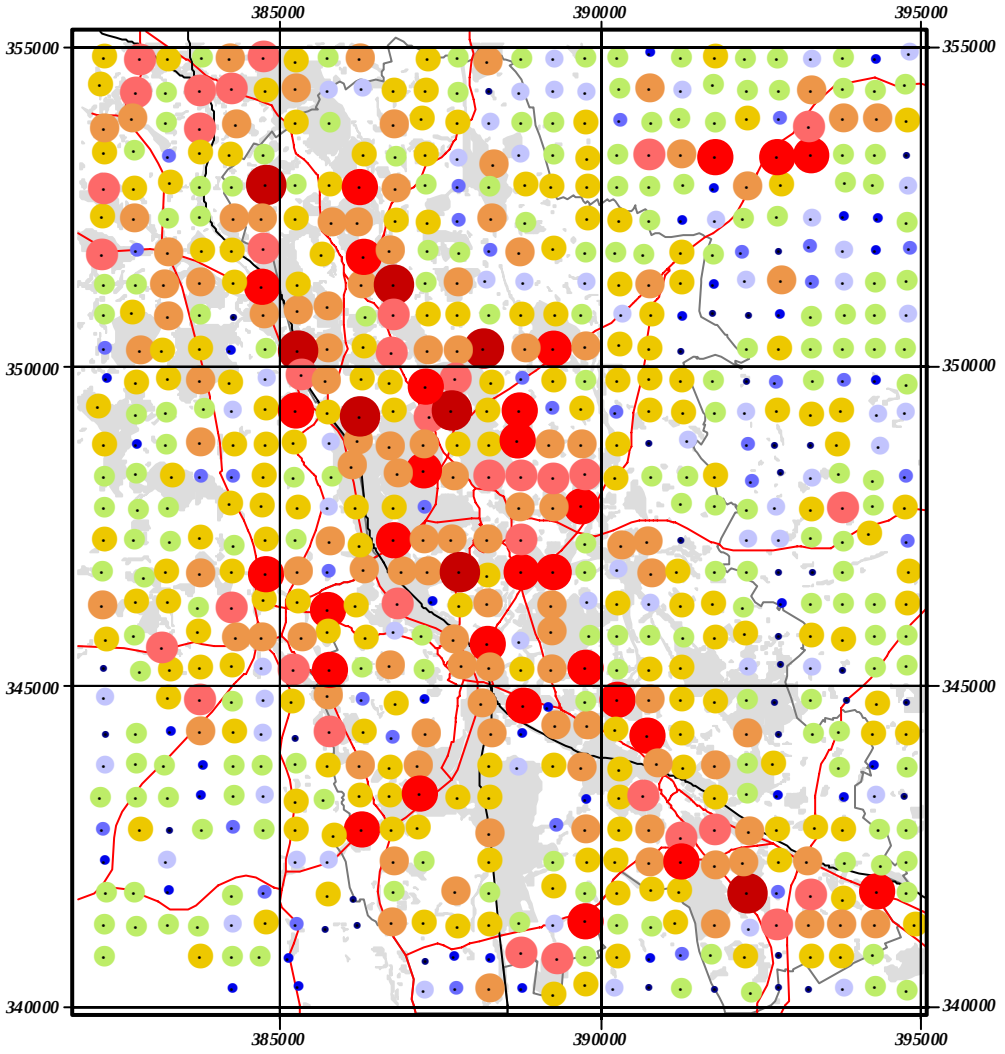
Concentration (ppm) 408 6 2 1 0.4 mg/kg

Calcium in Surface Soils



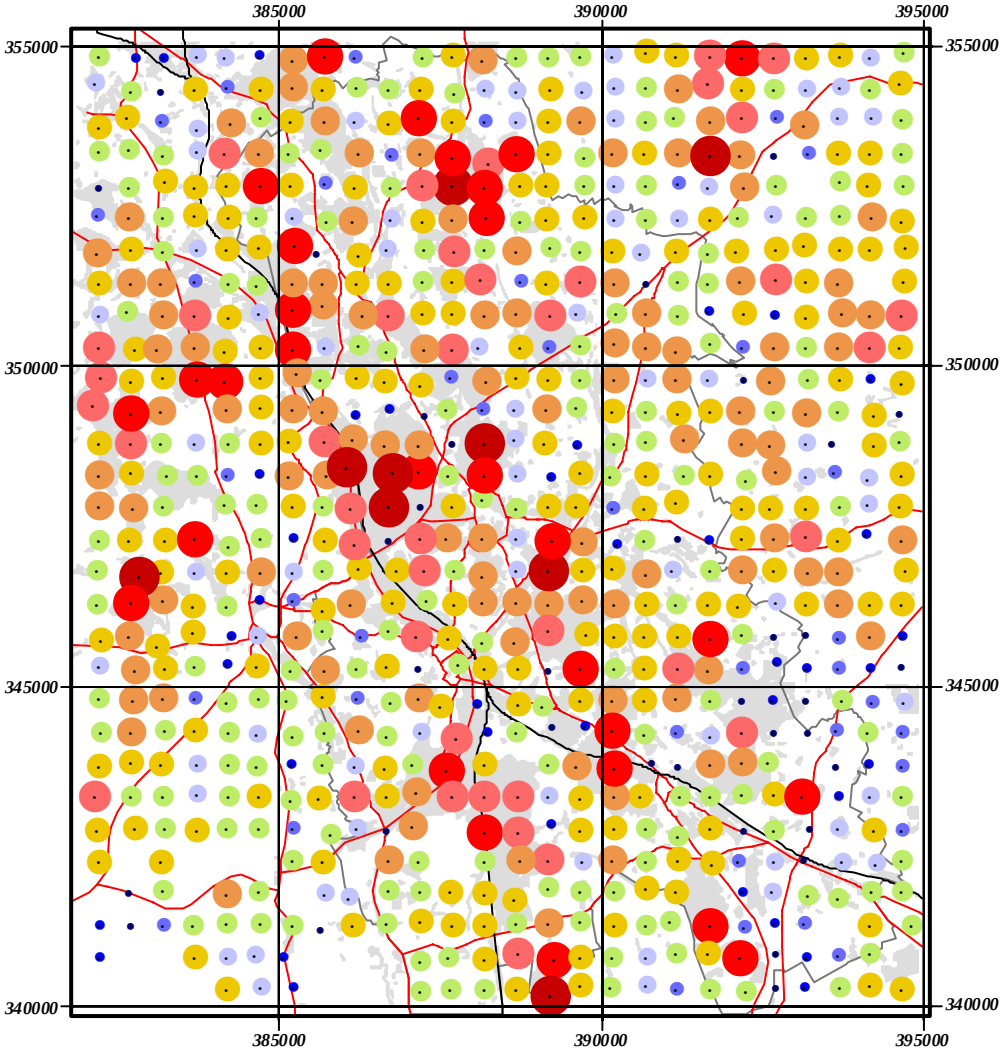
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	10.92	6.04	3.41	2.11	1.10	0.56	0.36	0.27	0.21	0.14	0.03

Calcium in Profile Soils



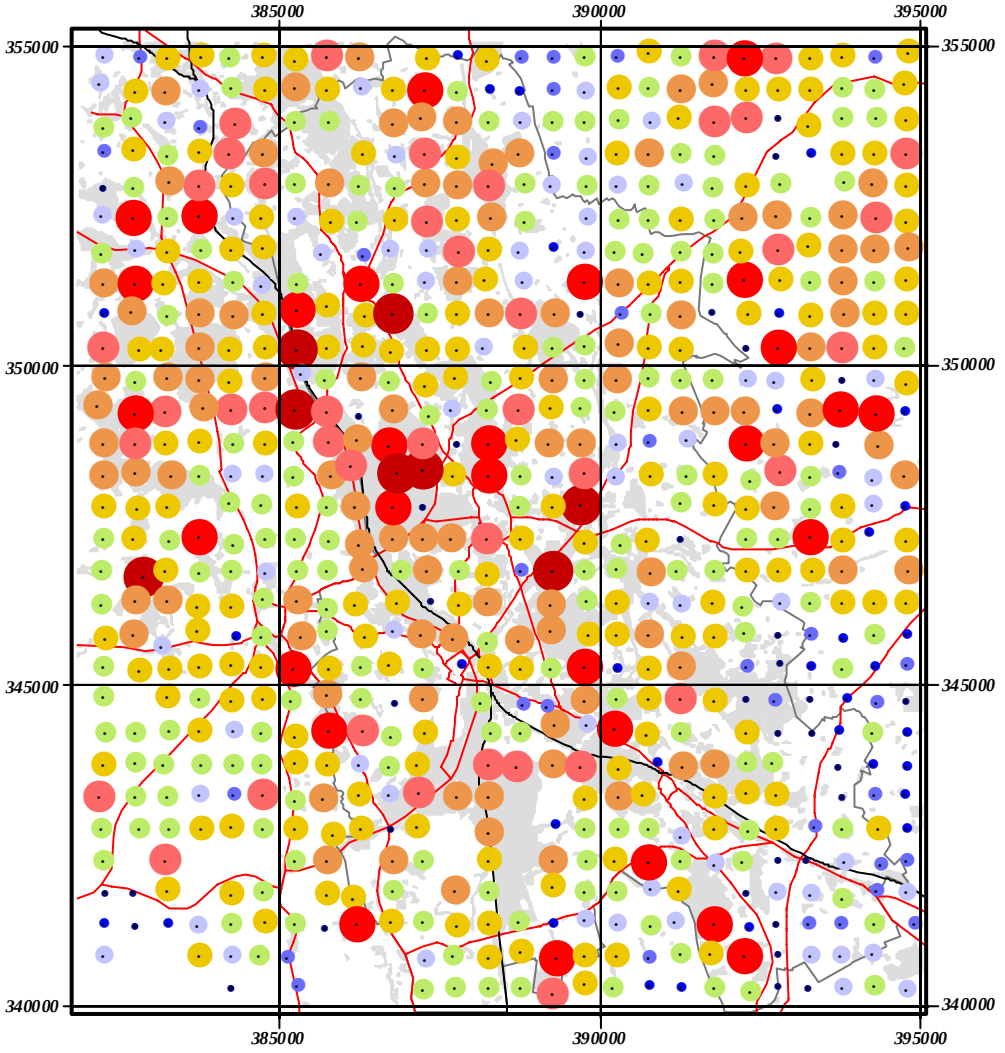
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	17.80	7.97	4.19	2.86	1.14	0.44	0.29	0.22	0.16	0.10	0.03

Chromium in Surface Soils



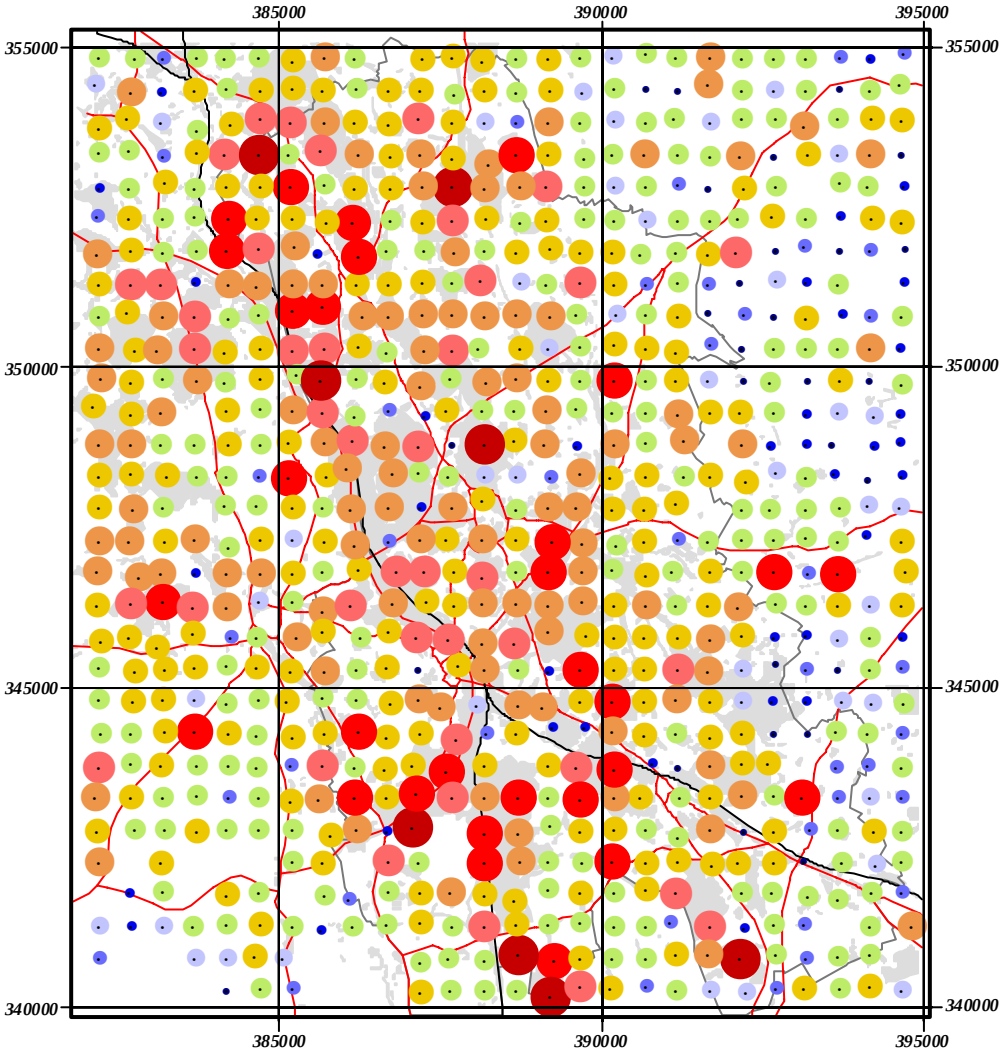
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	441	148	113	102	86	73	63	56	51	42	22

Chromium in Profile Soils



Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	574	183	125	115	103	92	82	77	72	66	41

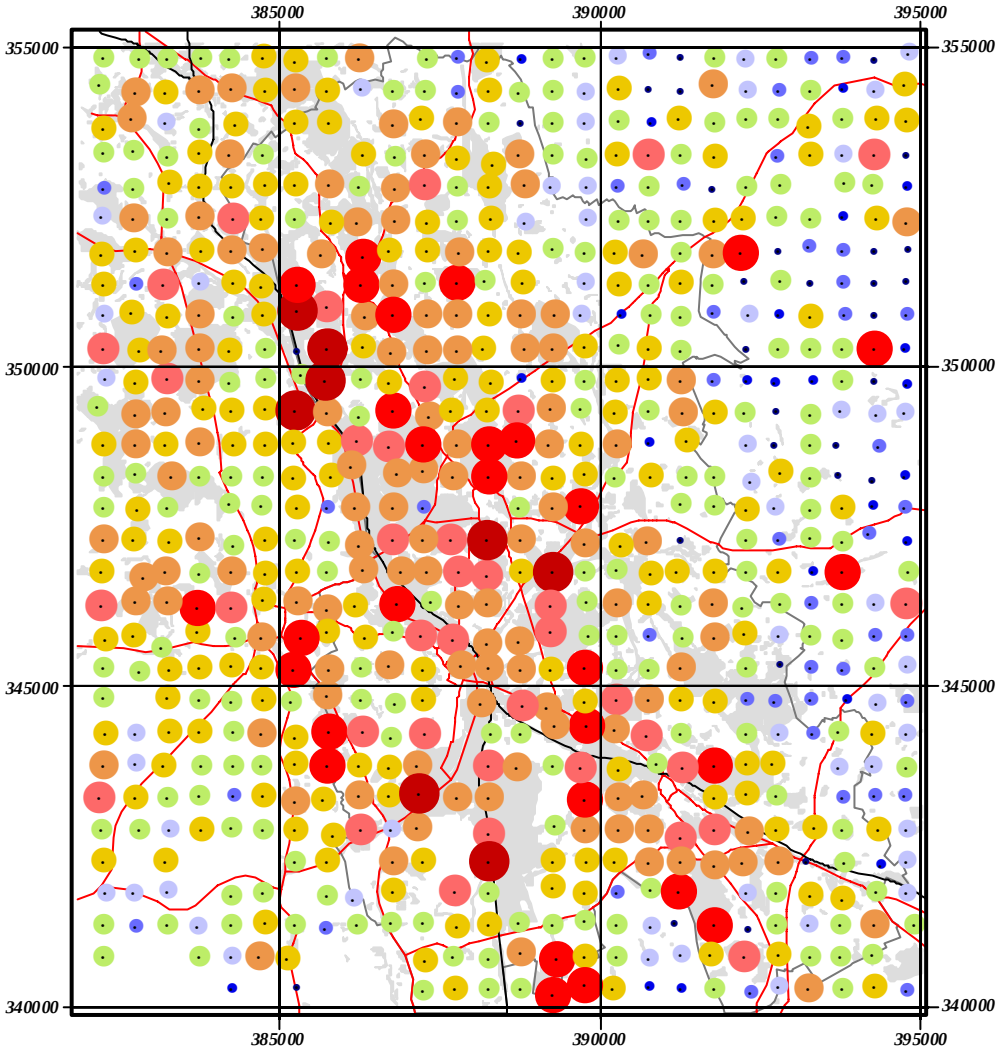
Cobalt in Surface Soils



Percentile 100 99 95 90 75 50 25 15 10 5 0

Concentration (ppm) mg/kg 452 65 45 39 30 22 16 13 11 9 4

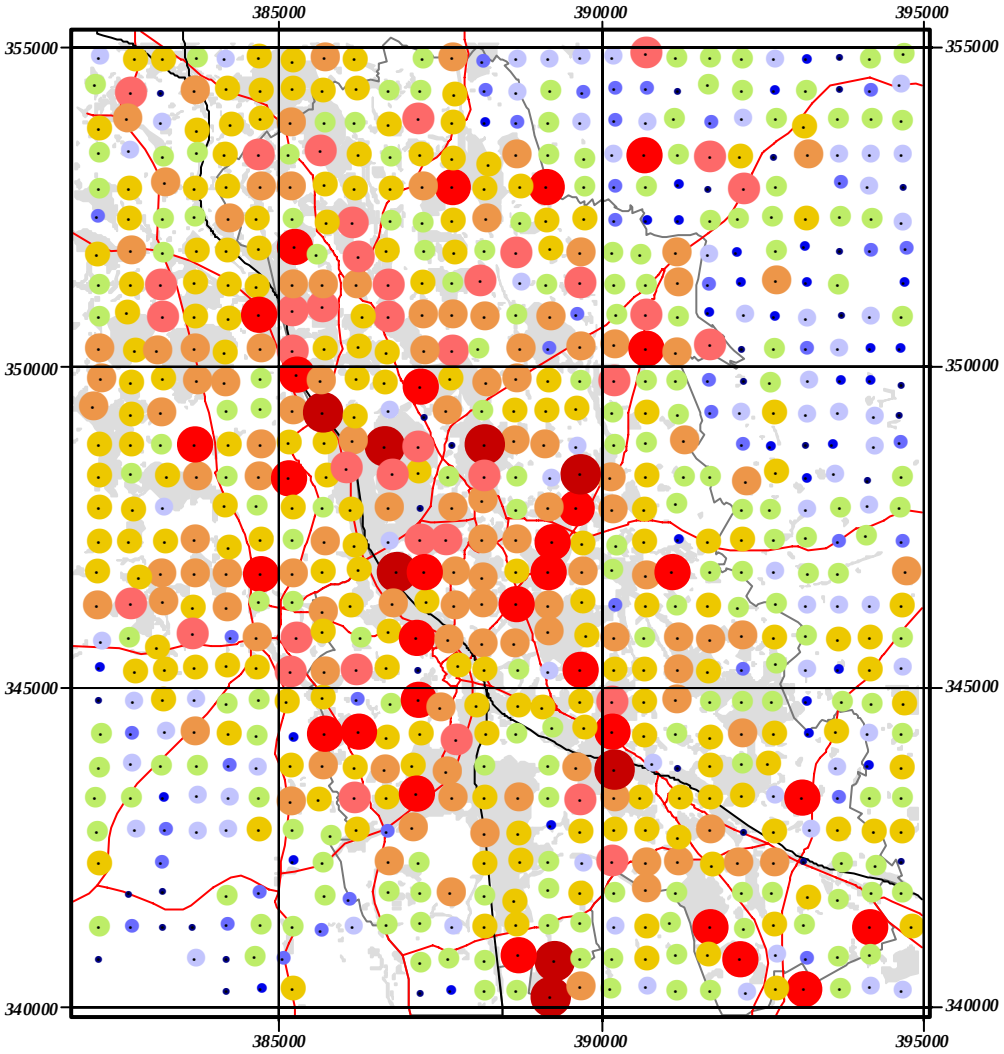
Cobalt in Profile Soils



Percentile 100 99 95 90 75 50 25 15 10 5 0

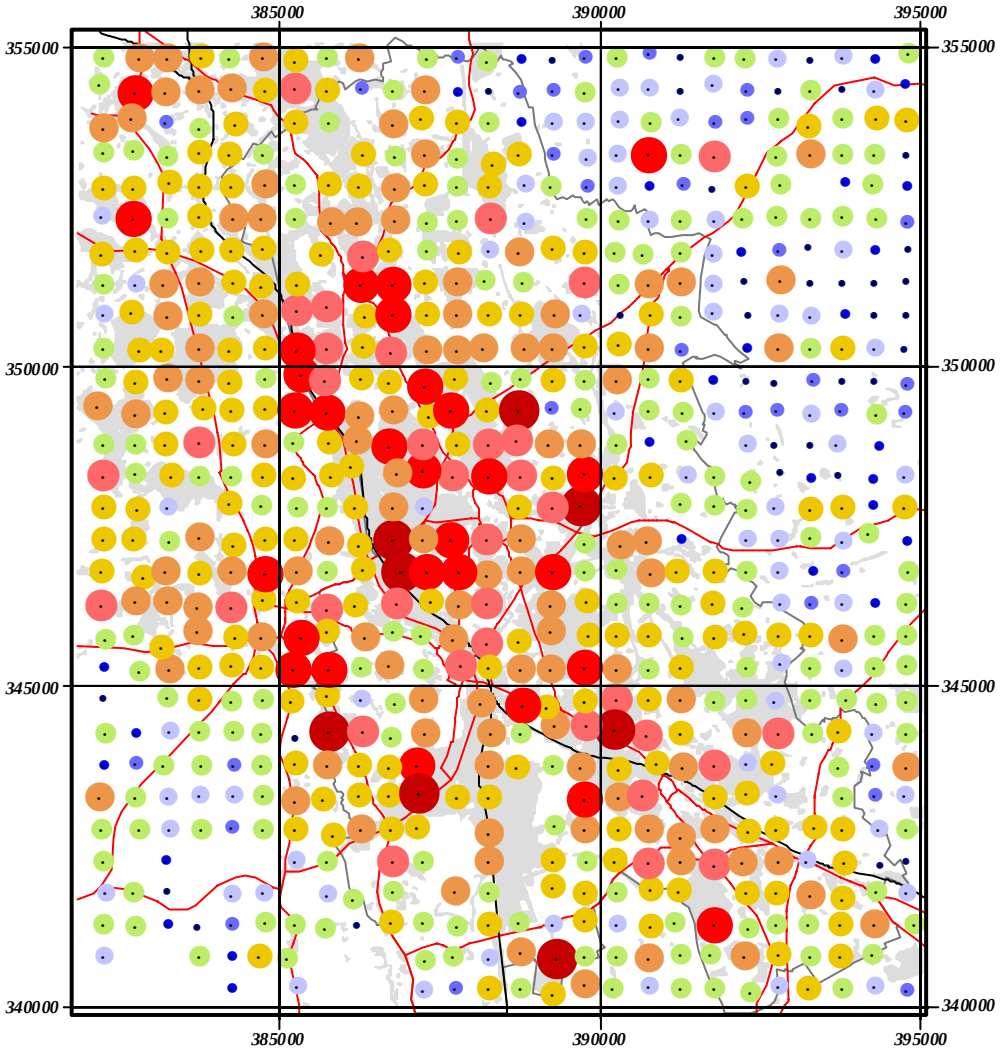
Concentration (ppm) mg/kg 133 80 53 43 33 26 19 17 14 12 1

Copper in Surface Soils



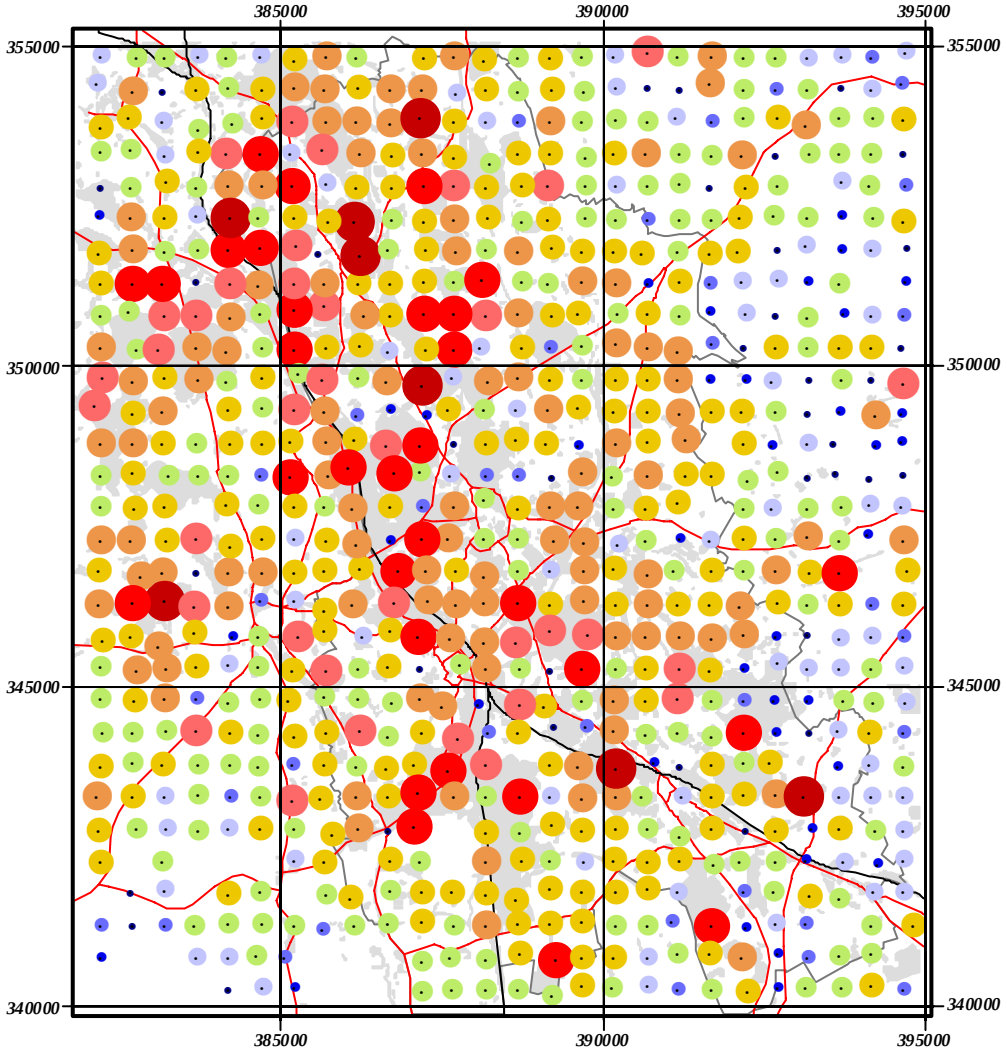
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	1729	289	129	86	52	33	22	18	16	14	7

Copper in Profile Soils



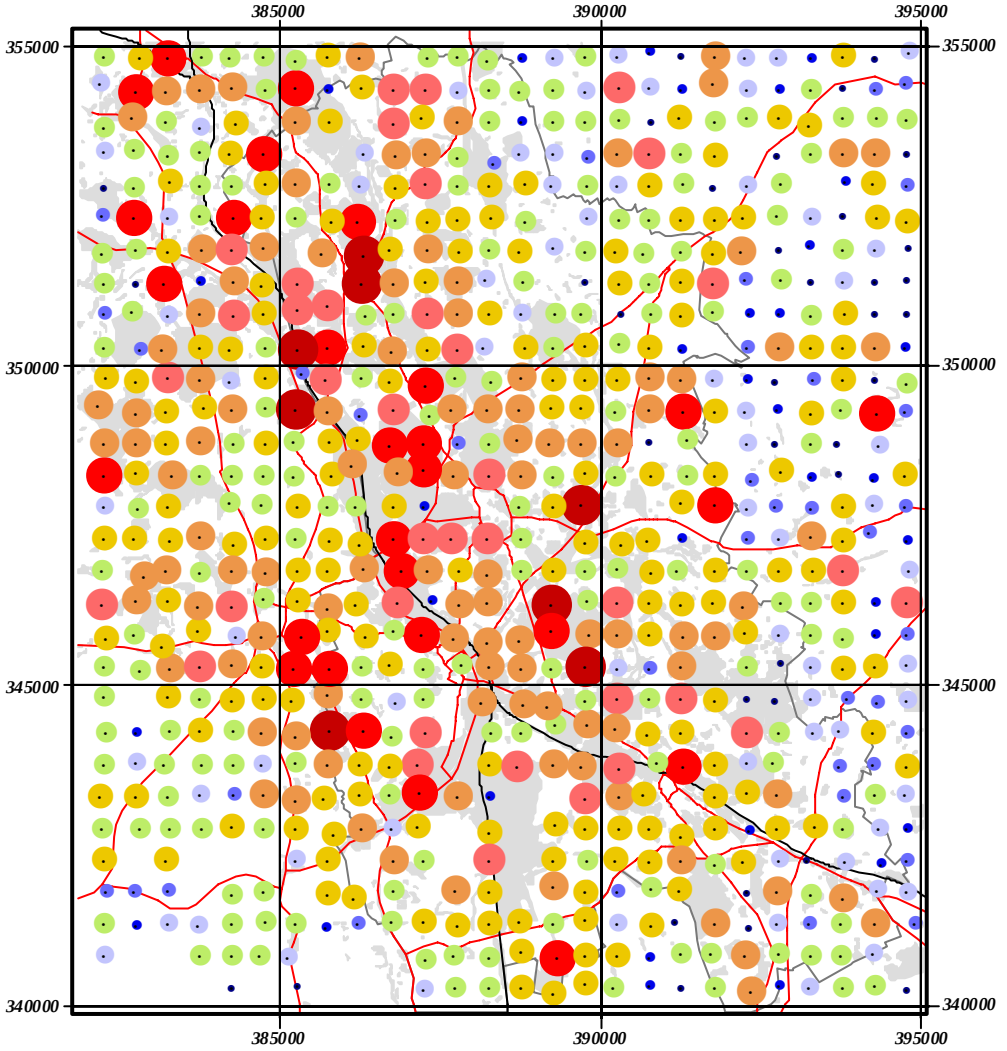
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	1260	520	161	105	56	33	20	16	14	12	7

Iron in Surface Soils



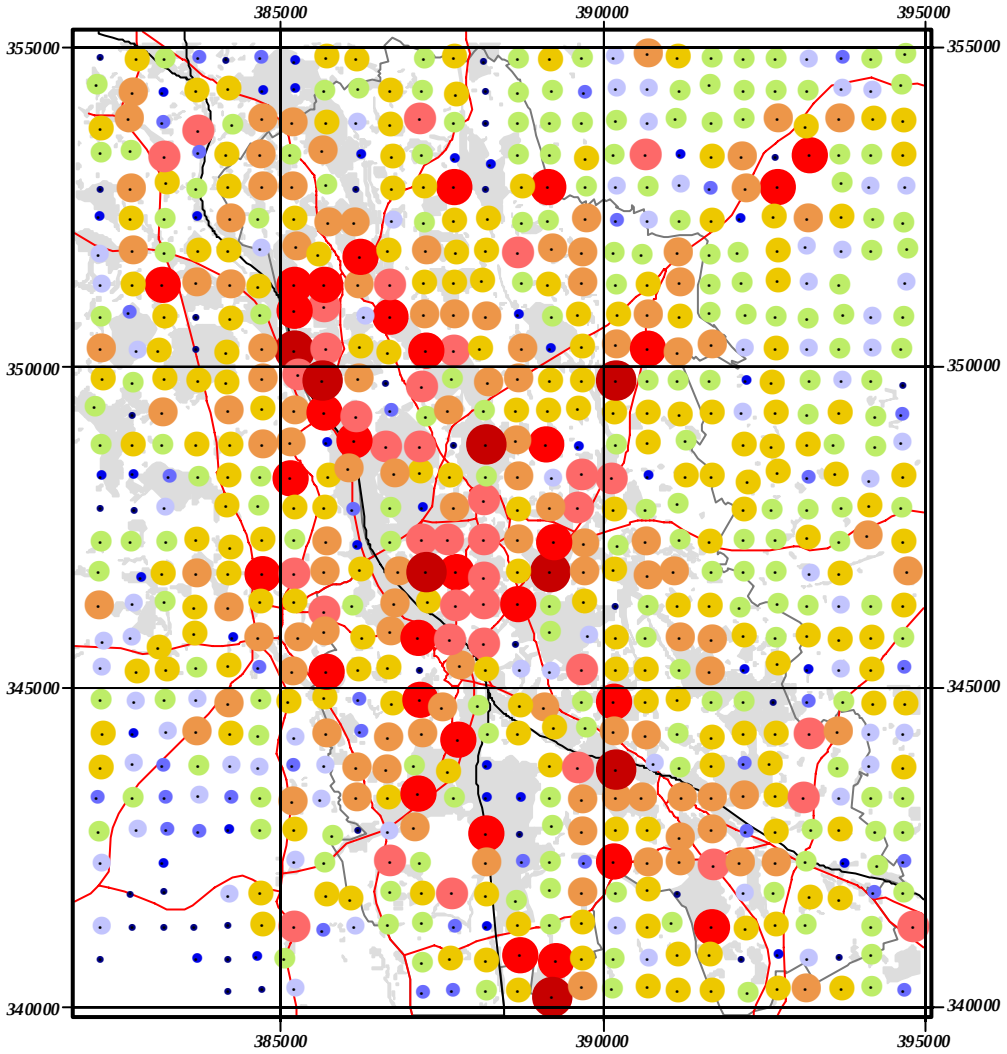
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	32.300	14.403	10.121	8.901	6.822	5.212	4.002	3.252	2.860	2.342	0.600

Iron in Profile Soils



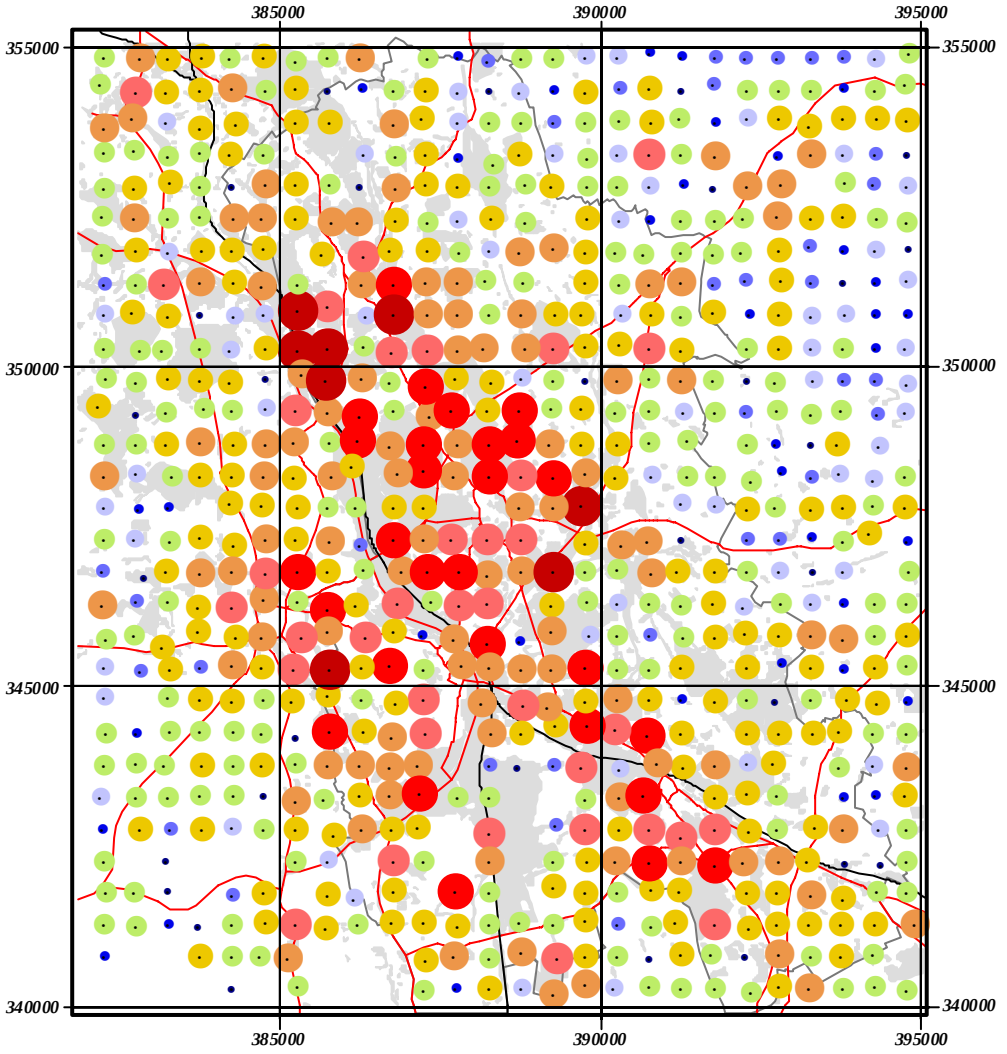
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	43.700	18.996	11.520	9.967	7.817	6.468	5.040	4.497	4.107	3.349	1.700

Lead in Surface Soils



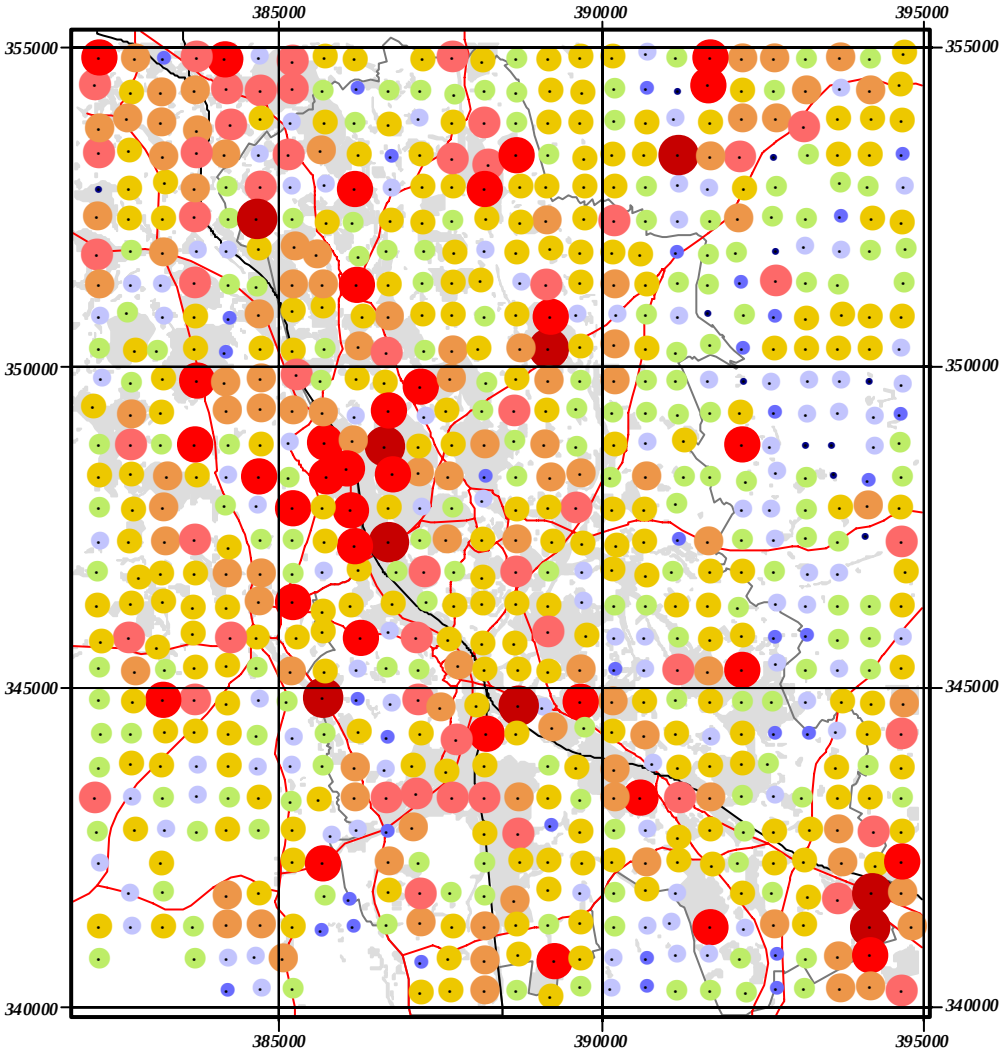
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	4208	1356	565	341	159	93	66	54	50	38	10

Lead in Profile Soils



Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	4207	1525	633	380	134	61	37	32	30	26	15

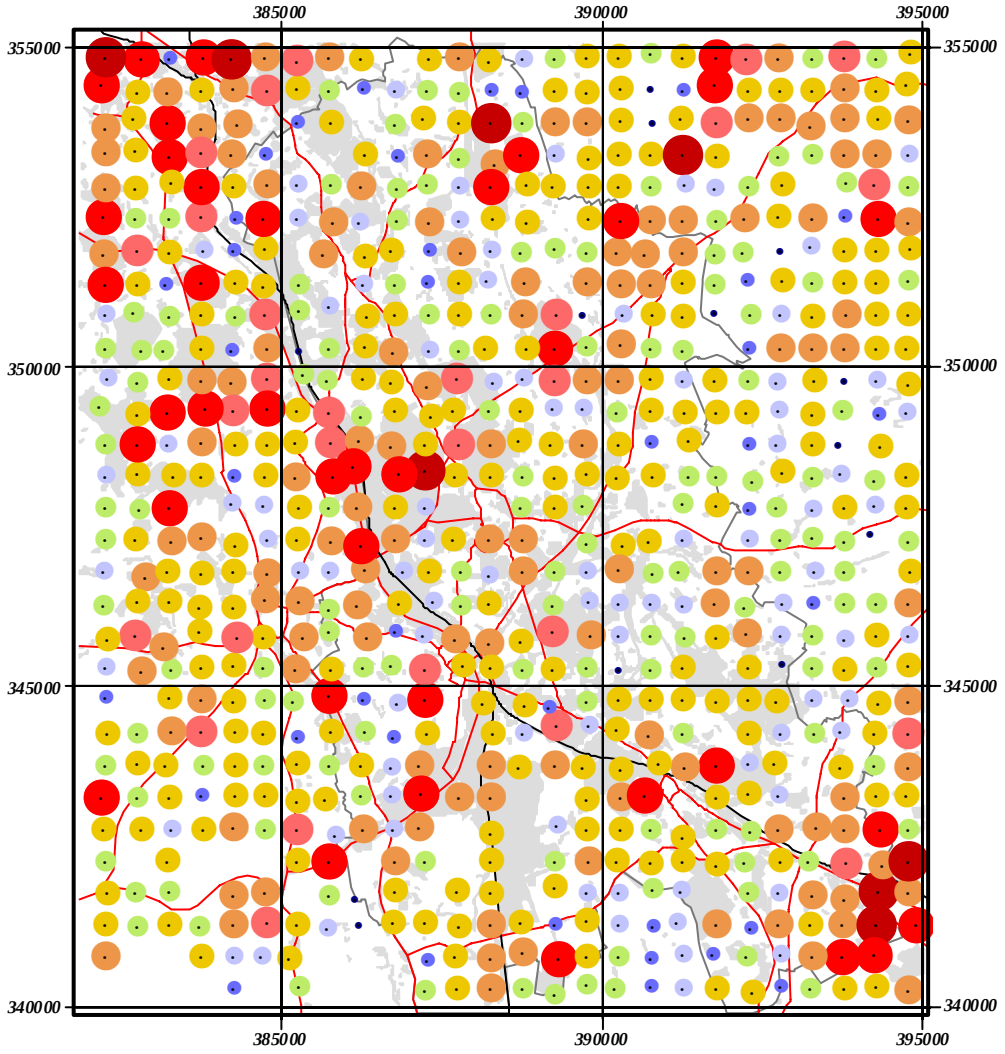
Magnesium in Surface Soils



Percentile 100 99 95 90 75 50 25 15 5 0

Concentration (wt %) 3.0 2.0 1.2 1.0 0.8 0.6 0.5 0.4 0.3 0.1

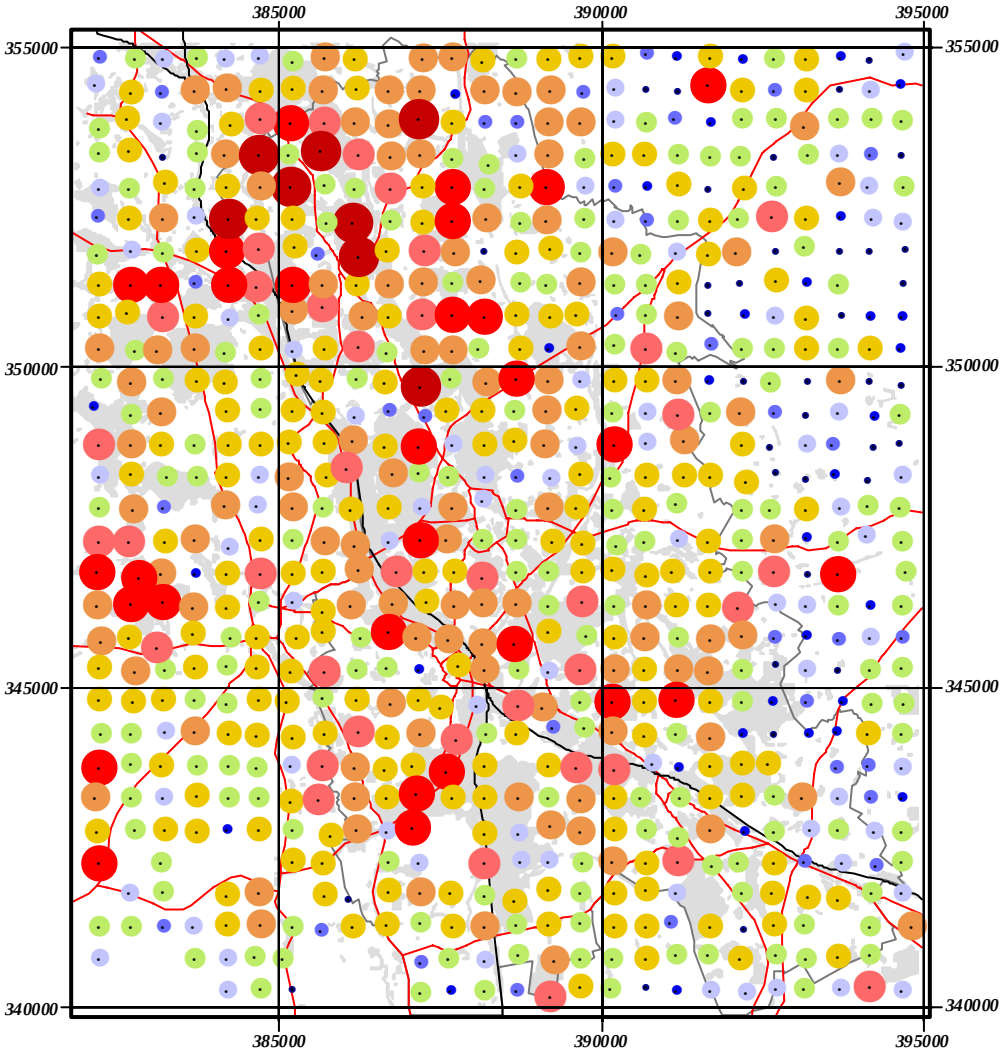
Magnesium in Profile Soils



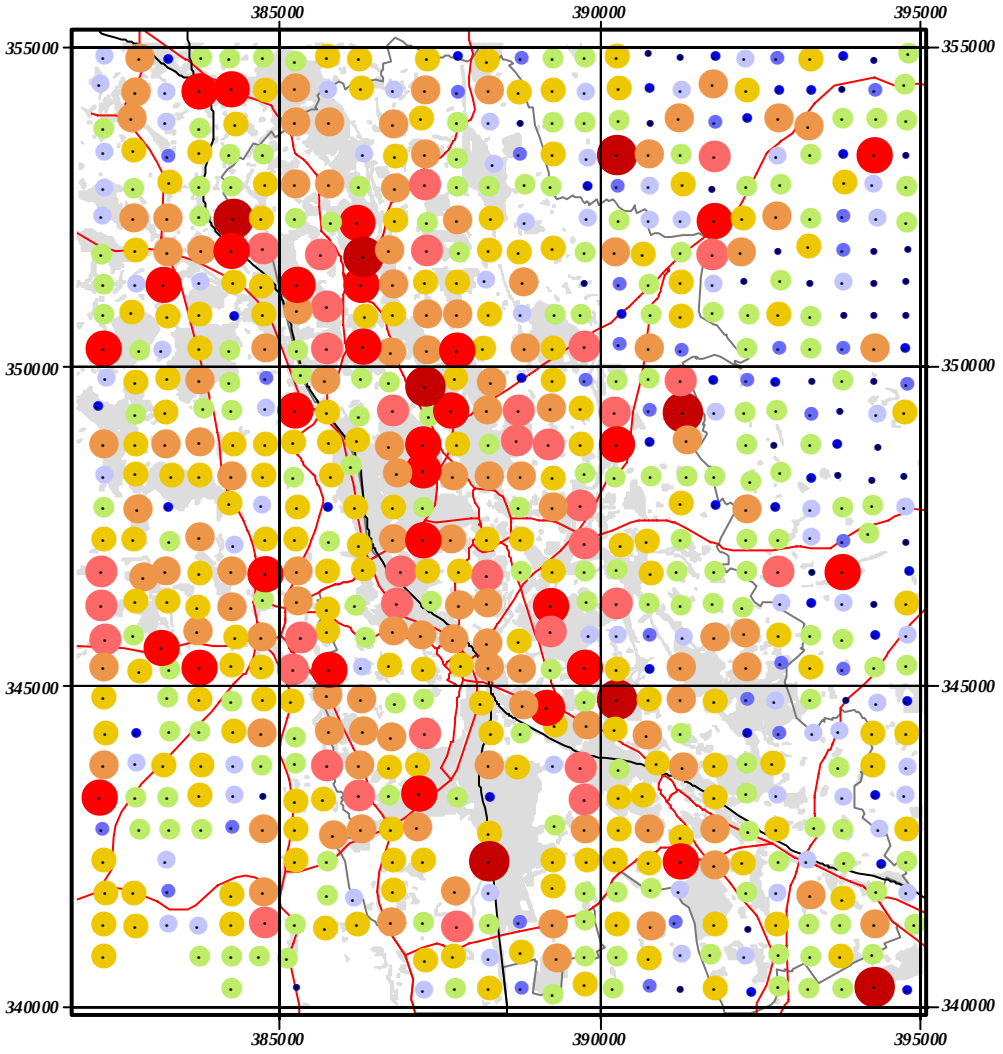
Percentile 100 99 95 90 75 50 25 15 5 0

Concentration (wt %) 3.7 2.0 1.4 1.2 0.9 0.7 0.6 0.5 0.4 0.1

Manganese in Surface Soils



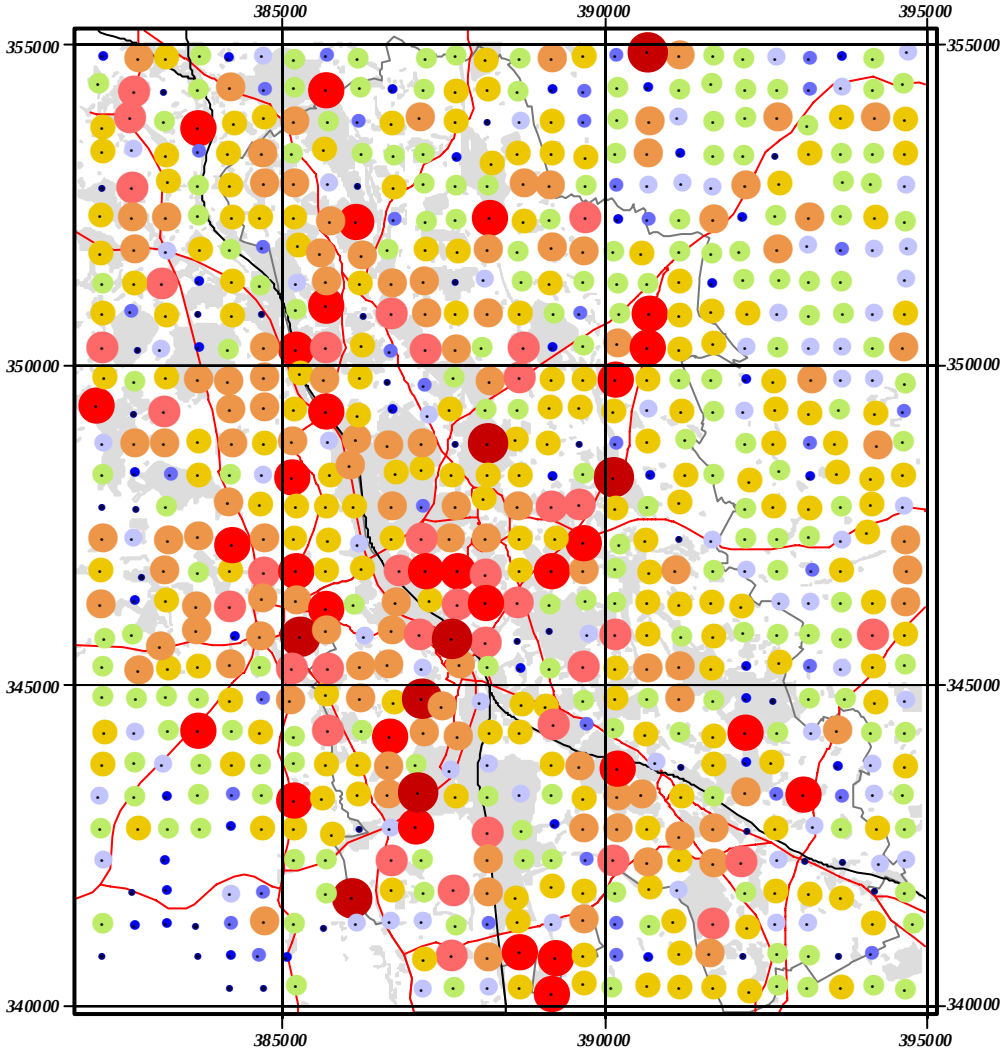
Manganese in Profile Soils



Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	0.6700	0.506	0.323	0.258	0.189	0.128	0.085	0.066	0.058	0.044	0.030

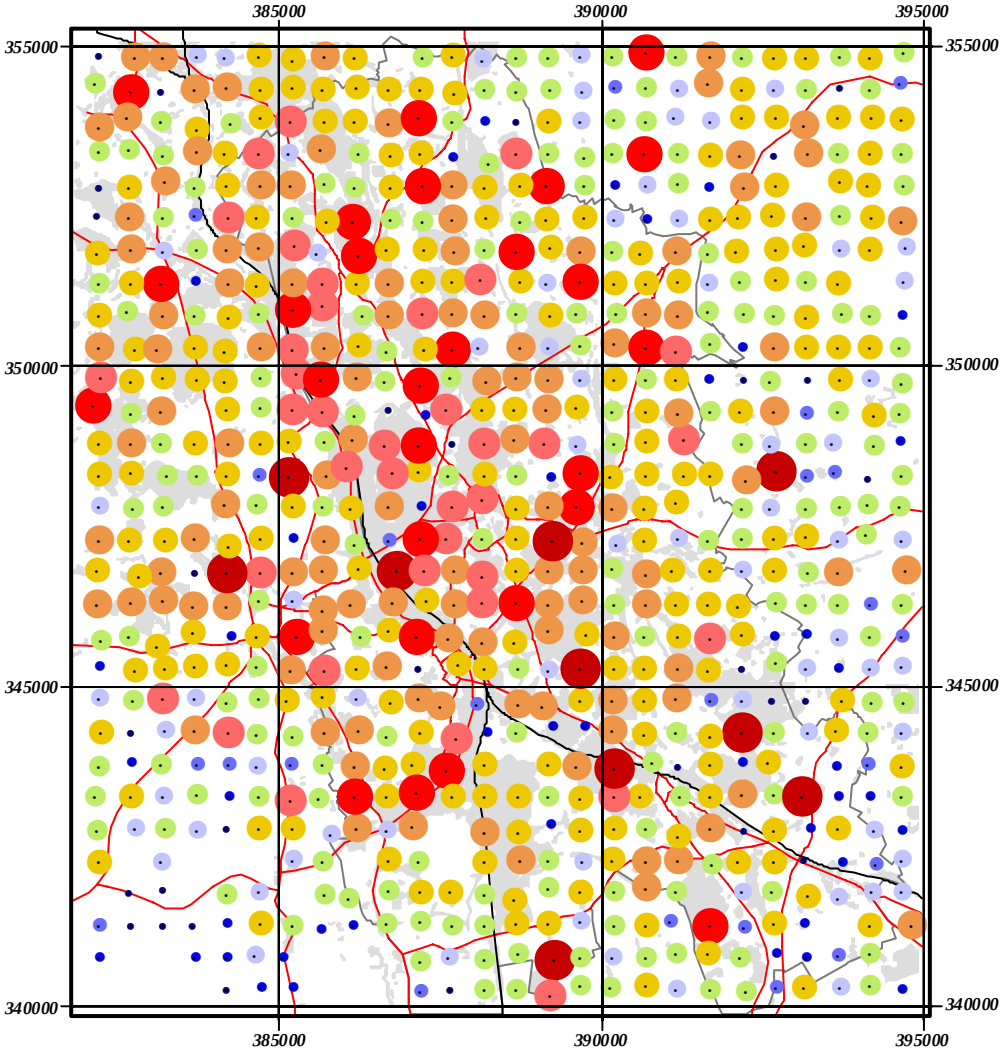
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	1.0700	0.571	0.372	0.302	0.206	0.138	0.089	0.067	0.054	0.038	0.020

Mercury in Surface Soils



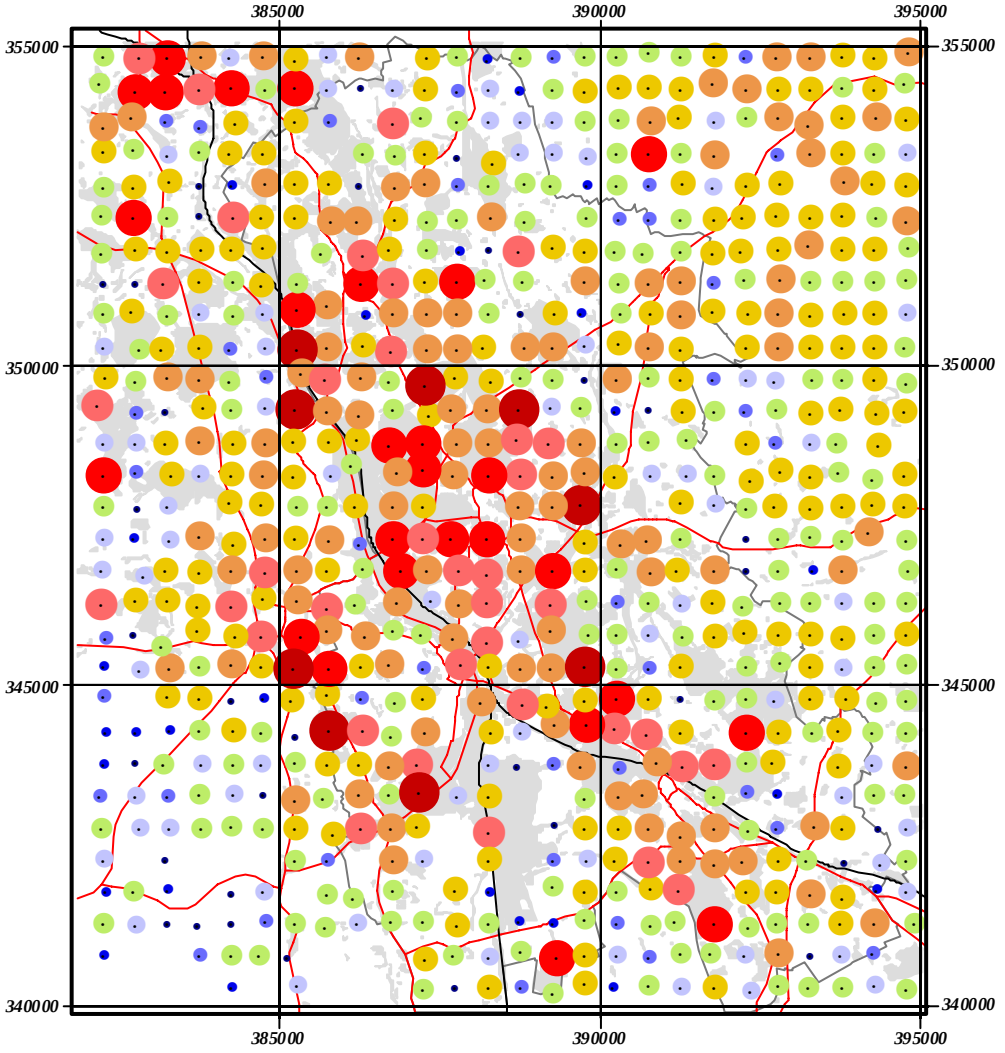
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	7.220	2.527	0.684	0.416	0.229	0.143	0.101	0.084	0.074	0.058	0.005

Molybdenum in Surface Soils



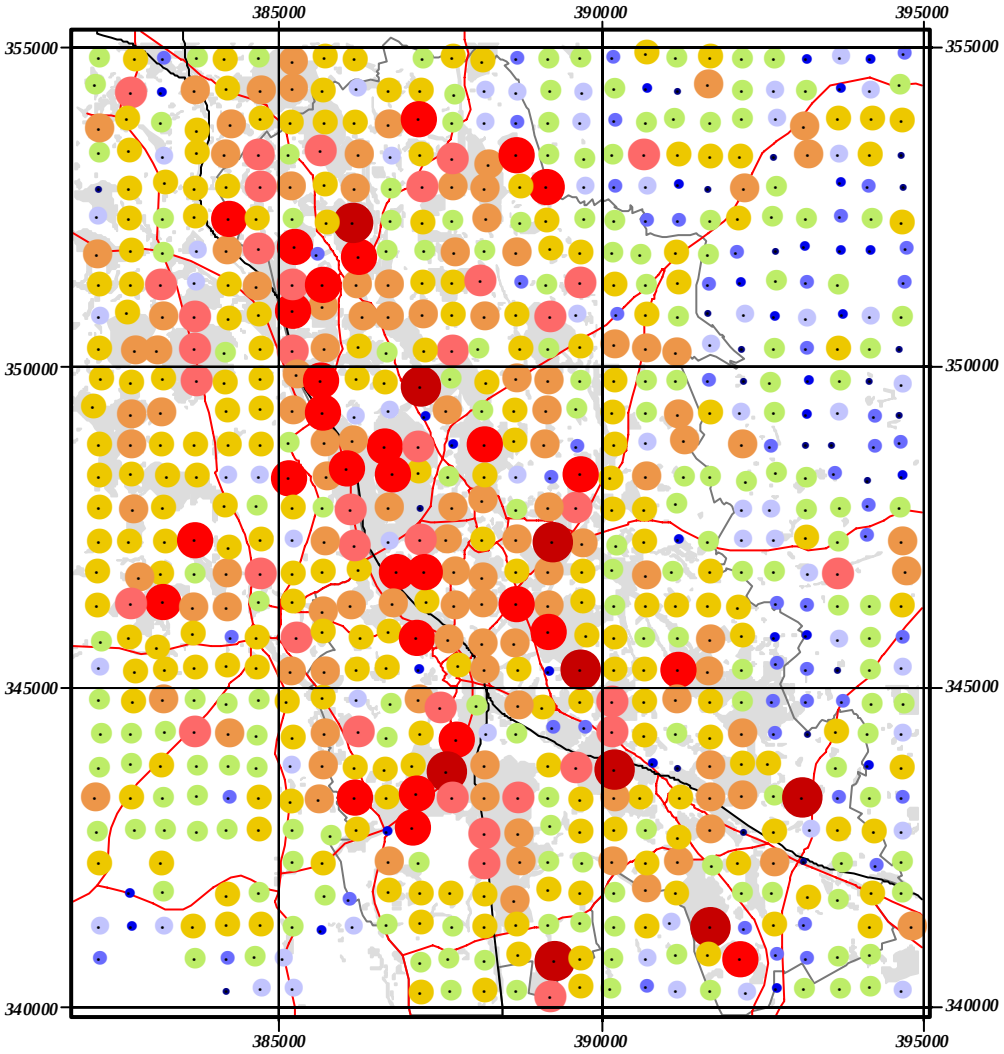
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	25.8	10.4	6.9	5.2	3.3	2.4	1.8	1.5	1.4	1.1	0.6

Molybdenum in Profile Soils



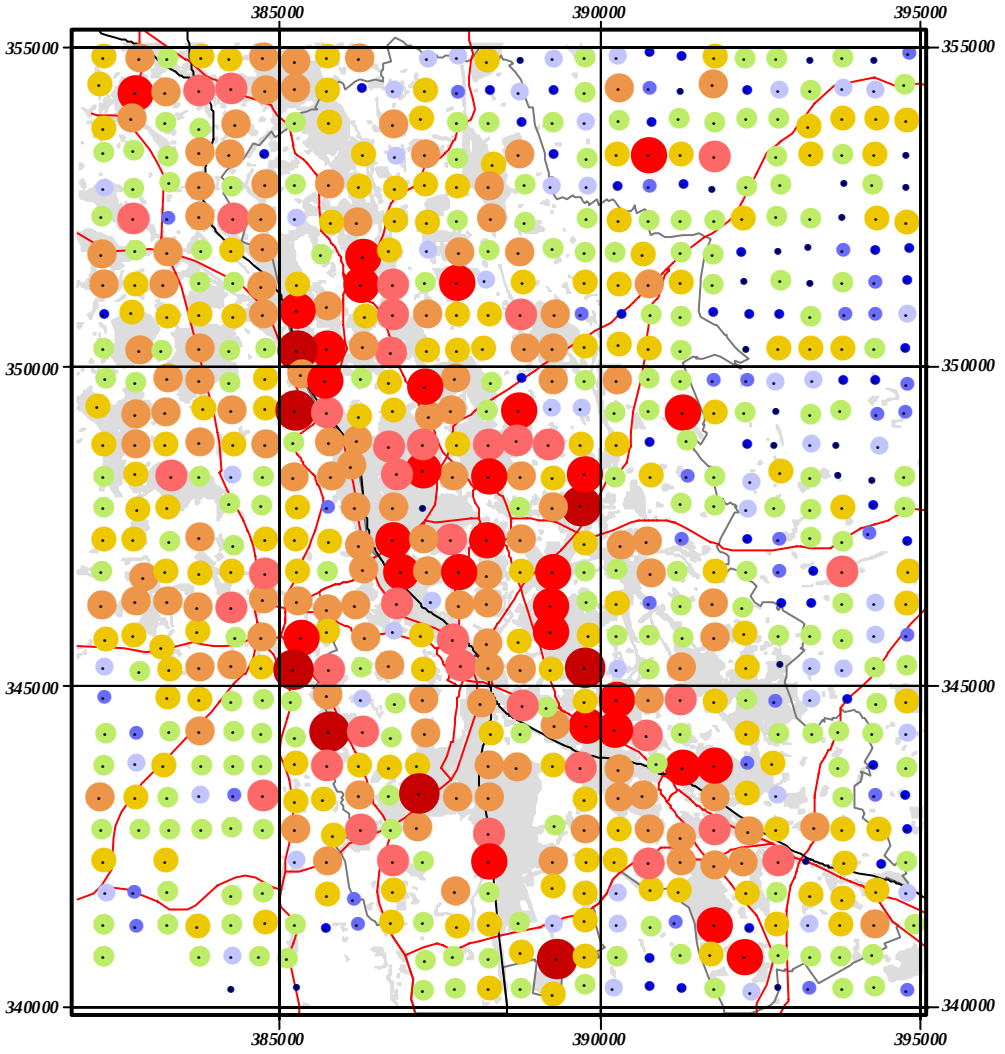
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	69.1	22.3	11.3	7.6	4.4	2.7	2.0	1.7	1.5	1.4	0.2

Nickel in Surface Soils



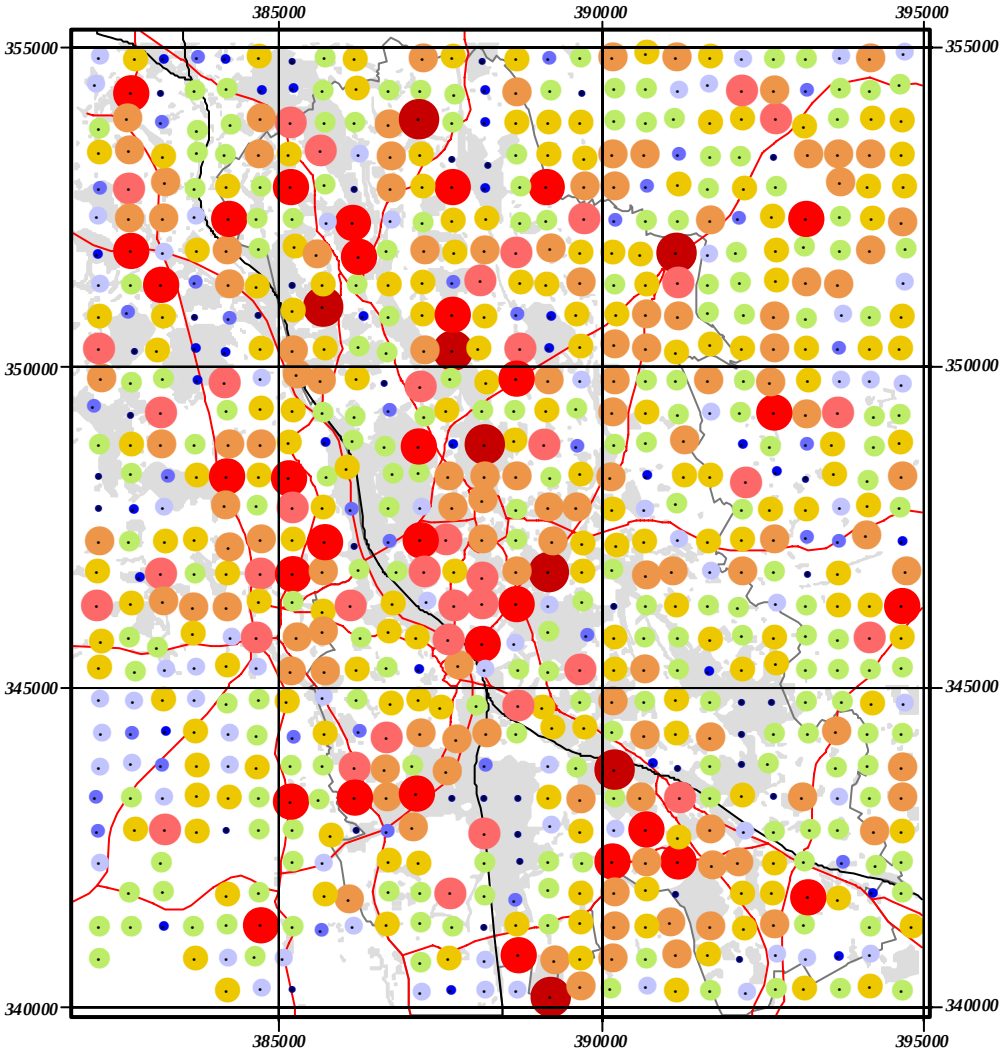
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	124	79	55	46	34	23	17	15	12	10	5.0

Nickel in Profile Soils



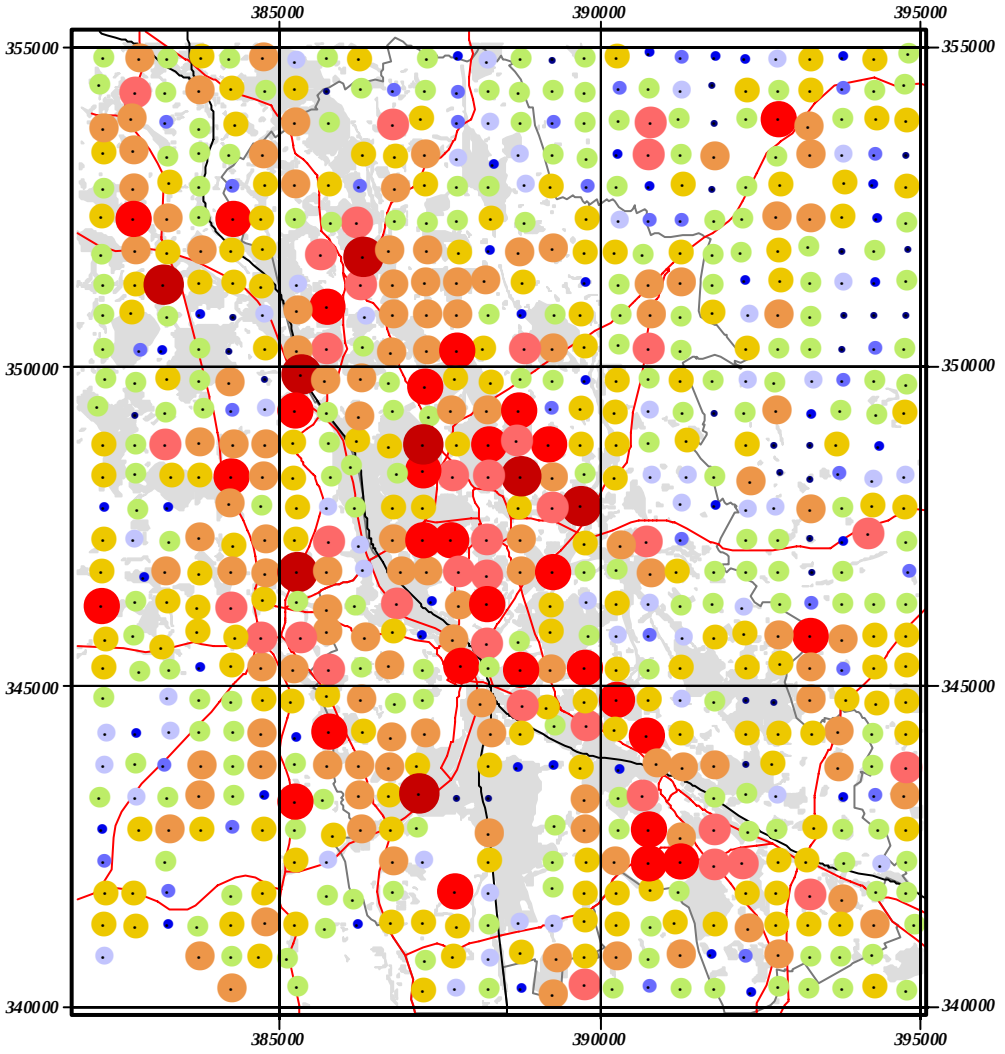
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	250	121	73	54	40	30	21	19	17	14	6.0

Phosphorus in Surface Soils



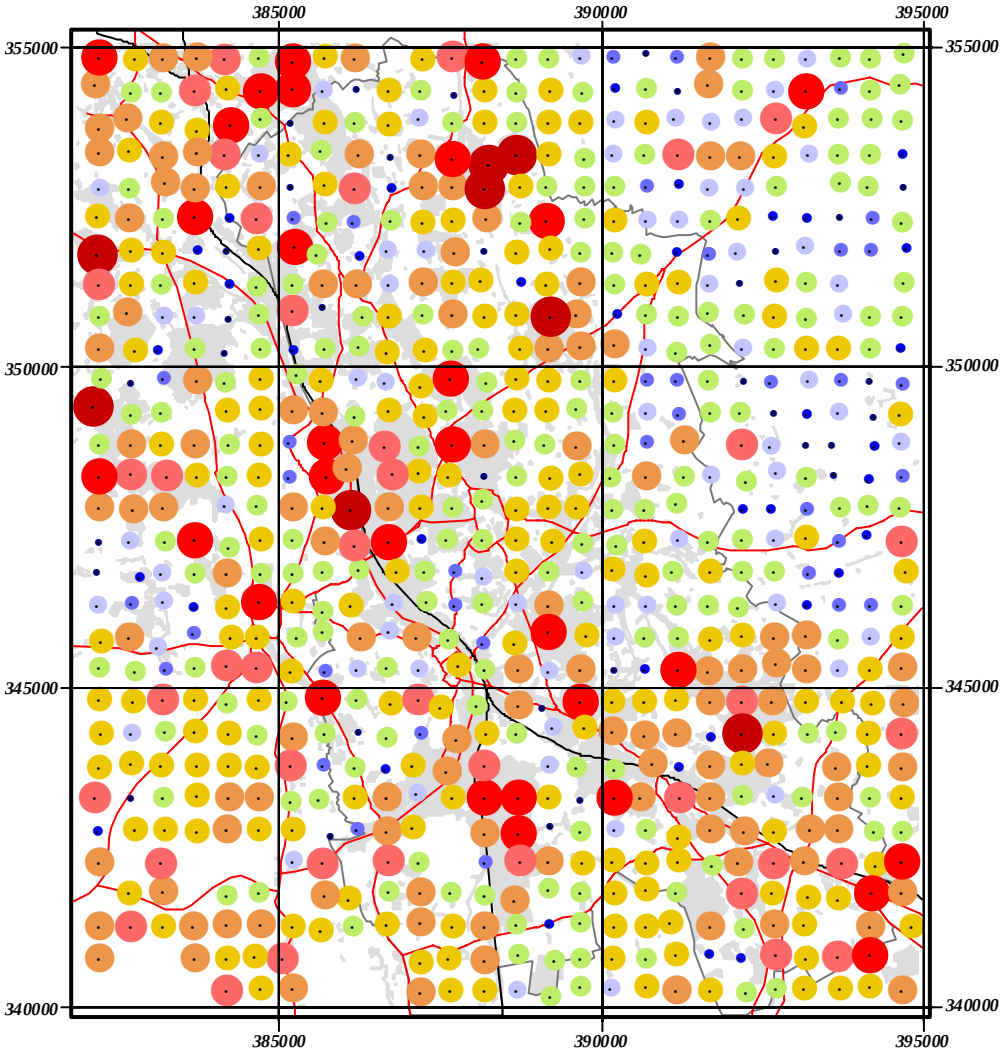
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	3.74	1.07	0.69	0.54	0.39	0.30	0.21	0.17	0.15	0.13	0.06

Phosphorus in Profile Soils



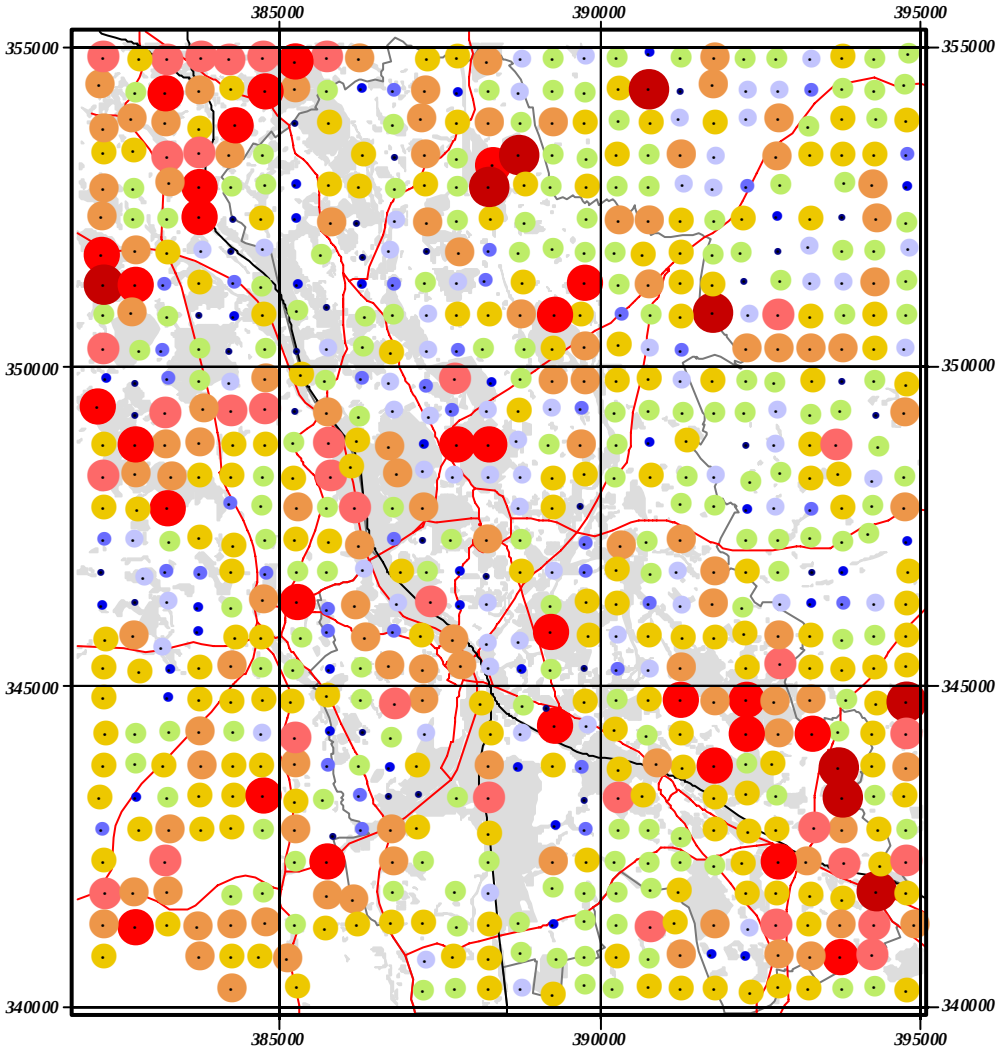
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	1.42	0.89	0.60	0.46	0.28	0.19	0.12	0.10	0.09	0.07	0.03

Potassium in Surface Soils



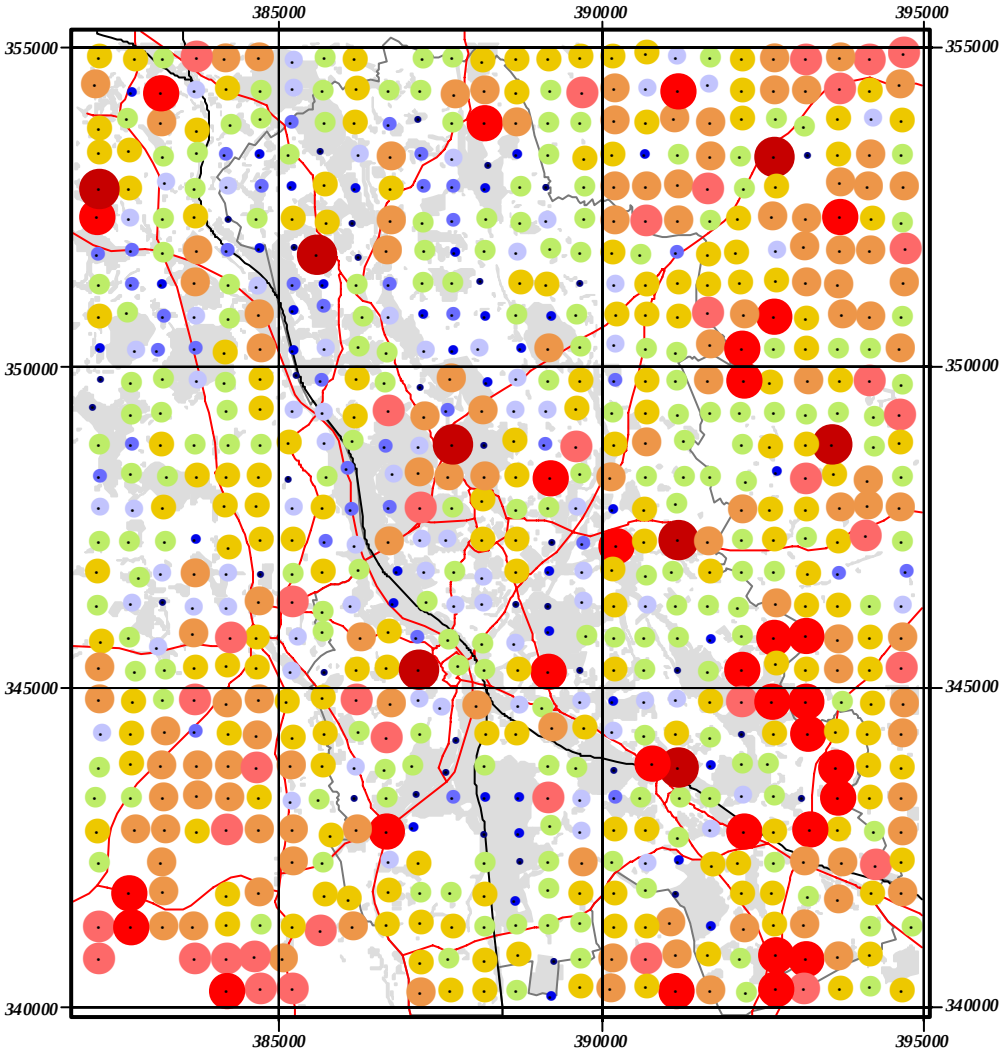
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	3.60	2.99	2.24	2.05	1.75	1.52	1.30	1.21	1.13	1.01	0.53

Potassium in Profile Soils



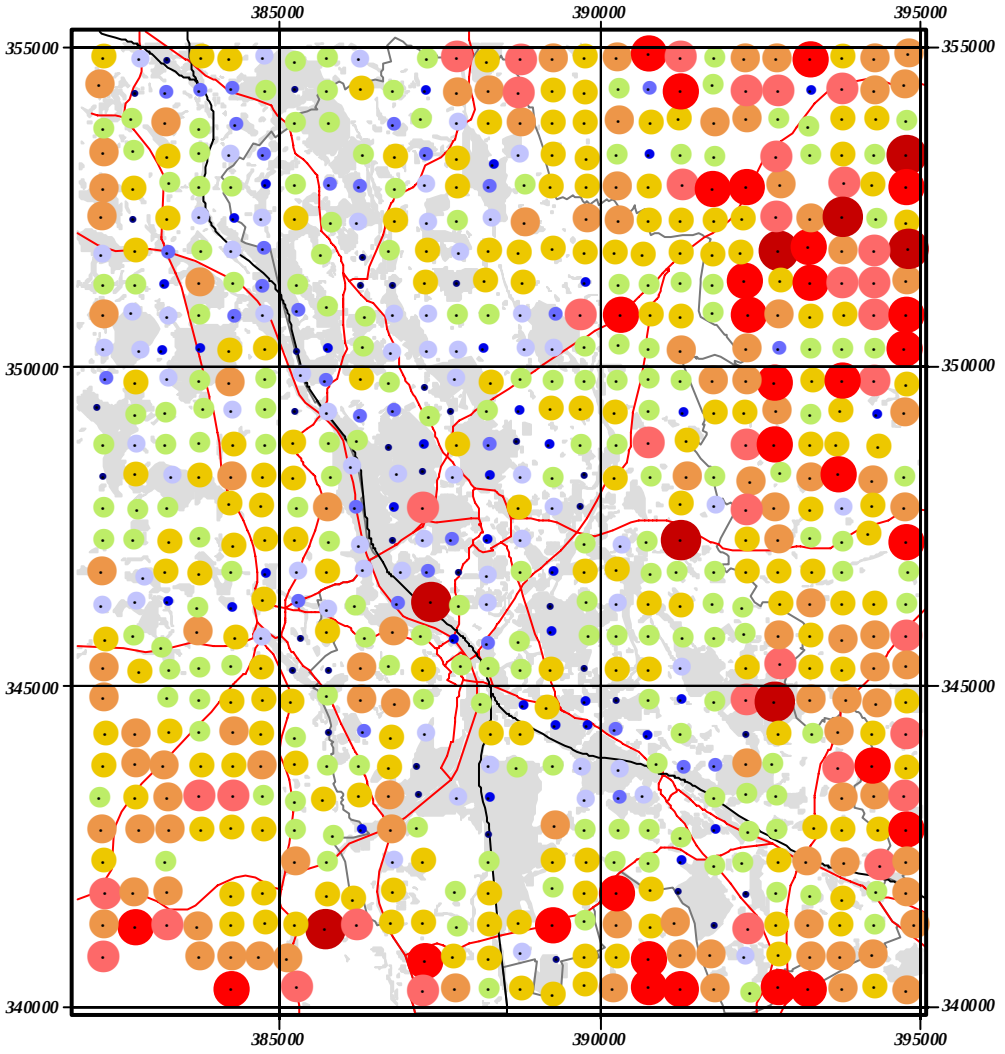
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	4.20	3.58	2.97	2.65	2.20	1.85	1.62	1.49	1.37	1.20	0.42

Silicon in Surface Soils



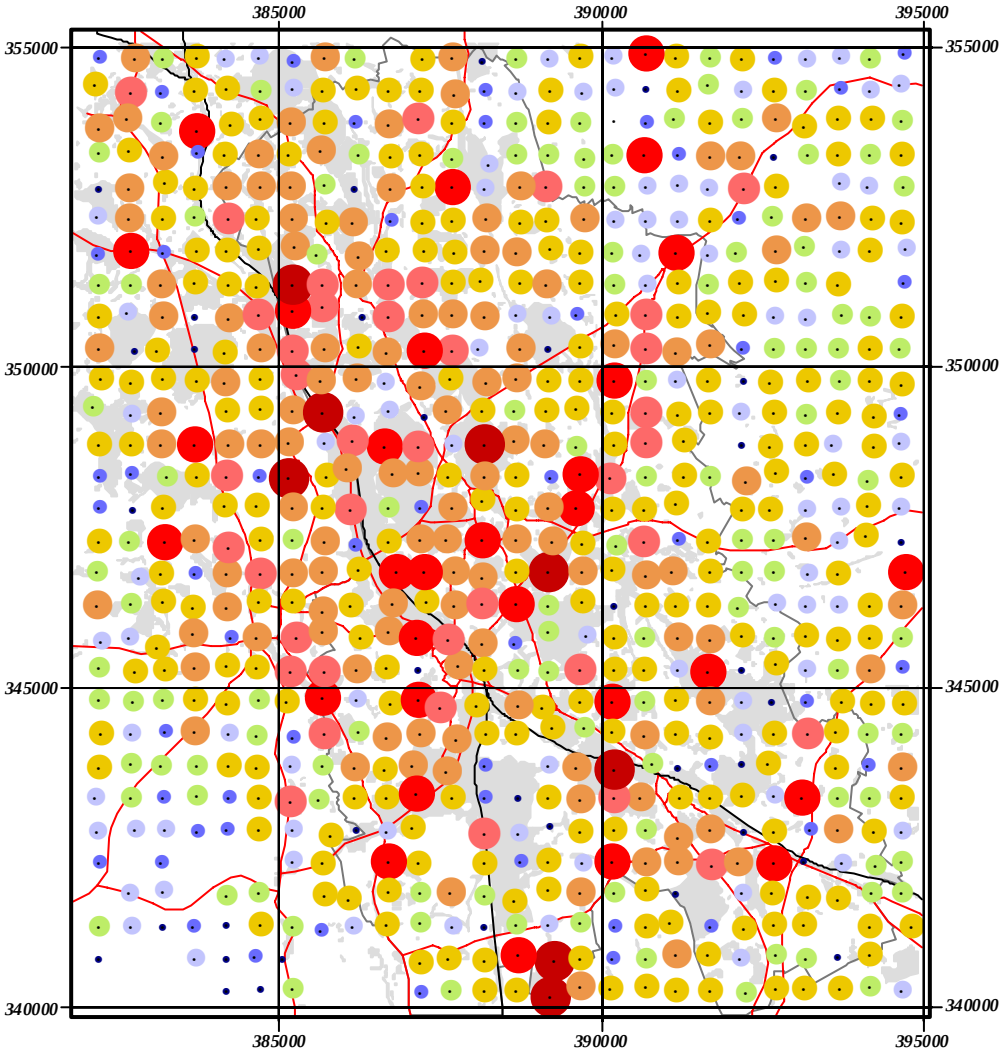
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	78.1	74.2	70.3	68.0	64.7	61.0	56.1	53.3	50.8	46.8	20.6

Silicon in Profile Soils



Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	76.9	72.5	68.3	66.6	63.3	59.3	54.3	51.6	49.3	45.4	12.6

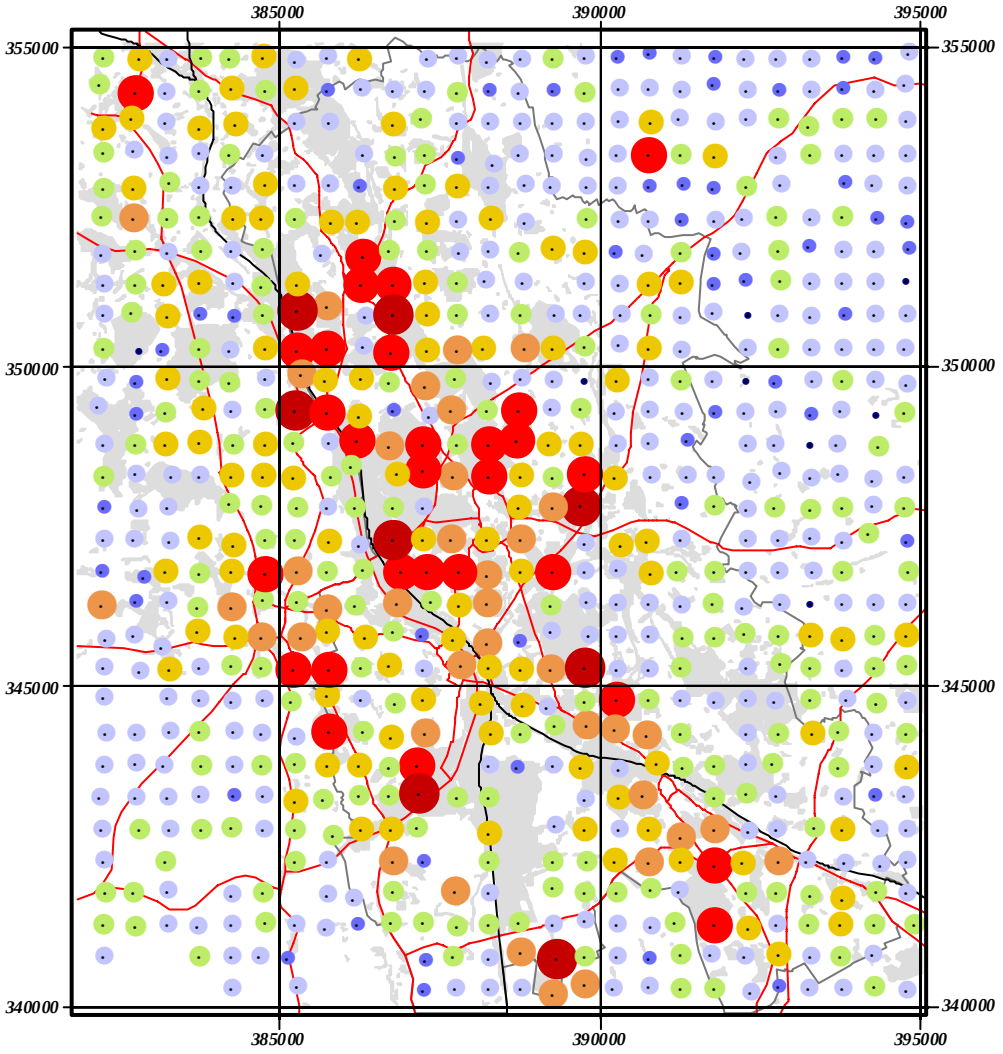
Tin in Surface Soils



Percentile 100 99 95 90 75 50 25 15 10 0

Concentration (ppm) 662 195 48 25 12 7 6 5 4 1 **mg/kg**

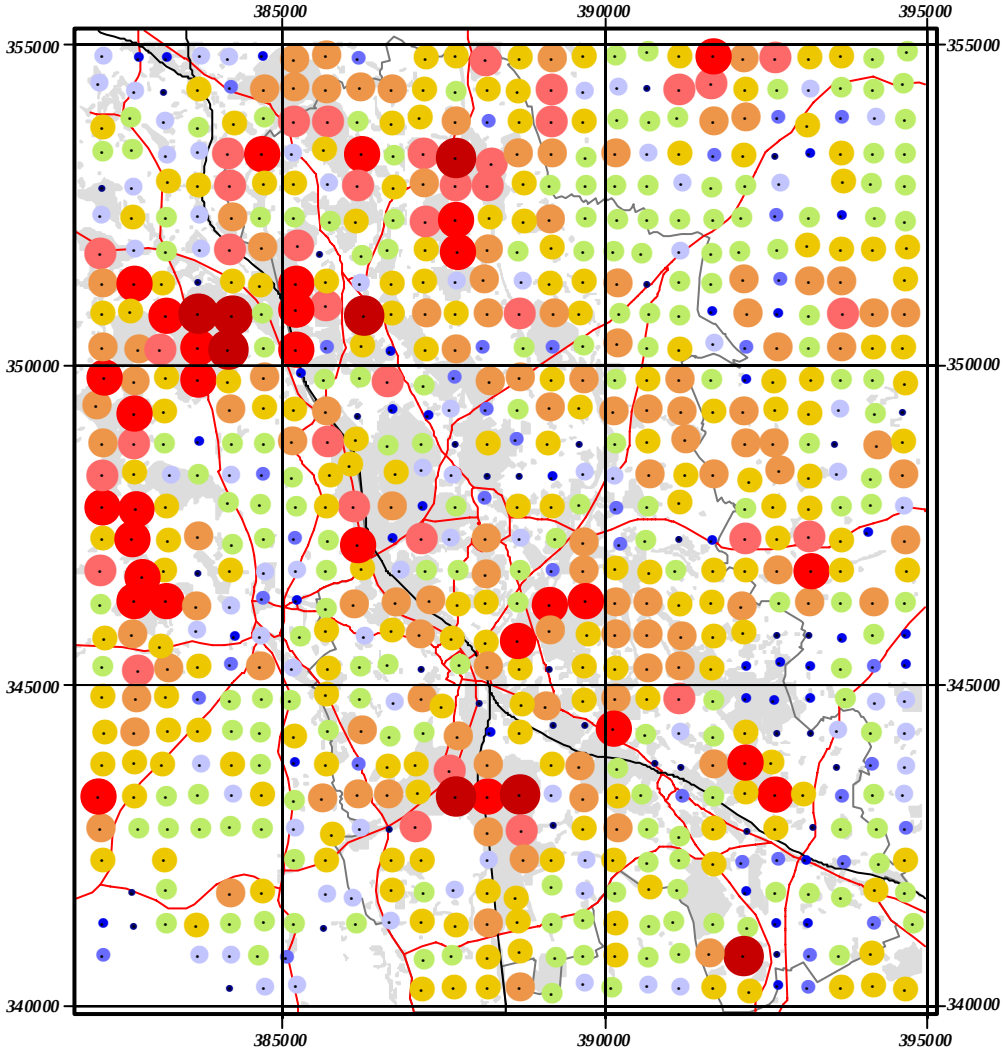
Tin in Profile Soils



Percentile 100 99 95 90 75 50 25 5 0

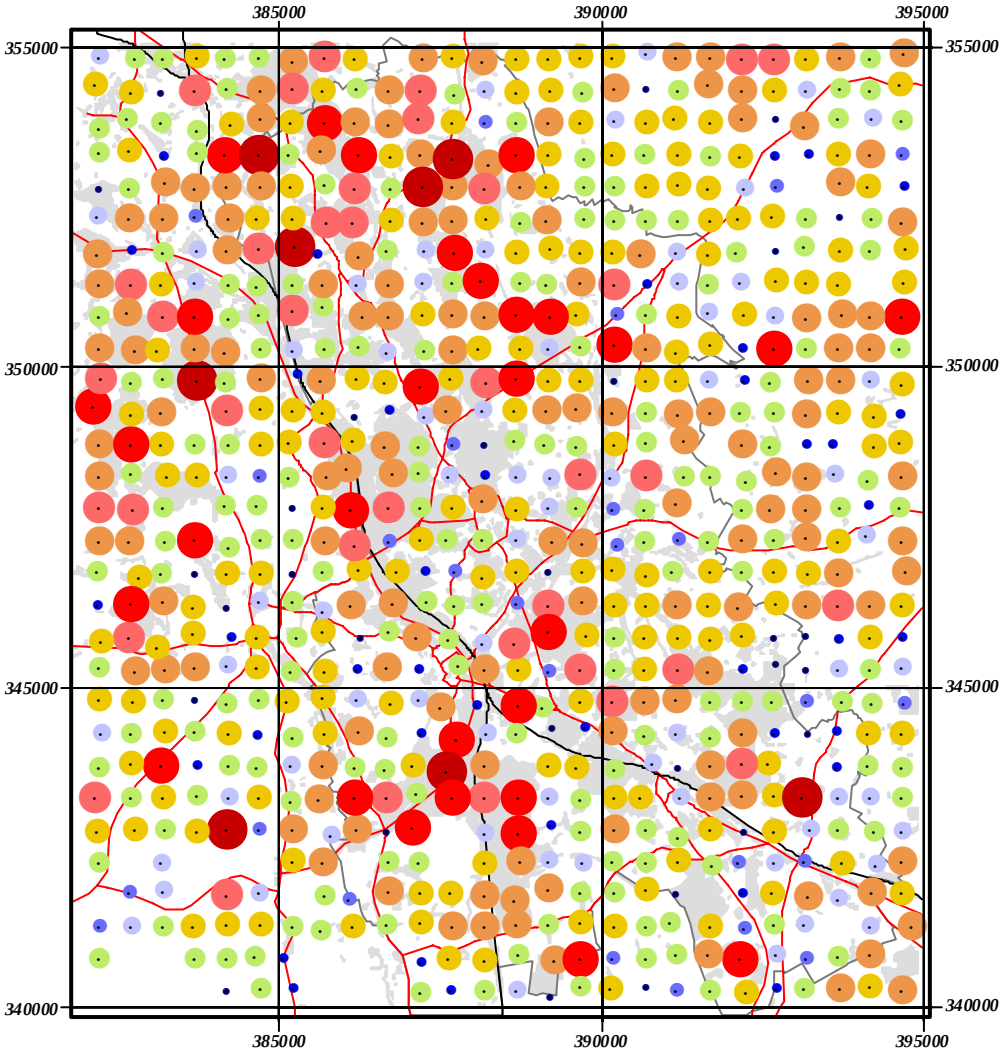
Concentration (ppm) 657 145 46 25 11 6 4 3 2 **mg/kg**

Titanium in Surface Soils



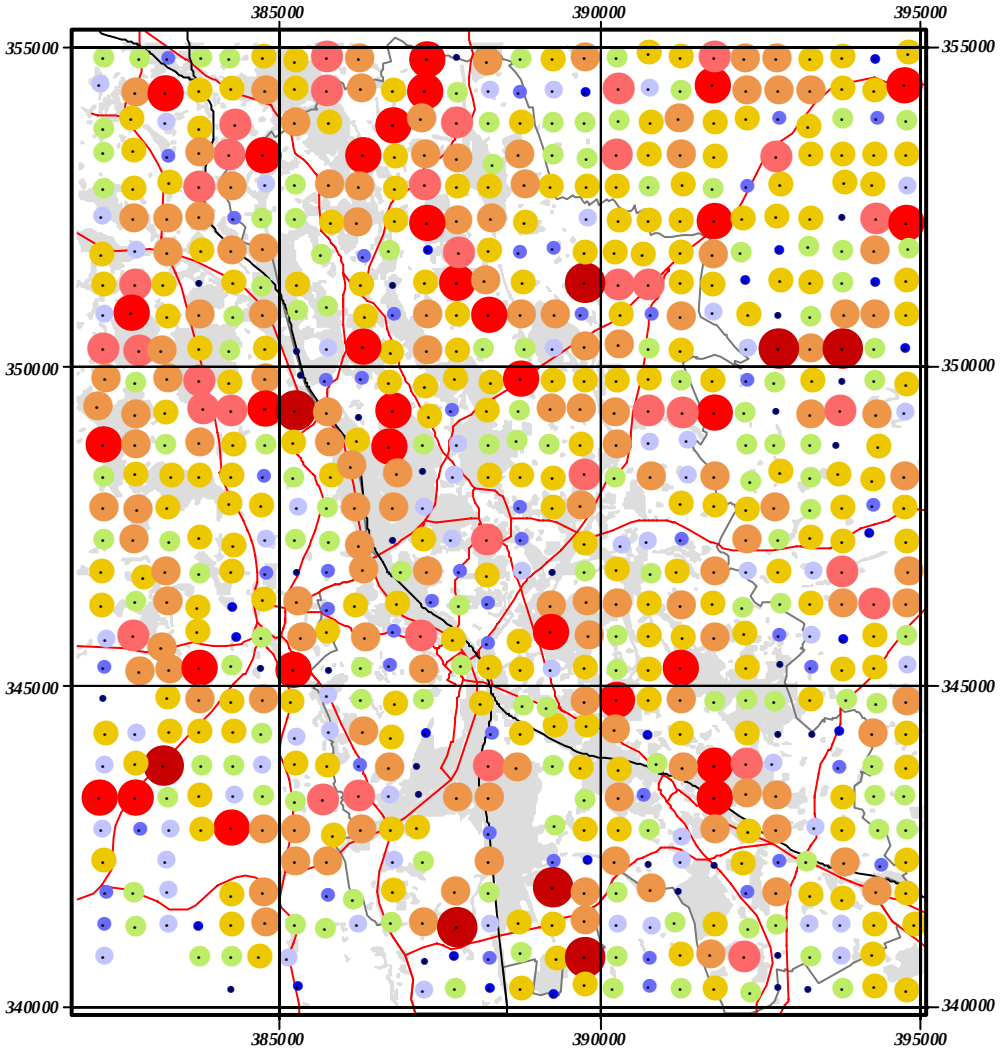
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (wt %)	1.393	1.051	0.909	0.851	0.740	0.617	0.509	0.424	0.384	0.315	0.096

Uranium in Surface Soils



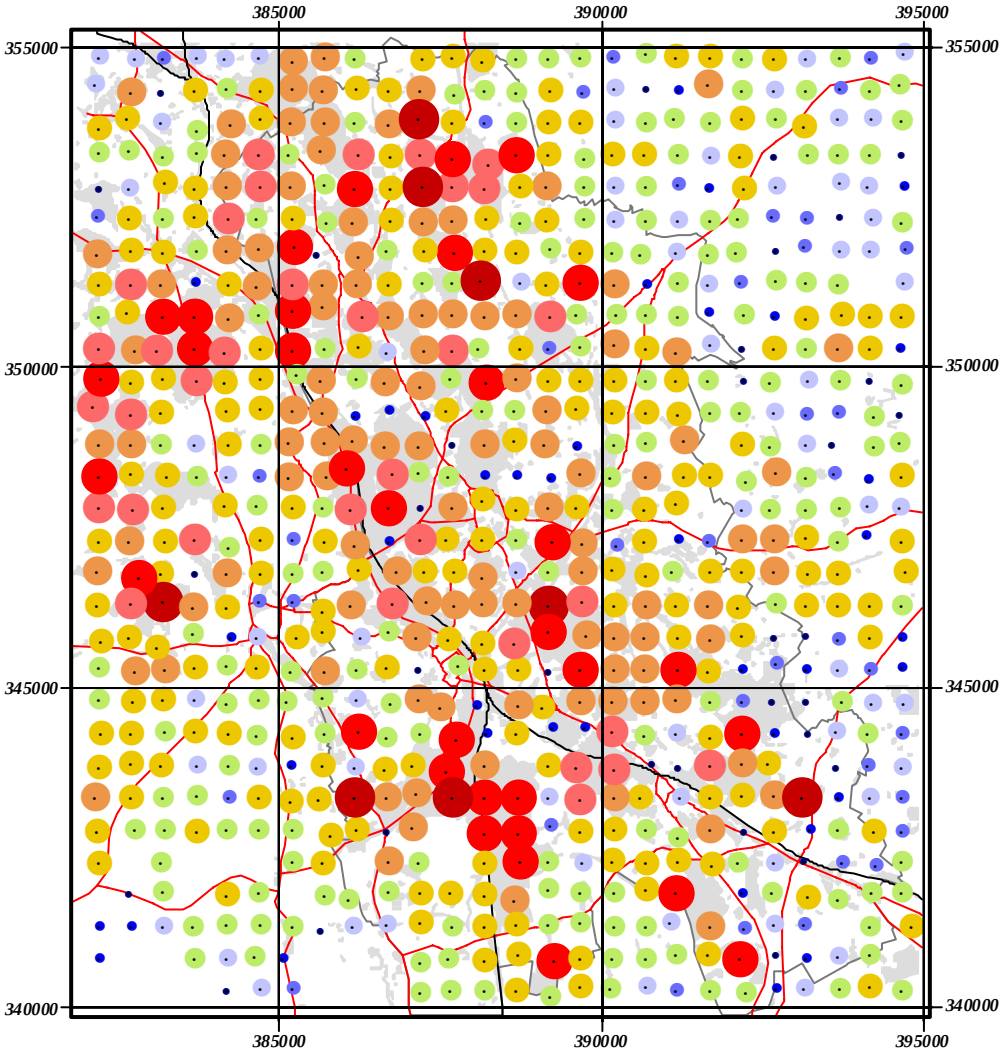
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	4.9	3.5	2.7	2.4	1.8	1.5	1.1	0.9	0.8	0.6	0.3

Uranium in Profile Soils



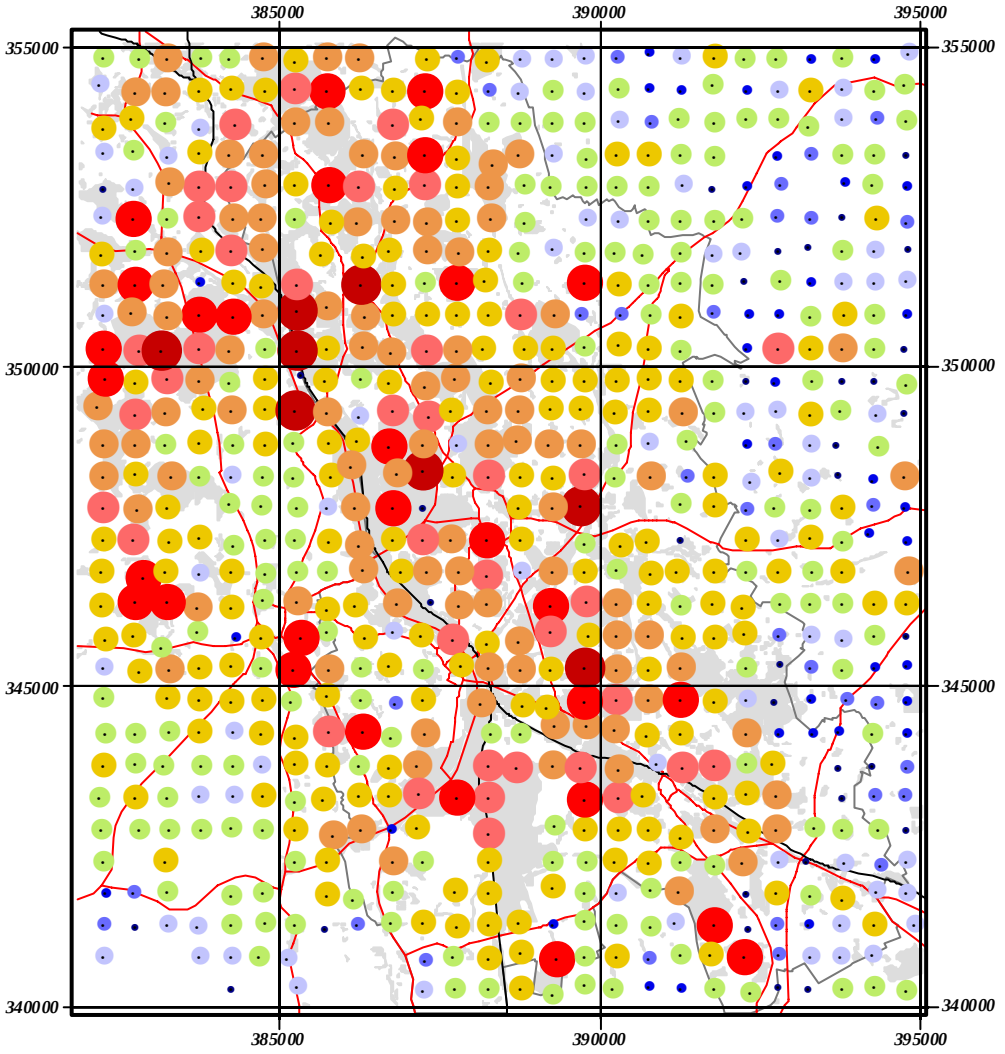
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	7.0	4.5	3.5	3.3	2.8	2.4	2.0	1.8	1.6	1.5	0.3

Vanadium in Surface Soils



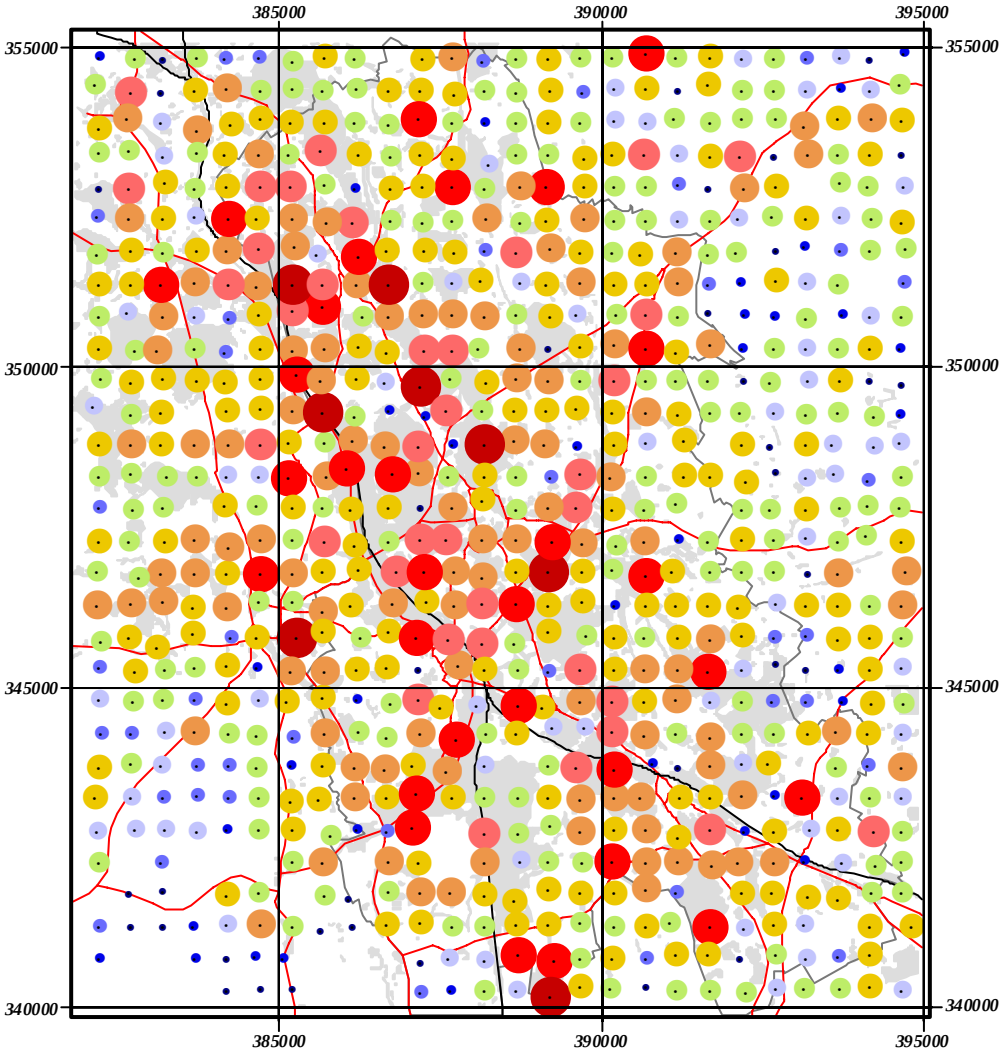
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	241	190	160	142	113	89	72	64	57	48	23

Vanadium in Profile Soils



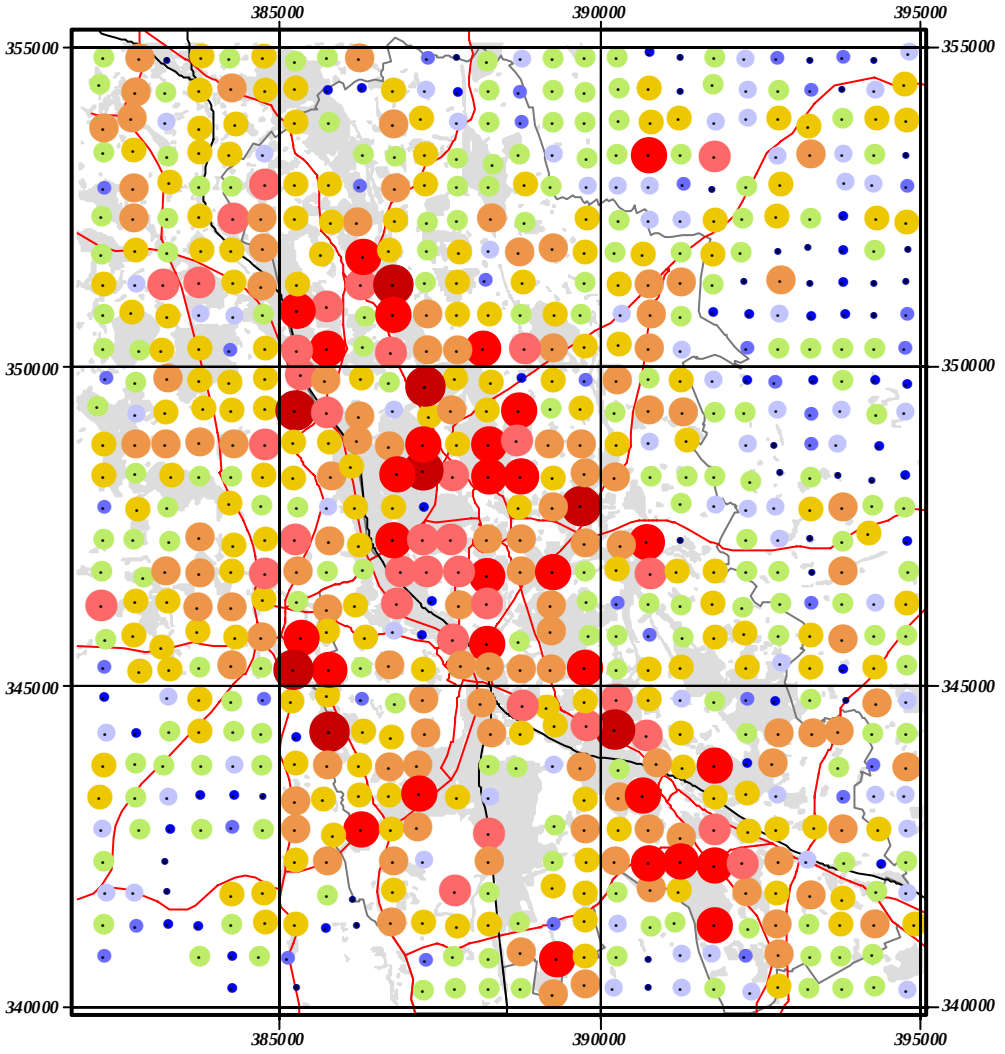
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	296	222	173	159	135	108	88	79	74	66	41

Zinc in Surface Soils



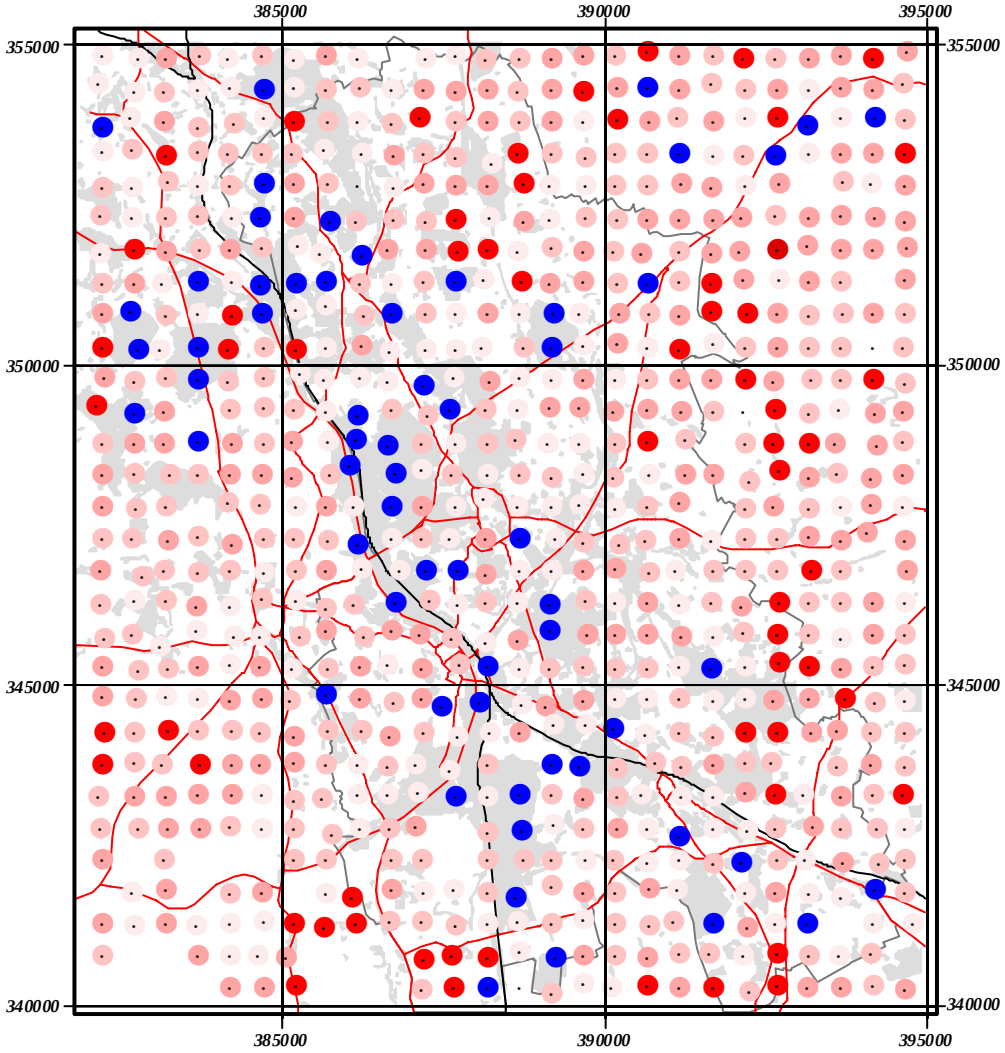
Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	2589	949	413	265	161	108	76	62	54	44	6

Zinc in Profile Soils

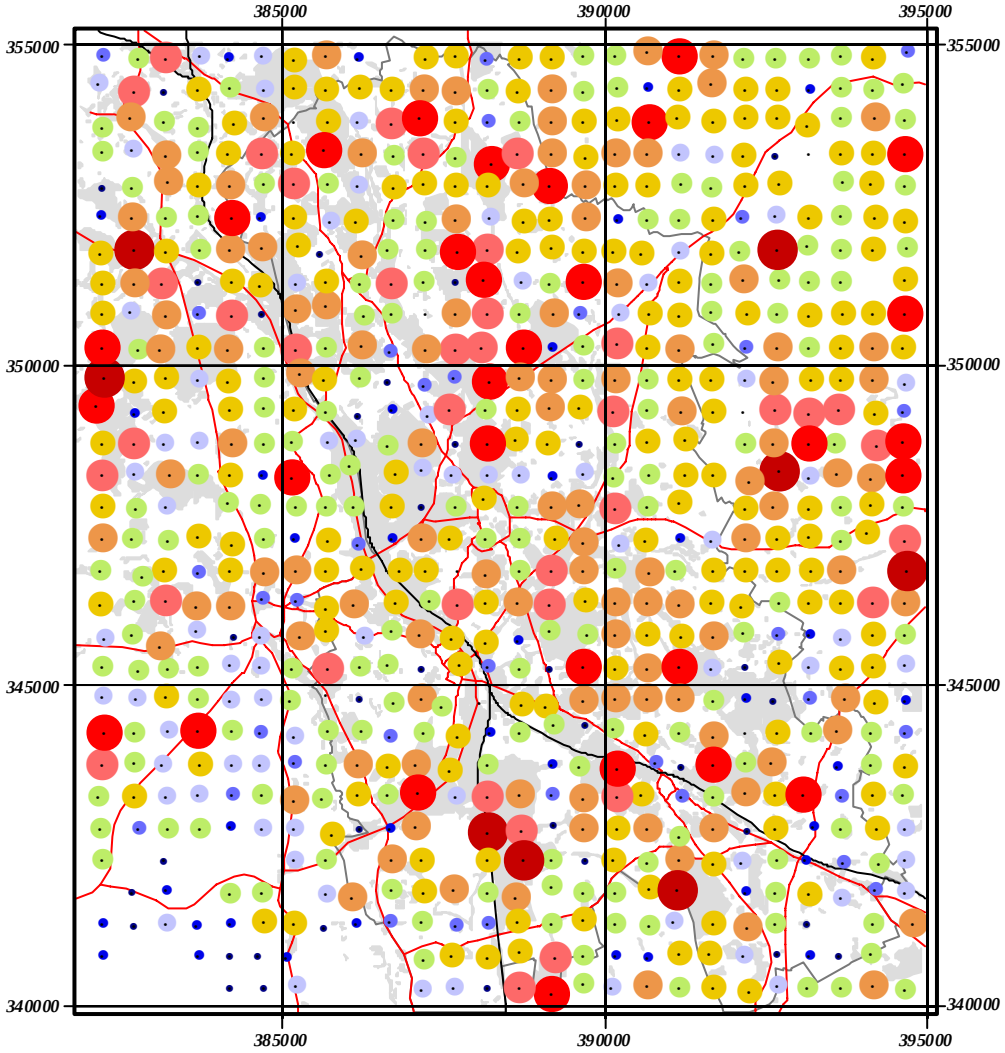


Percentile	100	99	95	90	75	50	25	15	10	5	0
Concentration (ppm) mg/kg	7408	1235	466	313	153	90	63	53	47	39	20

pH of Surface Soils



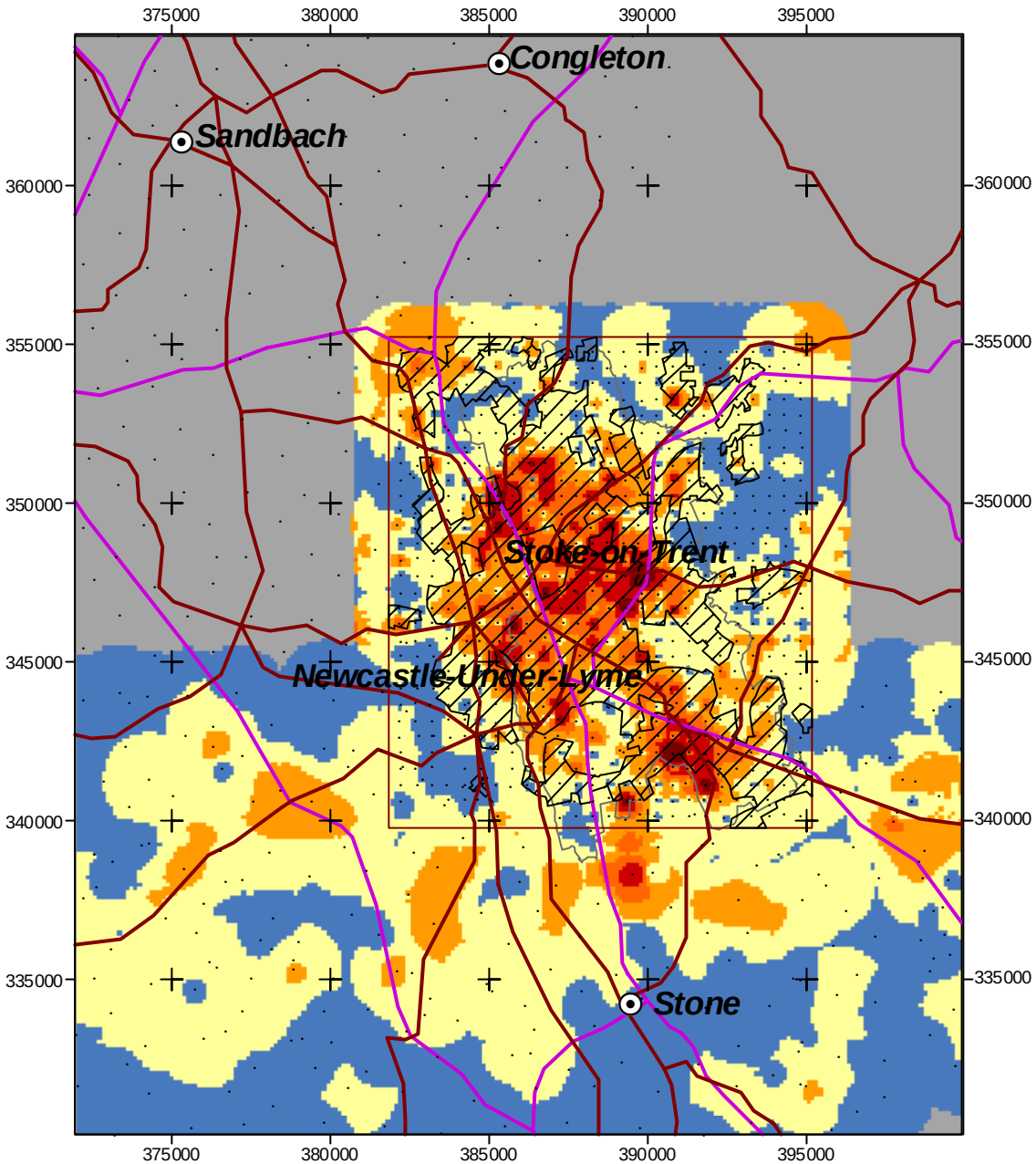
Loss on Ignition of Surface Soils



Percentile	100	99	95	90	75	50	25	15	10	5	0
% of Total Weight Lost	73.3	28.6	22.3	19.0	14.7	11.7	9.2	7.8	7.2	6.2	0.6

ANNEX 2. Interpolated Geochemical Maps of Stoke-on-Trent Rural and Urban Profile Soils

Combined Rural and Urban Profile (0.45m) Soil Data - Antimony



Sample Site Locations

Limit of Urban Study Area

Stoke City Boundary

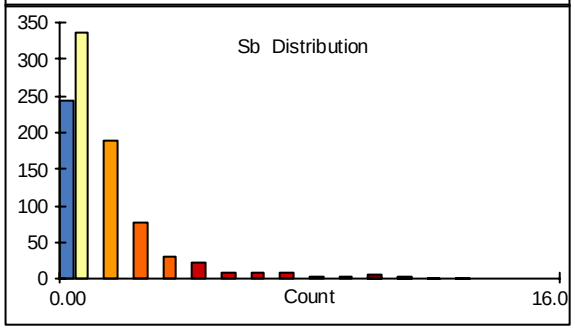
Limits of Urban Areas

Roads

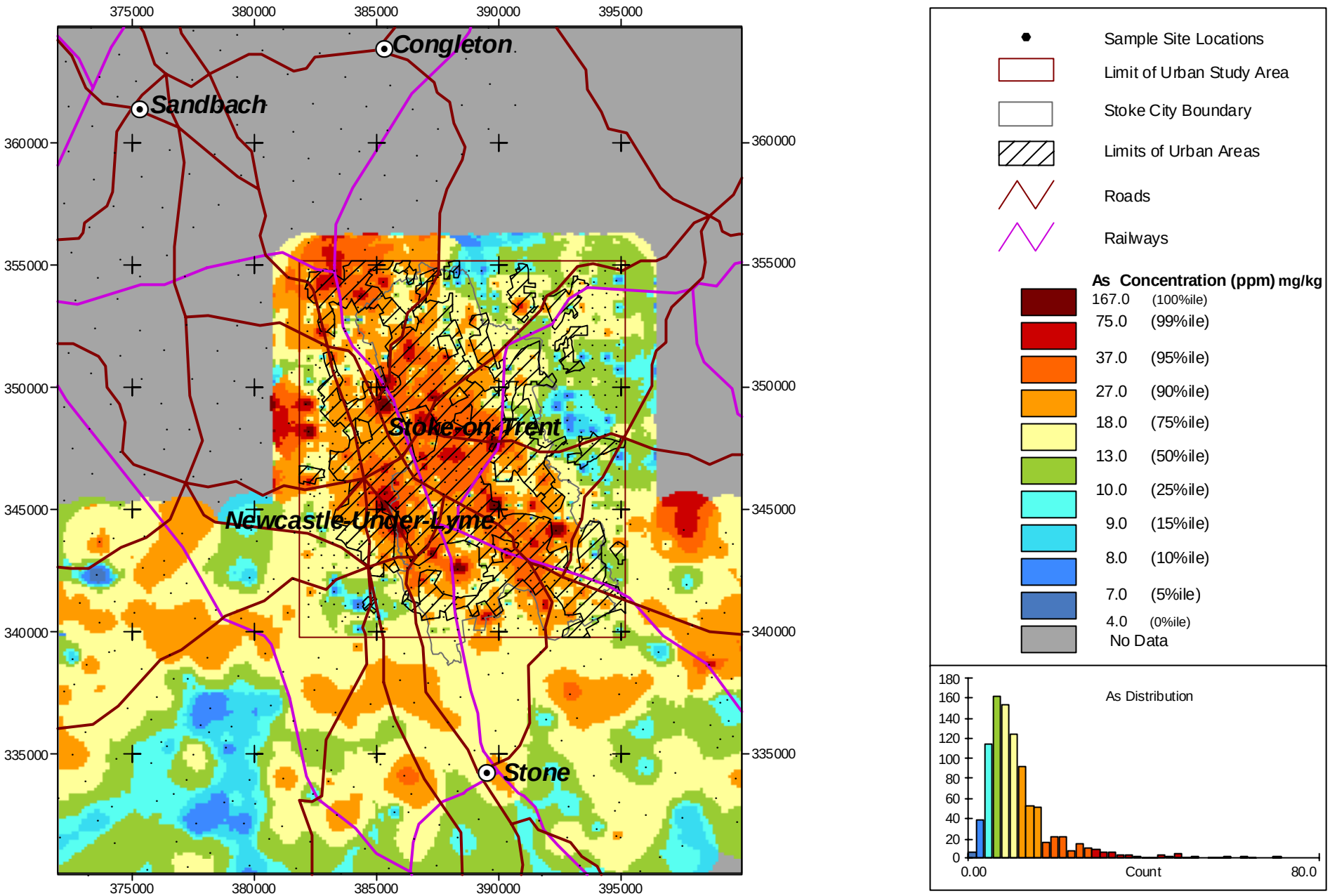
Railways

Sb Concentration (ppm)mg/kg

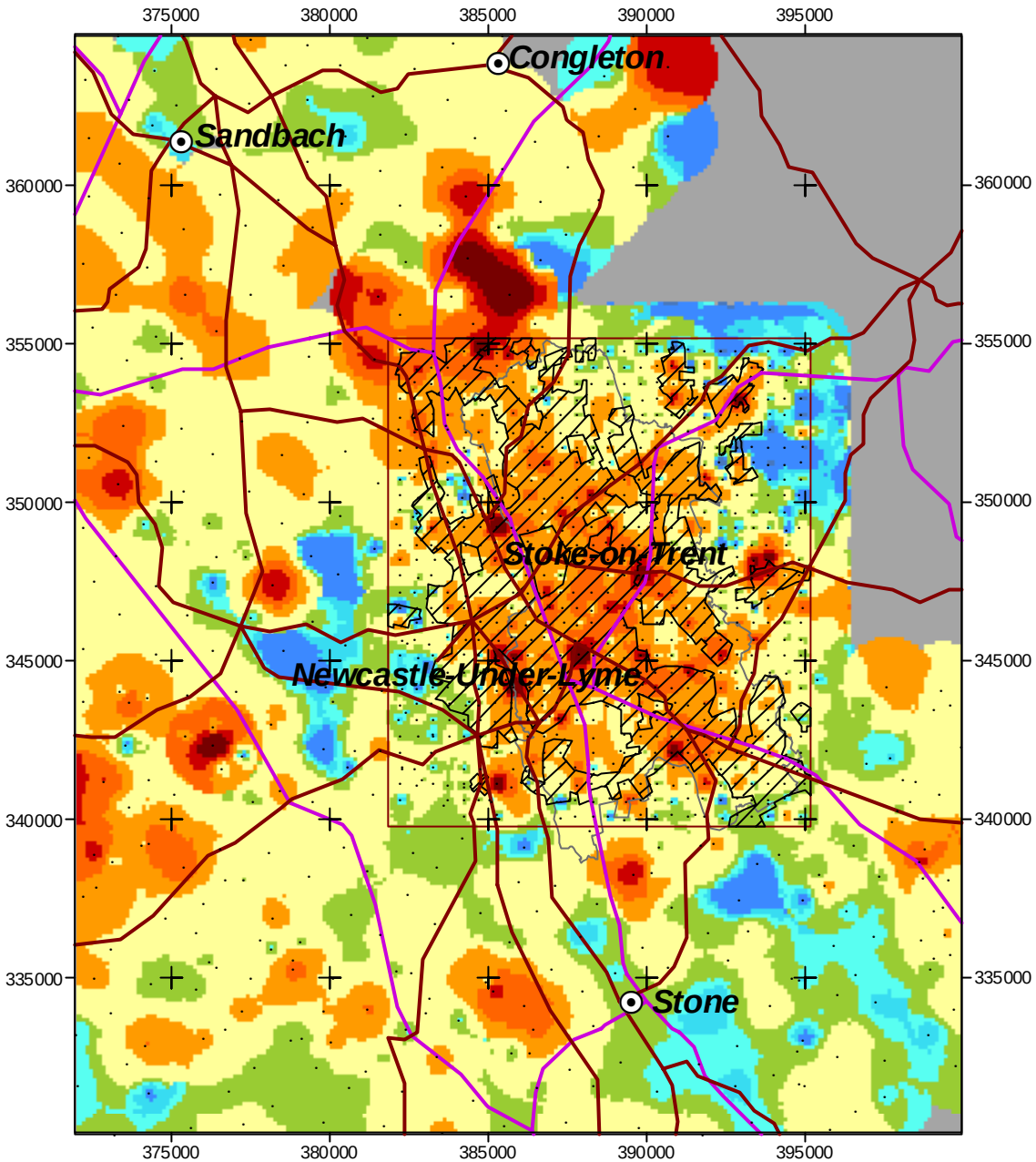
71.0	(100%ile)
15.7	(99%ile)
6.0	(95%ile)
4.0	(90%ile)
2.0	(75%ile)
1.0	(50%ile)
0.5	(0%ile)
No Data	



Combined Rural and Urban Profile (0.45m) Soil Data - Arsenic



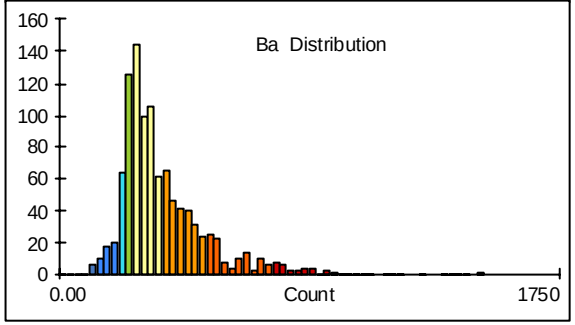
Combined Rural and Urban Profile (0.45m) Soil Data - Barium



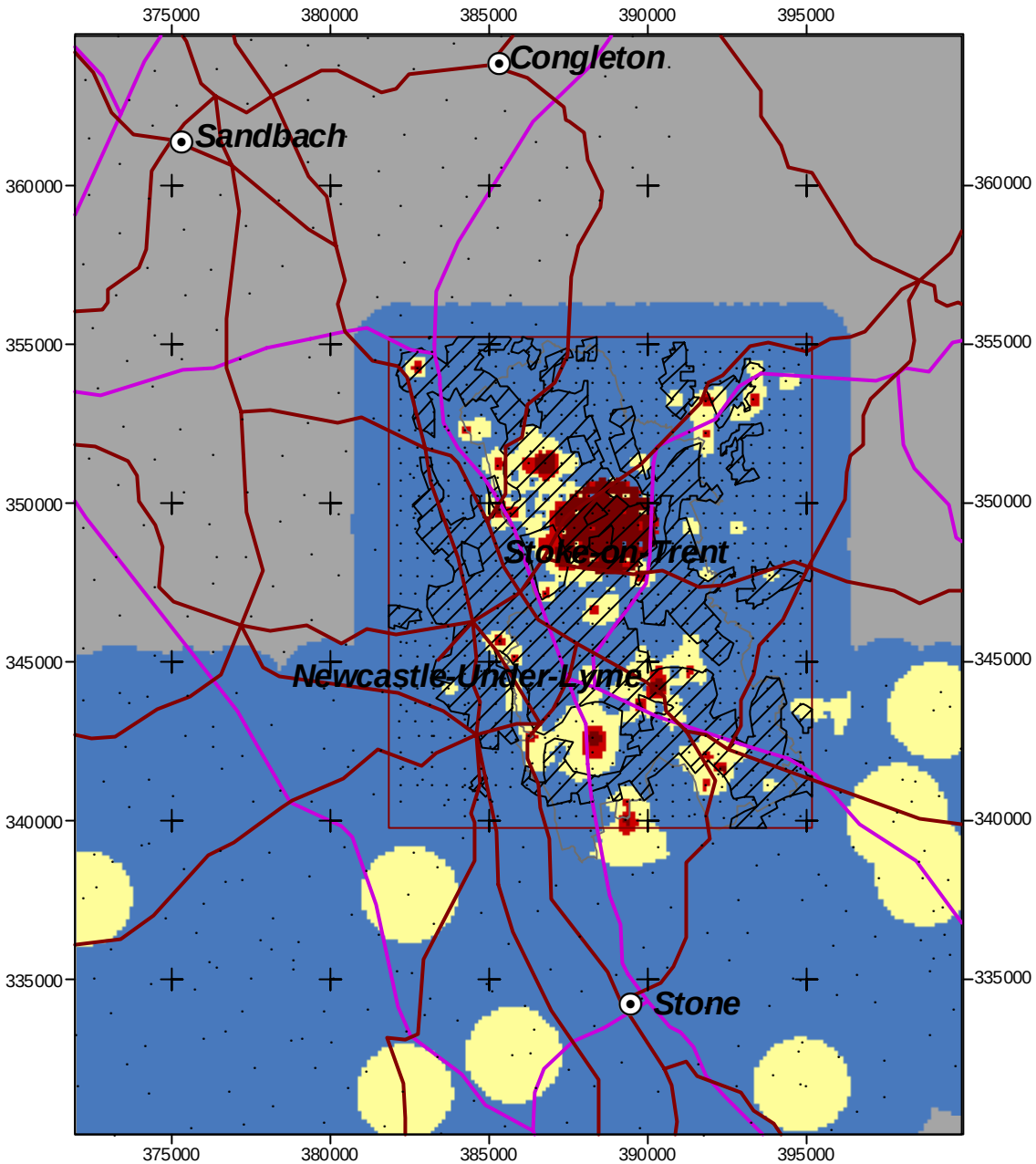
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Ba Concentration (ppm)mg/kg

4269	(100%ile)
1711	(99%ile)
950	(95%ile)
790	(90%ile)
600	(75%ile)
479	(50%ile)
417	(25%ile)
397	(15%ile)
381	(10%ile)
355	(5%ile)
146	(0%ile)
No Data	



Combined Rural and Urban Profile (0.45m) Soil Data - Cadmium



Sample Site Locations

Limit of Urban Study Area

Stoke City Boundary

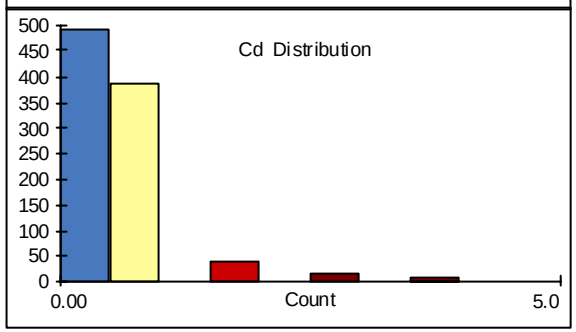
Limits of Urban Areas

Roads

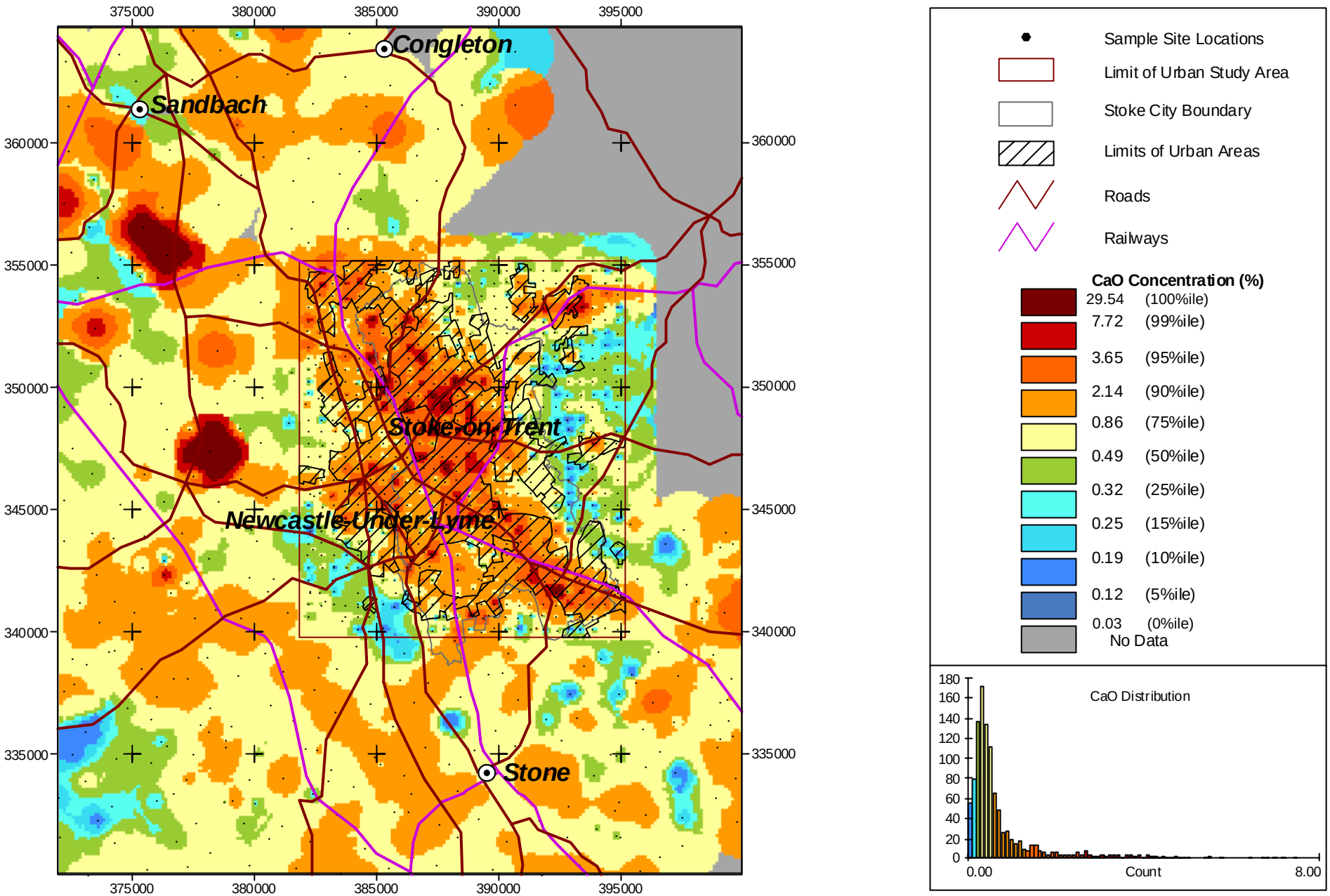
Railways

Cd Concentration (ppm) mg/kg

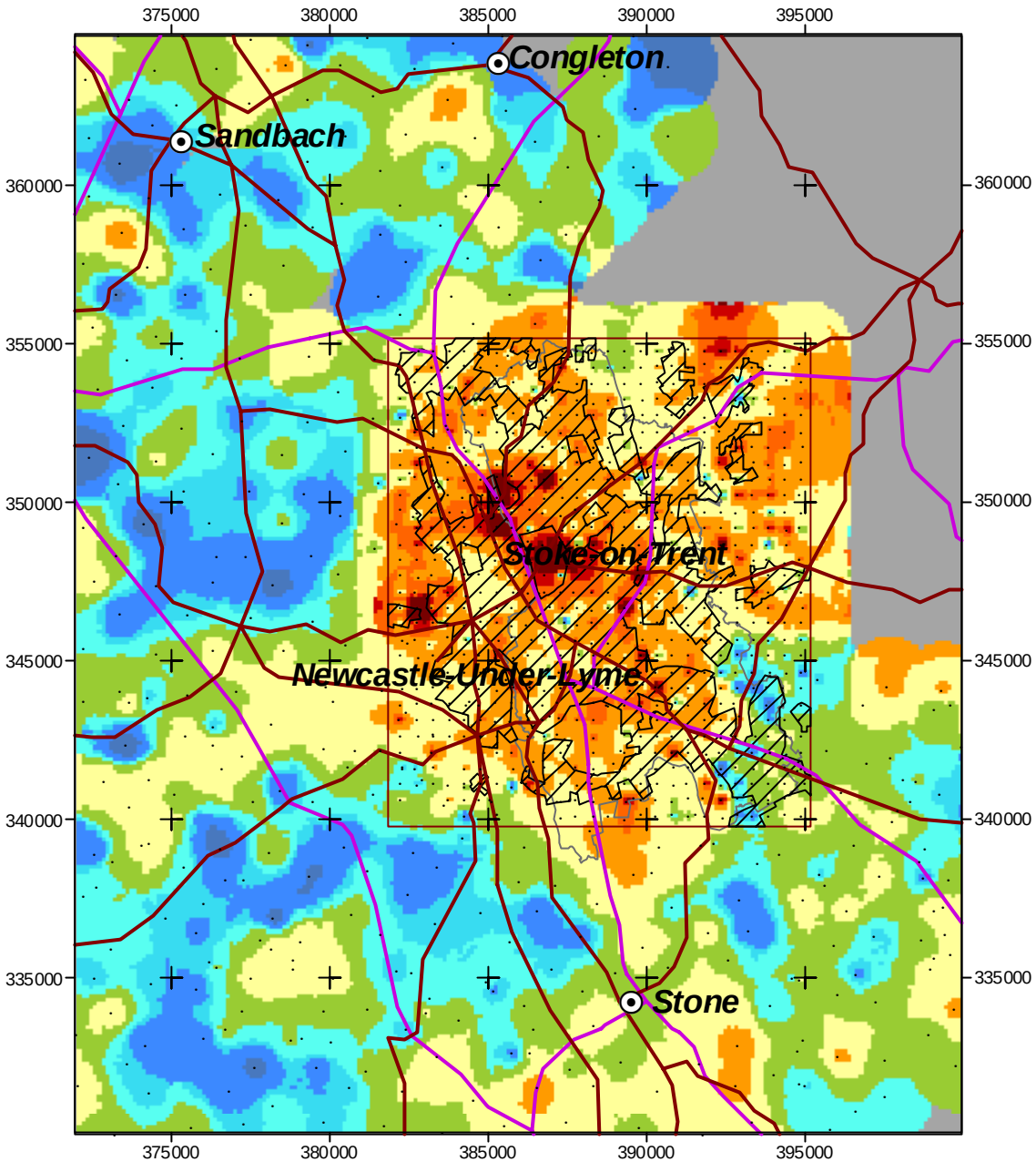
408.0	(100%ile)
4.4	(99%ile)
2.0	(95%ile)
1.0	(90%ile)
0.4	(0%ile)
No Data	



Combined Rural and Urban Profile (0.45m) Soil Data - Calcium Oxide



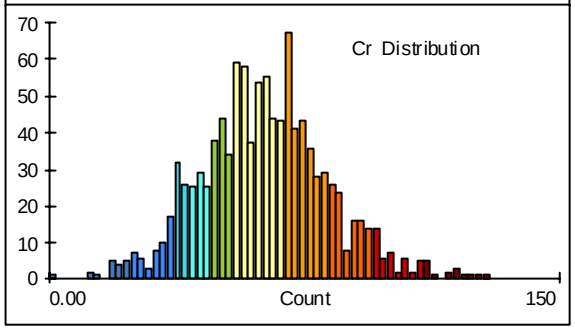
Combined Rural and Urban Profile (0.45m) Soil Data - Chromium



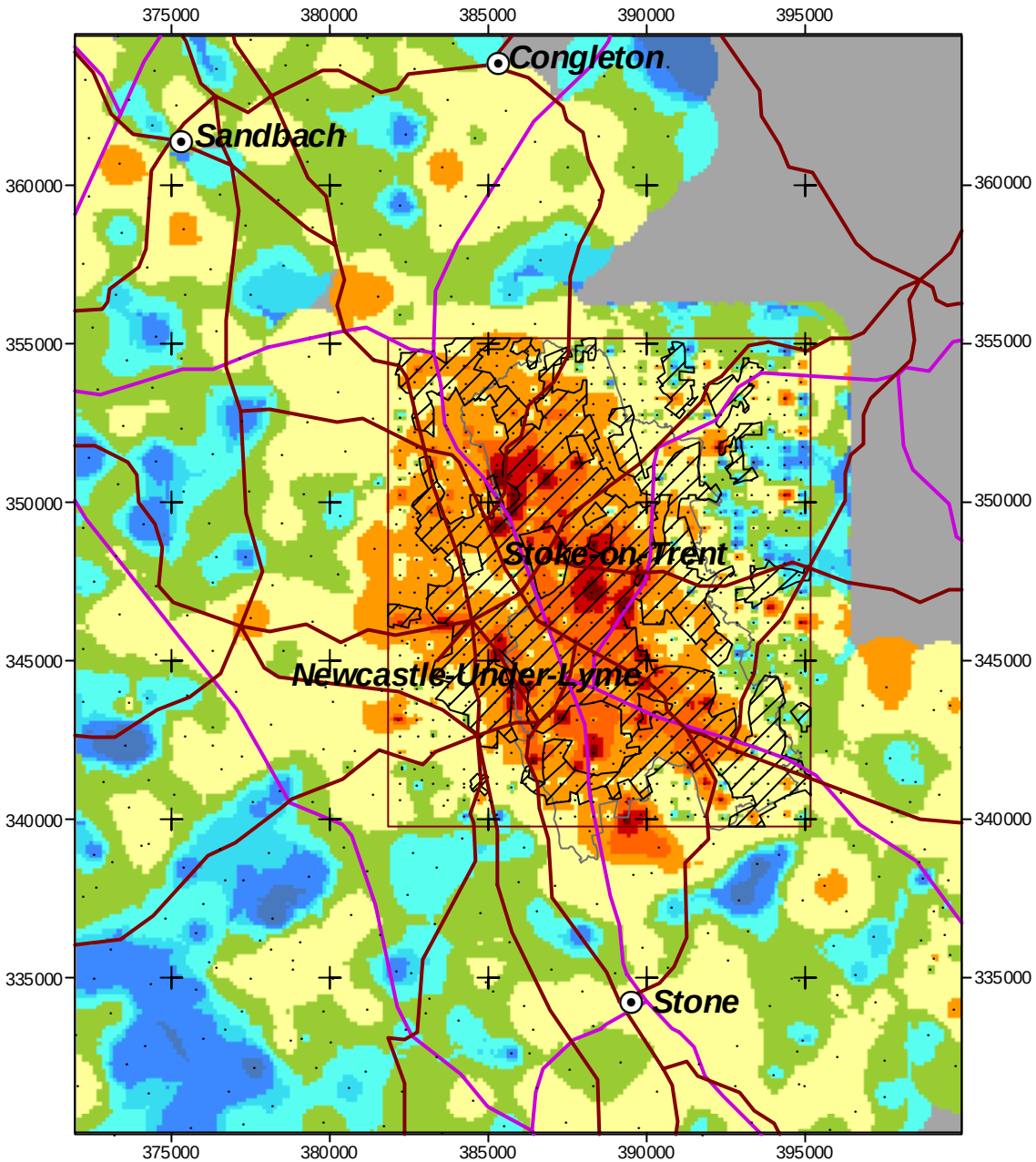
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Cr Concentration (ppm) mg/kg

574	(100%ile)
144	(99%ile)
118	(95%ile)
110	(90%ile)
97	(75%ile)
85	(50%ile)
73	(25%ile)
66	(15%ile)
62	(10%ile)
57	(5%ile)
23	(0%ile)
No Data	



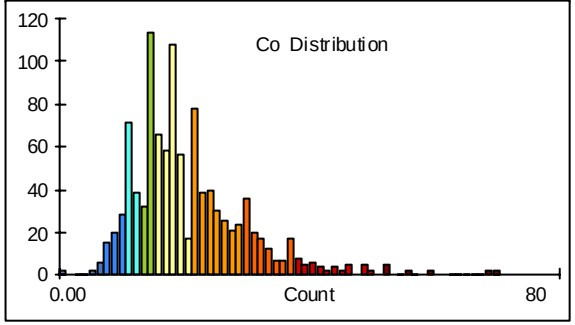
Combined Rural and Urban Profile (0.45m) Soil Data - Cobalt



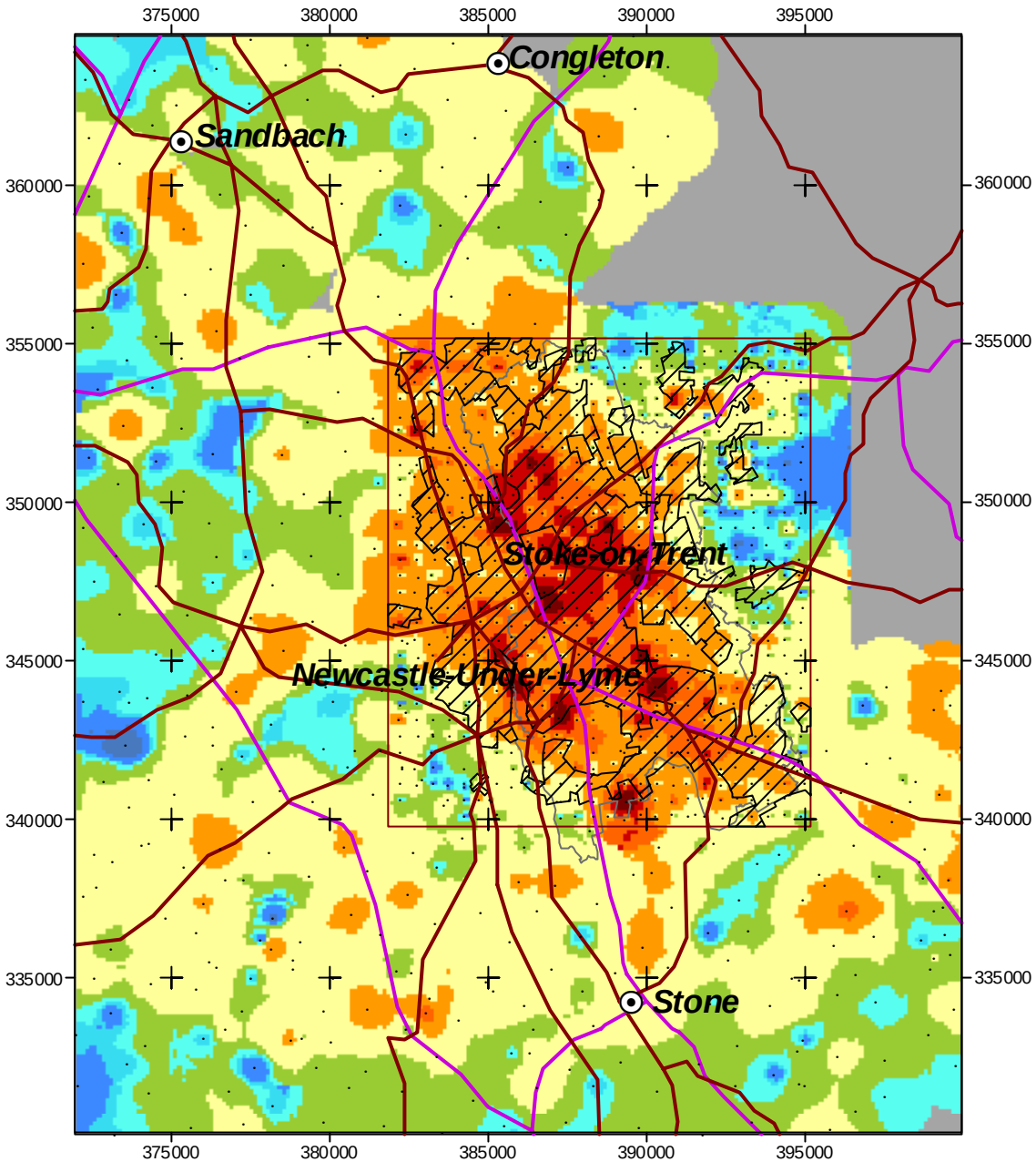
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Co Concentration (ppm)mg/kg

133	(100%ile)
77	(99%ile)
47	(95%ile)
38	(90%ile)
29	(75%ile)
22	(50%ile)
17	(25%ile)
15	(15%ile)
14	(10%ile)
12	(5%ile)
1	(0%ile)
No Data	



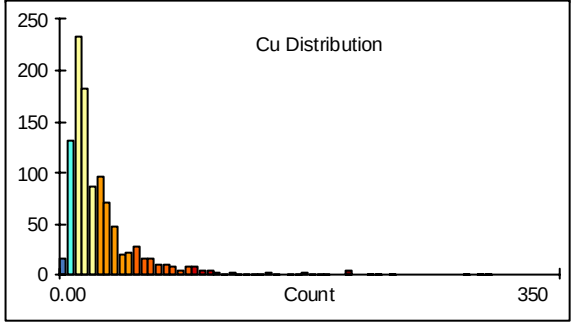
Combined Rural and Urban Profile (0.45m) Soil Data - Copper



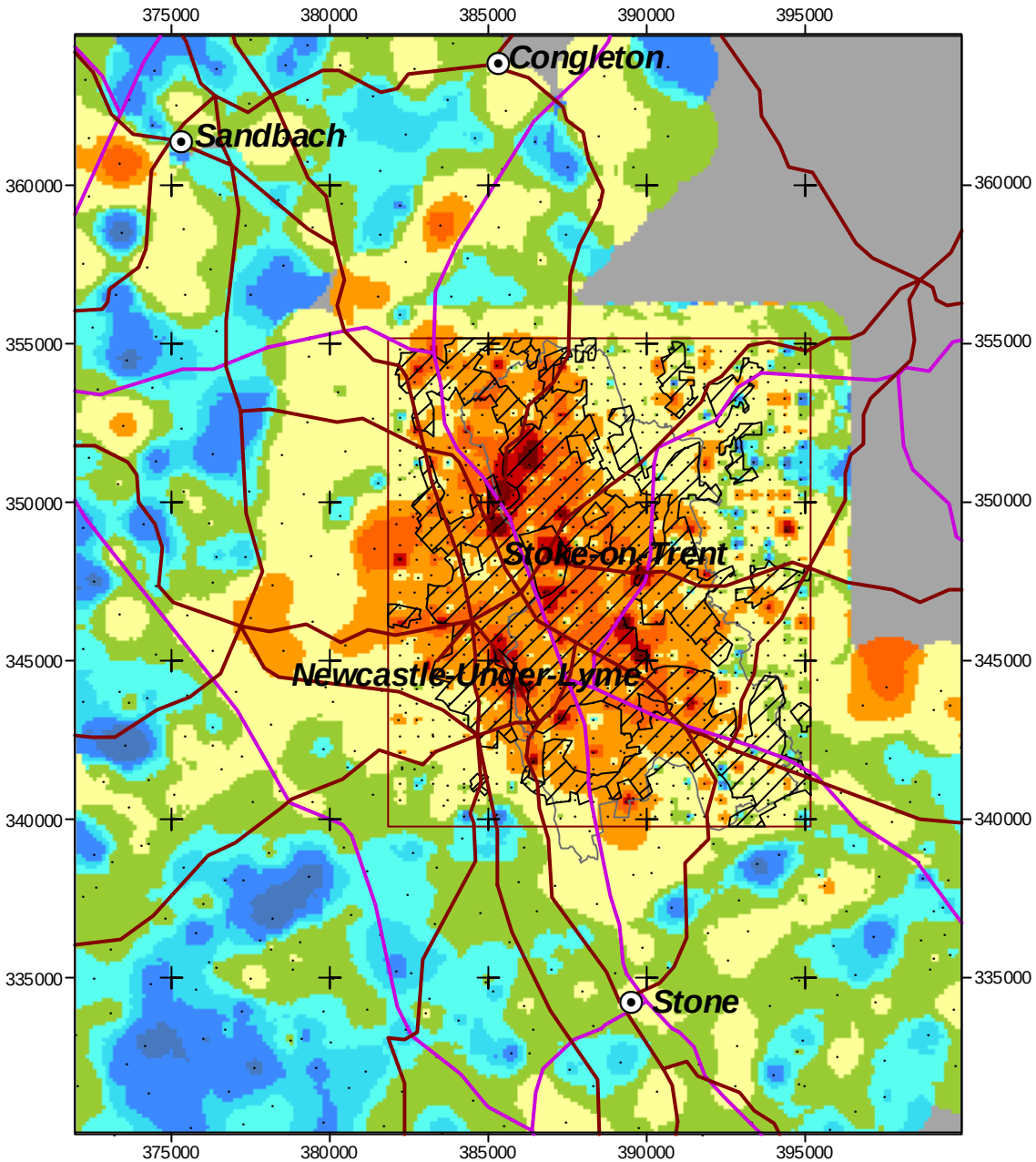
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Cu Concentration (ppm) mg/kg

1260	(100%ile)
349	(99%ile)
121	(95%ile)
81	(90%ile)
44	(75%ile)
27	(50%ile)
19	(25%ile)
16	(15%ile)
14	(10%ile)
12	(5%ile)
4	(0%ile)
No Data	



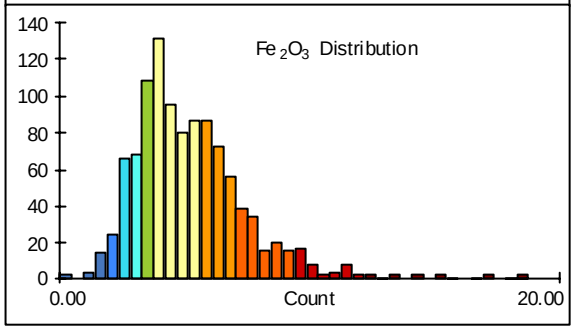
Combined Rural and Urban Profile (0.45m) Soil Data - Iron Oxide



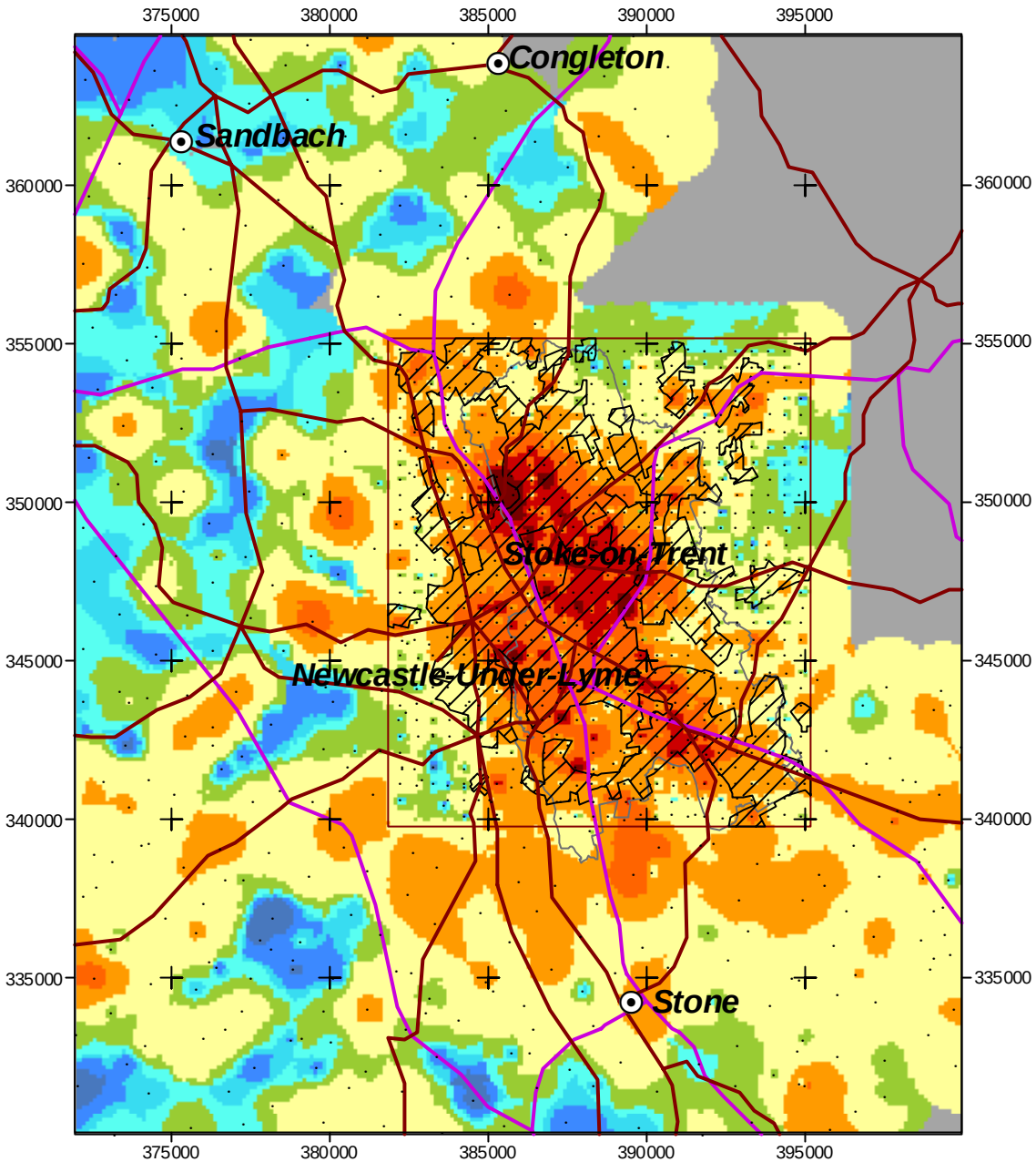
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Fe_2O_3 Concentration (%)

43.700	(100%ile)
17.834	(99%ile)
10.556	(95%ile)
9.130	(90%ile)
7.170	(75%ile)
5.570	(50%ile)
4.353	(25%ile)
3.890	(15%ile)
3.464	(10%ile)
3.132	(5%ile)
0.600	(0%ile)
No Data	



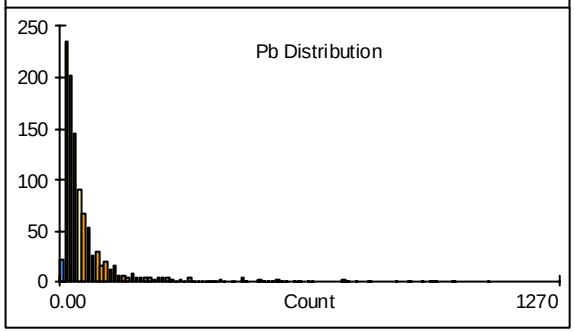
Combined Rural and Urban Profile (0.45m) Soil Data - Lead



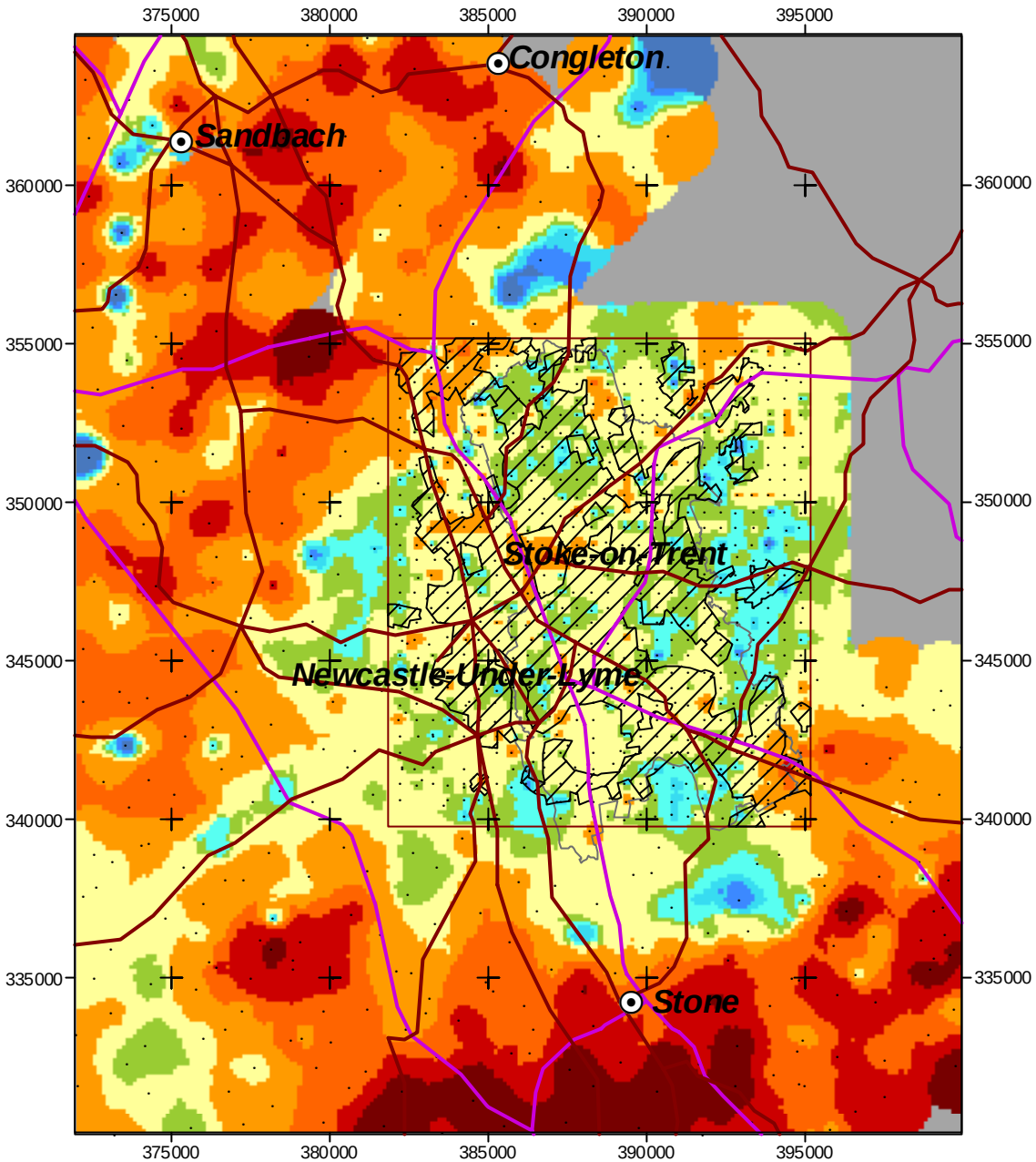
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Pb Concentration (ppm) mg/kg

4207	(100%ile)
1268	(99%ile)
505	(95%ile)
248	(90%ile)
97	(75%ile)
53	(50%ile)
35	(25%ile)
30	(15%ile)
28	(10%ile)
25	(5%ile)
9	(0%ile)
No Data	



Combined Rural and Urban Profile (0.45m) Soil Data - Magnesium Oxide



Sample Site Locations

Limit of Urban Study Area

Stoke City Boundary

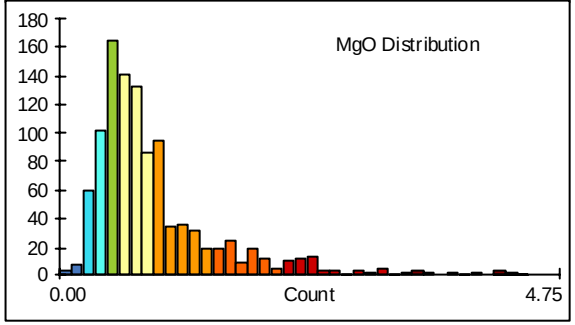
Limits of Urban Areas

Roads

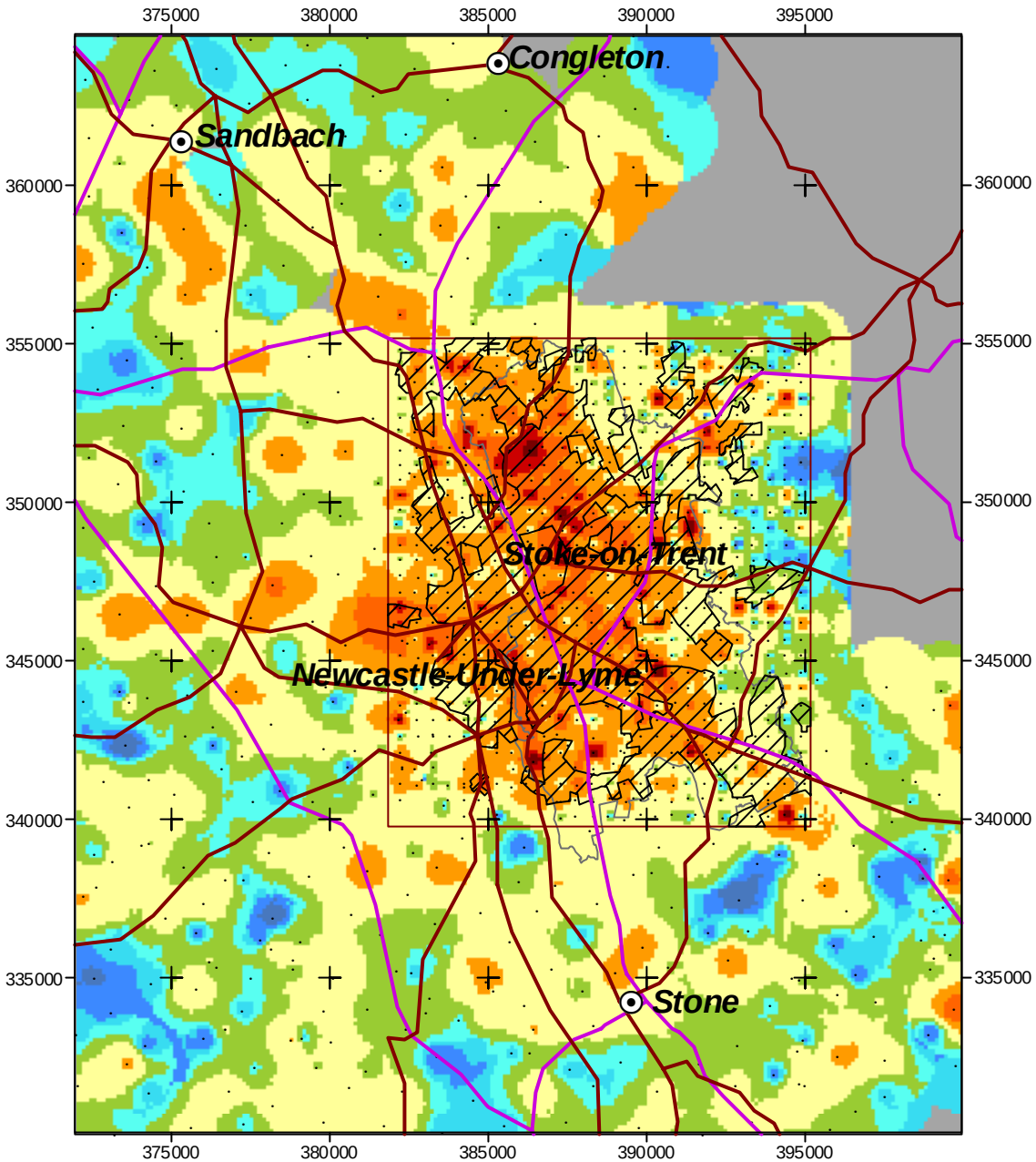
Railways

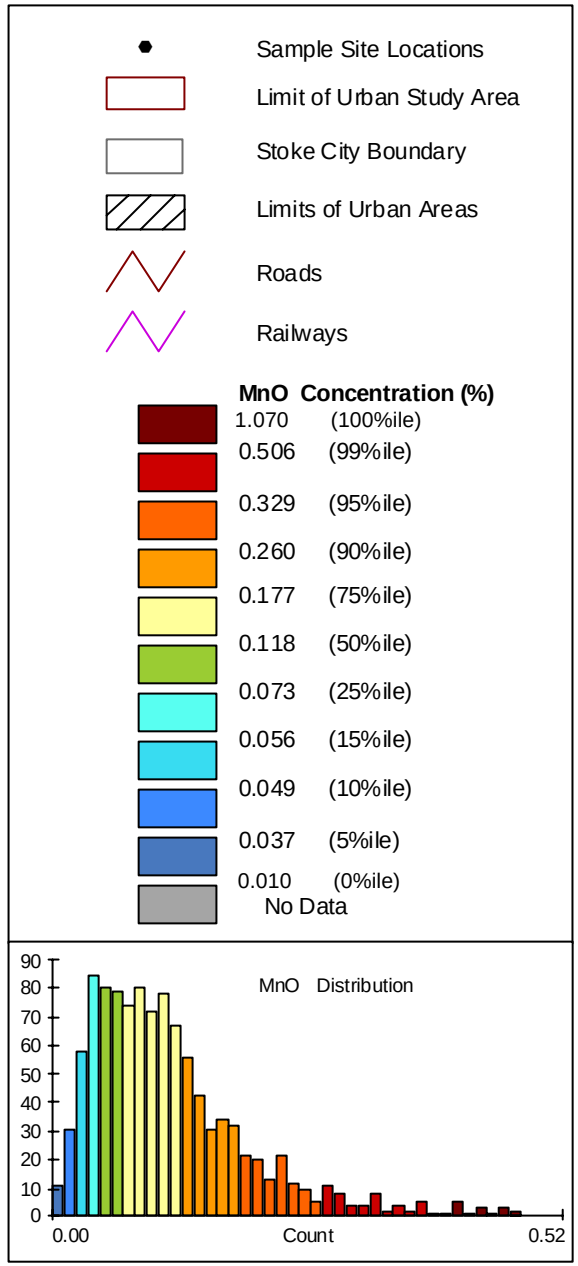
MgO Concentration (%)

8.20	(100%ile)
4.57	(99%ile)
2.60	(95%ile)
2.00	(90%ile)
1.20	(75%ile)
0.80	(50%ile)
0.60	(25%ile)
0.50	(15%ile)
0.45	(10%ile)
0.40	(5%ile)
0.10	(0%ile)
No Data	

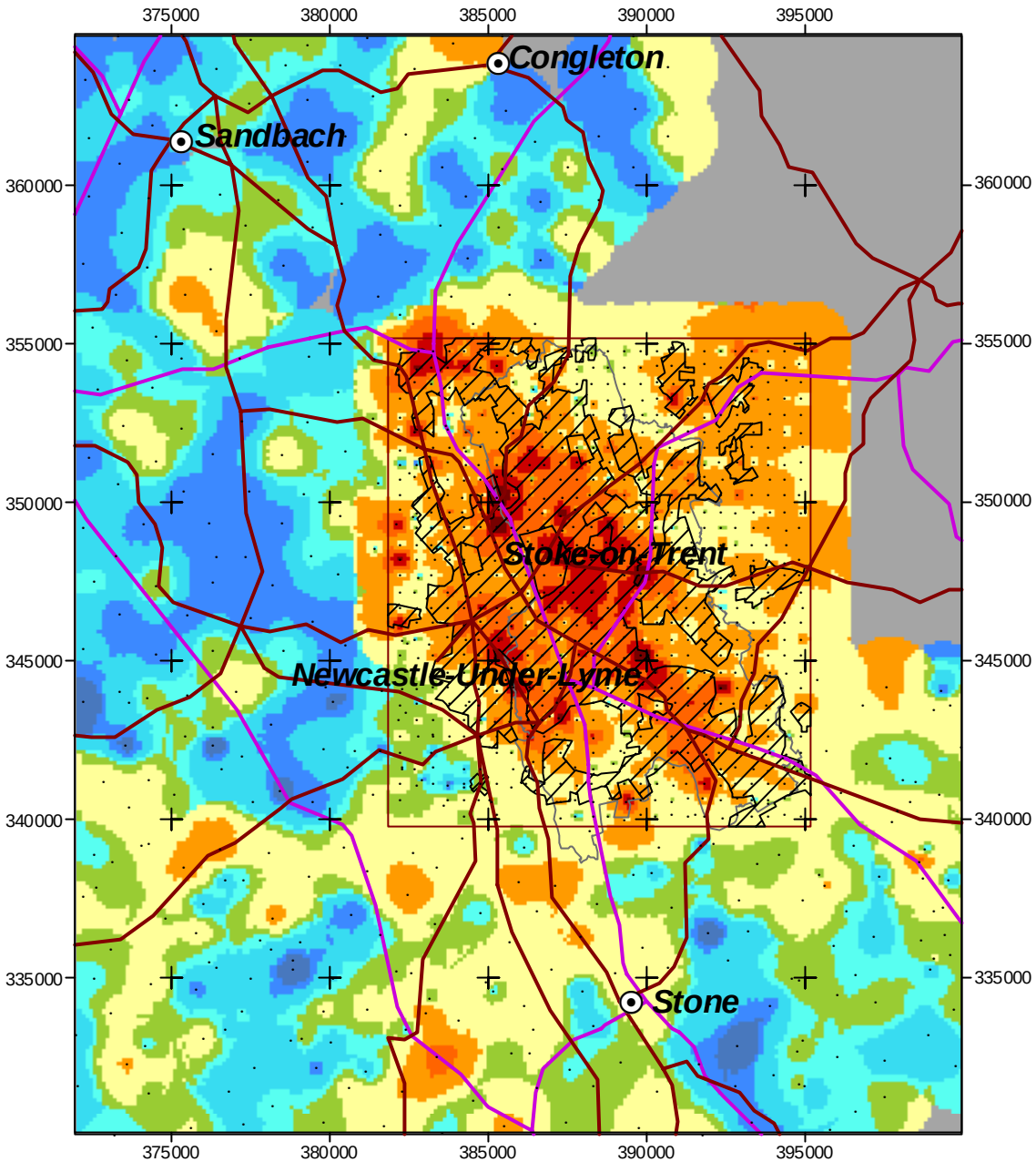


Combined Rural and Urban Profile (0.45m) Soil Data - Manganese Oxide





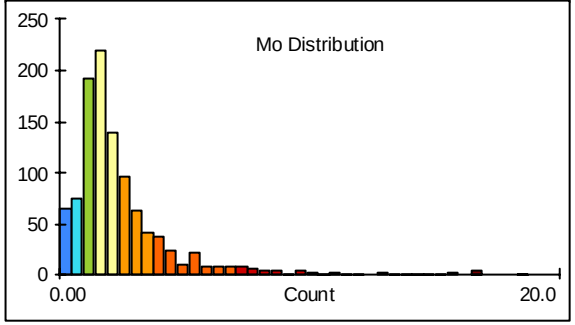
Combined Rural and Urban Profile (0.45m) Soil Data - Molybdenum



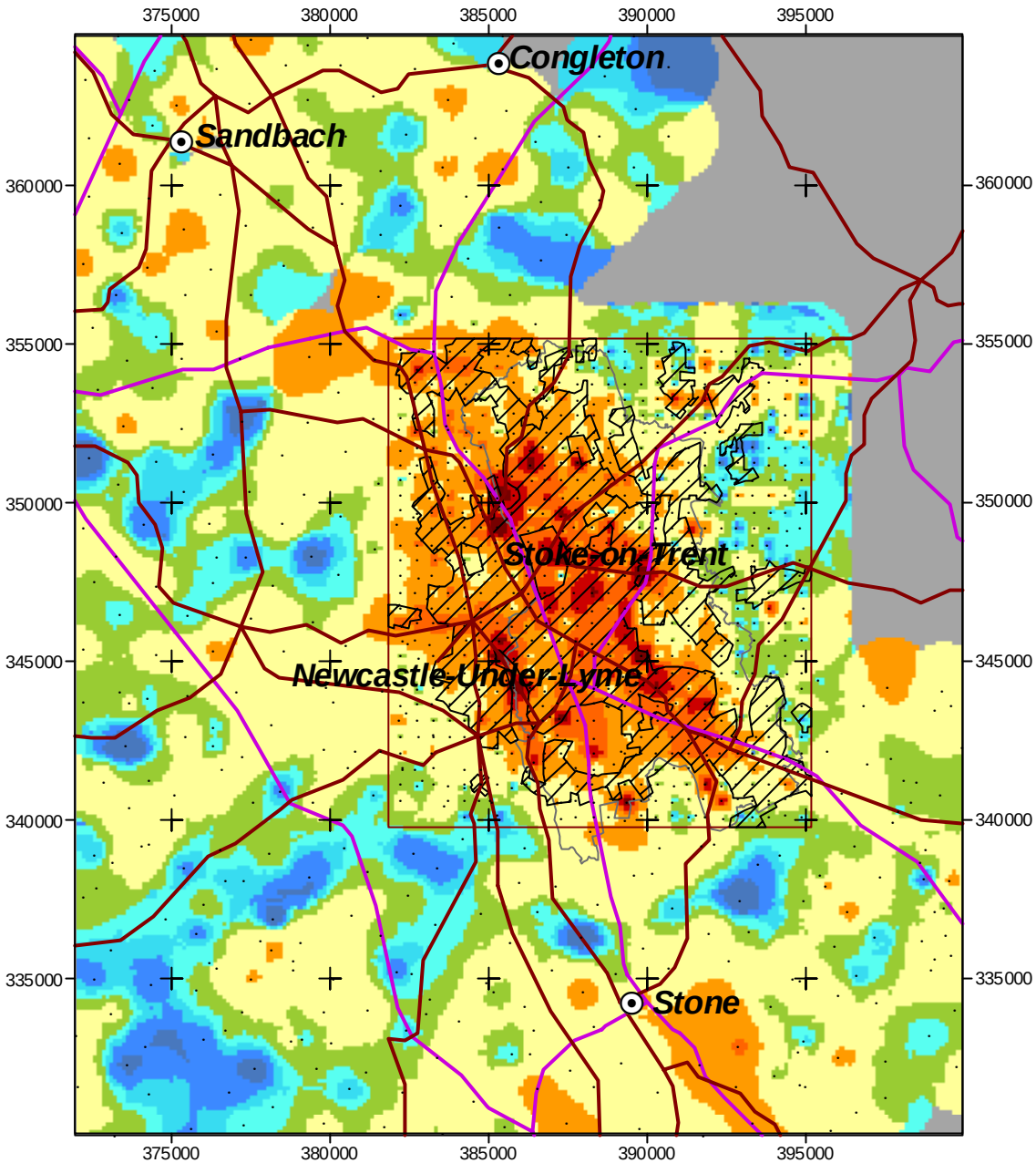
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Mo Concentration (ppm) mg/kg

69.1	(100%ile)
18.2	(99%ile)
8.7	(95%ile)
5.8	(90%ile)
3.3	(75%ile)
2.1	(50%ile)
1.5	(25%ile)
1.2	(15%ile)
1.0	(10%ile)
0.6	(5%ile)
0.2	(0%ile)
No Data	



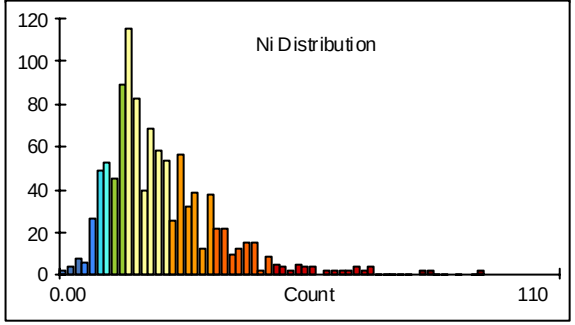
Combined Rural and Urban Profile (0.45m) Soil Data - Nickel



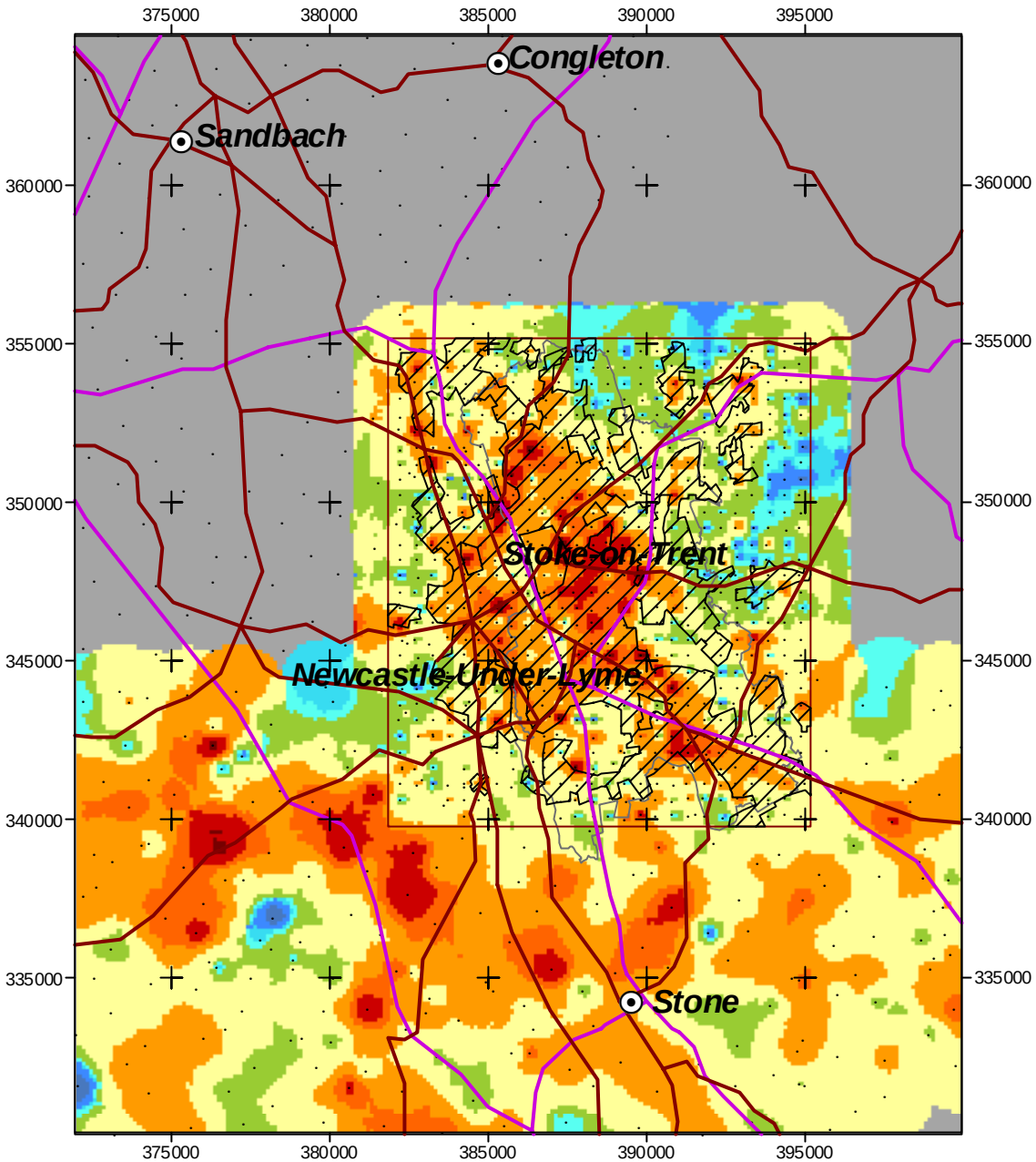
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Ni Concentration (ppm) mg/kg

250	(100%ile)
104	(99%ile)
61	(95%ile)
49	(90%ile)
36	(75%ile)
26	(50%ile)
20	(25%ile)
18	(15%ile)
16	(10%ile)
14	(5%ile)
5	(0%ile)
No Data	



Combined Rural and Urban Profile (0.45m) Soil Data - Phosphorous



Sample Site Locations

Limit of Urban Study Area

Stoke City Boundary

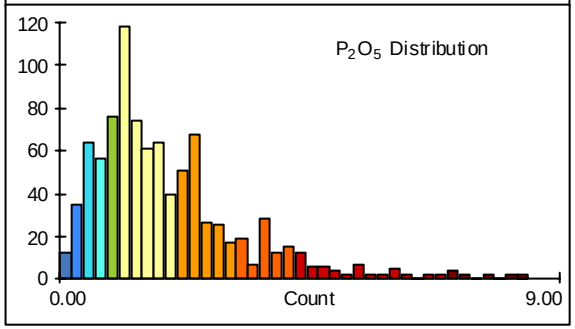
Limits of Urban Areas

Roads

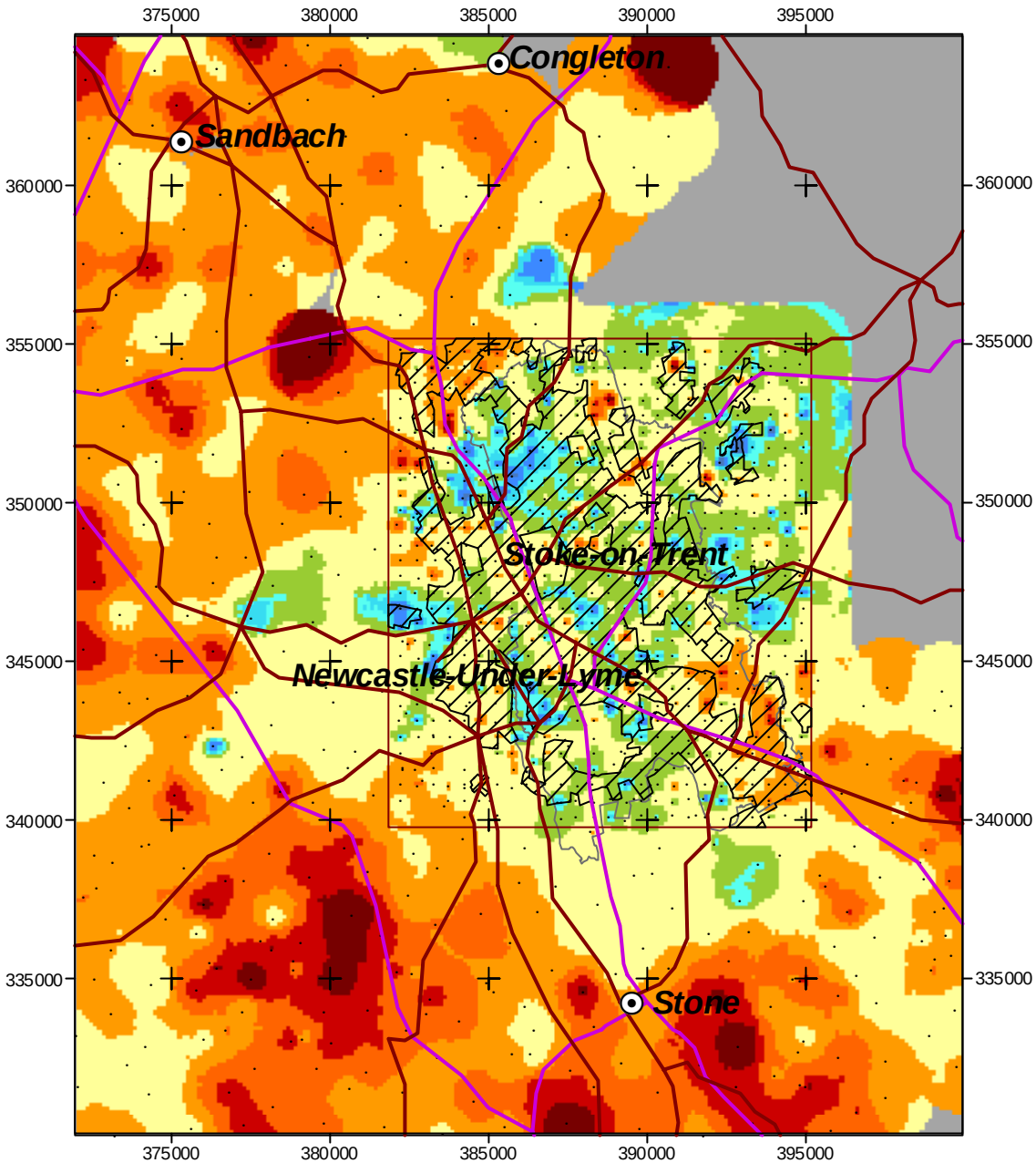
Railways

P_2O_5 Concentration (%)

1.42	(100%ile)
0.87	(99%ile)
0.57	(95%ile)
0.44	(90%ile)
0.29	(75%ile)
0.20	(50%ile)
0.13	(25%ile)
0.11	(15%ile)
0.09	(10%ile)
0.08	(5%ile)
0.03	(0%ile)
No Data	



Combined Rural and Urban Profile (0.45m) Soil Data - Potassium Oxide



Sample Site Locations

Limit of Urban Study Area

Stoke City Boundary

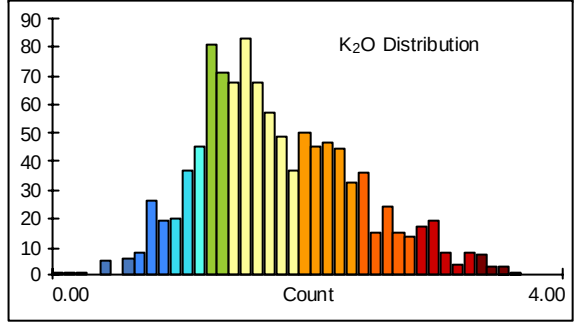
Limits of Urban Areas

Roads

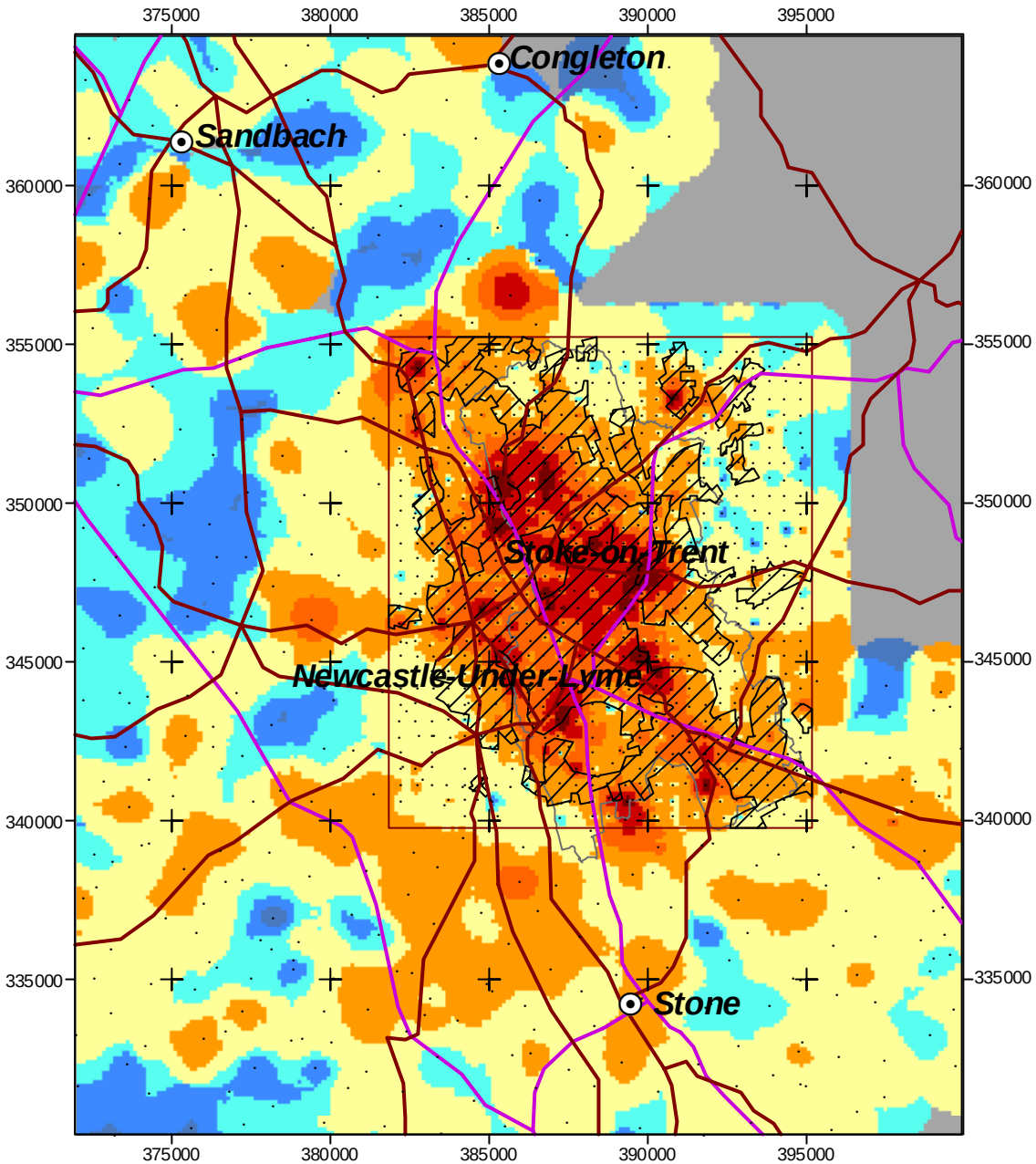
Railways

K_2O Concentration (%)

5.74	(100%ile)
3.88	(99%ile)
3.32	(95%ile)
3.02	(90%ile)
2.55	(75%ile)
2.04	(50%ile)
1.70	(25%ile)
1.58	(15%ile)
1.46	(10%ile)
1.27	(5%ile)
0.42	(0%ile)
No Data	



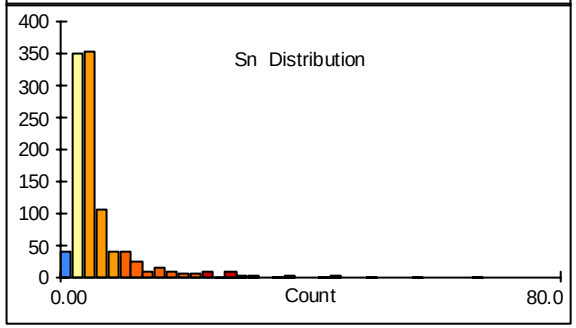
Combined Rural and Urban Profile (0.45m) Soil Data - Tin



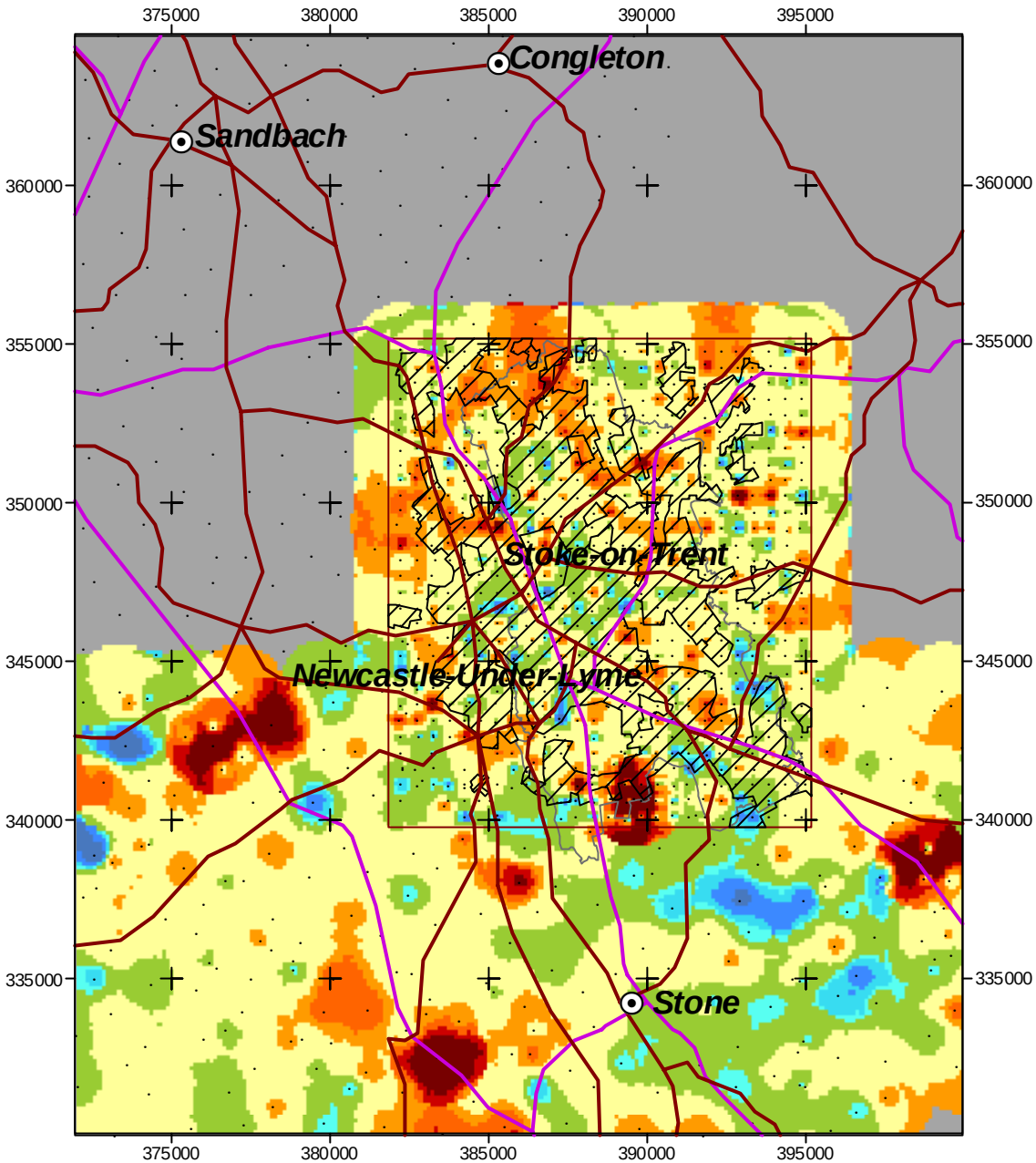
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

Sn Concentration (ppm)mg/kg

657.0	(100%ile)
131.0	(99%ile)
31.0	(95%ile)
17.0	(90%ile)
8.0	(75%ile)
5.0	(50%ile)
4.0	(15%ile)
3.0	(5%ile)
1.0	(0%ile)
No Data	



Combined Rural and Urban Profile (0.45m) Soil Data - Uranium



Sample Site Locations

Limit of Urban Study Area

Stoke City Boundary

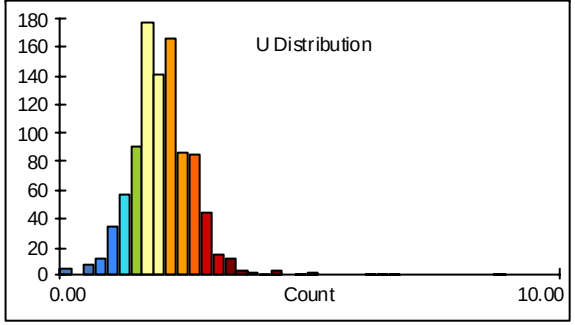
Limits of Urban Areas

Roads

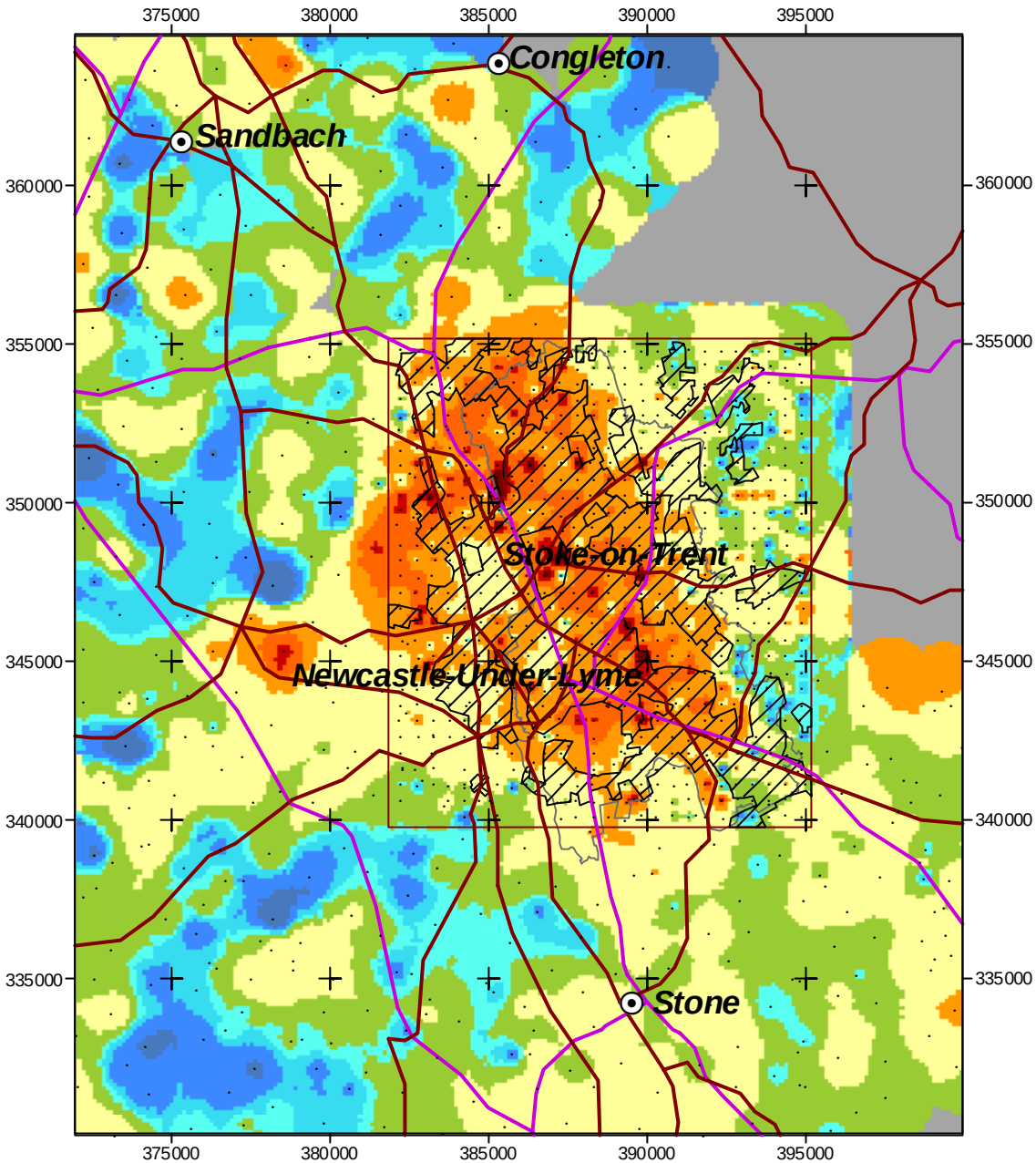
Railways

U Concentration (ppm) mg/kg

44.5	(100%ile)
4.8	(99%ile)
3.4	(95%ile)
3.2	(90%ile)
2.8	(75%ile)
2.4	(50%ile)
2.0	(25%ile)
1.8	(15%ile)
1.7	(10%ile)
1.5	(5%ile)
0.3	(0%ile)
No Data	



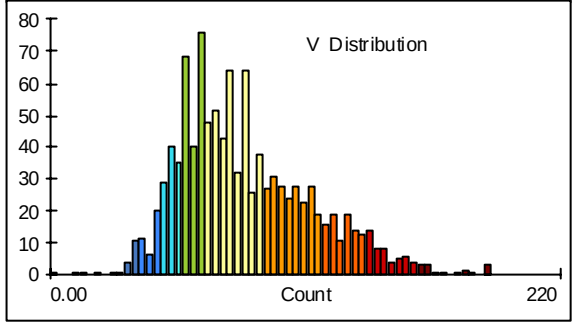
Combined Rural and Urban Profile (0.45m) Soil Data - Vanadium



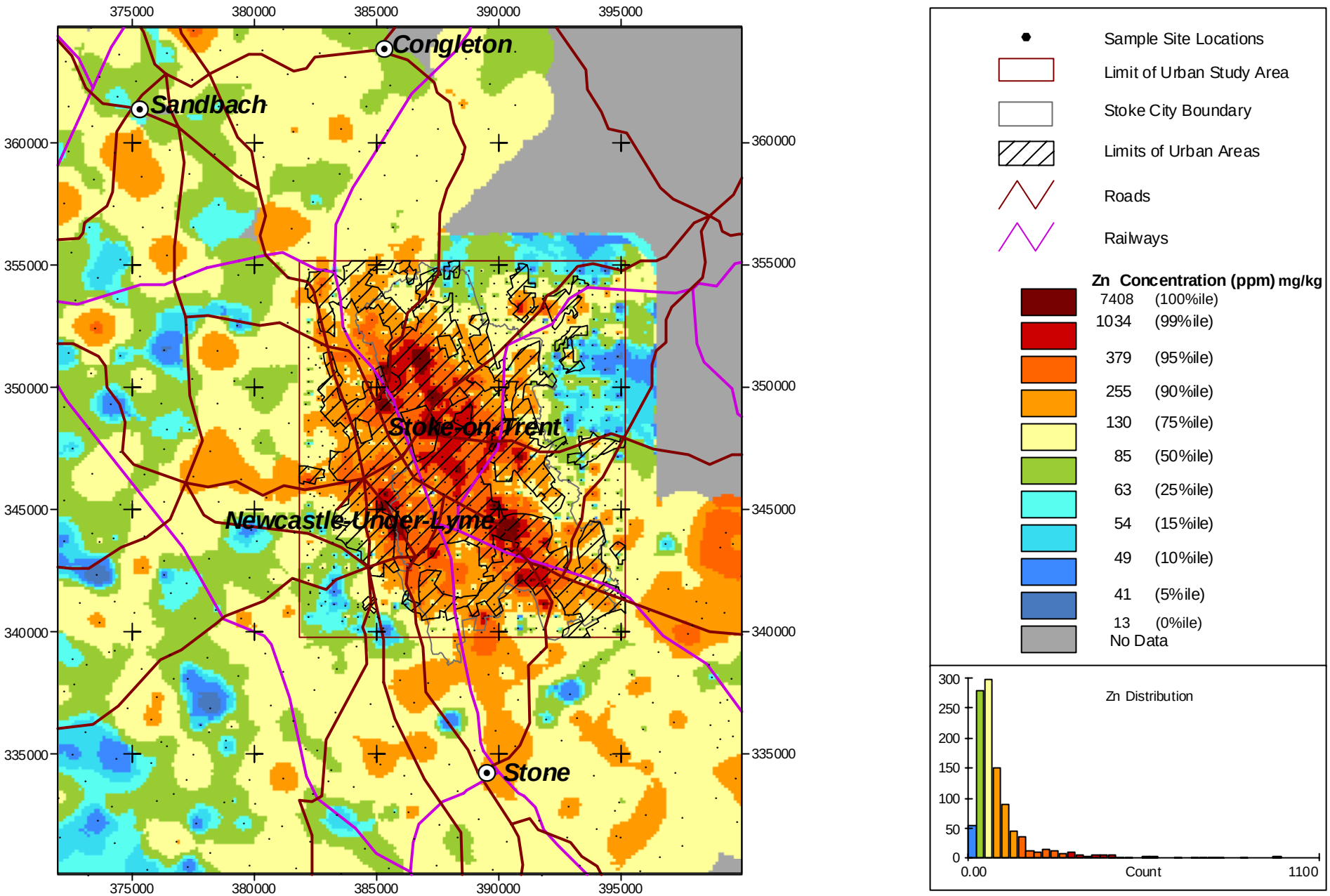
Sample Site Locations
Limit of Urban Study Area
Stoke City Boundary
Limits of Urban Areas
Roads
Railways

V Concentration (ppm) mg/kg

296	(100%ile)
213	(99%ile)
165	(95%ile)
153	(90%ile)
125	(75%ile)
97	(50%ile)
80	(25%ile)
73	(15%ile)
68	(10%ile)
63	(5%ile)
11	(0%ile)
No Data	

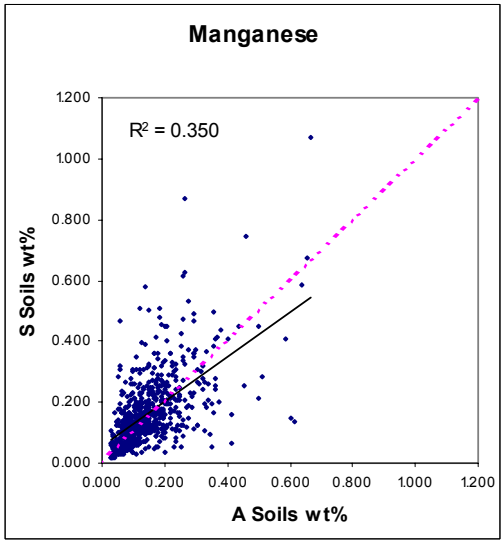


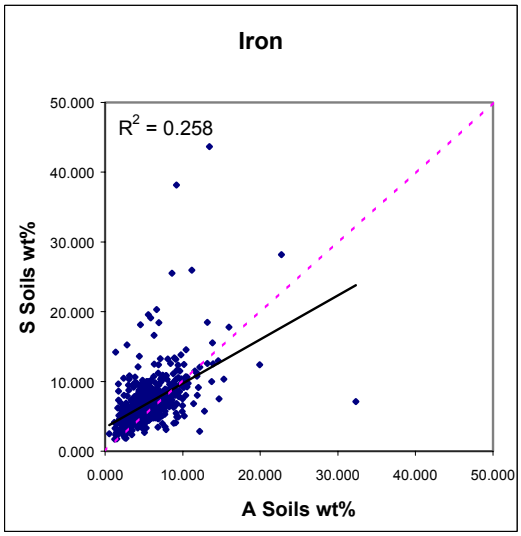
Combined Rural and Urban Profile (0.45m) Soil Data - Zinc

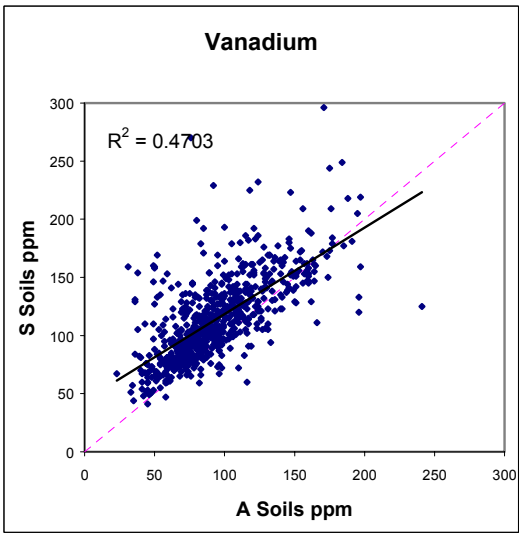


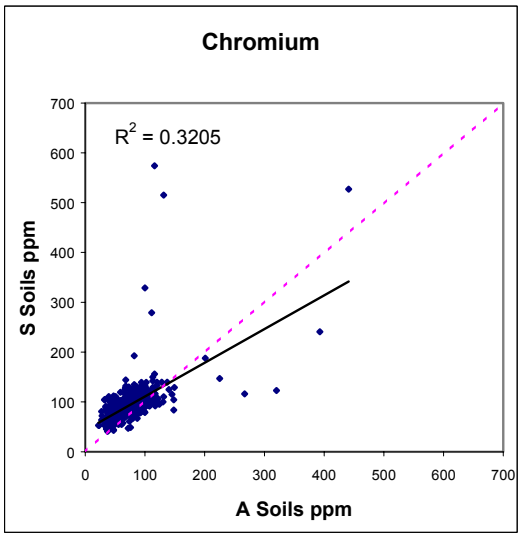
ANNEX 3. PLOTS OF ELEMENT CONCENTRATIONS IN 747 STOKE-ON-TRENT SURFACE (A) VERSUS PROFILE (S) SOILS SHOWING BEST-FIT LINES.

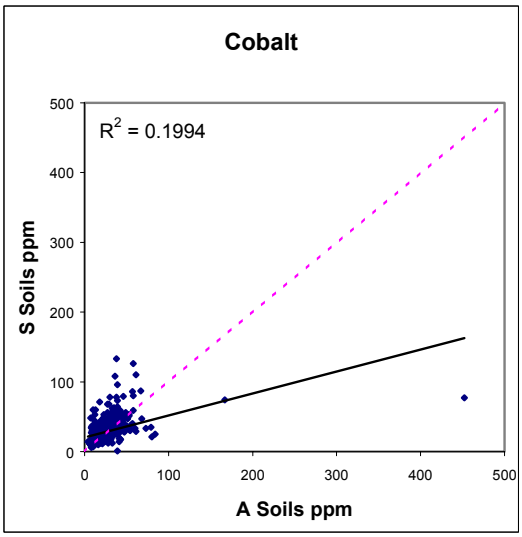
ppm = mg/kg

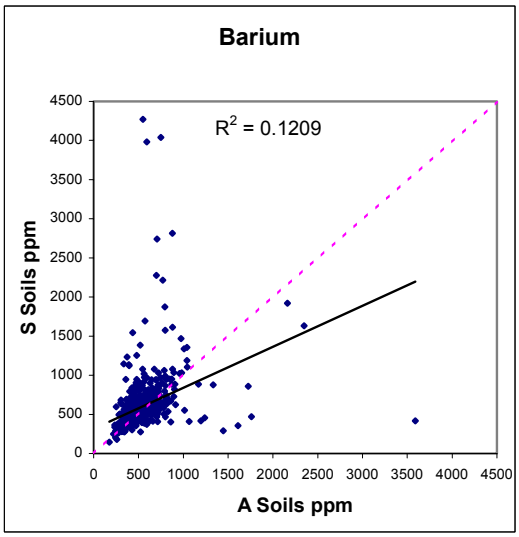


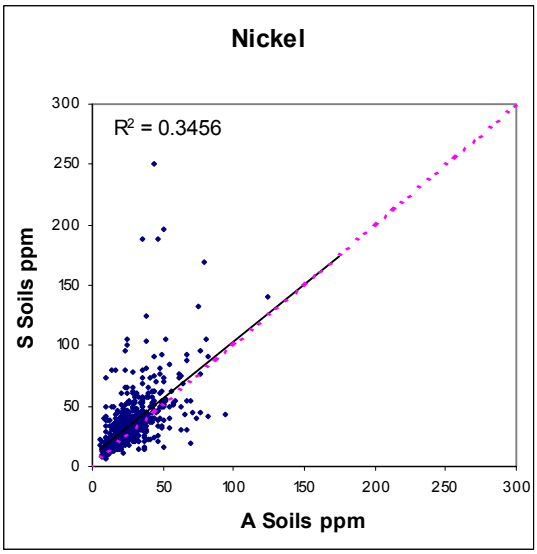


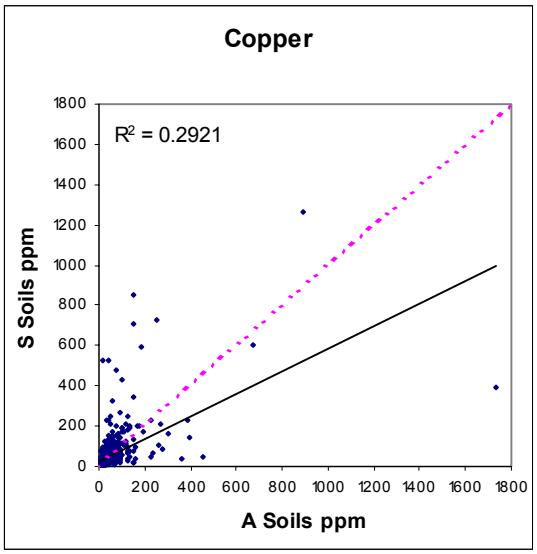


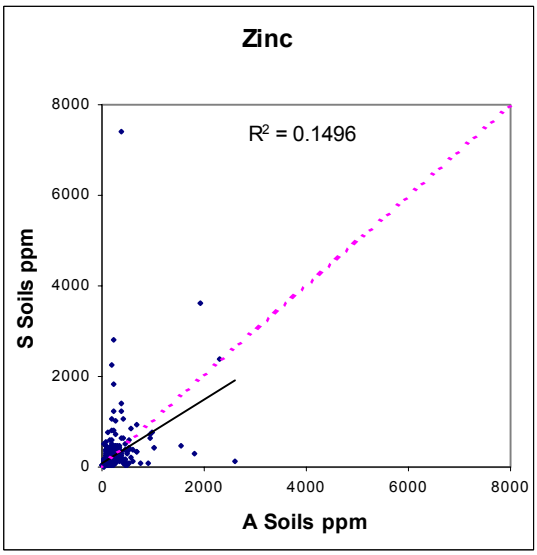


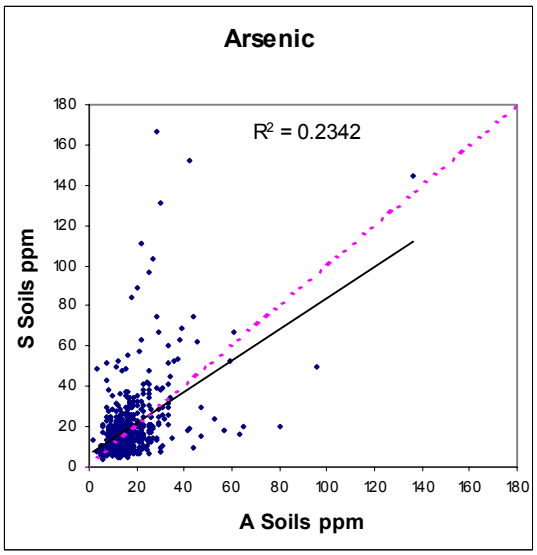


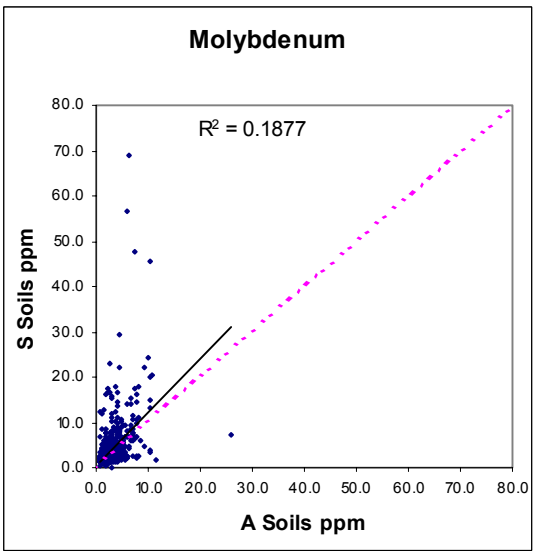


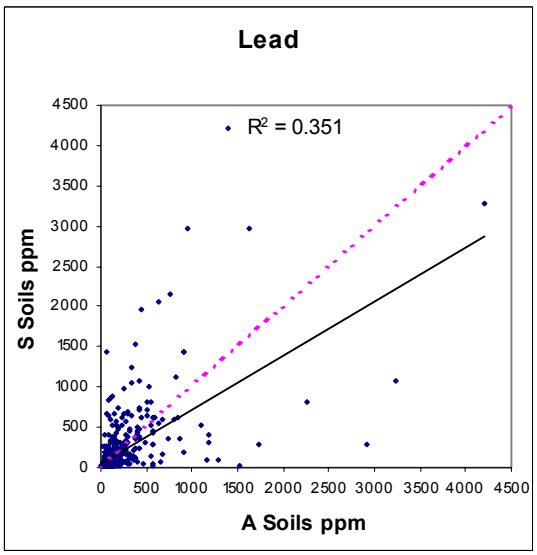

Nickel
R² = 0.3456
S Soils ppm
A Soils ppm
0
50
100
150
200
250
300

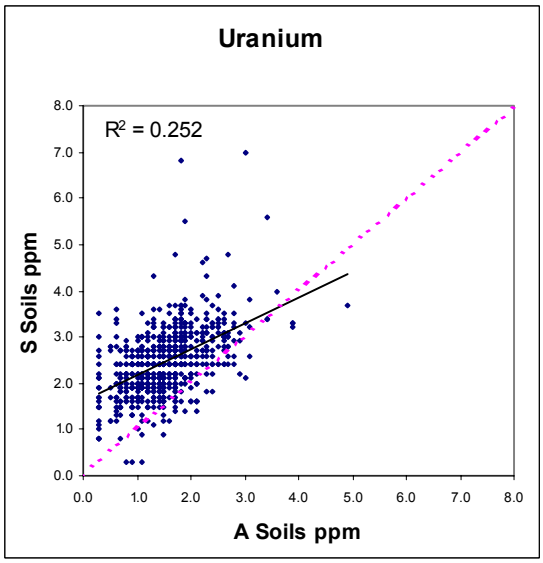

Copper
R² = 0.2921
S Soils ppm
A Soils ppm
0
200
400
600
800
1000
1200
1400
1600
1800

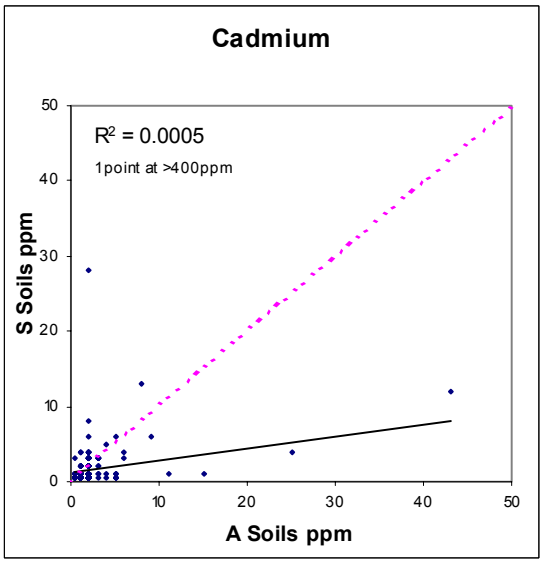

Zinc
R² = 0.1496
S Soils ppm
A Soils ppm
0
2000
4000
6000
8000

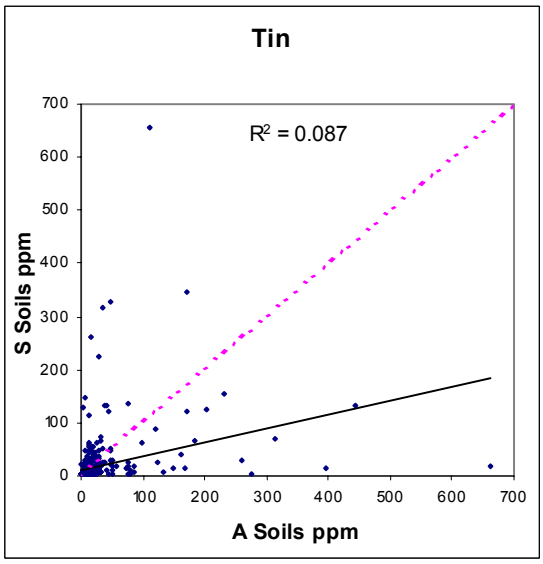

Arsenic
R² = 0.2342
S Soils ppm
A Soils ppm
0
20
40
60
80
100
120
140
160
180

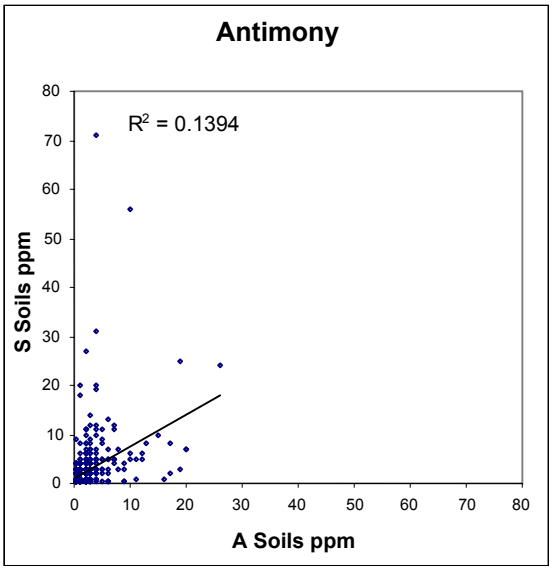

Molybdenum
R² = 0.1877
S Soils ppm
A Soils ppm
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0

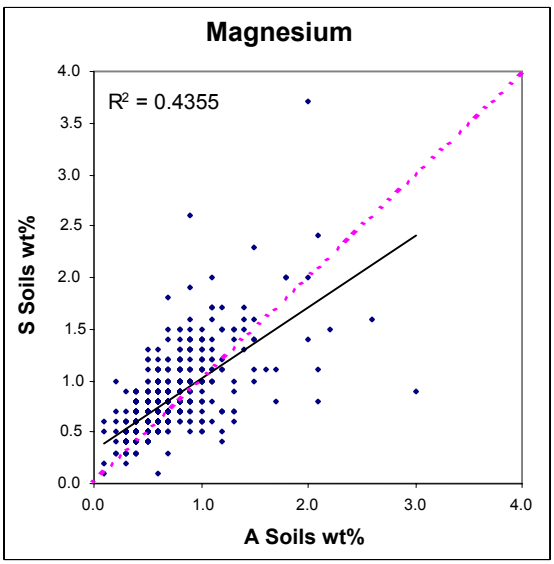

Lead
R² = 0.351
S Soils ppm
A Soils ppm
0
500
1000
1500
2000
2500
3000
3500
4000
4500

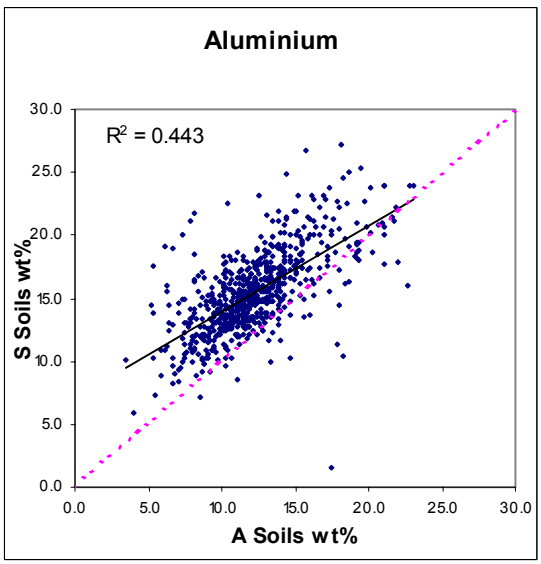

Uranium
R² = 0.252
S Soils ppm
A Soils ppm
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

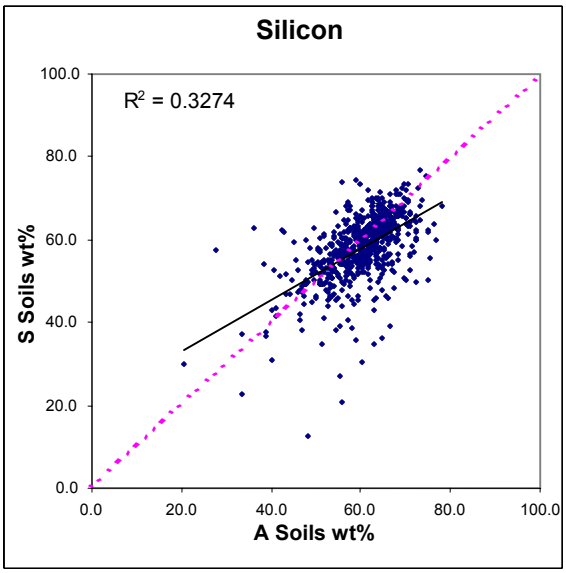

Cadmium
R² = 0.0005
1point at >400ppm
S Soils ppm
A Soils ppm
0
10
20
30
40
50

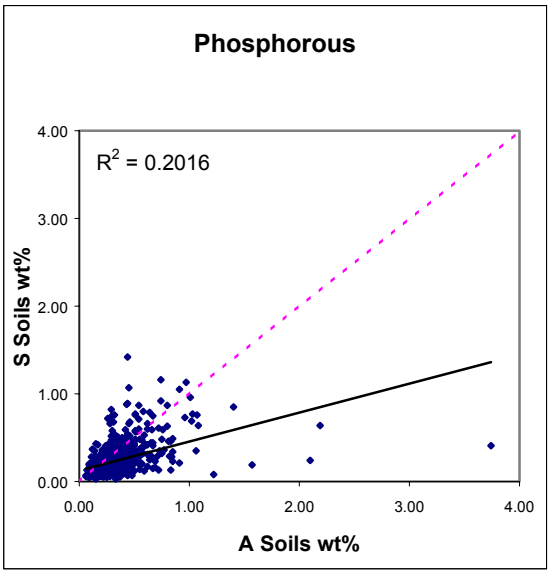

Tin
R² = 0.087
S Soils ppm
A Soils ppm
0
100
200
300
400
500
600
700

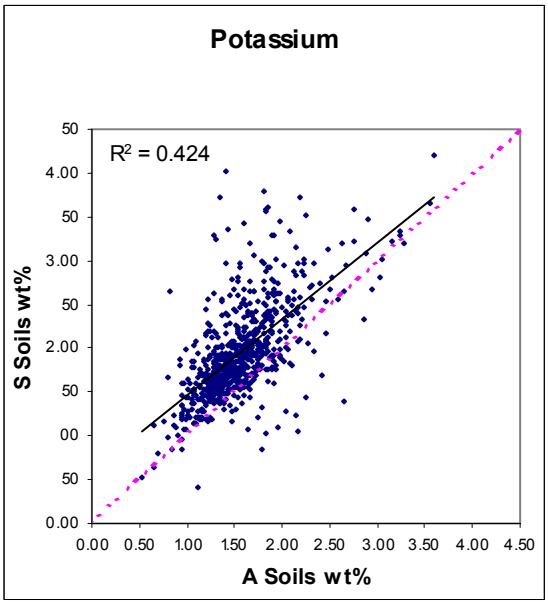

Antimony
R² = 0.1394
S Soils ppm
A Soils ppm
0
10
20
30
40
50
60
70
80

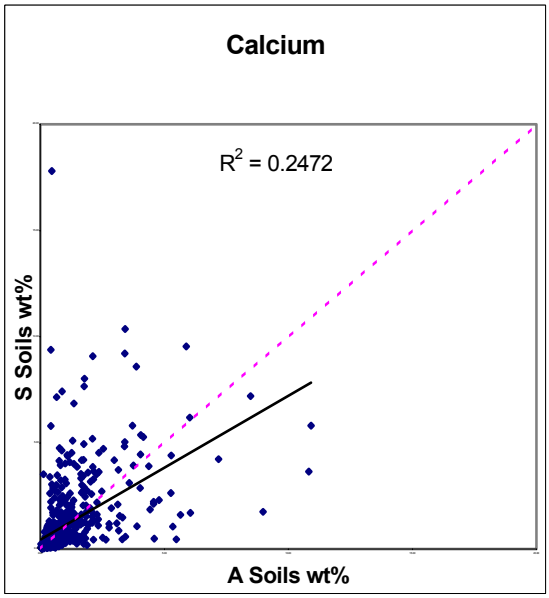

Magnesium
R² = 0.4355
S Soils wt%
A Soils wt%
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0


Aluminium
R² = 0.443
S Soils wt%
A Soils wt%
0.0
5.0
10.0
15.0
20.0
25.0
30.0


Silicon
R2 = 0.3274
S Soils wt%
A Soils wt%
0.0
20.0
40.0
60.0
80.0
100.0


Phosphorous
R2 = 0.2016
S Soils wt%
A Soils wt%
0.00
1.00
2.00
3.00
4.00


Potassium
R2 = 0.424
S Soils wt%
A Soils wt%


Calcium
R2 = 0.2472
S Soils wt%
A Soils wt%