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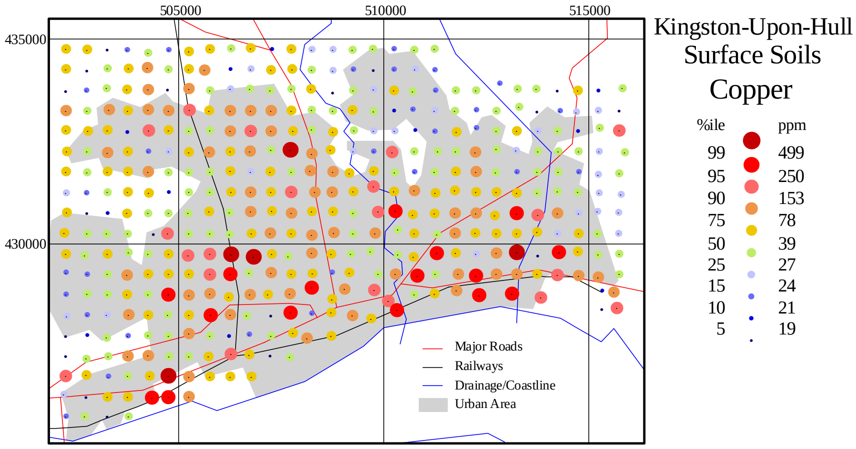
Geochemical baseline data for the urban area of Kingston-upon-Hull

Urban Geoscience and Geological Hazards Programme

Internal Report IR/02/080



BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/02/080

Geochemical baseline data for the urban area of Kingston-upon-Hull

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Front cover

Copper in Kingston-upon Hull surface soils.

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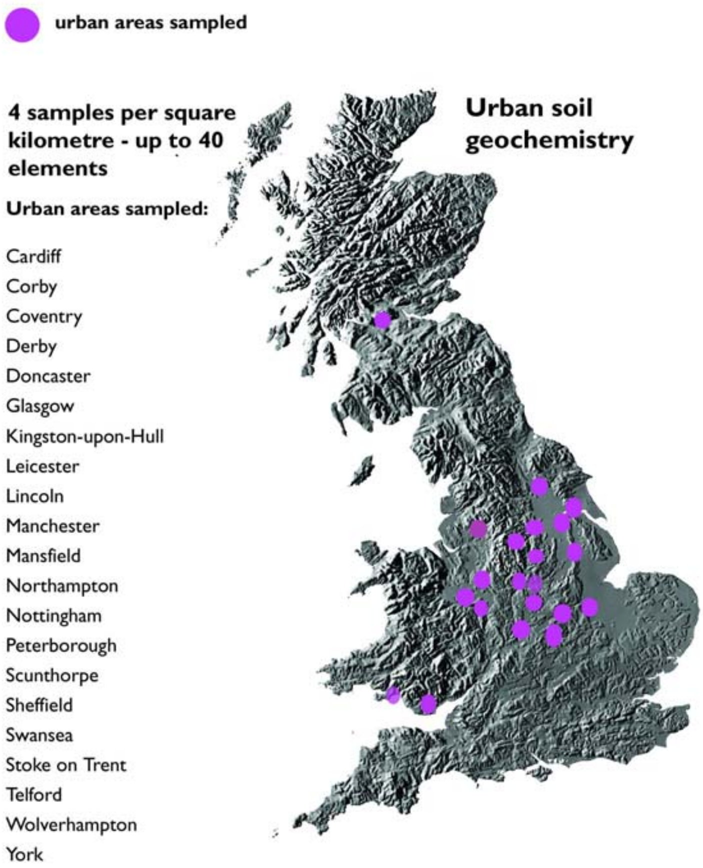
The soil geochemical data presented in this report (and other urban reports from this series) are from individual sites which were sampled as part of a baseline geochemical survey. The results should only be used to set a regional context, not as the basis for interpretations concerning specific sites. Interpretations relating to specific sites should be based on follow-up investigations. The data in this report, in addition to all geochemical data held by BGS, are available under licence. Its use is subject to the terms of a licensing agreement.

Foreword

This report is a product of the British Geological Survey's (BGS) Geochemical Surveys of the Urban Environment (GSUE) project. Work is funded by the Office of Science and Technology and is part of the national Geochemical Baseline Survey of the Environment (G-BASE) project. The report forms part of a series, which seeks to make GSUE urban soil geochemistry data publicly available with a minimum of interpretation, displaying the data as a series of proportional symbol maps.

A number of urban centres have been surveyed using the same soil sampling procedures; the status of completed sampling is indicated by the figure below. Wolverhampton, Manchester and Glasgow have been sampled as part of larger multi-disciplinary projects.



Map showing urban areas that have been soil sampled (end of 2003)

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Summary

This report describes and interprets the results of a systematic urban geochemical baseline survey carried out in the Kingston-upon-Hull area.

The concentrations of trace elements vary widely over different rock types. Baseline geochemical data enables natural concentrations to be determined and these provide a benchmark with which to compare the levels of contaminants in industrialised and urban areas.

Soil samples were taken at a density of four per square kilometre. Sampling was carried out on the least disturbed area of unbuilt ground, such as domestic gardens, allotments, parks or (in the worst instance) road verges or made ground. Details of the sampling and analysis of Hull soils are summarised in Table 1.

Preliminary interpretation of the data can then be carried out and related back to the past and present industrial history of Kingston-upon-Hull. Elevated levels of As, Cu, Sn, Pb, Sb and Zn are identified in the soils of Kingston-upon-Hull, in relation to the surrounding countryside.

Table 1 Summary of Kingston-upon-Hull soil sampling information

Date Sampled:	Summer 1996
Area Sampled:	160 km^2 (min E 500000; max E 517000; min N 424000; and max N 436000)
Number of Samples:	411 surface and 405 profile soils
Elements determined by XRFS: *(elements in italics determined in surface samples only)*	*TiO_2*, Fe_2O_3, MnO, Cr, Mo, Pb, Zn, As, Cd, Cu, Ni, Sb, U, Ba, Co, Sn, V.

1 Introduction

This report summarises the results and methodology of a soil geochemical survey of the urban area of Kingston-upon-Hull, undertaken by the British Geological Survey as part of the Geochemical Surveys of the Urban Environment Project (GSUE), which is funded by the Office of Science and Technology. The project is part of a wider national survey known as the Geochemical Baseline Survey of the Environment Project (G-BASE).

The G-BASE Programme is undertaking a systematic regional geochemical survey of soils, stream sediments and stream waters of the British Isles. The data obtained provide information on the surface chemical environment, which can be used to define the soil geochemical baseline and the extent of surface contamination. The data has a range of applications, including the assessment of risk to human health, with respect to potentially harmful elements through environmental exposure.

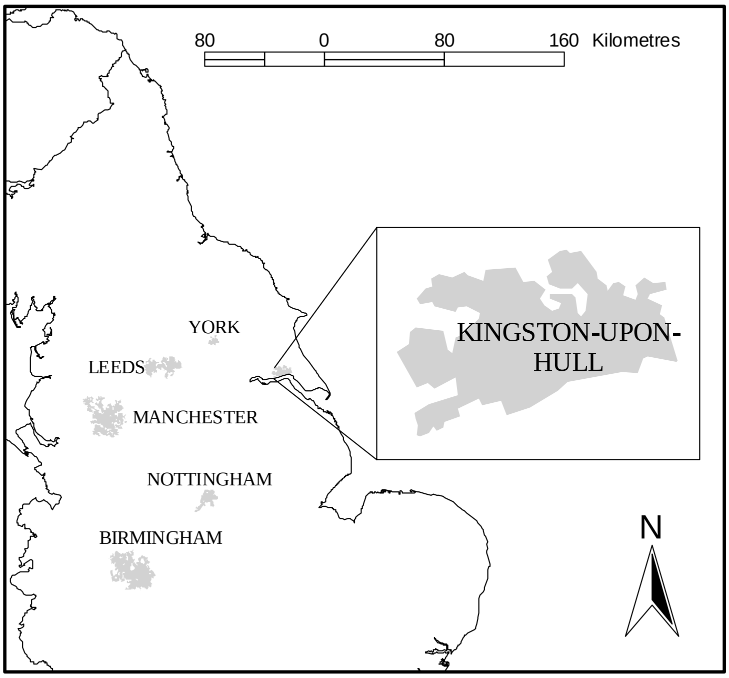

Figure 1 Location map for Kingston-upon-Hull

Kingston-upon-Hull is a port situated on the east coast of England (Figure 1). It has had a varied industrial history, related to steel production, associated metal processing (especially tin, copper and nickel smelting), and chemical manufacture.

The distributions of trace metals in the surface environment of Kingston-upon-Hull are described in this report in the context of present and historical land use. The concentrations of trace metals are also considered in relation to the underlying geology and placed in context with respect to the typical background concentrations obtained from G-BASE regional data sets.

2 Study area

2.1 HISTORICAL LAND USE

Kingston-upon-Hull originated in the 12th century as a port for the wool trade and later for the whaling and fishing industries. In 1794 – 1798 the first artificial dock was dug on the site of the north defences of the old town. Further docks were opened in 1809 and 1829 along the west side of the old town (Allison, 1976). Industry that developed around the port area included oilseed crushing mills, paintworks and corn mills. Two cotton mills were also established in 1836 and 1845. The flat low-lying ground around the area of Kingston-upon-Hull lent itself to rapid Victorian housing development, to the north, east and west of the old city centre (Allison, 1976). It is still a major port today; having a long history of importing and exporting goods, including sand and gravel. The docks are still used as a landing port for marine dredged aggregates, although many of the buildings along the sea front are now derelict. Coal, oil and gas exploration in the area was common for most of the 20th century. Many of the surrounding towns in this area have been large industrial centres for ironstone, aggregates and metal smelting.

A world-leading tin smelter, known as Capper Pass, operated for over fifty years in the town of Melton, North Ferriby, to the west of Kingston-upon-Hull. At Capper Pass, Sn-bearing raw materials brought from around the world were converted into pure Sn and other metals. It should be noted that the smelter did not exploit the natural resources of the area around Kingston-upon-Hull, only imported products. The first blast furnace was commissioned in 1937 and the plant operated until 1991. The original 200 ft high chimney, built in 1938 was replaced in 1971 with a 600 ft high chimney.

From the British Geological Survey Geoscience Data Index[1] it can be seen that Kingston-upon-Hull has a few abandoned and active quarries owned by the local council. There are also many waste disposal sites around the city and its suburbs; many of the sites have the potential to be a risk to ground or surface water.

2.2 AREA SAMPLED

An area of 160 km^2 was surveyed during the summer of 1996, in which a total of 411 sites for surface soils (0-15 cm depth) and 405 sites for profile soils (30-45 cm depth) were sampled (Table 1). This extends from British National Grid (BNG) grid references 500000 m east to 517000 m east and from 424000 m north to 436000 m north, and includes the areas of Kingston-upon-Hull city centre, and Cottingham. The survey area is shown in Figure 2. The shaded urban area represents the boundary between the built up area and open countryside.

[1] http://www.bgs.ac.uk/geoindex

2.3 SOLID AND DRIFT GEOLOGY

Geological information for the Kingston-upon-Hull area was obtained from the BGS memoirs for the area (British Geological Survey, 1992) and BGS 1:50 000 scale DigmapGB data[2]. The area sampled is almost entirely underlain by Upper Cretaceous Chalk, of the Flamborough, Burnham, Welton and Ferriby Formations. The succession generally increases in age towards the west (younging direction towards the east), with a small outcrop of Jurassic mudstone from the Ancholme Group present in the southwest of the sampling area.

Quaternary deposits underlie over 90 % of Kingston-upon-Hull, and are comprised predominantly of alluvium, glaciofluvial deposits (sand and gravel) and Diamicton till. Around the Humber Estuary, tidal flat deposits are common, being composed of clay, silt and sand. The drift and solid geology can be seen on Figure 4 and Figure 5 respectively.

[2] Ew072_Beverley; Ew080_Hull; Ew081_Patrington; Ew082_Spurn. Drift and solid geology.

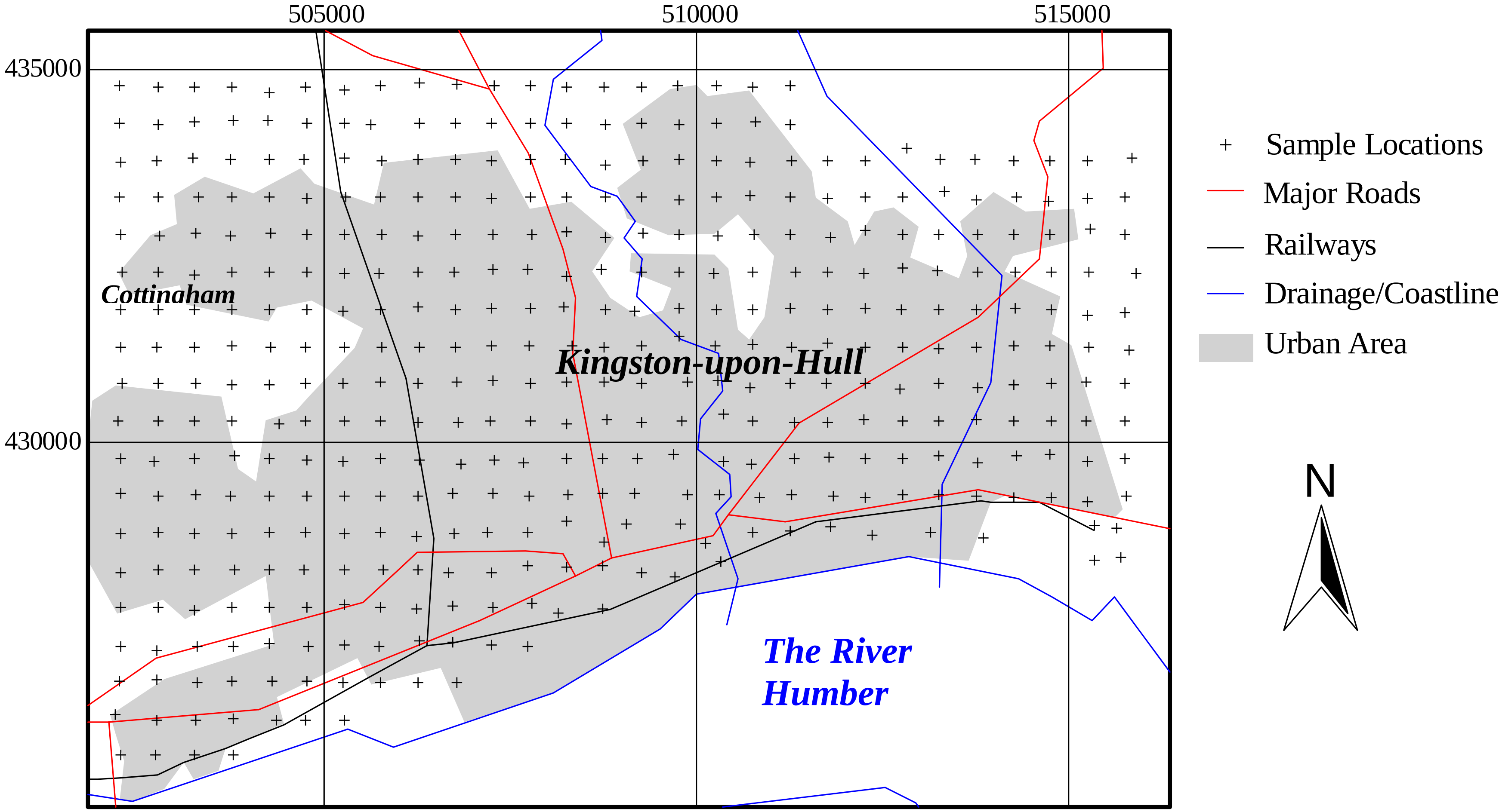

Figure 2 Map of Kingston-upon-Hull sampling area (Grid squares shown at 5 km intervals)

Figure 3 Topographical map of sampling area

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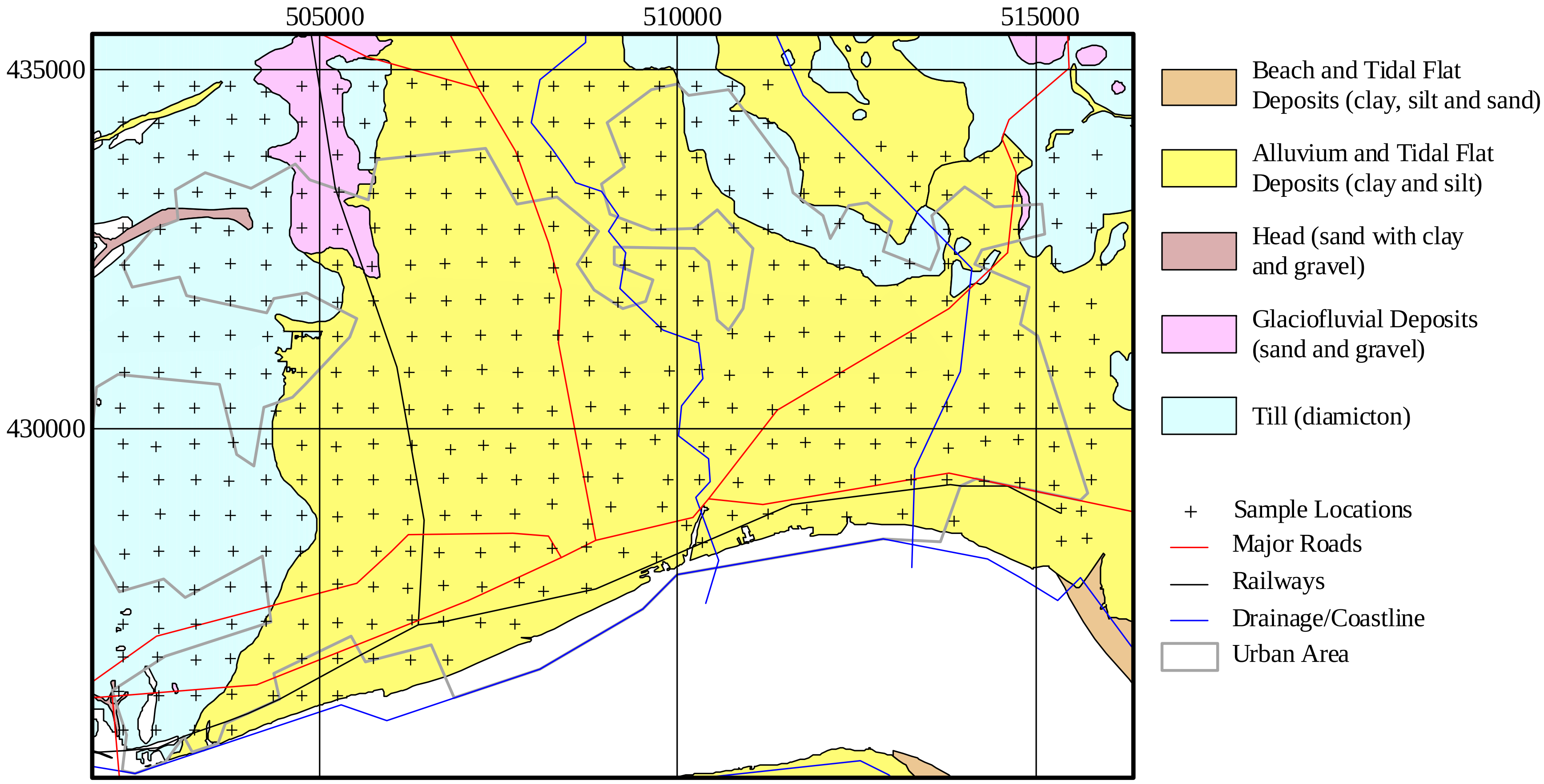

Figure 4 Drift cover of Kingston-upon-Hull and surrounding area (Grid squares shown at 5 km intervals)

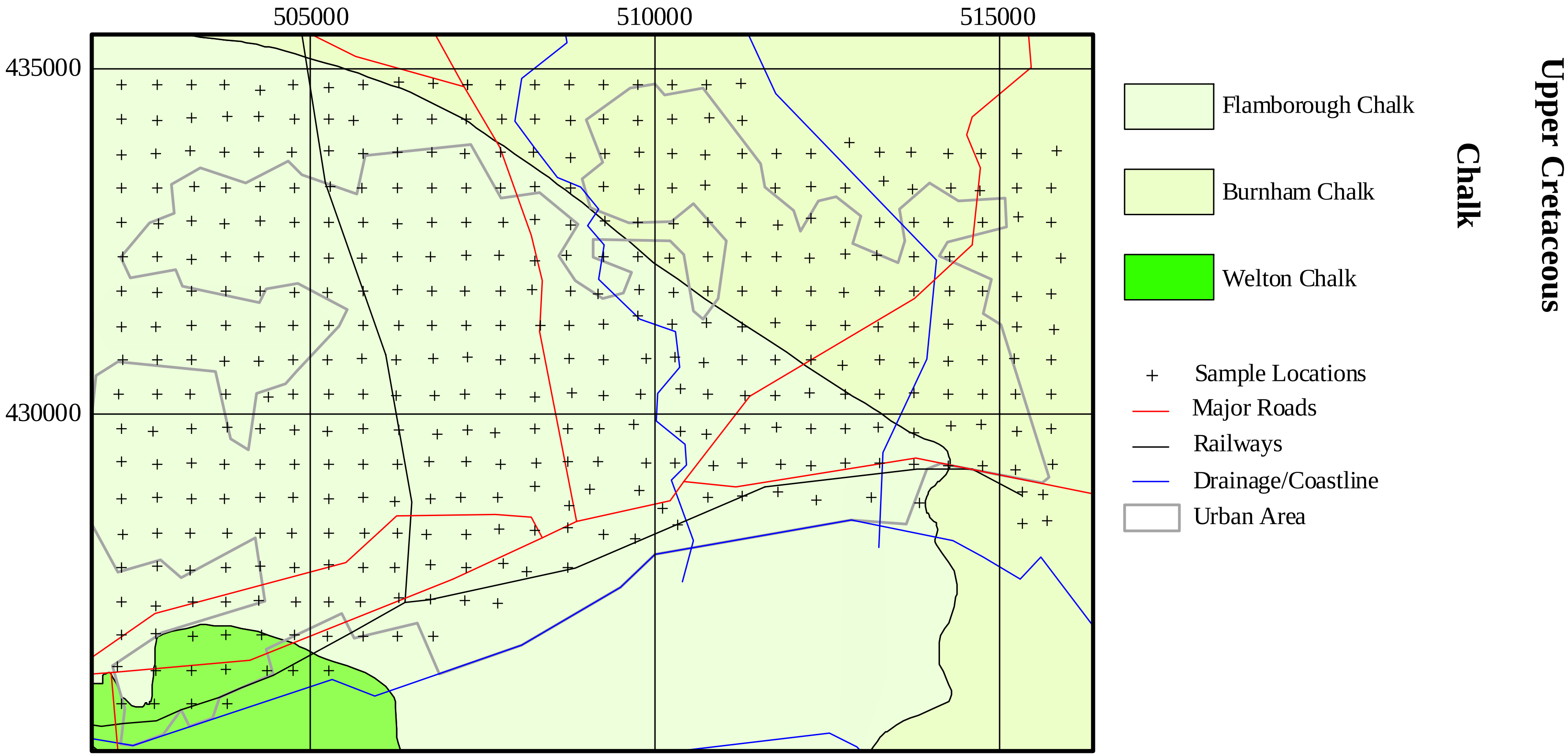

Figure 5 Underlying solid geology of Kingston-upon-Hull and surrounding area (Grid squares shown at 5 km intervals)

2.4 SOIL TYPE

Urban and industrial areas have not been surveyed for soil type by the National Soil Resources Institute (formally the Soil Survey of England and Wales). No information therefore exists on soil type for the main city area of Kingston-upon-Hull, although limited data is available for the outskirts of the urban area. This was obtained from a map of the Soils of Northern England (Soil Survey of England and Wales, 1983).

Basic information for the urban soils of Kingston-upon-Hull is available from the G-BASE field cards (see Appendix A), which are filled in "on-site" during sampling. These contain data such as soil colour, texture, sample depth, clasts that are contained in the soil, as well as land use and any physical contamination that is observed. The field codes used were extracted from Harris and Coats (1992).

The area around Kingston-upon-Hull is characterised by stony, silty or clay loams, belonging to the Brown Calcareous Earth soil classification. These are characterised by fine silty material overlying lithoskeletal chalk, usually occurring in well-drained areas.

3 Methodology

3.1 SOIL SAMPLING

Sample sites were arranged on a regular grid pattern at a density of 4 samples per km^2. Sample spacing was kept as regular as possible, namely 500 m apart, but was constrained by the actual conditions that were encountered on the ground (such as buildings and other constructions). Soil samples were collected from the closest open area to the allocated sample point, using the least disturbed area of unbuilt ground, such as domestic gardens, allotments, parks or (in the worst instance) road verges or made ground. In urban areas it is often difficult to find sample sites that obey this ideal, but wherever possible samples were taken so as to preserve as near as possible the regular sampling grid.

Soil samples were collected using a Dutch style hand auger with a 3 cm bore. Two samples were collected at different depths at each site. Surface samples were labelled A and were collected from a depth of 0-15 cm. They were made up of a three point composite sample based on a 2 x 2 m square. The deeper "profile" samples were labelled S and collected at a standard depth of 30-45 cm. These were composed of 3 sub-samples from the same 2 x 2 m square as the A sample. Duplicate sampling is described in section 3.3.2.

Information from the field cards is entered onto an Access database and sample positions recorded onto a stable base and archived. This data is then stored in the corporate geochemical database (Harris and Coats, 1992).

3.2 SAMPLE PREPARATION

Samples were dried in an oven at temperatures below 20 ºC and then sieved. Surface soils were sieved to obtain the <2 mm fraction and profile soils to obtain the <150 µm fraction. The sieved material was coned and quartered and a split of the sample was ground using an agate ball mill until 95 % reached a grain size finer than 53 µm. A 12 g split of the ground material was combined with 3 g of elvacite binder and pressed into a pellet for analysis by X-Ray Fluorescence Spectrometry analysis (XRFS) (see section 3.4).

Excess sieved and ground sample material is retained in the National Geoscience Records Centre sample store at the BGS.

3.3 ERROR CONTROL PROCEDURES

The accuracy and precision of the geochemical data was monitored using the methods of Plant et al (1975), which are briefly described below.

3.3.1 Random numbering of samples

Samples were allocated numbers according to a random numbering system (Plant, 1973), but were analysed in numerical order. This allows any systematic error in either sampling or analytical methodologies to be identified and attributed to the appropriate process. At each site the A and the S samples were assigned unique numbers according to the random number lists. Therefore within each batch of one hundred samples there were 50 A and 50 S samples.

3.3.2 Duplicate and sub-samples

Within each batch of one hundred samples, a pair of sample numbers were assigned to a sampling duplicate, resulting in a duplicate pair for both A and S samples. Duplicate samples were collected using identical sampling methodology adjacent to the original sample. At the sample preparation stage each of the duplicate samples were split to obtain a sub-sample. Each sub-sample was assigned a different number and treated as a separate sample for analytical purposes.

The collection of duplicate samples enables the sampling error, or sampling variation, to be estimated, thus providing a measure of the between-sample variance. Sub-sampling allows the analytical error or variance to be estimated. The variation in the results between original and sub-sample gives an indication of the variation introduced by sample preparation and analysis.

The components of variance were estimated using analysis of variance (ANOVA). This statistical technique is used to determine the residual variance (introduced by sub-sampling, sample preparation and chemical analysis); the between-sample variance (attributed to within-site variation and variability introduced during sample collection); and between-site variance (representing the natural variation in element concentrations across the survey area). All of the analyses form part of a single randomised dataset and a random nested model of ANOVA was therefore used (Snedecor and Cochran, 1989). Due to the relatively low number of duplicate samples collected in a single urban area, the ANOVA calculations were performed using replicate soils collected from 11 different urban centres: Cardiff, Swansea, Stoke, Telford, York, Hull, Doncaster, Mansfield, Scunthorpe, Lincoln and Sheffield (Lister, 2002, In prep.). A total of 50 replicate sets were measured for urban profile soils, while up to 37 were measured for urban surface soils. All elements except Cd and U (both horizons) and TiO_2 (surface soils) were log transformed to produce a distribution approaching the required Gaussian. The ANOVA calculations were performed using the NESTED procedure from the statistical software package, MINITAB^{TM}. The results of the ANOVA indicate that for most elements the between-site variability is greater than 80% of the total variance (Table 2). This suggests that geochemical variation is the principal control over element concentrations in urban areas. The between-site variance of cadmium is significantly lower than the other elements, with nearly half the variation in the surface soils attributed to residual factors. This is an indication of analytical error, most likely to result from low overall concentrations with respect to the detection limit.

3.3.3 Standards

G-BASE internal reference standards were analysed within each batch of field samples in order to monitor analytical instrument performance, and to provide continuity of data between different analytical campaigns. Internal standards were assigned unique sample ID's and inserted into each batch of field samples. In the case of Hull, G-BASE internal reference standards S13, S15 and S24 were inserted during analysis of surface (A) and profile (S) soil samples. The reference standards S13 and S24 were inserted into both the surface and profile soil batches three times, while S15 was inserted four times.

The inclusion of G-BASE internal reference standards throughout all G-BASE and GSUE projects maintains data integrity between such projects. Kingston-upon-Hull lies within the Humber-Trent regional atlas area, and it is therefore essential that data for the urban centre of Hull is compatible with that of the surrounding regional dataset, which consists of the XRFS analyses of approximately 7000 soil sample sites (British Geological Survey, In Prep). A number of G-BASE standards were routinely analysed throughout the entire duration of analysis of samples from the Humber-Trent area. Mean element concentrations determined for standards S13, S15 and S24 during analysis of Hull urban samples may be compared with those generated for the same standards during analysis of the Humber-Trent regional samples (Table 3).

Where values differed significantly, conditioning of the data was carried out. Simple X-Y plots and regression calculations were generated in Excel in order to carry out this task.

Table 2 Percentage of variance in surface and profile soils attributable to between-site, between sample and residual variance.

Surface Soils	Variance				Profile Soils	Variance			
Element	Number of Replicate Sets	Between Site (%)	Between Sample (%)	Residual (%)	Element	Number of Replicate Sets	Between Site (%)	Between Sample (%)	Residual (%)
Sb	16	88.03	1.15	10.82	Sb	50	87.68	3.05	9.27
As	37	97.69	2.02	0.29	As	50	97.87	1.82	0.31
Ba	37	97.63	1.79	0.58	Ba	50	97.39	2.56	0.05
Cd	27	47.88	6.77	45.35	Cd	50	65.44	3.95	30.61
Cr	37	94.14	3.07	2.79	Cr	50	93.46	5.55	0.99
Co	37	96.35	0.00	3.65	Co	50	94.00	5.62	0.38
Cu	37	97.63	1.66	0.72	Cu	50	98.87	1.08	0.06
Fe_2O_3	37	97.69	2.06	0.25	Fe_2O_3	50	96.62	3.36	0.01
Pb	27	97.48	2.23	0.29	Pb	50	96.51	3.43	0.06
MnO	37	98.28	1.39	0.33	MnO	50	96.03	3.92	0.05
Mo	33	94.24	0.71	5.05	Mo	50	93.59	3.23	3.17
Ni	37	98.06	1.59	0.34	Ni	50	95.96	3.83	0.21
Sn	36	93.45	2.91	3.63	Sn	50	95.77	2.42	1.81
TiO_2	37	96.58	2.65	0.77	TiO_2	-	-	-	-
U	37	85.95	1.24	12.81	U	47	76.92	10.99	12.09
V	37	97.89	1.79	0.32	V	50	97.85	2.09	0.06
Zn	37	94.77	5.16	0.07	Zn	50	92.64	7.34	0.02

Table 3 Mean G-BASE bulk sediment standard values.

Sample Type Standard ID	Humber Trent S13	Hull A S13	Hull S S13	Humber Trent S15	Hull A S15	Hull S S15	Humber Trent S24	Hull A S24	Hull S S24
Cd	<1	<1	1	<1	<1	2	3	<1	2
Sn	3	2	2	5	4	3	6	6	5
Sb	<1	<1	<1	1.1	<1	0.3	7.9	6.7	7.7
TiO_2	0.817	0.876	-	0.392	0.427	-	1.122	1.224	-
MnO	0.128	0.105	0.120	0.082	0.060	0.067	0.458	0.426	0.489
Fe_2O_3	6.88	6.91	7.12	1.88	1.93	2.01	10.22	10.27	10.51
V	97	85	93	35	23	31	140	128	138
Cr	98	96	99	41	30	36	123	124	125
Co	29	22	23	9	5	6	97	84	84
Ba	1704	1758	1888	291	385	375	983	1051	1019
Ni	36	34	35	12	10	11	45	43	44
Cu	17	14	15	6	3	4	64	62	63
Zn	113	112	114	30	28	29	387	392	396
As	15	15	15	9	9	9	124	127	129
Mo	1.6	1.3	0.8	0.7	0.4	1.2	1.9	2.0	1.1
Pb	109	108	109	24	25	23	1070	1009	1048
U	2.5	2.6	3.1	1.2	1.4	1.8	1.7	1.7	2.1

3.4 ANALYTICAL PROCEDURES

All samples were analysed at the BGS laboratories for a range of elements by Wavelength Dispersive X-ray Fluorescence Spectrometry (Ingham and Vrebos, 1994). Three sequential XRF spectrometers were used. A Philips PW1480 fitted with a 216 position sample changer and a 3 kW/ 100 kV tungsten anode X-ray tube was used to determine Cd, Sn and Sb. Two Philips PW2400 spectrometers fitted with 102 position sample changers and with 3 kW/ 60 kV rhodium anode x-ray tubes were used to determine TiO_2, MnO, Fe_2O_3, V, Cr, Co, and Ba in one suite and Ni, Cu, Zn, As, Mo, Pb, and U in another. The results for trace elements are reported in parts per million (ppm). One part per million is equivalent to one microgram per gram (µg/g or $\mu g\ g^{-1}$) or one milligram per kilogram (mg/kg or $mg\ kg^{-1}$). Major elements are reported as weight percent of the element in its oxide form (WT % oxide).

The elements determined and the lower limits of detection (LLD) and upper and lower reporting limits (URL and LLR) for each analyte are shown in Table 4.

The quoted LLDs are theoretical values for the concentration equivalent to three standard deviations above the background count rate for the analyte in a pure silica matrix. High instrumental stability results in practical values for these materials approaching the theoretical.

Table 4 Lower limits of detection (LLD) and upper reporting limit (URL) values for XRFS analysis of G-BASE urban soil samples, Humber-Trent region

Analyte	LLD (ppm)	LLD (%)	URL (ppm)	URL (%)
TiO_2*	-	0.01	-	100.0
MnO	-	0.01	-	10.0
Fe_2O_3	-	0.01	-	100.0
V	2.4	-	20000	-
Cr	3	-	250000	-
Co	1.9	-	10000	-
Ni	0.9	-	4000	-
Cu	0.9	-	6500	-
Zn	1	-	10000	-
As	0.9	-	10000	-
Mo	0.3	-	1000	-
Cd	0.9	-	500	-
Sn	1.1	-	10000	-
Sb	1.2	-	10000	-
Ba	2.9	-	600000	-
Pb	1.2	-	10000	-
U	0.5	-	650	-

* A horizon only.

3.5 DATA INTERPRETATION

Once full error control and data quality procedures were completed, the Kingston-upon-Hull geochemical and location data were loaded into an Arcview© GIS software package. Proportional symbol geochemical maps for surface and profile soils were then generated (see Appendix C).

4 Geochemical Interpretation

A total of 17 major and trace elements were measured in the surface soils collected in Kingston-upon-Hull; antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (expressed as Fe_2O_3), lead (Pb), manganese (expressed as MnO), molybdenum (Mo), nickel (Ni), tin (Sn), titanium (expressed as TiO_2), uranium (U), vanadium (V) and zinc (Zn). All elements except TiO_2 were additionally measured in the profile soils.

4.1 GEOCHEMICAL VARIATION WITH DEPTH

In a comparison of surface and profile soils, it should again be noted that during sample preparation the two horizons are sieved to different size fractions. Surface soils are sieved to <2 mm, while profile soils are sieved to <150 µm. The sieved profile soil therefore has a much larger surface area and will contain more clay particles (which possess the ability to attract and bind heavy metal ions (Brady and Weil, 1999)). In an urban area, higher concentrations of elements derived from anthropogenic sources would typically be expected in the surface soils, all other factors being equal; however, due to the analysis of the finer fraction in the profile soils, their element concentrations may naturally be higher than in the surface soils.

In Kingston-upon-Hull, the majority of analytes are present at higher concentrations in the profile soils than in the surface soils, and they also have larger ranges in concentration than the surface soils. This is likely to be related to the difference in size fraction, although there may be other explanations for the higher levels. For example, it is possible that in areas of contamination, fresh topsoil has been brought in for a remediation exercise, resulting in the contaminated soil being buried. Certain soil properties such as pH and redox potential (Eh) can affect the mobility of potentially toxic elements, such as As and Cd. Under appropriate conditions, elements can dissolve into solution and leach downwards, taking elements from the upper A horizon soil and re-precipitating them into the deeper B horizon, or into groundwater in the underlying strata. Leaching may also reach surface waters i.e. rivers. Elements present in higher concentrations within the surface soils of Hull (Sn, Pb, Zn, and Co) are likely to represent the most significant contaminants in this urban area.

4.2 BACKGROUND LEVELS

In order to aid the interpretation of the geochemical data for Kingston-upon-Hull it is useful to be aware of typical background concentrations in the environment in order to put the concentrations seen in Hull into context. This is discussed by Rawlins et al. (2003) for soils in eastern England. The median elemental concentrations for 6561 topsoil samples are shown in Table 5 and the median elemental concentrations for 6877 profile soils are shown in Table 6, these data can be used to give an indication of the typical magnitude of the elemental concentrations throughout the Humber-Trent region (in which Kingston-upon-Hull is located) as a whole (British Geological Survey, In Prep).

Table 5 Comparison of median concentrations in regional surface soil samples, Humber-Trent atlas area and in Kingston-upon-Hull surface soil samples

Analyte	Units	Median Regional	Median Hull
As	ppm	13	20
Ba	ppm	376	448
Cd	ppm	<1	<1
Co	ppm	19	28
Cr	ppm	71	83
Cu	ppm	18	39
Fe_2O_3	wt%	4.66	5.98
MnO	wt%	0.080	0.077
Mo	ppm	2.2	2.7
Ni	ppm	22	34
Pb	ppm	43	116
Sb	ppm	<1	1
Sn	ppm	4	11
TiO_2	wt%	0.680	0.714
U	ppm	2.1	2.0
V	ppm	83	101
Zn	ppm	72	132

Table 6 Comparison of median concentrations in regional profile soil samples, Humber-Trent atlas area and in Kingston-upon-Hull profile soil samples

Analyte	Units	Median Regional	Median Hull
As	ppm	12	20
Ba	ppm	388	453
Cd	ppm	<1	1
Co	ppm	21	25
Cr	ppm	83	97
Cu	ppm	20	31
Fe_2O_3	wt%	5.04	6.30
MnO	wt%	0.104	0.093
Mo	ppm	1.8	2.5
Ni	ppm	27	37
Pb	ppm	38	81
Sb	ppm	3	1
Sn	ppm	4	7
TiO_2	wt%	0.735	-
U	ppm	2.5	2.7
V	ppm	88	109
Zn	ppm	77	117

Almost all the median values for elements in surface and profile soils are higher in Kingston-upon-Hull, than on a regional scale (Tables 5 and 6). The parent materials of the city are comprised of Quaternary drift deposits overlying Chalk (section 2.3). Natural mineralisation is unlikely in this type of geological environment; however, in a coastal or near-coastal setting such as the Humber Estuary, accumulations of major and trace elements in drift deposits and soils are commonly derived from sea-spray. The elevated levels observed across the whole range of elements analysed does nevertheless indicate some level of urban contamination.

4.3 SOIL GEOCHEMISTRY OF KINGSTON-UPON-HULL IN RELATION TO OTHER HUMBER-TRENT URBAN AREAS

The results for selected elements from surface soils in Kingston-upon-Hull are presented in Figure 6 in the context of six other urban areas from the Humber-Trent region (Doncaster, Lincoln, Mansfield, Scunthorpe, Sheffield and York) and the results from the regional survey for the Humber-Trent area. Eight elements that may be affected by anthropogenic contamination in urban areas (As, Cd, Cu, Pb, Mo, Sn, Sb and Zn) were selected, while TiO_2 was included to represent the closest approximation to a conservative element, unaffected by contamination.

While concentrations of TiO_2 are normally distributed in each urban area and fall within the range in concentration found on the regional scale, the levels of the other selected elements are in general positively skewed (indicated by a mean value significantly exceeding the median) and are higher than the regional values. This may reflect the influence of anthropogenic contamination, elevating the concentrations of certain elements above the typical regional levels and generating anomalously high values, which create skewed distributions. In the case of Mo, however, this pattern is only observed in Sheffield.

The main controls over variation in concentrations between different urban areas include population and past and present industrial activities. Recent work carried out by the British Geological Survey (Rawlins et al., 2003) has also identified the importance of parent material type in determining the geochemical composition of soils. This work is, however, largely outside the scope of this report.

Soil Guideline Values (SGV) produced by the Contaminated Land Exposure Assessment (CLEA) model (Department of the Environment Food and Rural Affairs and the Environment Agency, 2002a, b) for residential areas with plant uptake are shown on Figure 6 for Cd and As. The levels of Cd in Hull are particularly low in relation to the regional values and the other urban areas, falling well below the guideline values provided for this element. Concentrations of As are, however, relatively high in Hull, exceeding the 20 ppm guideline value in half the samples analysed. Areas in which soil concentrations exceed 20 ppm may be of concern to human health; however, it should be noted that the regional values indicate high levels of background As in the Humber-Trent region. Although levels of As are significantly higher in Hull than in other urban areas in the region, the results are comparable with Sheffield and Scunthorpe.

Alongside As, Figure 6 demonstrates high levels of Cu, Pb, Zn, Sn and Sb in Hull surface soils, in relation to most other urban centres included and to the regional levels. This may, in part, be related to an emission plume from the Capper Pass tin smelter.

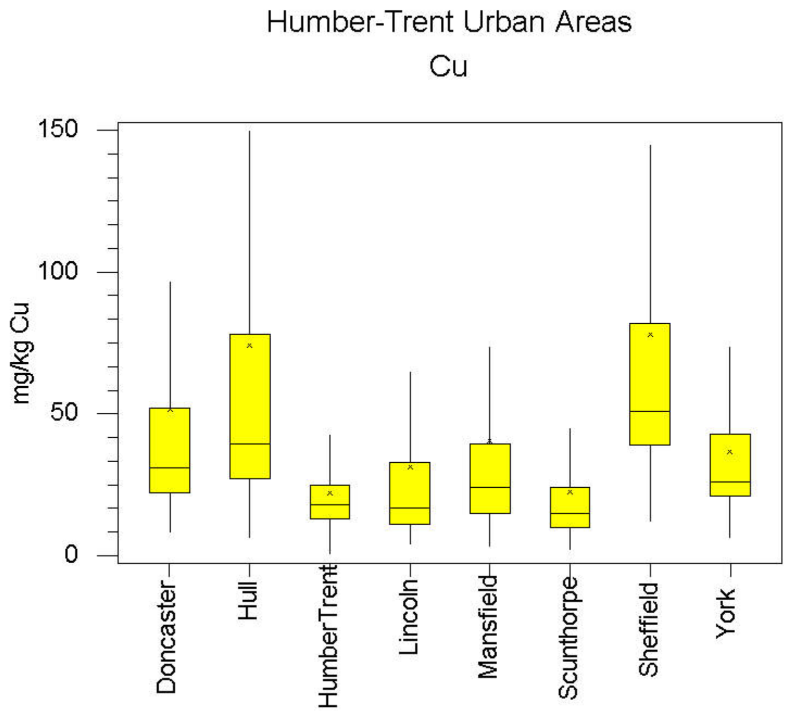

Figure 6: (a) Copper in surface soil

Figure 6 (*(a) - (i)*). Box and Whisker Plots for selected elements in surface soils from six urban areas in the Humber-Trent region presented with the regional Humber-Trent data. Soil Guideline Values (SGVs) for soils in residential areas involving plant uptake (derived using the CLEA model) are shown in red for As and Cd. Note that for Pb (450 mg/kg) and Cd (pH = 8, 8 mg/kg) SGV values are outside plot area (boxes show inter-quartile range, median is a straight line and the mean value a cross)

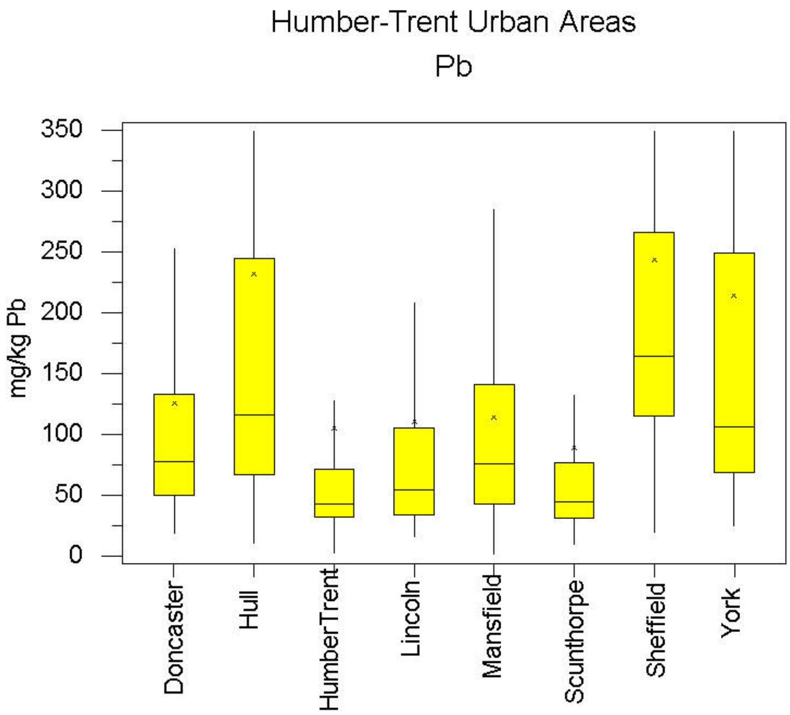

Figure 6: (b) Lead in surface soil

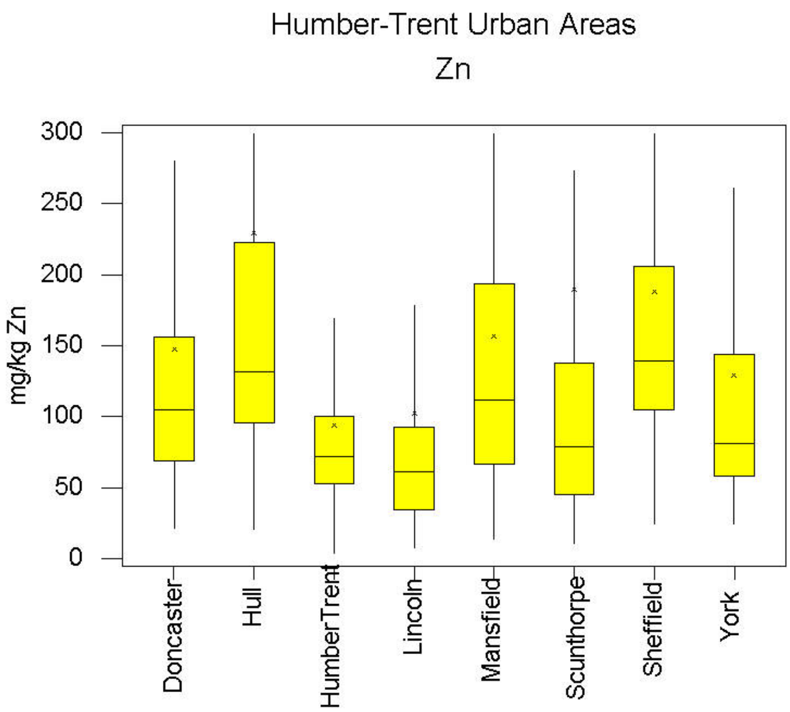

Figure 6: (c) Zinc in surface soil

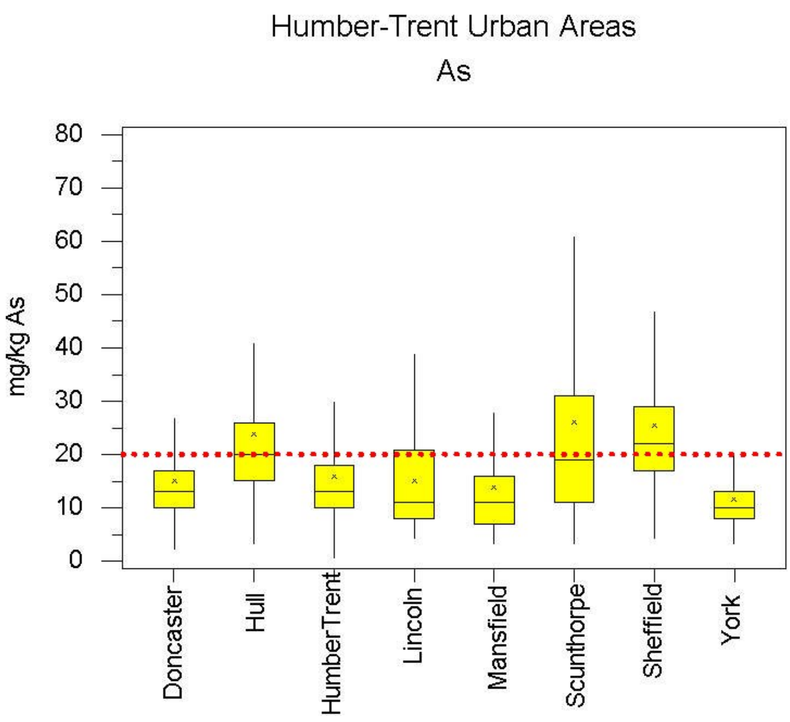

Figure 6: (d) Arsenic in surface soil

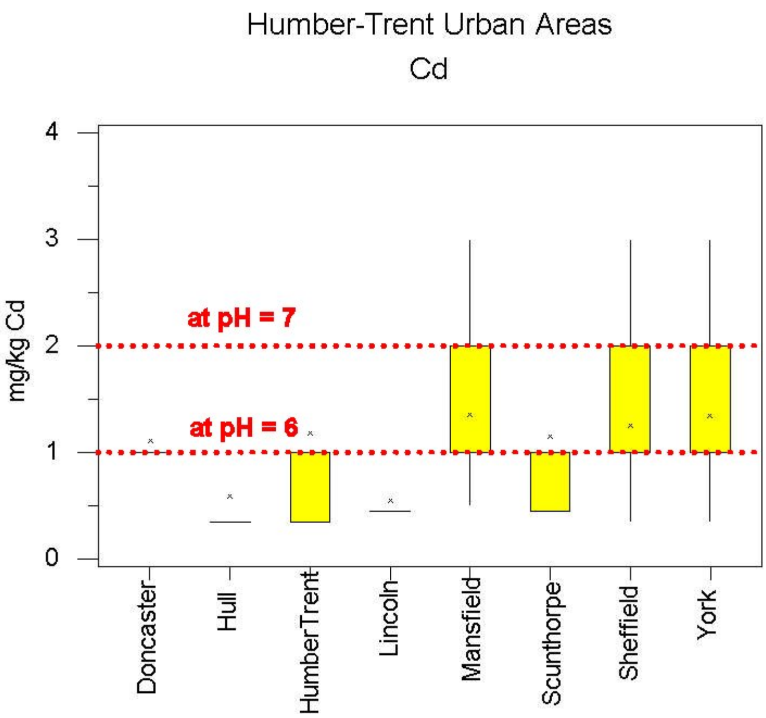

Figure 6: (e) Cadmium in surface soil

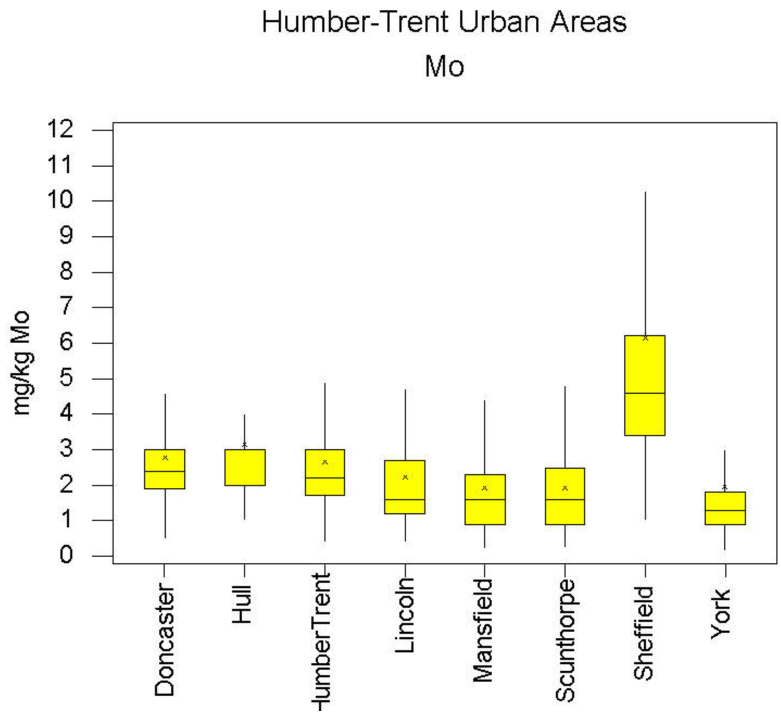

Figure 6: (f) Molybdenum in surface soil

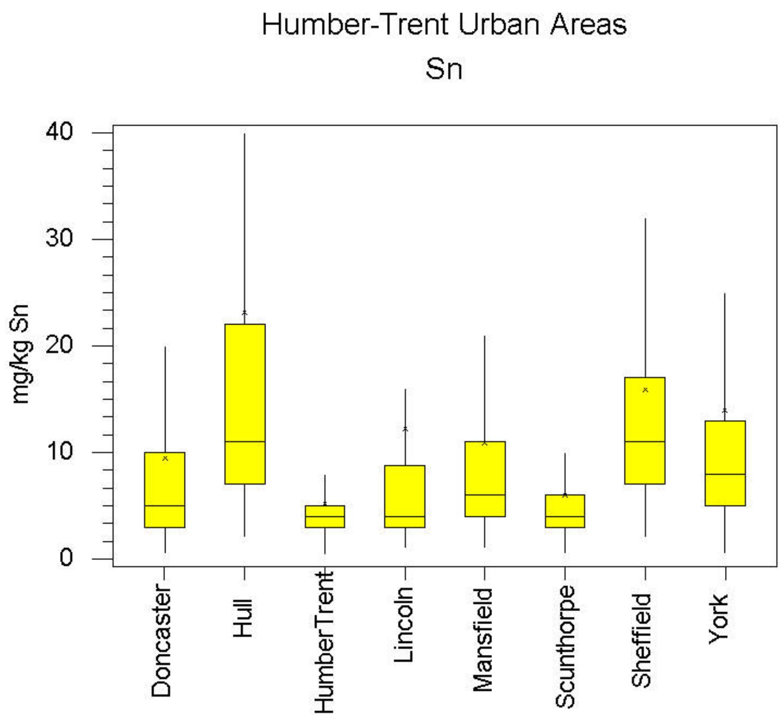

Figure 6: (g) Tin in surface soil

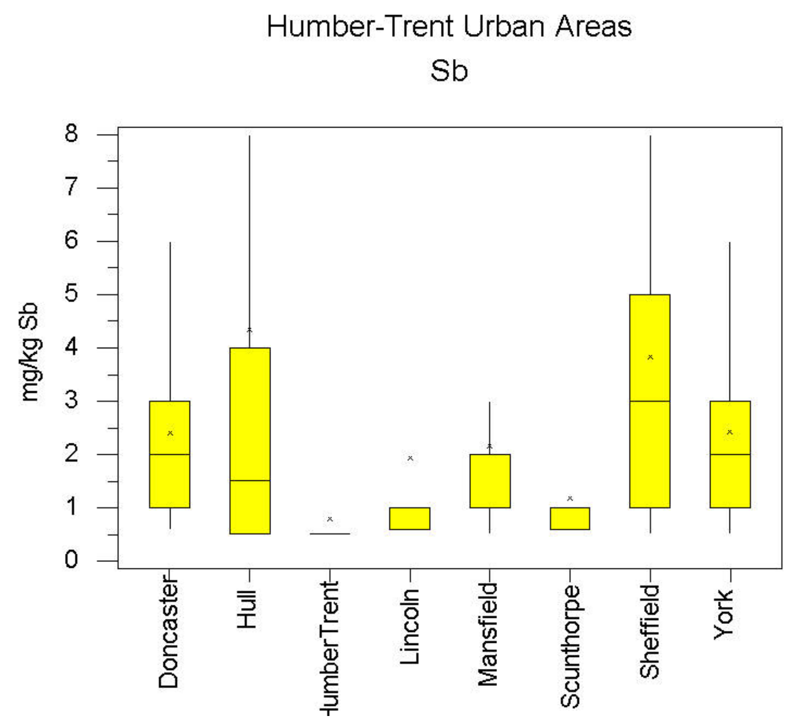

Figure 6: (h) Antimony in surface soil

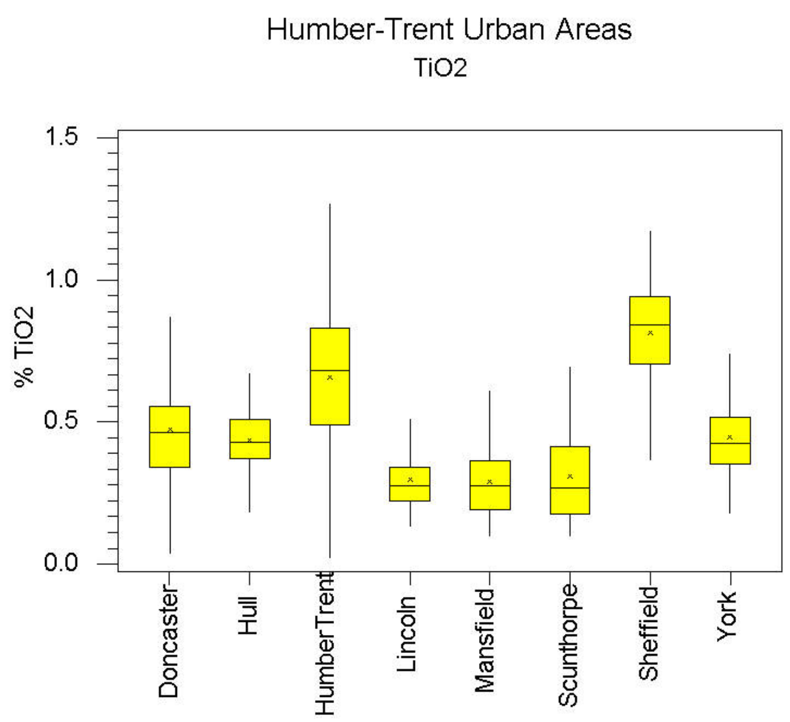

Figure 6: (i) Titanium oxide in surface soil

4.4 THE CAPPER PASS TIN SMELTER

A study of urban soil geochemistry undertaken by BGS (O'Donnell and Rawlins, 2003) identified particularly high levels of tin in Kingston-upon-Hull, in relation to regional Humber-Trent samples collected over the same parent material types. The median values were elevated by over 300% in the urban area. Estimated concentrations of tin in the surface soils of Hull and the surrounding non-urban area were plotted in a kriged map (Figure 7) to highlight the possible causes of the elevated levels in this area. The map identifies a possible contamination plume, originating in the region of the smelter, and trending in the prevailing wind direction (SW-NE). The proportional symbol map for Sn indicates that smelter emissions are unlikely to be the sole anthropogenic source of this element in the soils of Kingston-upon-Hull.

4.5 GEOCHEMICAL CHARACTERISTICS WITHIN THE KINGSTON-UPON-HULL DATASET

In general, the levels of As, Cu, Pb, Zn, Sn and Sb are higher towards the centre of the shaded urban area, with lower levels on the outskirts of Hull. This suggests that urban contamination has a significant influence on soil geochemistry. High levels of Pb, Sb and to some extent Sn, appear to be associated with the city's transport networks (rivers, roads and railways), while concentrations of Cu are higher towards the coastline, particularly in the dockside region to the east of the city (Figure 3). Higher levels of As, Pb, Sn and Sb are also apparent in this region. Excluding this area, however, concentrations of Sn are generally higher in the surface soils collected in the western part of the city, than towards the east. This may reflect the influence of the smelter.

All other elements analysed demonstrate some level of enrichment around the dockside area, suggesting that this is a major region of contamination in Hull. Strong similarities in the distributions of Ni, Mo, Cr, Co, Cu, Fe_2O_3 and V are observed in this area. As already mentioned (section 2.1), the Capper Pass tin smelter received imports of tin-bearing raw materials from overseas. These ores would have therefore been delivered to docks along the Humber Estuary, along with other imports of raw materials for industry. The complex tin ores (mainly from Bolivia) are likely to have contained As, Cu, Sb and other chalcophilic elements. Additionally, industrial waste products, such as metal-rich furnace slags and ballast from ships may have been used in the construction of the docks, providing a further source of contamination. Industrial activity in the dockside area of Hull is likely to provide a continued source of contamination to the present day. High levels of heavy metals also occur in the area of Hessle (to the south-east of Hull), appearing in a small and isolated number of samples. This is likely to reflect industrial activity in the area.

In addition to Pb, Sb and Sn, high concentrations of Ba, Mo and Zn are found in proximity to routes of transportation (rivers, roads and railways) and similar patterns are observed for Cr and Co. Prior to 2000, tetra-ethyl Pb was added to petrol as an anti-knocking agent and was widely released in vehicle emissions. Other elements may also be present as impurities in petroleum products. Barium has been identified as a possible alternative tracer to Pb for vehicle emissions in surface soils as it can be found in petrol, as well as in unleaded petrol and diesel oil (Monaci and Bargagli, 1997). Many industries develop close to important transport routes and therefore provide other sources of soil contamination in these areas.

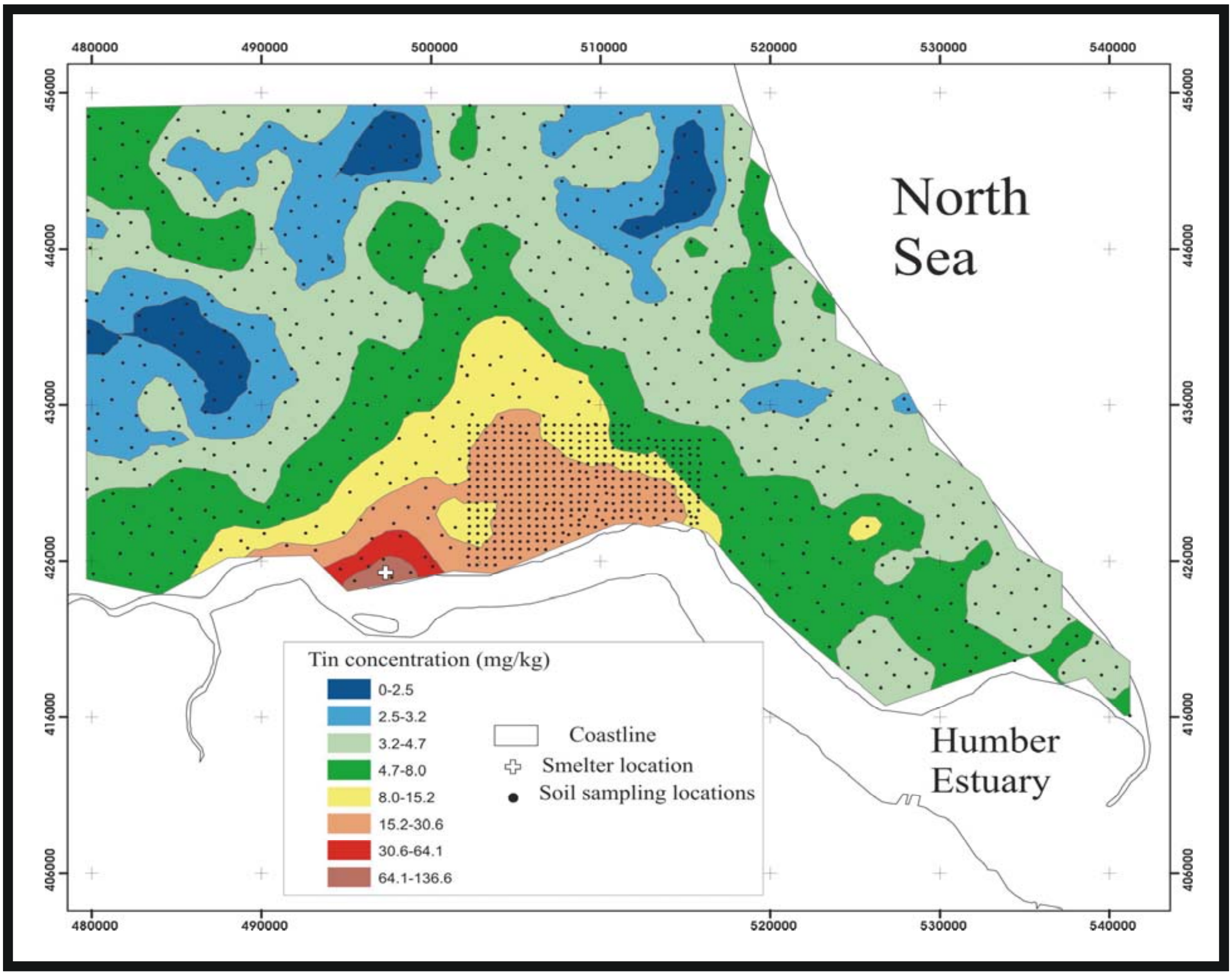

Figure 7 Kriged map of tin (Sn) concentrations in top-soil for the Kingston-upon-Hull area, combining urban and rural soil geochemical data. The impact of aerially deposited particulates, most probably derived from the smelter at North Ferriby (shown by the white cross) can be seen in the ENE trending plume extending towards the North Sea. Coordinates are in metres of the British National Grid.

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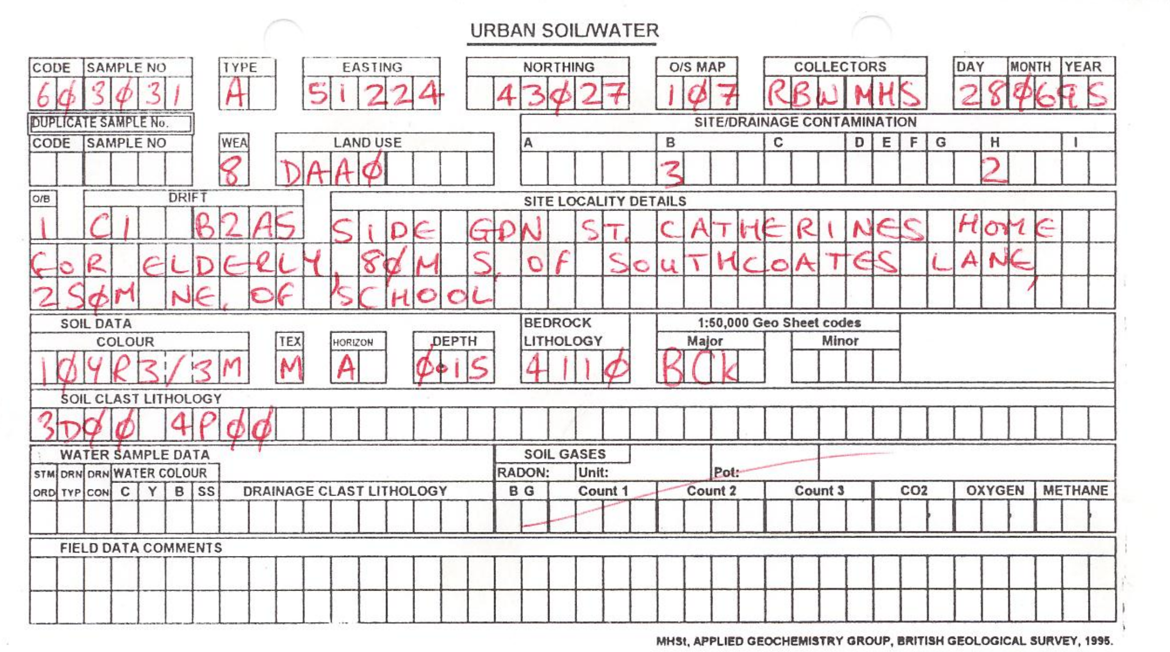
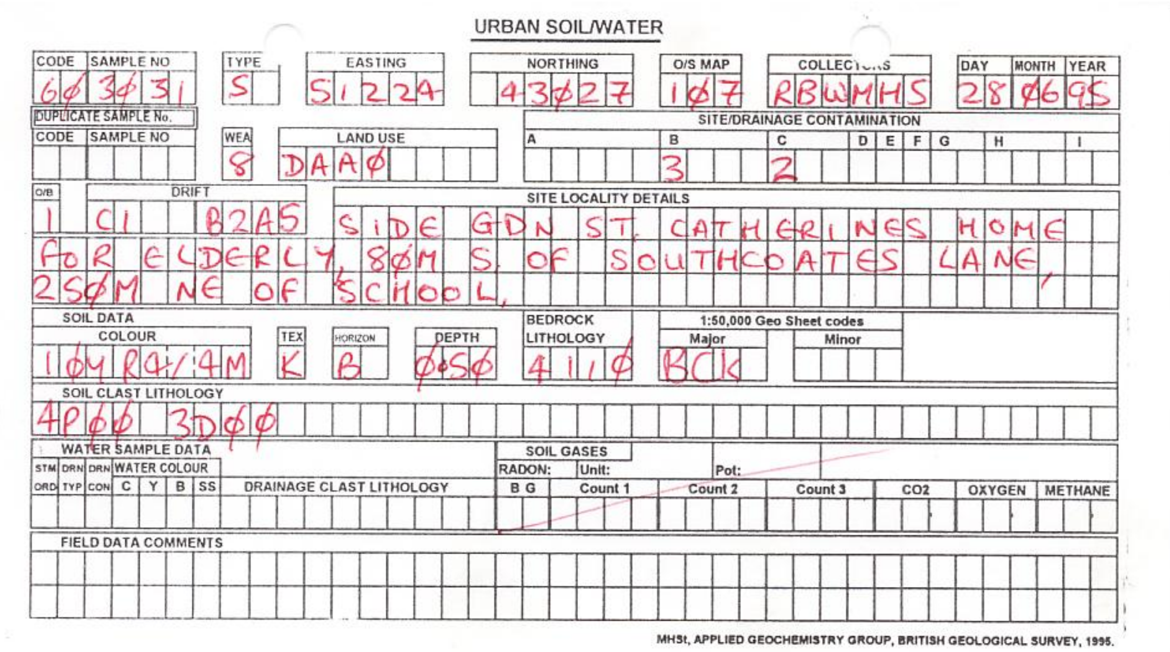
Appendix A: Examples of urban surface and profile field cards from Kingston-upon-Hull.





Appendix B: Percentile calculations for Kingston-upon-Hull soil

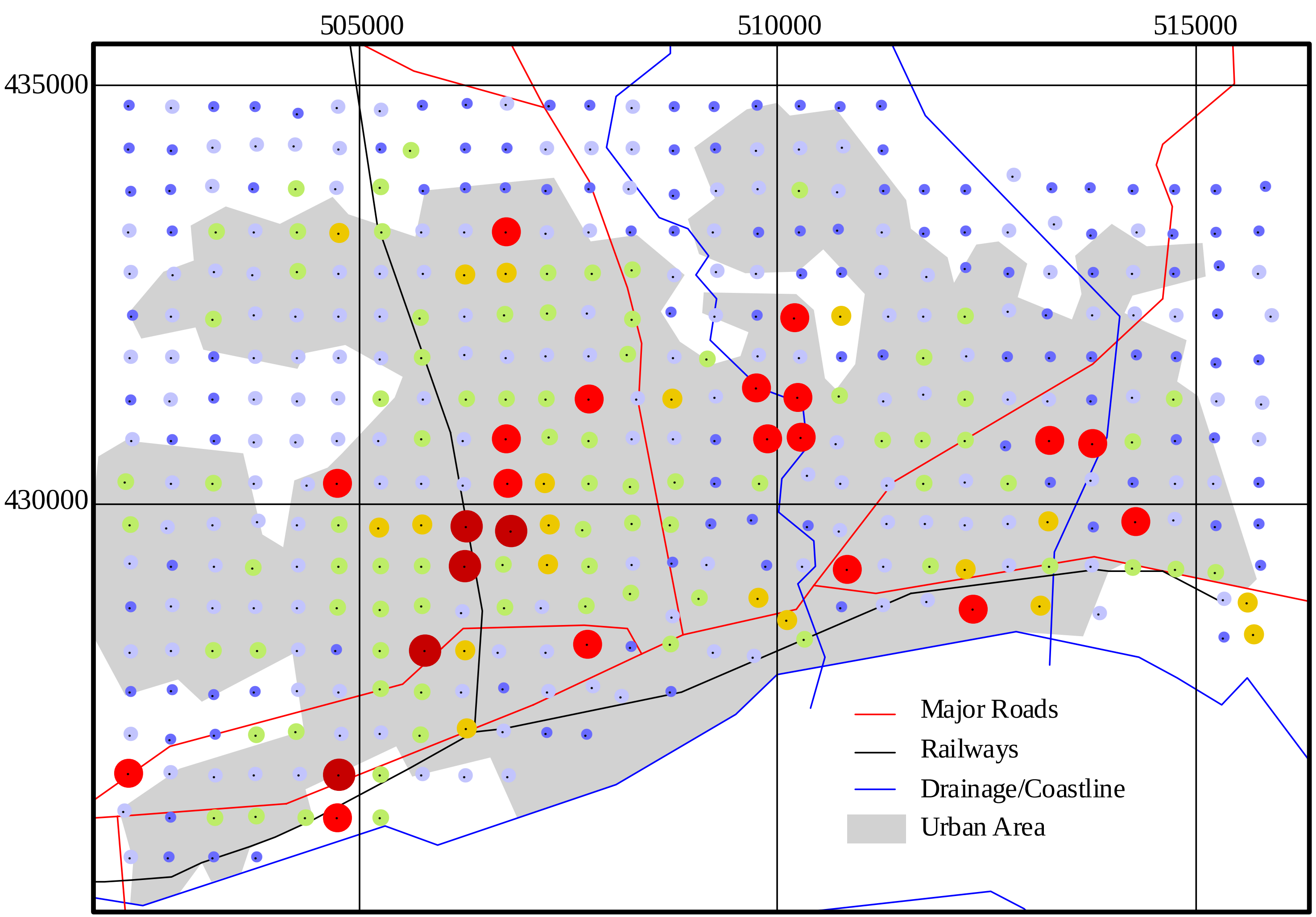
Percentiles	Fe_2O_3	Fe_2O_3	MnO	MnO	TiO_2	Ni	Ni	Sn	Sn	V	V	Ba	Ba	Pb	Pb	Zn	Zn
	WT %	WT %	WT %	WT %	WT %	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
5%	3.68	3.84	0.042	0.045	0.445	19	20	5	3	62	68	334	386	42	26	65	61
10%	4.08	4.37	0.048	0.054	0.511	21	24	5	3	71	77	352	398	49	29	72	67
15%	4.37	4.64	0.054	0.061	0.561	23	26	6	3	75	82	372	409	56	33	80	73
25%	4.80	5.11	0.061	0.072	0.622	26	29	7	4	82	90	396	427	67	40	96	85
50%	5.98	6.30	0.077	0.093	0.714	34	37	11	7	101	109	448	453	116	81	132	117
75%	7.20	7.49	0.095	0.116	0.849	42	45	22	16	129	137	520	526	244	224	221	191
90%	8.09	8.91	0.114	0.148	0.969	49	55	47	45	146	156	705	718	545	506	415	370
95%	9.02	9.99	0.129	0.183	1.007	56	62	68	81	157	166	871	928	766	761	623	587
99%	15.62	15.55	0.203	0.256	1.085	95	112	240	248	206	289	2069	2499	1600	2196	1769	1991
Max	31.66	27.41	0.338	0.413	1.404	141	204	633	1394	323	346	4901	11641	2900	3900	5800	4358
Min	1.50	1.64	0.017	0.013	0.168	7	11	2	1	30	39	148	202	10	13	20	34
Mean	6.22	6.56	0.081	0.099	0.728	36	40	23	24	107	116	524	576	231	228	229	220
Median	5.98	6.30	0.077	0.093	0.714	34	37	11	7	101	109	448	453	116	81	132	117

	Cd*	Cd*	Cu	Cu	Mo	Mo	Sb*	Sb*	U*	U*	Co	Co	As	As	Cr	Cr	
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
5%	0.35	0.35	19	15	1.8	1.4	0.5	0.5	1.1	1.71	20	18	11	10	54	66	
10%	0.35	0.35	21	18	1.9	1.5	0.5	0.5	1.3	2.1	21	19	12	11	59	74	
15%	0.35	0.35	24	19	2.1	1.6	0.5	0.5	1.5	2.3	23	20	13	12	62	79	
25%	0.35	0.35	27	21	2.3	1.8	0.5	0.5	1.7	2.4	25	21	15	15	67	83	
50%	0.35	1	39	31	2.7	2.5	1	1	2.0	2.7	28	25	20	20	83	97	
75%	0.35	2	78	69	3.4	3.5	4	4	2.4	3.1	33	29	26	26	107	114	
90%	1	2	153	161	4.42	5.4	10	9	2.8	3.4	37	34	37	40	120	125	
95%	2	3	250	262	5.7	7.9	15	15	3.0	3.9	41	37	48	51	143	137	
99%	3	4	499	657	11.0	21.5	40.9	61.9	4.28	5.0	67	59	93	85	258	203	
Max	5	19	1123	930	21.0	42.0	73	98	6.0	6.7	85	82	205	253	1809	530	
Min	0.35	0.35	6	9	1.3	0.9	0.5	0.5	0.25	0.25	10	11	3	6	22	28	
Mean	0.60	1.21	74	71	3.1	3.4	4.3	4.5	2.08	2.77	30	26	24	25	94	101	
Median	0.35	1	39	31	2.7	2.5	1	1	2	2.7	28	25	20	20	83	97	

Surface soils in yellow. *Minimum value reported as half detection limit.

Appendix C: Proportional symbol geochemical maps for Kingston-upon-Hull surface and profile soils

Antimony
Arsenic
Barium
Cadmium
Chromium
Cobalt
Copper
Iron
Lead
Manganese
Molybdenum
Nickel
Tin
Titanium
Uranium
Vanadium
Zinc



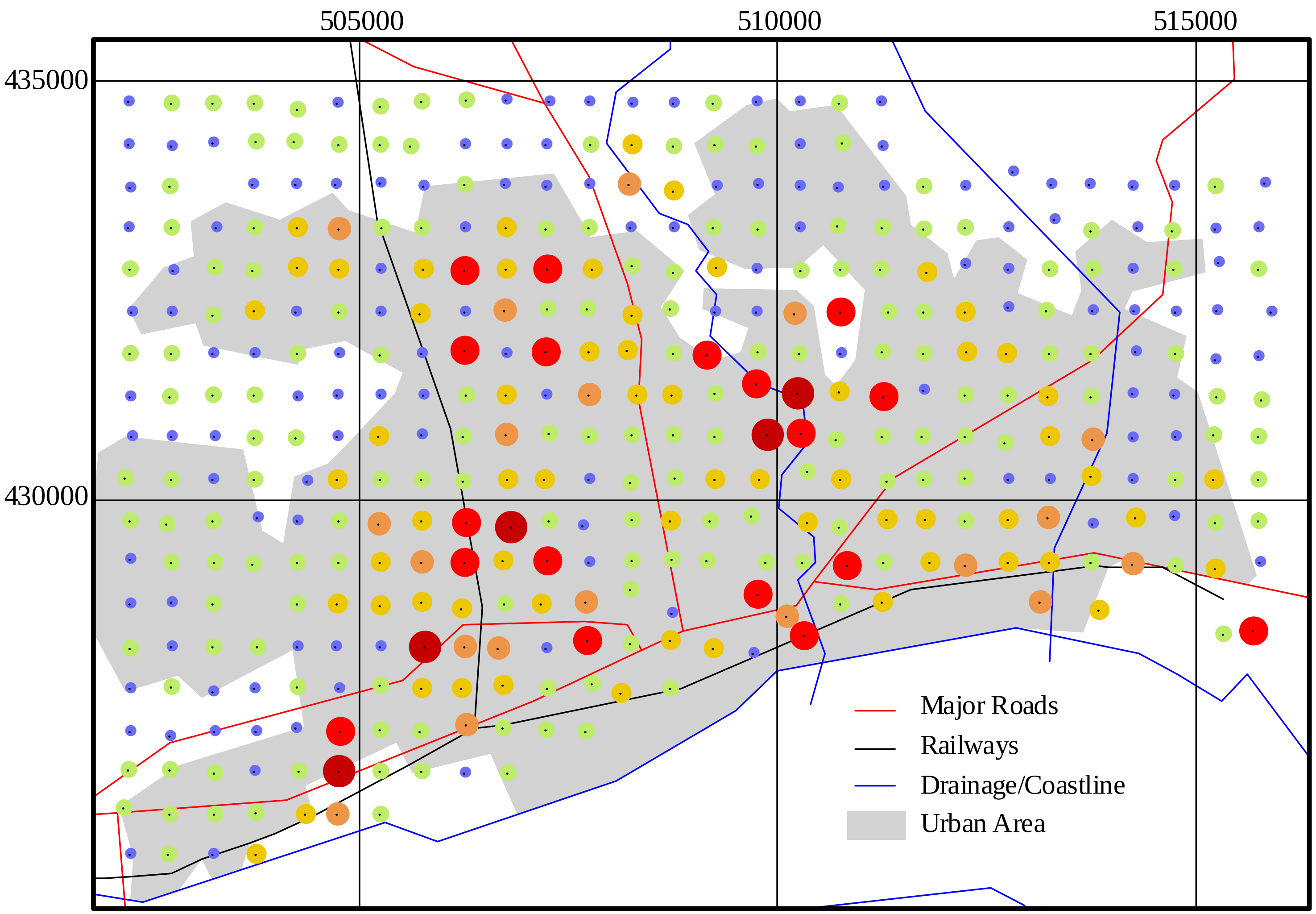
Kingston-Upon-Hull Surface Soils

Antimony

%ile	ppm
99	40.9
95	15
90	10
75	4
50	1
25	0.5

surface soil	Sb (ppm)
number	409
minimum	0.5*
maximum	73
median	1
mean	4.3

* minimum value quoted as half detection limit

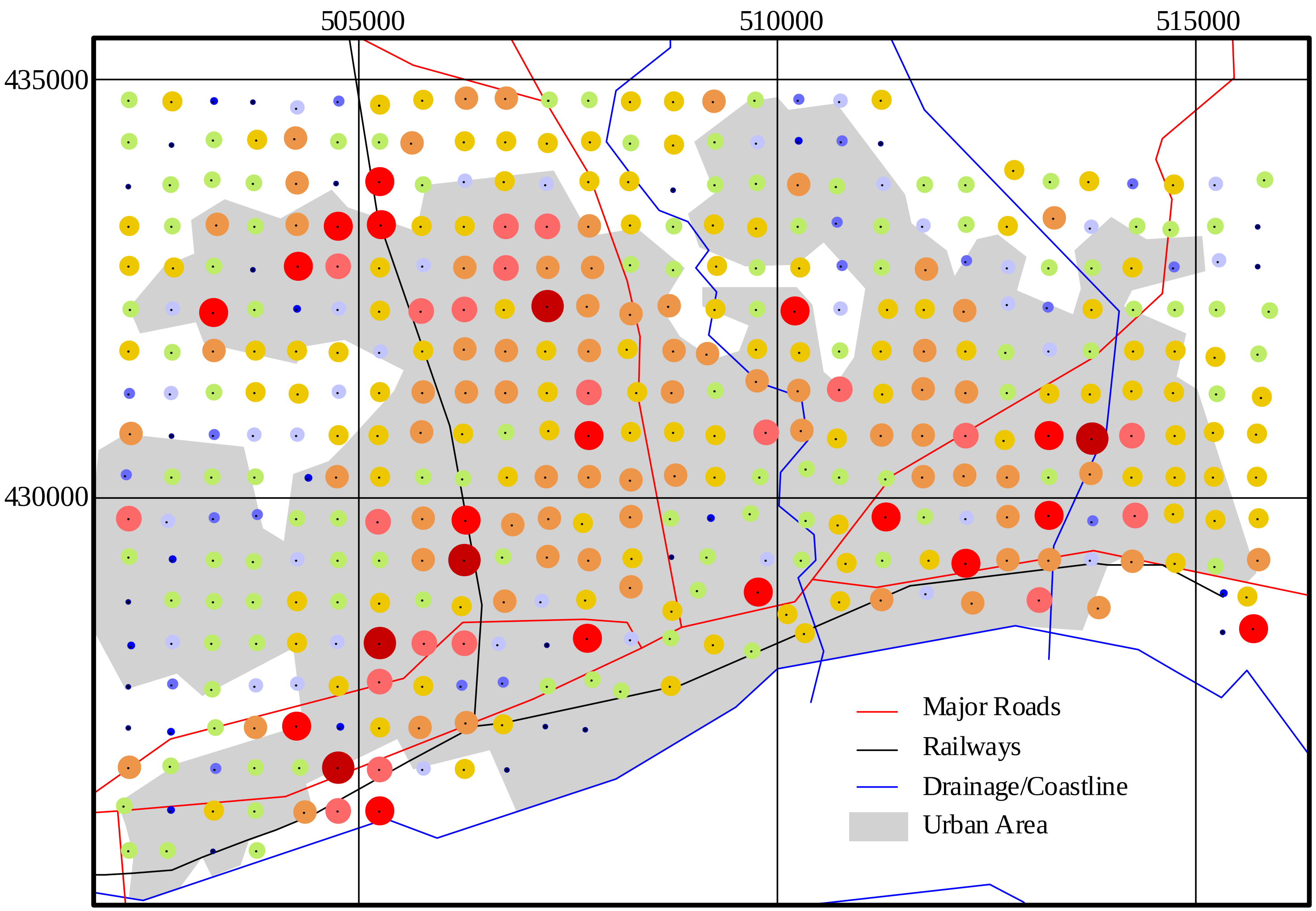


Kingston-Upon-Hull Profile Soils Antimony

%ile	ppm
99	61.9
95	15
90	9
75	4
50	1
25	0.5

profile soil	Sb (ppm)
number	402
minimum	0.5*
maximum	98
median	1
mean	4.5

* minimum value quoted as half detection limit



Kingston-Upon-Hull Surface Soils

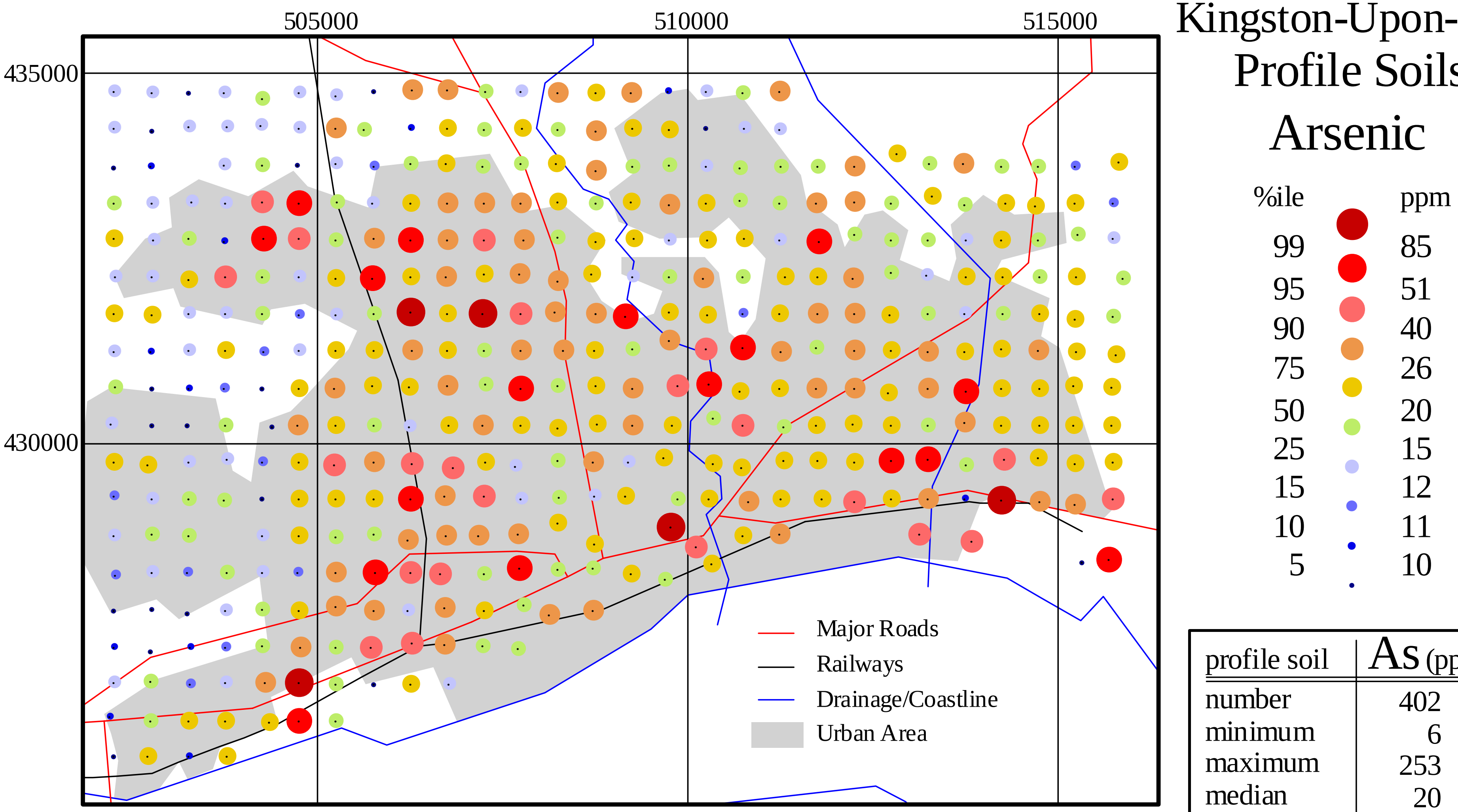
Arsenic

%ile	ppm
99	93
95	48
90	37
75	26
50	20
25	15
15	13
10	12
5	11

surface soil	As (ppm)
number	409
minimum	3
maximum	205
median	20
mean	24

Kingston-Upon-Hull Profile Soils

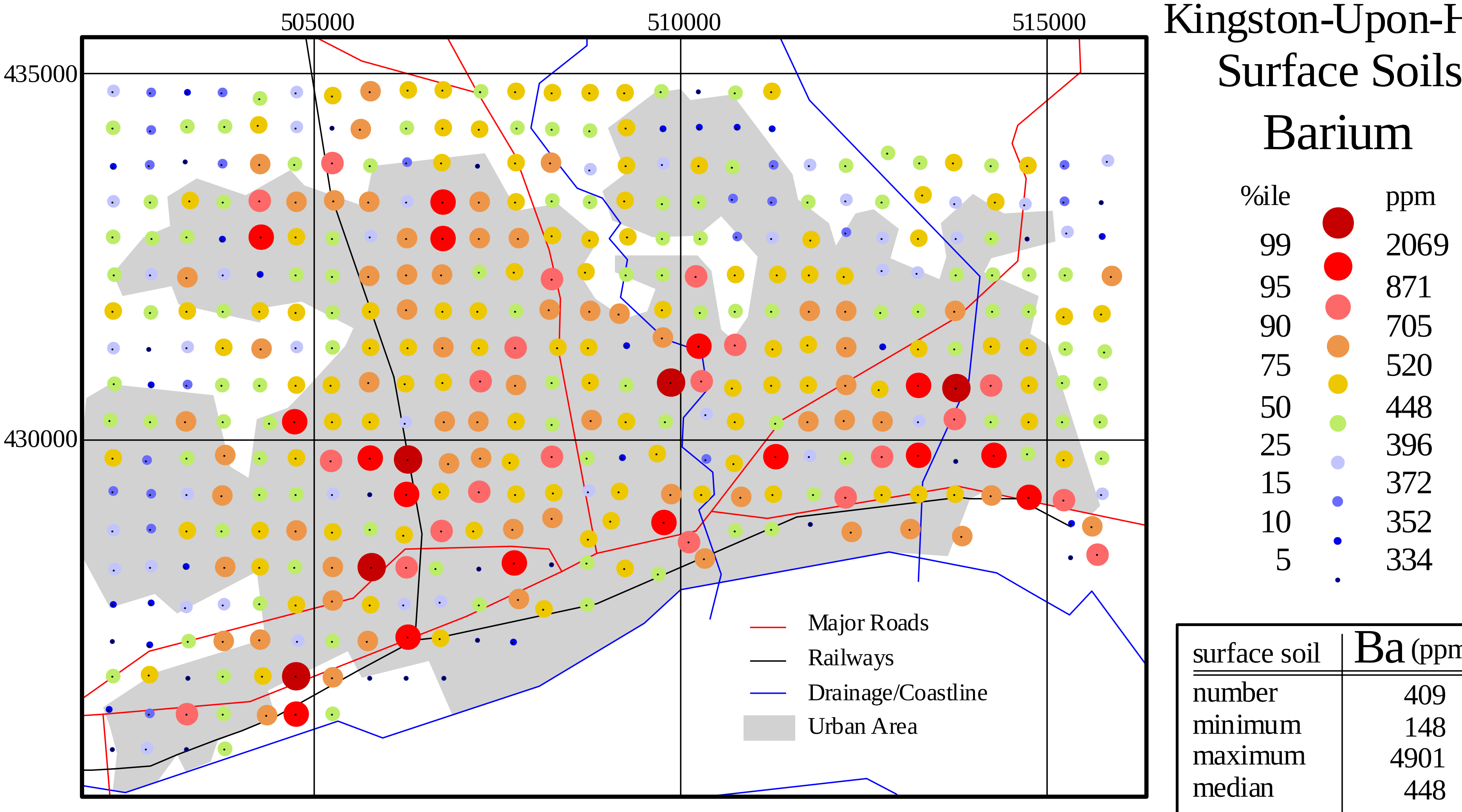
Arsenic



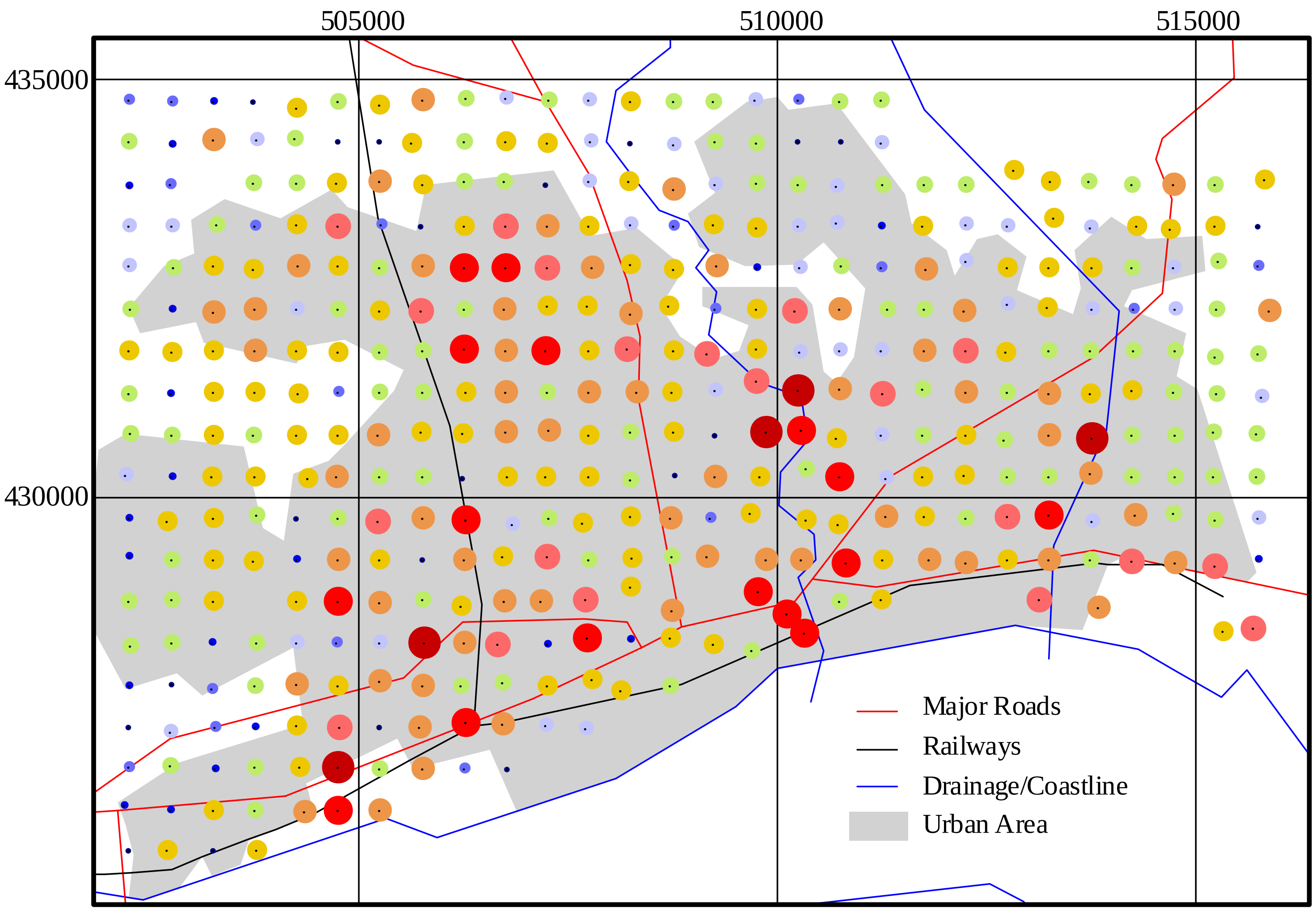
profile soil	As (ppm)
number	402
minimum	6
maximum	253
median	20
mean	25

Kingston-Upon-Hull Surface Soils

Barium



surface soil	Ba (ppm)
number	409
minimum	148
maximum	4901
median	448
mean	524

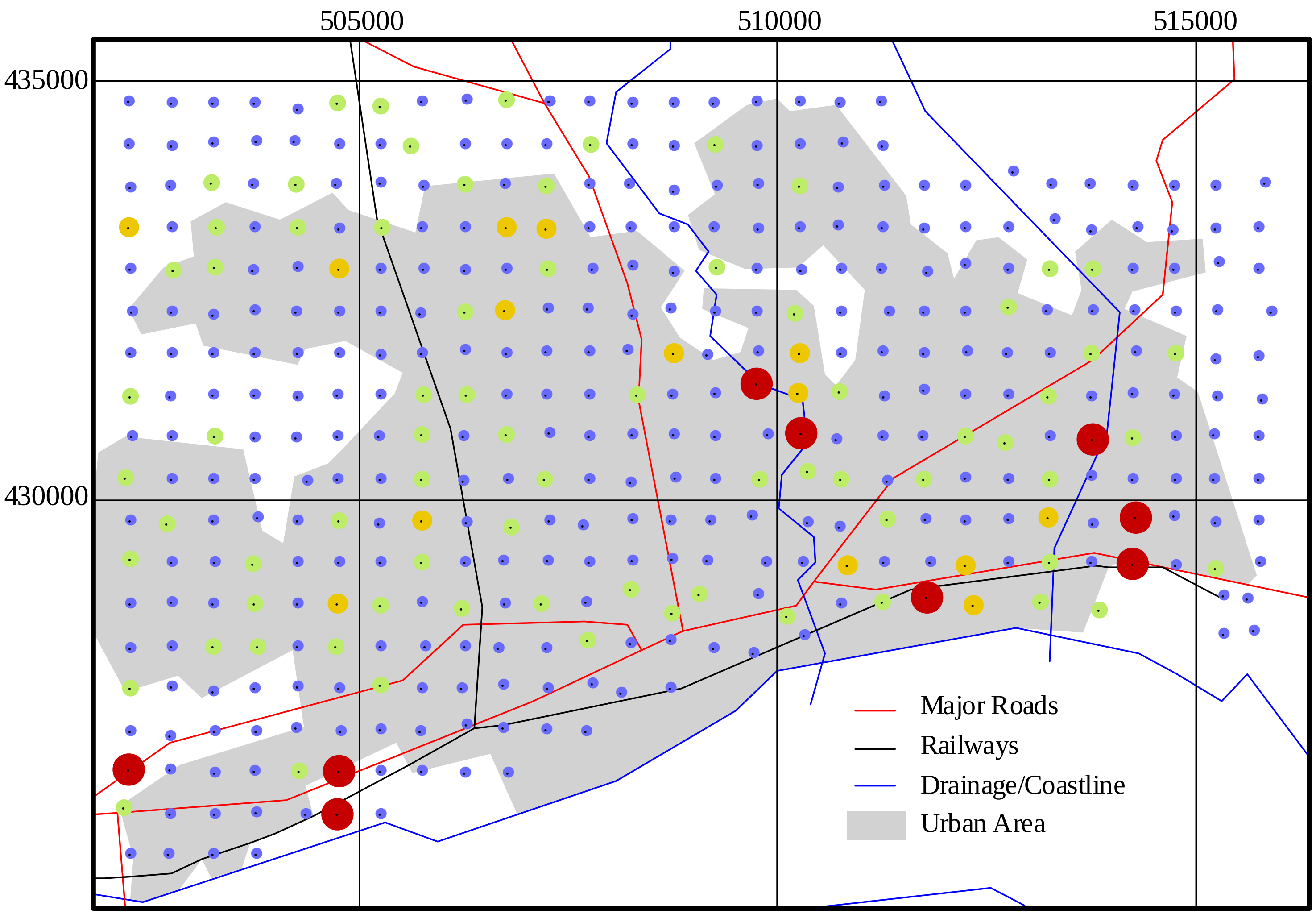


Kingston-Upon-Hull
Profile Soils
Barium

%ile	ppm
99	2499
95	928
90	718
75	526
50	453
25	427
15	409
10	398
5	386

profile soil	Ba (ppm)
number	402
minimum	202
maximum	11641
median	453
mean	576

Kingston-Upon-Hull
Surface Soils
Cadmium

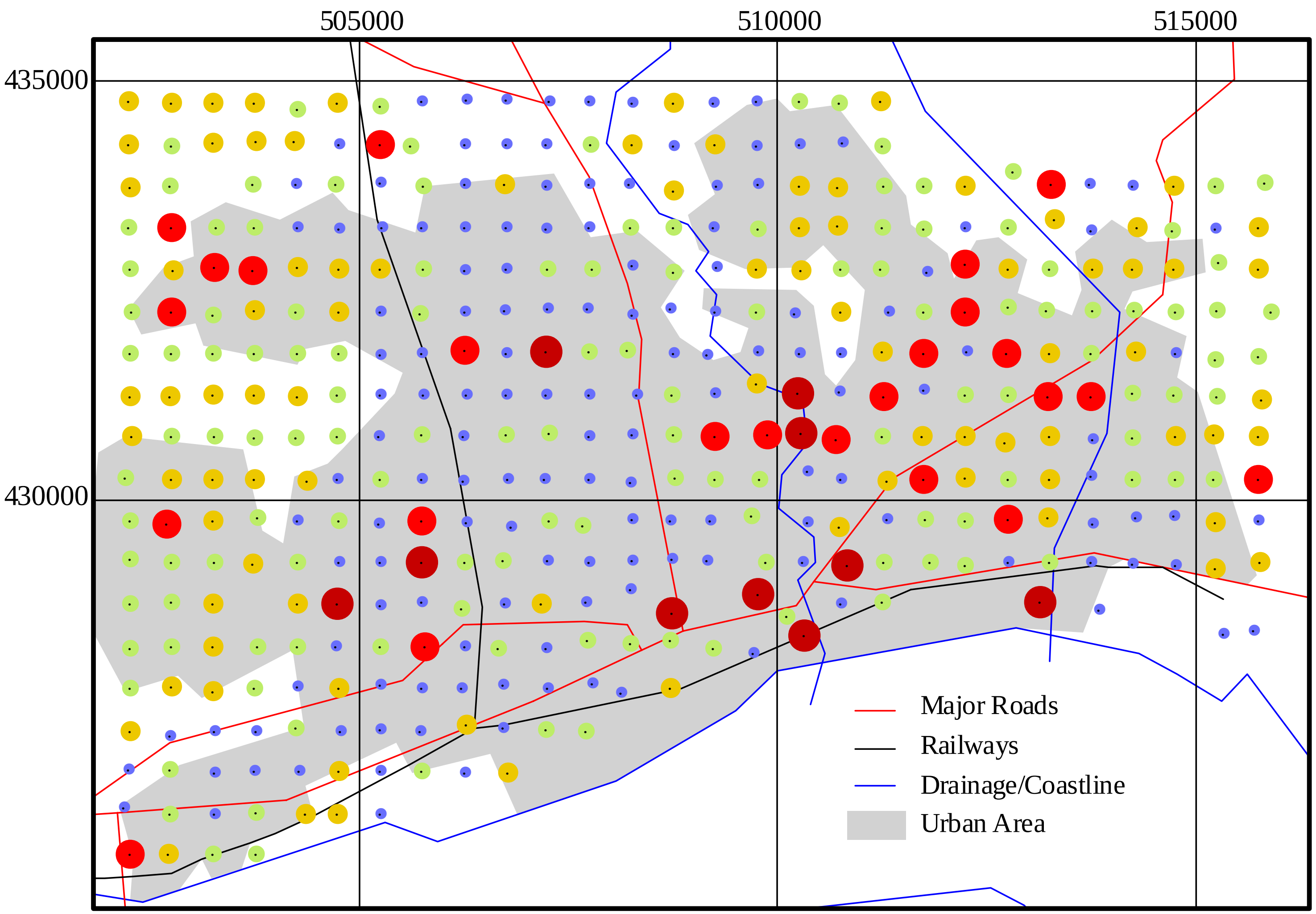


%ile	ppm
99	3
95	2
90	1
75	0.35

surface soil	Cd (ppm)
number	409
minimum	0.35*
maximum	5
median	0.35
mean	0.6

* minimum value quoted as half detection limit

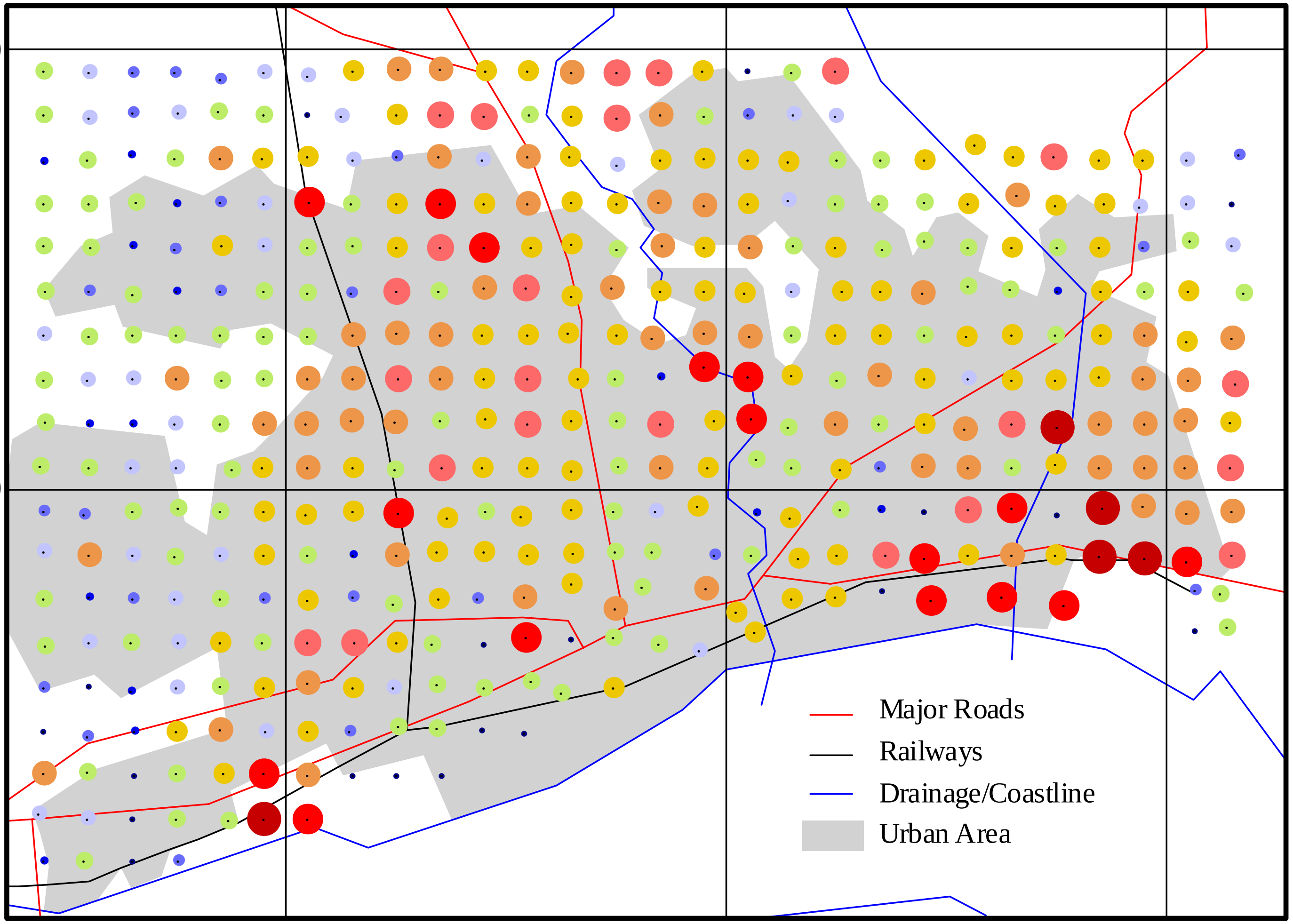
Kingston-Upon-Hull Profile Soils Cadmium



%ile	ppm
99	4
95	3
90	2
50	1
25	0.35

profile soil	Cd (ppm)
number	402
minimum	0.35*
maximum	19
median	1
mean	1.21

* minimum value quoted as half detection limit

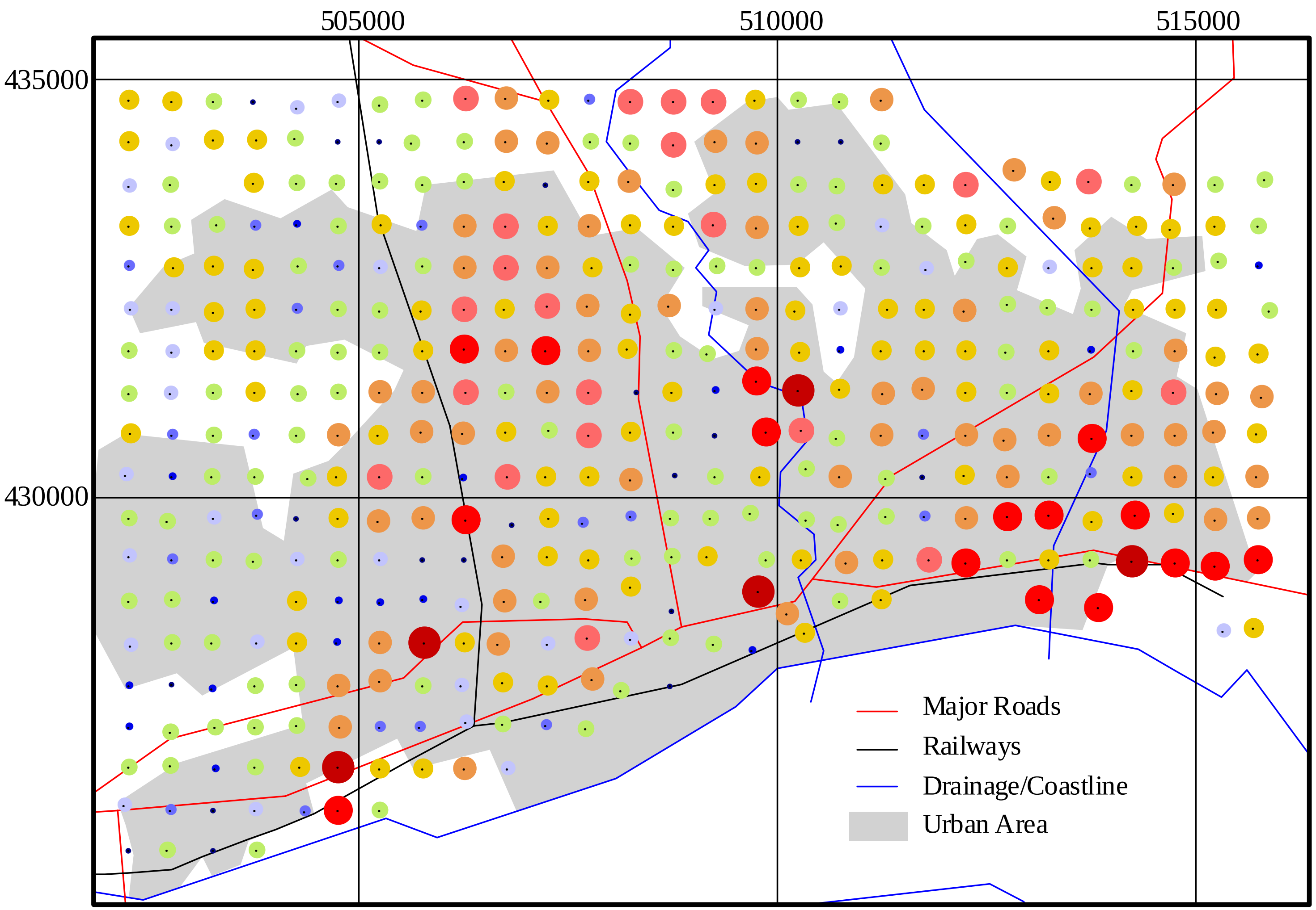


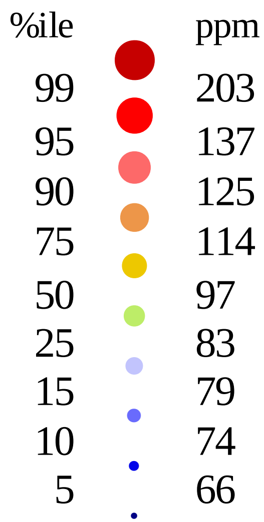
Kingston-Upon-Hull Surface Soils Chromium

%ile	ppm
99	258
95	143
90	120
75	107
50	83
25	67
15	62
10	59
5	54

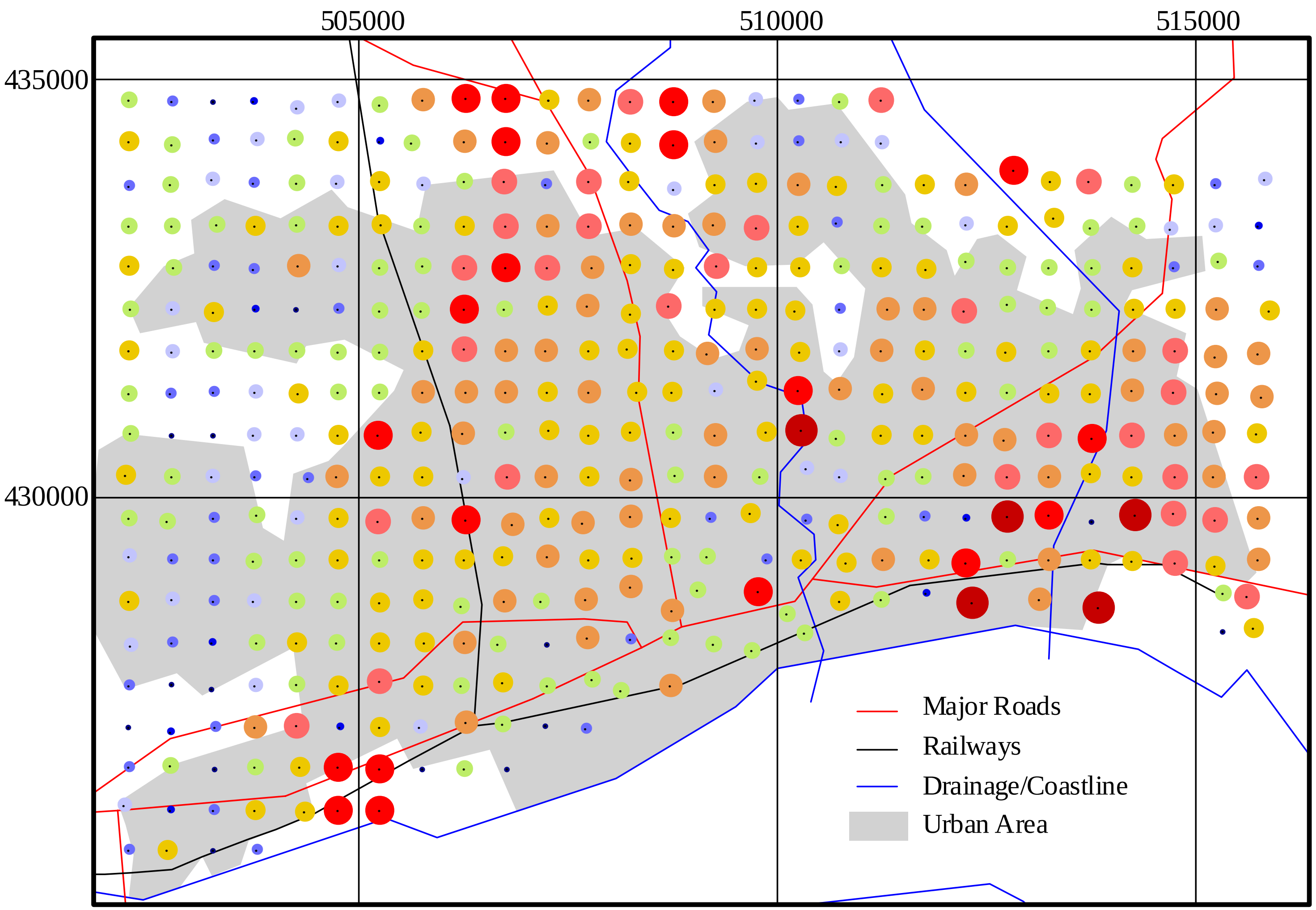
surface soil	Cr (ppm)
number	409
minimum	22
maximum	1809
median	83
mean	94

Kingston-Upon-Hull Profile Soils Chromium





profile soil	Cr (ppm)
number	402
minimum	28
maximum	530
median	97
mean	101



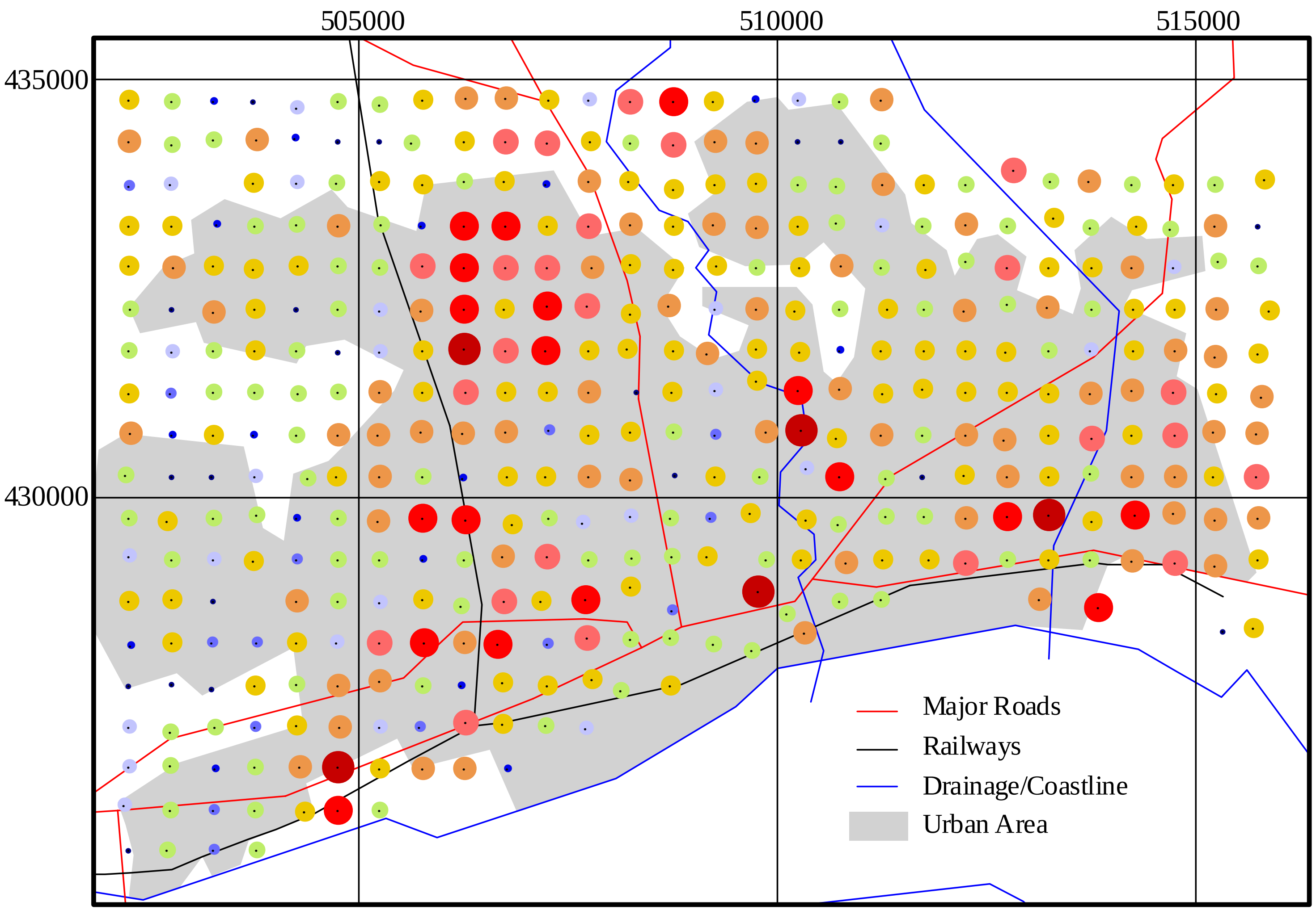
Kingston-Upon-Hull Surface Soils

Cobalt

%ile	ppm
99	67
95	41
90	37
75	33
50	28
25	25
15	23
10	21
5	20

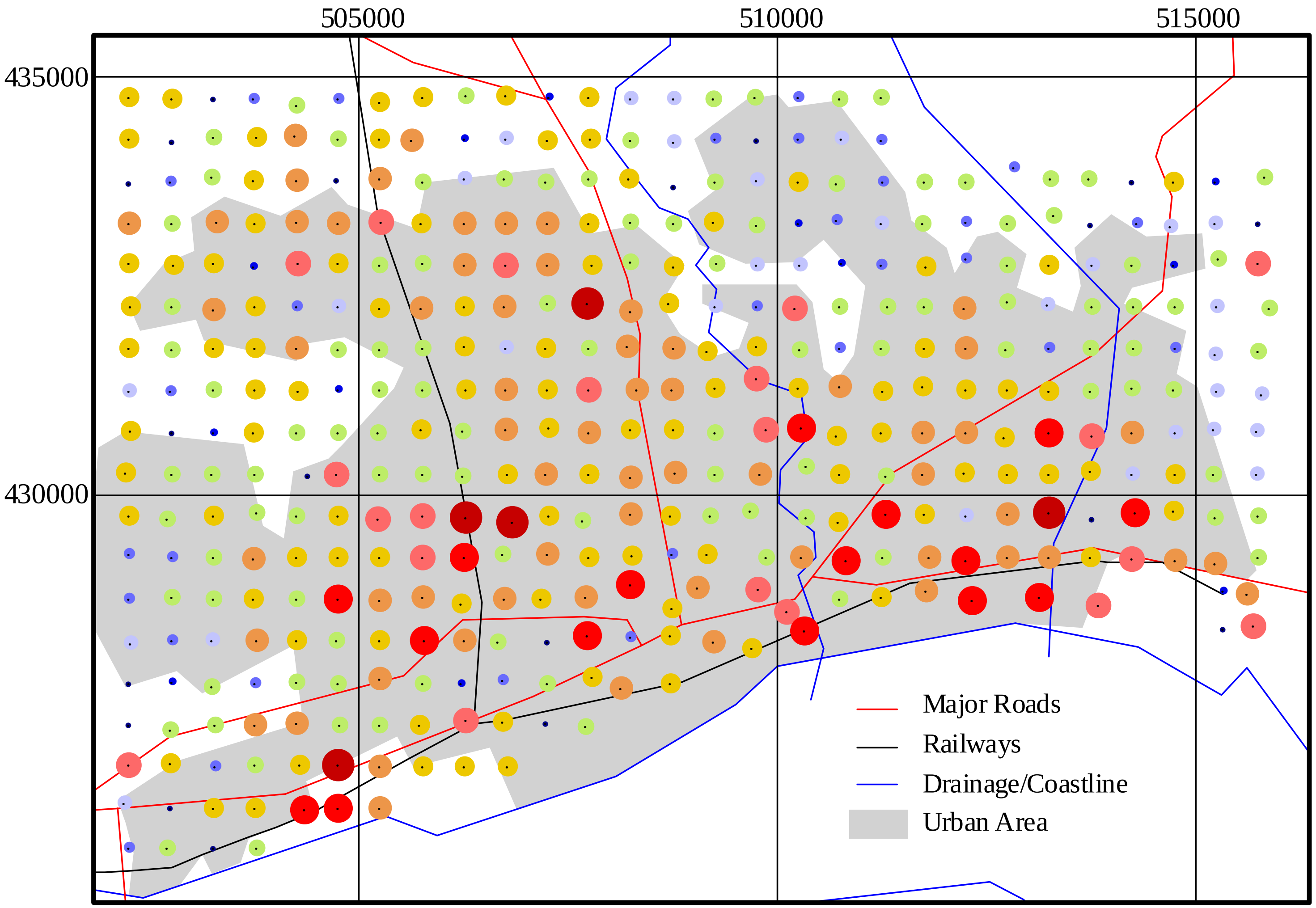
surface soil	Co (ppm)
number	409
minimum	10
maximum	85
median	28
mean	30

Kingston-Upon-Hull Profile Soils Cobalt



%ile	ppm
99	59
95	37
90	34
75	29
50	25
25	21
15	20
10	19
5	18

profile soil	Co (ppm)
number	402
minimum	11
maximum	82
median	25
mean	26

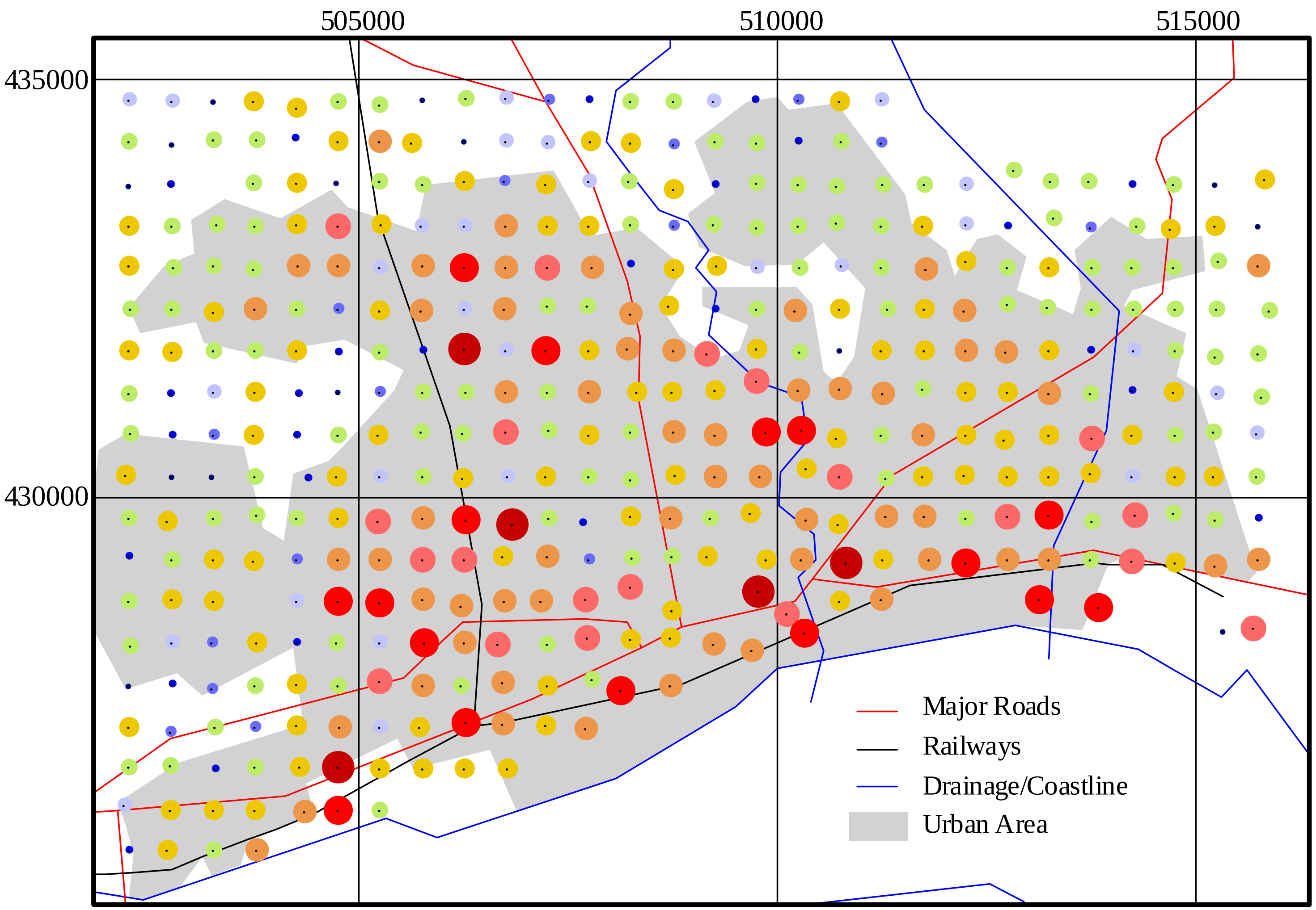


Kingston-Upon-Hull Surface Soils

Copper

%ile	ppm
99	499
95	250
90	153
75	78
50	39
25	27
15	24
10	21
5	19

surface soil	Cu (ppm)
number	409
minimum	6
maximum	1123
median	39
mean	74

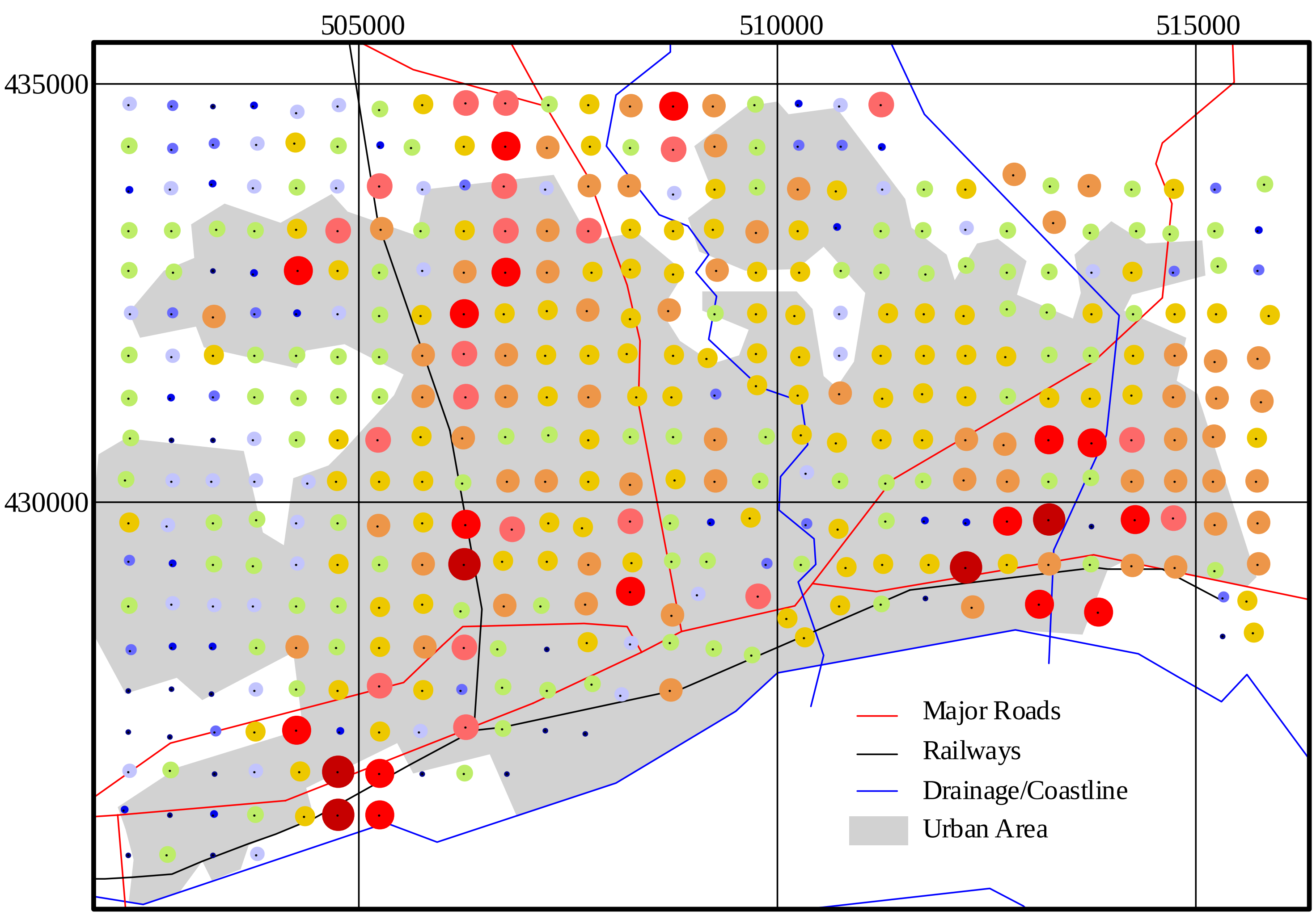


Kingston-Upon-Hull Profile Soils

Copper

%ile	ppm
99	657
95	262
90	161
75	69
50	31
25	21
15	19
10	18
5	15

profile soil	Cu (ppm)
number	402
minimum	9
maximum	930
median	31
mean	71



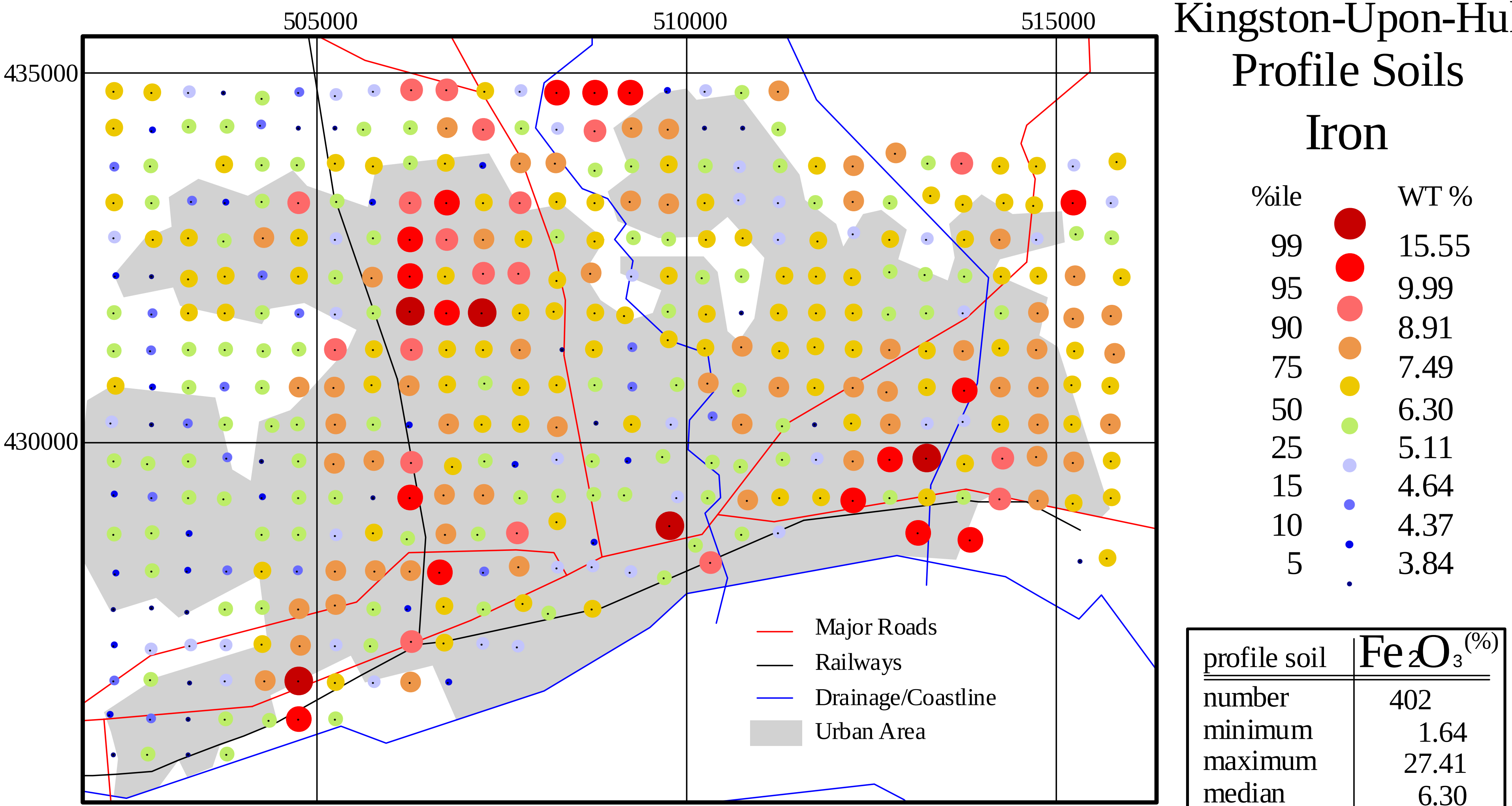
Kingston-Upon-Hull Surface Soils

Iron

%ile	WT %
99	15.62
95	9.02
90	8.09
75	7.20
50	5.98
25	4.80
15	4.37
10	4.08
5	3.68

surface soil	Fe_2O_3 (%)
number	409
minimum	1.50
maximum	31.66
median	5.98
mean	6.22

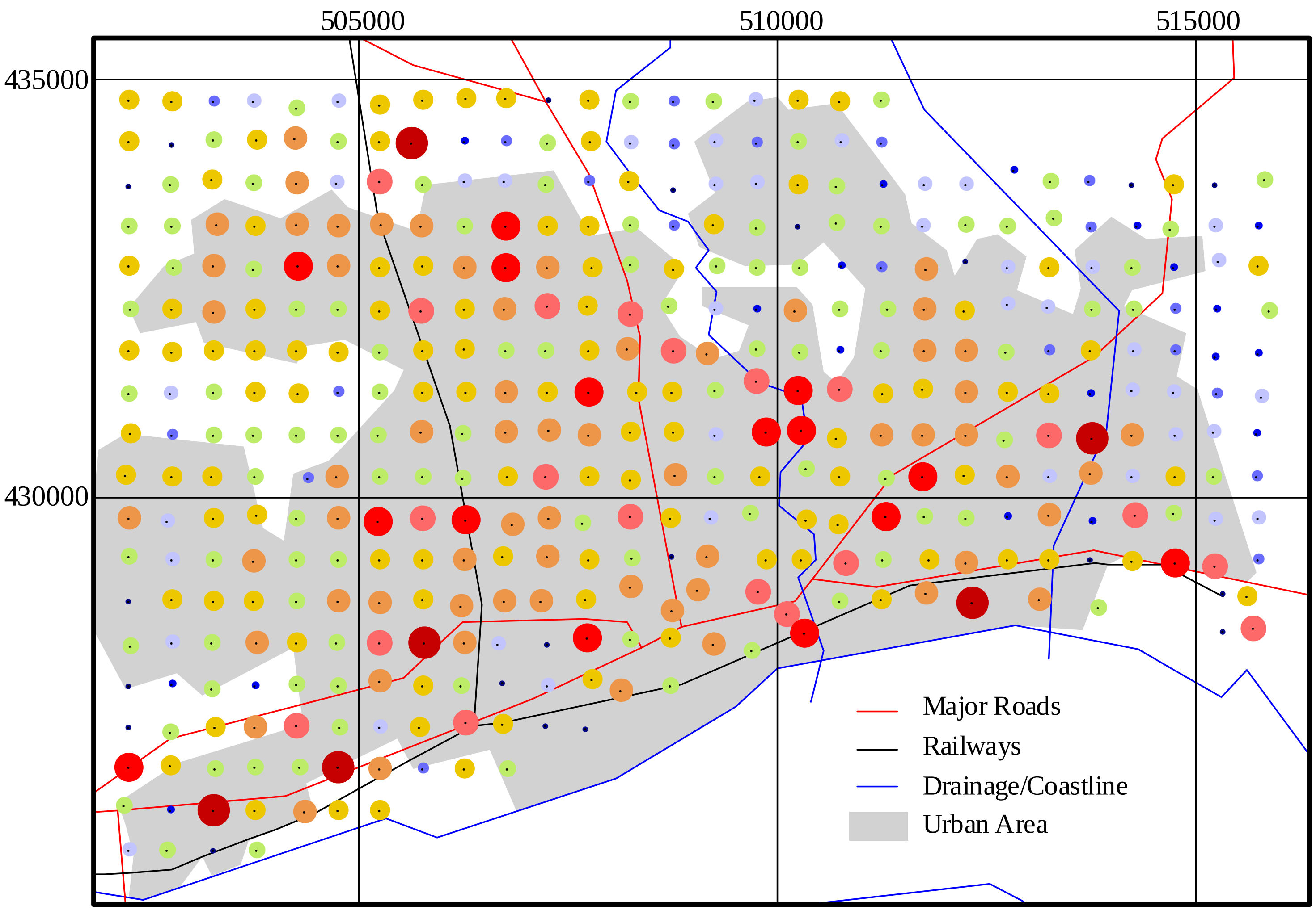
Kingston-Upon-Hull
Profile Soils
Iron



profile soil	Fe_2O_3 (%)
number	402
minimum	1.64
maximum	27.41
median	6.30
mean	6.56

Kingston-Upon-Hull Surface Soils

Lead

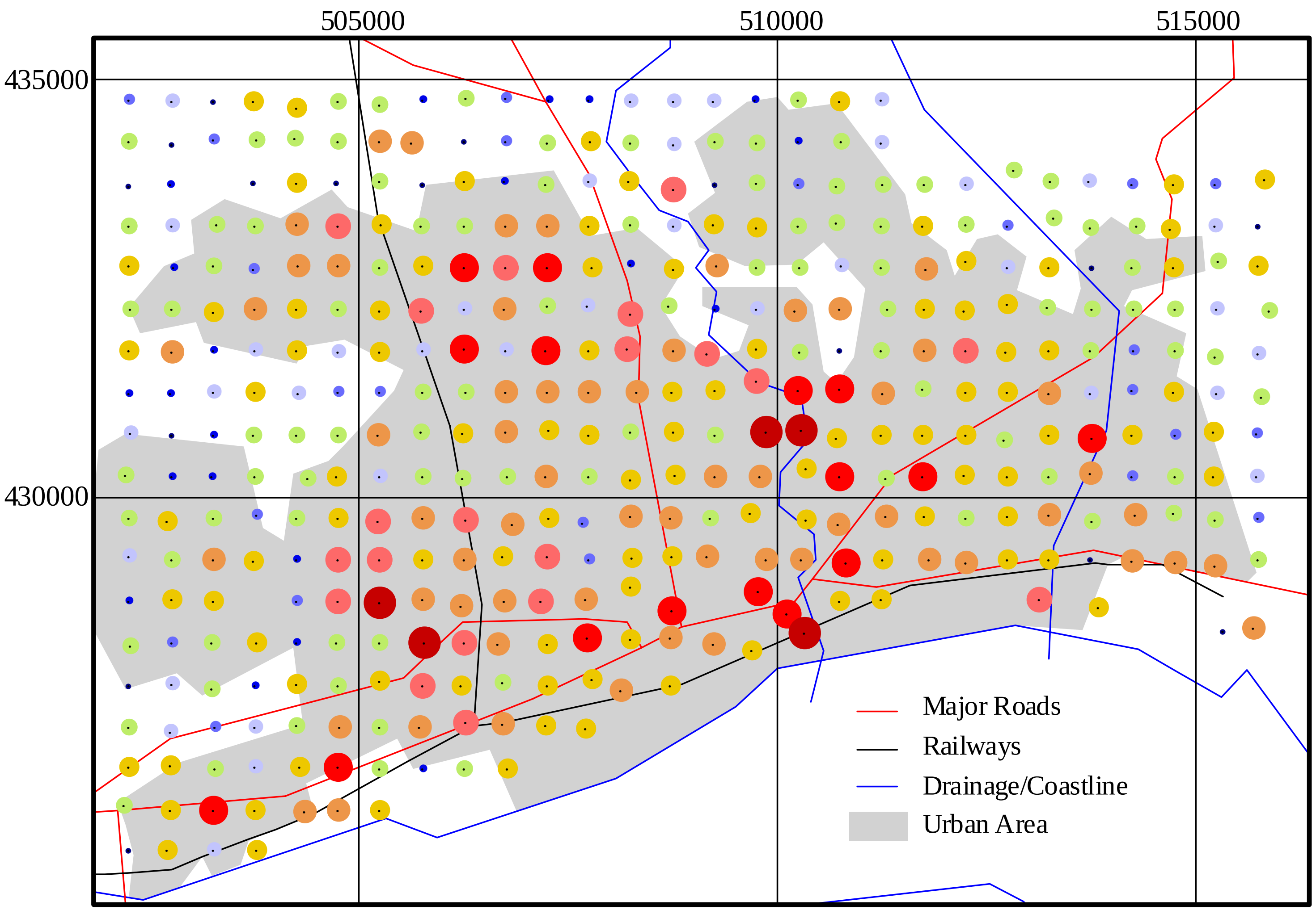


%ile	ppm
99	1600
95	766
90	545
75	244
50	116
25	67
15	56
10	49
5	42

surface soil	Pb (ppm)
number	409
minimum	10
maximum	2900
median	116
mean	231

Kingston-Upon-Hull Profile Soils

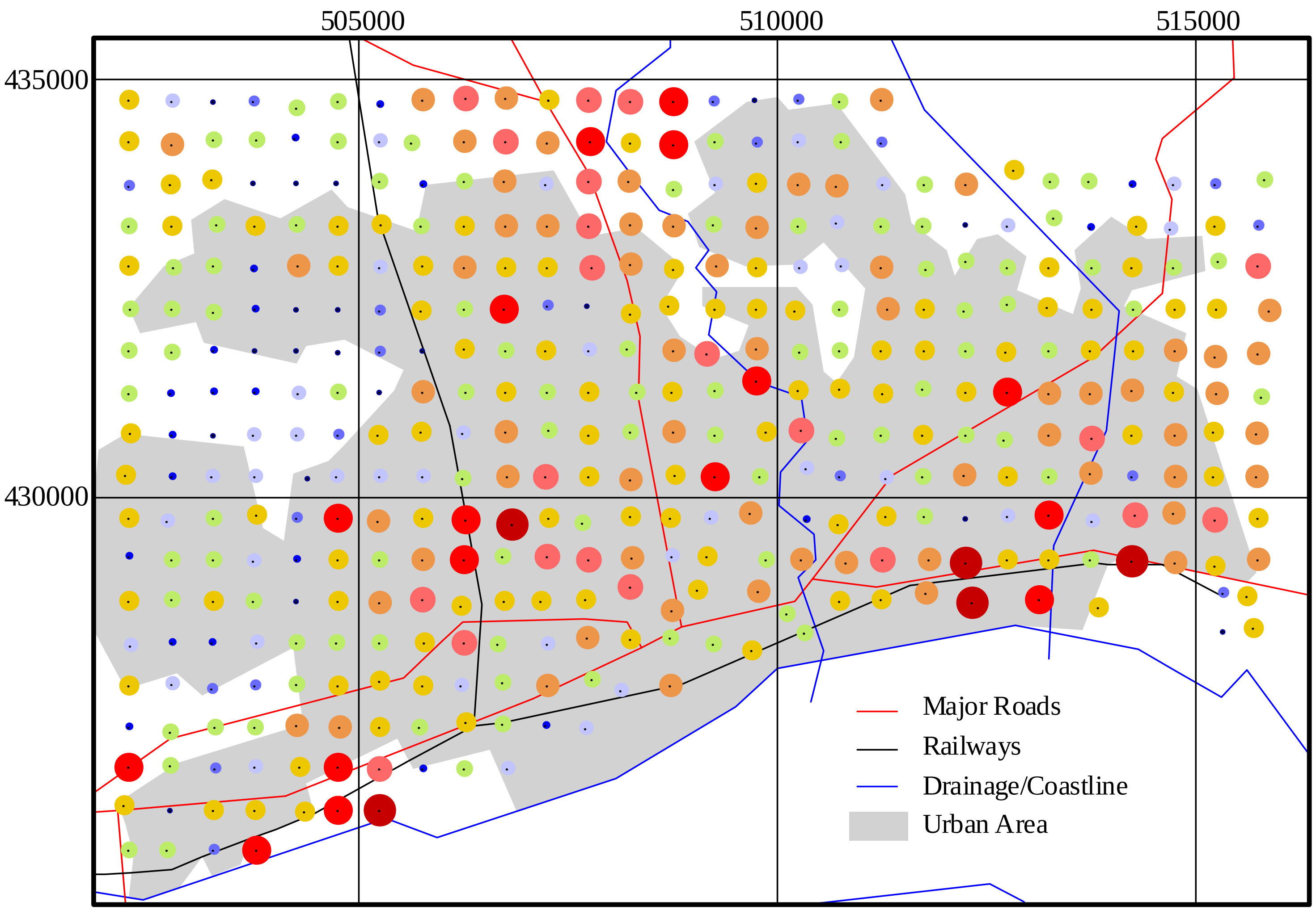
Lead



%ile	ppm
99	2196
95	761
90	506
75	224
50	81
25	40
15	33
10	29
5	26

profile soil	Pb (ppm)
number	402
minimum	13
maximum	3900
median	81
mean	228

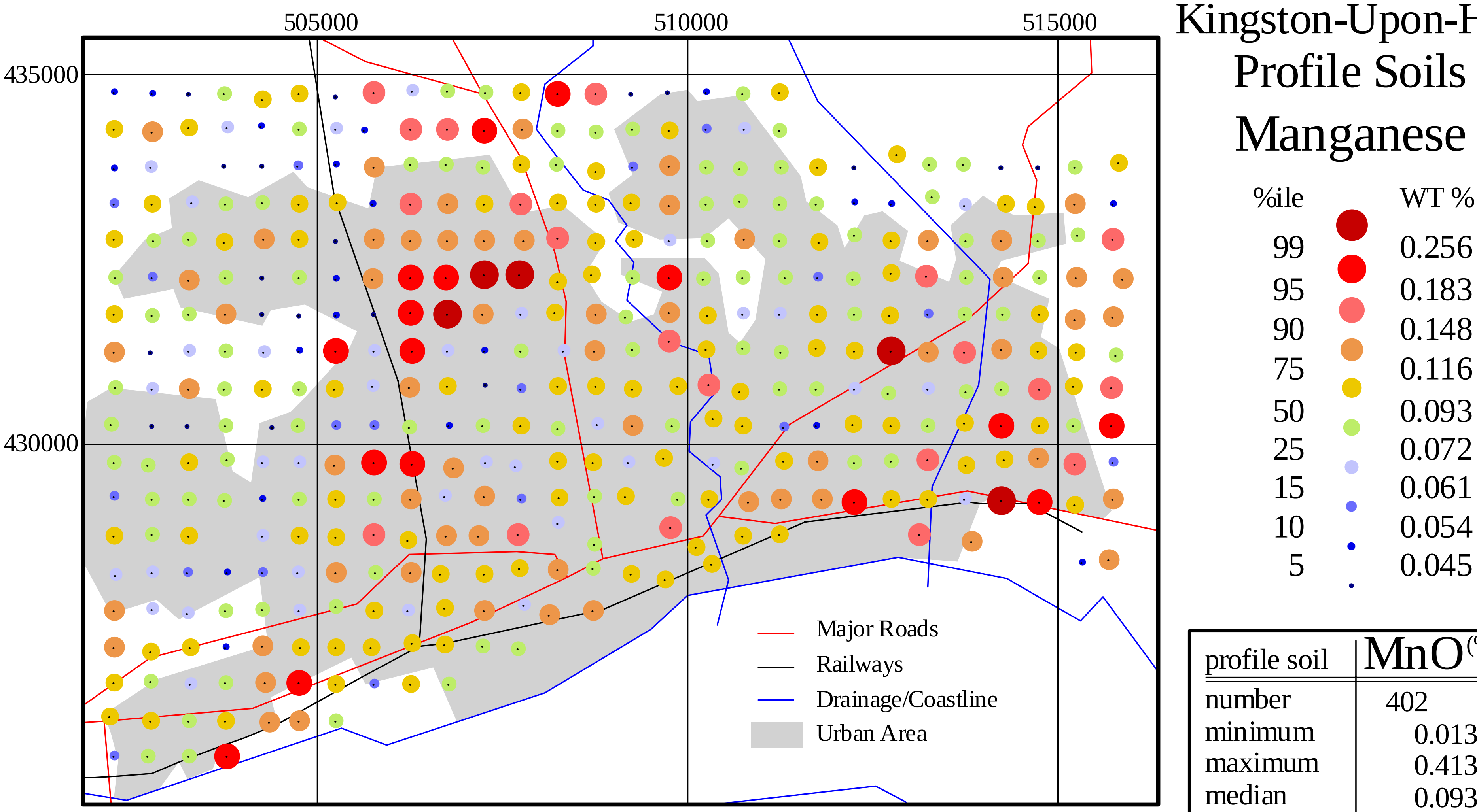
Kingston-Upon-Hull Surface Soils Manganese



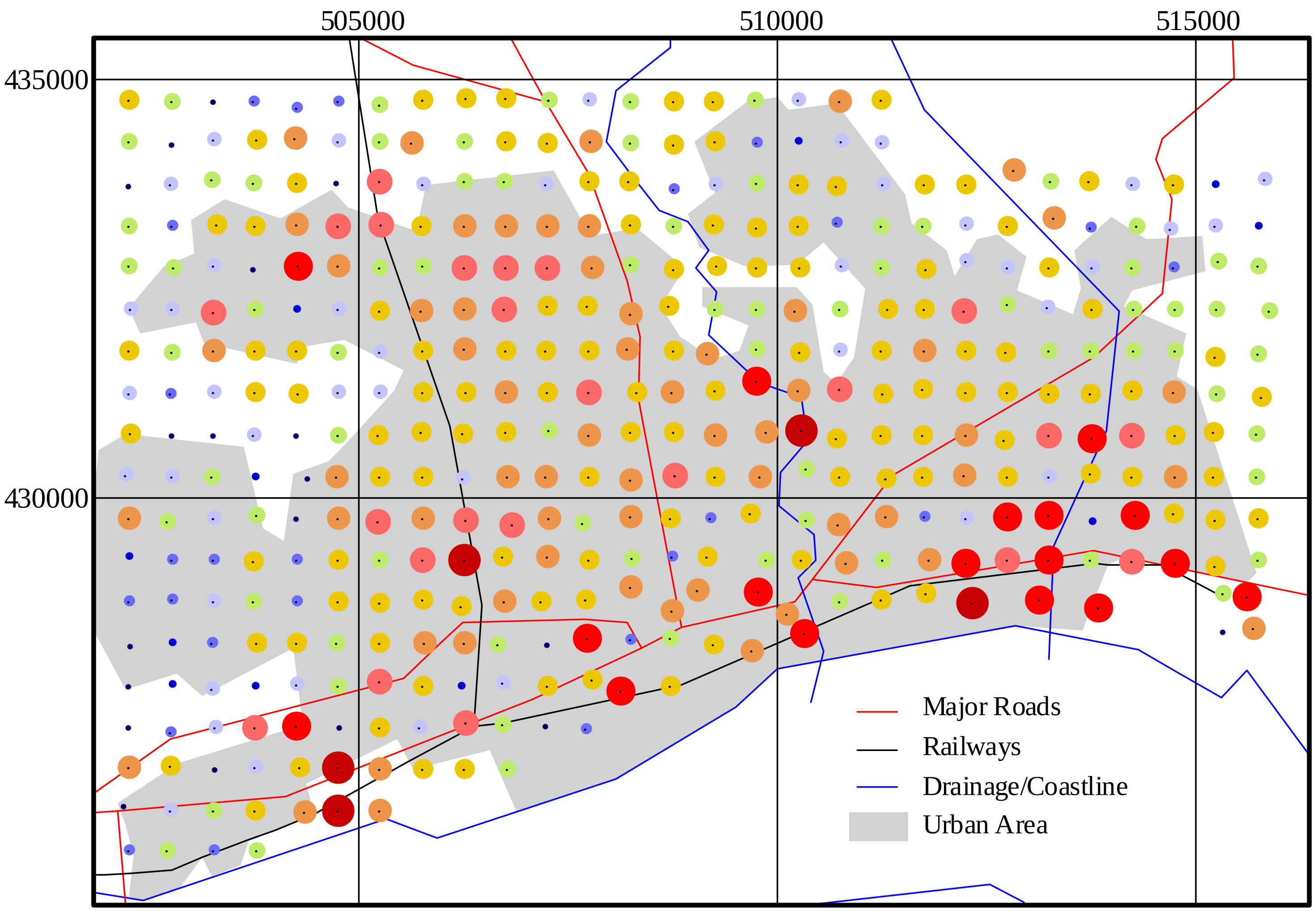
%ile	WT %
99	0.203
95	0.129
90	0.114
75	0.095
50	0.077
25	0.061
15	0.054
10	0.048
5	0.042

surface soil	MnO (%)
number	409
minimum	0.017
maximum	0.338
median	0.077
mean	0.081

Kingston-Upon-Hull Profile Soils Manganese



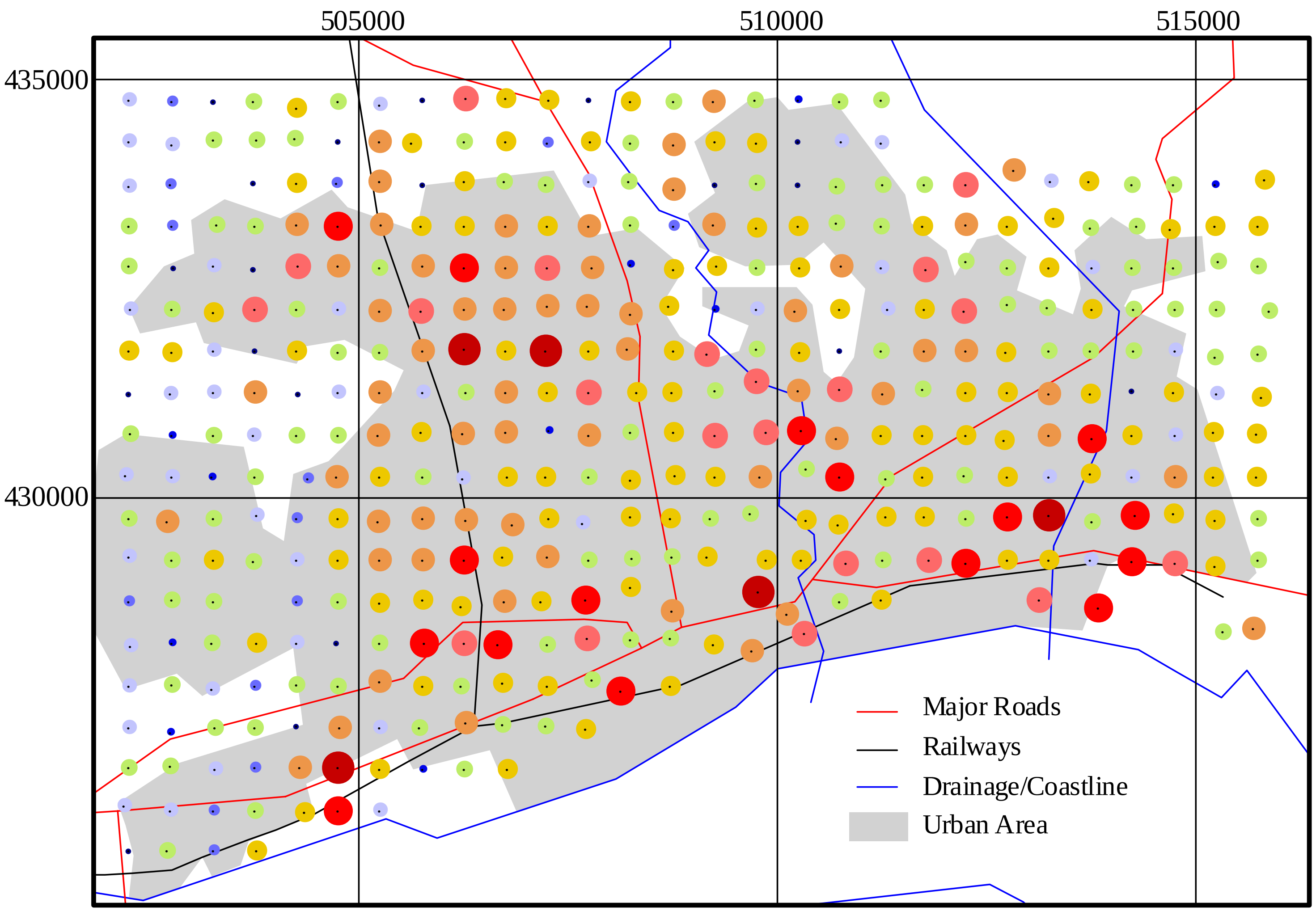
profile soil	MnO (%)
number	402
minimum	0.013
maximum	0.413
median	0.093
mean	0.099



Kingston-Upon-Hull Surface Soils Molybdenum

%ile	ppm
99	11.0
95	5.7
90	4.4
75	3.4
50	2.7
25	2.3
15	2.1
10	1.9
5	1.8

surface soil	Mo (ppm)
number	409
minimum	1.3
maximum	21.0
median	2.7
mean	3.1

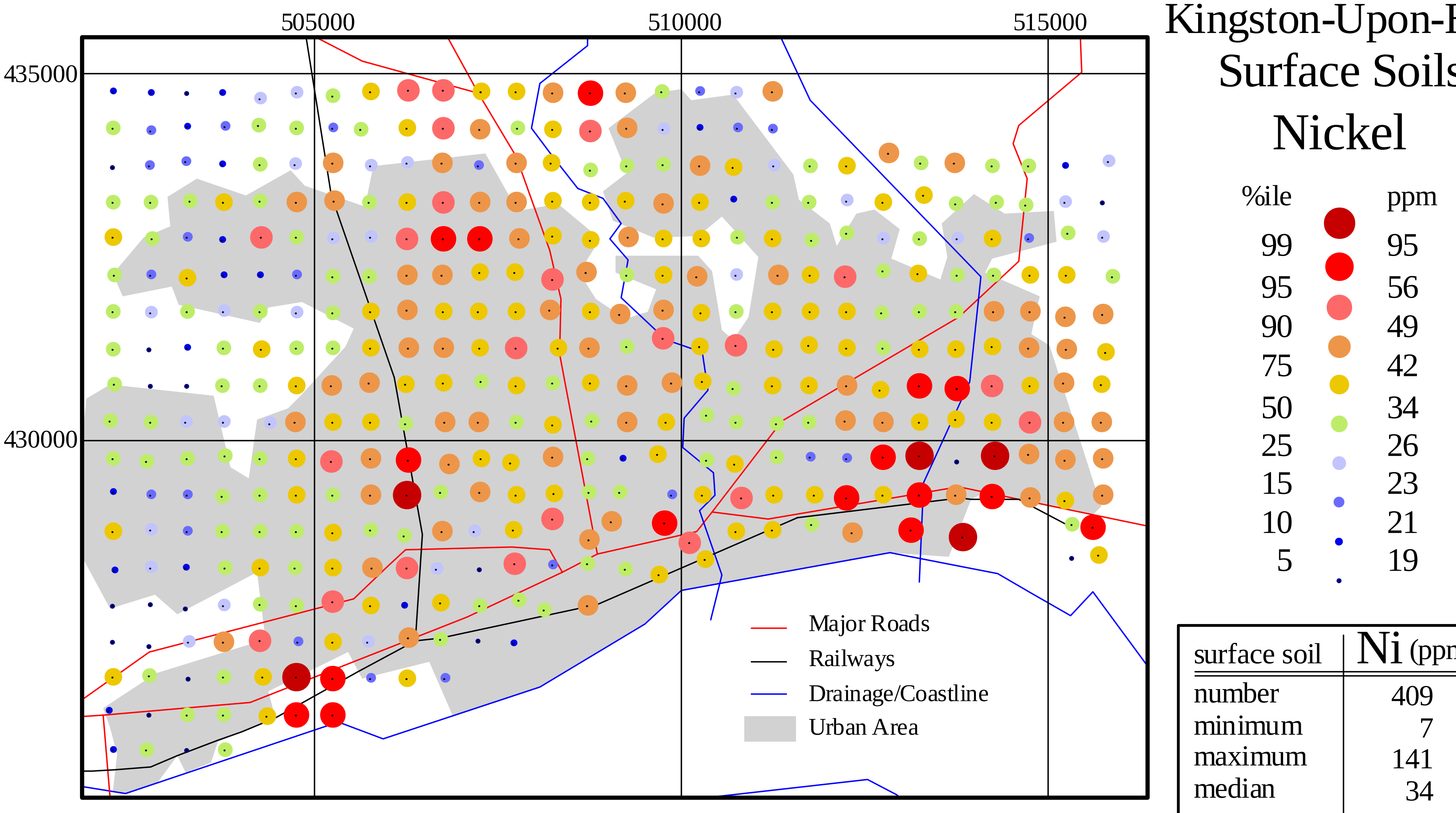


Kingston-Upon-Hull Profile Soils Molybdenum

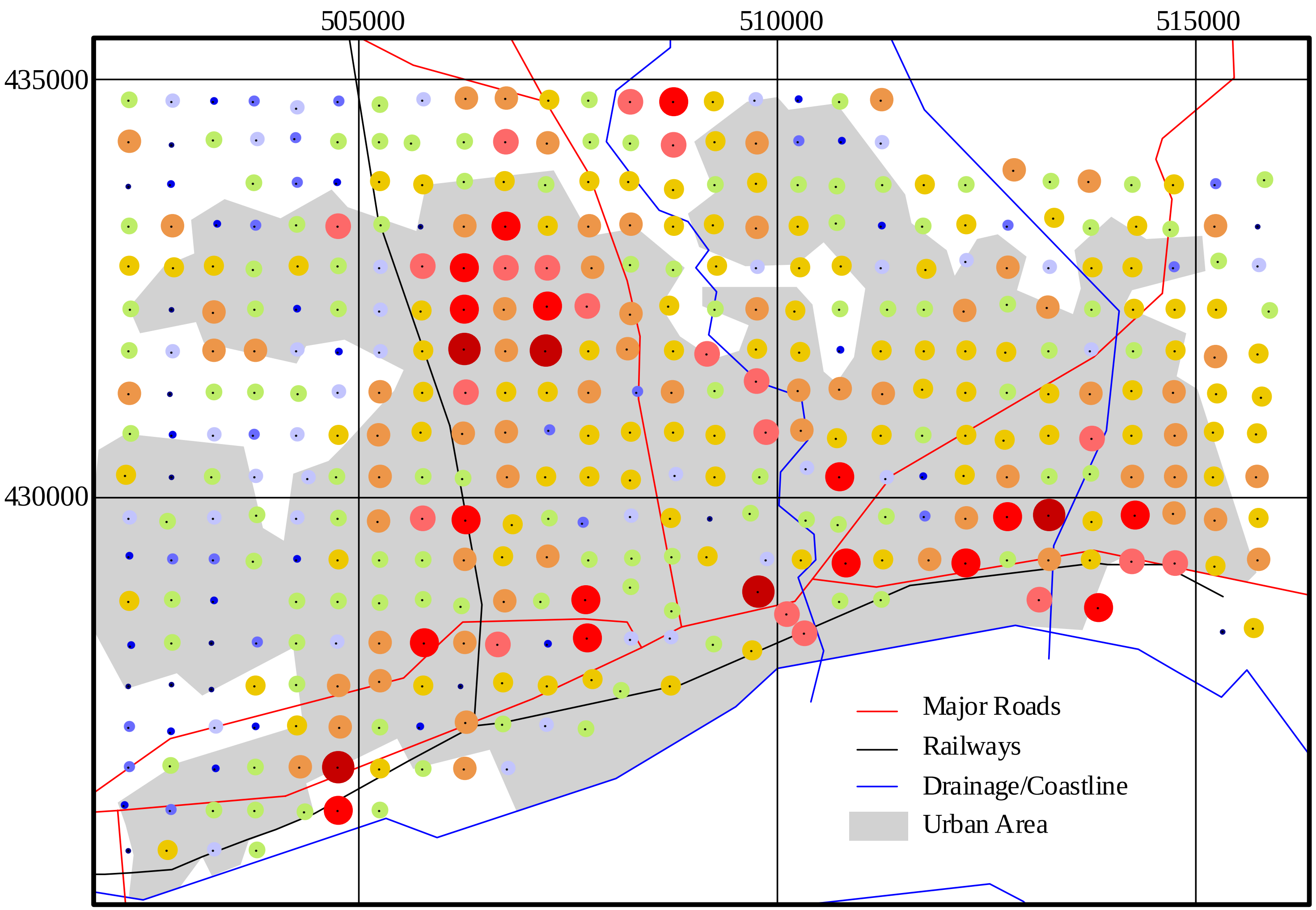
%ile	ppm
99	21.5
95	7.9
90	5.4
75	3.5
50	2.5
25	1.8
15	1.6
10	1.5
5	1.4

profile soil	Mo (ppm)
number	402
minimum	0.9
maximum	42
median	2.5
mean	3.4

Kingston-Upon-Hull Surface Soils Nickel



surface soil	Ni (ppm)
number	409
minimum	7
maximum	141
median	34
mean	36



Kingston-Upon-Hull Profile Soils

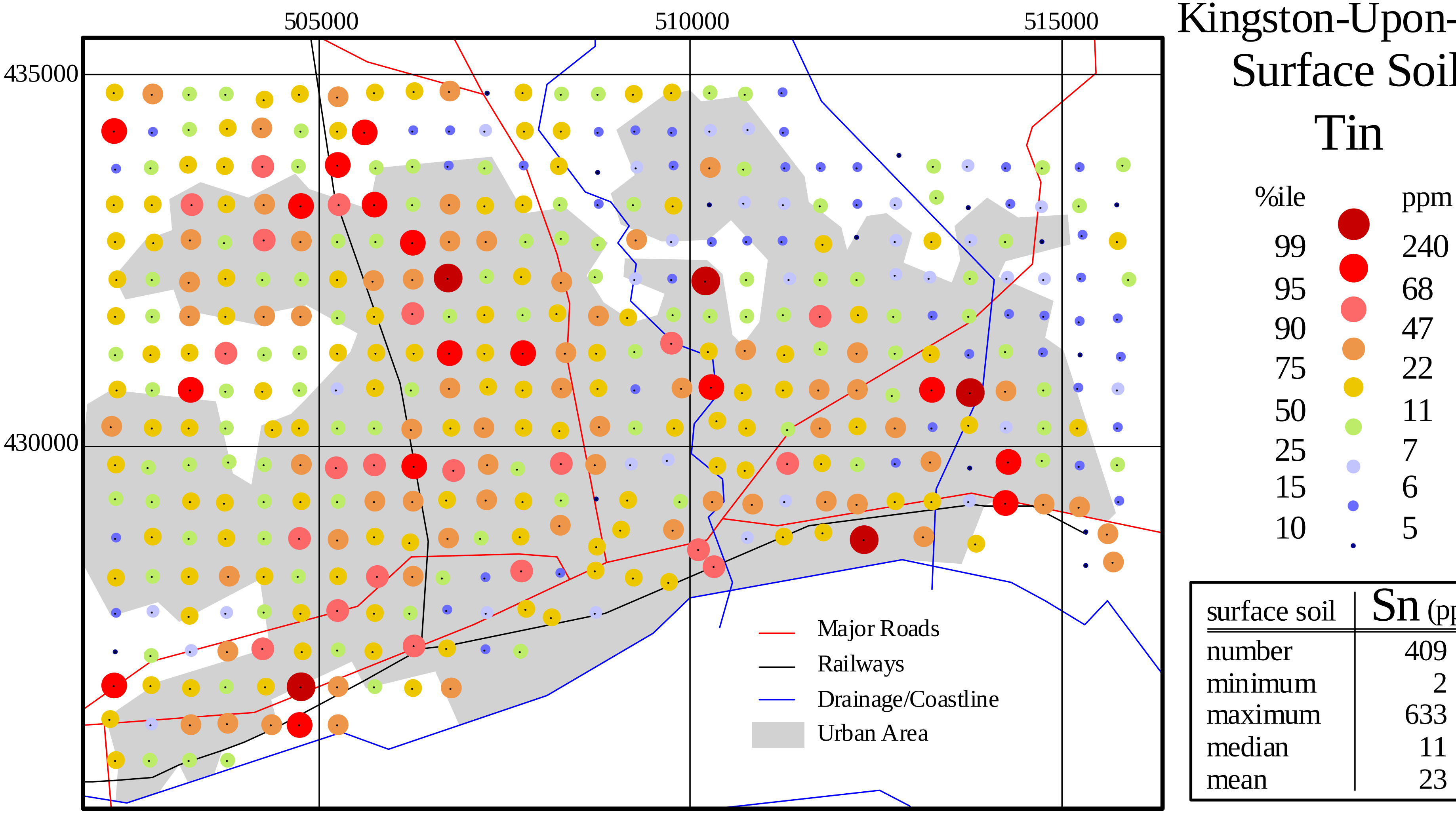
Nickel

%ile	ppm
99	112
95	62
90	55
75	45
50	37
25	29
15	26
10	24
5	20

profile soil	Ni(ppm)
number	402
minimum	11
maximum	204
median	37
mean	40

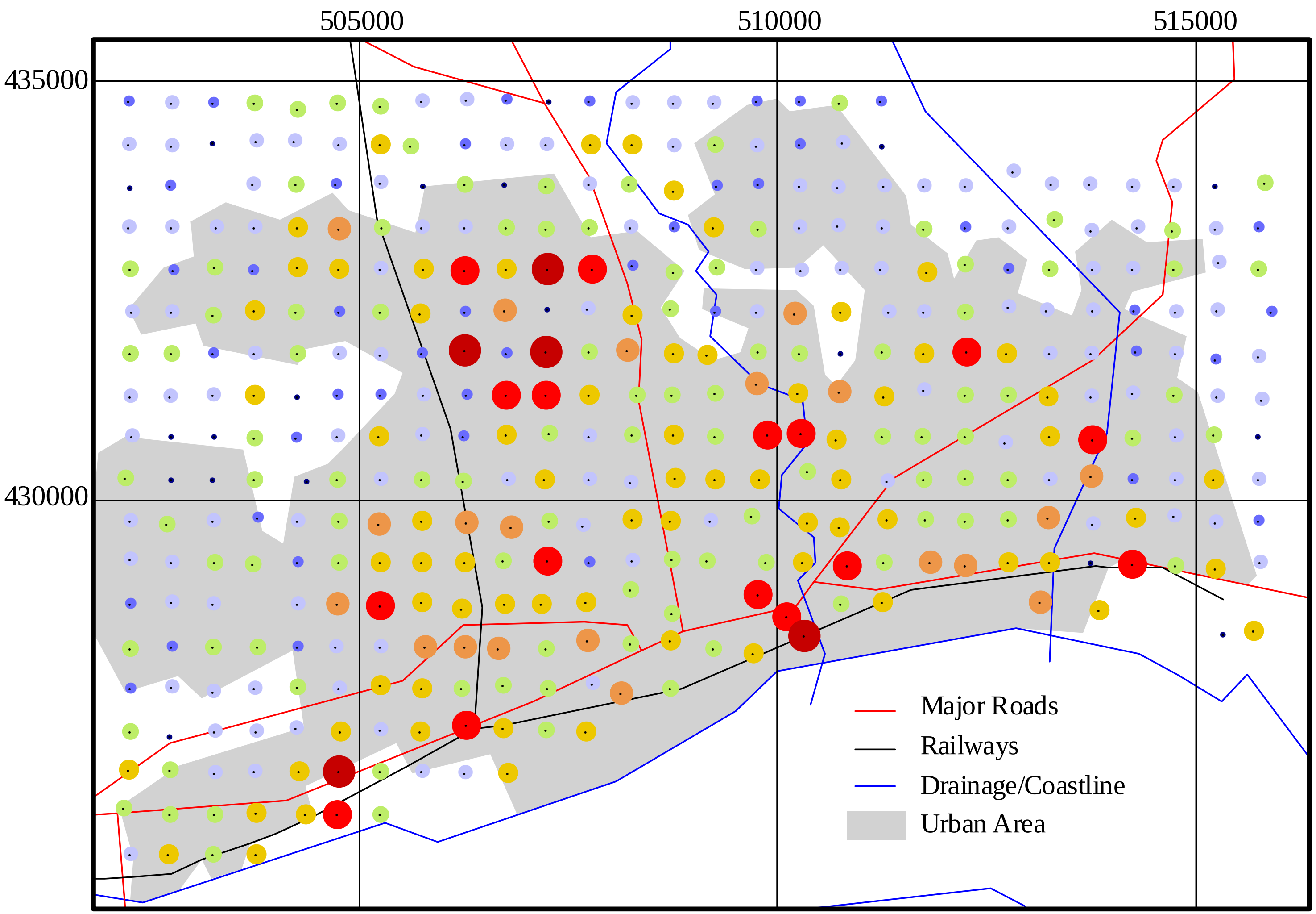
Kingston-Upon-Hull Surface Soils

Tin



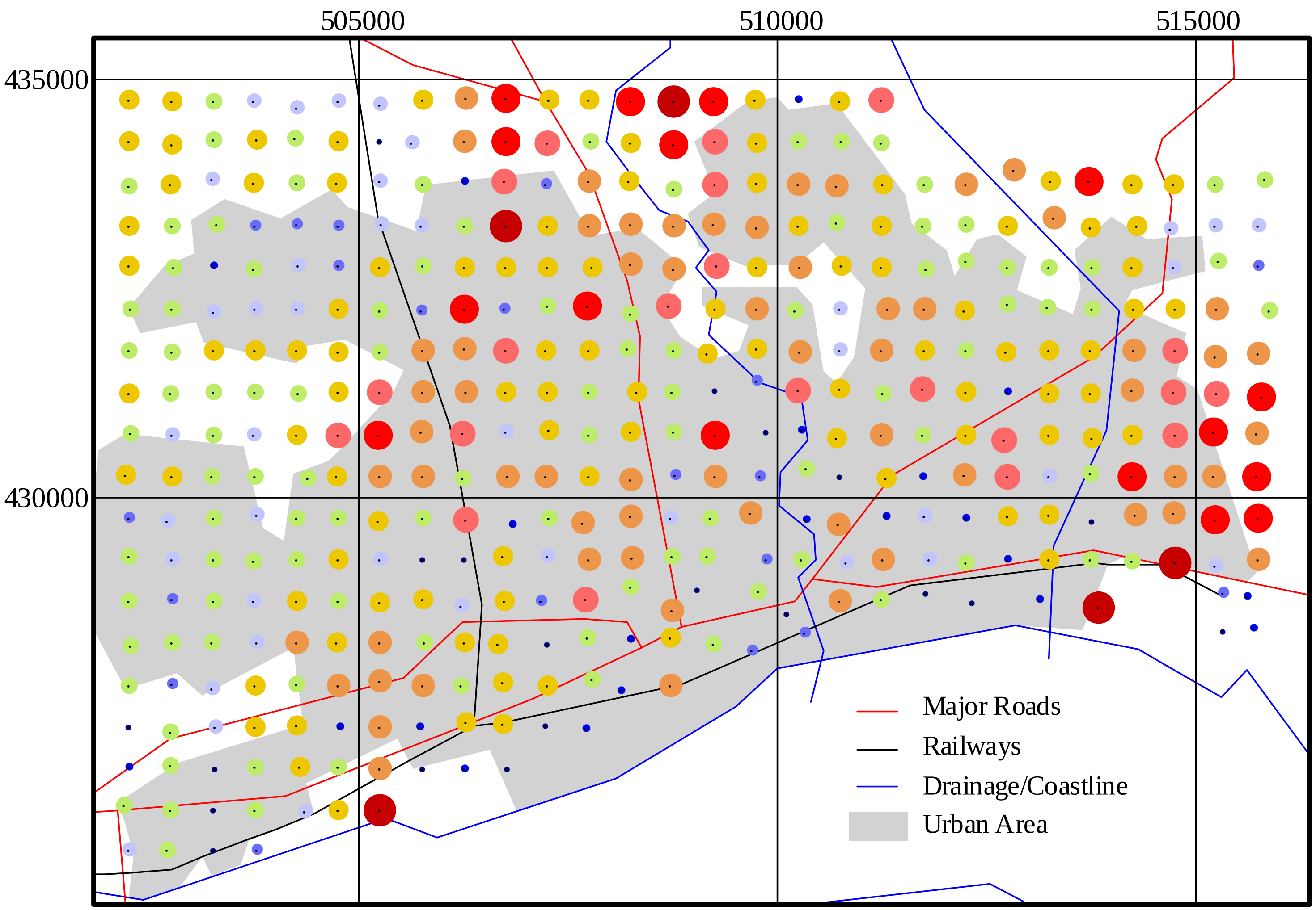
surface soil	Sn (ppm)
number	409
minimum	2
maximum	633
median	11
mean	23

Kingston-Upon-Hull
Profile Soils
Tin



%ile	ppm
99	248
95	81
90	45
75	16
50	7
25	4
15	3

profile soil	Sn (ppm)
number	402
minimum	1
maximum	1394
median	7
mean	24



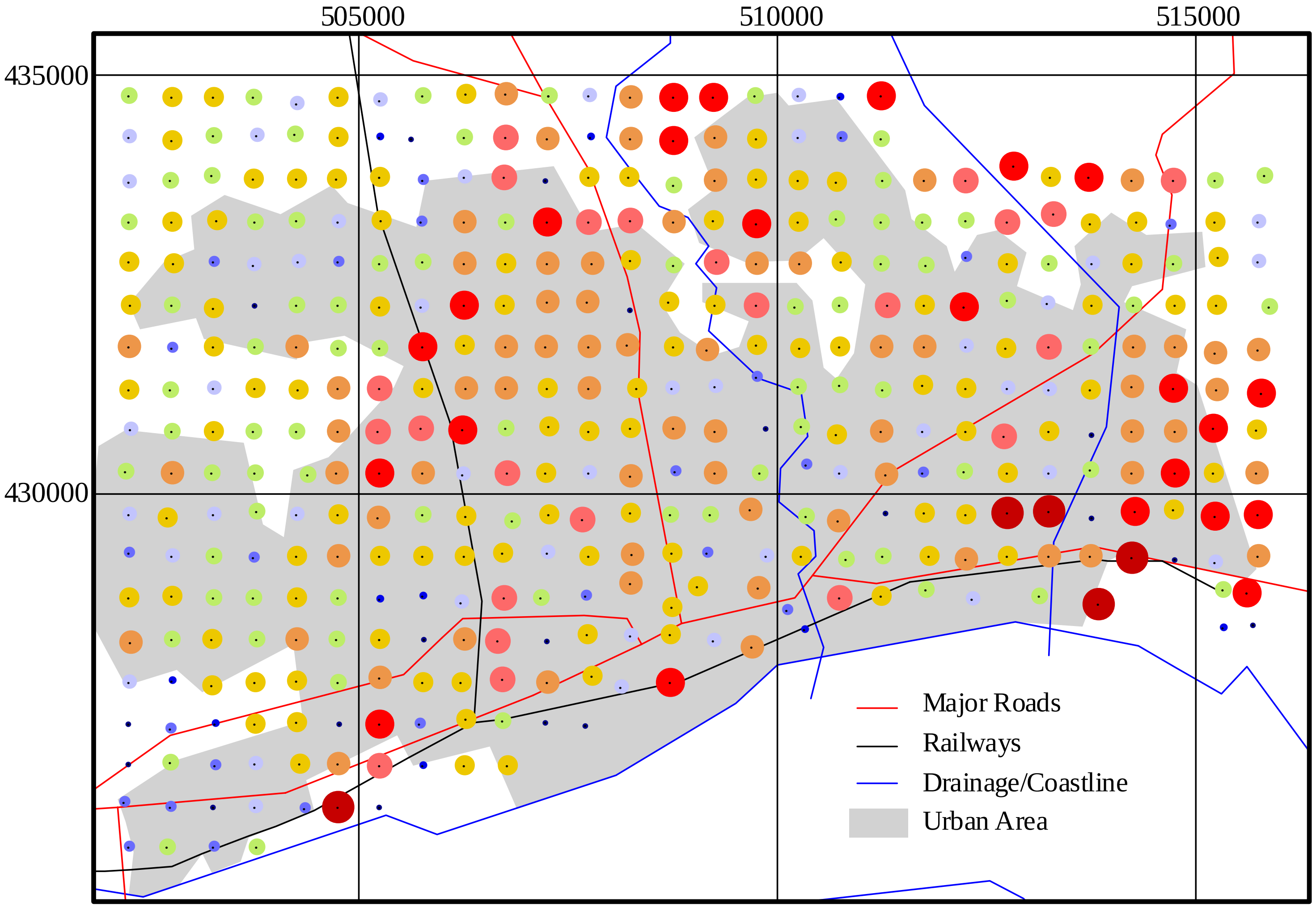
Kingston-Upon-Hull Surface Soils Titanium

%ile	WT %
99	1.085
95	1.007
90	0.969
75	0.849
50	0.714
25	0.622
15	0.561
10	0.511
5	0.445

surface soil	TiO_2 (%)
number	409
minimum	0.168
maximum	1.404
median	0.714
mean	0.728

Titanium was not determined in the Profile Soils

Kingston-Upon-Hull
Surface Soils
Uranium



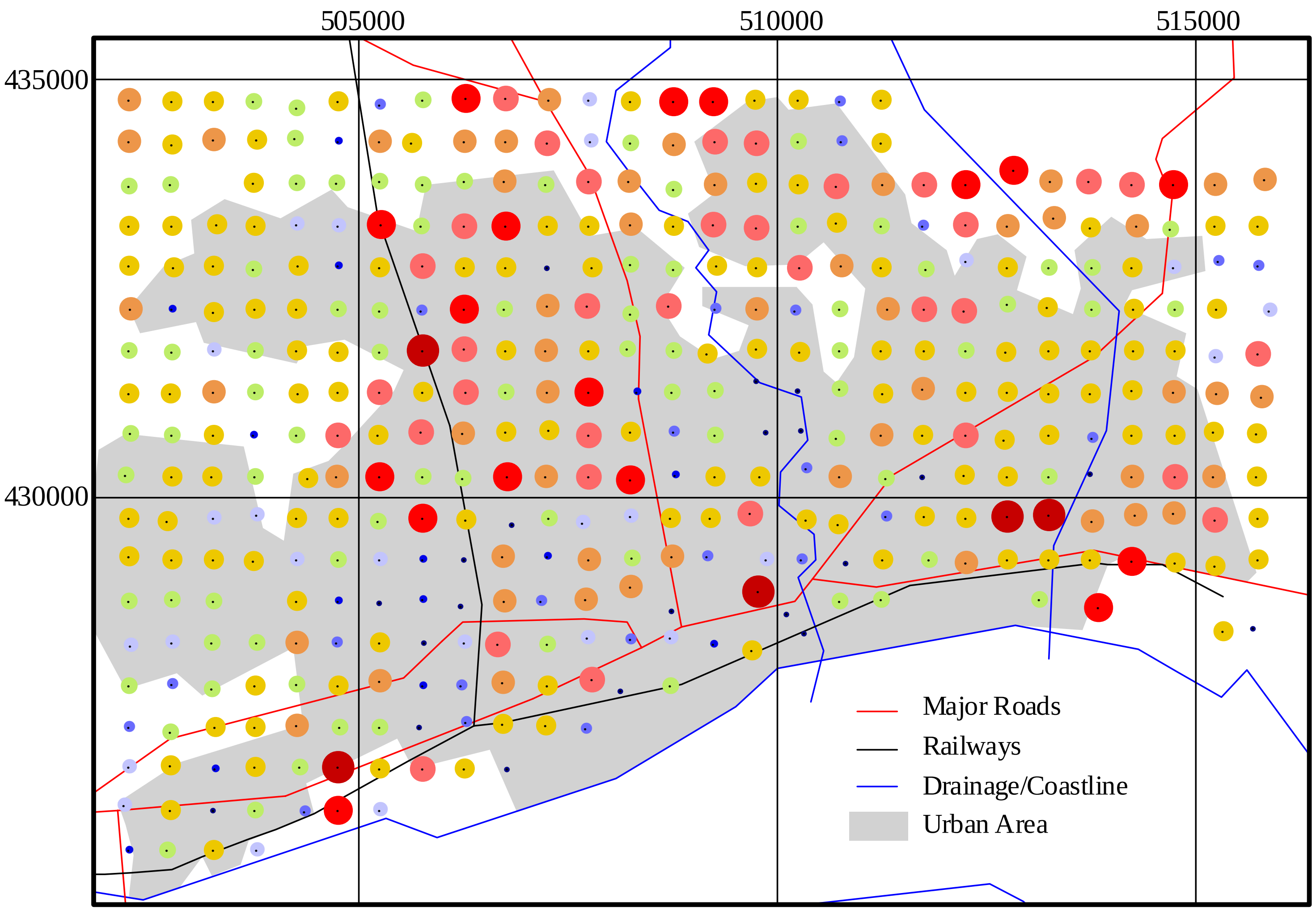
%ile	ppm
99	4.28
95	3.00
90	2.80
75	2.40
50	2.00
25	1.70
15	1.50
10	1.30
5	1.10

surface soil	U(ppm)
number	409
minimum	0.25*
maximum	6.0
median	2.0
mean	2.08

* minimum value quoted as half detection limit

Kingston-Upon-Hull Profile Soils

Uranium

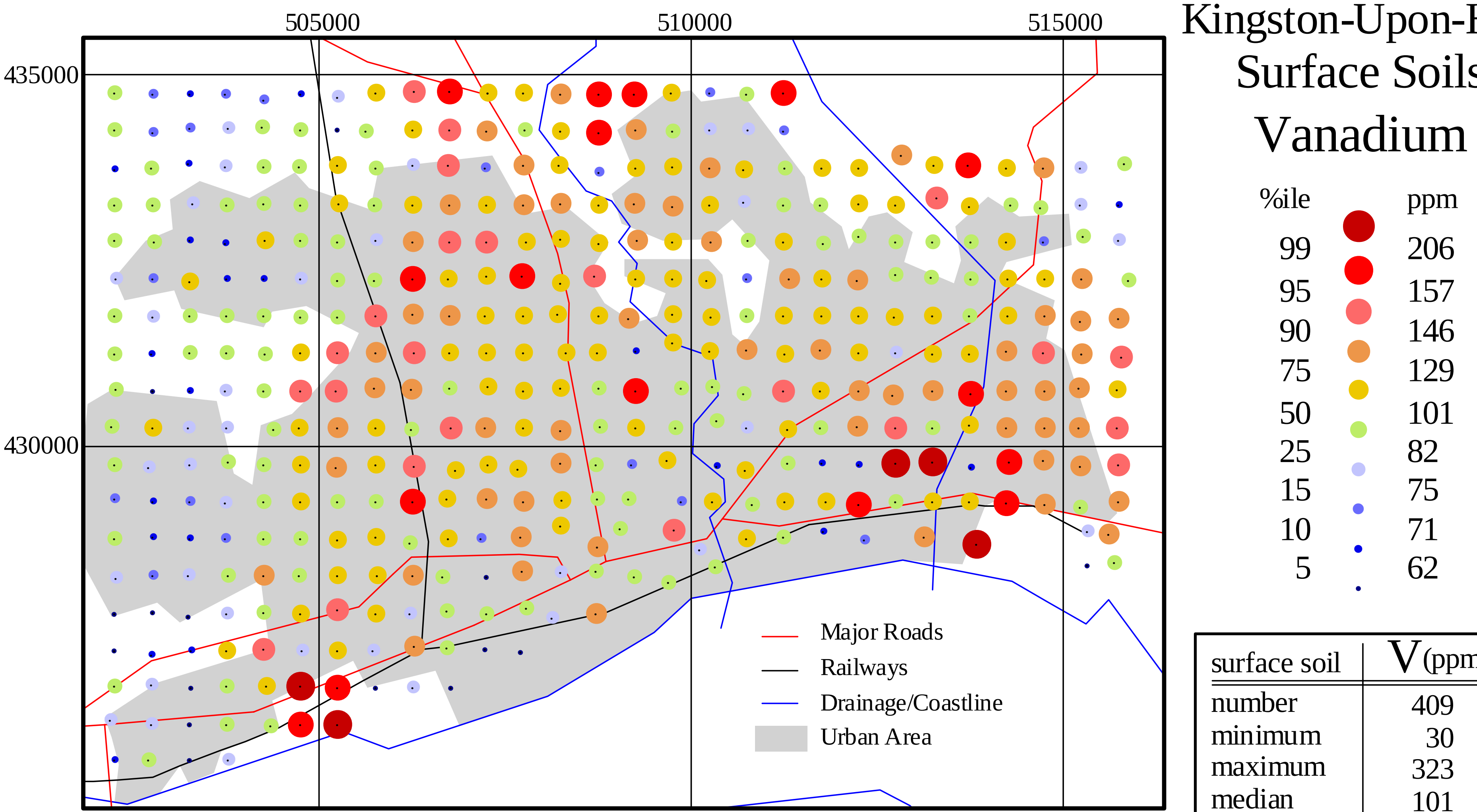


%ile	ppm
99	5.0
95	3.9
90	3.4
75	3.1
50	2.7
25	2.4
15	2.3
10	2.1
5	1.71

profile soil	U(ppm)
number	402
minimum	0.25*
maximum	6.7
median	2.7
mean	2.77

* minimum value quoted as half detection limit

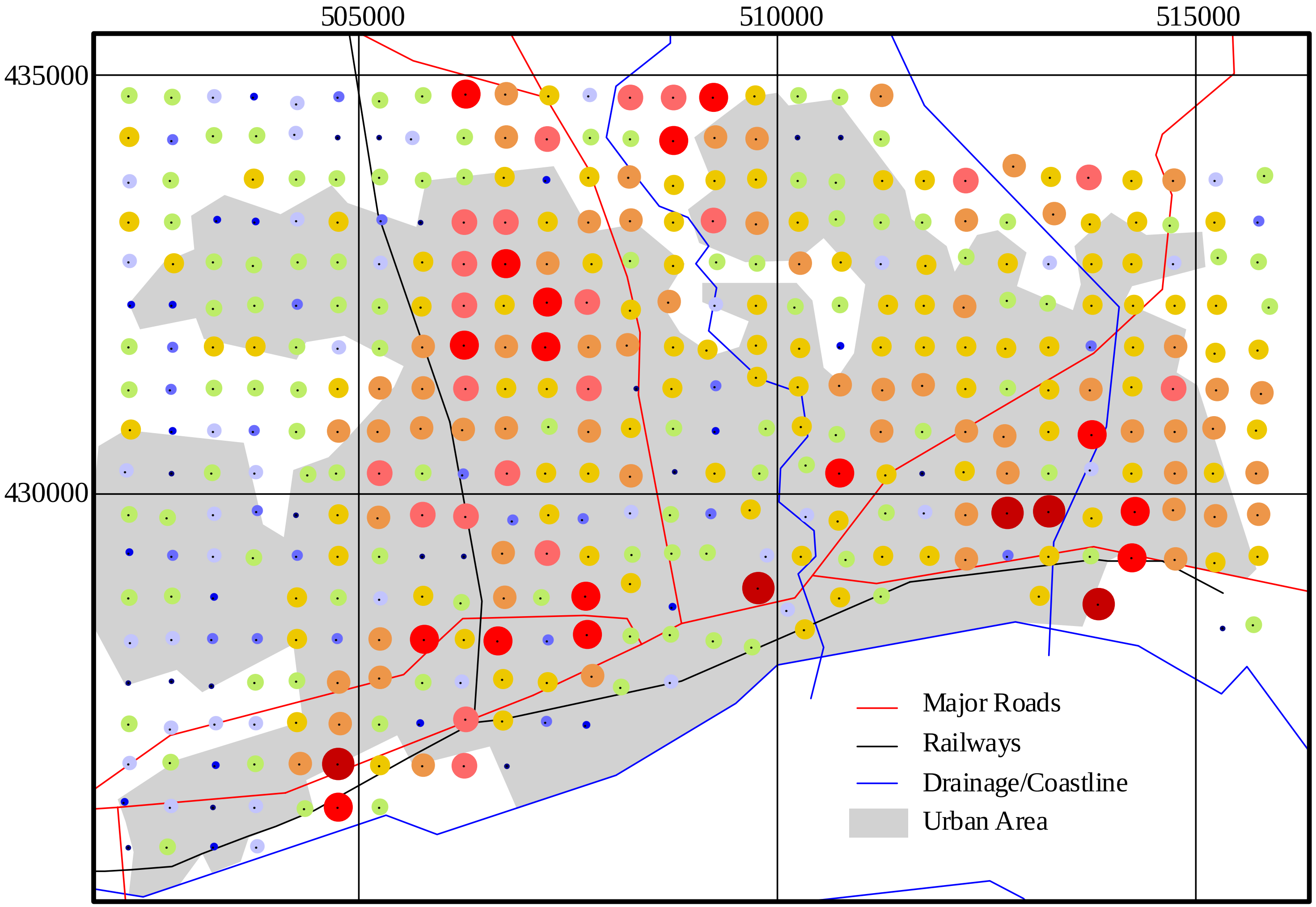
Kingston-Upon-Hull Surface Soils Vanadium



surface soil	V (ppm)
number	409
minimum	30
maximum	323
median	101
mean	107

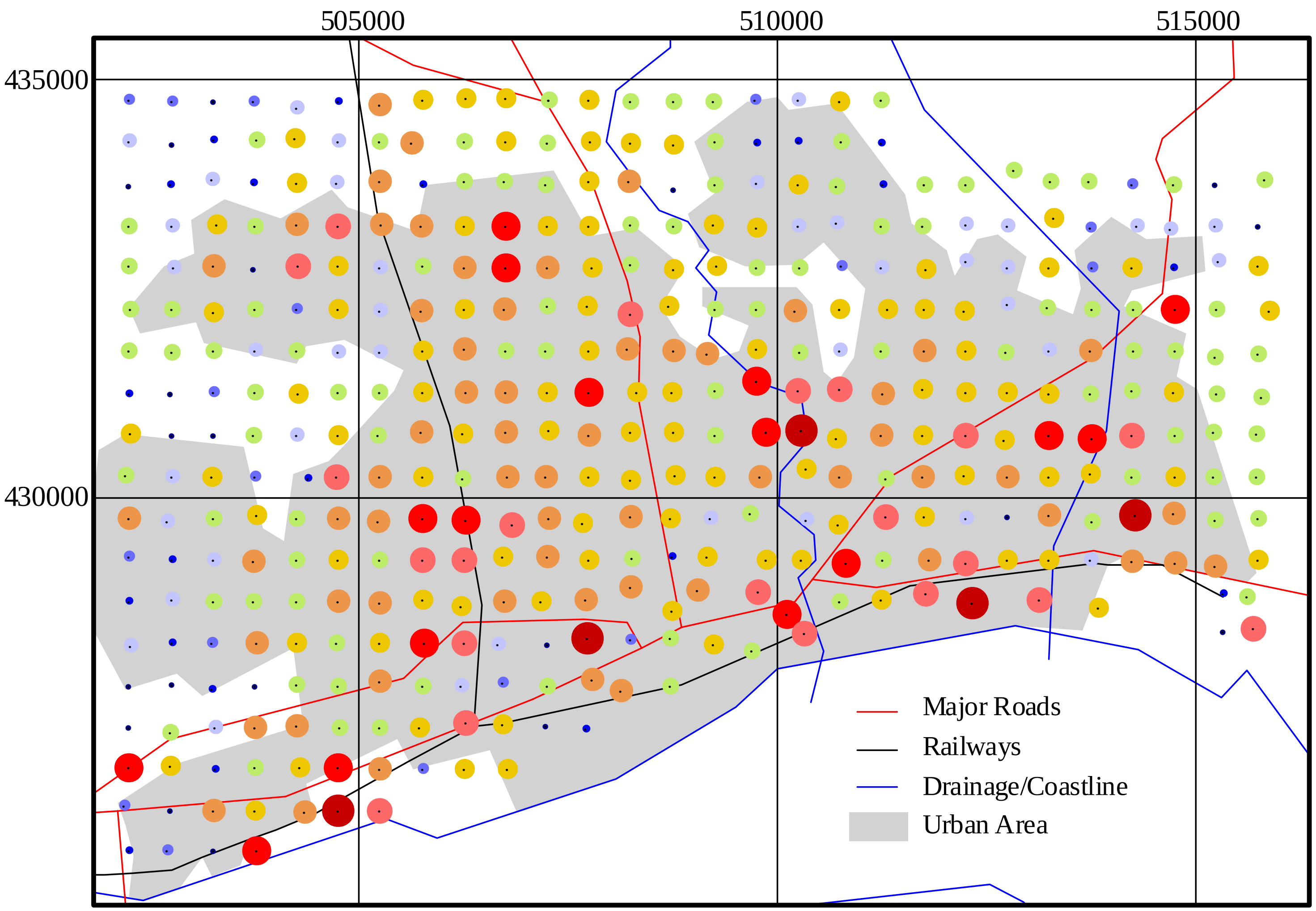
Kingston-Upon-Hull Profile Soils

Vanadium



%ile	ppm
99	289
95	166
90	156
75	137
50	109
25	90
15	82
10	77
5	68

profile soil	V(ppm)
number	402
minimum	39
maximum	346
median	109
mean	116

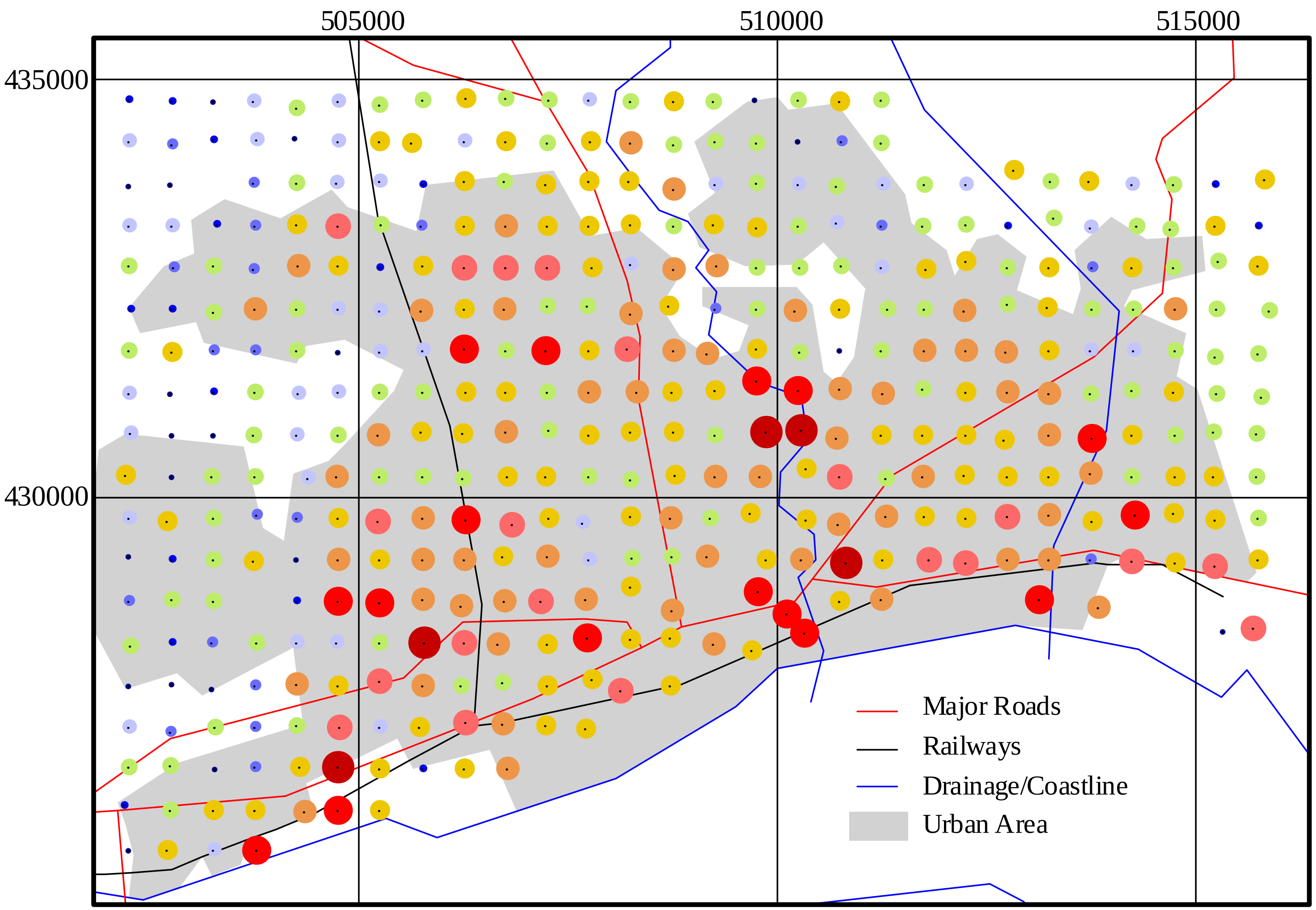


Kingston-Upon-Hull Surface Soils

Zinc

%ile	ppm
99	1769
95	623
90	415
75	221
50	132
25	96
15	80
10	72
5	65

surface soil	Zn (ppm)
number	409
minimum	20
maximum	5800
median	132
mean	229



Kingston-Upon-Hull Profile Soils

Zinc

%ile	ppm
99	1991
95	587
90	370
75	191
50	117
25	85
15	73
10	67
5	61

profile soil	Zn (ppm)
number	402
minimum	34
maximum	4358
median	117
mean	220