



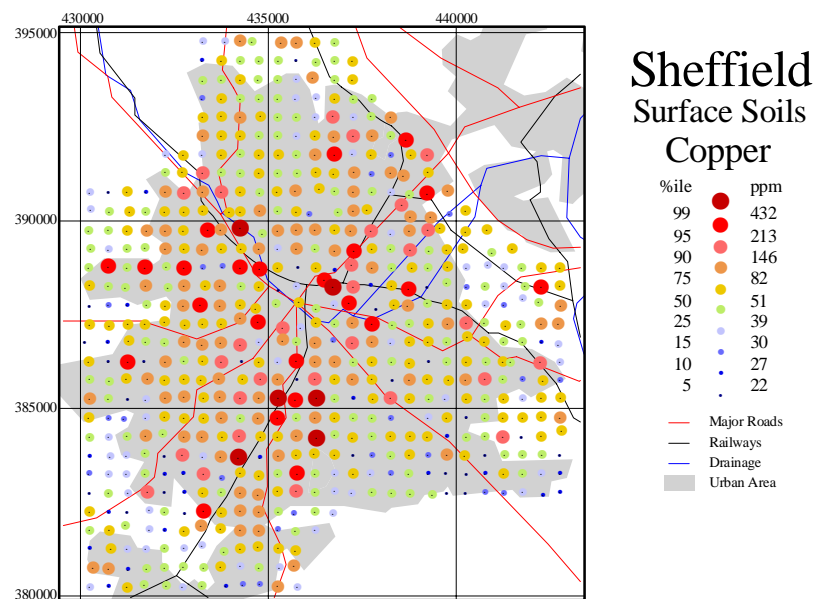
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Geochemical baseline data for the urban area of Sheffield

Urban Geoscience and Geological Hazards Programme

Internal Report IR/02/084



BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/02/084

Geochemical baseline data for the urban area of Sheffield

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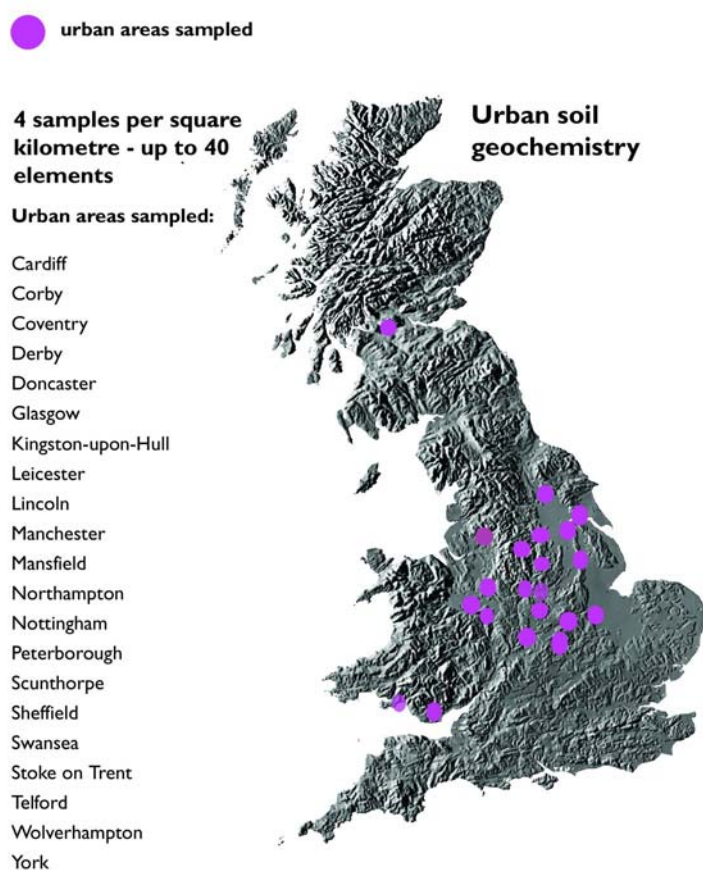
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The soil geochemical data presented in this report (and other urban reports from this series) are from individual sites which were sampled as part of a baseline geochemical survey. The results should only be used to set a regional context, not as the 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 Sheffield 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 Sheffield 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 Sheffield.

Table 1 Summary of Sheffield soil sampling information

Date Sampled:	Summer 1996
Area Sampled:	160 km ² (min E 430000; max E 442000; min N 380000; and max N 395000)
Number of Samples:	575 surface and 542 profile soils
Elements determined by XRFs: (<i>elements in italics determined in surface samples only</i>)	<i>Al₂O₃, CaO, SiO₂, P₂O₅, K₂O, TiO₂, MgO, Fe₂O₃, MnO, Cr, Mo, Pb, Zn, As, Cd, Cu, Ni, Sb, U, Ba, Co, Sn, V.</i>

1 Introduction

This report summarises the results and methodology of a soil geochemical survey of the urban area of Sheffield, 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 much 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 environmental baselines 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.

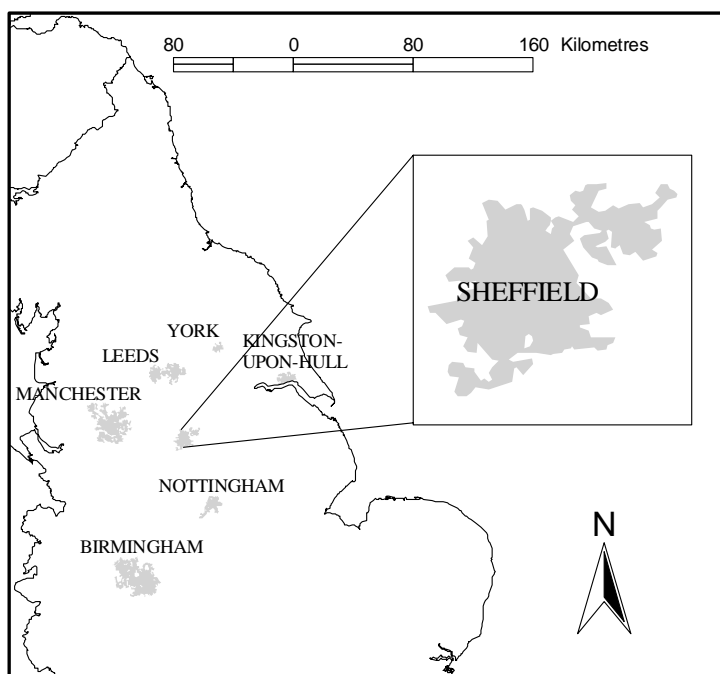


Figure 1 Location map for Sheffield

Sheffield is situated in the county of South Yorkshire, just to the east of the Peak District National Park (Figure 1). It has had a varied industrial history related predominantly to coal mining and steel production.

The distributions of trace metals in the surface environment of Sheffield are described in this report in the context of present and historical land use. The concentrations of the 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

Sheffield has a past history of iron working and coal mining. In 1161, ironstone began to be quarried in a crude form from the Coal Measures. By the 14th century, the making of cutlery was becoming established. The local phosphorus-rich ores were found to be of little use in making steel; therefore, this led to the importing of iron and steel from elsewhere, such as continental Europe. Sheffield developed as a large conurbation due to its topography; it is situated in a valley, becoming a meeting place for the many rivers that feed into the drainage basin. During the Industrial Revolution, the rivers were used to power machinery and water mills. Other nearby towns such as Rotherham, Renishaw and Staveley also developed this heavy industry. The coal industry in Sheffield did not develop until the late 17th and early 18th century when steam engines were invented, helping to transport the coal from site, to many areas of the U.K. In the late 20th century there were many pit closures in Sheffield and all over the U.K. due to poor economic conditions.

From the British Geological Survey Geoscience Data Index¹ it can be seen that Sheffield has many abandoned quarries owned by brickwork and reclamation companies. There are also many waste disposal sites (some containing toxic oil and sludge) around the city and its suburbs; many of the sites have the potential to be a risk to groundwater.

2.2 AREA SAMPLED

An area of 160 km² was surveyed during the summer of 1996, in which a total of 575 surface soils (0-15 cm depth) and 542 profile soils (30-45 cm depth) were sampled (Table 1). This extends from British National Grid (BNG) grid references 430000 m east to 442000 m east and from 380000 m north to 395000 m north, and includes the areas of Sheffield city centre and its suburbs. The survey area is shown in Figure 2 and Figure 3. 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 Sheffield area was obtained from the BGS memoirs for the area (Eden et al., 1957). The area sampled is entirely underlain by Carboniferous deposits of Westphalian and Namurian age. The geology here is complex compared to other urban centres sampled, due to the highly faulted and folded nature of the rocks, leading to discontinuous outcrops. To the east of the city centre, the Middle Coal Measures Formation outcrops; this is composed of sandstone interlayered with undifferentiated cyclic sediments and is Westphalian in age. Underlying the city centre is the Lower Coal Measures Formation composed of sandstone interlayered with undifferentiated cyclic sediments, which are also Westphalian in age. To the west of the city centre, rocks of the Millstone Grit Group outcrop; these outcrops comprise the Rough Rock Formation, which is composed of sandstone; the Millstone Grit mudstone and the Red Mires Flagstone. The succession generally increases in age towards the west.

Quaternary deposits cover approximately 10 % of Sheffield. These are predominantly composed of silt alluvium, which infills the river valleys around and in the city of Sheffield. Small outcrops of river terrace deposits composed of sand and gravel also infill the valleys; peat and Diamicton Till appear in small deposits to the east and west of the city centre. The drift and solid geology can be seen in Figure 4 and Figure 5 respectively.

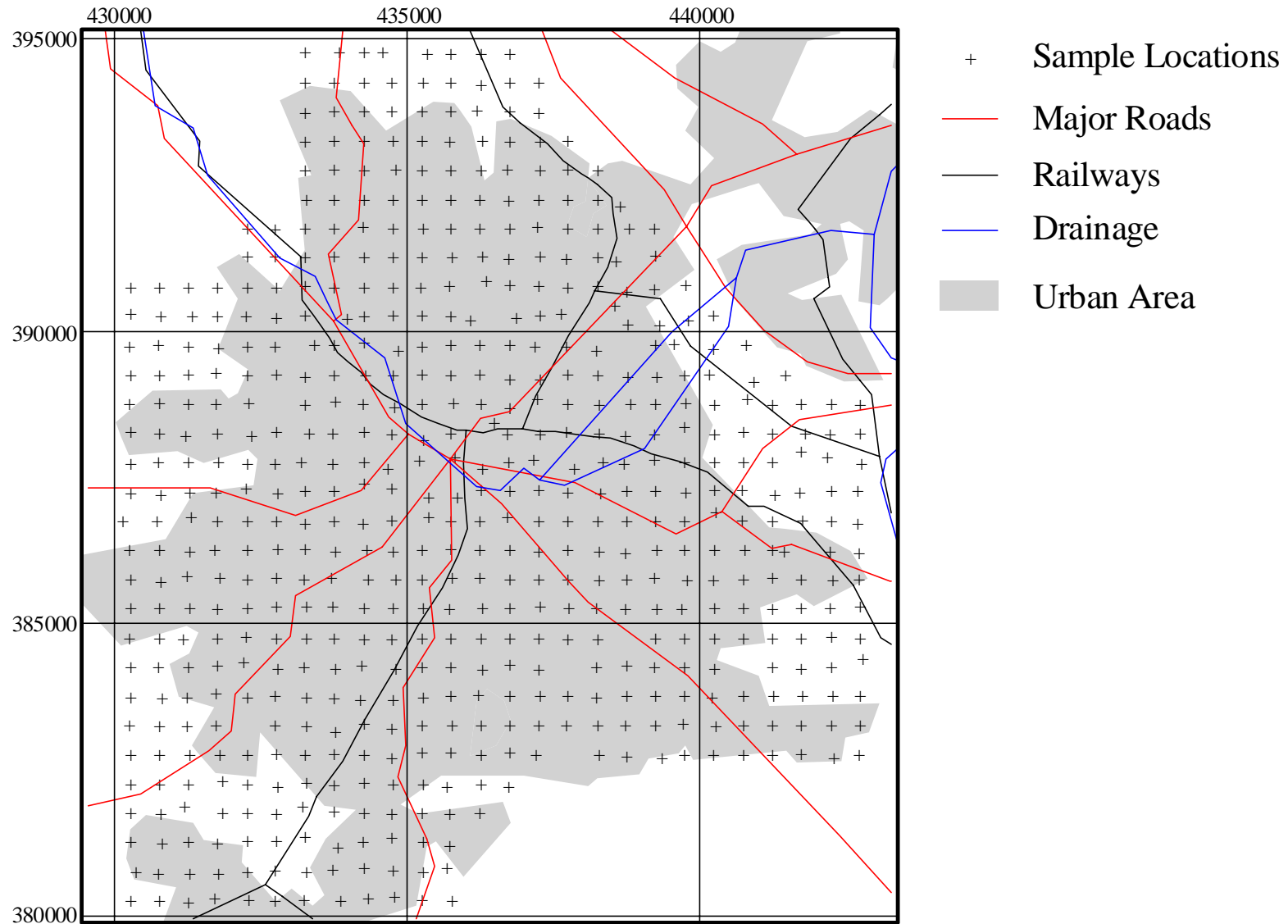


Figure 2 Map of Sheffield sampling area (Grid squares shown at 5 km intervals)

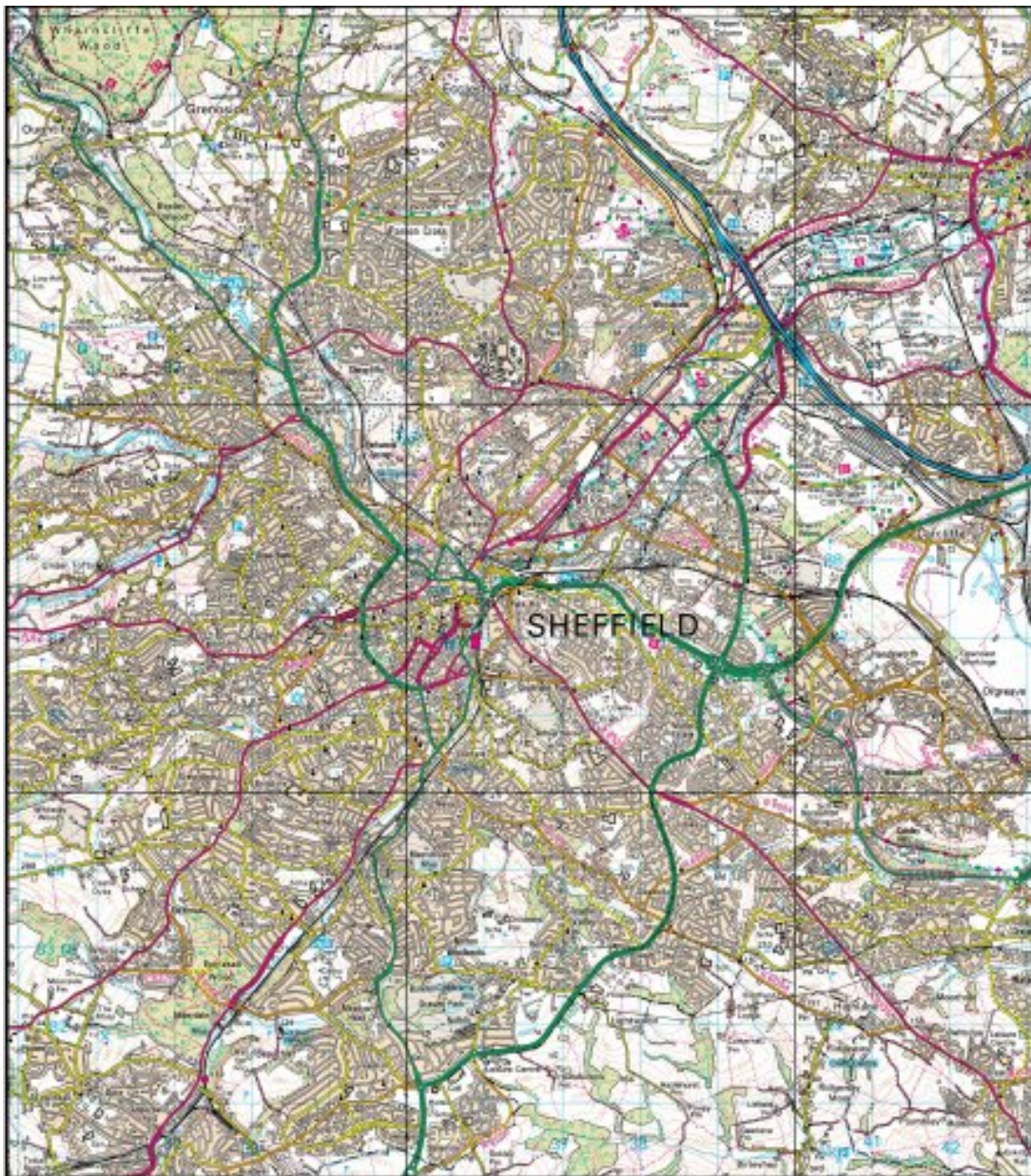


Figure 3 Topographical map of Sheffield sampling area (Grid squares shown at 5 km intervals)

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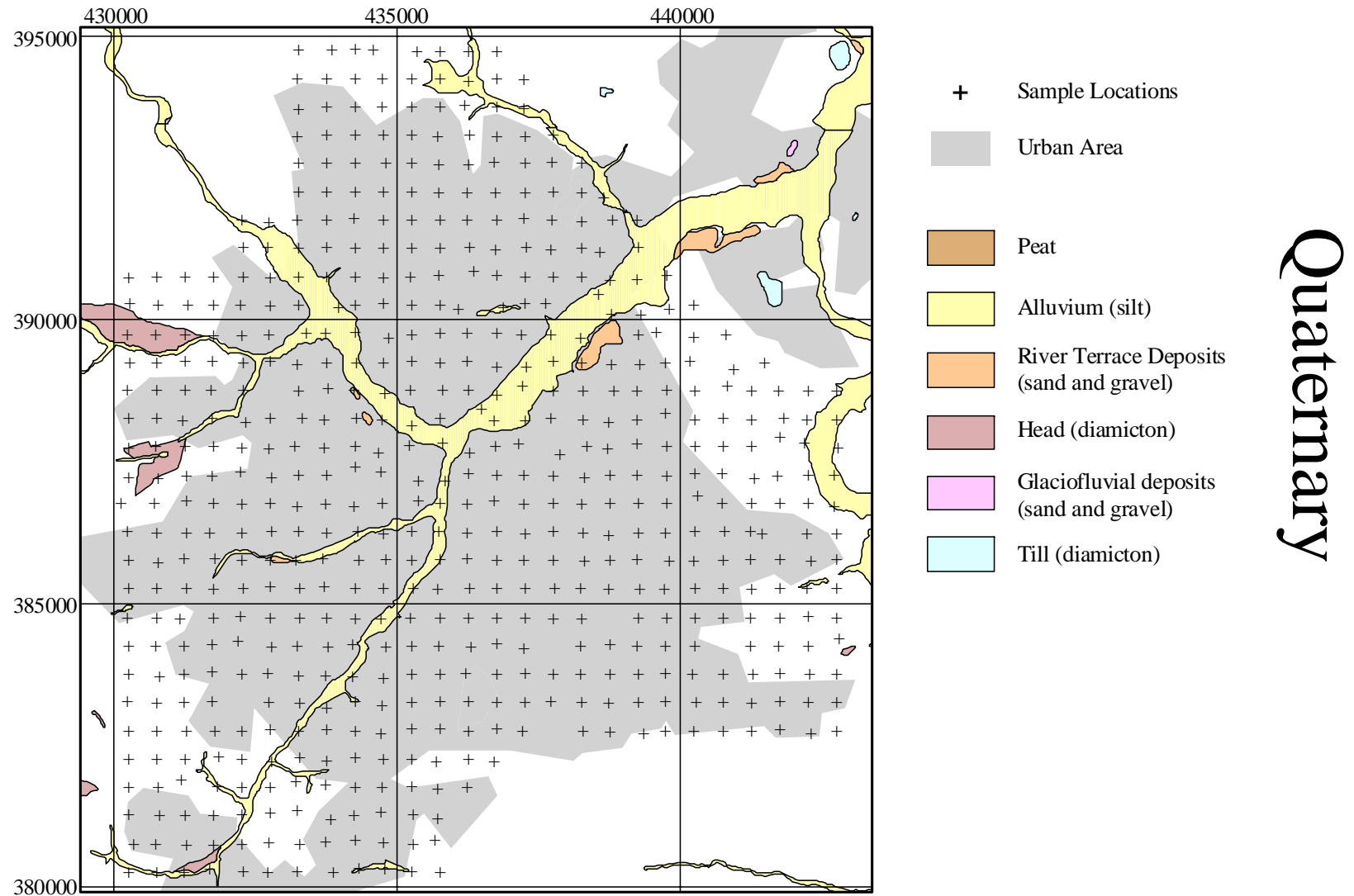


Figure 4 Drift cover of Sheffield and surrounding area (Grid squares shown at 5 km intervals)

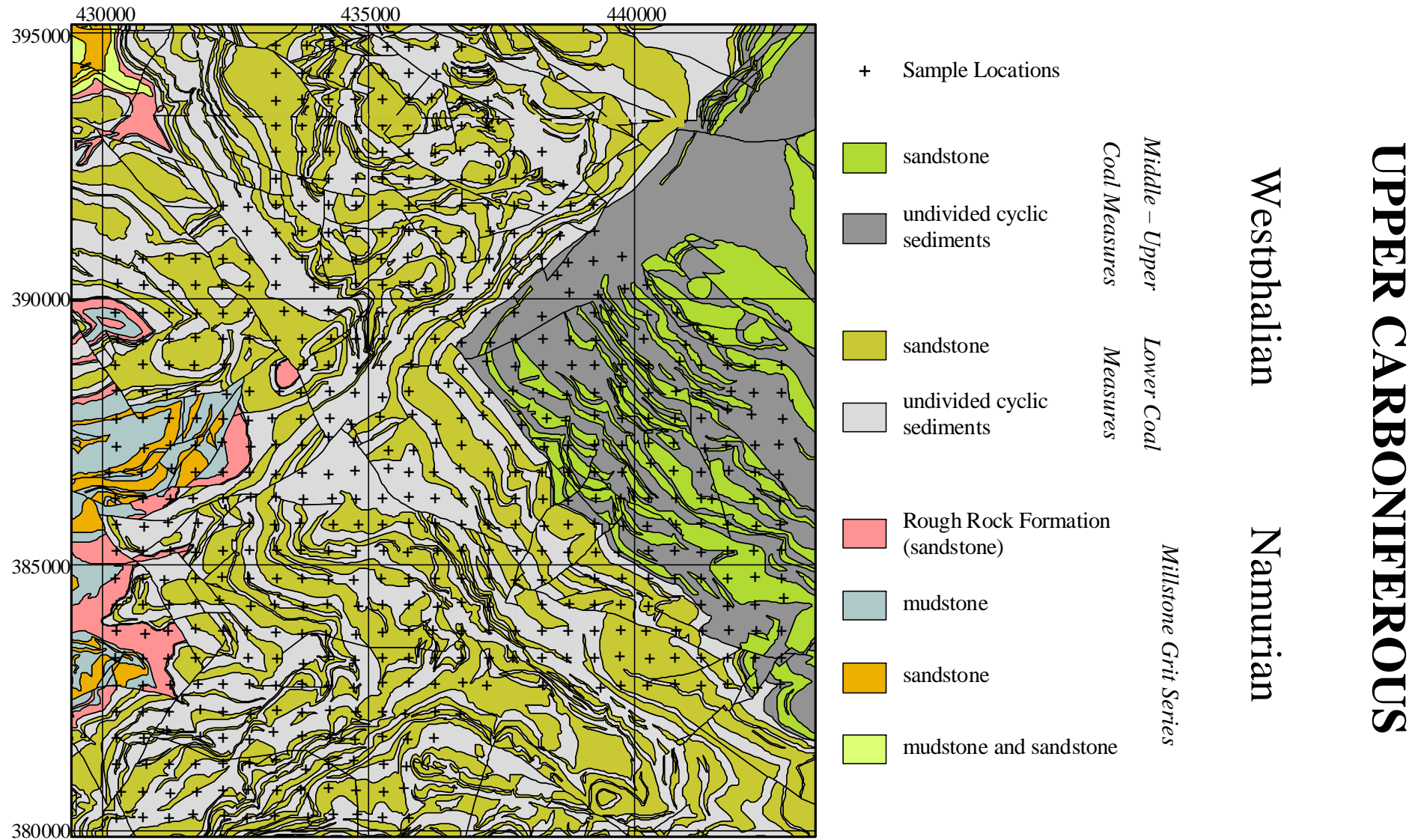


Figure 5 Underlying solid geology of Sheffield and surrounding area (Grid squares shown at 5 km intervals)

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 Sheffield, although limited data is available for the outskirts of the urban area. This was obtained from a map of the Soils of South and West Yorkshire (Soil Survey of England and Wales, 1979).

Basic information for the urban soils of Sheffield 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 Sheffield city centre is characterised by sandy soils, belonging to the Acid Brown Earth soil classification. This type of soil is associated with the Coal Measures geology and therefore occurs over much of the sampling area. To the west of the city centre, loamy and silty soil occurs, belonging to the Non-Calcareous Gley soil classification; also west of the city centre, organic peat soil occurs in small outcrops.

3 Methodology

3.1 SOIL SAMPLING

Sample sites were arranged on a regular grid pattern at a density of 4 samples per km². 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 are 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 °C 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; Lister, 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 TiO₂ (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, MINITABTM. 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.

The ANOVA analysis was not carried out on Al₂O₃, CaO, K₂O, P₂O₅, SiO₂ or MgO, as these major elements were not analysed routinely in the urban sampling programme.

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 Sheffield, G-BASE internal reference standards S13, S15 and S24 were inserted during analysis of surface (A) and profile (S) soil samples. The standards S13 and S15 were inserted five times with the surface soils and five times with the profile soils, while S24 was inserted four times with the surface soils and four times with the profile soils. Mean concentrations for all elements in each standard are illustrated in Table 3.

The inclusion of G-BASE internal reference standards throughout all G-BASE and GSUE projects maintains data integrity between such projects. Sheffield lies within the Humber-Trent regional atlas area, and it is therefore essential that data for the urban centre of Sheffield is compatible with that of the surrounding regional dataset, which consists of the XRF analyses of approximately 7000 soil sample sites (British Geological Survey, In Prep). A number of G-BASE standards, including S13, S15 and S24, 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 Sheffield urban samples may be compared with those generated for the same standards during analysis of 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					Profile Soils				
Element	Number of Replicate Sets	Variance			Element	Number of Replicate Sets	Variance		
		Between Site (%)	Between Sample (%)	Residual (%)			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 ₂ O ₃	37	97.69	2.06	0.25	Fe ₂ O 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	Sheffield A S13	Sheffield S S13	Humber Trent S15	Sheffield A S15	Sheffield S S15
Cd	<1	<1	1	<1	<1	1
Sn	3	2	2	5	4	2
Sb	<1	<1	0.1	1	<1	1.1
TiO ₂	0.817	0.888	-	0.392	0.430	-
MnO	0.13	0.11	0.12	0.08	0.06	0.07
Fe ₂ O ₃	6.88	6.95	7.10	1.88	1.93	2.02
V	97	86	93	35	23	31
Cr	98	96	99	41	34	40
Co	29	23	24	9	5	6
Ba	1704	1809	1808	291	380	375
Ni	36	35	36	12	10	11
Cu	17	15	15	6	3	3
Zn	113	112	113	30	28	29
As	15	16	15	9	8	9
Mo	1.6	1.7	0.3	0.7	0.9	0.4
Pb	109	109	110	24	25	24
U	2.5	3.0	3.1	1.2	1.7	2.1
MgO	1.2	1.1	-	0.6	0.5	-
SiO ₂	-	56.4	-	-	75.1	-
Al ₂ O ₃	-	18.0	-	-	6.7	-
P ₂ O ₅	0.13	0.13	-	0.09	0.09	-
K ₂ O	2.17	2.17	-	2.27	2.18	-
CaO	0.35	0.33	-	0.20	0.17	-

Sample Type Standard ID	Humber Trent S24	Sheffield A S24	Sheffield S S24
Cd	3	<1	4
Sn	6	6	5
Sb	8	9	7
TiO ₂	1.122	1.237	-
MnO	0.46	0.42	0.49
Fe ₂ O ₃	10.22	10.29	10.54
V	140	130	137
Cr	123	123	125
Co	97	85	83
Ba	983	1061	1036
Ni	45	44	45
Cu	64	63	63
Zn	387	390	401
As	124	128	129
Mo	1.9	2.0	0.5
Pb	1070	1015	1046
U	1.7	1.8	2.5
MgO	1.1	1.1	-
SiO ₂	-	45.5	-
Al ₂ O ₃	-	23.1	-
P ₂ O ₅	0.18	0.18	-
K ₂ O	3.40	3.45	-
CaO	0.32	0.32	-

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 Al₂O₃, CaO, K₂O, MgO, P₂O₅, SiO₂, TiO₂, MnO, Fe₂O₃, 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 ($\mu\text{g/g}$ or $\mu\text{g g}^{-1}$) 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 (%)
MnO	-	0.01	-	10.0
Fe ₂ O 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	-
TiO ₂ *	-	0.01	-	100.0
SiO ₂ *	-	0.1	-	100.0
Al ₂ O ₃ *	-	0.1	-	100.0
P ₂ O ₅ *	-	0.05	-	1.5
K ₂ O*	-	0.05	-	15.0
CaO*	-	0.05	-	60.0
MgO	-	0.1	-	50.0

* A horizon only.

3.5 DATA INTERPRETATION

Once full error control and data quality procedures were completed, the Sheffield 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

4.1 BACKGROUND LEVELS

In order to aid the interpretation of the geochemical data for Sheffield, it is useful to be aware of typical background concentrations in the environment, in order to put the concentrations seen in Sheffield into context. This is discussed by Rawlins *et al.* (2003) for surface soils from Eastern England. The urban area of Sheffield is located over the Upper Carboniferous Westphalian Coal Measures (section 2.3). These measures are naturally enriched in a number of elements and consequently, the background values for soils in Sheffield are likely to be higher than the typical values for soils in the east of England. The median values for 818 surface soil samples and 818 profile soil samples collected over the Coal Measures are shown in Tables 5 and 6, respectively. These samples were extracted from a dataset of 6561 surface and 6877 profile soils collected across the Humber-Trent region, as part of the G-BASE project (British Geological Survey, In Prep) and represent all the samples collected over the Coal Measures in this area.

Table 5 Median concentrations in regional surface soil samples overlying Carboniferous Coal Measures, Humber-Trent atlas area and in Sheffield surface soil samples

Analyte	Units	Coal Measures	Sheffield A
Al ₂ O ₃	wt%	14.2	13.0
As	ppm	18	22
Ba	ppm	437	390
CaO	wt%	0.6	0.77
Cd	ppm	1	1
Co	ppm	27	27
Cr	ppm	84	102
Cu	ppm	31	51
Fe ₂ O ₃	wt%	6.65	6.74
K ₂ O	wt%	<0.05	1.66
MgO	wt%	0.8	0.8
MnO	wt%	0.15	0.18
Mo	ppm	3.3	4.6
Ni	ppm	24	32
Pb	ppm	79	164
P ₂ O ₅	wt%	0.3	0.31
Sb	ppm	0.5	3
SiO ₂	wt%	-	55.2
Sn	ppm	6	11
TiO ₂	wt%	0.91	0.841
U	ppm	2.6	2.5
V	ppm	103	103
Zn	ppm	101	139

Table 6 Median concentrations in regional profile soil samples overlying Carboniferous Coal Measures, Humber-Trent atlas area and in Sheffield profile soil samples

Analyte	Units	Coal Measures	Sheffield S
Al ₂ O ₃	wt%	<0.1	-
As	ppm	13	15
Ba	ppm	388	346
CaO	wt%	0.43	-
Cd	ppm	0.35	1
Co	ppm	25	25
Cr	ppm	88	94
Cu	ppm	25	39
Fe ₂ O ₃	wt%	5.99	6.2
K ₂ O	wt%	1.86	-
MgO	wt%	0.9	-
MnO	wt%	0.149	0.14
Mo	ppm	1.9	2.8
Ni	ppm	26	31
Pb	ppm	46	91
P ₂ O ₅	wt%	0.173	-
Sb	ppm	4	1
SiO ₂	wt%	-	-
Sn	ppm	5	8
TiO ₂	wt%	0.88	-
U	ppm	2.7	2.5
V	ppm	97	98
Zn	ppm	86	108

4.2 KEY GEOCHEMICAL CHARACTERISTICS OF THE SHEFFIELD DATASET

At the median value, the concentrations of almost all the elements analysed are higher in the surface soils than in the profile soils. This is despite the fact that the profile soils are sieved to a finer size fraction (<150 µm), resulting in a larger surface area and a higher proportion of clay particles. Clay minerals possess the ability to attract and bind heavy metal ions (Brady and Weil, 1999). It is therefore likely that the surface soils in Sheffield have been subjected to some level of anthropogenic contamination.

A number of the trace elements analysed are higher at the median value than the regional median values for samples overlying the Coal Measures, most notably Pb, as well as Cr, Cu, Sn, Ni and Zn. The same elements are also elevated in concentration in the Sheffield profile soils, with respect to the regional values, suggesting that the deeper soils may also be affected by urban contamination.

4.2.1 Geochemical distribution of soils within the urban area of Sheffield.

Coal mining played a substantial part in the industry of Sheffield throughout many areas of the city. The combustion products of coal and other fossil fuels have elevated levels of trace metals (e.g. Sn, Cr, Co, Mo, Ni) associated with them and therefore can contribute to high levels of trace elements in soil through atmospheric deposition. Sheffield was also a very large centre for the production of steel, therefore many of the elements associated with steel making, such as Fe, Cr and Ni (Alloway, 1995), show higher levels in and around the city centre, and out to the northeast of the city centre.

The northeast of the sampling area is bound by the course of the M1 motorway (Figure 3). There are elevated levels of a number of major and trace elements in this area (in both the surface and profile soils). In the shaded urban area of Sheffield (Figure 2), there are some industrial works, railway lines and a retail centre close to the M1. The River Don also flows through this area, out of the city. There are particularly high levels of Cr and Co around this part of Sheffield and also elevated levels of other trace elements, such as As and Ba. On the north side of the M1 (in the outskirts of Rotherham), there is a large sewage works, alongside the River Don. This is outside of the sample area, and also downstream, so is unlikely to provide a major contamination source for the soils studied.

To the east of the sampling area is a region which lies outside the shaded urban area, extending towards the M1. This area contains opencast workings and a large steel works, which is located between a complex railway network and the River Don (approximate GR: 440000, 389000). Significantly high levels of Al₂O₃ and K₂O occur throughout this area and elevated levels of MgO, TiO₂, Cr, U and V are also observed. High levels of, in particular Mo and Ni, along with Cr, Co, MnO, U and V are associated with the steel works and some nearby opencast workings. Stainless steel manufacture represents the single largest use of Cr and Ni (Alloway, 1995). Elements such as Cr, Ni and Mo are released to the atmosphere through melting and smelting operations and the burning of fossil fuels.

A number of elements demonstrate significant relationships with the main transport routes of Sheffield, particularly the railways, including Sb (surface soils), As, Cd (surface soils), Cr, Co, Cu, Fe₂O₃, Pb, MgO (to the north of the city only), Mo, Ni, Sn and Zn. This is likely to reflect the industrial history of Sheffield, with coal, steel products and other industrial materials transported by rail into and out of Sheffield. High levels of Pb may be related to vehicle emissions. Prior to 2000, tetra-ethyl Pb was added to petrol as an anti-knocking agent. Other trace elements may be present as impurities in petroleum products.

4.3 SOIL GEOCHEMISTRY OF SHEFFIELD IN RELATION TO OTHER HUMBER-TRENT URBAN AREAS

The results for selected elements from surface soils in Sheffield are presented in Figure 6 in the context of six other urban areas from the Humber-Trent region (Doncaster, Hull, Lincoln, Mansfield, Scunthorpe and York) and the results from the regional survey for the Humber-Trent region. Eight elements that may be affected by anthropogenic contamination in urban areas (Sb, As, Cd, Cu, Pb, Mo, Sn and Zn) were selected, while TiO₂ was included to represent the closest approximation to a conservative element, unaffected by contamination.

While concentrations of TiO₂ 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 demonstrated 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, Department of the Environment Food and Rural Affairs and the Environment Agency, 2002b) for residential areas with plant uptake are shown on Figure 6, for Cd and As. From the 75th percentile, cadmium concentrations in Sheffield are above the SGV value for soils with a pH of 6, but are largely below the level given for pH 7 soils. The levels are comparable with Mansfield and York, but are higher than the remaining 4 urban areas, which are very low in Cd. More than half of the surface soil samples in Sheffield contain levels of As that are above the SGV value for soils in residential areas involving plant uptake. On a regional scale, the median concentration for As in surface soils overlying the Coal Measures is 18 ppm, which suggests that levels of As are naturally high in Sheffield. The median value over the whole of the Humber-Trent region is lower than over the Coal Measures alone (13 ppm), which may in part explain the high levels of As in Sheffield, relative to some of the other urban areas in the region.

All the elements included in Figure 6 (including TiO₂) are relatively high in Sheffield, when compared to the regional Humber-Trent values and to other urban areas within the region. This is likely to reflect the enriched geochemistry of the underlying Coal Measures and the strong industrial history of Sheffield, largely based around the exploitation of the Coal Measures resources.

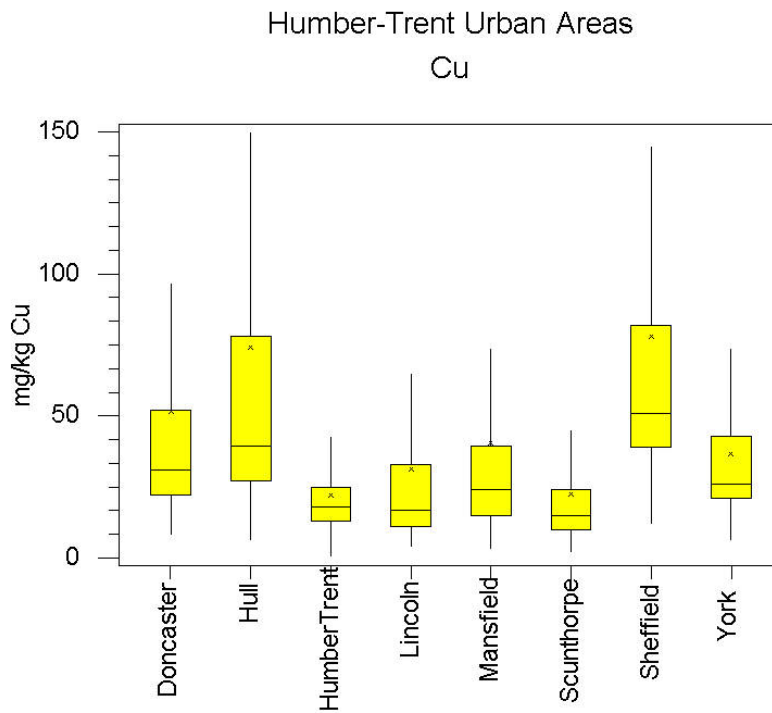


Figure 6: (a) Copper in surface soil

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)

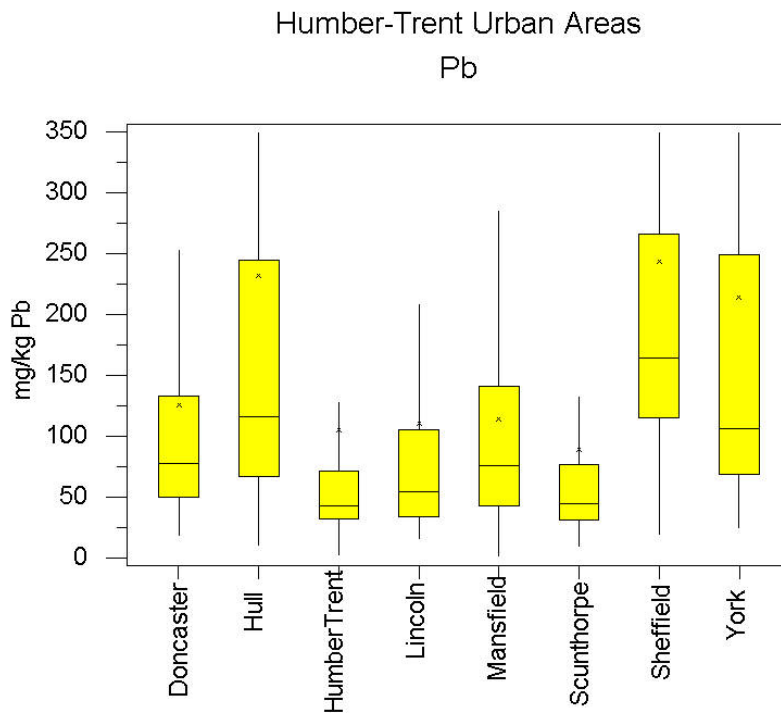


Figure 6: (b) Lead in surface soil

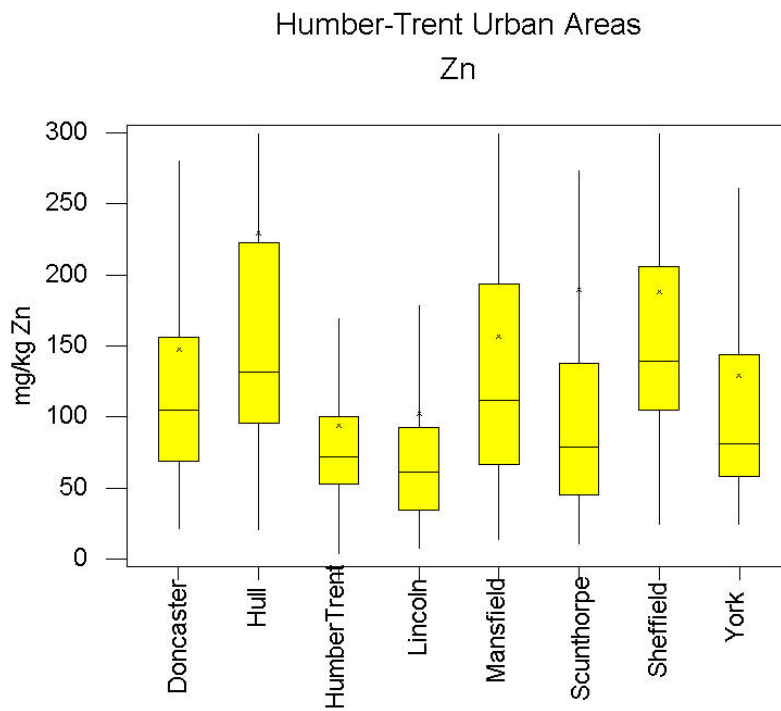


Figure 6: (c) Zinc in surface soil

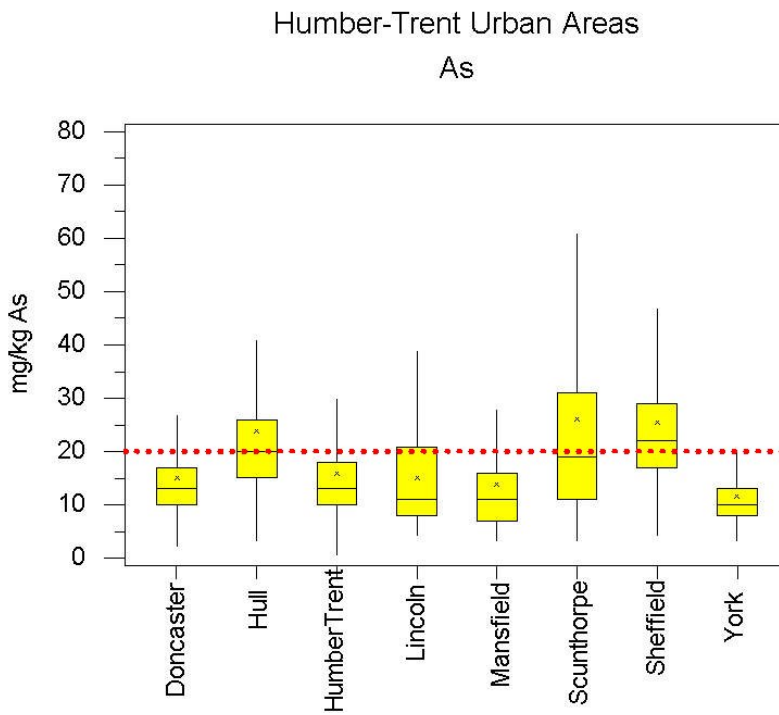


Figure 6: (d) Arsenic in surface soil

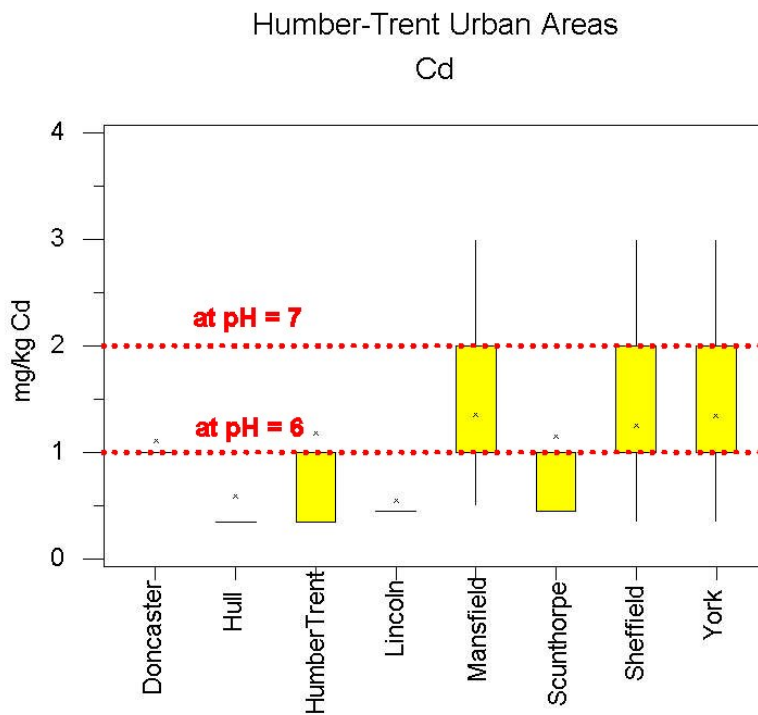


Figure 6: (e) Cadmium in surface soil

Humber-Trent Urban Areas
Mo

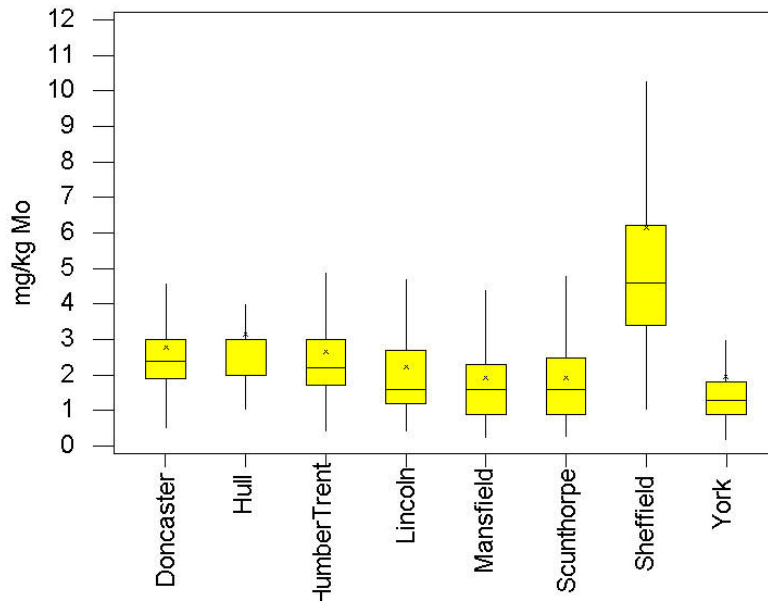


Figure 6: (f) Molybdenum in surface soil

Humber-Trent Urban Areas
Sn

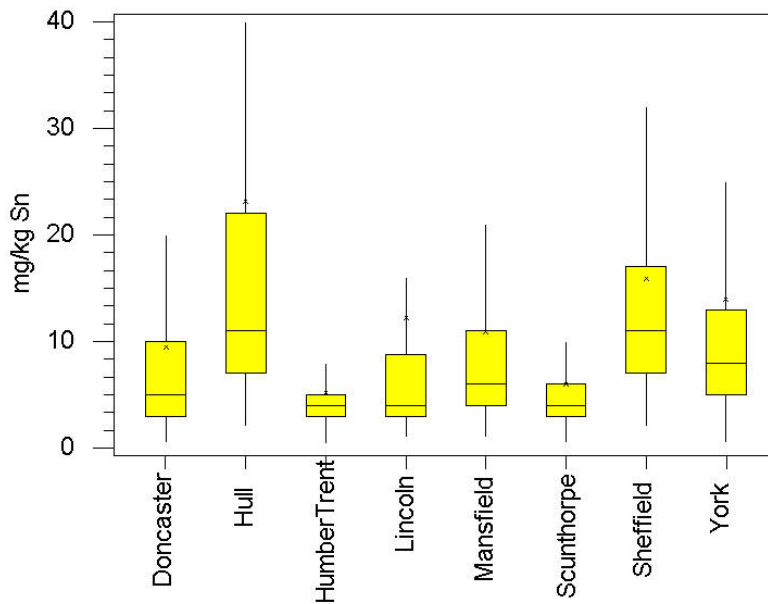


Figure 6: (g) Tin in surface soil

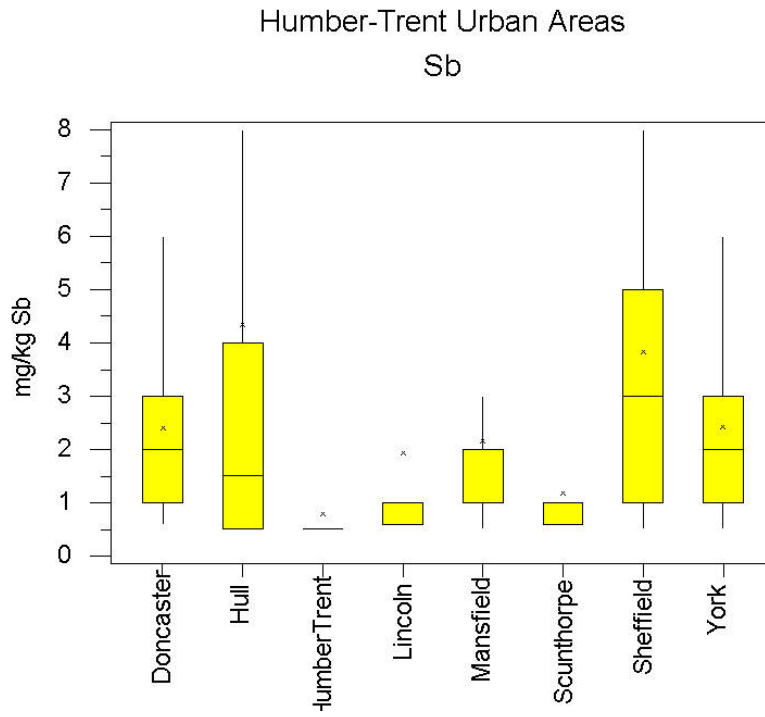


Figure 6: (h) Antimony in surface soil

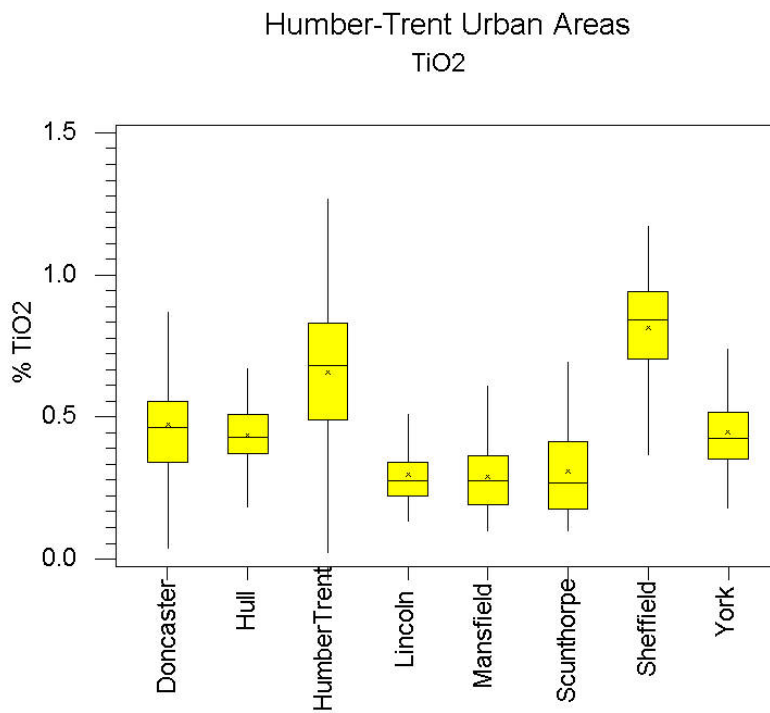


Figure 6: (i) Titanium oxide in surface soil

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Appendix A: Examples of urban surface and profile field cards from Sheffield.

URBAN SOIL/WATER

CODE	SAMPLE NO	TYPE	EASTING	NORTHING	O/S MAP	COLLECTORS	DAY	MONTH	YEAR							
604153		A	43478	38870	111	RBWMTS	24	06	96							
DUPLICATE SAMPLE No.																
CODE	SAMPLE NO	WEA	LAND USE	SITE/DRAINAGE CONTAMINATION												
		8	DACA EA 00	A	B	C	D	E	F	G	H	I				
					3											
O/B	DRIFT	SITE LOCALITY DETAILS														
1	CI	FRONT AREA - HAYES METALS FCTRY														
20M N CRS RDS BETWN BOYLAND ST + BARDWELL																
RD. 130M N POST OFFICE, PHILADELPHIA																
SOIL DATA																
COLOUR		TEX	HORIZON	DEPTH	BEDROCK LITHOLOGY	1:50,000 Geo Sheet codes										
25Y	3/10	C	A	0.15	4P00	Major	Minor									
SOIL CLAST LITHOLOGY																
4P00 3D00																
WATER SAMPLE DATA																
STM	DRN	DRN	WATER COLOUR	SOIL GASES		RADON: Unit: Pot: 352										
ORD	TYP	CON	C	Y	B	SS	DRAINAGE CLAST LITHOLOGY	B	G	Count 1	Count 2	Count 3	CO2	OXYGEN	METHANE	
										10	115	62	38			
FIELD DATA COMMENTS																

MHSI, APPLIED GEOCHEMISTRY GROUP, BRITISH GEOLOGICAL SURVEY, 1998.

URBAN SOIL/WATER

CODE	SAMPLE NO	TYPE	EASTING	NORTHING	O/S MAP	COLLECTORS	DAY	MONTH	YEAR							
604153		S	43478	38870	111	RBWMTS	24	06	96							
DUPLICATE SAMPLE No.																
CODE	SAMPLE NO	WEA	LAND USE	SITE/DRAINAGE CONTAMINATION												
		8	DACA EA 00	A	B	C	D	E	F	G	H	I				
					23	1										
O/B	DRIFT	SITE LOCALITY DETAILS														
1	CI	FRONT AREA - HAYES METALS FCTRY														
20M N CRS RDS BETWN BOYLAND ST + BARDWELL																
RD. 130M N POST OFFICE, PHILADELPHIA																
SOIL DATA																
COLOUR		TEX	HORIZON	DEPTH	BEDROCK LITHOLOGY	1:50,000 Geo Sheet codes										
25Y	3/10	C	A	0.30	4P00	Major	Minor									
SOIL CLAST LITHOLOGY																
7011 3D00																
WATER SAMPLE DATA																
STM	DRN	DRN	WATER COLOUR	SOIL GASES		RADON: Unit: Pot:										
ORD	TYP	CON	C	Y	B	SS	DRAINAGE CLAST LITHOLOGY	B	G	Count 1	Count 2	Count 3	CO2	OXYGEN	METHANE	
FIELD DATA COMMENTS																

MHSI, APPLIED GEOCHEMISTRY GROUP, BRITISH GEOLOGICAL SURVEY, 1998.

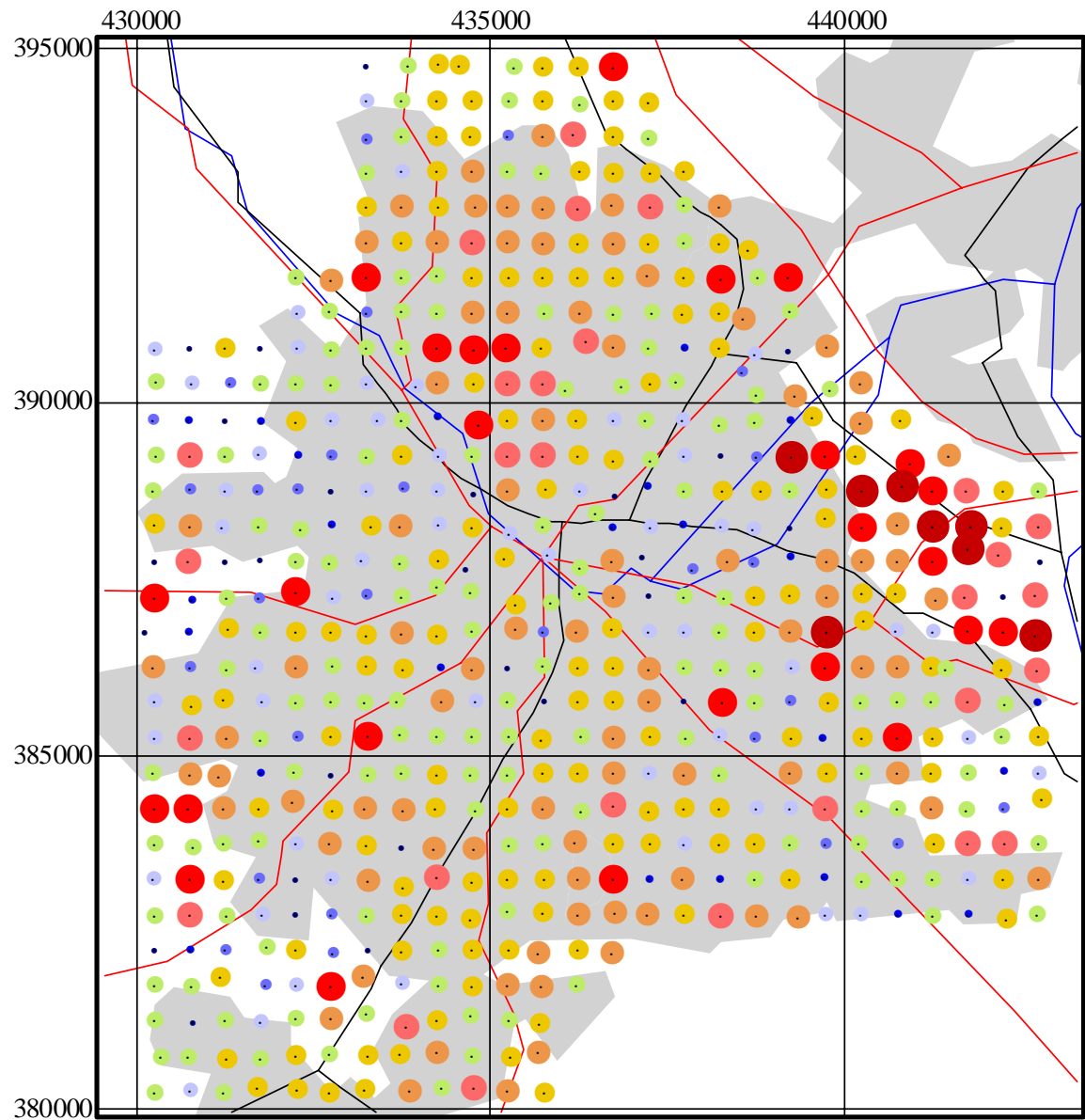
Appendix B: Percentile calculations for Sheffield soil

Percentiles	MgO	SiO ₂	Al ₂ O ₃	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	MnO	Fe ₂ O ₃	Fe ₂ O ₃	V	V	Pb	Pb	Cd*	Cd*	Cu	Cu	
	WT %	WT %	WT %	WT %	WT %	WT %	WT %	WT %	WT %	WT %	WT %	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
99%	2.3	67.3	20.4	1.01	3.29	7.87	1.086	0.43	0.46	16.76	15.52	199	225	1226	1269	6	5.59	432	530	
95%	1.6	63.0	17.6	0.66	2.67	4.06	1.033	0.29	0.29	9.89	10.27	151	148	676	597	3	3	213	224	
90%	1.3	60.9	16.0	0.54	2.25	2.78	1.002	0.25	0.24	8.94	8.85	136	133	493	349	2	2	146	137	
75%	1.0	58.1	14.6	0.41	1.95	1.49	0.941	0.21	0.18	7.67	7.23	117	114	266	183	2	2	82	66	
50%	0.8	55.2	13.0	0.31	1.66	0.77	0.841	0.18	0.14	6.74	6.20	103	98	164	91	1	1	51	39	
25%	0.6	52.3	11.2	0.23	1.39	0.45	0.708	0.14	0.10	5.81	5.46	87	85	115	47	1	1	39	26	
15%	0.5	50.0	10.5	0.20	1.25	0.30	0.643	0.11	0.08	5.21	5.03	80	79	89	35	0.35	0.35	30	22	
10%	0.5	48.5	9.9	0.18	1.15	0.24	0.590	0.10	0.06	4.83	4.76	75	75	72	31	0.35	0.35	27	21	
5%	0.4	43.6	9.3	0.14	1.08	0.14	0.520	0.08	0.04	4.05	4.39	65	69	55	25	0.35	0.35	22	19	
Min	0.1	19.7	3.4	0.05	0.54	0.03	0.175	0.02	0.01	1.28	3.21	38	45	19	13	0.35	0.35	12	7	
Max	5.9	73.2	22.0	1.51	4.02	15.43	1.175	0.48	1.58	26.37	20.81	382	403	4300	4000	8	9	1575	4088	
Mean	0.9	54.6	13.0	0.34	1.71	1.28	0.815	0.18	0.15	6.96	6.63	105	103	244	174	1.26	1.46	78	78	
Median	0.8	55.2	13.0	0.31	1.66	0.77	0.841	0.18	0.14	6.74	6.20	103	98	164	91	1	1	51	39	
Percentiles	Cr	Cr	As	As*	Ni	Ni	Zn	Zn	Mo	Mo	Ba	Ba	U*	U*	Sn	Sn	Co	Co	Sb*	Sb*
	ppm	ppm	Ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
99%	767	500	86	101	183	258	838	861	32.0	26.6	1295	1455	4.53	6.6	107	98	64	90	21.3	19
95%	283	232	50	53	84	87	429	369	17.7	11.4	737	682	3.4	3.9	40	51	39	45	10.3	11
90%	198	154	40	36	60	59	327	241	10.0	7.9	617	564	3.2	3.4	28	31	35	35	8	6
75%	130	113.8	29	24	42	41	206	157	6.2	4.5	470	433	2.8	2.9	17	15	31	30	5	3
50%	102	94	22	15	32	31	139	108	4.6	2.8	390	346	2.5	2.5	11	8	27	25	3	1
25%	87	81	17	11	24	25	105	82	3.4	1.8	330	273	2.1	2.0	7	5	22	23	1	1
15%	80	75	14	10	21	23	88.1	74	2.9	1.6	291	247	1.9	1.9	6	4	20	21	1	0.5
10%	74	72	13	9	18	20	80.4	68	2.6	1.4	264	228	1.8	1.7	6	4	18	20	1	0.5
5%	66	67	11	7	16	17	67	58	2.1	1.2	216	204	1.4	1.5	5	3	16	17	0.5	0.5
Min	43	44	4	0.5	8	9	24	22	1.0	0.6	78	59	0.25	0.25	2	1	7	10	0.5	0.5
Max	1251	1490	239	156	473	1358	2678	11000	58.3	115	6241	3788	8.8	10.5	199	378	1273	323	47	65
Mean	135	117	26	21	40	43	189	169	6.2	4.3	440	399	2.49	2.58	16	15	30	28	3.8	3
Median	102	94	22	15	32	31	139	108	4.6	2.8	390	346	2.5	2.5	11	8	27	25	3	1

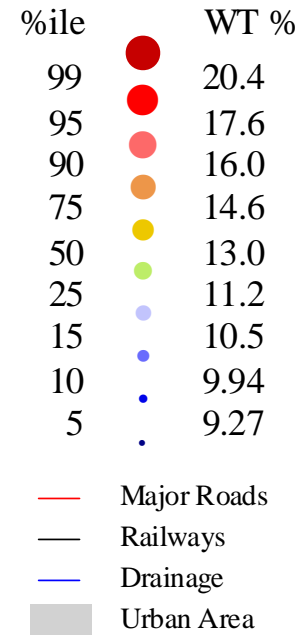
Surface soils in yellow. *Minimum value reported as half detection limit.

Appendix C: Proportional symbol geochemical maps for Sheffield surface and profile soils

Aluminium (surface soils only)
Antimony
Arsenic
Barium
Cadmium
Calcium (surface soils only)
Chromium
Cobalt
Copper
Iron
Lead
Magnesium (surface soils only)
Manganese
Molybdenum
Nickel
Phosphorous (surface soils only)
Potassium (surface soils only)
Silicon (surface soils only)
Tin
Titanium (surface soils only)
Uranium
Vanadium
Zinc

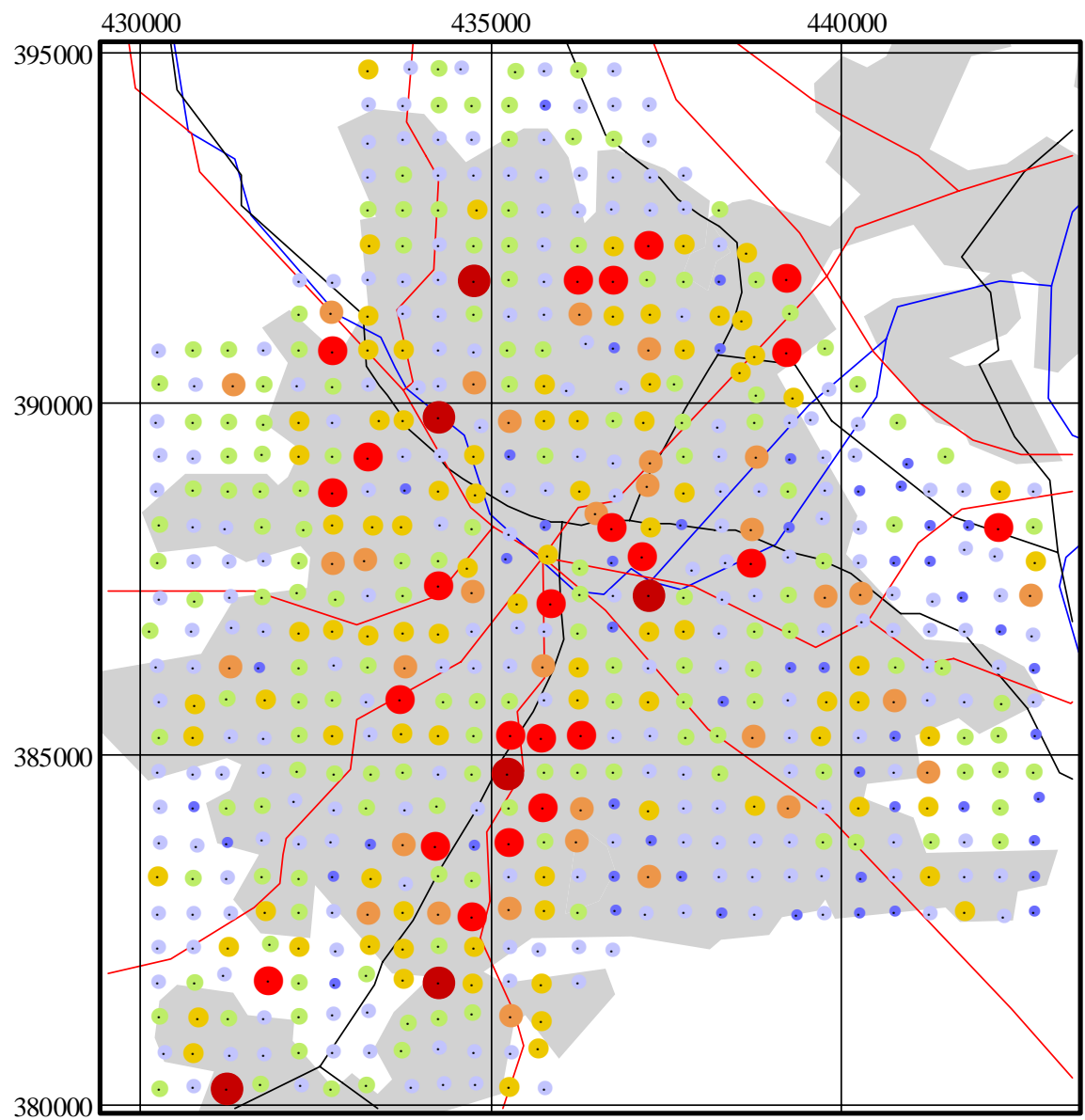


Sheffield Surface Soils Aluminium



surface soil	Al_2O_3 (%)
number	575
minimum	3.4
maximum	22.0
median	13.0
mean	13.0

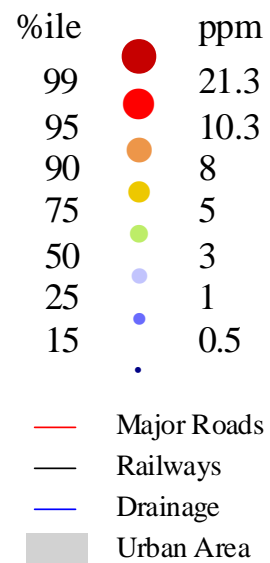
Aluminium was not determined in the profile soils



Sheffield

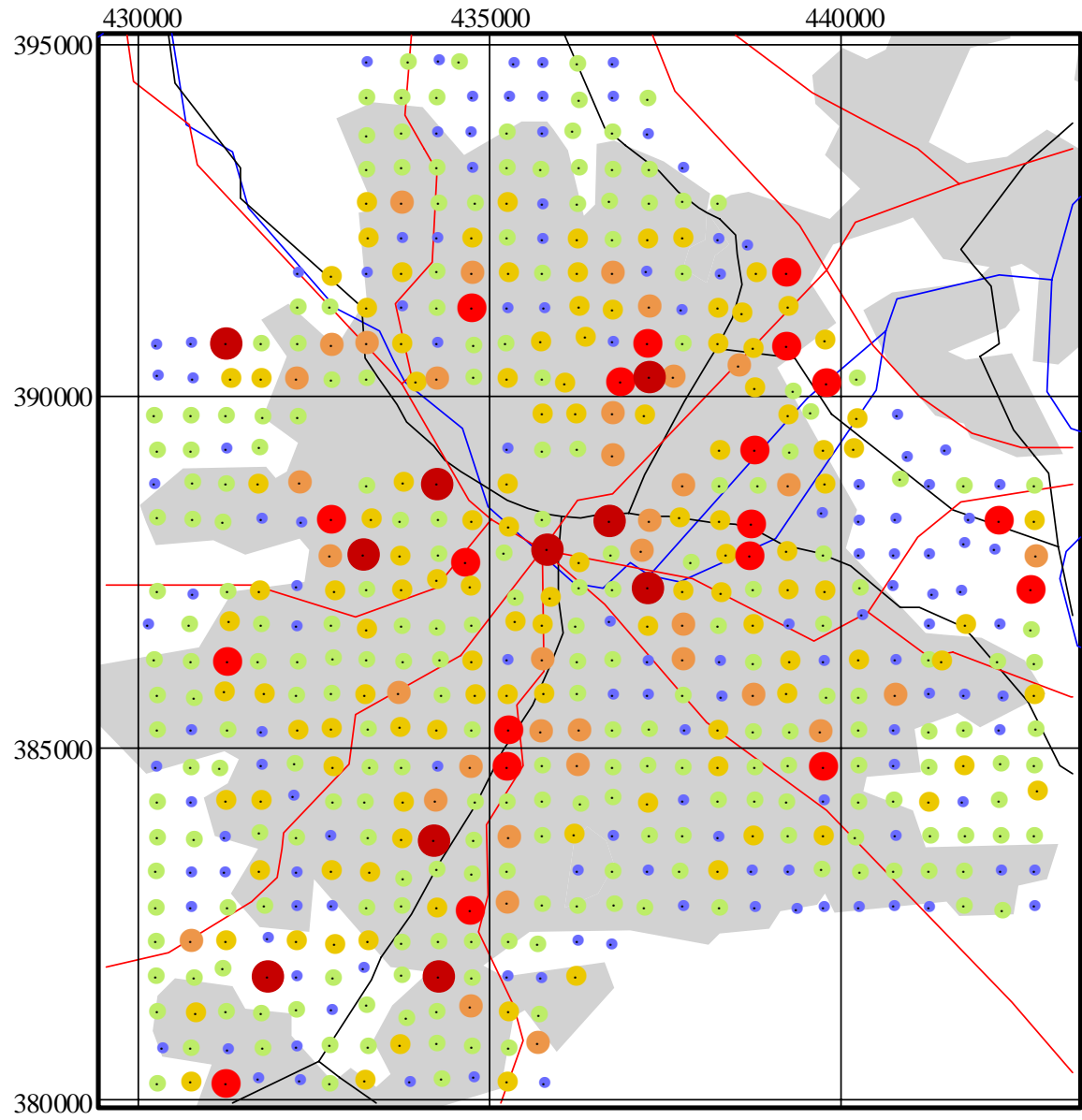
Surface Soils

Antimony

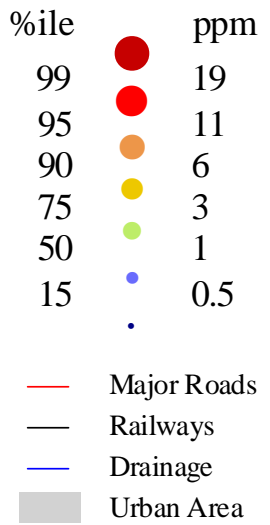


surface soil	Sb(ppm)
number	575
minimum	0.5*
maximum	47
median	3
mean	3.8

* minimum value reported as half detection limit

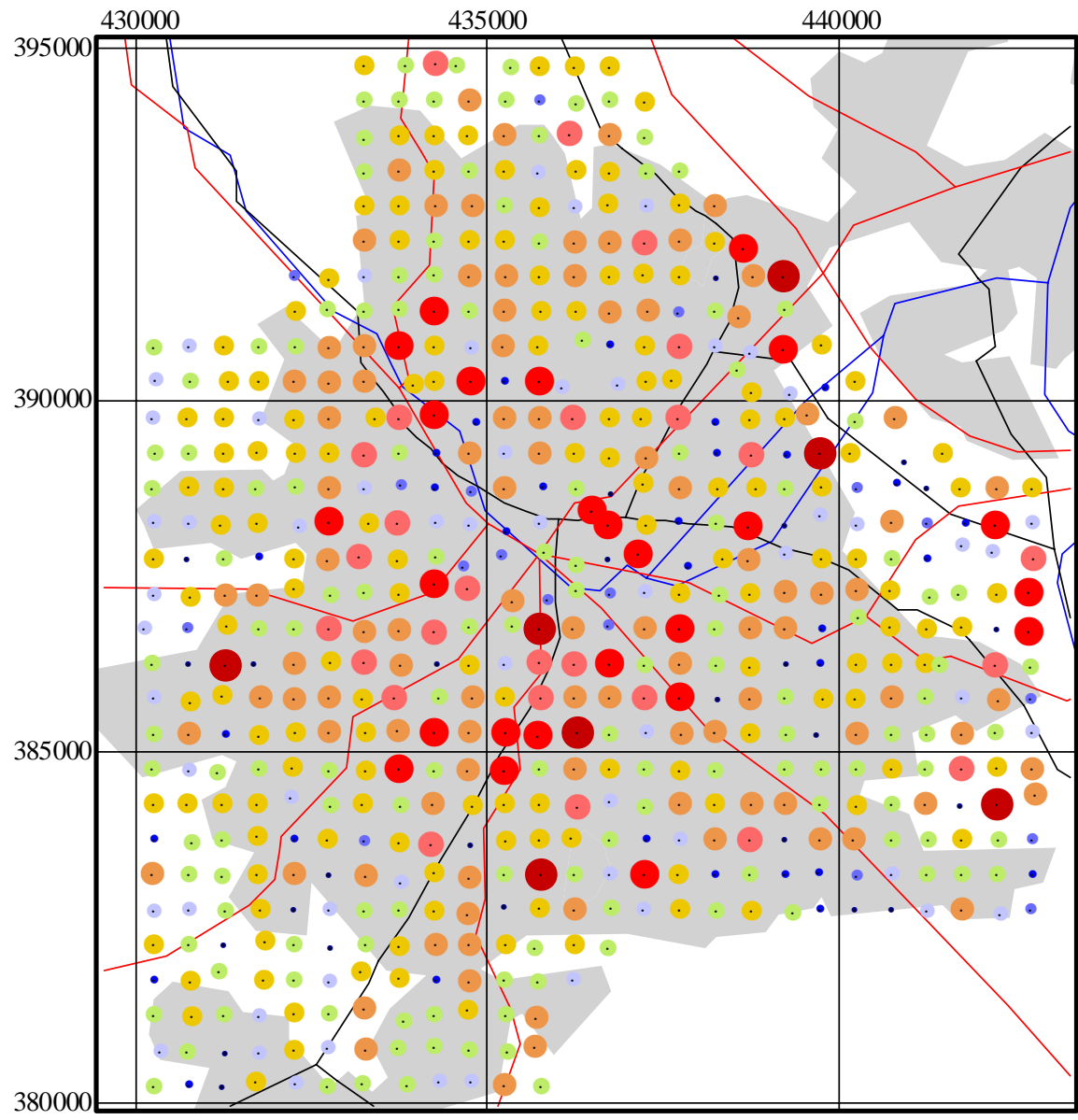


Sheffield Profile Soils Antimony



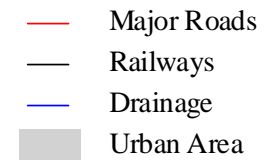
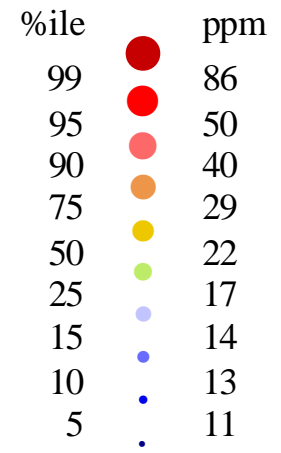
profile soil	Sb(ppm)
number	542
minimum	0.5*
maximum	65
median	1
mean	3

* minimum value quoted as half detection limit

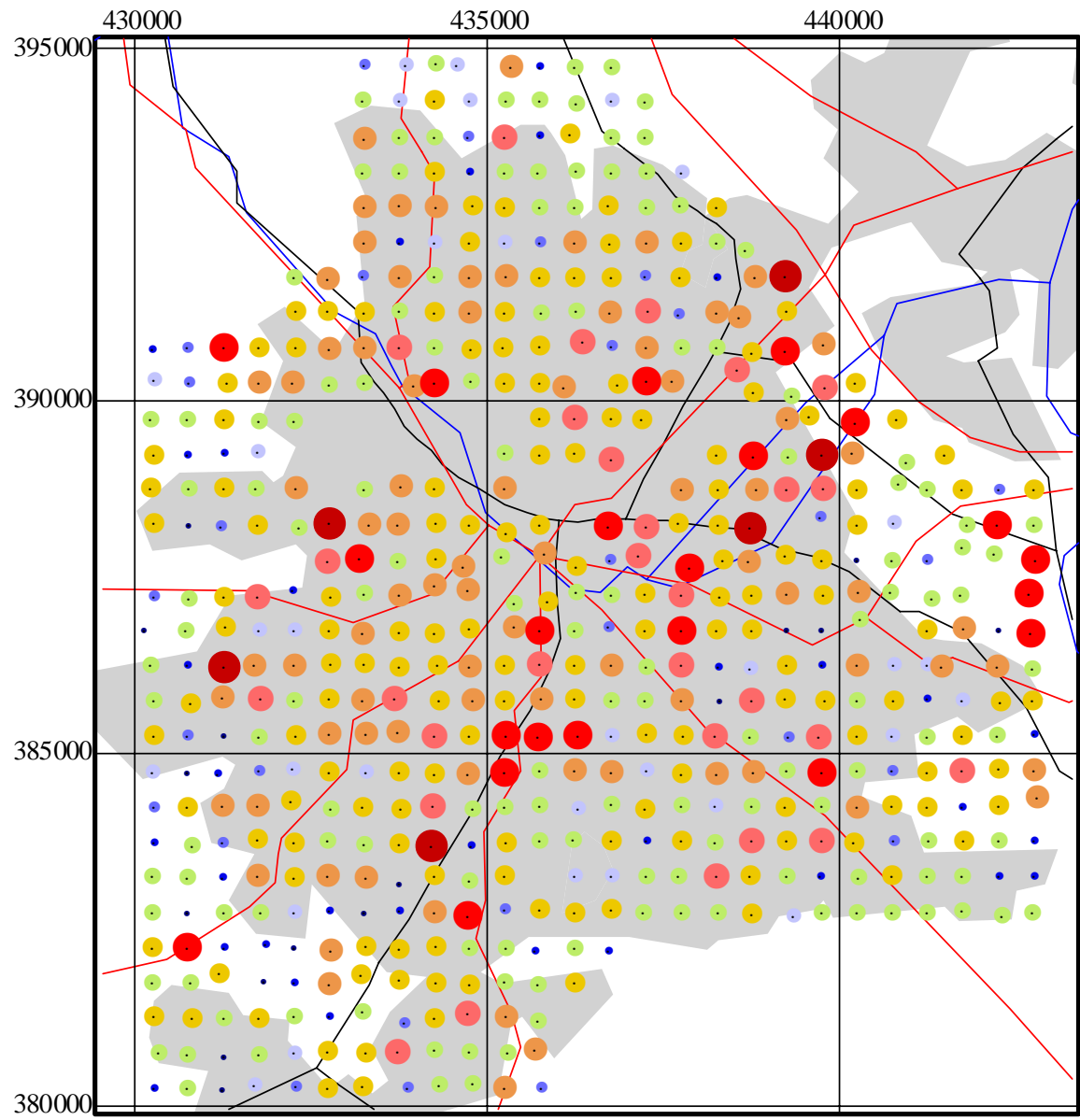


Sheffield Surface Soils

Arsenic

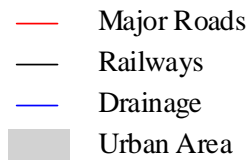
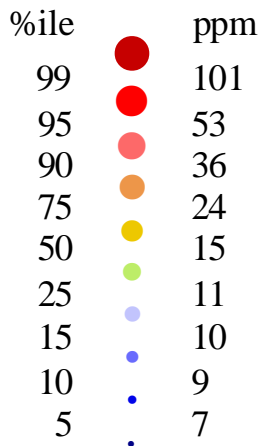


surface soil	AS (ppm)
number	575
minimum	4
maximum	239
median	26
mean	22



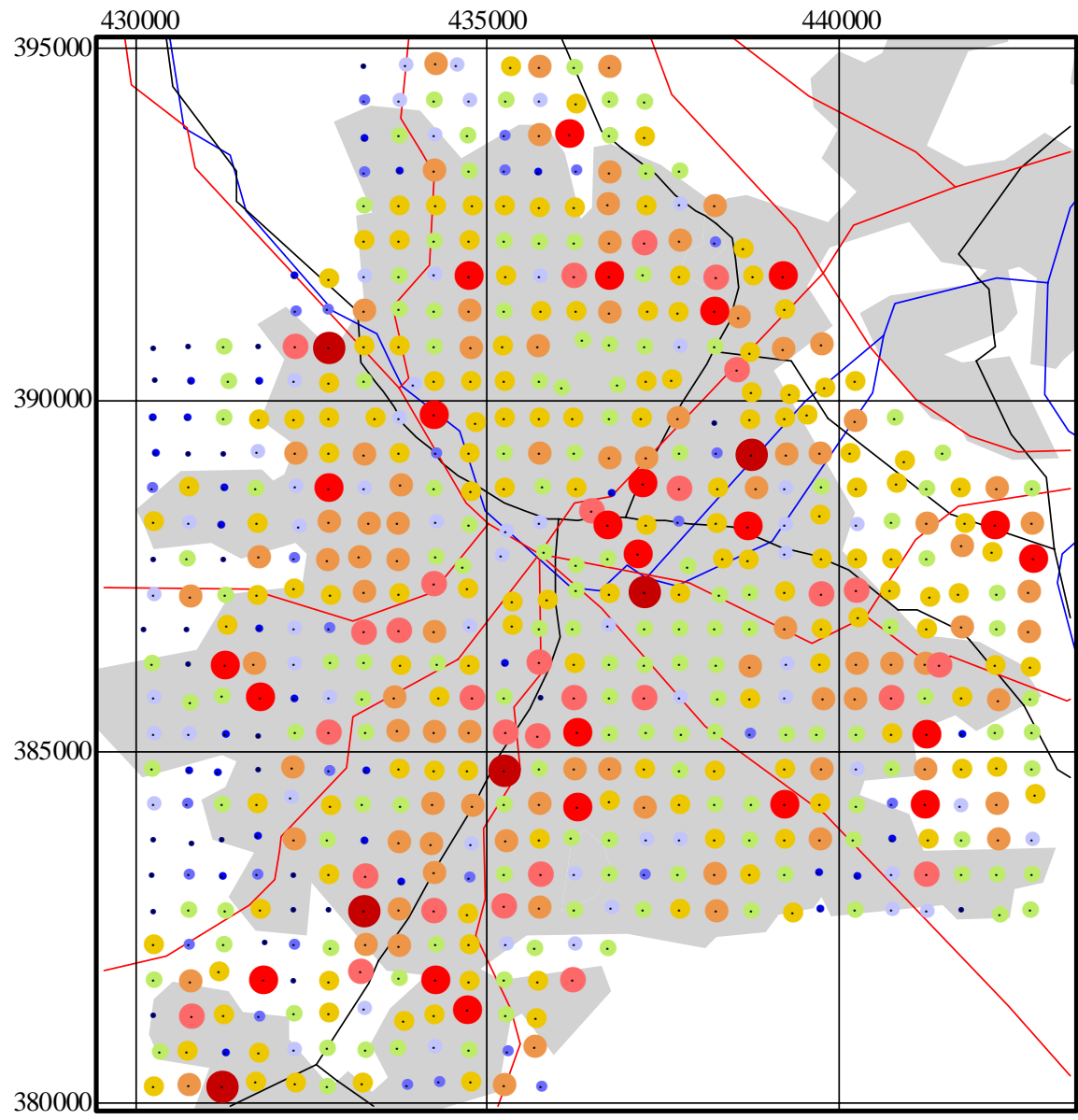
Sheffield Profile Soils

Arsenic



profile soil	AS (ppm)
number	542
minimum	0.5*
maximum	156
median	15
mean	21

* minimum value quoted as half detection limit



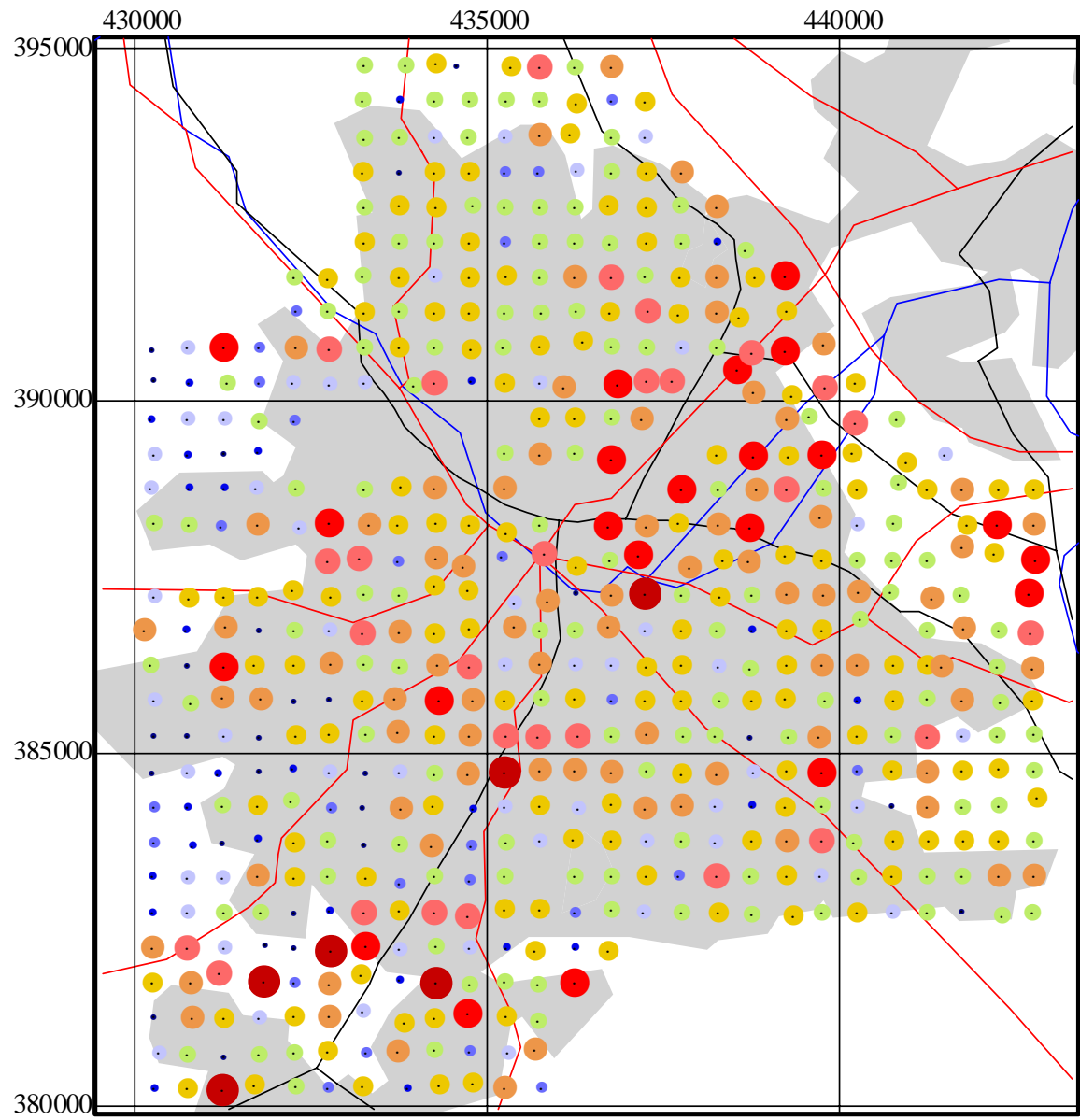
Sheffield

Surface Soils

Barium



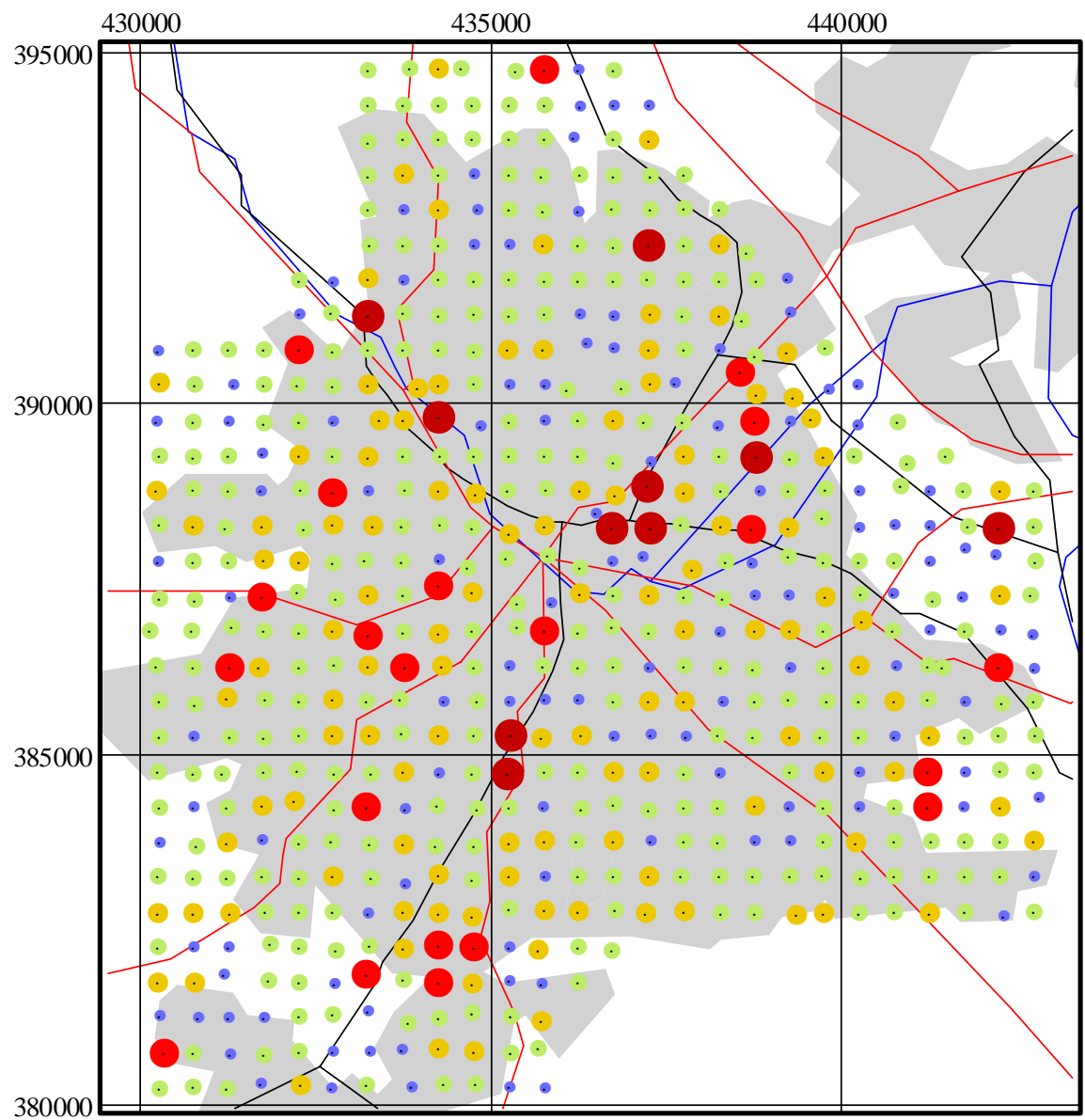
surface soil	Ba(ppm)
number	575
minimum	78
maximum	6241
median	390
mean	439



Sheffield Profile Soils Barium



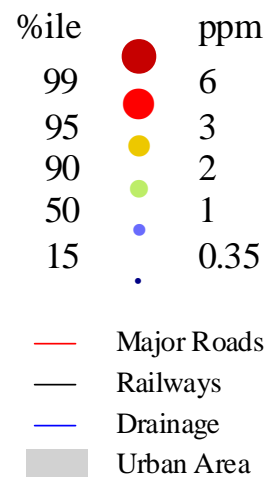
profile soil	Ba (ppm)
number	542
minimum	59
maximum	3788
median	346
mean	399



Sheffield

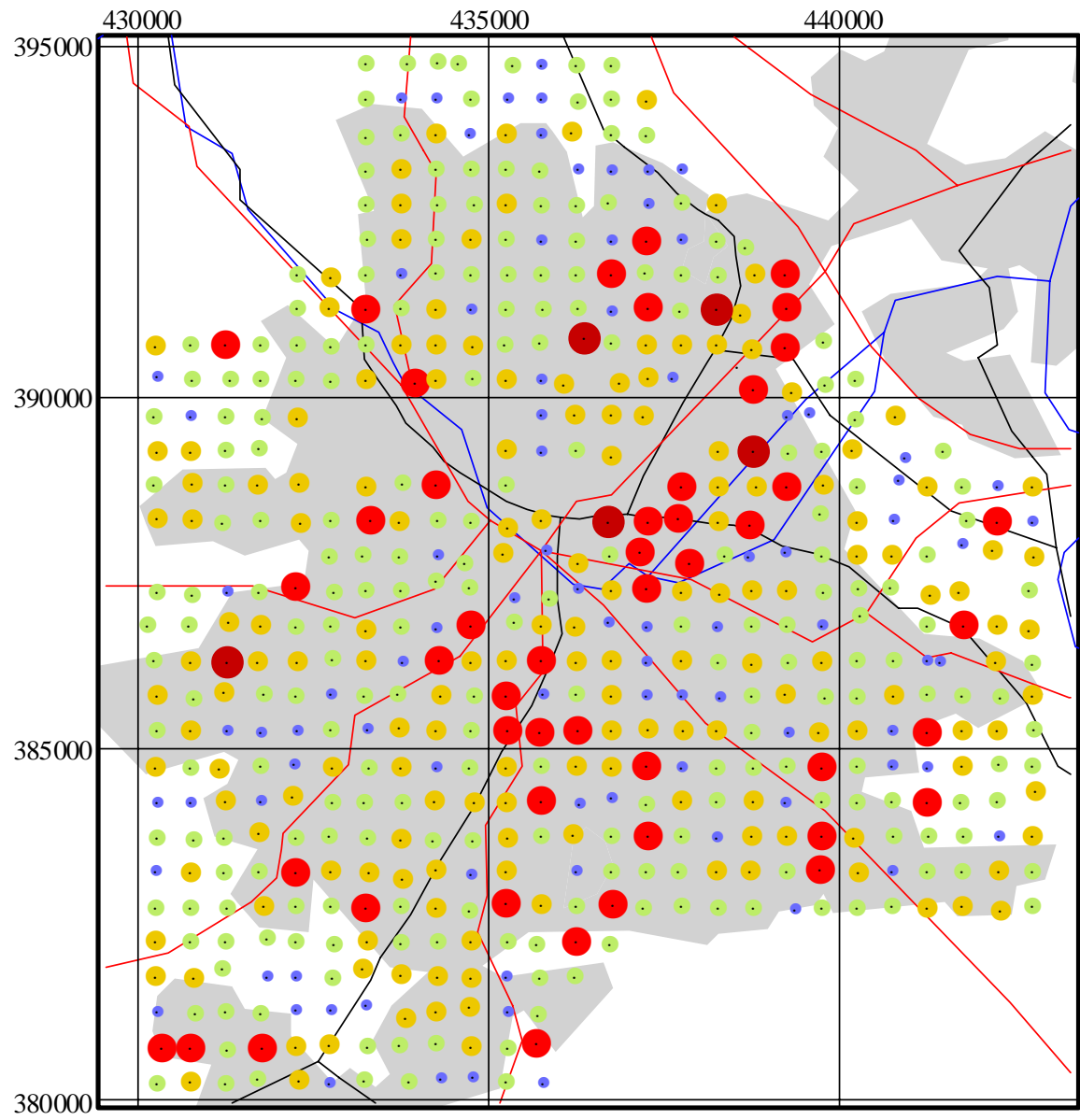
Surface Soils

Cadmium

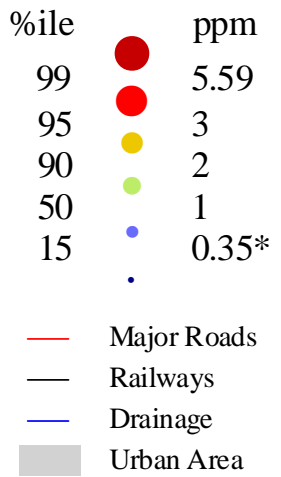


surface soil	Cd(ppm)
number	575
minimum	0.35*
maximum	8
median	1
mean	1.26

* minimum value reported as half detection limit

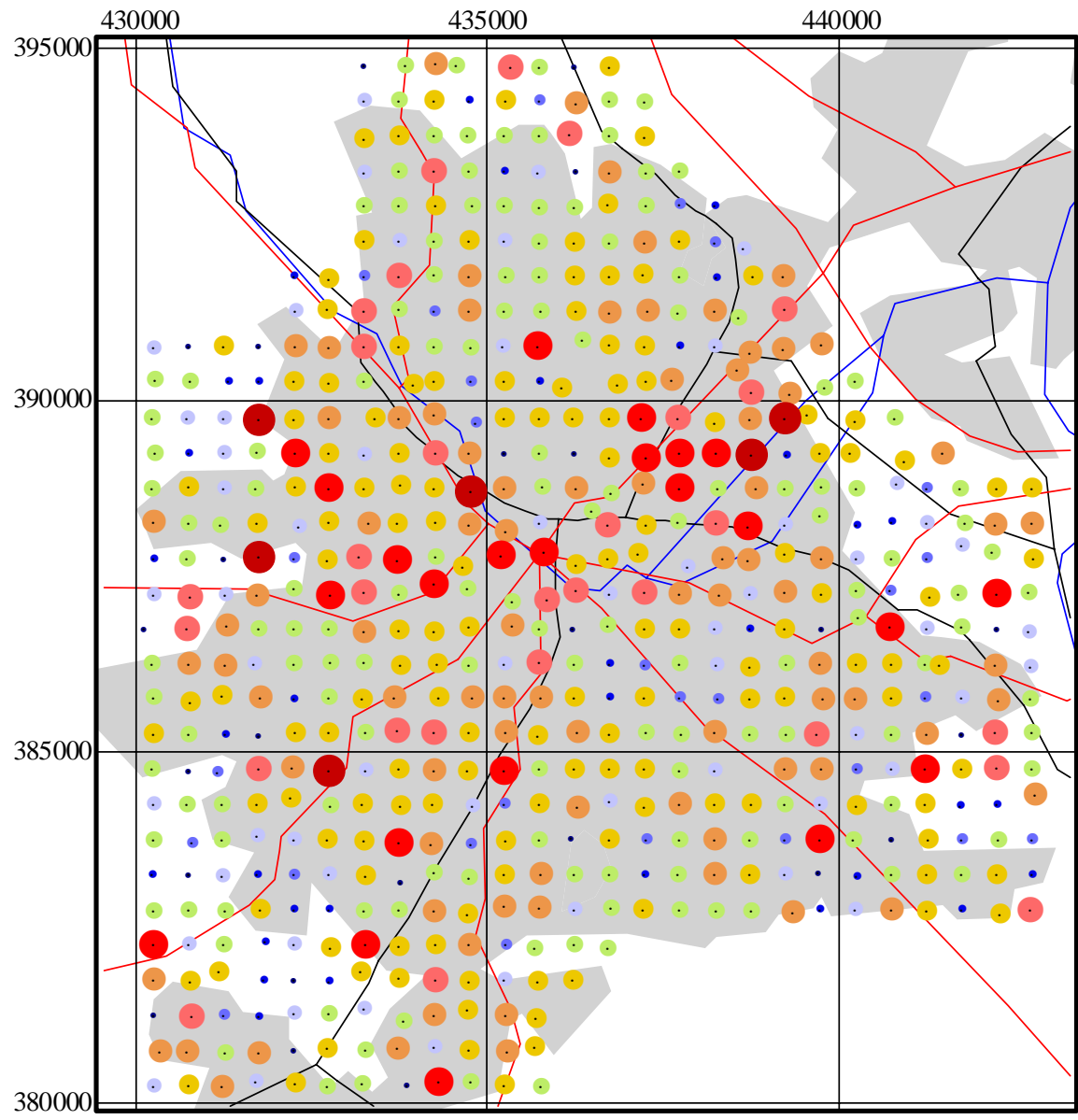


Sheffield Profile Soils Cadmium



profile soil	Cd (ppm)
number	542
minimum	0.35*
maximum	9
median	1
mean	1.46

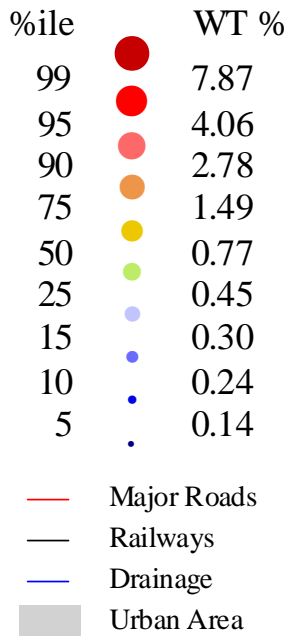
* minimum value quoted as half detection limit



Sheffield

Surface Soils

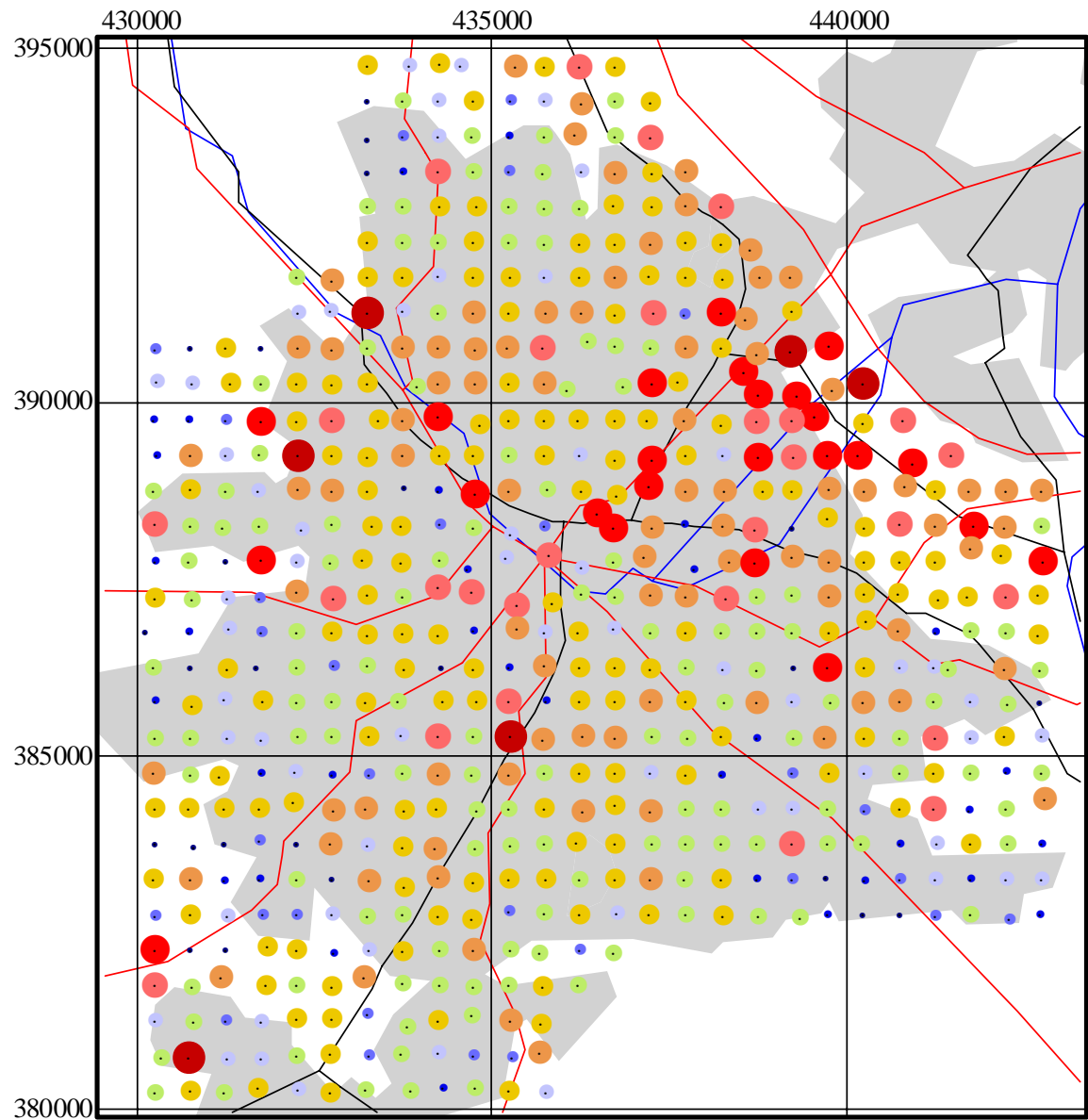
Calcium



surface soil	CaO (%)
number	575
minimum	0.025*
maximum	15.43
median	0.77
mean	1.28

* minimum value reported as half detection limit

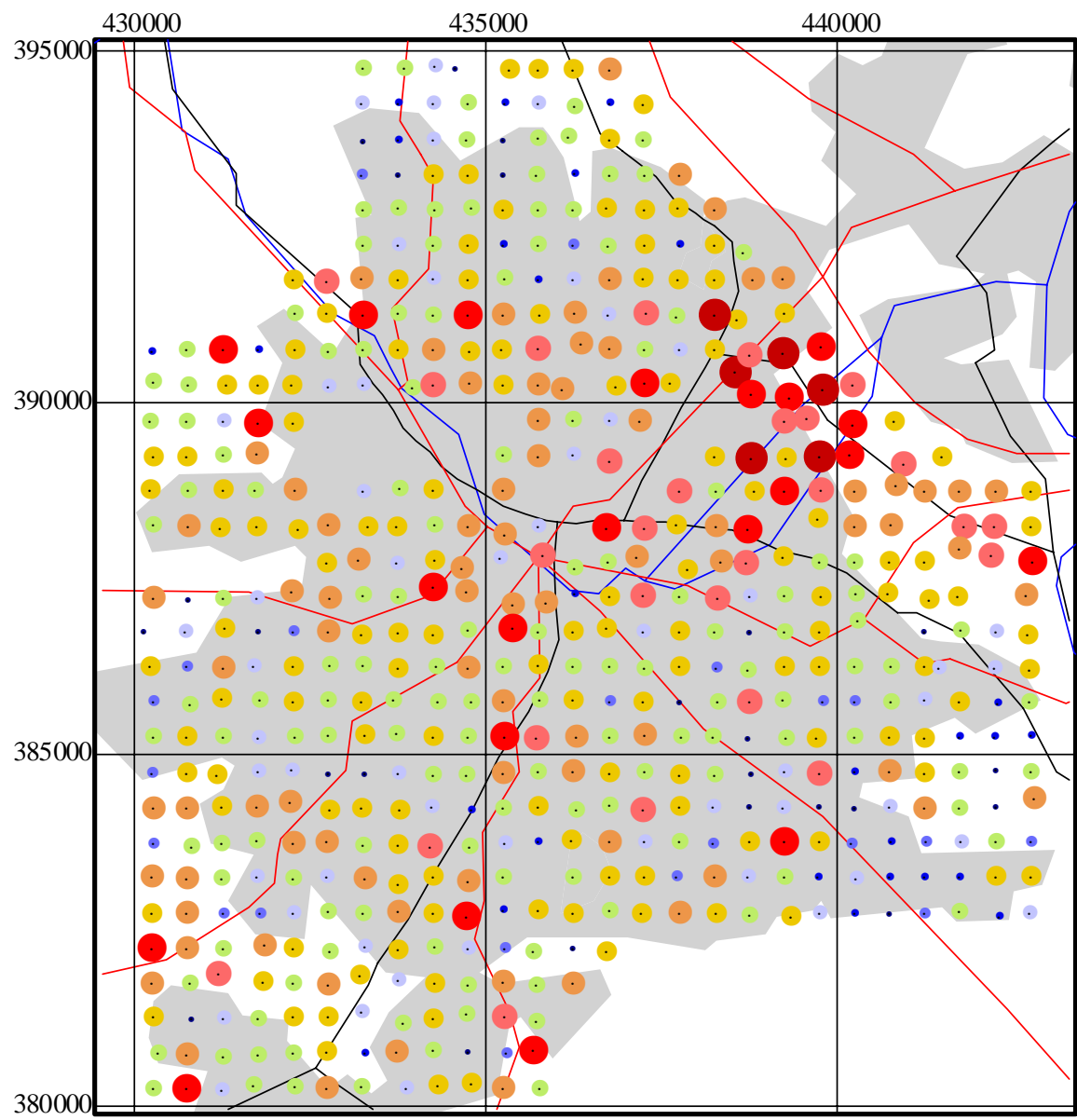
Calcium was not determined in the Profile Soils



Sheffield Surface Soils Chromium



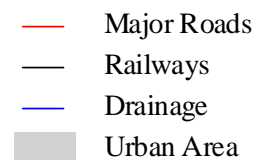
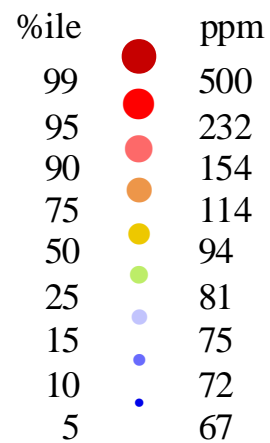
surface soil	Cr (ppm)
number	575
minimum	43
maximum	1251
median	102
mean	135



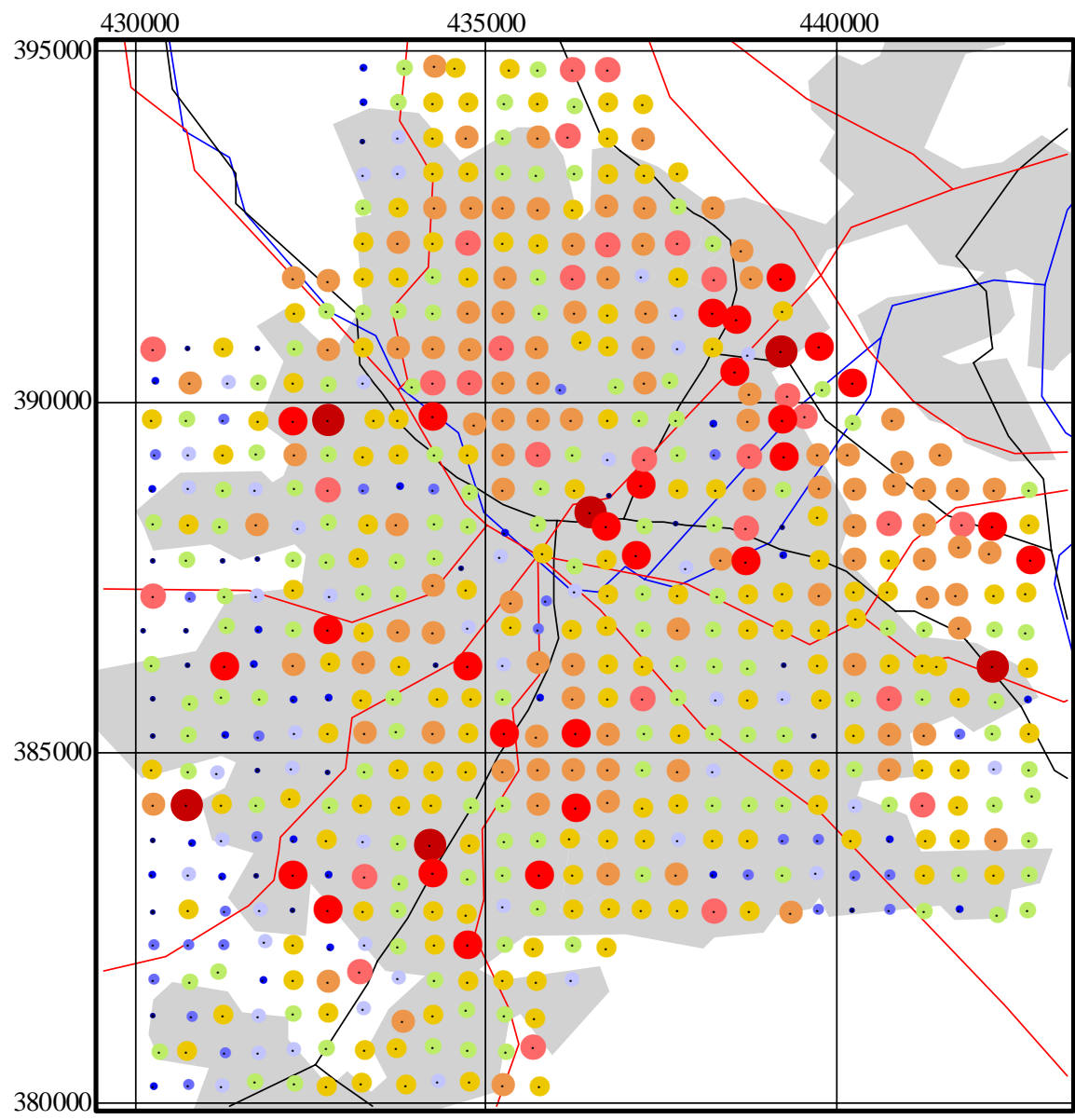
Sheffield

Profile Soils

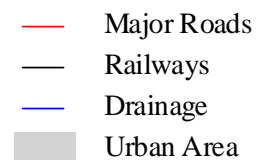
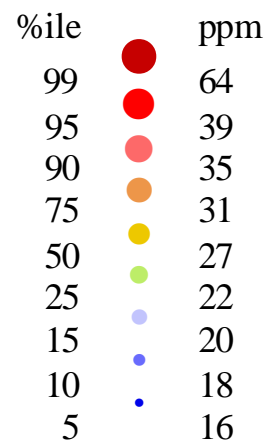
Chromium



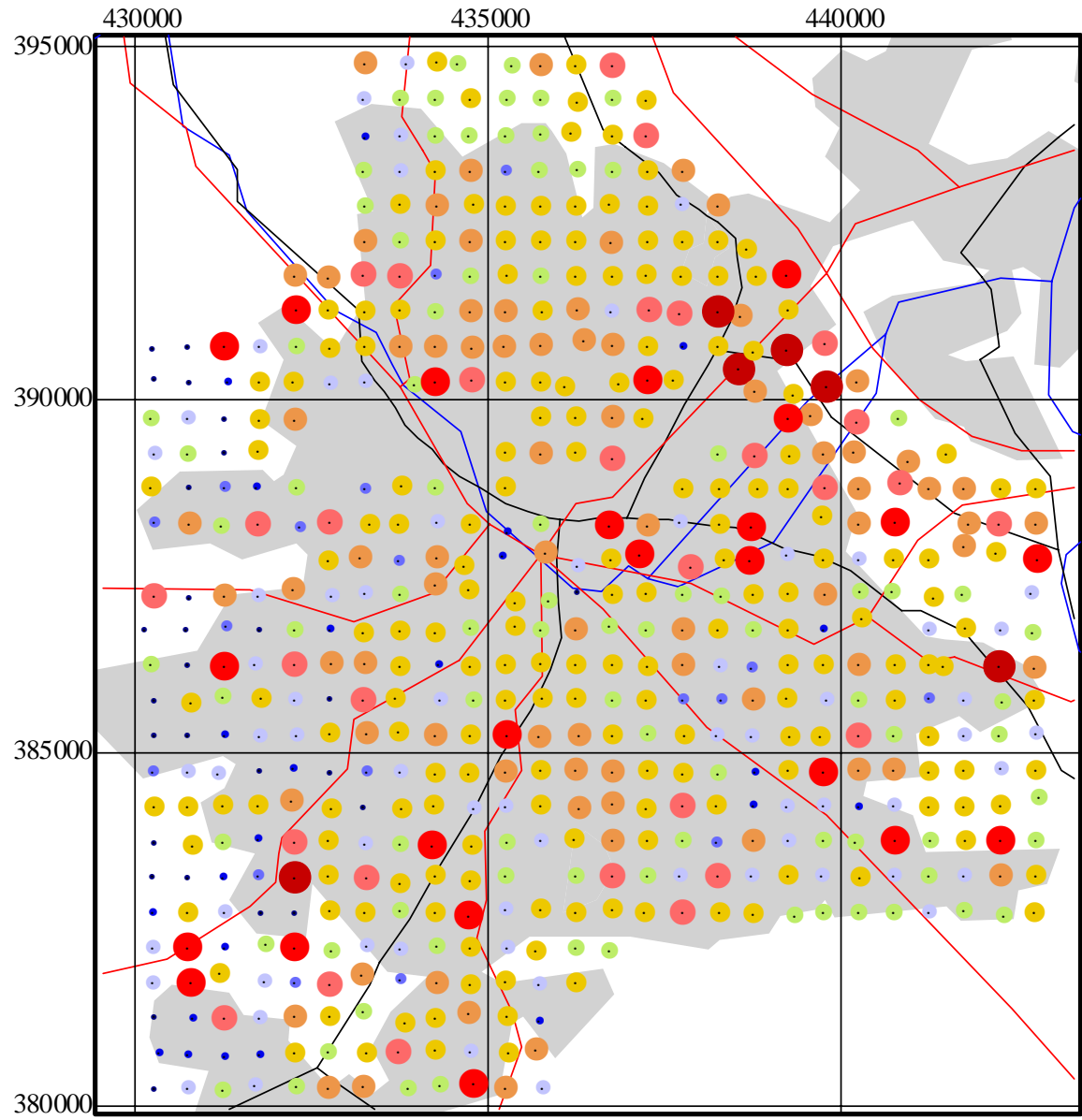
profile soil	Cr (ppm)
number	542
minimum	44
maximum	1490
median	94
mean	117



Sheffield Surface Soils Cobalt



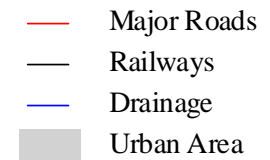
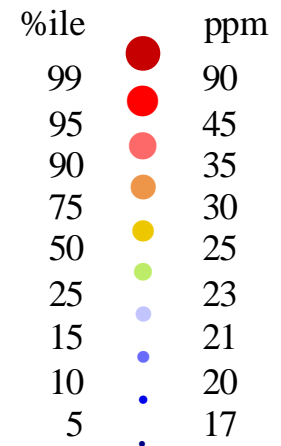
surface soil	Co (ppm)
number	575
minimum	7
maximum	1273
median	27
mean	30



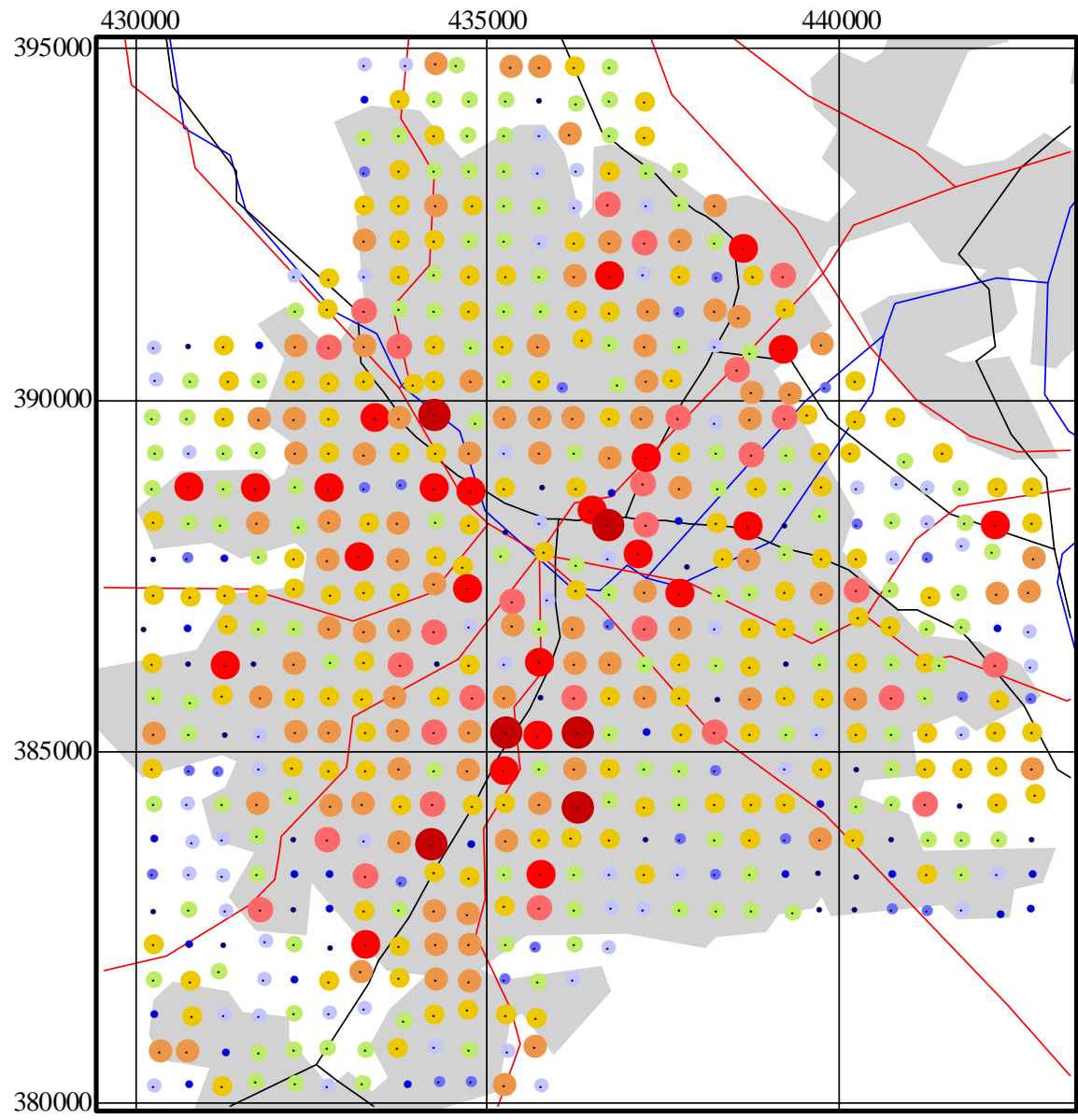
Sheffield

Profile Soils

Cobalt



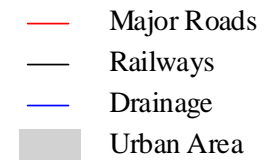
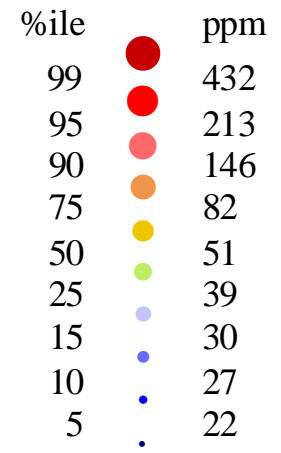
profile soil	Co (ppm)
number	542
minimum	10
maximum	323
median	25
mean	28



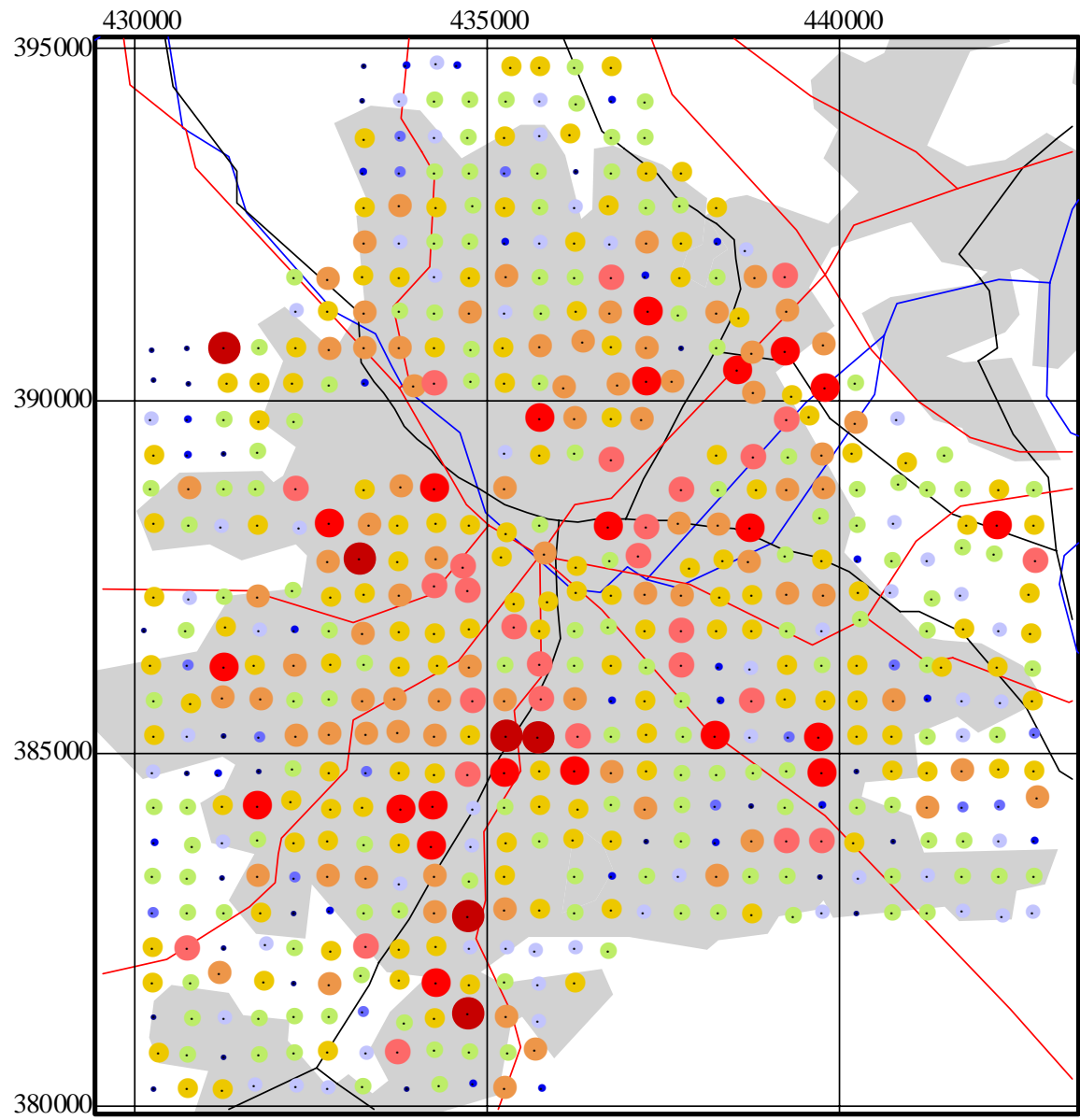
Sheffield

Surface Soils

Copper



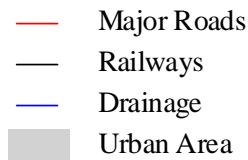
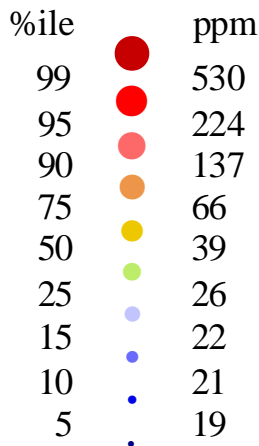
surface soil	Cu(ppm)
number	575
minimum	12
maximum	1575
median	51
mean	78



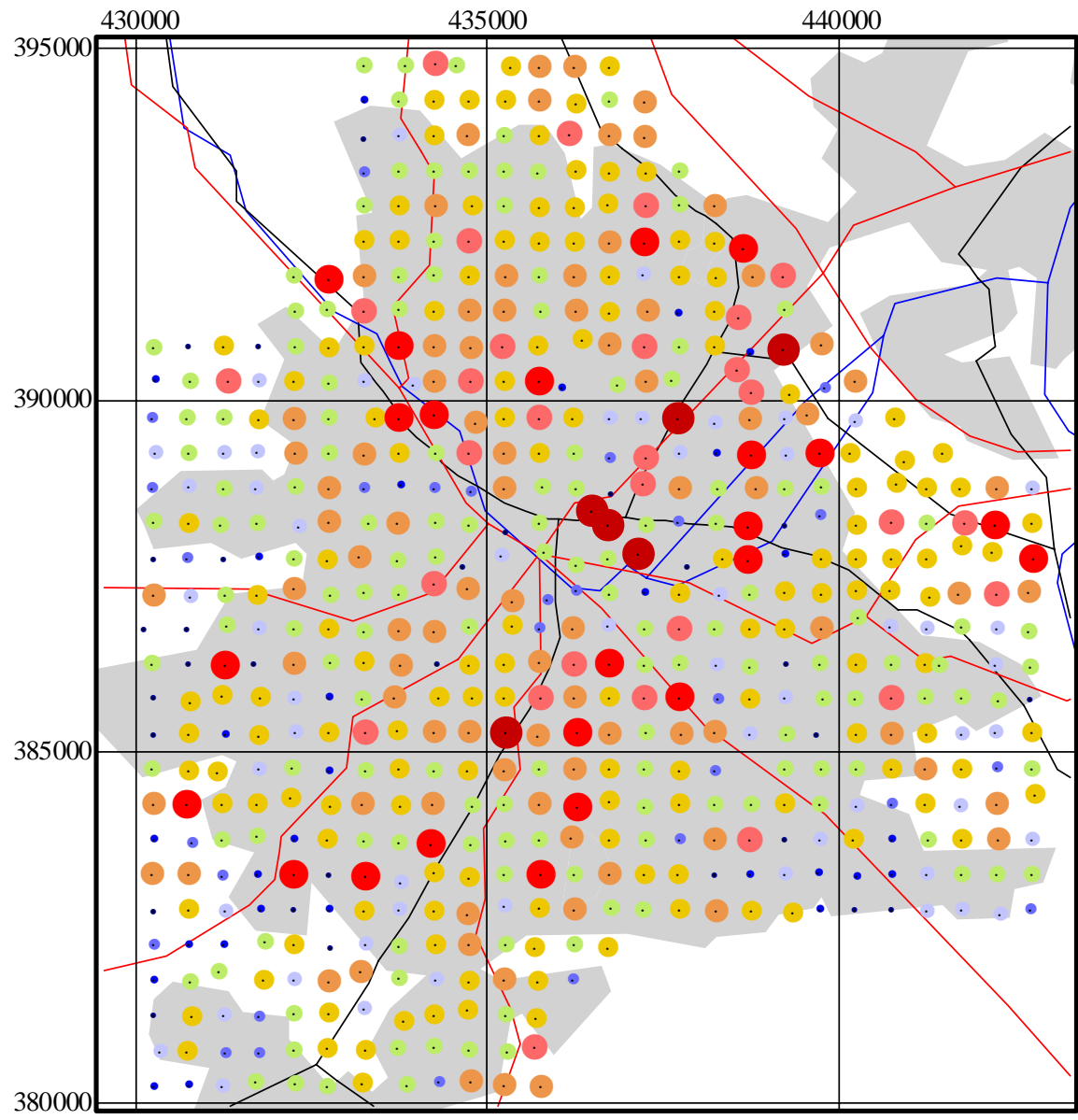
Sheffield

Profile Soils

Copper



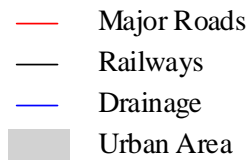
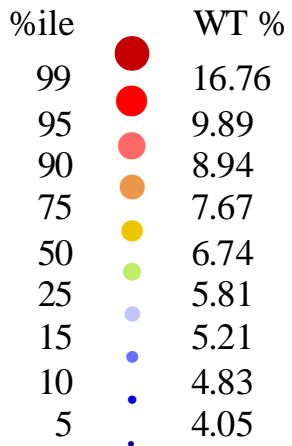
profile soil	Cu (ppm)
number	542
minimum	7
maximum	4088
median	39
mean	78



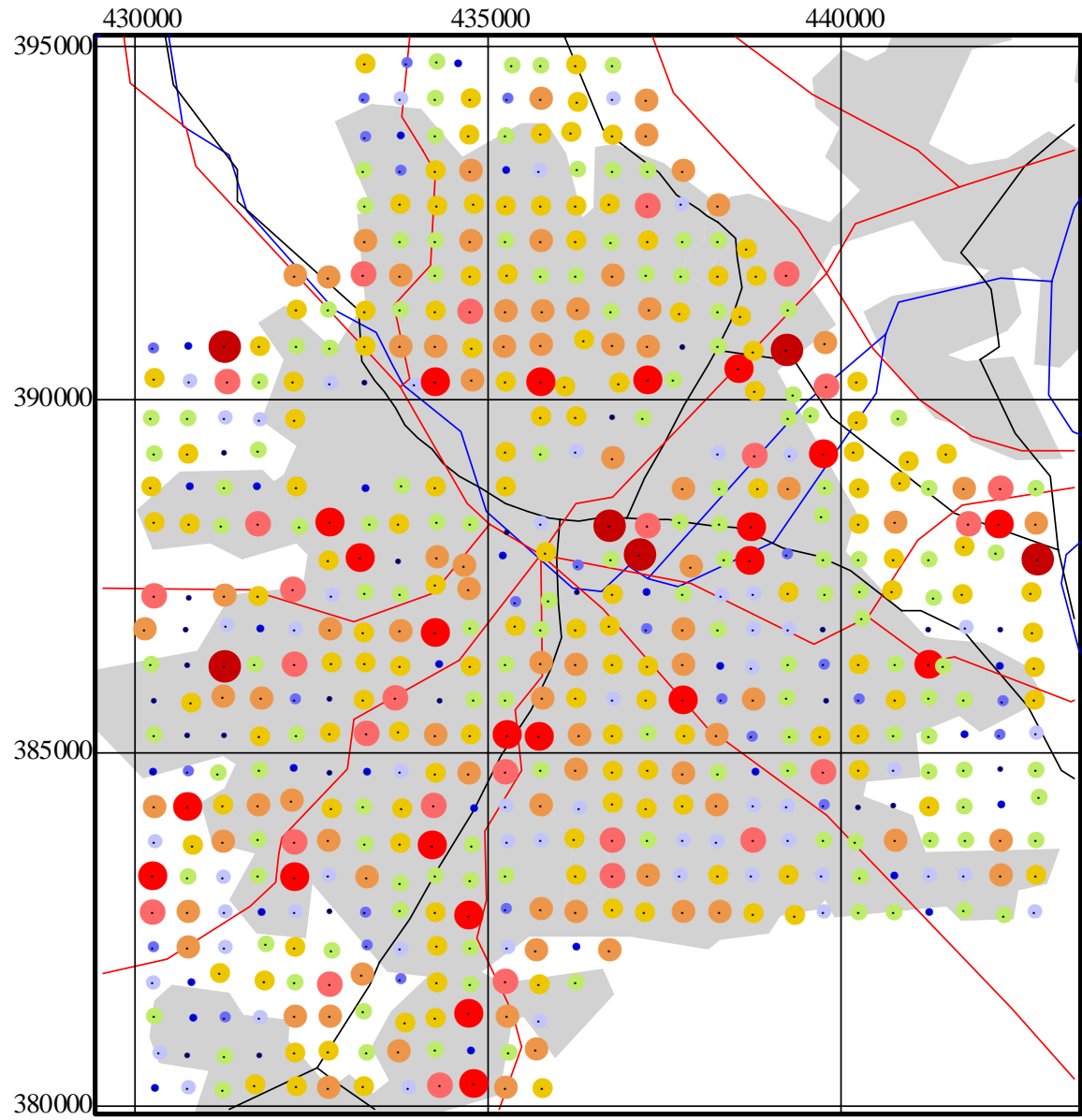
Sheffield

Surface Soils

Iron



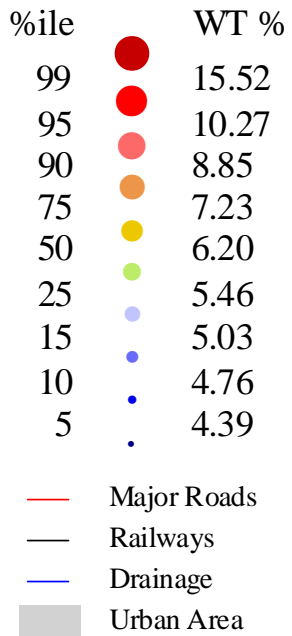
surface soil	Fe_2O_3 (%)
number	575
minimum	1.28
maximum	26.37
median	6.96
mean	6.74



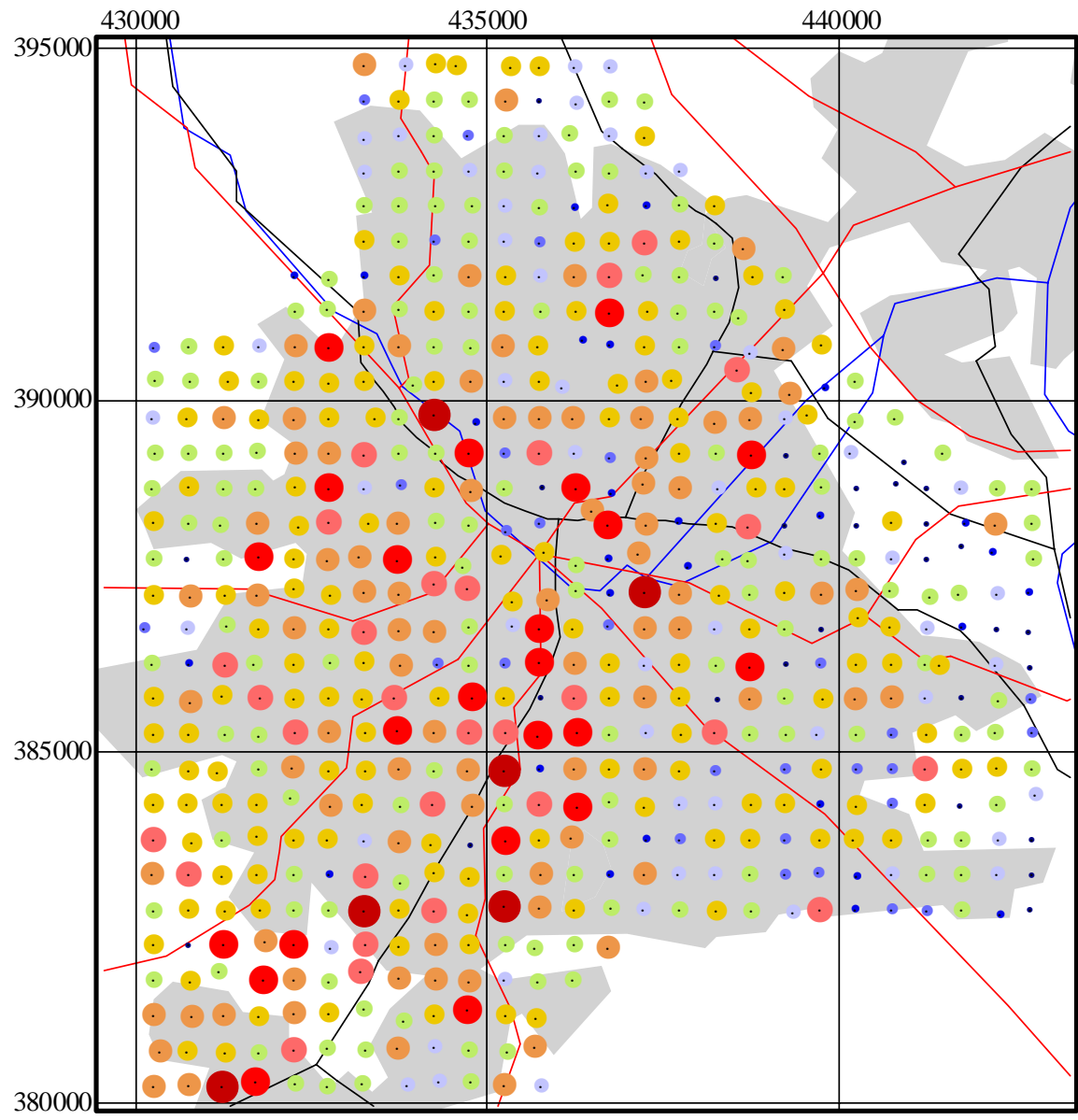
Sheffield

Profile Soils

Iron



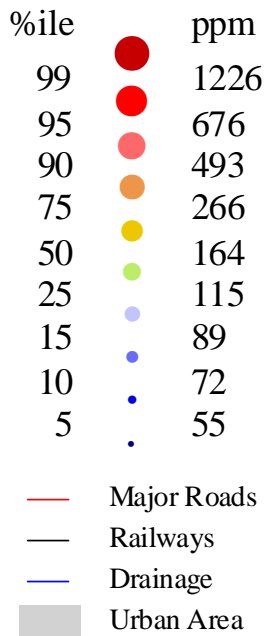
profile soil	Fe_2O_3 (%)
number	542
minimum	3.21
maximum	20.81
median	6.20
mean	6.63



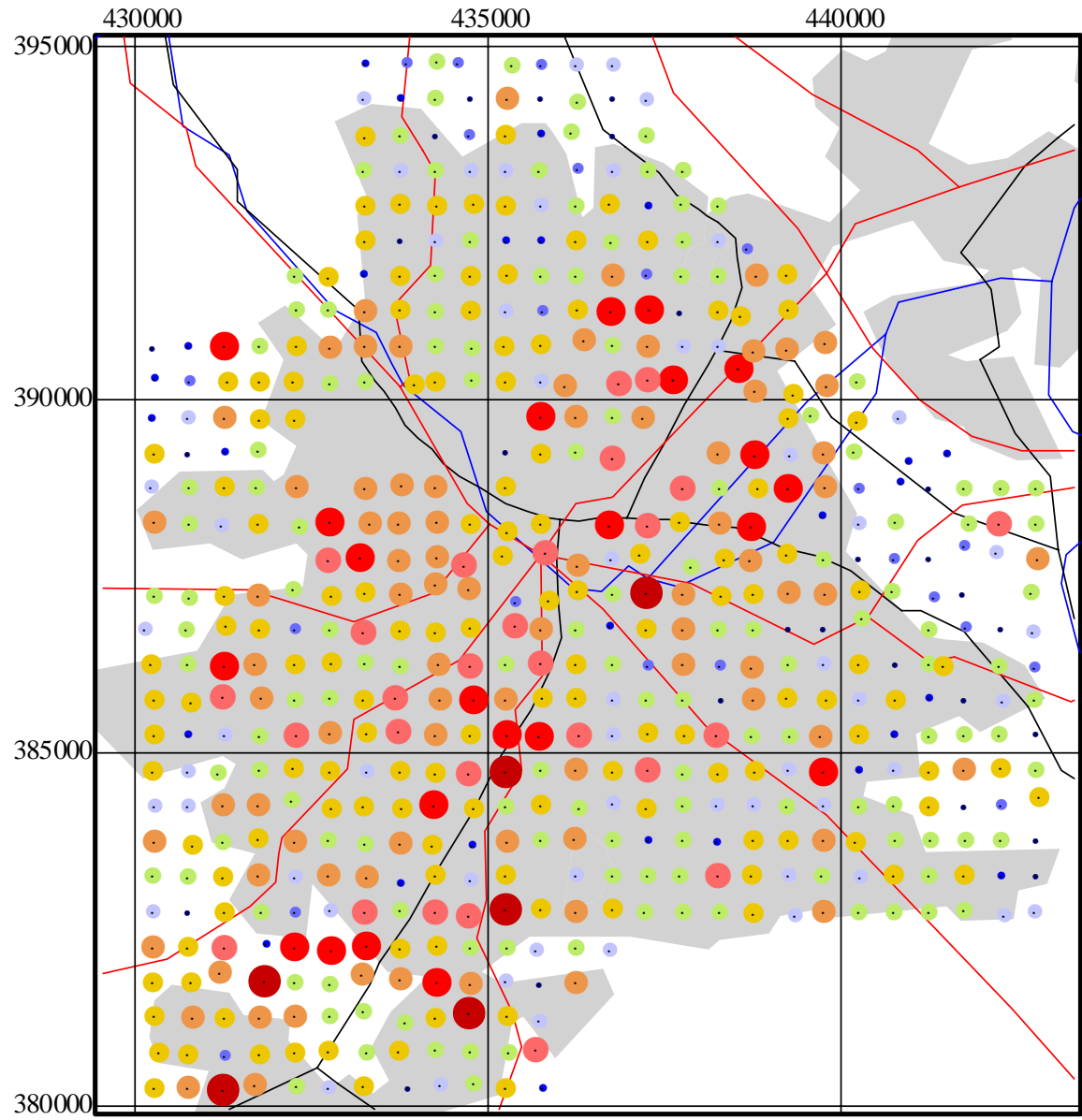
Sheffield

Surface Soils

Lead



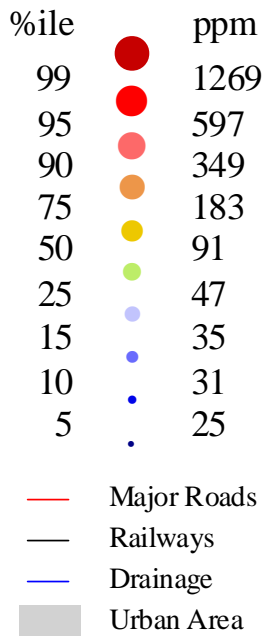
surface soil	Pb(ppm)
number	575
minimum	19
maximum	4300
median	164
mean	244



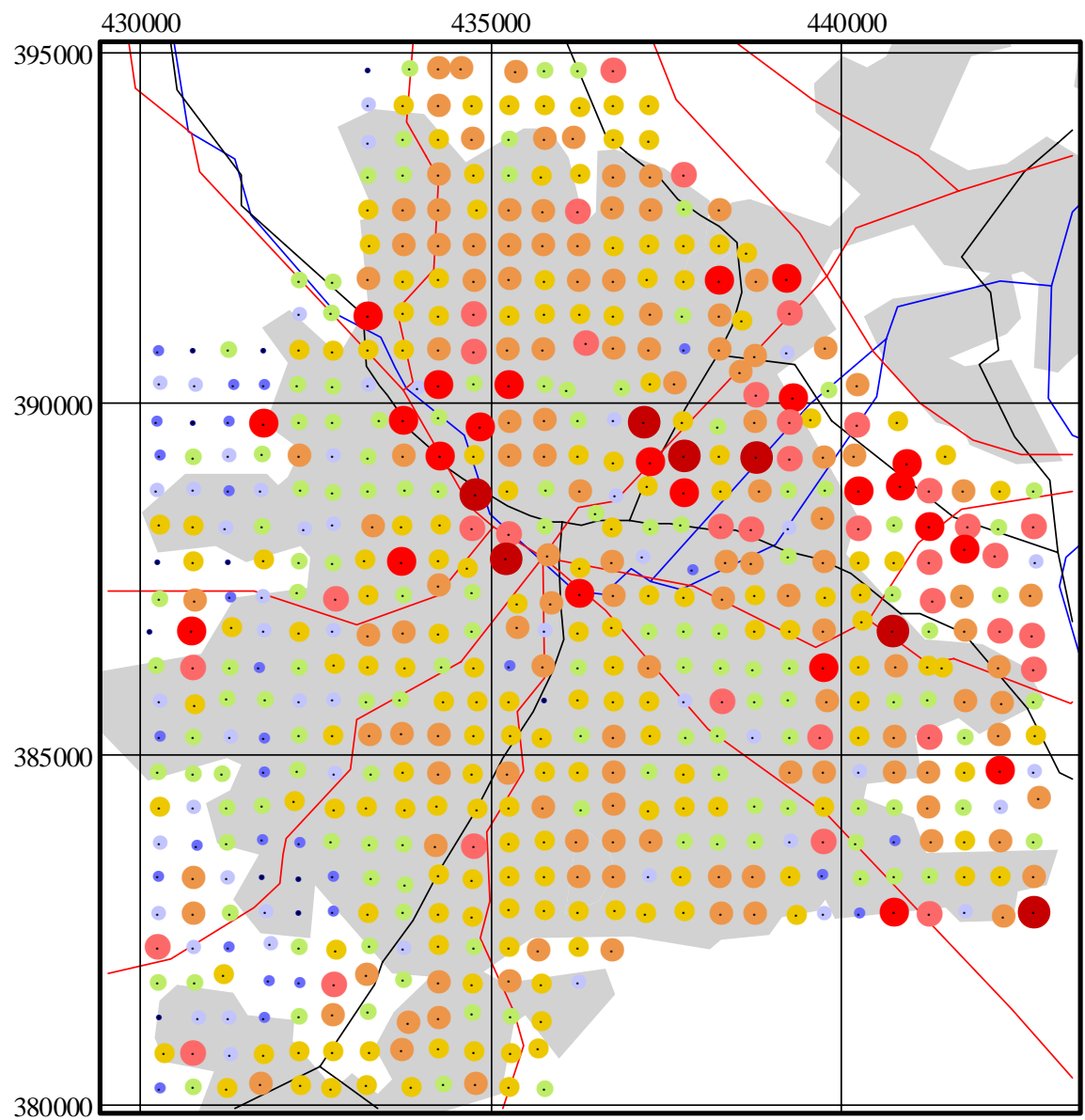
Sheffield

Profile Soils

Lead



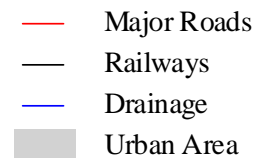
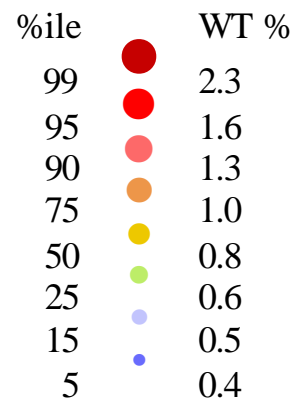
profile soil	Pb(ppm)
number	542
minimum	13
maximum	4000
median	91
mean	174



Sheffield

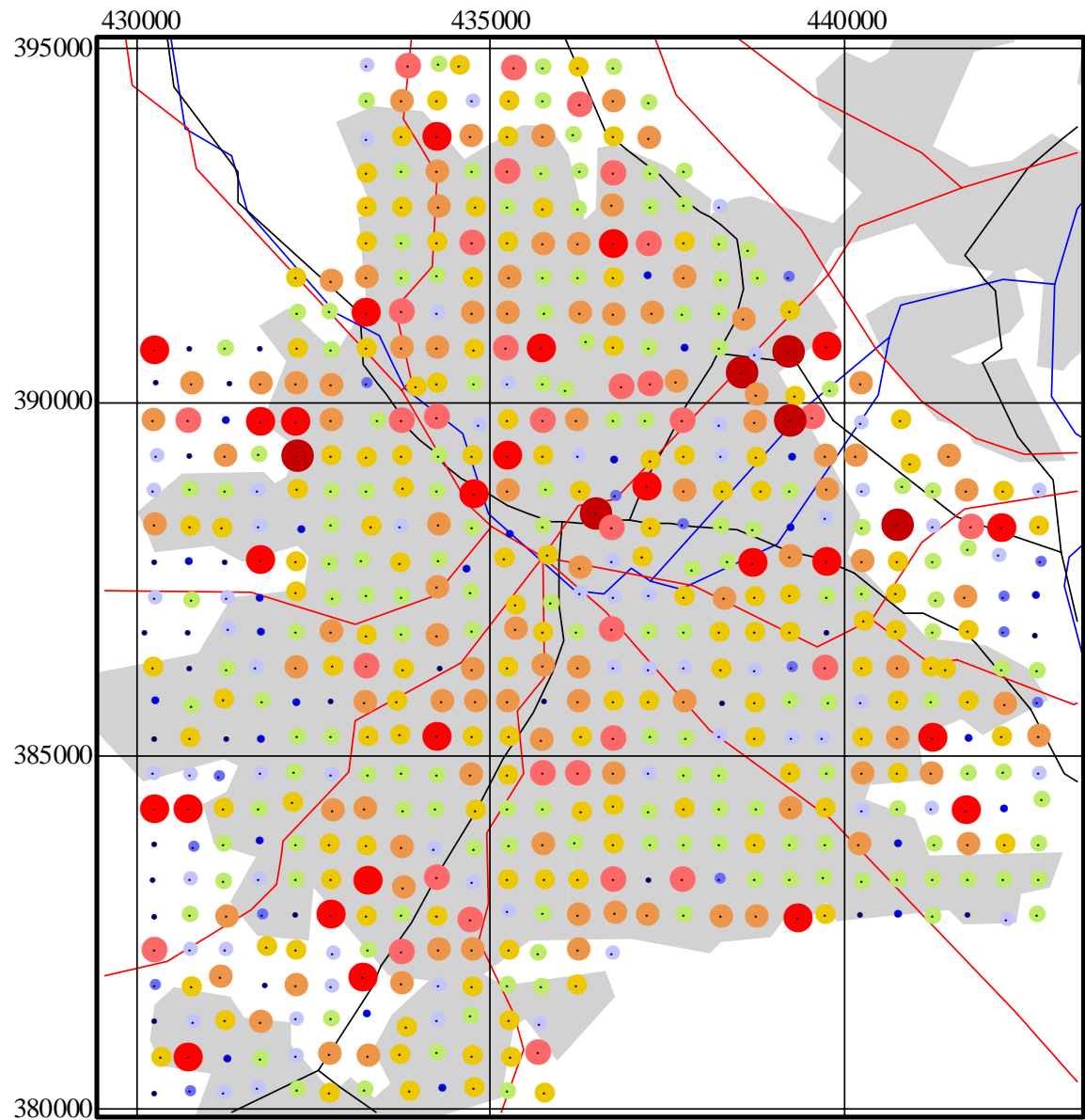
Surface Soils

Magnesium

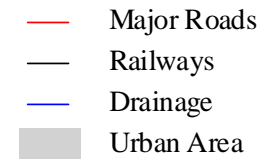
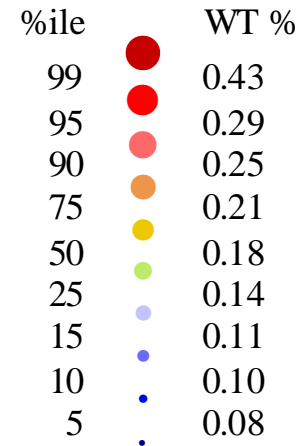


surface soil	MgO(%)
number	575
minimum	0.1
maximum	5.9
median	0.8
mean	0.9

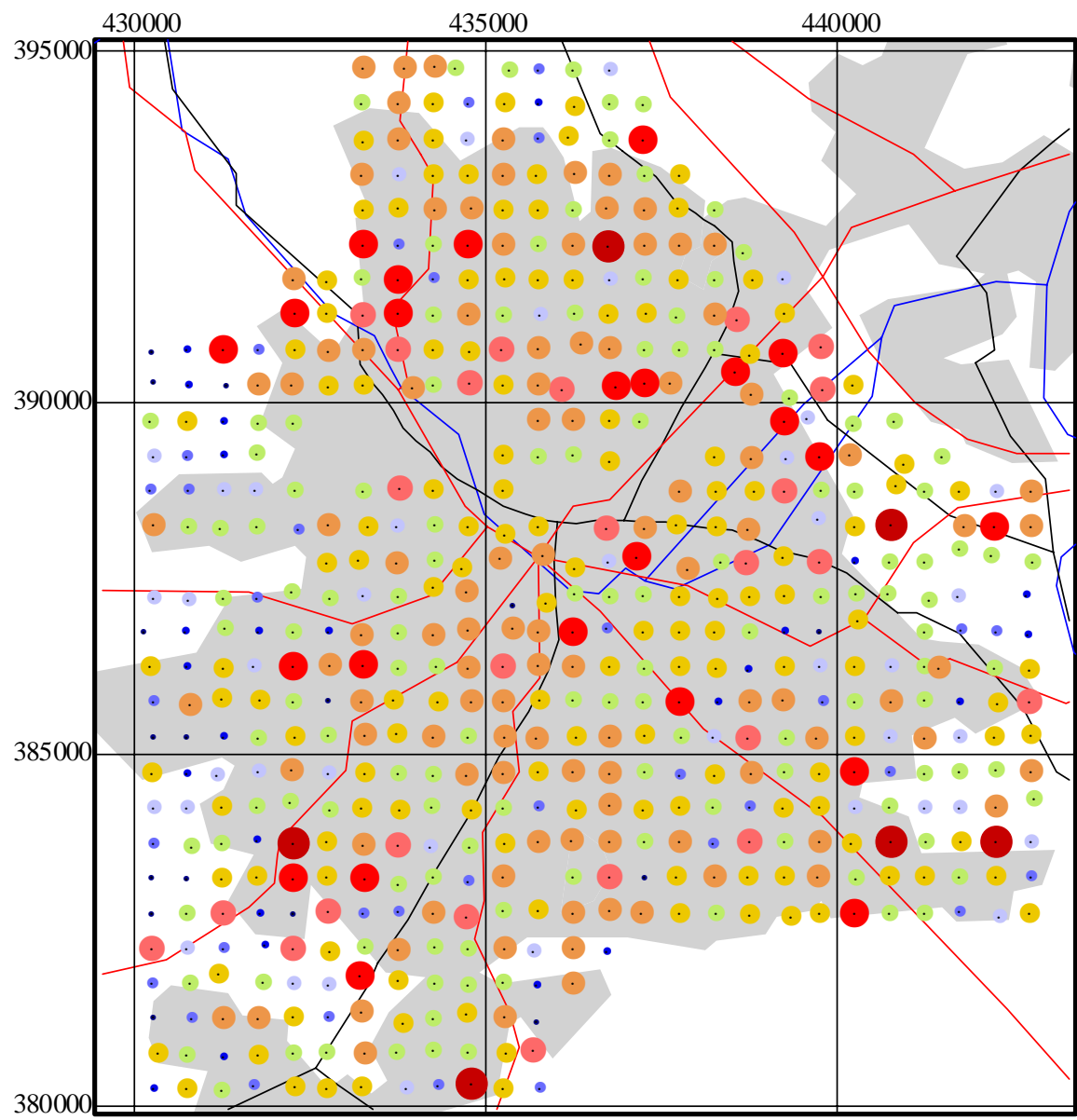
Magnesium was not determined in the Profile Soils



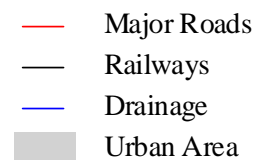
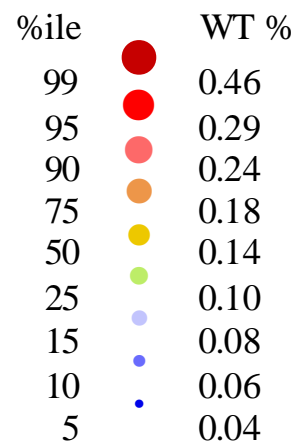
Sheffield Surface Soils Manganese



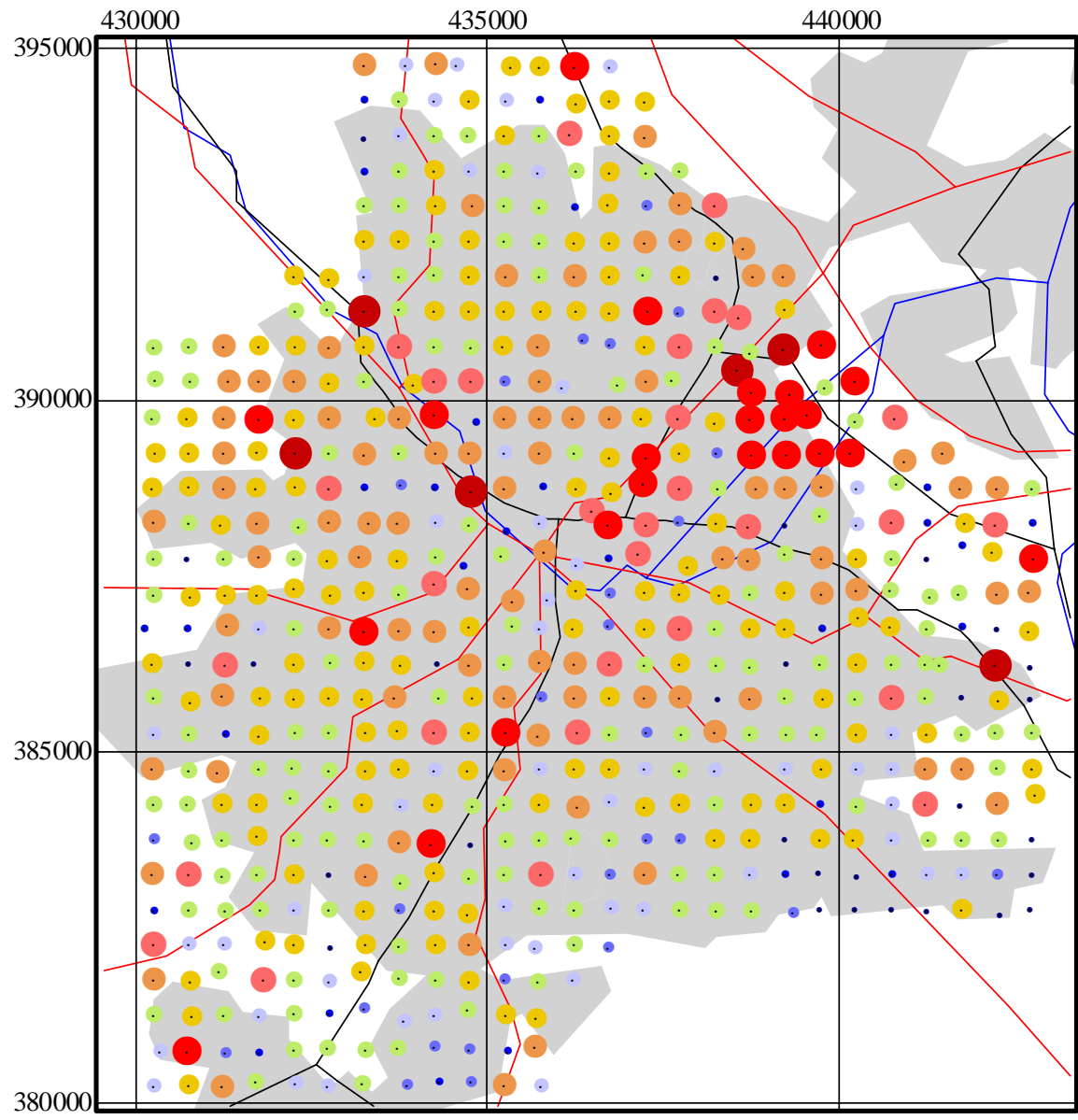
surface soil	MnO(%)
number	575
minimum	0.02
maximum	0.48
median	0.18
mean	0.18



Sheffield Profile Soils Manganese



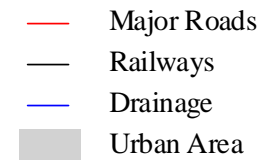
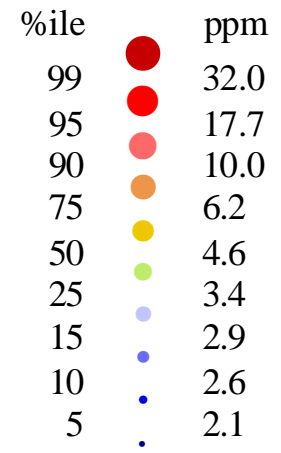
profile soil	MnO (%)
number	542
minimum	0.01
maximum	1.58
median	0.14
mean	0.15



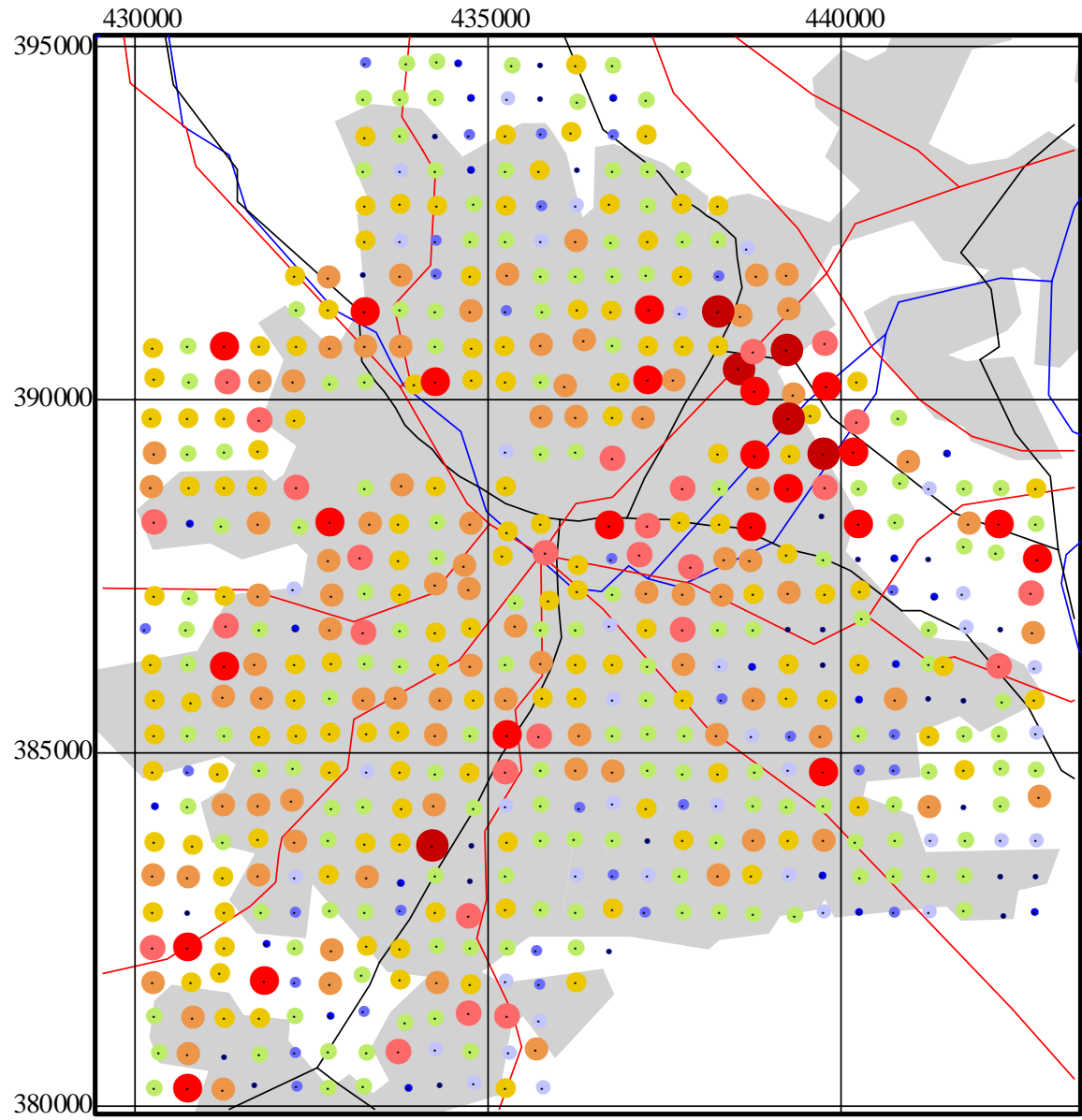
Sheffield

Surface Soils

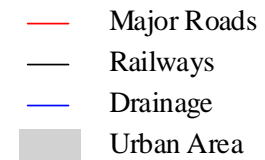
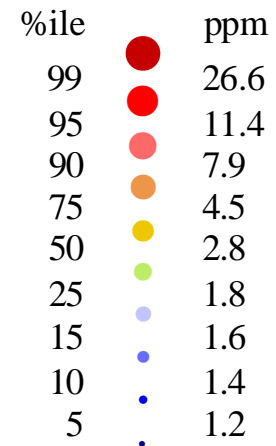
Molybdenum



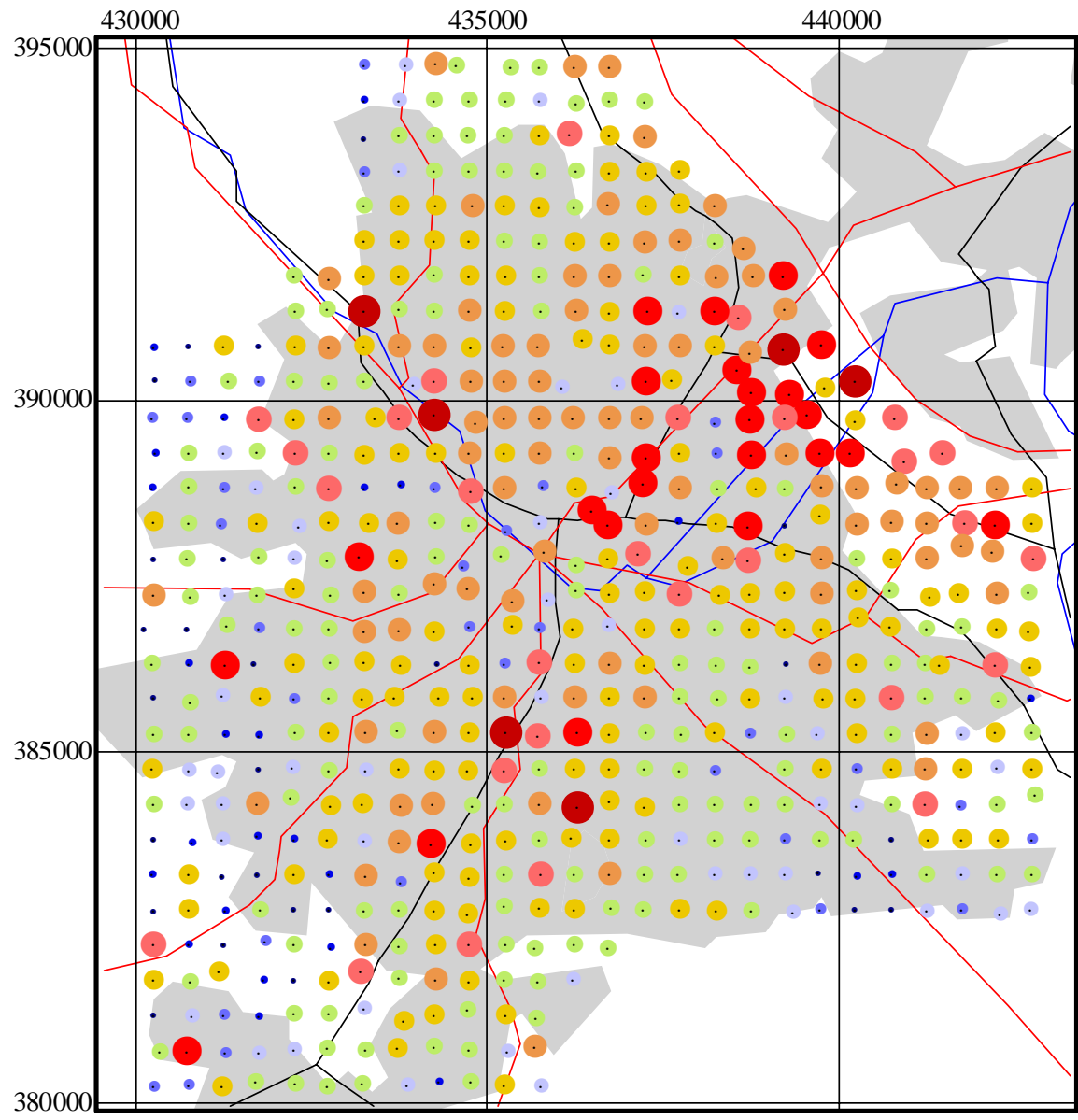
surface soil	Mo (ppm)
number	575
minimum	1
maximum	58.3
median	4.6
mean	6.2



Sheffield Profile Soils Molybdenum



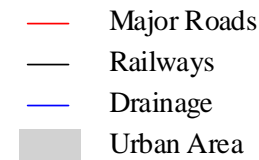
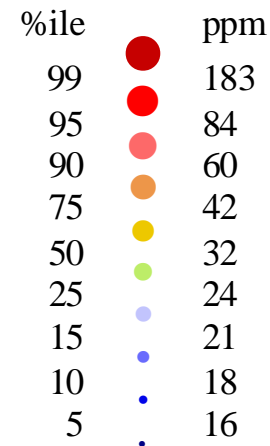
profile soil	Mo (ppm)
number	542
minimum	0.6
maximum	115
median	2.8
mean	4.3



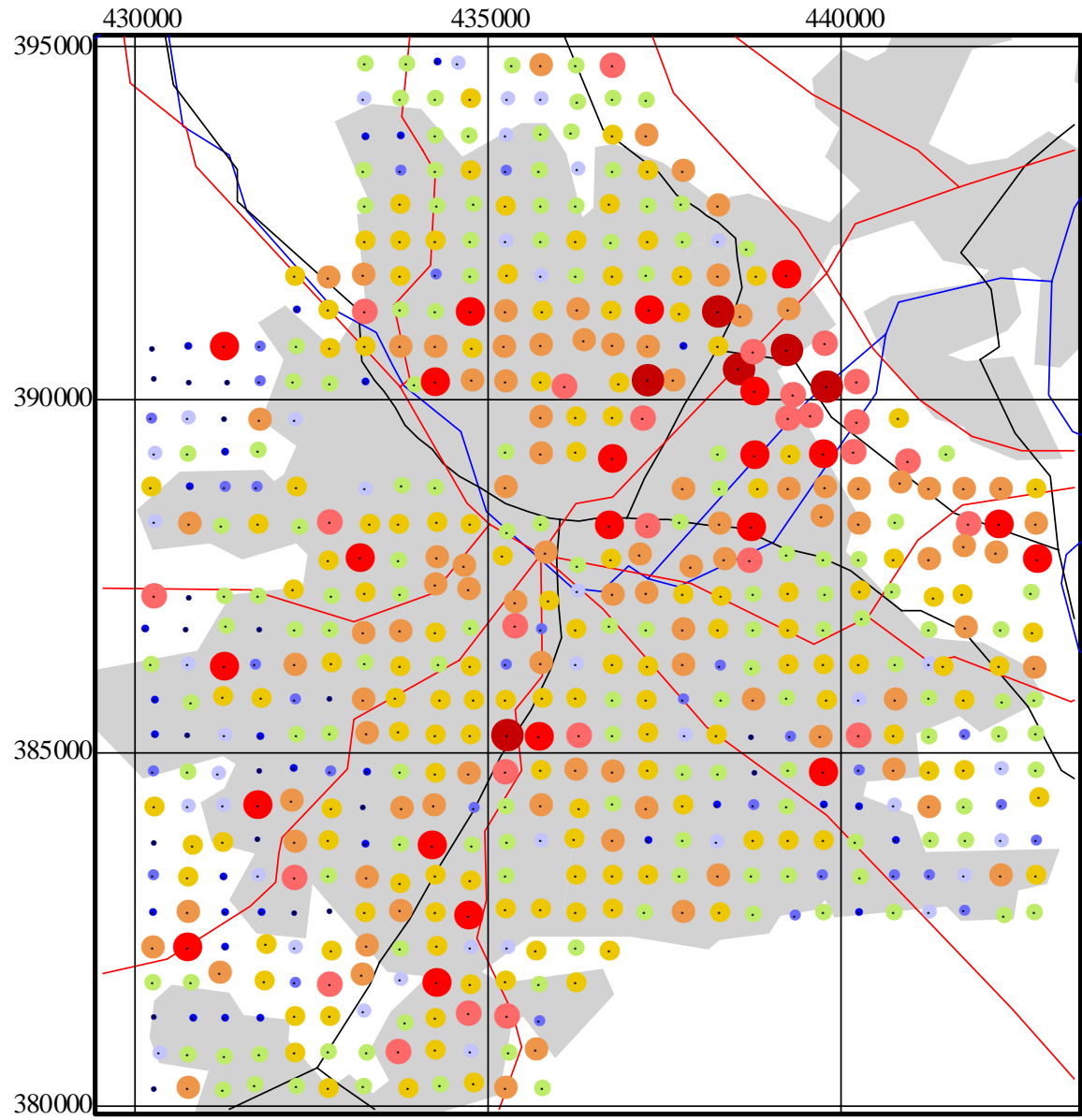
Sheffield

Surface Soils

Nickel



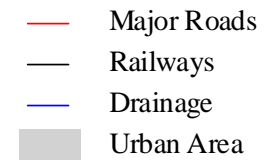
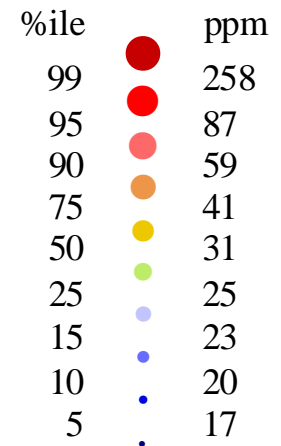
surface soil	Ni(ppm)
number	575
minimum	8
maximum	473
median	32
mean	40



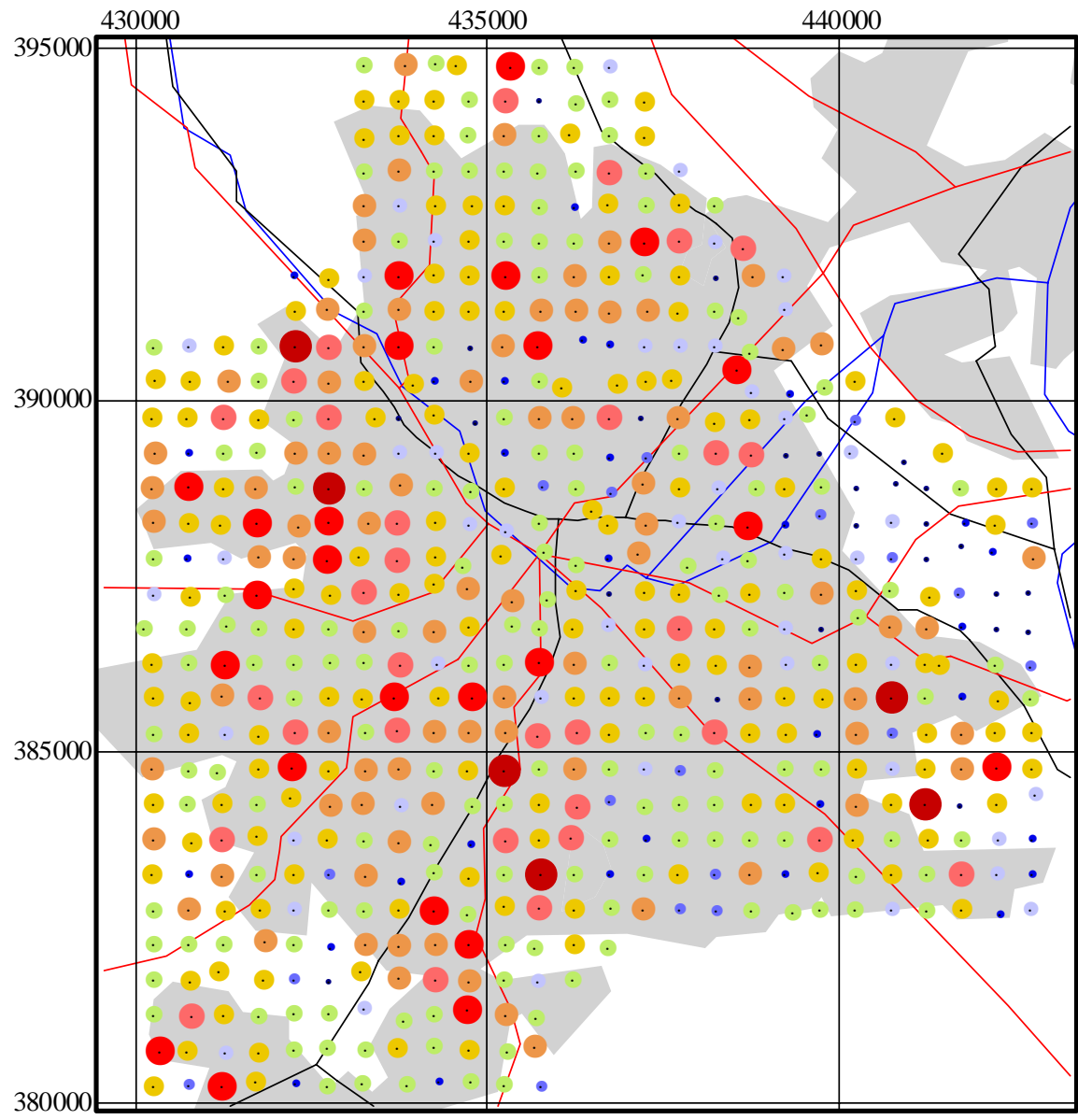
Sheffield

Profile Soils

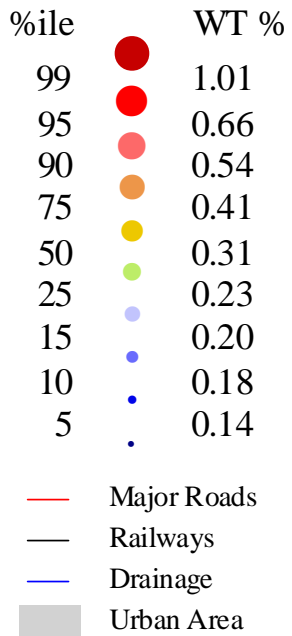
Nickel



profile soil	Ni (ppm)
number	542
minimum	9
maximum	1358
median	31
mean	43

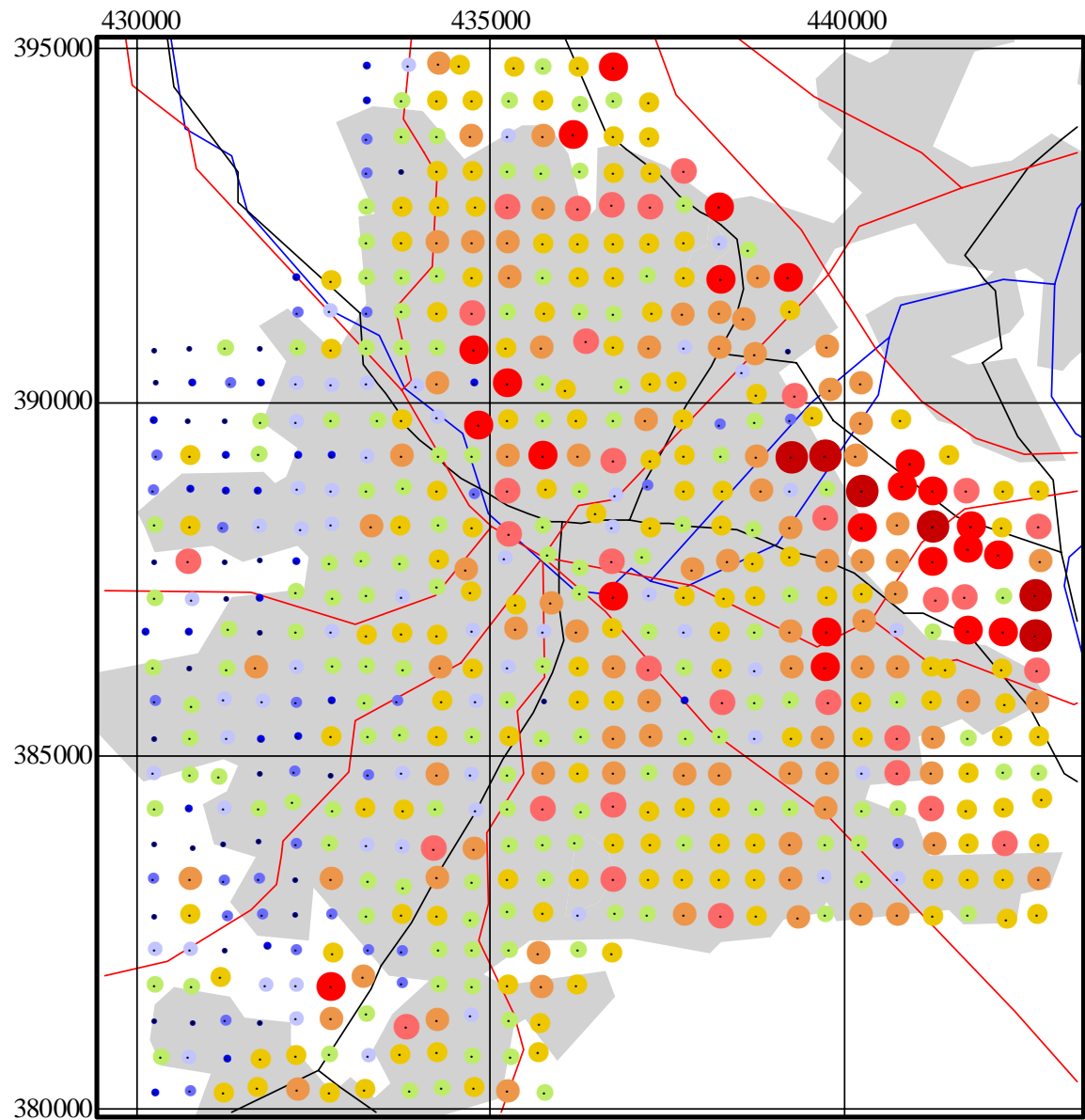


Sheffield Surface Soils Phosphorus



surface soil	P ₂ O ₅ (%)
number	575
minimum	0.05
maximum	1.51
median	0.31
mean	0.34

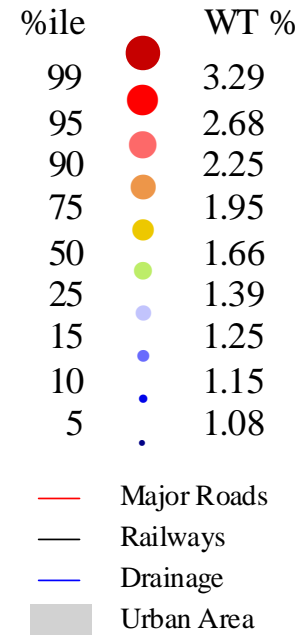
Phosphorus was not determined in the Profile Soils



Sheffield

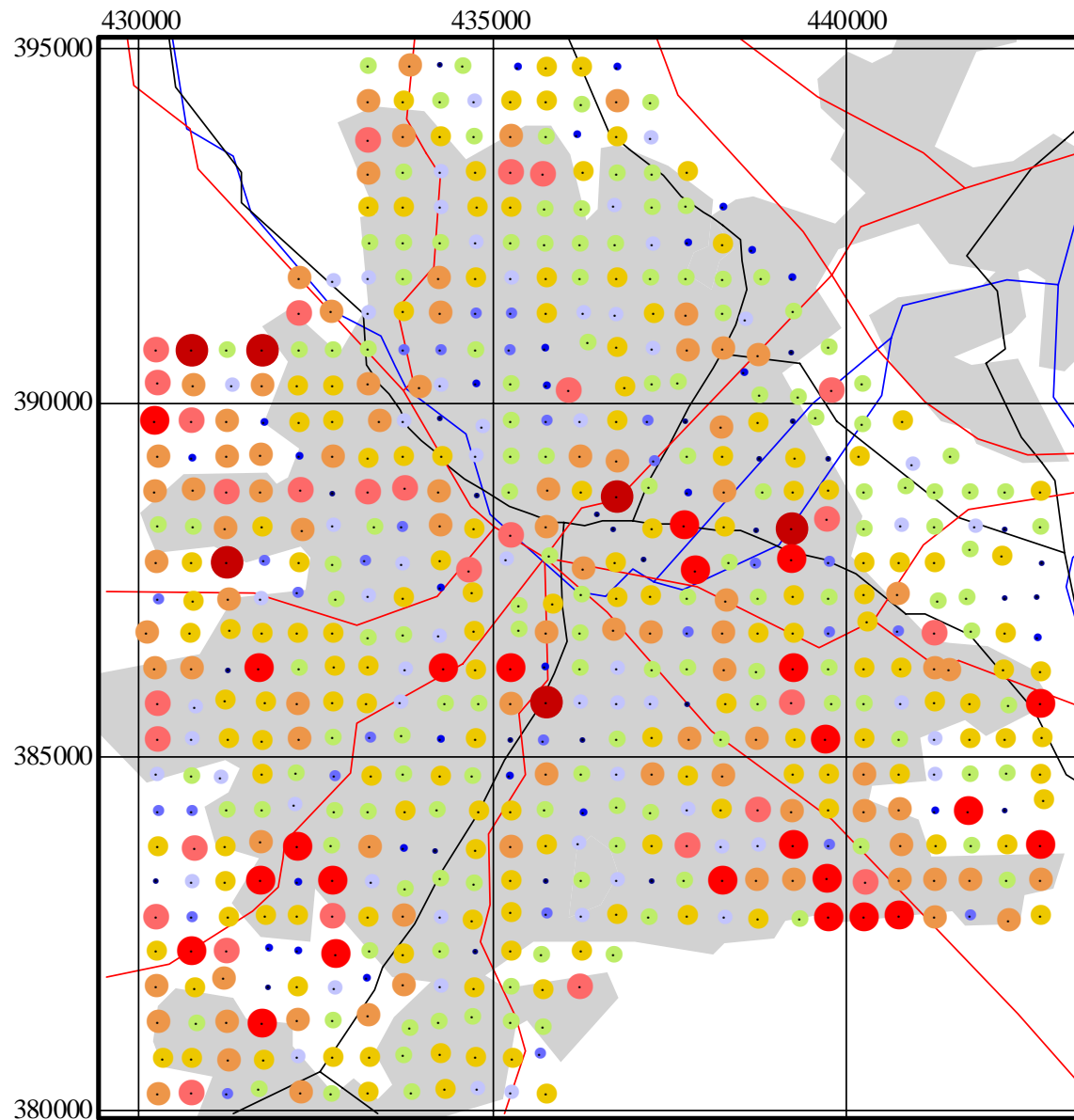
Surface Soils

Potassium



surface soil	K ₂ O (%)
number	575
minimum	0.54
maximum	4.02
median	1.66
mean	1.71

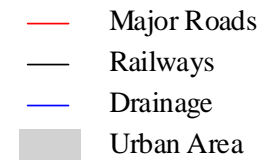
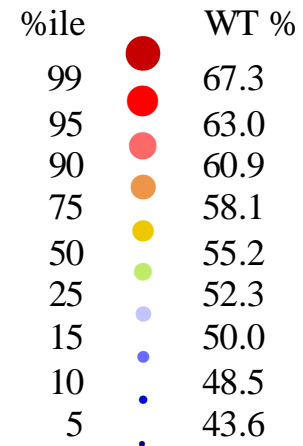
Potassium was not determined in the Profile Soils



Sheffield

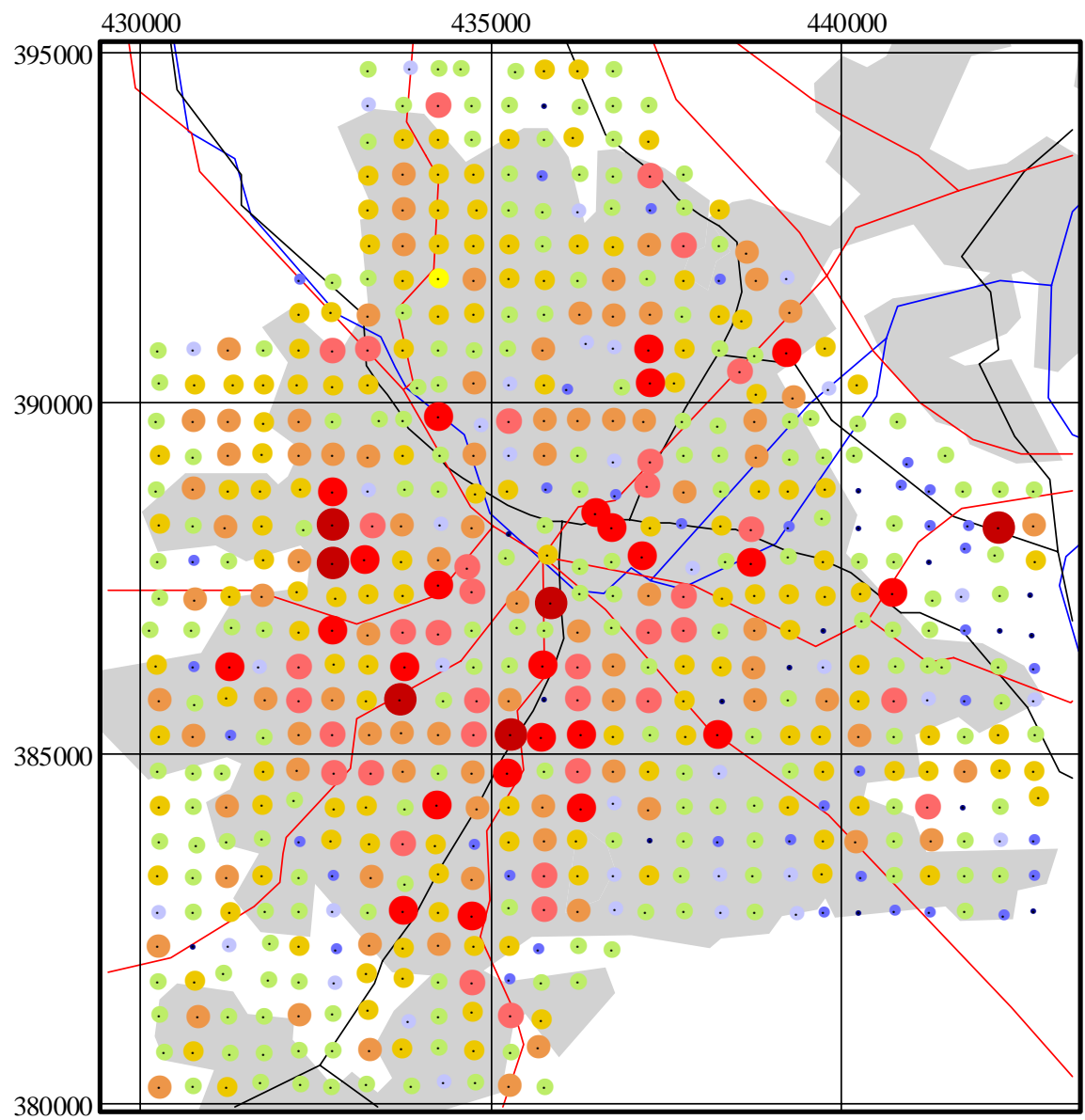
Surface Soils

Silicon



surface soil	SiO ₂ (%)
number	575
minimum	19.7
maximum	73.2
median	55.2
mean	54.6

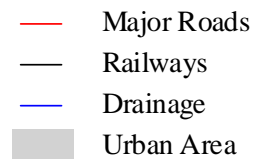
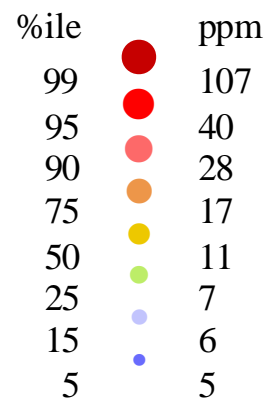
Silicon was not determined in the Profile Soils



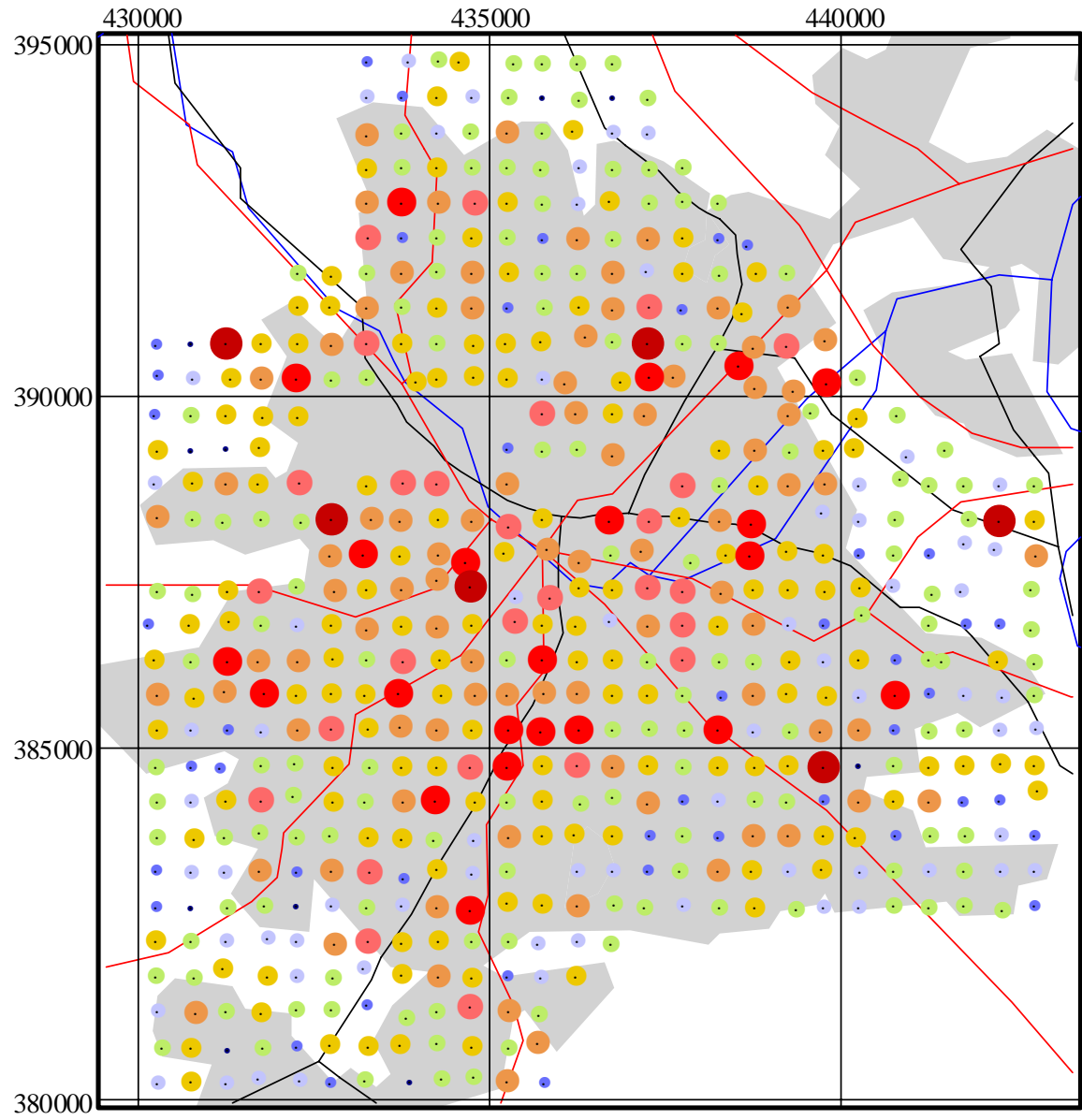
Sheffield

Surface Soils

Tin



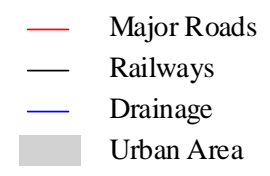
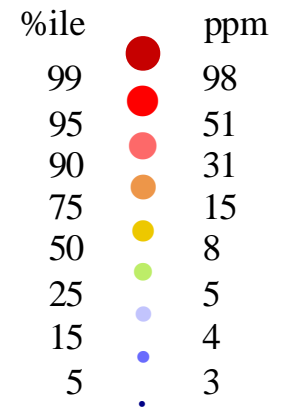
surface soil	Sn (ppm)
number	575
minimum	2
maximum	199
median	16
mean	11



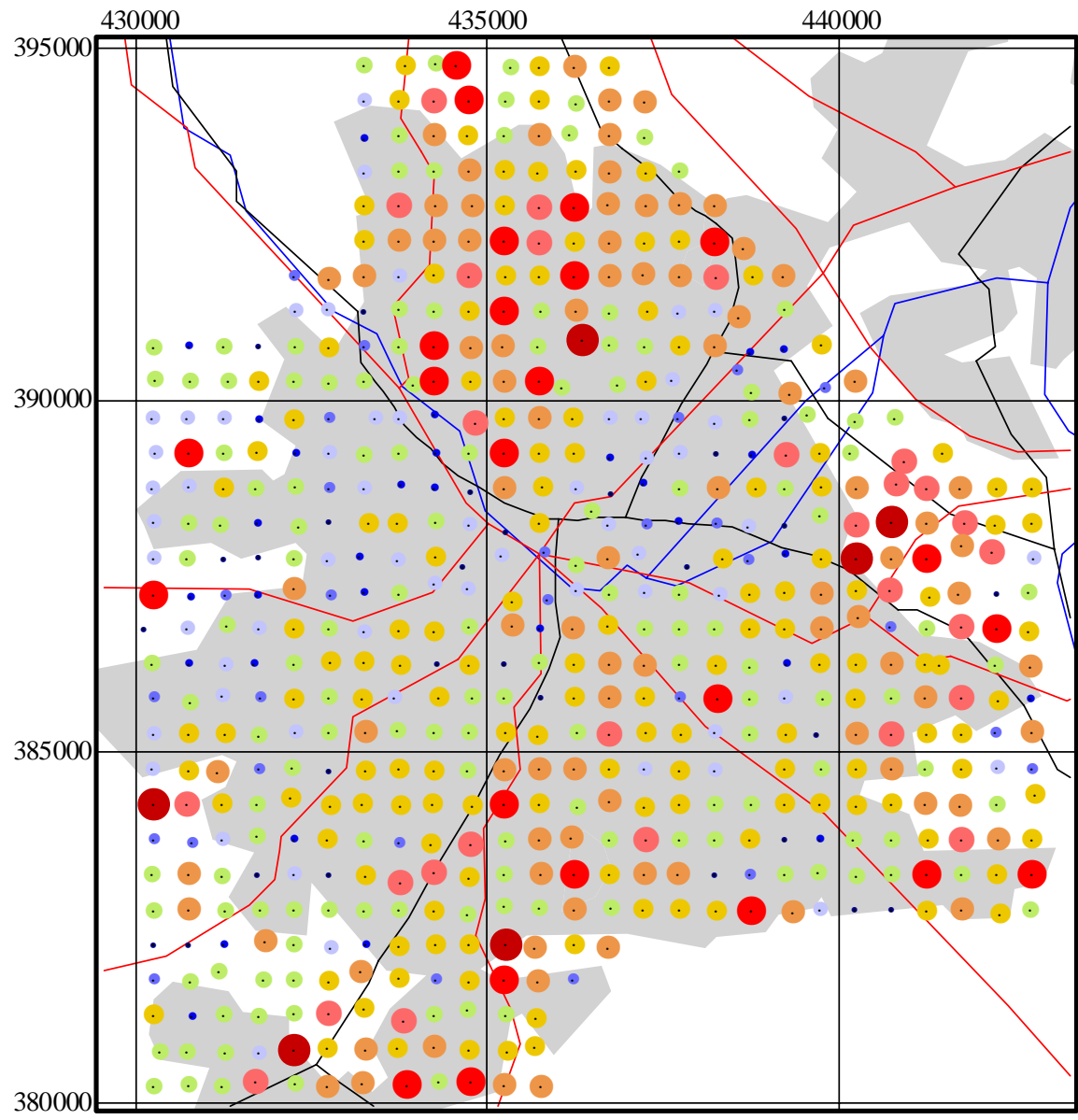
Sheffield

Profile Soils

Tin



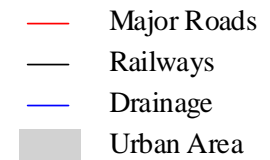
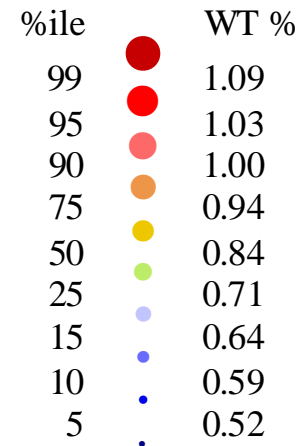
profile soil	Sn(ppm)
number	542
minimum	1
maximum	378
median	8
mean	15



Sheffield

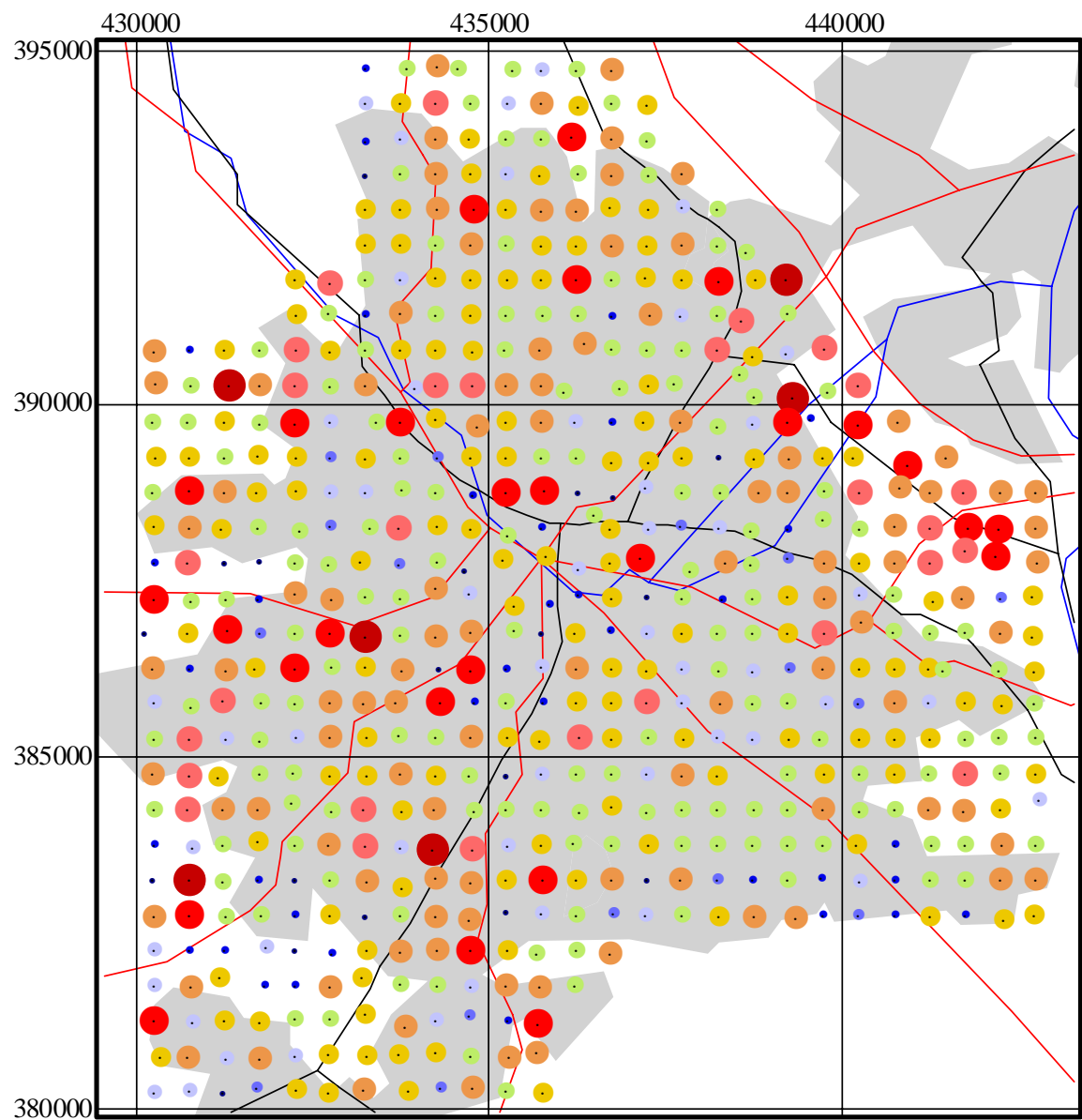
Surface Soils

Titanium



surface soil	TiO ₂ (%)
number	575
minimum	0.18
maximum	1.18
median	0.84
mean	0.82

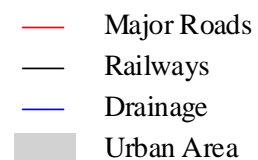
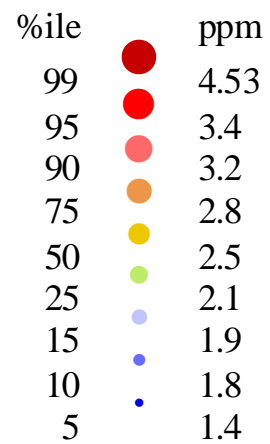
Titanium was not determined in the Profile Soils



Sheffield

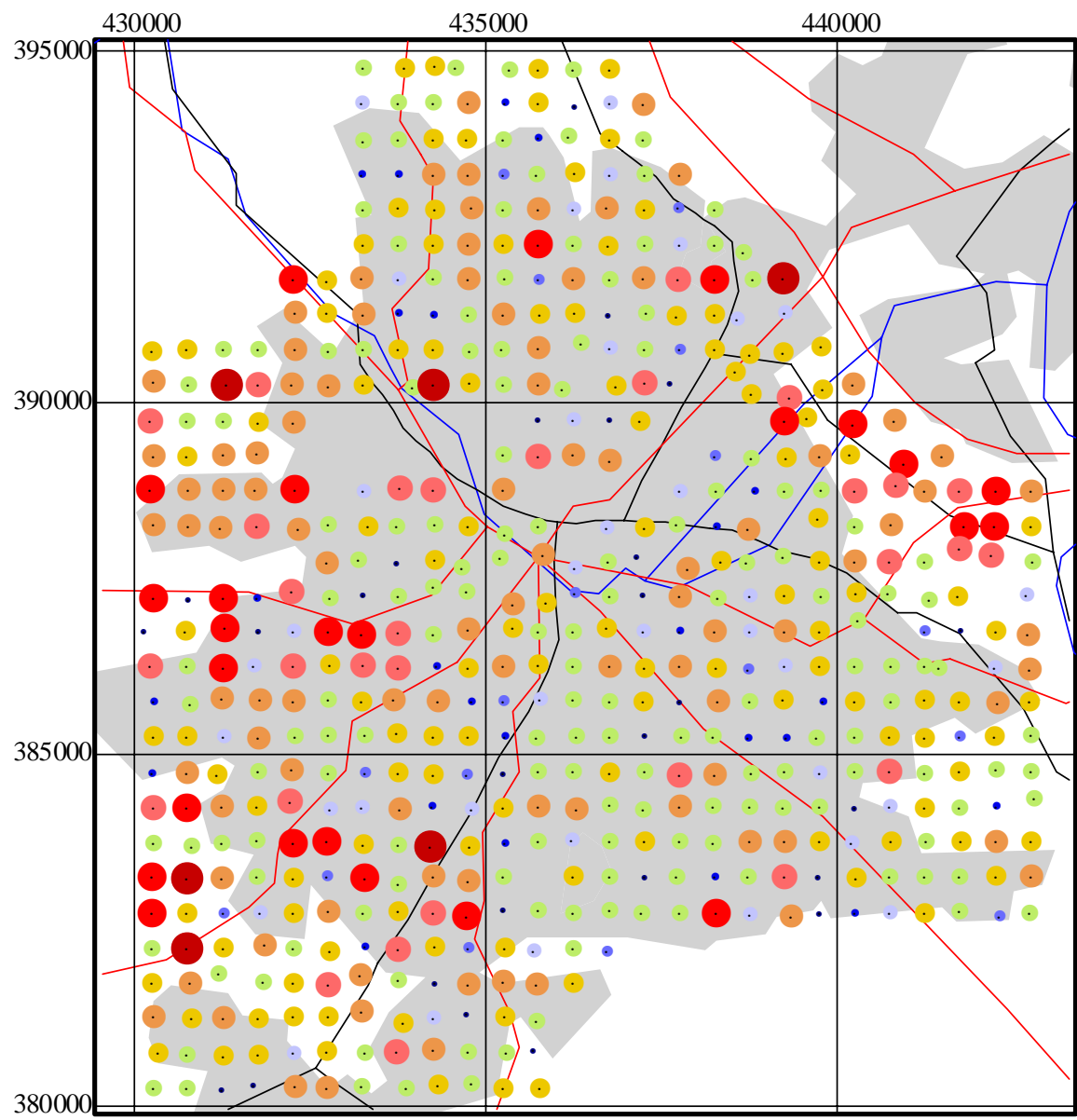
Surface Soils

Uranium



surface soil	U(ppm)
number	575
minimum	0.25*
maximum	8.8
median	2.5
mean	2.49

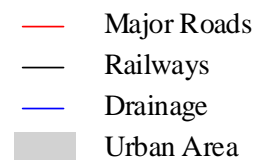
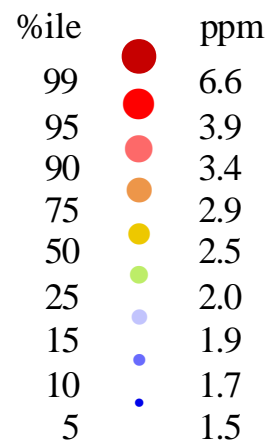
* minimum value reported as half detection limit



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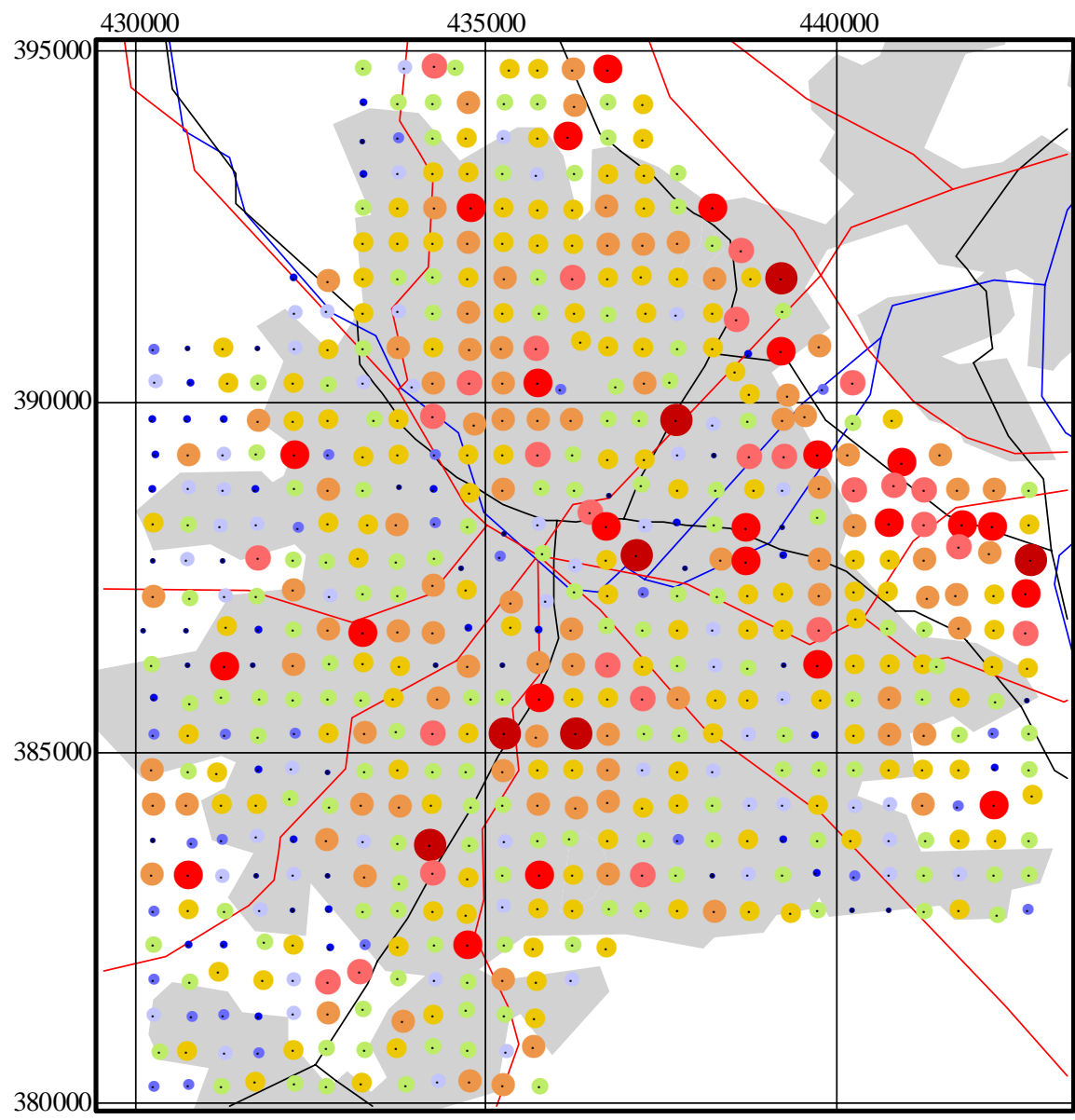
Profile Soils

Uranium



profile soil	U (ppm)
number	542
minimum	0.25*
maximum	10.5
median	2.5
mean	2.58

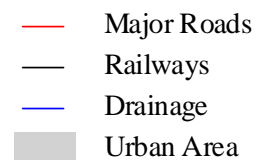
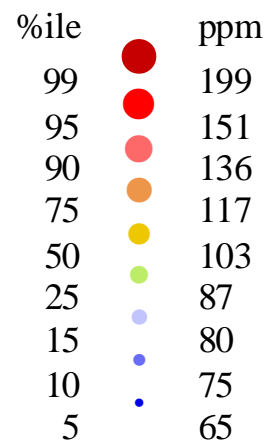
* minimum value quoted as half detection limit



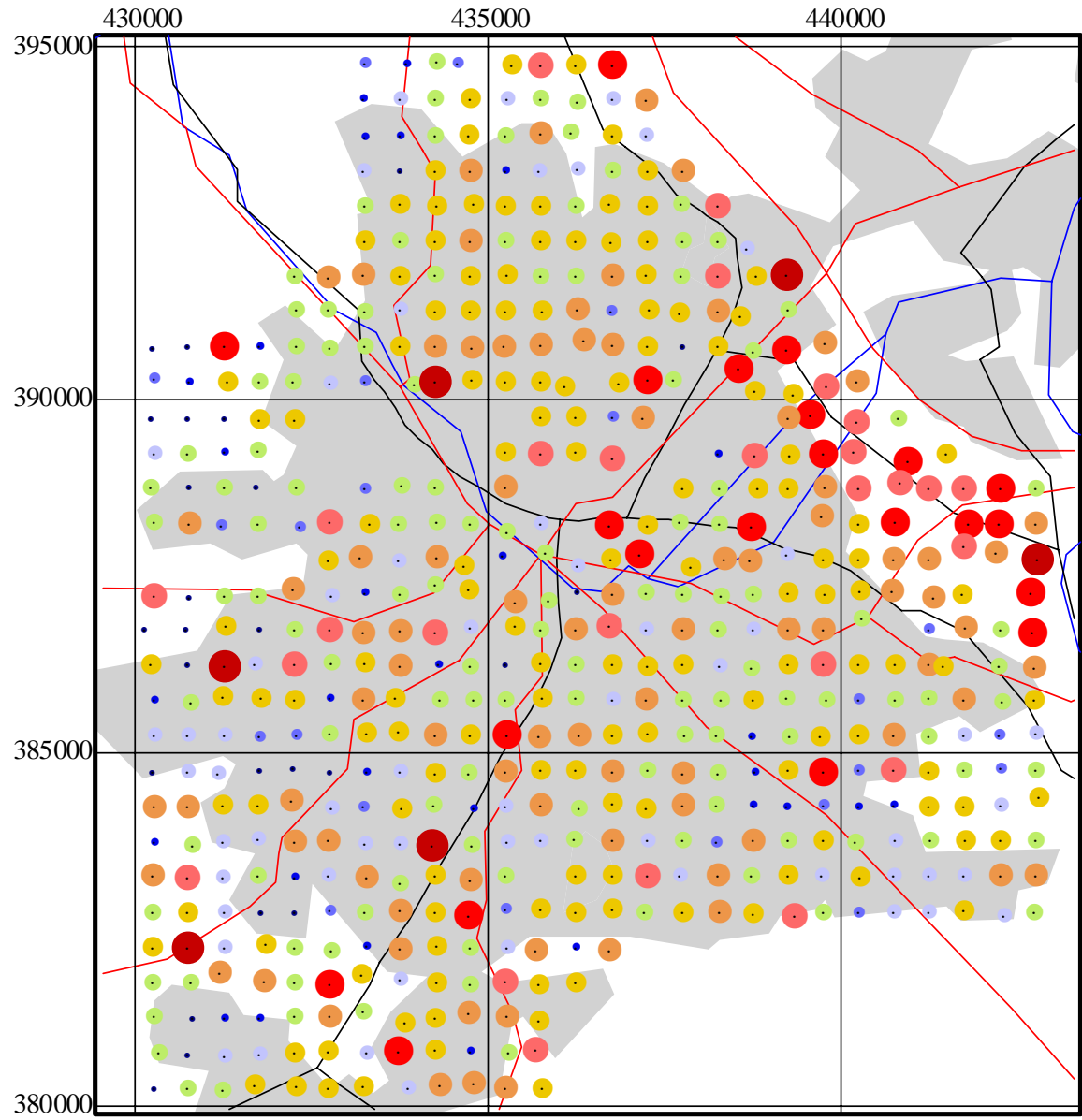
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Surface Soils

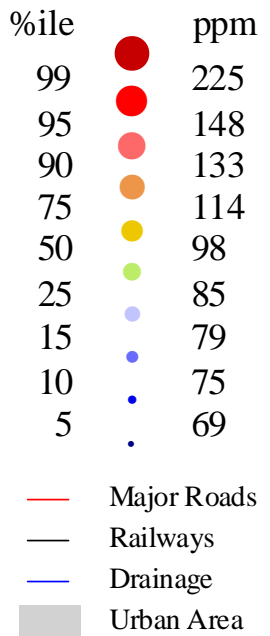
Vanadium



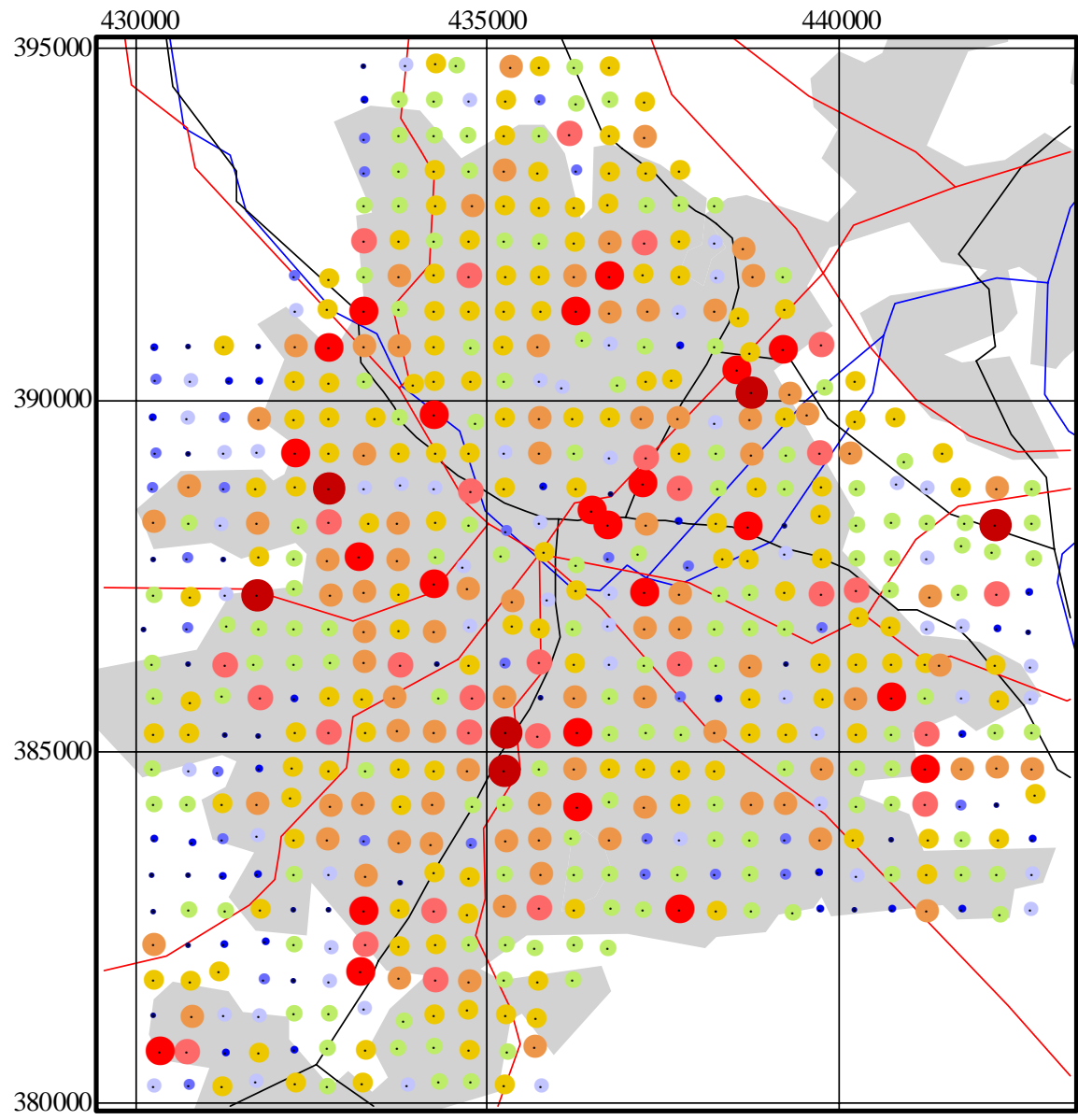
surface soil	V(ppm)
number	575
minimum	38
maximum	382
median	103
mean	105



Sheffield Profile Soils Vanadium



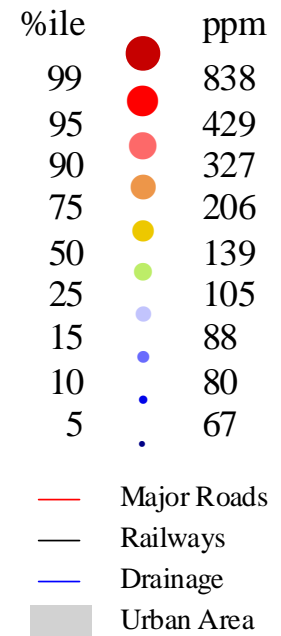
profile soil	V (ppm)
number	542
minimum	45
maximum	403
median	98
mean	103



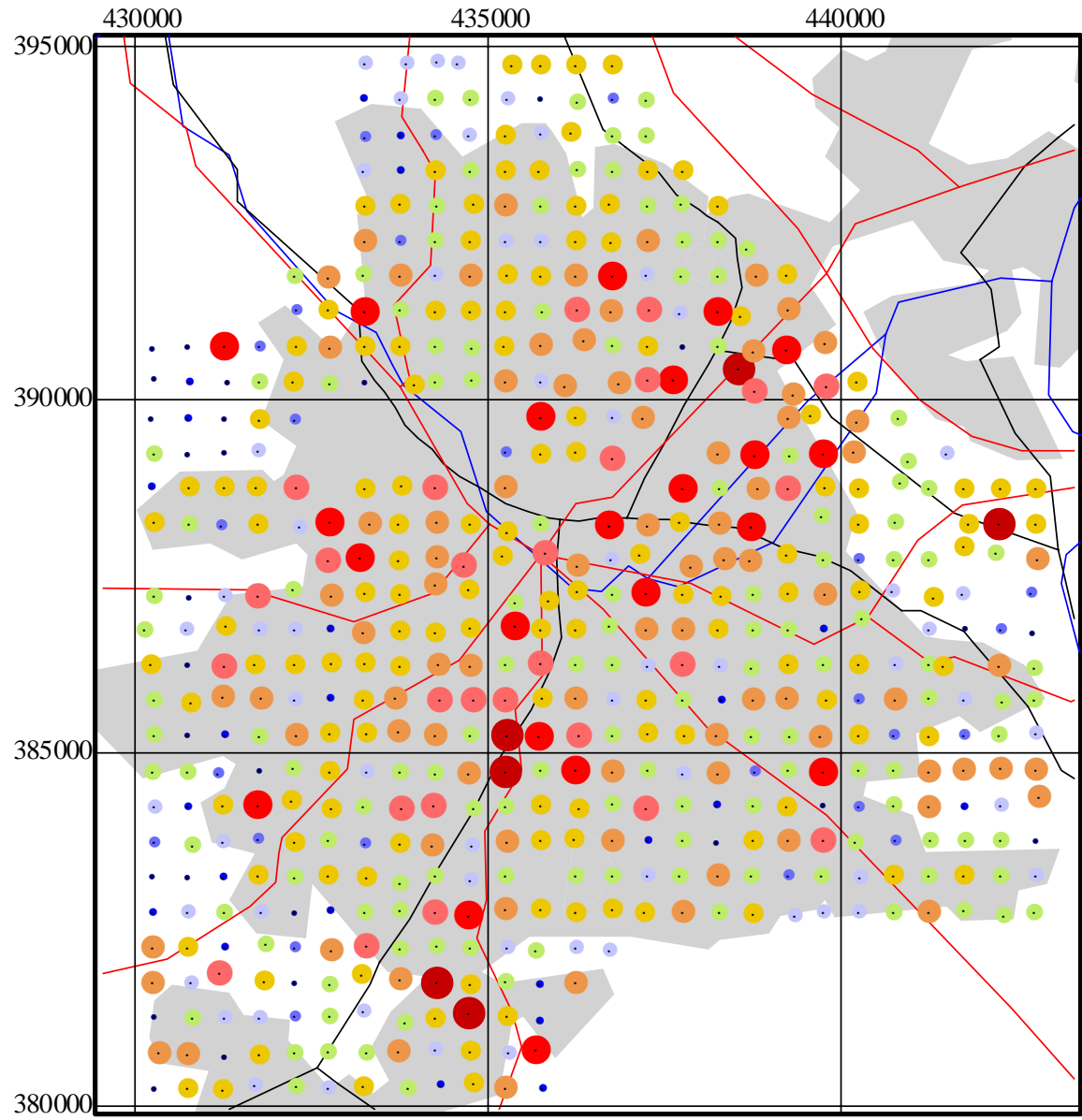
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Surface Soils

Zinc



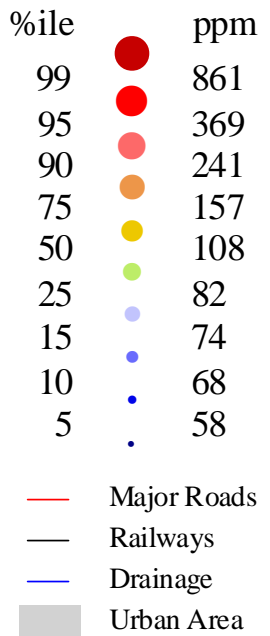
surface soil	Zn (ppm)
number	575
minimum	24
maximum	2678
median	139
mean	189



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Profile Soils

Zinc



profile soil	Zn(ppm)
number	542
minimum	22
maximum	11000
median	108
mean	169