Geochemical survey of the Tamar catchment (south-west England)

BGS Economic Minerals and Geochemical Baselines Programme
Environment Agency (SW Region)
Report CR/03/027N

BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/03/027 N

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Front cover

Monitoring site for daily, stream water quality sampling at catchment outflow (Gunnislake), Devon and Cornwall border. Photo courtesy of Miss Sarah Brown.

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Foreword

This report is the published product of a geochemical survey of soil, stream sediment and stream water undertaken by the British Geological Survey (BGS) and the Environment Agency during September 2002 in the Tamar catchment. The catchment includes land in both Devon and Cornwall, the River Tamar forming much of the border between these two counties in south-west England.

Whilst every effort has been made to minimise the number of errors (both typographical and factual) in this report, undoubtedly a few may occur. The authors are keen to amend any errors in the report as soon as possible. Please send any comments on the report by e-mail to: bgr@bgs.ac.uk, or by mail to: Barry Rawlins, Kingsley Dunham Centre, BGS, Keyworth, Nottingham, NG12 5GG

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The staff involved in establishing the project were Dr Barry Rawlins, Dr Richard Scrivener and Misss Sarah Brown (BGS), Mr Mike Robins of the Environment Agency (SW England) and Dr Phil Haygarth (IGER).

A large number of individuals have contributed to the collection, preparation and analysis of the samples.

Fieldwork was planned and access to sites arranged by Miss Sarah Brown, Mrs Juliet Harvey, Ms Kirsten O'Donnell and Ms Susan Freestone (BGS).

The fieldwork teams were managed by Dr Barry Rawlins, Mr Bob Lister, Ms Susan Freestone, Ms Catherine Emery, Miss Sarah Brown and Dr Louise Ander (BGS) and Mr Paul Evans.

The fieldwork was undertaken by the team managers and the following fieldworkers from a range of universities and departments throughout the UK and AS from Germany:

Dr Marcus Cross, Ms Ruth Burgin, Mr Andreas Schieb, Mr Stuart Gilfillan, Ms Sarah Walker, Mr Joel Flitton, Mr Andrew Fallas, Ms Jemma Kennedy, Mr Jason Roberts, Ms Sarah Ling and Ms Claire Fox.

Sample preparation was undertaken at BGS Keyworth by the following BGS staff: Mr Mark Allen, Mr Barry Adkin, Mr Kevin Barker, Mr Charles Brettle and Mr Matthew Kirkham.

Water samples were analysed and the data quality assured by the following BGS staff:

Ms Jenny Cook, Ms Joanna Wragg, Mrs Kerry Johnson, Dr Helen Taylor, Mr Richard A Shaw, Mr Shaun Reeder, Ms Linda Ault, Mrs Kate Breward, Dr M J Watts, Mrs Kay Green, Ms Claire Carlick and Mr Ben Charlton.

Soil and sediment sample analysis by XRFS was undertaken by Mr Mark Ingham, Dr C J B Gowing, Mr S J Carter, Mr N D Eatherington and Miss L D Grimsley.

The molybdate reactive phosphorus analysis of stream water and the Olsen P analysis of soil was undertaken by Ms Patricia Butler (IGER). The pH and loss on ignition analysis of the soil samples was undertaken by Mrs Barbara Vickers, Miss Claire Carlick and Miss Vicky Moss-Hayes.

Data QA/QC of the field database was undertaken by Miss Sarah Brown and Mrs Juliet Harvey. The catchment areas for the first- and second order streams were created by Emilia Fiorini. Dr Louise Ander plotted the stream water Piper diagrams.

The authors would like to thank the landowners in the Tamar catchment for their permission to sample soil, sediment and stream water from their land.

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Summary

This report presents data and preliminary findings from a geochemical survey of the 920 km^2 Tamar catchment in south-west England undertaken in September 2002 (funded by the British Geological Survey and the Environment Agency - SW region).

The survey was undertaken to fulfil two overriding objectives. First, to further the BGS G-BASE (Geochemical Baseline Survey of the Environment) project in south-west England and establish the baseline geochemistry of the UK landmass. Second, to provide information on the water quality in the headwaters of the catchment, which subsequently flow into two SACs (Special Areas of Conservation) as designated under the EU Habitats Directive; the Tamar estuary and the Plymouth Sound.

The sampling included the collection of:

- 494 stream sediments and heavy mineral concentrates, and 492 stream waters from predominantly first and second order streams throughout the catchment
- daily samples of stream water at a second-order stream 'monitoring' site and at the catchment gauging station
- 468 topsoil (0-15 cm depth) and deeper (35-50 cm depth) samples from a non-aligned grid throughout the catchment.

With the exception of the deeper soils, all samples were analysed for their total concentration of up to 50 inorganic elements and other key geochemical parameters. The latter for topsoil samples included pH, organic matter content and available phosphorus. The analytical methods for determination of the total content of elements in topsoil and stream sediment were a combination of energy and wavelength dispersive X-Ray Fluorescence Spectrometry (XRFS), and in water samples a combination of ion chromatography, inductively coupled mass spectrometry (ICP-MS) and atomic emission spectrometry (ICP-AES). Excess material from the preparation of each soil and sediment sample was archived in the National Geoscience Data Centre as part of the G-BASE sample archive.

Results of the analysis from the spatial survey are presented as a series of geochemical maps for each element / parameter and summary statistics are presented in a series of tables. Temporal variations in stream water chemistry are presented as plots of concentration, load and discharge. A cluster analysis was applied to the spatial survey dataset for each of the three media and an interpretation of the spatial distribution of each of the variables undertaken on the basis of each cluster. The database of analytical results from the survey contains more than 70,000 individual determinations, and this report provides a preliminary assessment of this information. The data generated from this survey are available under licence from the British Geological Survey (Keyworth). The preliminary findings of environmental significance from the geochemical analysis of each of the sample media were as follows:

Stream-water

The following general conclusions apply to the water quality at the time of sampling; low flow (baseflow) conditions during the month of September. At other times of the year, when flow and climatic conditions are likely to be somewhat different, these statements would require modification:

- With the exception of phosphorus (P) and dissolved metal concentrations at a few sites close to historical mines, all the samples from the spatial survey conformed to the Environment Agency's list of EQS (Environmental Quality Standards), indicating that for 18 determinands, water quality in the catchment was generally very good.

- Around 10 % of the headwater streams had total reactive phosphorus concentrations above the 60 µg P/l Agency *standard*, whilst 5 % of sites had values exceeding the 100 µg P/l, the Agency *threshold* for catchments with the geological characteristics of the Tamar.
- The distribution of reactive P in the catchment indicated several significant point sources of pollution, particularly in the north and west of the catchment, some of which may warrant further investigation.
- Based on a number of simplifying assumptions, it was estimated that 5% of the streams accounted for 50% of the dissolved reactive phosphorus load to the catchment system, and 10% of these streams accounted for 50% of the total phosphorus load. These calculations demonstrate the importance of concentrated sources of P to the total load of the receiving waters in the catchment.
- Streams around former mining sites in the south and west of the catchment had elevated total arsenic concentrations (5-30 µg/l). Private water supplies in these areas may have arsenic concentrations that exceed the drinking water guideline value of 10 µg l^{-1} (WHO, 1993).

Stream sediment

- The fine fraction of stream sediments around former mining areas (near Gunnislake and Callington) have concentrations of potentially toxic elements (arsenic, copper, lead and zinc) well above typical crustal abundance, and are clearly related to mineralisation and mining.
- When the sediment load of streams is high (during flood events), the suspended load of these elements to the estuary is likely to be larger than for other catchments where mining-related contamination is limited. It was beyond the scope of this study to determine the magnitude of these sources and their impact on the ecology of the Tamar estuary and Plymouth Sound.

Topsoil

- Approximately 60% of the sites throughout the catchment had total soil As values above the recently published Soil Guideline Value for residential land use of 20 mg/kg (DEFRA AND Environment Agency, 2002). The highest values were in the south of the catchment in areas of intense former mining activity. This does not imply that soils in these areas pose a significant risk to human health, but that further assessments would be needed to determine whether there is the possibility of significant harm.
- Around 20% of the land in the north of the catchment has Co concentrations below 5 mg/kg, a threshold below which Co deficiency in ruminant animals that graze grassland in these areas could occur. Further tests on the availability of Co in soils in these areas would be necessary to determine whether Co deficiency is problematic.
- Soils in parts of the north and south of the catchment have particularly low Mo concentrations (<0.35 mg/kg), which in these relatively acidic soils (pH values <5.5) may pose problems of Mo deficiency for certain crops. Further tests would be needed to determine the available Mo contents of these soils to establish whether Mo deficiency is likely.
- Around one third of the soils had ‘excessive’ available P contents for sites under grassland (according to MAFF guidelines), which accounts for approximately two-thirds of land use across the catchment. Such elevated concentrations may result in greater losses of P to watercourses and problems associated with eutrophication.

1 Introduction

1.1 AIMS OF THE SURVEY – HABITATS DIRECTIVE / WATER QUALITY

The Geochemical survey of the Tamar catchment was co-funded by the Environment Agency (SW England) and the BGS G-BASE (Geochemical Baseline Survey of the Environment) project. The aim of the G-BASE project is to establish the baseline geochemistry of the UK landmass. Having completed the survey of Scotland, Wales and much of northern and central England, the south-west of England was an area in which sampling had not been undertaken prior to 2002. At the same time, the Environment Agency wished to have a better understanding of the water quality in the headwater catchments which drain into two SACs (Special Areas of Conservation) as designated under the EU Habitats Directive; the Tamar estuary and Plymouth Sound (shown in Figure 1). Hence, the project was intended to further the geochemical survey of the UK and to provide important data to the Environment Agency.

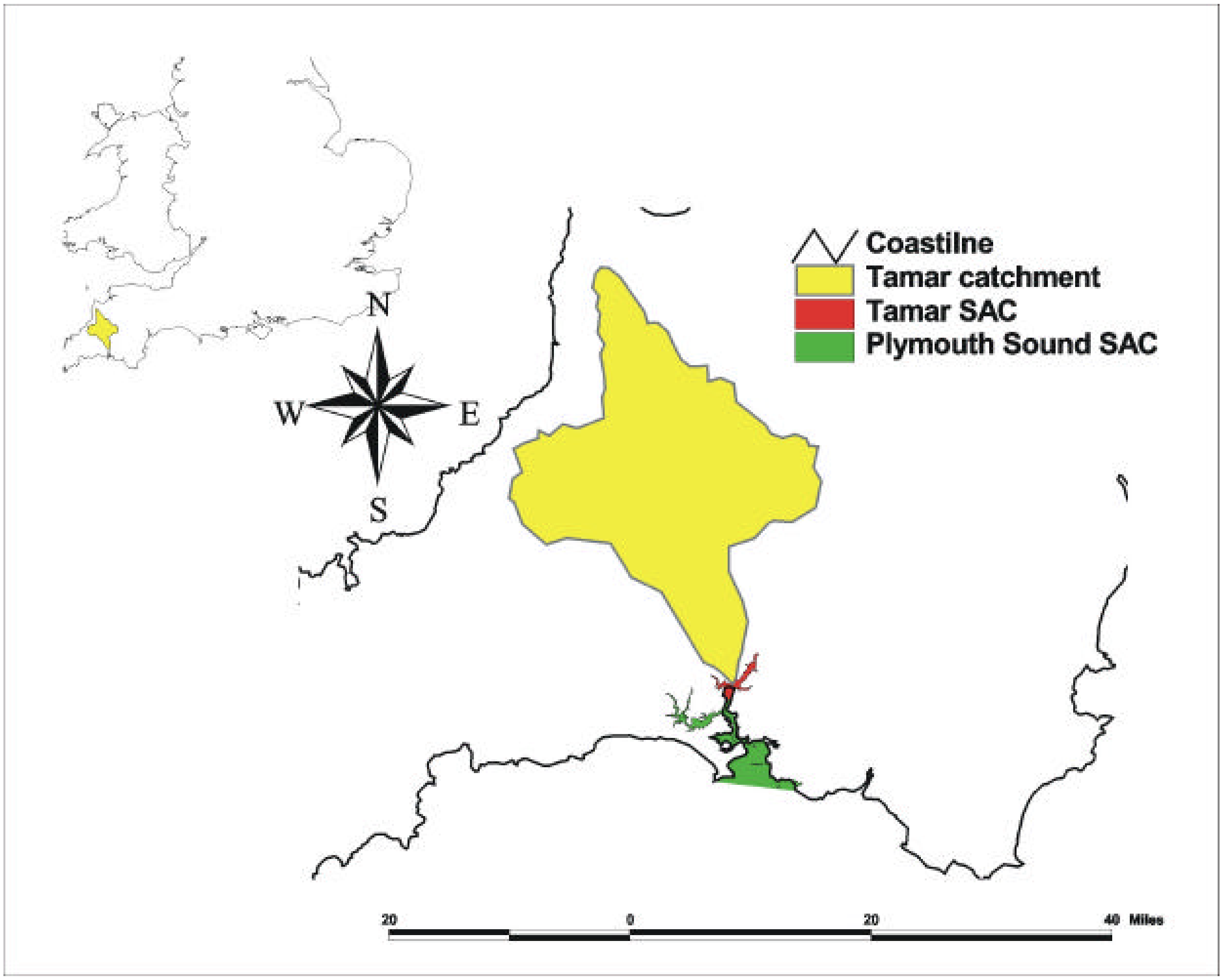

Figure 1 - Location of the Tamar Catchment and the SACs.

1.2 THE TAMAR CATCHMENT

1.2.1 Geology, topography and climate

Bedrock geology in the north of the catchment is predominantly interbedded sandstones and argillaceous (fine-grained) sedimentary rocks from the Carboniferous period (Figure 2). Further south, the Lower

Carboniferous rocks are dominated by fine-grained sedimentary sequences and chert (crystalline silica). Outcrops of granite occur on the eastern (Dartmoor) and western (Bodmin Moor) sides of the catchment, and are also interspersed with outcrops of Lower Carboniferous and Devonian slates. Given the distribution of historical metalliferous mine shafts (Figure 2), mineralisation throughout the area is most common in the south of the catchment associated with Upper Devonian, Lower Carboniferous lithologies and a range of igneous rocks, from small outcrops to larger outcrops of Dartmoor and Bodmin Moor. The British Geological Survey has carried out previous work investigating mining and mineralisation in this area, including Bennett et al. (1980), Jones (1981), Jones and Beer (1990), Cameron et al. (1994) and Leake et al. (1994); as well as geochemical investigations of the Bude and Crackington Formations: Haslam and Scrivener (1991) and Haslam (1990).

The only significant Quaternary deposits throughout the catchment are alluvial sediments along the larger rivers (not shown on the simplified geology map). The Tamar catchment covers an area of 916.9 square km, with a maximum altitude of 586 metres OD. The north of the catchment has an elevation of around 200 metres, rising to the east (>500 metres on Dartmoor) and to the west (>300 metres on Bodmin Moor); the remainder of the catchment towards the south has elevations of less than 200 metres. Annual average rainfall across the catchment between 1961 and 1990 was 1216 mm (Institute of Hydrology, 1993).

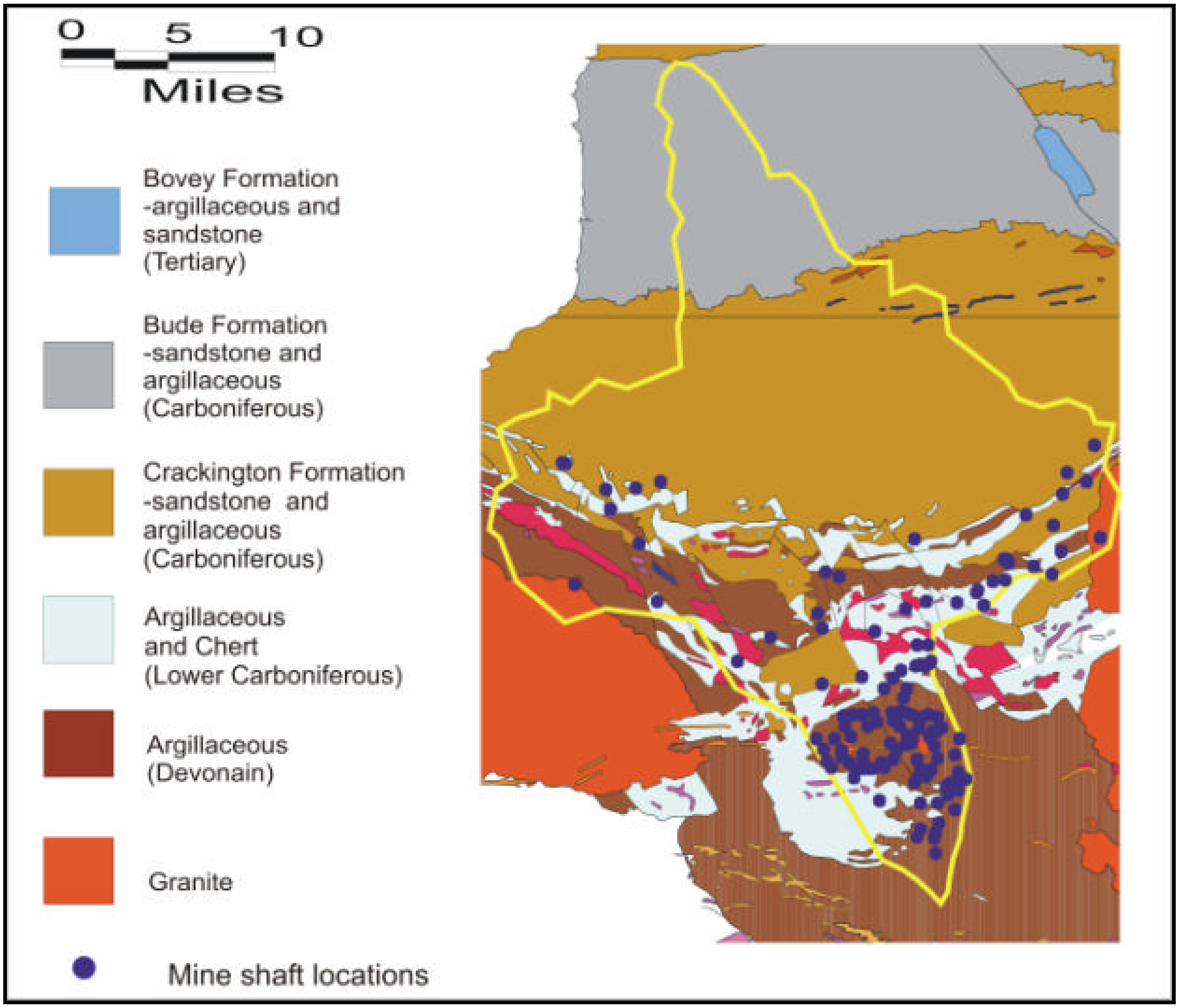

Figure 2 - Simplified geological map of the Tamar Catchment.

source: (British Geological Survey, 1985).

1.2.2 Hydrology and hydrogeology

The Tamar river at Gunnislake has a base flow index (BFI) of 0.47 (Institute of Hydrology, 1993) and is described as fairly responsive. The BFI is a measure of the proportion of the river runoff that derives from stored sources. This means that permeable bedrock, drift and soil store more water leading to higher sustained flow during dry weather. Catchments comprising impermeable bedrock have small BFI values (0.15 – 0.35), whilst rivers in catchments with permeable bedrock have larger BFI values (0.9). The more permeable lithologies in the Tamar catchment such as the grits and sandstones would tend to increase base flow, whilst the impermeable rock types such as slates and shales would lead to a more flashy response. Roadford reservoir may have a significant impact on discharge at low flows, although information on its operation was not available for incorporation into this study.

1.2.3 Soils

The soils of the Tamar catchment are dominantly comprised of typical brown earths (Soil Survey of England and Wales, 1983). These are well-drained, fine loamy soils, prone to slight seasonal waterlogging. The brown earths in the south of the catchment also contain a fine silty fraction. In the north of the region, overlying the Bude Formation, widespread mottled patches of pelo-stagnogley soils are dispersed through the brown earths. These clayey soils are slowly permeable, with seasonal waterlogging. They cover a broad region (6 km in width) covering much of the boundary between the Bude and Crackington Formations (Figure 2).

Brown earths cover large parts of the central region of the catchment between the two major granite bodies. Mottled areas of pelo-stagnogley soils occur around Roadford reservoir and further east and this soil type also overlies the course of the River Thrushel. Typical brown alluvial soils overlie the course of the River Tamar in the centre of the catchment. The main soil type overlying the Bodmin Moor Granite is an ironpan stagnopodzol. These soils are gritty, loamy and very acid, with a wet, peaty surface horizon. A thin ironpan is often present. To the north of this area, there are two bands of soil contrasting the typical brown earths. The band nearest to the granite is composed of a typical brown podzolic soil, while the second band is mainly composed of a ferric stagnopodzol. Both bands trend NW-SE. Over the western edge of the Dartmoor granite, the soils are largely comprised of humic brown podzolic soils, cambic stagnogley soils and ferric stagnopodzols. To the west of the granite, there are patches of cambic stagnogley soils, typical brown podzolic soils, ferric podzols and typical cambiogley soils.

Soils in the southern part of the catchment are mostly brown earths, although other soils of limited extent do occur. These include typical brown podzolic soils, which are mainly located around the River Tamar, cambic stagnogley soils and typical alluvial gley soils.

1.2.4 Land use

From the dominant land use types recorded at sample sites the relative proportions of the different land use types throughout the catchment during the survey were: Pasture (46%), Deciduous forest (36%), Rough Grazing (10%), Arable (7%), and Heather Moor and Coniferous Forest forming the remainder. The dominant land use types (pasture and deciduous forest) appear to be distributed relatively evenly throughout the catchment (Figure 3), whilst arable land appears to be most common in the north and west.

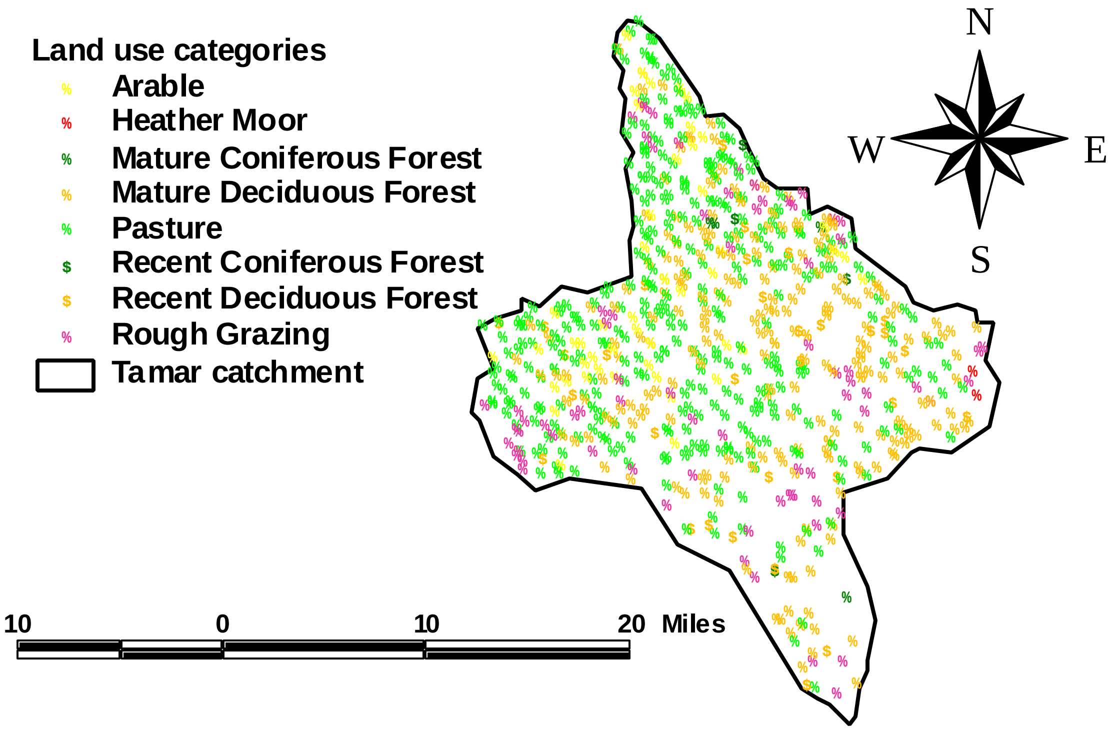

Figure 3 - Land use recorded at field sites during the survey (September 2002).

1.2.5 Historical mining activity

The most important mineral resources of the Tamar catchment area were found in a belt of country 12 miles long from east to west, and 4 miles wide, extending from the edge of the Dartmoor granite, westward across the Hingston Down and Kit Hill granites. The district has been more prolific in sulphide ores than in tin, and large yields of copper with significant pyrite and arsenopyrite have been obtained from nearly all the mines situated to the east of the Hingston Down granite (Dines, 1956). The Tavistock district of Devon forms part of this highly mineralised area and mines in this region prospered during the mid-nineteenth century.

According to a database which is currently being developed in BGS, there are 136 identified mine workings within the study area (Figure 2). These are largely shafts, with some adits and opencast mines. More than 60% of the workings are located towards the southern extent of the catchment, in the Kit Hill/Gunnislake and Tamar Valley areas. There are no workings north of Roadford Reservoir.

The earliest mines in the Tamar catchment date from pre-1750 (in the southern Tamar Valley area). Mining continued throughout the 19th century and the last mines were closed by around 1950. The Devon Great Consols mine [grid reference SX 426 733] on the east bank of the River Tamar in the Tavistock district was one of the most successful copper producers during Cornwall's global dominance of the copper mining industry in the 1800s. The mine which was derived from the consolidation of five adjacent mines, worked on lodes mainly consisting of chalcopyrite, pyrite and some mispickel and cassiterite with quartz, fluorspar and brecciated killas cemented by chlorite or siderite. In the 19th century Devon Great Consols was the richest and largest mine in the Tamar valley. The main product in the early years of operation was copper ore. Later attention turned to arsenic and an output of over 70 000 tons between 1848 and 1909 was recorded (Dines, 1956). In the 1870s half the world's arsenic production was estimated to come from half a dozen mines in the Callington and Tavistock area, including Devon Great Consols. Mining activity at Devon Great Consols ended in 1930.

In addition to copper, the mines of the Tamar catchment were worked for arsenic, lead, manganese, silver, iron ore, tin, tungsten, fluorite, zinc, gold and barytes. The mines in the central areas of Brentor to Lydford and Launceston were worked for fewer minerals than were extracted in the more densely mined areas towards the south. Significantly, arsenic, a commonly-mined mineral in the Kit Hill/Gunnislake and Tamar Valley areas was not produced further north. Mine waste is generally located in close proximity to the workings identified and attempts to rework waste dumps have revealed significant mineral enrichment in this material. Ore treatment facilities were also a source of contamination in the area. Materials from the Hingston and Clitters mines, for example, were processed in a mill below the Clitters mine, which lay on a slope descending towards the River Tamar (Figure 4).

Further information on the mining history of Devon and Cornwall can be obtained from Barton(1978) Barton (1989) and Johns (1986).

Figure 4 – Mill treating ores from the Hingston and Clitters mines.
The River Tamar can be seen on the right-hand side of the image; source (Trounson, 1980)

1.3 GEOCHEMICAL SAMPLING DESIGN

1.3.1 Spatial survey

The sampling schemes adopted by the G-BASE project have remained relatively consistent since its inception (around 1970), but have also evolved where necessary to adopt new, improved methods. Throughout the UK, stream sediment and stream water samples have been collected at an average resolution of 1 per 2 square kilometres on first and second order streams (British Geological Survey, 1999). This has been effective in identifying both point and diffuse sources of contamination (see for example Hutchins et al. (1999)). The sampling intensity has tended to be higher in areas of greater drainage density (i.e. where streams are more frequent). Likewise, soil samples have been collected at an average resolution of 1 site per 2 square kilometres (Rawlins et al., 2002). The same sampling intensities were adopted for the Tamar survey. A plan of the sampling sites indicated that around 460 samples of each of the three media (soil, sediment and water) would be collected based on these sampling intensities. It was estimated that four weeks would be required by the sampling teams to collect all of the above samples. The sampling was undertaken between the 2nd and 26th of September 2002.

1.3.2 Temporal monitoring of catchment outflow and stream water chemistry

It is well established that the concentration of dissolved solutes in surface water varies according to flow conditions, due in part to the varying residence times and flow paths caused by antecedent conditions and the intensity of precipitation. In undertaking a spatial survey over a period of four weeks, flow conditions throughout the catchment are liable to alter, to a greater or lesser extent, depending on the amount of precipitation that falls over the period and in the preceding weeks. One way to estimate the magnitude of the effect flow conditions have on stream water chemistry across the catchment is to undertake temporal monitoring at a specific site over the period of the spatial survey. A second order stream close to the field base (South Petherwin – near Launceston; Figure 5) was selected for this purpose and samples were collected at the same time each day (4 pm). In addition, samples were collected around the same time each day (5 pm) from the flow gauging station at Gunnislake [Grid reference: SX 426 725]. As the Environment Agency collect data on discharge (m^3/s) every 15 minutes, it is possible to calculate the dissolved load of the different solutes at Gunnislake in addition to their concentration.

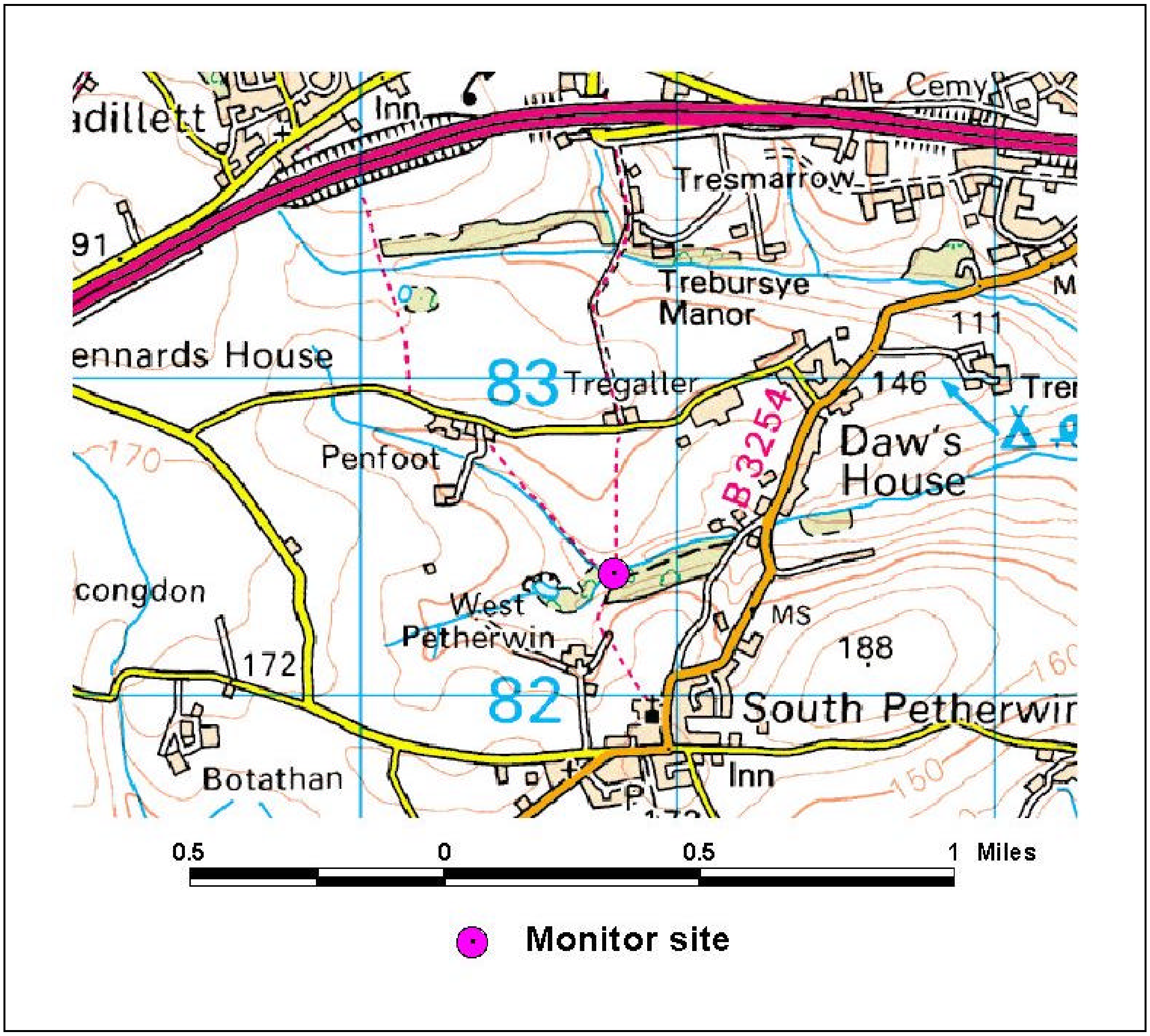

Figure 5 - Location of the second order stream monitor site at South Petherwin (grid reference SX307824).

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2 Sampling methods and sample preparation

2.1 GENERAL METHODS

Fieldworkers collected samples in pairs, but were interchanged daily to reduce the possibility of sampling bias being introduced by the use of individual procedures.

At each sample site, information on the location (recorded using a GPS), site and catchment geology, contamination, land use, and other features required for data interpretation was entered on a computer-compatible data card in a standard BGS format. The location was also plotted on a field copy of the 1:50 000 Ordnance Survey map. On completion of each day's fieldwork, the sample locations from the GPS were plotted on stable-base 1:50 000 Ordnance Survey maps using the data cards. Information on these data cards was transferred onto an electronic database after each day of sampling.

2.2 STREAM WATER AND SEDIMENT

As far as possible, samples were collected upstream of any potential source of contamination, such as habitation, industrial activity or any road or track crossing.

2.2.1 Stream water

Water samples were collected slightly upstream of the stream-sediment site to avoid contamination by disturbed sediment or pore water, and great care was taken during the sampling procedure to avoid any other contamination.

Four filtered samples were collected in new, 30 ml polystyrene bottles, two for multi-element analysis by ICP-AES and ICP-MS, the third for determination of chloride and nitrate, and the fourth for the analysis of dissolved (molybdate) reactive phosphorus (RP<0.45). These samples were filtered through 0.45 µm cellulose filters; the containers were rinsed with filtered water from the site before collection of the actual sample. The sample bottle containing the water sample for RP (<0.45) analysis was immediately placed in a cool bag to maintain its temperature at 4º C until it could be placed in a refrigerator at the same temperature, prior to analysis. All the RP (<0.45) samples were analysed within 72 hours of collection.

Unfiltered samples were collected in polythene bottles for the determination of pH and conductivity (30 ml), fluoride (30 ml), and alkalinity (250 ml). All containers were rinsed with stream water prior to sample collection and particular care was taken with the pH and alkalinity samples to eliminate air bubbles and hence minimise degassing.

On return to the field base, those samples intended for ICP-AES and ICP-MS analysis were acidified to 1% v/v using ultrapure, Aristar-grade, concentrated nitric acid.

2.2.2 Stream sediment

As far as possible, samples were collected from active sediment, upstream of any potential source of contamination, such as habitation, industrial activity or any road or track crossing. Water samples were collected in polyethylene bottles at each site, before the stream sediment was disturbed. The sediment sample was then collected after removal of the oxidised surface material and was wet-screened on site using a system devised by B A Toms (Department of Chemistry, University of Birmingham). This method uses a minimum of water to collect the fraction of sediment finer than 150 µm. Approximately 100 g of material was collected in a Kraft paper bag. A heavy-mineral concentrate was obtained at each site by screening the stream sediment through a 2 mm sieve and panning 2–3 kg of this sieved sediment, using the method described by Leake and Aucott (1973).

2.3 SOIL

Sample sites for the soil were selected from every second kilometre square of the British National Grid by random choice within each square, subject to the avoidance of roads, tracks, railways, domestic and public gardens, and other seriously disturbed ground. At each site, topsoil (0-15 cm) was taken from five holes augered at the corners and centre of a square with a side of length 20 m with a hand auger and combined to form a bulked sample of around 1 kg. Deeper soil samples (35-50 cm) were collected from the same auger holes and bulked to form a composite sample. These are archived at National Geoscience Data centre (Keyworth).

2.4 SEDIMENT AND SOIL SAMPLE PREPARATION

All samples of soil were dried, disaggregated, and sieved to pass through a 2 mm mesh. The sub 150 micron stream sediments were freeze dried at a field laboratory following initial air-drying. All samples were coned and quartered and a 50 g sub-sample ground in an agate planetary ball mill until 95% was less than 53 µm. The pulverised material was further sub-sampled to obtain portions for analysis.

3 Analytical methods

3.1 STREAM WATER

3.1.1 Measurement of stream water parameters

On return to the field base each evening, pH was determined using a temperature-compensated glass combination electrode connected to a high-performance pH meter (Radiometer Model PHM 80), and conductivity was determined using a standard 1 cm path-length cell in conjunction with an EIL conductivity bridge. Samples for ICP-AES determination were acidified to 1% v/v using ultrapure Aristar-grade concentrated nitric acid.

Alkalinity was determined by titration the day after sample collection, using a Hach digital titrator with sulphuric acid (0.8 M or 0.08 M) and bromocresol green indicator. The results are presented as mg/l bicarbomate (HCO_3^-).

Chloride, nitrite and nitrate were determined by Ion Chromatography.

Fluoride was determined using an Orion Model 94-09 fluoride ion selective electrode with an Orion Model 90-01 single-junction reference electrode connected to an Orion Model 420A ISE meter. The fluoride electrode was calibrated with a series of standards, ranging from 10 to 10 000 µg/l fluoride. The standards were run at regular intervals to check the calibration. The lowest quantifiable concentration was 10 µg/l. Total Ionic Strength Adjustment Buffer (TISAB) was added to all standard and sample solutions to maintain a high and constant ionic strength relative to the variable concentrations of fluoride.

Analysis of non-purgeable organic carbon (NPOC) in a filtered water sample determines its dissolved organic carbon (DOC) content. The determination of NPOC is carried out using a Shimadzu TOC 5000 analyser (Serial No. 28604210) with associated ASI 5000 auto-sampler (Serial No. 29D07360). Samples are automatically pre-treated by the addition of a small volume of 10% HCl and sparged with inert gas to remove any inorganic carbon in the sample. Technically, any organic species that are volatile on acidification are also removed - although such species are rare in natural waters. The remaining organic carbon in the sparged sample is then combusted in a furnace, evolving carbon dioxide which is measured using a non-dispersive infra-red (NDIR) gas analysis system. Samples are calibrated against a series of standards, and the method is subject to stringent quality control and proficiency testing regimes. The determination of NPOC is accredited by UKAS.

Inductively coupled plasma atomic-emission spectrometry (ICP-AES) was used to determine the concentration of 9 major and trace elements. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentration of 23 trace elements. The detection limits and analytical method for each element is shown in Table 3.

3.1.2 Determination of reactive Phosphorus (RP<0.45) in water by flow injection analysis

In describing the fractions of P (phosphorus) determined in stream water we have adopted the terminology proposed by Haygarth and Sharpley (2000). Hence, **TP (<0.45)**, refers to total (dissolved) phosphorus which has passed through a 0.45 µm filter. The other fraction, **RP (<0.45)** refers to molybdate reactive phosphorus which has also passed through a 0.45 µm filter.

The aqueous sample is injected into a water carrier stream and merged with a second carrier stream to avoid matrix effects. Phosphate reacts with acidic molybdate solution to form a yellow heteropolymolybdic complex, with phosphorus as the central coordinating atom:

$$H_3PO_4 + 12H_2MoO_4 \Rightarrow H_3P(Mo_3O_{10})_x + 12H_2O$$

On partial reduction with tin (II) chloride, some of the Mo^{6+} is converted to Mo^{3+} and/or Mo^{5+} and the complex assumes a blue colour. The colour is then measured using a spectrophotometer calibrated with P standards.

3.2 STREAM SEDIMENT AND SOIL

3.2.1 XRFS analysis

Major, minor and trace element determinations for stream-sediment and soil samples were carried out by wavelength-dispersive X-ray fluorescence spectrometry (Ingham and Vrebos, 1994) and energy-dispersive X-ray fluorescence spectrometry.

Two Philips PW2400 sequential x-ray fluorescence spectrometers fitted with rhodium-anode X-ray tubes (3 kW 60 kV) were used for Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Sc, V, Cr, Co, Cs, Ba, La, Ce, Nd and Sm as one suite and Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Hf, Ta, W, Tl, Pb, Bi, Th and U as another. The Philips spectrometers were controlled using Philips SuperQ application software package, version 3.0H, running under MicroSoft ™ Windows2000 operating system.

A Spectro X-LAB2000 energy-dispersive, polarised, x-ray fluorescence spectrometer fitted with a palladium-anode X-ray tube (400 W 54 kV) was used for Ag, Cd, Sn, Sb, Te and I. The Spectro X-LAB2000 was controlled using X-LABPRO application software package, version 2.4, running under MicroSoft ™ Windows2000 operating system.

3.2.1.1 SAMPLE PREPARATION

A 12 g aliquot of milled material was mixed thoroughly with 3 g of binder for 3 minutes in an agate planetary ball mill. This mixture was then pressed into a 40 mm diameter pellet at 250 kN using a Herzog (HTP-40) semi-automatic press. The binder consists of 9 parts EMU120FD styrene co-polymer (BASF plc) and one part Ceridust 3620 a micronised polyethylene wax (Hoechst), after van Zyl (1982).

3.2.1.2 WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

The pellet was irradiated by X-rays, which induce secondary X-ray fluorescence of the atoms within the sample. This secondary radiation was collimated onto a diffraction crystal and its intensity at selected peak and background positions in the X-ray spectrum was measured using either a proportional gas flow or a scintillation detector mounted on a goniometer.

The net intensity at each of the peak positions was calibrated against known synthetic standards and Reference Materials (RMs). Trace elements whose characteristic X-ray lines lie on the long-wavelength side of the Fe absorption edge (Sc, V, Cr, Cs, Ba, La, Ce, Nd and Sm) are affected by absorption from major elements (Fe, Mn and Ti), and this absorption is not corrected for by this calibration method. Therefore, the results for these trace elements are not as accurate as those for others.

The calibration lines were established using numerous RMs, placing the slope to give the best fit through the average of the predominantly silicate RMs. If the sample composition differs widely from this average it may produce erroneous results. The elements Ni, Cu, Zn, Sr, Zr, Ba and Pb, which are usually present at trace levels, will cause interference if they are present at concentrations above ca. 0.5%, leading to uncorrected errors in most analytes.

3.2.1.3 ENERGY DISPERSIVE, POLARISED, X-RAY FLUORESCENCE SPECTROMETRY

In the energy dispersive (X-LAB2000) spectrometer, the primary X-radiation is scattered off a secondary or polarisation target, which is used to optimise the effectiveness of the exciting X-radiation and to minimise the spectral background. Three different secondary/polarisation targets are used to give optimal coverage of 52 elements from Na to U; all elements are measured to improve the accuracy of the corrections on the analytes of interest. As in WD-XRFS, rather than being diffracted the whole of the emitted X-ray spectrum is detected simultaneously using a Si (Li) detector.

For both WD-XRFS and ED(P)XRFS mineralogical and particle-size effects contribute to the overall analytical error. The calibrations were validated by analysis of RMs and regularly corrected for instrumental drift.

3.2.1.4 LIMIT OF QUANTIFICATION

The theoretical lower limits of detection (LLD) were calculated using Equation 1 (Jenkins and de Vries, 1970) from count rates collected from synthetic standards on calibration. The background count rate was collected from the peak position on a ‘blank’ SiO_2 pellet on calibration.

Equation 1. Detection limit (3 sigma)

$$\text{Detection limit} = \frac{3}{m}\sqrt{\frac{Rb}{Tb}}$$

Where: Rb = background count rate (c/s)

Tb = time on background (s)

m = counts per second per percent (c/s/%)

The lower limits of detection (LLD) are shown in Table 7 with lower limits of reporting for the major elements and upper reporting limits based on the calibration standard or validation RM with the highest concentration. The LLDs are theoretical values for the concentration equivalent to three standard deviations above the background count rate for the analyte in a silica matrix. High instrumental stability results in practical values for these materials approaching the theoretical.

Individual results are not reliable below the quoted lower limits, but reliable estimates of average or typical values over an area may be obtained at lower levels of concentration; meaningful patterns may thus be recognised for some elements at levels lower than the LLD and LRL. Reliability also decreases above the URL, but results do, nevertheless, give an indication of the concentration in the sample. Results outside the limits were therefore reported and entered into the database.

3.2.2 LABORATORY QUALITY CONTROL PROTOCOLS

Batch to batch continuity is monitored by the analysis of six RMs at the beginning and end of the analysis of each batch of 500 samples. An example of the RMs is plotted in Figure 6 showing arsenic values for a soil RM measured for over three years. The results have ±3 sigma control limits of ±2.58 mg/kg but are better than the ±2 sigma warning limits of ±1.7 mg/kg. Each pellet is measured a maximum of five times on each face then a fresh aliquot is taken and a new pellet prepared.

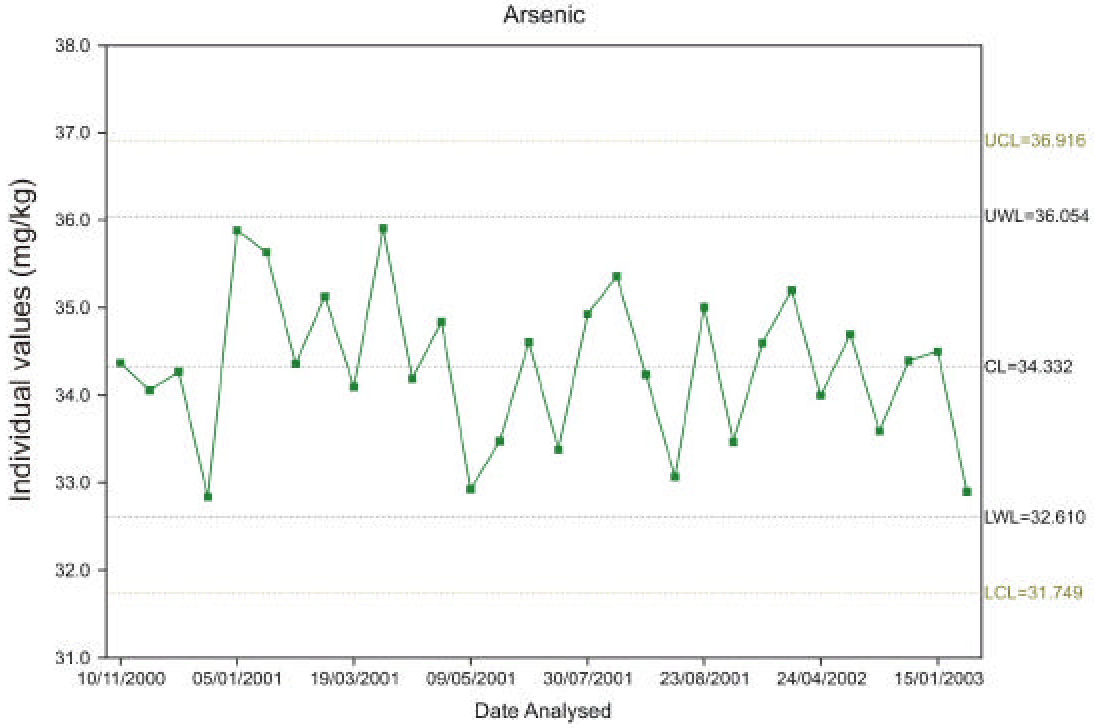

Figure 6 - Long term continuity measured for arsenic using a soil RM GSS-1

Quality Control (QC) is monitored by analysis of two silica glass samples spiked with a wide range of trace elements: BGS Low has trace element concentrations in the range 20-40 mg/kg and BGS High has trace elements concentrations in the range 250-350 mg/kg. One of these samples is analysed in approximately every 50 unknown samples.

QC charting and verification are carried out using Shewhart (1931) control charts, onto which are plotted the mean and control and warning limits of the QC data. Sample data from an analytical run are not used if the QC data fall outside ±3s control limits or if two or more consecutive QCs fall outside ±2s warning limits, unless authorised by the XRFS laboratory manager. QC data are also monitored for drift and bias, and analytical data may not be used if the mean QC values for 10 out of 11 consecutive analytical runs fall one side of the mean, or if 8 consecutive mean QC values successively rise or fall. Any batches of samples governed by a failing QC sample are re-analysed.

3.2.2.1 PROFICIENCY TESTING

The method is subjected to proficiency testing using the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL) International Soil-analytical Exchange (ISE) scheme. Soil samples are analysed on a regular basis and the data from these can be used to independently assess the accuracy of the method. To comply with the WEPAL regulations, the z-scores for the BGS data calculated by reference to all participating laboratories have to be less than three.

Figure 7 shows the z-score performance over four years for arsenic to be better than two. Points outside of two are explained on the graph. With each testing round a separate blind aliquot of a bulk material is also included and the z-scores are shown in Figure 8 and their corresponding concentrations in Figure 9. The equation used for calculating z-scores is shown in equation 2 below. Sample 921 is a river clay from the Netherlands.

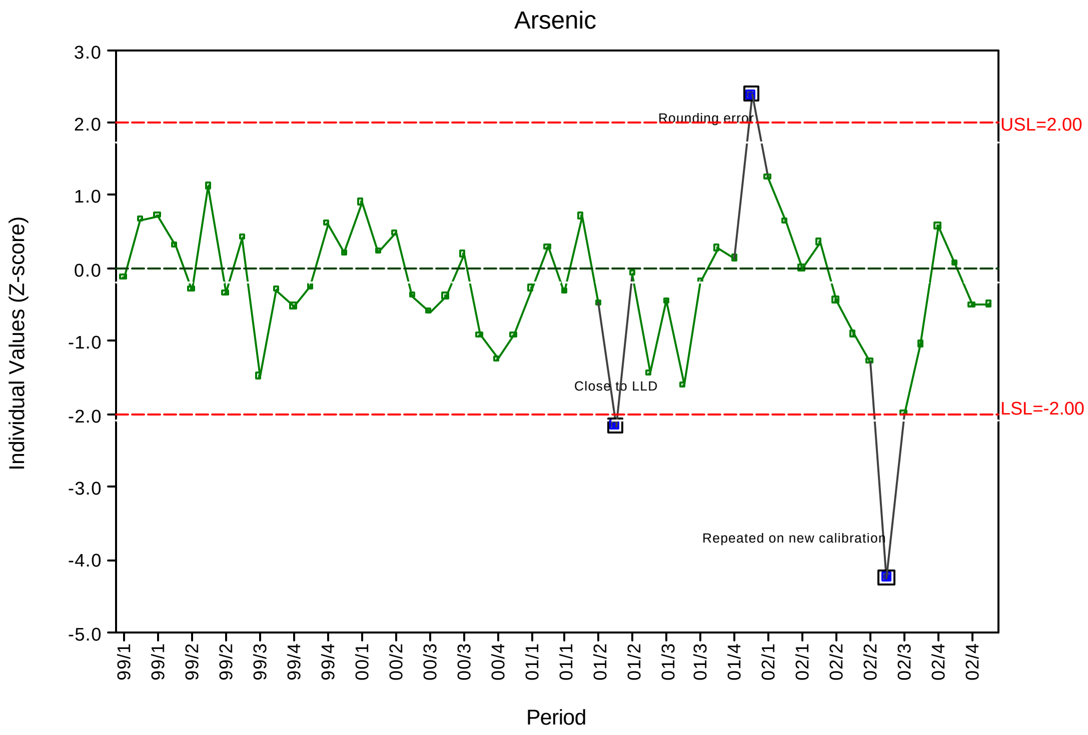

Figure 7 - Z-score performance for arsenic over 4 years of proficiency testing

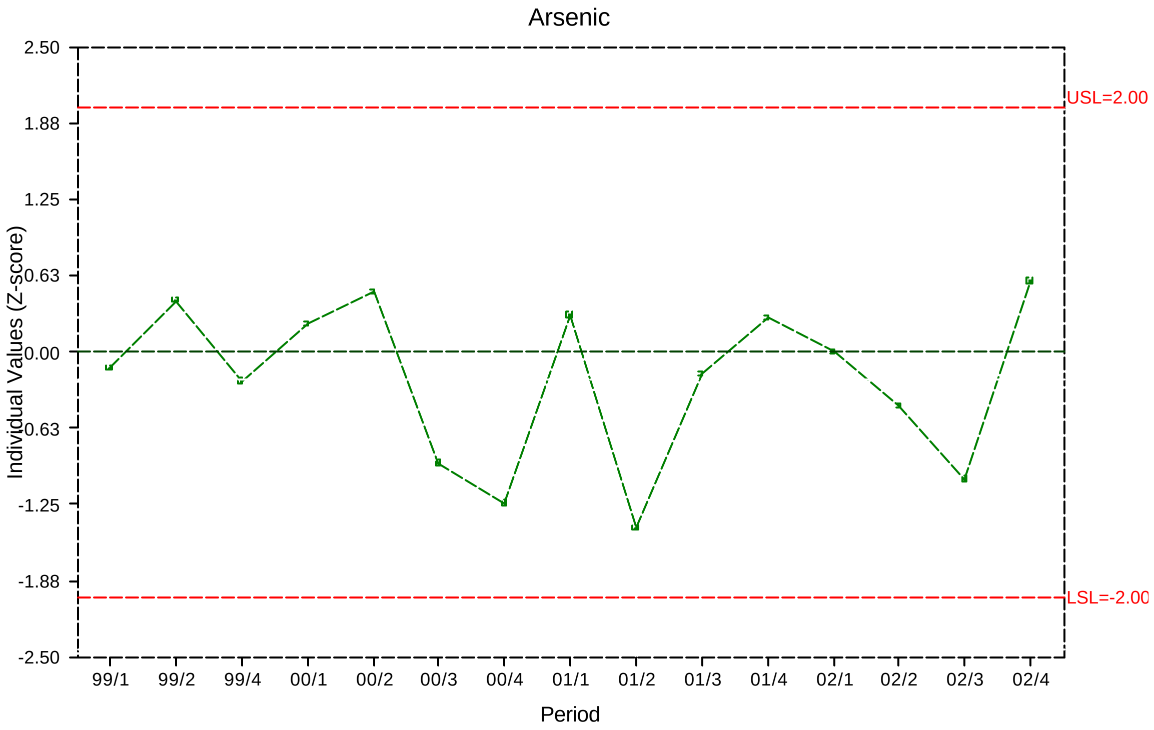

Figure 8 - Individual z-scores for sample 921, a bulk soil sample analysis over 3 years

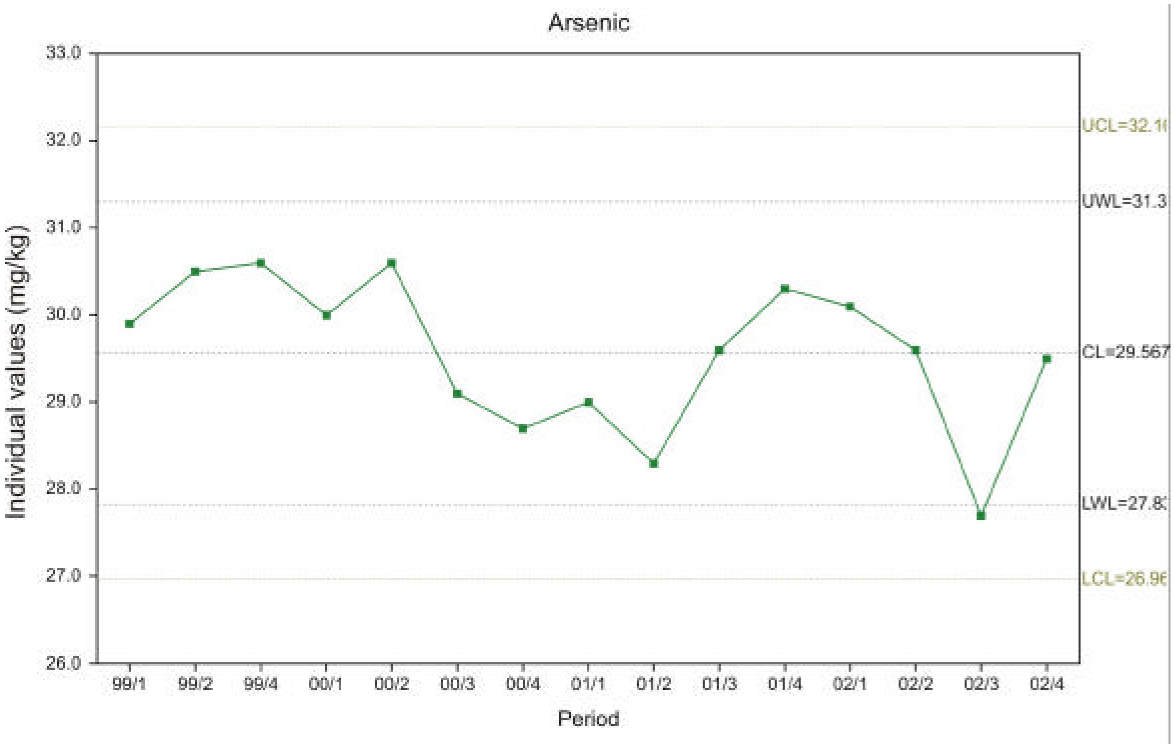

Figure 9 - Individual concentration values for sample 921 a bulk soil over 3 years

The individual z-scores for the bulk soil are better than two over the four years which would correspond to plus or minus three sigma of 2.6 mg/kg.

Equation 2. Statistical Z-score

$$\text{Z-score} = \frac{X - Xmean}{Sd}$$

Where: X = the reported value
$Xmean$ = the robust mean of all used values
Sd = standard deviation of all used values

3.2.3 Soil pH

The pH of each soil was determined using a standard protocol (Rowell, 1994). The pH was measured using a glass slurry electrode and Orion 720A meter. The pH meter was calibrated to 4 and 7 or 7 and 9 depending on the pH of the slurry to be measured. To 10.0 g of the <2mm sample, 25 ml of 0.01 M calcium chloride solution was added, the samples were magnetically stirred for one minute and then left to settle for 15 minutes. Prior to recording of the pH value the samples were stirred to reform the suspension.

3.2.4 Organic carbon (by Loss on ignition)

The organic carbon content of each sample was estimated by measuring the weight loss due to the combustion of organic matter, which occurs when a soil is heated to a specified temperature of 450°C. This method has been widely adopted in soil science because of its ease of use, it is inexpensive, rapid, requires no specialized training, and strong statistical relationships commonly exist between organic matter and organic carbon contents estimated by standard dry combustion procedures (Sutherland, 1998). Samples were initially dried at 105°C to remove any residual water. Each soil was weighed prior to and after heating, the decrease in weight was calculated as a proportion of the initial weight and expressed as a percentage weight loss. Samples were heated in a furnace at 450°C for four hours and allowed to cool in a dessicator prior to weighing to produce loss on ignition data, which was used as a measure of the organic carbon content of the sample. It has been reported that the average carbon content of organic matter is approximately 58% (Broadbent, 1953), therefore an estimate of carbon content was calculated by multiplying the organic matter content (%) by 0.58.

3.2.5 Available phosphorus (Olsen's method)

A soil P availability index is typically determined by extracting the P from the soil using a sodium bicarbonate solution (referred to as the Olsen method) and measuring the fraction using a phosphomolybdate method. The precise weight of approximately 2.5g of air-dry soil was recorded and the soil transferred to a glass bottle. 50 ml of sodium bicarbonate solution was added and mechanically shaken for 20 minutes at 20° C. The solution was then filtered through a Whatman 125 filter paper. The concentration of P in the solution was determined using an ammonium molybdate solution and spectrophotometer calibrated with P standards (for further details see Rowell (1994)).

4 Presentation and interpretation of geochemical data

4.1 DATA HANDLING

The lower limits of detection (LLD) and upper and lower reporting limits (URL and LRL) are shown in the tables of summary statistics (section 6, 7 and 8). Individual results are not reliable below the quoted lower limits, but reliable estimates of average or typical values over an area may be obtained at lower levels of concentration; meaningful patterns may thus be recognised for some elements at levels lower than the LLD and LRL. Reliability also decreases above the URL, but results do, nevertheless, give an indication of the concentration in the sample. Results outside the limits were therefore reported and entered into the database.

Long-term analytical drift was monitored by analysing a series of standards representing the range of concentration for each element. The standards included several bulk stream-sediment samples collected over representative rock types, which were analysed in every batch of 100 samples. Time-versus-concentration plots for each of these standard samples were used to identify shifts in the analytical data, and simple arithmetic factors were calculated to enable the data to be normalised for systematic drift. Values below the lower limit of detection were assigned to a value of one half of the detection limit, as recommended by Abert and Horowitz (1995), prior to statistical treatment of the dataset.

Where certain trace elements (As, Cu, W and Zn) had unusually high vales (>1000 mg/kg) the values reported should be treated as estimates of the concentration. For a more accurate determination these samples would need to be re-analysed using a small proportion of the sample diluted with silica.

4.2 PRESENTATION OF GEOCHEMICAL DATA

For generating, processing and editing the geochemical images, an in-house extension to ArcView 3.2 called Gridder was used. The geochemical data were interpolated by Gridder to produce grids for each chemical element, where each grid cell (pixel) represents 250 by 250 m on the ground. The grids were produced by interpolation of the data using the method of Inverse Distance Weighting. In this technique, each grid cell is given a calculated value derived from data for nearby sample sites. The calculation uses data from all sample sites within 1500 m, weighted in accordance with distance (r) such that the weighting is proportional to distance squared.

The gridded data were then used to produce percentile colour-classified images generally based on class boundaries set at the 5, 10, 15, 25, 50, 75, 90, 95 and 99 percentile levels. For elements in which the concentration classes did not correspond to those above (due to poor analytical resolution), the exact percentile values are quoted. The continuous colour images presented in the appendices to this report are a useful visualisation method and provide estimates of the element concentrations; the exact values are only known at the sample locations. In cases where more than half the data were below the analytical limit of detection, maps showing individual symbols proportional to concentration were generated.

4.3 GROUPING GEOCHEMICAL VARIABLES FOR INTERPRETATION

There are several ways to describe and interpret regional geochemical data as presented in the images in Appendices A-C. In doing so, it was our intention to avoid repetition in the interpretation of the spatial distributions. We grouped the elements and parameters in each media (stream water, sediment and soil) on the basis of a multi-variate cluster analysis. The results suggested several logical groupings based on geochemical associations inherited from bedrock lithology, mining and related activities, agriculture and land use/topography.

4.4 CONTROLS ON STREAM WATER CHEMISTRY

Groundwater flow, residence time, topography, climate and land use are all important determinants of stream-water chemistry. The chemistry of stream water at a sampling location is dependent on biological and hydrological processes as well as chemical processes. The water in streams is a mixture of waters that have passed through different environments. This mixing takes place in the unsaturated and saturated zones, in the riparian zone and within the stream channel. The relative proportions of these components are dependent on catchment properties such as topography and the characteristics of the bedrock. For example, soil and rock permeability and hydraulic connectivity determine the importance of groundwater in contributing to stream flow. Present and antecedent weather conditions also influence the proportions of these components, and thereby stream-flow discharge and current catchment hydrological status. Once water has reached the stream channel, in-stream processes can have a significant influence in modifying stream-water chemistry, particularly of the less mobile elements.

Factors controlling the chemical composition of stream waters include:

- Atmospheric deposition and rain-water composition
- Bedrock and soil type, long-term weathering and leaching processes
- Processes controlling the chemistry of soil solution
- The influence of terrestrial organisms
- Occurrence of drift deposits
- Mineral weathering and groundwater composition
- Catchment hydrology
- Anthropogenic influences
- In-stream processes

In areas where bedrock is very resistant to chemical weathering and in areas of blanket bog the chemistry of atmospheric deposition may be as significant as weathering reactions in determining stream-water composition. Bulk deposition data indicate that the main components of atmospheric deposition are marine-derived sea salts (principally Na, Cl^-, Ca, Mg and SO_4^{2-}).

The mineralogical and chemical composition of soil reflects the underlying regolith, which may include drift deposits of local and non-local origin, as well as bedrock. Soil composition is also determined by the degree to which the developing profile has been modified, notably through leaching. Chemical weathering is the term used to describe the low-temperature transformation of the minerals of the bedrock and regolith, many of which were formed at high pressures and temperatures within the earth, into more stable secondary minerals and solute species through interaction with dilute waters close to the earth's surface. In general, there are three products of the weathering process:

- Solute species
- Secondary minerals, such as clays and oxides
- Residual unweathered materials, such as quartz

The weathering of a rock can be described simply by a general mass balance:

Rock + water ? solid residue + dissolved species

The ability of rain water to dissolve minerals is largely due to the fact that it is slightly acidic due to the presence of dissolved CO_2 (producing carbonic acid) derived from the atmosphere. Soil waters may be more acidic, because of CO_2 derived from biological activity and the decomposition of organic matter. The presence of strong acid components due to industrial pollution may give rise to acid rain, which causes increased weathering rates. The chemical processes which control weathering include hydration, hydrolysis, redox reactions and complex formation, although the exact mechanisms are poorly understood in detail.

The different minerals present in rocks have an extremely wide range of weathering rates, covering several orders of magnitude. The relative reactivity of common minerals increases in the order quartz < K-feldspar < Na-feldspar < muscovite < ferromagnesian silicates < carbonates. One consequence of this is that weathering is very selective, and the most reactive minerals (e.g. calcite) contribute a disproportionate amount of dissolved matter to the water. The presence of calcite, for example, may dominate the chemistry of water even if the mineral is only a minor component of the rock.

4.4.1 Description and interpretation of stream water chemistry

It is well established that the chemical composition of stream water varies over short temporal scales (days and weeks), and that the magnitude of this variation is greater than for soil and stream sediment chemistry over such time-scales. Hence, when describing variations in stream water chemistry, it is reported here in the past tense (sections 5 and 6), while the stream sediment and soil geochemistry are reported in the present tense (section 7 and 8). Given the range and complexity of the processes which can influence stream water chemistry (see above), it is only possible in this study to provide an initial, broad interpretation on the most significant factors which lead to variation in stream water chemistry throughout the catchment.

5 Temporal monitoring of stream water chemistry

5.1 PRESENTATION OF TEMPORAL VARIATION IN STREAM WATER CHEMISTRY

Images showing the variation in stream water chemistry at the monitor site (South Petherwin) and at the gauging station (Gunnislake) are provided in part I of Appendix A. Each graph shows the variation from the 2nd to 26th of September of four variables:

1. The concentration of solute in stream water at the Gunnislake gauging station
2. The concentration of solute in stream water at the monitor site (South Petherwin)
3. The solute load at the Gunnislake gauging station
4. The discharge of the River Tamar at the Gunnislake gauging station

5.2 CATCHMENT GAUGING STATION – GUNNISLAKE

Comparison of Figure 10 and Figure 11 shows that discharge at the gauging station throughout the sampling period was generally typical for the month of September, with low flows ranging from 2.7 to 3.9 m^3/s. The majority of the water sampled in the survey will therefore have been derived from groundwater sources as opposed to more near surface flow paths. Flow regime in the River Tamar is affected by operation of Roadford Reservoir (Lawson et al., 1991), which drains around 3% of the catchment. It was beyond the scope of this study to estimate its influence on water quality. Flow was relatively consistent throughout the month (2.7 – 3.7 m^3/s), which suggests that variations in hydrological conditions were unlikely to have had a significant impact on the concentration of solutes *between* sites during the sampling period. However, there was a small increase in flow (rising limb of the hydrograph) due to rainfall between the fourth and 10th of September. Flow subsequently declined (falling limb) to around 2.7 m^3/s.

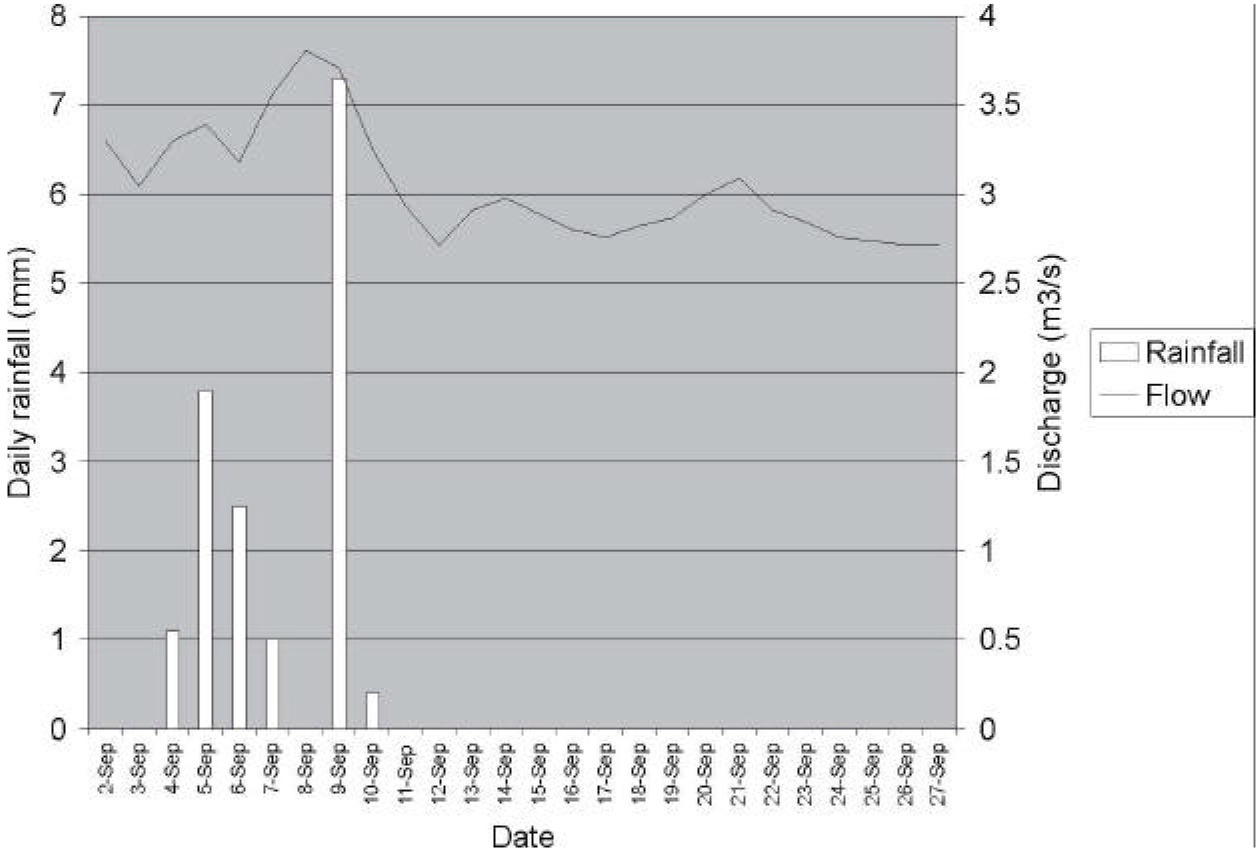

Figure 10 - Daily rainfall measured at Mill Hill (Grid ref:SX 4553 7452) and flow at the catchment gauging station (Gunnislake).

Data supplied by the Environment Agency.

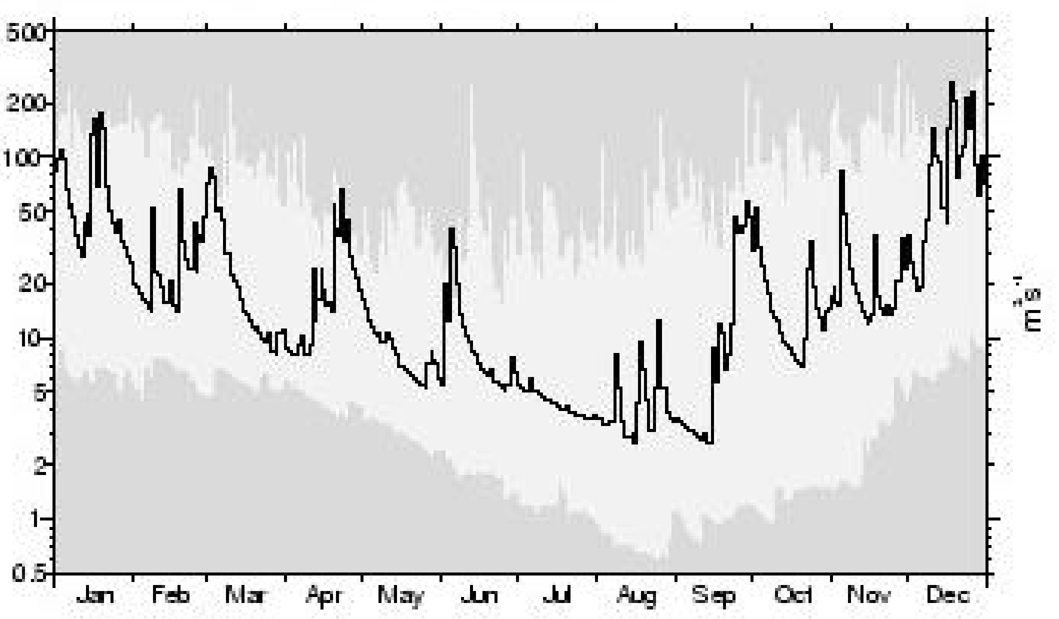

Figure 11 - Maximum and minimum daily flows from 1956 to 1999 and flow during 1999 - black line; mean flow 26.4 m^3 s^{-1}

source: Centre for Ecology and Hydrology (http://www.nwl.ac.uk/ih/nrfa/station_summaries/047/001.html)

For much of the monitoring period, the concentration of many major and trace elements in the Tamar River were relatively constant (**As, B, Cl^-, Ca, Mg, Mn, Na, Si, SO_4^{2-}, Sr** – see Appendix A). The slight decline in the total dissolved load of these elements can be attributed to the small reduction in discharge over this period. There were increased concentrations of several major and trace elements at the gauging station (Al, Cd, Cu, F^-, Mn, U and Zn) on the rising limb of the hydrograph (Figure 10) around the 7th of September following the rainfall over the preceding few days. The concentrations of Pb and Ni reached their highest concentrations on the falling limb of the hydrograph (10th September), at the end of the rainfall events which were spread over this period. This corresponds with a reduction in pH (from 8.2 to 7.6) and a corresponding increase in the **H^+** ion, the more acidic conditions accounting for the increase in dissolved metal concentrations. Despite the short term variation in their concentrations, the dissolved loads of **Pb** and **Ni** were also relatively consistent across the month of sampling, with a general reduction in load due to the reduction in discharge (Figure 10).

The chemistry of River Tamar at the catchment guaging station reflects the mixing of stream and groundwater across the entire catchment. Comparison of the cation and anion dominance of streams across the catchment and the chemistry at the outflow gauging station (Gunnislake) shown in Figure 12 indicates that a greater proportion of the flow is derived from the more bicarbonate (HCO_3^-) dominated waters as they are skewed towards this part of the trilinear diagram.

By contrast, nutrient (**TP<0.45, RP<0.45 and nitrate**) concentrations and loads showed a general decline over the month of monitoring. This may be related to a combination of factors; seasonal decline in temperature leading to a reduction in mineralisation of organic matter, or the reduction of diffuse and point sources of pollution throughout the catchment over the month. In combination with the reduction in discharge this led to a more significant decline in dissolved load for these elements over the month compared to the other elements.

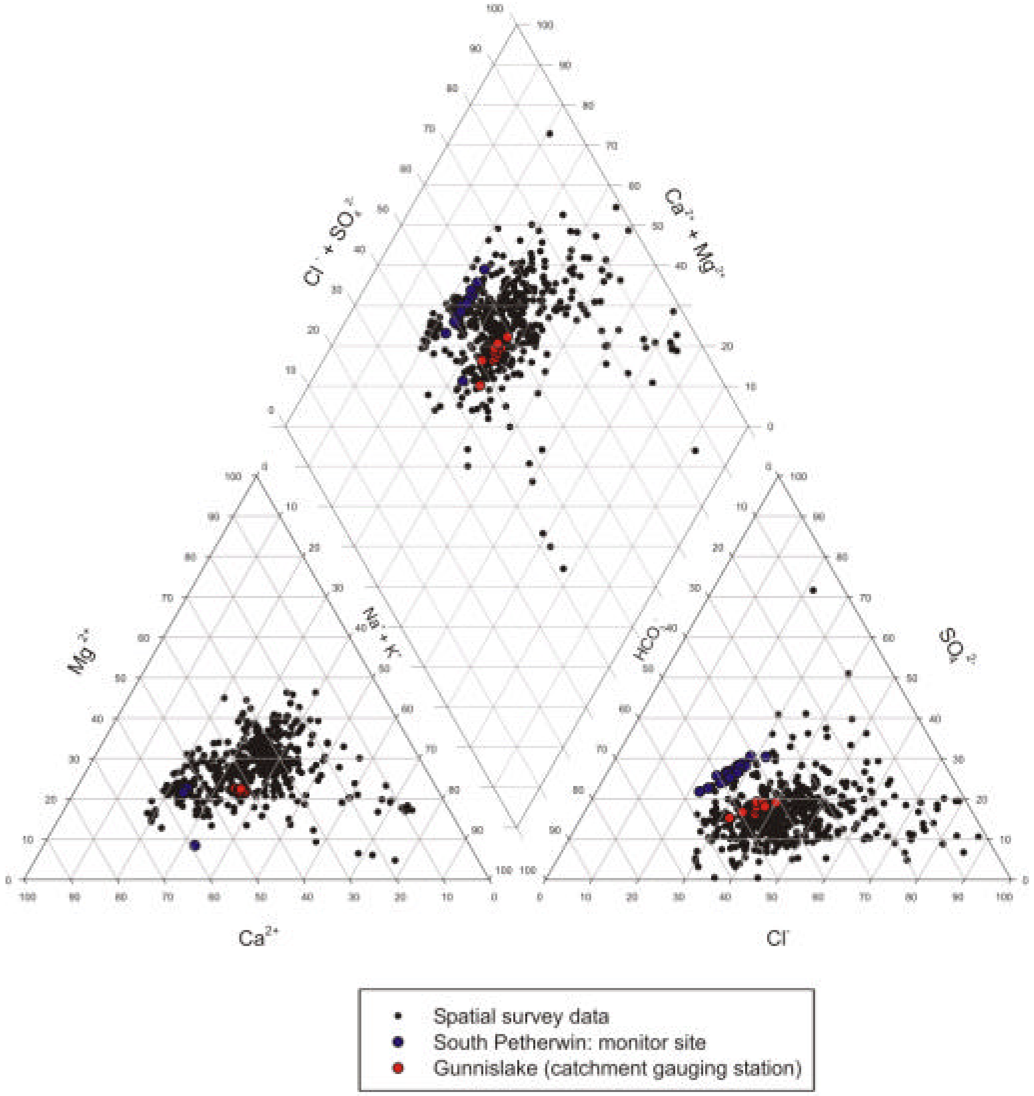

Figure 12 – Piper diagram showing the dominance of major cations and anions in stream water samples from the spatial survey and the monitor sites.

Table 1 - Summary statistics for stream water chemistry at the gauging station (Gunnislake) from 2nd to 26th September (n=20).

	Min	Max	Median	Mean	St. Dev.	Skewness
Al (µg/l)	8.00	57.10	11.1	14.3	10.8	3.7
As (µg/l)	3.80	4.50	4.20	4.1	0.2	-0.2
B (µg/l)	0.01	0.04	0.03	0.0	0.0	-0.1
Ba (µg/l)	4.06	5.21	4.46	4.5	0.3	0.9
Be (µg/l)	0.00	0.11	0.01	0.0	0.0	3.2
Br (mg/l)	0.07	0.10	0.09	0.1	0.0	-0.4
Ca(mg/l)	18.4	20.7	19.3	19.3	0.6	0.4
Cd (µg/l)	0.03	0.07	0.04	0.0	0.0	2.2
Ce (µg/l)	0.01	0.44	0.02	0.0	0.1	4.4
Cl (mg/l)	23.10	25.60	23.90	24.1	0.6	0.8
Co (µg/l)	0.27	0.39	0.35	0.3	0.0	-0.6
Cond (µS/cm)	7.64	211.0	194.5	185.2	42.9	-4.1
Cr (µg/l)	0.03	0.31	0.09	0.1	0.1	2.1
Cs (µg/l)	0.14	0.22	0.17	0.2	0.0	1.6
Cu (µg/l)	4.00	8.20	4.40	4.6	0.9	3.5
DOC (mg/l)	1.87	4.54	2.11	2.3	0.6	4.0
RP<0.45 (µg/l)	32.0	66.0	46.0	47.4	12.2	0.3
F (mg/l)	0.06	0.14	0.07	0.1	0.0	3.3
Fe (mg/l)	0.07	0.19	0.13	0.1	0.0	0.1
HCO3 (mg/l)	37.4	191.8	41.5	50.0	33.7	4.3
K (mg/l)	3.01	3.49	3.18	3.2	0.1	0.6
La (µg/l)	0.01	0.85	0.01	0.1	0.2	4.5
Li (µg/l)	3.81	4.68	4.15	4.2	0.2	0.5
Mg (mg/l)	5.74	6.47	6.07	6.1	0.2	0.3
Mn (µg/l	15.7	27.4	19.2	19.3	2.5	1.8
Mo (µg/l)	0.17	0.34	0.20	0.2	0.0	2.2
Na (mg/l)	15.7	18.8	16.9	17.0	0.7	0.5
Nb (µg/l)	0.01	0.00	0.00	0.0	0.0	-0.7
Ni (µg/l)	2.30	2.90	2.50	2.5	0.1	0.9
NO2 (mg/l)	0.01	0.02	-0.01	0.0	0.0	3.0
NO3 (mg/l)	7.47	9.24	8.25	8.2	0.5	0.4
TP<0.45 (µg/l)	0.05	0.09	0.07	0.1	0.0	0.0
Pb (µg/l)	0.03	3.28	0.06	0.2	0.7	4.4
PH	7.59	8.47	8.18	8.1	0.2	-0.9
Rb (µg/l)	2.80	3.40	2.95	3.0	0.2	1.3
Sb (µg/l)	0.12	0.21	0.16	0.2	0.0	0.5
Si (mg/l)	0.64	2.05	1.63	1.3	0.5	-0.2
Sn (µg/l)	0.08	0.29	0.13	0.1	0.1	1.5
SO4 (mg/l)	15.1	16.7	15.5	15.7	0.5	1.1
Sr (mg/l)	0.06	0.07	0.07	0.1	0.0	0.1
Th (µg/l)	0.00	0.01	0.00	0.0	0.0	4.5
U (µg/l)	0.05	0.10	0.06	0.1	0.0	1.7
V (µg/l)	0.10	0.33	0.16	0.2	0.1	1.6
Y (µg/l)	0.02	0.05	0.03	0.0	0.0	1.5
Zn (µg/l)	3.40	12.7	5.45	5.9	2.0	2.2
Zr (µg/l)	0.01	0.03	0.01	0.0	0.0	1.5

5.3 SOUTH PETHERWIN MONITOR SITE (2ND ORDER STREAM)

The dissolved concentration of the majority of the elements at the monitor site at South Petherwin was relatively consistent across the month of monitoring (Appendix A). The sample collected on the 15th of September had markedly lower concentrations for the majority of its parameters than for the other days throughout the month, the cause of which is unknown. Notable exceptions to the general pattern include:

- the large variations in Mn concentrations for the sampling period which may reflect changes in the dissolved oxygen content of the stream (redox potential).
- the significant increases in pH and bicarbonate concentrations on the 23rd of September.
- the low U concentrations reported for the 12th and 15th September.

There were also significant changes in the anion dominance in stream water at the site through time, the bicarbonate ion (HCO_3^-) becoming increasingly dominant in comparison to chloride and sulphate (Figure 12).

Table 2 – Summary statistics for stream water chemistry at the monitor site (South Petherwin) from 2nd to 26th September (n=25).

	Min	Max	Median	Mean	St. Dev.	Skewness
Al (µg/l)	4	17.3	9.1	9.68	2.69	1.5
As (µg/l)	0.2	0.9	0.8	0.73	0.13	-2.8
B (µg/l)	0.02	0.04	0.03	0.03	0.01	0.1
Ba (µg/l)	1.39	4.03	1.77	1.85	0.48	4.2
Be (µg/l)	0	0.02	0.01	0.01	0.01	-0.2
Br (mg/l)	0.005	0.101	0.088	0.09	0.02	-3.9
Ca(mg/l)	15.4	34.1	31.3	30.7	3.38	-4.2
Cd (µg/l)	0	0.02	0.01	0.01	0.01	-0.3
Ce (µg/l)	0	0.02	0.01	0.01	0.00	0.0
Cl (mg/l)	16.2	23.2	22.3	22.1	1.31	-4.0
Co (µg/l)	0.04	0.31	0.24	0.23	0.07	-1.7
Cond (µS/cm)	203	258	238	237	14.0	-0.6
Cr (µg/l)	0.01	1.93	0.06	0.20	0.50	3.3
Cs (µg/l)	0.1	0.13	0.11	0.11	0.01	0.6
Cu (µg/l)	0.9	10.6	1.5	1.86	1.84	4.8
DOC (mg/l)	1.15	2.91	1.55	1.69	0.40	1.7
RP<0.45 (µg/l)	10	29	18	18.4	3.78	0.4
F (mg/l)	0.035	0.055	0.049	0.05	0.00	-1.8
Fe (mg/l)	0.00	0.14	0.09	0.08	0.03	-1.5
HCO3 (mg/l)	37.4	72.2	56.5	55.3	6.7	-0.2
K (mg/l)	0.94	3.70	3.21	3.12	0.51	-3.4
La (µg/l)	0	0.01	0	0.00	0.00	0.8
Li (µg/l)	2.35	7.9	6.73	6.65	1.02	-3.2
Mg (mg/l)	1.32	8.38	7.57	7.34	1.29	-4.6
Mn (µg/l	0.05	55.3	24.1	24.3	11.9	0.0
Mo (µg/l)	0.01	0.48	0.39	0.38	0.09	-3.6
Na (mg/l)	9.1	14.3	13.4	13.2	0.92	-4.0
Nb (µg/l)	0.01	0	0	0.00	0.00	-1.3
Ni (µg/l)	0.5	4	3.3	3.18	0.63	-3.3
NO2 (mg/l)	0.005	0.2	-0.005	0.00	0.04	5.0
NO3 (mg/l)	2.71	10.2	8.37	8.10	1.47	-2.1
TP<0.45 (µg/l)	0.00	0.05	0.03	0.03	0.01	-0.8
Pb (µg/l)	0.03	0.28	0.03	0.04	0.06	2.9
PH	7.64	8.27	7.81	7.81	0.13	1.9
Rb (µg/l)	1.8	3.4	2.1	2.13	0.30	3.3
Sb (µg/l)	0.07	0.21	0.19	0.18	0.03	-3.1
Si (mg/l)	2.07	3.45	3.03	3.04	0.27	-1.6
Sn (µg/l)	0.0	0.32	0.11	0.12	0.07	0.9
SO4 (mg/l)	21.4	31.6	29.2	29.4	2.12	-2.3
Sr (mg/l)	0.02	0.10	0.09	0.09	0.01	-4.6
Th (µg/l)	0	0	0	0.00	0.00	n/a
U (µg/l)	0.01	0.11	0.09	0.08	0.02	-2.1
V (µg/l)	0.05	0.64	0.1	0.14	0.15	3.0
Y (µg/l)	0	0.05	0.04	0.03	0.01	-1.9
Zn (µg/l)	0.1	32	1.1	2.55	6.29	4.7
Zr (µg/l)	0	0.03	0.02	0.02	0.01	-0.8

6 Interpretation of spatial stream water chemistry

6.1 SYNOPSIS OF SPATIAL STREAM WATER CHEMISTRY

Data from monitoring the temporal variation (section 5) showed that flow conditions throughout the month of September 2003 were likely to have only a limited impact on the dissolved (<0.45 µm) stream water chemistry, indicating that comparison of the spatial survey samples would be meaningful. Stream waters in the Tamar catchment are of relatively low ionic strength in comparison to much of England and Wales, reflecting the low solubility of the minerals derived from soil and bedrock. There were significant regional trends in the distributions of many marine derived aerosols (most notably sodium and chloride) highlighting the importance of marine inputs on the spatial distribution of many major and trace elements. A cluster analysis of all the elements and parameters appeared to be of limited success in identifying clear geochemical associations. However, there were some clear groups including major elements and parameters, heavy metals, nutrients and rare-earth elements.

Total and reactive phosphorus (P) concentrations indicated several point sources of pollution which could contribute to problems associated with nutrient enrichment of water courses (eutrophication). The high concentrations of total and reactive phosphorus, many of which exceed the Agency standards and thresholds for streams draining this type of terrain indicates that phosphorus loss is probably the most significant and widespread surface water quality issue in the Tamar cathcment. The significance of these high P loads to the catchment system are investigated further in section 9.1.

Several stream samples had elevated total dissolved arsenic (As) concentrations above the World Health Organisation (1993) drinking water guideline value of 10 µg/l. Many of these stream water samples were in the vicinity of human habitation that may have private water supplies (wells). In such areas, there is a potential threat to human health through their use as a supply of drinking water, although further analysis would be required to determine the concentration of As in the drinking water supply and assess exposure.

Based on the water hardness of each sample, Environmental Quality Standards (EQS) were exceeded at a few stream water sample sites, some of which were close to sites of former metal mining. The elements for which EQS were exceeded includes copper (Cu), lead (Pb), cadmium (Cd) and cobalt (Co). However, with the exception of P, the spatial survey and termporal monitoring of stream water chemistry indicates that the dissolved water quality throughout the catchment is generally very good.

6.2 PRESENTATION OF SPATIAL STREAM WATER CHEMISTRY

Images showing the variation in each of the 45 stream water chemistry parameters are provided in part II of Appendix A.

6.3 SUMMARY STATISTICS

Table 3 - Summary statistics and detection limits for stream water geochemistry (n=490).

Element/parameter	*Method	Min	Max	Median	Mean	St. Dev.	Skewness	Detection limit
Al (µg/l)	ICP-MS	0.6	134	7.8	11.9	14.2	4.7	0.2
As (µg/l)	ICP-MS	0.2	33.8	0.7	1.43	2.66	6.5	0.2
B (µg/l)	ICP-AES	0.001	0.34	0.02	0.03	0.02	7.1	0.04
Ba (µg/l)	ICP-MS	0.0015	0.081	0.01	0.01	0.01	2.4	0.003
Be (µg/l)	ICP-MS	0.005	0.23	0.01	0.01	0.02	5.5	0.01
Br (mg/l)	IC	0.005	2.86	0.091	0.11	0.15	13.8	0.01
Ca (mg/l	ICP-AES	0.01	70.9	16.0	16.8	8.16	1.3	0.025
Cd (µg/l)	ICP-MS	0.0025	5.93	0.013	0.05	0.31	15.8	0.005
Ce (µg/l)	ICP-MS	0.0025	0.36	0.03	0.04	0.05	3.4	0.005
Cl (mg/l)	IC	8.47	966	22.5	27.2	47.8	17.1	1
Co (µg/l)	ICP-MS	0.02	17.1	0.33	0.61	1.26	8.3	0.01
Cond. (us/cm)		42	1650	188	192.2	96.2	8.1	n/a
Cr (µg/l)	ICP-MS	0.025	1.99	0.08	0.12	0.20	5.8	0.05
Cs (µg/l)	ICP-MS	0.01	3.82	0.07	0.18	0.35	5.4	0.02
Cu (µg/l)	ICP-MS	0.2	118.8	1	1.73	6.42	15.2	0.3
DOC (mg/l)		0.25	15.6	3.18	3.52	2.05	1.5	0.1
F (mg/l)	IC	0.015	1.6	0.076	0.09	0.08	12.8	0.01
Fe (mg/l	ICP-AES	0.005	9.54	0.21	0.37	0.62	8.4	0.01
HCO3 (mg/l)		0.42	208	40.7	42.0	24.0	2.2	0.2
K (mg/l	ICP-AES	0.05	95.0	2.76	3.78	5.21	11.8	0.1
La (µg/l)	ICP-MS	0.0025	0.94	0.015	0.03	0.06	10.2	0.005
Li (µg/l)	ICP-MS	0.2	37.1	4.8	5.59	3.91	2.9	0.04
Mg (mg/l	ICP-AES	0.03	93.1	7.37	7.79	5.21	9.4	0.06
Mn (mg/l	ICP-MS	0.0015	4.617	0.037	0.09	0.29	11.2	0.003
Mo (µg/l)	ICP-MS	0.02	1.32	0.13	0.18	0.17	2.9	0.04
Na (mg/l	ICP-AES	0.09	691	14.2	17.31	34.2	16.9	0.075
Ni (µg/l)	ICP-MS	0.1	35.5	2.8	3.24	3.05	4.8	0.1
NO2 (mg/l)	IC	0.0025	1.09	0.0025	0.04	0.13	4.8	0.005
NO3 (mg/l)	IC	0.0025	131	4.93	7.44	9.04	6.0	0.005
† TP<0.45 (mg/l)	ICP-AES	0.005	1.70	0.034	0.06	0.14	7.7	0.07
Pb (µg/l)	ICP-MS	0.01	18.7	0.07	0.23	1.26	11.9	0.02
PH		4.46	8.24	7.425	7.38	0.33	-2.3	n/a
Rb (µg/l)	ICP-MS	0.2	61.6	2.4	3.05	3.83	10.4	0.1
†† RP<0.45 (µg/l)		0	1772	13	39.1	141.9	9.0	4.3
Sb (µg/l)	ICP-MS	0.005	4.76	0.08	0.13	0.26	13.3	0.01
Si (mg/l)	ICP-AES	0.08	9.13	3.91	4.24	1.62	0.6	0.08
Sn (µg/l)	ICP-MS	0.02	0.52	0.09	0.10	0.06	2.3	0.04
SO4 (mg/l)	IC	0.25	101	11.4	12.9	8.66	4.9	0.12
Sr (mg/l)	ICP-AES	0.001	0.559	0.064	0.06	0.04	6.1	0.001
Tl (µg/l)	ICP-MS	0.001	0.37	0.006	0.01	0.02	9.5	0.002
U (µg/l)	ICP-MS	0.0015	0.48	0.02	0.04	0.05	4.7	0.003
V (µg/l)	ICP-MS	0.03	3.29	0.09	0.14	0.23	8.6	0.06
Y (µg/l)	ICP-MS	0.004	0.547	0.043	0.06	0.07	3.6	0.005
Zn (µg/l)	ICP-MS	0.2	2735	2	13.3	130.6	19.1	0.2
Zr (µg/l)	ICP-MS	0.0025	0.359	0.027	0.03	0.04	3.6	0.005

* The main analytical methods were inductively coupled plasma atomic-emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC).

† Total phosphorus (<0.45)

†† Reactive Phosphorus (<0.45)

Table 4 - Correlation coefficients (r) between elements determined in stream water samples (based on n=460 in which there was a full suite of elements).

Correlations greater than 0.5 in bold.

	pH	*Cond	HCO3	F	Cl	Br	NO3	SO4	DOC	**RP	Li	Be	Al	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Y	Zr	Mo	Cd	Sn	Sb	Cs	Ba	La	Ce	Tl	Pb	Th	U	B	Ca	Fe	K	Mg	Na	†TP	Si	Sr
PH	1.00
*Cond	0.35	1.00
HCO3	0.50	**0.67**	1.00
F	0.01	0.19	0.32	1.00
Cl	0.04	0.45	0.28	**0.77**	1.00
Br	0.05	**0.52**	0.33	**0.68**	**0.95**	1.00
NO3	0.17	0.28	0.21	-0.11	0.02	0.03	1.00
SO4	0.15	0.48	0.21	0.46	**0.60**	**0.54**	0.07	1.00
DOC	0.05	0.25	0.37	0.16	0.08	0.07	-0.07	-0.07	1.00
**RP	0.14	0.34	0.38	-0.03	0.07	0.17	0.26	0.03	0.06	1.00
Li	-0.20	0.04	-0.07	0.23	0.08	0.05	-0.11	0.41	-0.07	-0.08	1.00
Be	-0.52	-0.27	-0.33	-0.03	-0.07	-0.07	-0.09	-0.25	-0.02	-0.04	-0.02	1.00
Al	-0.35	-0.13	-0.20	-0.07	-0.04	-0.03	0.02	-0.22	0.24	0.08	-0.15	**0.61**	1.00
V	0.12	0.13	0.13	-0.15	-0.10	-0.07	0.28	-0.12	0.09	0.27	-0.18	-0.01	0.36	1.00
Cr	0.13	0.11	0.10	-0.04	0.03	0.06	0.16	-0.01	0.08	0.15	-0.16	-0.04	0.19	**0.61**	1.00
Mn	-0.13	0.13	0.13	0.16	0.17	0.20	-0.03	0.14	0.10	-0.02	0.18	0.01	-0.02	-0.03	-0.04	1.00
Co	-0.20	0.09	-0.01	0.04	0.03	0.07	-0.04	0.27	0.12	0.02	0.42	0.03	0.06	-0.03	-0.04	**0.69**	1.00
Ni	-0.14	0.09	0.02	0.10	0.00	-0.01	-0.13	0.34	0.29	-0.04	**0.51**	-0.01	0.00	-0.06	-0.08	0.27	**0.72**	1.00
Cu	-0.07	0.01	-0.07	0.12	0.01	0.00	0.11	0.13	-0.01	0.12	0.32	0.08	0.19	0.22	0.04	0.07	0.30	0.34	1.00
Zn	-0.13	0.01	-0.09	0.07	-0.01	-0.01	-0.01	0.41	-0.10	0.01	0.43	0.01	-0.02	-0.04	-0.06	0.29	**0.64**	**0.54**	0.21	1.00
As	-0.08	0.03	-0.05	0.08	0.04	0.10	0.23	0.04	-0.18	0.23	0.17	0.09	0.06	0.13	0.05	0.09	0.21	0.11	**0.55**	0.16	1.00
Rb	0.03	0.42	0.43	0.11	0.15	0.17	**0.54**	0.09	0.40	0.32	0.09	0.05	0.19	0.41	0.18	0.10	0.15	0.23	0.32	0.02	0.21	1.00
Y	-0.46	-0.23	-0.34	-0.14	-0.06	-0.03	-0.01	-0.25	0.18	0.00	-0.05	**0.61**	**0.73**	0.18	0.09	0.17	0.22	0.10	0.26	0.00	0.14	0.15	1.00
Zr	-0.06	0.10	0.14	0.05	0.02	0.03	0.05	-0.13	**0.72**	0.07	-0.09	0.09	0.49	0.31	0.18	0.09	0.15	0.25	0.19	-0.05	-0.09	0.42	0.40	1.00
Mo	0.15	0.40	0.36	0.28	0.32	0.29	0.02	0.36	0.36	0.07	0.11	-0.17	-0.08	0.14	0.12	0.13	0.14	0.33	0.08	-0.05	-0.01	0.40	-0.09	0.31	1.00
Cd	-0.16	0.00	-0.10	0.13	-0.01	-0.02	0.00	0.39	-0.11	0.00	0.41	0.03	-0.01	-0.04	-0.07	0.27	**0.59**	**0.51**	0.24	**0.96**	0.17	0.02	0.00	-0.05	-0.04	1.00
Sn	-0.05	0.06	0.01	0.04	0.05	0.09	-0.01	0.05	-0.12	0.13	0.16	0.07	0.04	0.09	-0.07	0.15	0.19	0.10	0.12	0.13	0.21	0.05	0.05	0.01	0.05	0.14	1.00
Sb	-0.01	0.08	0.05	0.20	0.01	-0.02	0.11	0.19	-0.09	0.05	0.00	-0.08	0.00	0.08	-0.02	-0.02	-0.01	-0.02	0.17	0.17	0.08	0.09	-0.07	-0.03	0.09	0.36	0.11	1.00
Cs	-0.13	0.01	-0.12	0.09	0.00	0.00	0.23	0.16	-0.26	0.04	0.36	0.16	-0.03	0.00	-0.08	0.02	0.21	0.22	**0.50**	0.20	**0.59**	0.23	0.10	-0.17	0.00	0.24	0.16	0.21	1.00
Ba	0.05	0.15	0.22	0.09	0.03	0.02	-0.05	-0.05	0.26	0.00	-0.01	-0.04	0.10	0.26	0.05	0.09	0.06	0.15	0.06	-0.02	-0.11	0.17	-0.01	0.28	0.05	-0.03	-0.04	-0.07	-0.13	1.00
La	-0.35	-0.16	-0.26	-0.04	-0.04	-0.04	0.06	-0.12	-0.04	0.01	0.22	0.48	0.37	0.06	0.01	0.07	0.19	0.15	0.47	0.09	0.36	0.13	**0.63**	0.10	-0.11	0.11	0.13	-0.03	0.46	-0.03	1.00
Ce	-0.40	-0.13	-0.17	-0.06	-0.04	-0.03	-0.01	-0.24	0.37	0.02	-0.07	**0.55**	**0.79**	0.27	0.12	0.10	0.17	0.13	0.24	-0.02	0.14	0.28	**0.80**	**0.58**	0.00	-0.02	0.05	-0.07	0.02	0.14	**0.55**	1.00
Tl	-0.19	-0.09	-0.20	0.11	-0.03	-0.05	0.04	0.19	-0.16	0.00	0.41	0.13	0.03	-0.06	-0.05	0.08	0.34	0.37	**0.66**	0.28	**0.58**	0.10	0.15	-0.07	0.08	0.35	0.15	0.27	**0.63**	-0.12	0.41	0.07	1.00
Pb	-0.06	0.02	-0.01	0.11	0.00	-0.01	0.00	0.03	0.04	0.00	0.00	0.02	0.07	0.04	-0.01	-0.02	0.04	0.04	0.05	0.08	-0.01	0.03	0.01	0.11	0.01	0.17	0.10	0.34	0.00	0.15	-0.01	0.05	0.10	1.00
Th	-0.08	0.05	0.11	0.07	0.01	0.02	-0.07	-0.14	**0.54**	0.06	-0.04	0.16	**0.50**	0.35	0.16	0.21	0.19	0.23	0.20	-0.03	-0.02	0.29	0.42	**0.78**	0.26	-0.03	0.11	-0.02	-0.07	0.27	0.17	**0.60**	-0.05	0.11	1.00
U	0.19	0.35	0.41	0.17	0.24	0.23	0.18	0.27	0.08	0.10	-0.06	0.08	0.10	0.20	0.06	0.05	-0.01	0.03	0.00	-0.05	0.00	0.31	-0.01	0.01	0.48	-0.04	0.01	0.08	0.10	0.04	-0.03	0.03	0.03	-0.04	0.06	1.00
B	0.14	0.49	0.36	**0.73**	**0.74**	**0.67**	-0.01	**0.53**	0.23	0.16	0.15	-0.13	-0.05	-0.05	0.02	0.10	0.04	0.08	0.11	0.04	0.04	0.14	-0.15	0.12	0.27	0.04	0.02	0.05	0.01	0.07	-0.05	-0.06	0.01	0.03	0.11	0.18	1.00
Ca	**0.53**	**0.51**	**0.65**	0.29	0.36	0.34	0.32	**0.50**	0.02	0.15	-0.11	-0.44	-0.29	0.12	0.13	0.09	-0.05	-0.08	-0.03	-0.02	0.01	0.17	-0.40	-0.11	0.39	-0.01	-0.01	0.21	0.02	0.02	-0.28	-0.34	-0.08	-0.01	-0.09	**0.53**	0.28	1.00
Fe	-0.11	0.08	0.19	0.13	0.03	0.03	-0.17	-0.02	0.34	-0.05	0.11	0.01	0.04	-0.03	-0.03	0.46	0.33	0.29	-0.02	0.07	-0.01	0.08	0.05	0.33	0.26	0.06	0.03	-0.08	-0.06	0.22	0.00	0.19	-0.03	0.07	**0.51**	-0.01	0.08	-0.03	1.00
K	0.11	**0.54**	**0.55**	0.24	0.33	0.33	**0.53**	0.23	**0.50**	0.23	0.06	-0.07	0.03	0.17	0.11	0.11	0.12	0.21	0.07	-0.02	0.05	**0.87**	-0.01	0.37	0.45	-0.02	-0.02	0.06	0.08	0.16	-0.02	0.14	-0.01	0.03	0.18	0.32	0.27	0.31	0.12	1.00
Mg	0.19	**0.50**	**0.51**	**0.82**	**0.83**	**0.75**	-0.02	**0.60**	0.26	-0.02	0.21	-0.22	-0.18	-0.09	0.00	0.18	0.07	0.16	-0.01	0.03	-0.09	0.18	-0.26	0.09	0.40	0.02	-0.03	-0.01	-0.07	0.23	-0.17	-0.14	-0.13	0.00	0.09	0.23	**0.78**	0.46	0.20	0.39	1.00
Na	0.07	0.45	0.34	**0.77**	**0.98**	**0.96**	0.00	**0.56**	0.06	0.18	0.06	-0.07	-0.04	-0.08	0.06	0.16	0.02	-0.03	0.01	-0.01	0.06	0.14	-0.07	0.00	0.29	-0.02	0.07	0.00	-0.02	0.03	-0.05	-0.05	-0.05	-0.01	0.00	0.24	**0.74**	0.36	0.02	0.30	**0.81**	1.00
†TP	0.05	0.01	0.05	0.11	0.00	-0.01	-0.05	-0.09	0.15	-0.02	0.01	0.02	0.11	-0.01	0.01	-0.02	0.03	0.07	0.03	0.01	-0.01	0.01	0.03	0.17	0.01	0.01	0.03	-0.02	-0.03	-0.01	0.02	0.08	-0.03	0.03	0.20	-0.03	0.26	-0.10	0.10	-0.02	0.08	0.02	1.00
Si	0.12	0.18	0.33	0.17	-0.04	-0.05	-0.19	-0.07	0.38	0.01	0.18	-0.15	-0.12	0.00	-0.03	0.02	0.06	0.24	-0.04	-0.04	-0.23	0.08	-0.20	0.23	0.11	-0.06	-0.13	-0.20	-0.24	**0.54**	-0.16	-0.04	-0.21	0.04	0.21	-0.08	0.18	-0.08	0.26	0.16	0.34	-0.03	0.10	1.00
Sr	0.32	**0.56**	**0.61**	**0.63**	**0.74**	**0.69**	0.08	**0.58**	0.24	0.09	-0.02	-0.32	-0.20	0.02	0.08	0.19	-0.01	0.02	-0.03	-0.06	-0.06	0.20	-0.26	0.07	0.46	-0.06	-0.04	0.06	-0.09	0.23	-0.21	-0.17	-0.13	0.00	0.08	0.47	**0.61**	**0.75**	0.14	0.40	**0.80**	**0.72**	-0.03	0.16	1.00

* conductivity

** reactive phosphorus (RP<0.45)

† total phosphorus (TP<0.45)

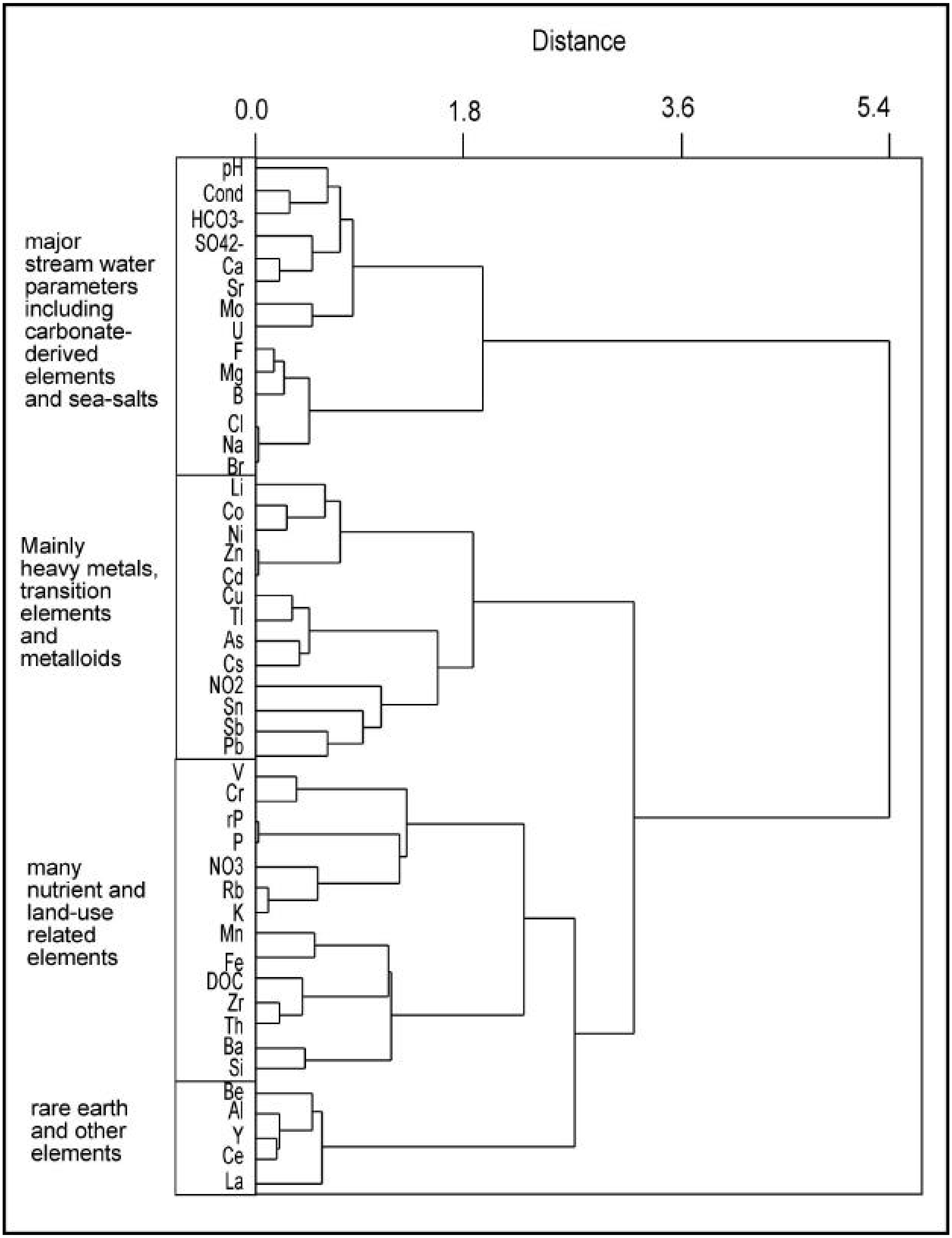

Figure 13 - Dendogram showing the clustering of stream water chemical parameters.

The dendogram is based on a cluster analysis of all variables based on Ward's linkage method (Ward, 1963). Cluster analysis is an agglomerative hierarchical method that begins with all variables separate, each forming its own cluster. In the first step, the two variables closest together are joined. In the next step, either a third variable joins the first two, or two other variables join together into a different cluster. This process will continue until all clusters are joined. The groupings can be used to assign certain geochemical associations or groupings (as shown). Greater distances at which clusters are joined implies they are not closely related.

Table 5 – Environmental Quality Standards (EQS) and drinking water quality guideline values.

Determinand	Freshwater EQS (μg/l)	Drinking water guideline * (μg/l)	Comments
Arsenic (dissolved)	50 AA	10	Statutory EQS, list II substance
Boron	2000 AA		Statutory EQS, list II substance
Cadmium	5 AA total	3	Statutory EQS, list II substance
Chlorine	250000 AA		Environment Agency Non-Statutory Standard
Chromium	EQS 1 EQS 2 0-50mg CaCO3 5 150 50-100mg CaCO3 10 175 100-150mg CaCO3 20 200 150-200mg CaCO3 20 200 200-250mg CaCO3 50 250 >250mg/l CaCO3 50 250	50	Statutory EQS, list II substance
Cobalt (dissolved)	3 AA 100 MAC		Proposed DETR EQS, Environment Agency Non-Statutory Standard
Copper (dissolved)	EQS 1 EQS 2 0-50mg CaCO3 1 1 50-100mg CaCO3 6 6 100-150mg CaCO3 10 10 150-200mg CaCO3 10 10 200-250mg CaCO3 10 10 >250mg/l CaCO3 28 28	2000	Statutory EQS, list II substance
Fluoride	1500 AA		Environment Agency Non-Statutory Standard
Iron	1000 AA		Statutory EQS, list II substance
Lead	EQS 1 EQS 2 0-50mg CaCO3 4 50 50-100mg CaCO3 10 125 100-150mg CaCO3 10 125 150-200mg CaCO3 20 250 200-250mg CaCO3 20 250 >250mg/l CaCO3 20 250	50	Statutory EQS, list II substance
Manganese (dissolved)	30 AA 300 MAC		Environment Agency Non-Statutory Standard
Nickel (dissolved)	EQS 1 EQS 2 0-50mg CaCO3 50 50 50-100mg CaCO3 100 100 100-150mg CaCO3 150 150 150-200mg CaCO3 150 150 200-250mg CaCO3 200 200 >250mg/l CaCO3 200 200	20	Statutory EQS, list II substance
NO_3^-		50 (mg/l)	none
pH	6 - 9 95%ile		Statutory EQS, list II substance
Phosphorus	Salmonid 65 MAC Cyprinid 130 MAC		Environment Agency EAL. Operational standard used for the protection of fisheries
Silver	0.05 AA 0.1 MAC		Environment Agency Non-Statutory Standard
Sulphate	400		Environment Agency Non-Statutory Standard
Uranium		2	none
Vanadium	EQS 1 EQS 2 0-50mg CaCO3 20 20 50-100mg CaCO3 20 20 100-150mg CaCO3 20 20 150-200mg CaCO3 20 20 200-250mg CaCO3 60 20 >250mg/l CaCO3 60 20		Environment Agency Non-Statutory Standard
Zinc		5000	

Notes
MAC = Maximum Allowable Concentration
AA = Annual Average
95%ile = 95% samples
EQS 1 = for the protection of sensitive aquatic species (e.g. salmonids)
EQS 2 = for the protection of other aquatic species (e.g. Cyprinids)
* collation of guideline values published by the World Health Organization in 1993

6.4 METHOD FOR CALCULATING SUB-CATCHMENT AREAS

By combining a DEM (digital elevation model) of the catchment and the stream sampling locations in the GIS package ArcGIS, it was possible to calculate the drainage areas of each sample site by mapping each sub-catchment based on its topography. The total area covered by the sub-catchments of the 490 stream sampling locations was 671 km^2, approximately 73% of the entire catchment area (920 km^2). Of this 671 km^2, first and second order streams accounted for 38.5 and 41% of the drainage area respectively (Table 6).

Table 6 – Area and proportion total catchment area of streams in different stream orders.

Stream Order	Count	Total area (km^2)	Proportion of area (%)
1	293	259	38.5
2	154	276	41
3	39	89	13.2
4	8	47	7
Total	494	671	

6.5 PRESENTATION OF SPATIAL STREAM WATER CHEMISTRY

For the majority of elements and parameters the variation in concentrations across the catchment show relatively smooth variation, comparable to autocorrelation where samples close together are more similar on average than those further apart. In the case of total and reactive phosphorus, there is significant short-scale variation due to a variety of non-natural diffuse and point sources. There is little or no autocorrelation in these spatial data, hence the sample values are not interpolated but presented as proportional symbols.

6.6 CONTROLS ON STREAM WATER CHEMISTRY AND TEMPORAL VARIATION

6.6.1 Major ions and stream water parameters

The hydrochemical facies of waters collected over the Bude and Crackington Formations are plotted in Figure 14. The Piper (1944) diagram demonstrates that the waters are not strongly dominated by any of the three major cation or anion classes. The Crackington Formation samples produce a more widely dispersed hydrochemistry than the samples collected over the Bude Formation. Samples demonstrating a dominance of **chloride** (**Cl^-**) and **sodium** (**Na**) are likely to have been influenced by marine aerosols. Samples from the Crackington Formation had a greater range of cation and anion dominance, which may be explained in part by its broader geographical coverage (cf. Figure 2). Samples collected over igneous lithologies have been plotted in Figure 15. The hydrochemistry is broadly similar to that of the major catchment lithologies, with no significant ionic dominance for the majority of the samples.

Most natural waters fall in the **pH** range 5 to 9 (Drever, 1988), although drainage from mines and peat bogs may be considerably more acid. In the Tamar catchment, stream water **pH** at the time of sampling ranged from approximately 6.7 to 7.7, between the 5th and the 99th percentiles. The lowest **pH** values (<6.7) were predominantly associated with the granite intrusions, where the overlying soils are acidic (<pH 4.5) and poorly-buffered. Low **pH** values were also obtained around the most intensive area of mining activity, surrounding the Devon Great Consols mine. Despite the distinctively low values in this area, water acidity was generally high over the rest of the mineralised zone (>pH 7.4), with respect to typical concentrations across the whole catchment.

A significant positive correlation (r=0.67) was calculated between **conductivity** and **bicarbonate** (**HCO_3^-**) concentration in the stream waters. The dominant control on the pattern of stream water **conductivity** is the solubility of minerals in soils, drift cover and bedrock. **Conductivity** values may be modified as a result of human activities, including mining, the application of fertilisers and agricultural lime, and point-source contamination. **Bicarbonate** (**HCO_3^-**) in surface and ground water is derived from CO_2 present in the atmosphere and in the soil atmosphere above the water table, and from the dissolution of carbonate minerals. Both **conductivity** and **HCO_3^-** appear to show strong topographic affinities (at the time of sampling), with high levels in the lower-lying region traversing the central part of the catchment, broadly trending north to south, and lower values over areas at greater elevation (the east and west of the survey area). The lowest values (conductivities<90 µs/cm; **HCO_3^-** <9 mg/l) were found in association with the two granite intrusions, reflecting the poor buffering capacity of the soil and bedrock minerals. Similarly, **conductivity** and **HCO_3^-** were low in the Kit Hill/Gunnislake area, corresponding with low pH. Sea-spray is likely to have contributed to stream water **conductivity**, particularly approaching the northern and southern extents of the catchment.

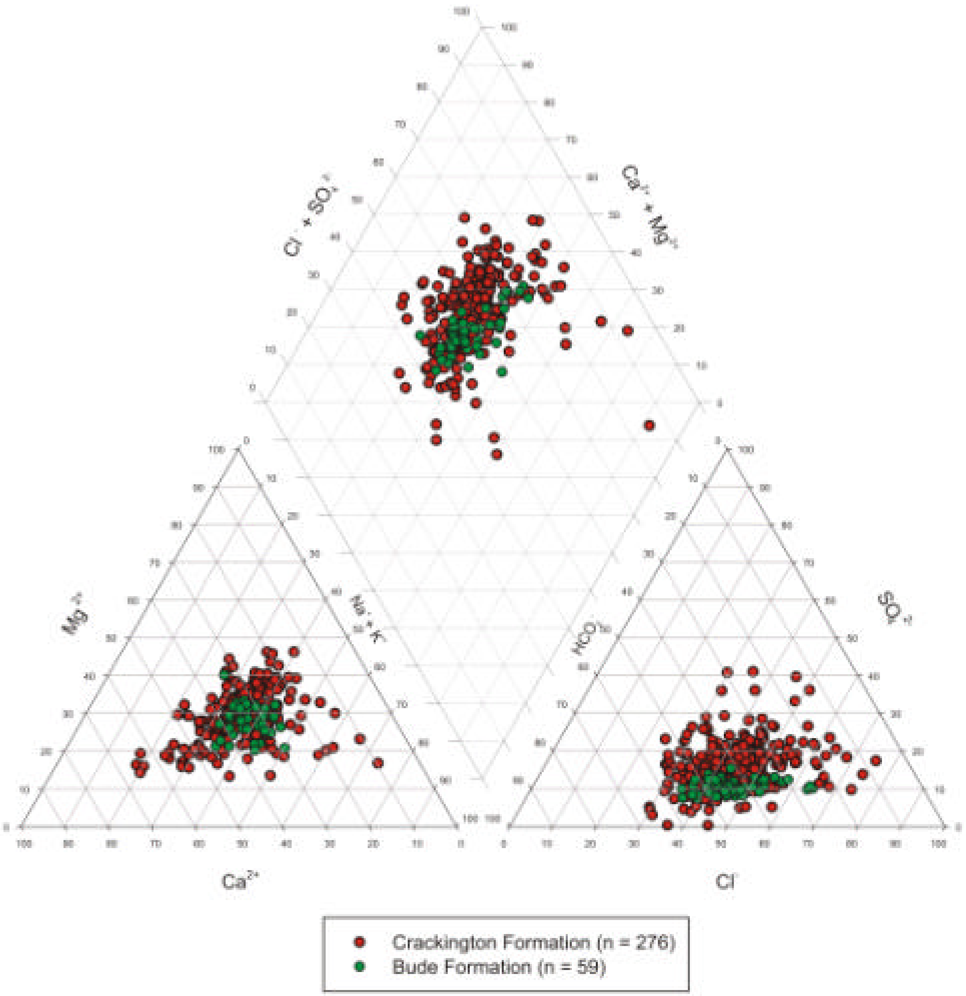

Figure 14 – Piper diagram showing the dominance of major cations and anions in stream water samples for catchments over the Bude and Crackington Formations.

A comparison of stream water **conductivity** and **bicarbonate** with a larger G-BASE survey, that of Wales, which comprises 13,444 samples (British Geological Survey, 1999), indicates that these parameters were generally low in the Tamar catchment. At the 50th percentile, **conductivity** and **HCO_3^-** in the catchment were 171 µs/cm and 35 mg/l, respectively, while the equivalent median values for Wales were 320 µs/cm and 97 mg/l, respectively.

The distribution of **water hardness** across the Tamar catchment, at the time of sampling, was very similar to that of **HCO_3^-**, demonstrating the strong contribution of carbonate mineral dissolution to **bicarbonate** alkalinity in the stream waters. **Water hardness** is defined as the concentration of ions in water that will react with a sodium soap to precipitate an insoluble residue (Drever, 1988) and is generated from the dissolution of carbonate mineral phases. The principal mineral phases involved are calcium carbonate ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). On the basis of a number of assumptions, **hardness** can be calculated as a function of the **Ca** and **Mg** ion concentrations in water and is defined as equivalent $CaCO_3$:

Equivalent $CaCO_3$ = 2.5(mg Ca/l) + 4.1(mg Mg/l) see Drever (1988)

Water hardness is significant for the purpose of environmental assessment and in the application of the Environment Agency's Freshwater Environmental Quality Standards (EQS). A number of potential contaminants are classified by **water hardness**, with lower maximum concentrations admissible where $CaCO_3$ concentrations are low (Table 5). **Water hardness** in the Tamar catchment generally fell within the range 50-100mg/l at the time of sampling, however 25% of the samples fell within the lowest range for **hardness** (0-50 mg/l).

A significant relationship (r=0.65) occurred between **Ca** and **HCO_3^-** concentrations in the Tamar catchment stream waters, consistent with the suggested influence of carbonate mineral dissolution. Very low **Ca** concentrations (<5 mg/l) occurred in association with the granite intrusions, as **Ca**-bearing minerals derived from granite are relatively insoluble. Concentrations were also low around the Devon Great Consols mine (the Kit Hill/Gunnislake area), corresponding with low **HCO_3^-**. The highest concentrations were generally clustered towards the centre and south of the catchment, overlying the mineralised region. The highest concentration (71 mg/l) was obtained from the southernmost point of the catchment and possibly reflects mixing with brackish waters in the estuary. A relationship with topography is also apparent, with higher concentrations towards the centre of the valley.

The major cations, **magnesium** (**Mg**) and **sodium** (**Na**) were strongly correlated in these stream waters (r=0.81); however, neither element had a strong relationship with **Ca**. They were additionally found to demonstrate very significant relationships with the major anions **chloride** (**Cl^-**), **fluoride** (**F^-**) and **bromide** (**Br^-**); r>0.75 for all five elements. The strongest relationship was calculated between **Na** and **Cl^-** (r=0.98). The distributions indicate that higher concentrations progressed from the north-west, across the catchment towards the central region. This almost certainly reflects the influence of sea-spray, dispersed inland from the coastal region directly to the north-west of the survey area. Very high concentrations of the major elements were also detected in the southernmost part of the catchment, probably reflecting the mixing of fresh and marine waters in the estuary. Very low concentrations of **Mg**, **Na**, **Cl^-** and **Br^-** (<3 mg/l, <8 mg/l, <14 mg/l and <0.04 mg/l, respectively) were found in stream waters overlying the granite intrusions.

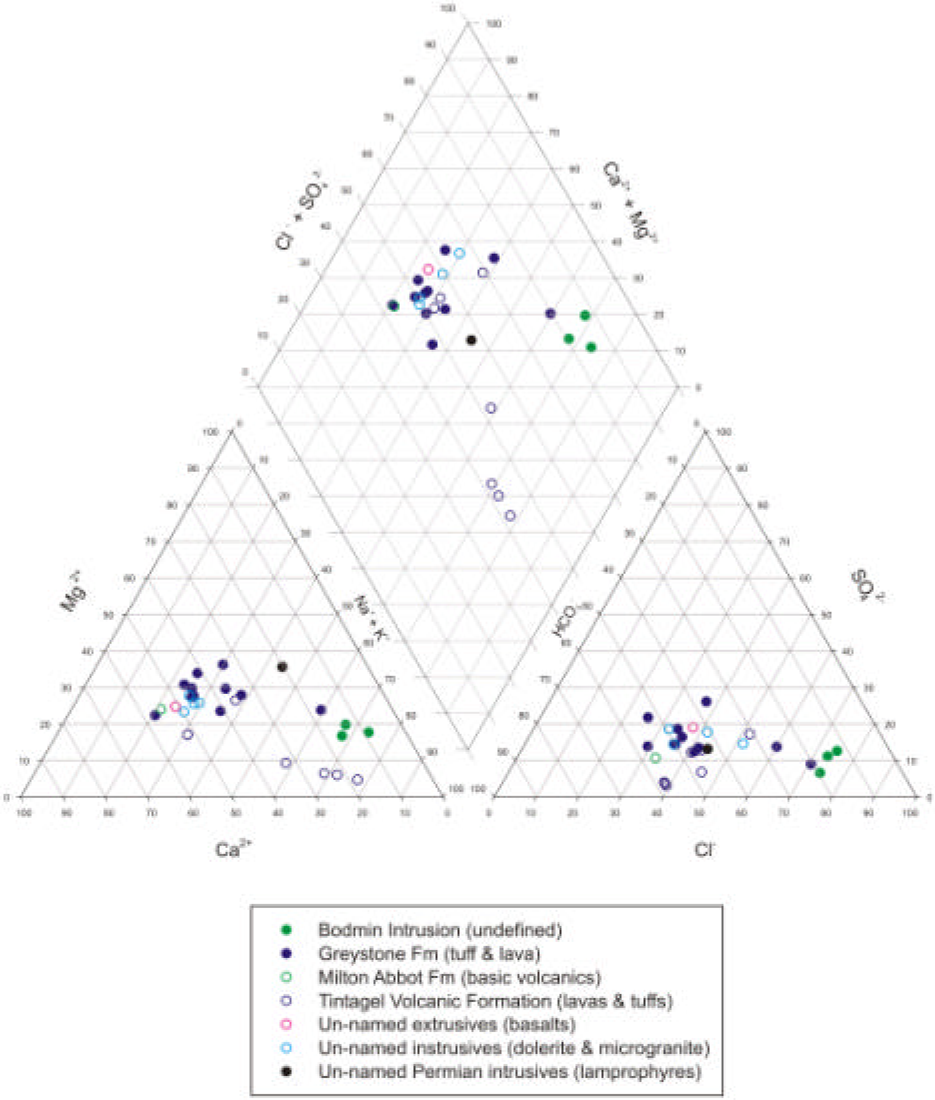

Figure 15 – Piper diagram showing the dominance of major cations and anions in stream water samples over various lithologies.

The correlations between **sulphate** (**SO_4^{2-}**) and the other major elements were slightly weaker for the samples collected. While high concentrations (>13 mg/l) towards the western margin of the catchment are likely to have reflected a sea-spray influence, elevated levels of this species over the southern region of the catchment, south of the Crackington Formation, may have been derived from sulphide-bearing minerals within this region of complex stratigraphy. Unusually, **SO_4^{2-}** concentrations were also low around the Devon Great Consols mine. Higher levels would be expected in this area, due to the low pH. The dissolution of sulphide minerals in mining regions is typically a major contributor to the generation of acidity in natural waters.

Of the trace elements measured, **strontium** (**Sr**), **molybdenum** (**Mo**), **uranium** (**U**) and **boron** (**B**) were most closely associated with these major ions and stream water parameters, according to the cluster diagram. **Strontium** demonstrated clear positive relationships (r>0.55) with **conductivity**, **HCO_3^-** and all associated major cations and anions, being most strongly associated with **Mg** (r=0.8). As these strong relationships are only apparent in the stream waters (not in the stream sediments or soils), the most logical cause is the association of **Sr** with **Mg**, **Ca**, **Na**, **Cl^-**, **Br^-** and **F^-** in sea-spray. **Strontium** concentrations were also low (<0.02 mg/l) over the granite intrusions and the mining region around the Devon Great Consols mine.

There were significant relationships (r>0.5) between boron (**B)** and the major cations and anions (described above), however, a marine influence is less apparent in the distribution of this element. The highest concentrations of **B** were found to be associated with the boundary between the Bude and Crackington formations, which is overlain by clay-rich soils. High concentrations were also located in the far south of the catchment, while the lowest values are again associated with the granites.

Uranium was determined to have a positive relationship with **Ca** (r=0.53), and although the range in **U** concentration was small (0.1 µg/l–0.13 µg/l between the 5th and 99th percentiles), the results were generally higher over the southern part of the catchment, overlying the mineralised area. Concentrations were again low around the Devon Great Consols mine (<0.1 µg/l), however, elevated levels of **U** (>0.05 µg/l) were present in stream waters over the granite intrusions. This reflects the strong association of **U** with this lithology.

6.6.2 Heavy metals, transition elements and metalloids

Arsenic (**As**) concentrations in stream waters collected from the Tamar catchment ranged between 0.4 and 7.3 µg/l, between the 5th and the 99th percentiles of the distribution. Higher levels were obtained from samples collected over the mineralised region in the southern half of the catchment. The drinking water guideline value for **As** is 10 µg/l (World Health Organisation, 1993). Due to the likely temporal variability of stream water **As** concentrations, values of 6 µg/l and above could represent a potential risk to human populations where they derive their drinking water from a private supply in the catchment of these streams.

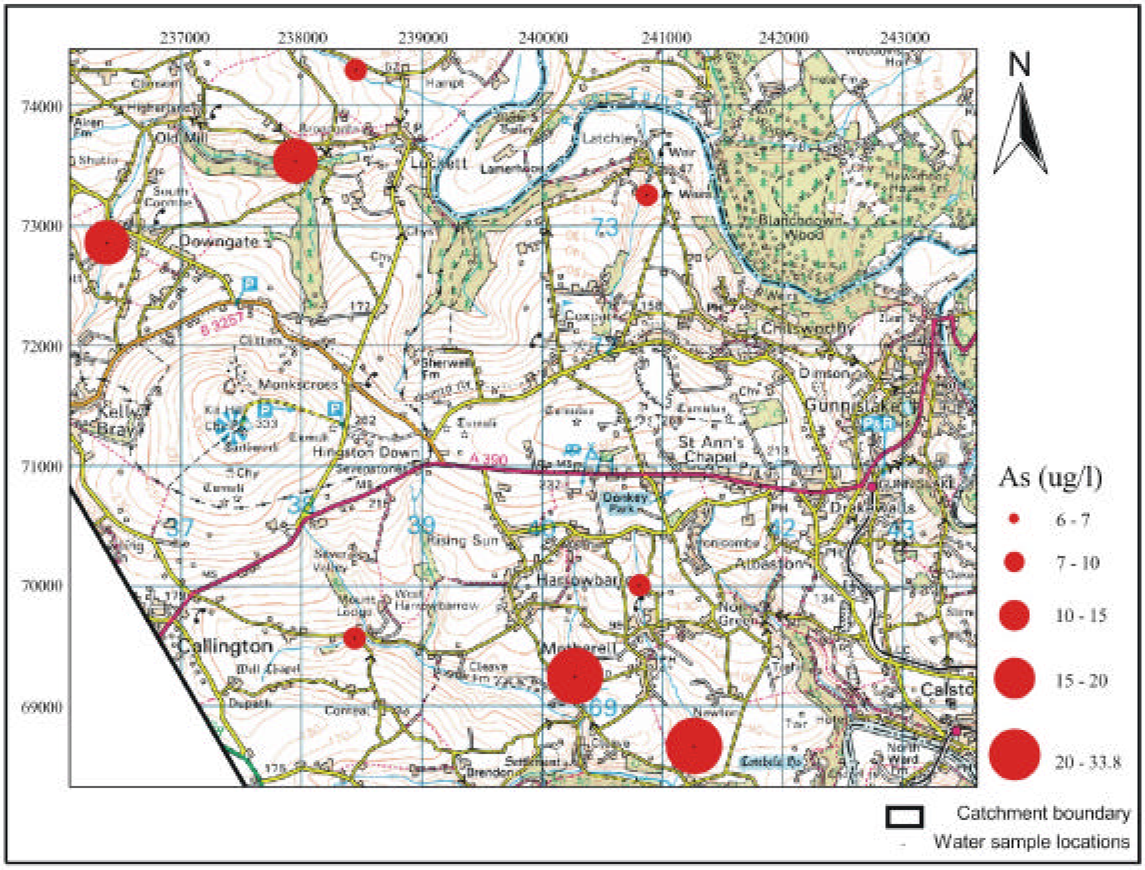

Figure 16 – Distribution of high arsenic concentrations (>6 mg/l) in stream waters of the Kit Hill / Gunnislake area, Tamar catchment.

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Most of the elevated concentrations (6 µg/l and above) were measured from stream water samples collected in close vicinity (within 1km^2) to areas of human habitation (generally small villages). Over the western extent of the catchment area, a sample containing 13.4 µg/l **As** [Grid reference: SX 233 839] was collected from a stream located approximately 0.5 km from the location of an ancient well site. The well lies directly to the east of the village of Laneast. High **As** levels may pose the most significant risk in the Kit Hill/Gunnislake area (Figure 16), as levels are generally higher in this region and the population density is greater. The highest concentration (33.8 µg/l) was measured in a sample collected from the small village of Treragin [Grid reference: SX 402 692], approximately 0.5 km downstream from the village of Harrowbarrow and directly west of Metherell. This area in particular may pose a significant risk to any individuals using private water supplies, as the sample obtained represents a three-fold exceedance of the drinking water guideline value.

The lowest levels of **copper** (**Cu**) were measured in stream waters collected over the granite intrusions (<0.45 µg/l). Although concentrations were generally lower over the southern part of the catchment, the highest **Cu** values obtained (>4 µg/l) were largely clustered around the Kit Hill/Gunnislake area (a region of intense mining activity in the south of the catchment). These sample locations were also characterised by low **water hardness** values (<50 mg/l). At **hardness** values below 50 mg/l, the freshwater EQS for **Cu** is 1 µg/l, both for the protection of sensitive and other aquatic species. There may therefore be a significant risk to aquatic life in this area. The highest value was measured at the same location as the highest **As** value [Grid reference: SX 402 692], with a **Cu** concentration of 118.8 µg/l and a **water hardness** value of 57.33 mg/l. (The EQS value for **Cu** rises to 6 µg/l for a **water hardness** of 50-100 mg/l). Despite the high values in this area, the effects appear to have been localised, as adjacent stream sites had relatively low concentrations of **Cu** below the EQS. Elevated concentrations further north in the catchment were also localised. A concentration of 70.4 µg/l was obtained from one sample overlying the Bude Formation [Grid reference: SS 307 095]. This enriched sample was collected in close proximity to the Bude Aqueduct (<1 km), but the high levels appear to have been rapidly diluted in downstream samples, to concentrations within EQS values for the appropriate **hardness** levels (50-100 mg/l). Humans can tolerate high concentrations of **Cu**, therefore the values obtained for the Tamar catchment stream waters do not represent a risk to drinking water supplies.

In contrast to the sediment and soil maps, the measurements for **lead** (**Pb**) in the stream waters were generally higher over the Crackington and Bude formations, than over the mineralised region in the south of the catchment. The highest concentrations were found in relatively isolated locations. Three sites exceeded the freshwater EQS for the protection of sensitive aquatic species (10 µg/l at 50-100 mg/l $CaCO_3$). The highest concentration (18.7 µg/l) was measured in a sample collected close to the boundary between the Bude and Crackington formations [Grid reference: SX 423 981]. This value falls significantly below the drinking water guideline value for **Pb** (50 µg/l), suggesting that **Pb** is not a hazard in terms of drinking water supply.

There appears to be have been a very strong correlation between **cadmium** (**Cd**) and **zinc** (**Zn**) concentrations in the stream waters, at the time of sampling (r=0.96). The highest levels of both elements were focused around the Kit Hill/Gunnislake area, although concentrations were generally found to be low over the mineralised region in the south of the catchment. A single sample [Grid reference: SX 427 769] contained the highest concentrations of **Zn** and **Cd** (2735 µg/l and 5.9 µg/l, respectively). Although significantly elevated in concentration with respect to the surrounding samples, the levels of **Zn** at this site did not exceed the guideline value for **Zn** in drinking water (5000 µg/l). The level of **Cd**, however, was higher than both the freshwater EQS (5 µg/l) and the drinking water guideline value (3 µg/l). One additional sample was found to exceed the drinking water guideline value for **Cd**, with a concentration of 3 µg/l [Grid reference: SX 434 662] and another sample contained 1.6 µg/l at the time of sampling [Grid reference: SX 402 692]. This stream may also represent a risk to drinking water supplies if levels are subject to any temporal increases. The **Cd** values with potential implications for human health through water consumption from a private water supply span the southern part of the catchment, from approximately SX660 to SX770.

The heavy metals **cobalt** (**Co**) and **nickel** (**Ni**) were significantly correlated in the stream waters (r=0.72) and were also positively correlated in concentration with **Cd** and **Zn** (r>0.5). This is likely to reflect the elevated levels of these elements obtained from streams overlying the Crackington Formation, with respect to the other major lithologies of the catchment. These elevated concentrations may be associated with higher rates of mineral dissolution from soils and rocks in this area. The highest **Ni** and **Co** concentrations were again found in conjunction with the highest **Zn** and **Cd** values [Grid reference: SX 427 769]. Although the value measured for **Ni** (35.5 µg/l) does not exceed any freshwater EQS values, it does exceed the drinking water guideline (20 µg/l). Two other sites exceeded the drinking water guideline for **Ni** [Grid reference: SX 402 693 and SX 293 942] and a further two sites contained **Ni** concentrations approaching the drinking water guideline

[Grid reference: SS 375 004 and SX 373 872]. The highest **Co** concentration (17.05 μg/l) obtained is several times higher than the annual average recommended in the freshwater EQS (3 μg/l). A further nine samples were found to contain **Co** above the average EQS and a number of samples, over the 99th percentile, were close to the EQS in concentration. The values obtained for **lithium** (**Li**) were again higher over the Crackington Formation and this element was found to have a positive correlation with **Ni** (r=0.51). Elevated levels of **Li** (>5.5 μg/l) were also found in the most intensely mined area, around the Devon Great Consols mine (Kit Hill/Gunnislake area).

Although the range in concentration obtained for **thallium** (**Tl**) was low (0-0.05 μg/l between the 5th and the 99th percentiles), this element had a significant correlation with **caesium** (**Cs**) in the Tamar catchment stream waters (r=0.63). Both elements were also positively correlated with **Cu** and **As** (r>0.5). The highest concentrations were found in the Kit Hill/Gunnislake area, with higher levels in general located to the south of the Bude Formation.

Tin (**Sn**) and **antimony** (**Sb**) were not found to have strong associations with the concentrations of any of the other elements that were determined. The distribution of **Sb** reflects a strong geogenic influence on stream water concentrations at the time of sampling, with an increase in concentration to the south of the Crackington Formation and low values over the granite intrusions and within the Kit Hill/Gunnislake area. **Tin** concentrations at the time of sampling were less variable spatially, with elevated concentrations to the north of the Bodmin Moor granite and over the southern tip of the catchment. The results obtained for **nitrite** (**NO_2**) in the Tamar catchment stream waters did not contain sufficient values above the detection limit to produce either an interpolated image or a proportional symbol image.

6.6.3 Mainly nutrient and land-use

The distributions of **TP (>0.45)** and **RP (<0.45)** were highly variable throughout the catchment representing a range of P sources: low concentrations in relatively pristine upland environments, moderate concentrations (which may be related to diffuse sources) and high concentrations (associated with point-sources of pollution). The greatest number of high **TP (<0.45)** and **RP (<0.45)** concentrations (>0.5 mg/l) in stream water occurred in the north and west of the catchment. It is beyond the scope of this study to attribute these high values to specific sources of phosphorus. The central and eastern parts of the catchment had generally low **TP (<0.45)** and **RP (<0.45)** concentrations (<0.05 mg/l).

Nitrate (**NO_3^-**) is a very soluble compound and has significant potential for migration into groundwater. Elevated levels of **NO_3^-** were found over the southern part of the catchment, below the boundary of the Crackington Formation. The highest value recorded for stream water **NO_3^-** was obtained from the central region of the catchment [Grid reference: SX 287 887]. The value obtained (131 mg/l) represents a more than two-fold increase with respect to the drinking water guideline value (50 mg/l), and is likely to reflect an isolated region of contamination. The **NO_3^-** distribution is most closely associated with **potassium** (**K**) and **rubidium** (**Rb**) in the stream water samples.

Potassium and **NO_3^-** were both found in relatively low concentrations in streams overlying the granite intrusions. The trace element **Rb** is commonly associated with **K** in the natural environment and the relationship between these two elements in the Tamar catchment stream waters is significant (r=0.87). The strongest similarities occurred towards the north of the catchment, overlying the Bude and Crackington Formations. A possible sea-spray influence is apparent towards the west of the Crackington Formation and high levels over the Bude Formation may have been related to clay-rich soils interspersed with the typical brown earths in this area (section 1.2.3).

The high concentrations of **Zr** over the Bude and Crackington Formations were probably associated with the sand-rich parent materials. This may also explain elevated concentrations of **silicon** (**Si**) in stream waters over the Bude and Crackington Formations (>3 mg/l). The distribution of **Si** in stream water was very similar to that of **barium** (**Ba**) in this region (r=0.54).

Iron (**Fe**) and **manganese** (**Mn**) concentrations were higher over the northern half of the catchment. At the 99th percentile, **Fe** concentrations exceeded the freshwater EQS (annual average), of 1 mg/l. The highest concentration is 9.5 mg/l, obtained from a stream located to the north of Launceton [Grid reference: SX 321 896]. **Manganese** levels exceeded the annual average freshwater EQS (0.03 mg/l) at the 75th percentile and were found to be above the maximum allowable concentration (0.3 mg/l) at the 99th percentile. **Chromium** (**Cr**) and **vanadium** (**V**) demonstrated a geochemical association in the stream waters (correlation coefficient, r=0.61), with the highest levels occurring in the mineralised region, between the two granite bodies.

6.6.4 Rare earth and other elements

The rare earth elements (REEs) **cerium** (**Ce**) and **lanthanum** (**La**) were found to be related in the stream waters (r=0.55) and were also strongly related to **yttrium** (**Y**), an element that has strong natural associations with the REEs. Concentrations were generally higher over the northern half of the catchment; however, levels of these elements were significantly elevated over the granite intrusions and in the Kit Hill/Gunnislake area, particularly **La** (>0.04 µg/l). **Aluminium** (**Al**) demonstrated strong associations with **Ce** and **Y** (r>0.7), with high concentrations (>18 µg/l) over the granite intrusions and generally elevated levels in the northern part of the catchment. **Beryllium** (**Be**) was also significantly related to **Al**, **Ce** and **Y** (r>0.5). Concentrations of this element were generally close to or below the detection limit (0.01 µg/l) across the catchment, higher values corresponding with greater elevations (the granites and the area to the north of Roadford Reservoir) and with the area of intense mining around Kit Hill and Gunnislake.

7 Interpretation of stream sediment geochemistry

7.1 SYNOPSIS OF STREAM SEDIMENT GEOCHEMISTRY

The chemical composition of active stream sediment represents a close approximation to a composite sample of the products of weathering and erosion of soil and rock in the catchment upstream of the sampling site. Chemical processes such as the precipitation of Mn and Fe oxides, and the co-precipitation and adsorption of certain trace elements can have a significant influence on the composition of the stream sediment sample. In addition, human activities such as mining and agriculture can significantly alter stream sediment geochemistry.

Stream sediments act as pollutant sinks for the catchment they drain, but also represent a pollutant source for the Tamar estuary and Plymouth sound further down the drainage network.

7.1.1 Mining-related contamination

The most significant feature in terms of impact on the Tamar estuary Special Area of Conservation is the elevated concentrations of potentially toxic elements (arsenic, copper, lead and zinc) in the fine fraction of stream sediments around the former mining areas near Gunnislake and Callington. When the sediment load of these streams is high (during flood events), the suspended load of these elements to the estuary is likely to be larger than for other catchments where mining-related contamination is limited. It is beyond the scope of this study to determine the significance of this impact on the ecology of the Tamar estuary and Plymouth Sound.

7.1.2 Phosphorus in stream sediment (sources and sinks)

The phosphorus content of stream sediment across the catchment largely reflects a combination of the natural background concentration derived from the parent material and any inputs from agricultural or effluent sources. Analysis of the **reactive phosphorus (RP<0.45)** content of stream water at each sediment sampling site across the catchment showed that a number of sites had elevated concentrations. All sites with a **(RP<0.45)** concentration of more than 50 µg l^{1} were selected from the streamwater database and paired with their phosphorus sediment content at the same site. Although there was no clear correlation between the two variates, the mean P_2O_5 concentration in this sediment subset was 0.28%, somewhat higher than the mean concentration throughout the catchment (0.22%). This suggests that phosphorus may have been precipitated at sites where stream water has elevated P concentrations, and that the sediments may be acting as a phosphorus sink. As the chemistry of stream water changes with time, sediments in such areas may also act as a source of P.

7.2 PRESENTATION OF STREAM SEDIMENT GEOCHEMISTRY

Images showing the variation in the total concentration of each element determined are provided in Appendix B.

7.3 SUMMARY STATISTICS

Table 7 - Summary statistics and detection limits for stream sediment geochemistry (n=494). All values in mg/kg unless otherwise stated.

Element	Min	Max	Median	Mean	St. Dev.	Skewness	Detection Limit (mg/kg)	Lower Reporting Limit (%)
Ag	0.25	34.5	0.25	0.4	1.7	18.2	0.5	0.5
Al_2O_3 (%)	8.3	25.1	18.7	18.4	2.7	-0.5	-	0.1
As	4.4	11000	19.2	73.1	505	20.9	0.9	1
Ba	161	1047	530	530	92.4	0.2	5.1	6
Bi	0.15	15.1	0.6	0.8	1.2	6.6	0.5	1
Br	0.6	222	11.7	19.2	24.7	4.2	0.4	1
CaO (%)	0.08	5.12	0.32	0.4	0.4	5.8	-	0.10
Cd	0.25	22.1	0.5	1.1	1.9	5.4	0.5	0.5
Ce	44	260	85	86.1	17.2	4.0	3.8	6
Co	5.7	218	31.2	38.4	26.7	3.2	1.2	2
Cr	44.7	397	119	128	46.0	3.4	1.3	2
Cs	2	47	7	8.7	7.0	1.8	2.2	4
Cu	11.4	8000	34.7	85.4	484	14.3	0.8	1
Fe_2O_3 (%)	1.84	22.1	7.92	8.1	2.1	1.3	-	0.01
Ga	8.2	37	20.7	20.5	4.0	-0.2	0.7	1
Ge	0.1	2.9	1.5	1.5	0.4	0.0	0.6	1
Hf	2.2	120	6.2	6.9	5.9	14.8	0.7	1
I	1	397	2	7.9	21.2	13.1	1.5	2
K_2O (%)	1.17	4.77	3.01	3.0	0.6	-0.2	-	0.05
La	26	135	45	46.0	10.4	3.4	3.5	6
MgO (%)	0.34	11.0	0.98	1.3	1.2	3.8	-	0.1
MnO (%)	0.03	6.56	0.22	0.4	0.5	6.7	-	0.010
Mo	0.15	9.4	0.15	0.8	1.4	3.1	0.2	1
Na_2O (%)	0.1	2.3	0.6	0.6	0.2	1.2	-	0.1
Nb	6.9	62.6	16.4	18.0	5.8	3.8	0.6	1
Nd	24	118	40	41.3	10.0	3.2	3.5	6
Ni	11.2	295	56.9	68.0	38.9	2.2	0.6	1
P_2O_5 (%)	0.05	0.85	0.19	0.2	0.1	1.9	-	0.05
Pb	13.2	450	31.05	42.5	41.7	5.8	0.5	1
Rb	40.2	394	132	134	40.7	1.3	0.5	1
Sb	0.5	59.4	1.9	3.5	4.7	5.6	0.9	1
Sc	5	31	17	17.2	3.2	-0.1	1.3	2
Se	0.1	11.6	1.16	1.6	1.5	2.2	0.2	1
SiO_2 (%)	22.7	71.8	57.4	56.9	5.2	-0.8	-	0.1
Sm	1	28	7	7.5	3.9	0.6	3.1	6
Sn	0.8	1500	3.4	33.0	142	7.4	0.8	1
Sr	36.9	195	89.6	90.9	20.0	0.7	0.6	1
Ta	0.1	53.6	1.5	1.9	3.3	12.4	0.7	1
Th	4.2	102	11.9	12.6	7.0	9.0	0.7	1
TiO_2 (%)	0.48	3.37	0.90	0.9	0.2	4.4	-	0.020
Tl	0.1	15.3	0.7	0.8	0.9	9.0	0.5	1
U	0.25	47.1	3.4	3.7	3.4	7.8	0.6	1
V	51.0	245	142	138	26.1	-0.1	1.3	2
W	0.1	1257	3.3	13.1	69.3	13.6	0.6	1
Y	20	103	30	31.2	6.4	4.8	0.8	1
Zn	48	1901	142	194	201	5.1	0.5	1
Zr	92.1	1341	231	258	110	4.9	0.8	1

Table 8 - Correlation coefficients (r) between elements determined in stream sediments (n=494).

Correlations greater than 0.5 in bold.

	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	MnO	Fe2O3	Sc	V	Cr	Co	Cs	Ba	La	Ce	Nd	Sm	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	MO	Hf	Ta	W	Tl	Pb	Bi	Th	U	Sn	Sb
Na2O	**1.00**																																											
MgO	-0.17	**1.00**																																										
Al2O3	0.01	-0.18	**1.00**																																									
SiO2	0.20	-0.52	-0.18	**1.00**																																								
P2O5	-0.26	0.41	-0.39	-0.51	**1.00**																																							
K2O	-0.15	-0.09	**0.84**	-0.42	-0.11	**1.00**																																						
CaO	-0.06	**0.63**	-0.35	-0.53	**0.62**	-0.19	**1.00**																																					
TiO2	-0.05	**0.76**	-0.07	-0.41	0.32	-0.10	0.47	**1.00**																																				
MnO	-0.27	0.16	-0.31	-0.34	0.38	-0.08	0.34	0.03	**1.00**																																			
Fe2O3	-0.29	0.44	-0.05	-0.73	0.43	0.15	0.34	0.33	0.29	**1.00**																																		
Sc	-0.29	**0.60**	0.47	-0.58	0.17	0.44	0.29	**0.60**	0.02	0.47	**1.00**																																	
V	-0.33	**0.57**	0.35	-0.51	0.22	0.34	0.26	**0.58**	0.11	**0.51**	**0.86**	**1.00**																																
Cr	-0.18	**0.89**	-0.03	-0.50	0.35	-0.03	**0.56**	**0.75**	0.10	0.44	**0.71**	**0.66**	**1.00**																															
Co	-0.33	0.26	-0.19	-0.48	0.36	0.01	0.25	0.11	**0.55**	**0.56**	0.22	0.25	0.26	**1.00**																														
Cs	-0.08	-0.01	0.19	-0.39	0.08	0.34	0.15	-0.03	0.01	0.13	0.13	0.10	-0.04	-0.02	**1.00**																													
Ba	-0.28	-0.18	0.37	0.05	-0.07	0.33	-0.25	-0.21	0.17	-0.01	0.15	0.15	-0.12	0.03	-0.21	**1.00**																												
La	-0.17	-0.10	0.27	-0.50	0.19	0.47	0.06	-0.06	0.11	0.23	0.11	0.03	-0.08	0.22	0.47	0.00	**1.00**																											
Ce	0.07	-0.21	0.27	-0.29	0.10	0.44	-0.03	-0.11	-0.06	0.06	-0.04	-0.12	-0.21	0.05	0.39	-0.10	**0.79**	**1.00**																										
Nd	-0.15	-0.11	0.20	-0.41	0.19	0.39	0.03	-0.07	0.09	0.17	0.07	-0.02	-0.10	0.22	0.40	-0.04	**0.92**	**0.77**	**1.00**																									
Sm	-0.07	-0.03	0.07	-0.14	0.05	0.13	0.00	0.00	-0.01	0.01	0.02	-0.02	-0.02	0.01	0.24	-0.04	0.41	0.48	0.40	**1.00**																								
Ni	-0.36	**0.61**	-0.22	-0.54	0.49	-0.04	**0.53**	0.42	**0.58**	**0.58**	0.50	**0.57**	**0.65**	**0.68**	-0.02	0.03	0.03	-0.15	0.03	-0.04	**1.00**																							
Cu	-0.15	0.00	-0.11	-0.35	0.35	0.00	0.20	-0.07	0.26	0.33	-0.05	-0.03	-0.03	0.31	0.10	-0.03	0.36	0.23	0.32	0.05	0.18	**1.00**																						
Zn	-0.34	0.20	-0.06	-0.46	0.44	0.13	0.28	0.09	0.29	0.42	0.18	0.17	0.16	0.45	0.10	0.07	0.33	0.15	0.32	0.04	0.40	**0.55**	**1.00**																					
Ga	-0.06	0.09	**0.85**	-0.52	-0.09	**0.89**	-0.03	0.12	-0.12	0.26	**0.61**	**0.52**	0.16	-0.02	0.34	0.24	0.42	0.40	0.32	0.12	0.03	0.00	0.11	**1.00**																				
Ge	0.05	0.01	0.37	-0.11	-0.18	0.36	-0.03	-0.04	-0.04	0.00	0.23	0.19	0.06	-0.11	0.13	0.15	0.01	0.03	-0.04	0.01	0.00	-0.17	-0.09	0.38	**1.00**																			
As	-0.11	0.03	-0.03	-0.21	0.25	0.05	0.03	-0.03	0.04	0.33	-0.01	-0.01	0.00	0.19	0.41	-0.04	0.32	0.31	0.30	0.04	0.02	**0.98**	**0.51**	0.08	-0.14	**1.00**																		
Se	-0.37	0.08	-0.20	-0.15	0.36	0.03	0.16	-0.03	0.42	0.27	0.15	0.40	0.07	0.31	0.09	0.17	0.02	-0.06	0.04	-0.01	0.46	0.07	0.22	-0.03	0.02	0.04	**1.00**																	
Br	-0.02	0.13	-0.20	-0.53	0.39	0.12	0.34	0.07	0.24	0.21	-0.03	-0.05	0.01	0.21	0.46	-0.34	0.49	0.41	0.47	0.22	0.15	0.25	0.33	0.09	-0.06	0.15	0.19	**1.00**																
Rb	-0.01	-0.14	**0.65**	-0.44	-0.06	**0.87**	-0.09	-0.18	-0.07	0.09	0.23	0.13	-0.13	-0.03	**0.54**	0.08	**0.62**	**0.64**	**0.56**	0.24	-0.13	0.06	0.17	**0.80**	0.29	0.12	-0.01	0.39	**1.00**															
Sr	0.33	0.15	0.38	-0.12	-0.05	0.23	0.12	0.21	-0.02	0.06	0.32	0.23	0.26	-0.09	-0.22	0.29	-0.11	-0.06	-0.17	-0.13	0.05	-0.11	-0.13	0.34	0.22	-0.07	-0.17	-0.27	0.07	**1.00**														
Y	-0.18	-0.04	-0.02	-0.28	0.21	0.18	0.08	-0.04	0.13	0.13	0.08	0.00	-0.08	0.21	0.37	-0.11	**0.60**	0.48	**0.64**	0.29	0.09	0.16	0.22	0.16	-0.05	0.19	0.21	**0.56**	0.38	-0.28	**1.00**													
Zr	0.32	-0.16	-0.47	0.35	-0.08	-0.43	-0.05	-0.13	-0.11	-0.36	-0.56	-0.62	-0.28	-0.19	0.04	-0.37	-0.11	0.07	-0.04	0.04	-0.33	-0.11	-0.19	-0.48	-0.19	-0.04	-0.23	0.19	-0.15	-0.25	0.13	**1.00**												
Nb	0.01	**0.72**	-0.20	-0.41	0.40	-0.08	**0.53**	**0.80**	0.10	0.28	0.42	0.39	**0.66**	0.09	0.12	-0.31	0.09	0.12	0.10	0.07	0.43	-0.03	0.11	0.08	-0.04	0.03	0.04	0.29	0.00	0.13	0.20	0.04	**1.00**											
MO	-0.32	-0.06	-0.15	-0.11	0.28	0.02	0.06	-0.18	0.38	0.30	0.02	0.27	-0.05	0.26	0.10	0.24	0.16	0.08	0.15	0.05	0.32	0.23	0.22	-0.02	-0.03	0.21	**0.71**	0.15	0.04	-0.20	0.26	-0.22	-0.08	**1.00**										
Hf	0.25	-0.12	-0.26	0.08	0.00	-0.13	0.00	-0.13	-0.01	-0.19	-0.34	-0.41	-0.22	-0.08	0.17	-0.33	0.11	0.27	0.15	0.08	-0.20	0.05	-0.06	-0.17	-0.08	0.06	-0.08	0.38	0.18	-0.21	**0.52**	**0.92**	0.20	-0.15	**1.00**									
Ta	-0.14	0.12	-0.11	-0.43	0.40	0.01	0.29	0.04	0.30	0.38	0.04	0.06	0.07	0.34	0.17	-0.07	0.39	0.27	0.34	0.08	0.27	**0.96**	**0.54**	0.05	-0.15	**0.91**	0.13	0.32	0.10	-0.08	0.20	-0.11	0.11	0.23	0.09	**1.00**								
W	-0.08	0.03	-0.03	-0.26	0.28	0.10	0.14	0.00	0.02	0.23	-0.07	-0.11	-0.01	0.12	0.21	-0.13	0.45	**0.51**	0.43	0.13	-0.01	**0.65**	**0.51**	0.10	-0.15	**0.86**	-0.14	0.29	0.26	-0.11	0.20	0.00	0.11	0.14	0.11	**0.64**	**1.00**							
Tl	-0.14	-0.10	0.09	-0.17	0.18	0.16	0.14	-0.14	0.13	0.19	0.07	0.16	-0.06	0.15	0.10	0.13	0.13	0.13	0.07	0.00	0.14	0.21	0.05	0.25	0.03	0.00	0.32	0.09	0.13	0.01	0.16	-0.23	-0.14	0.35	-0.12	0.18	-0.11	**1.00**						
Pb	-0.26	0.11	0.01	-0.39	0.34	0.22	0.14	0.03	0.17	0.37	0.13	0.11	0.04	0.24	0.21	0.05	0.38	0.27	0.38	0.08	0.16	**0.50**	**0.79**	0.18	-0.08	**0.60**	0.14	0.39	0.29	-0.14	0.30	-0.12	0.11	0.21	0.03	**0.50**	**0.58**	-0.02	**1.00**					
Bi	-0.14	0.02	0.10	-0.32	0.16	0.18	0.22	0.03	0.11	0.12	0.14	0.04	0.05	0.08	0.27	0.05	0.46	0.20	0.41	0.17	0.08	0.29	0.30	0.20	-0.06	0.14	-0.04	0.31	0.31	-0.09	0.28	-0.09	0.05	0.12	0.03	0.30	0.24	-0.02	0.29	**1.00**				
Th	0.19	-0.13	0.14	-0.22	0.08	0.35	0.04	-0.12	-0.07	-0.05	-0.19	-0.25	-0.20	-0.05	0.36	-0.24	**0.60**	**0.82**	**0.59**	0.28	-0.18	0.15	0.10	0.30	0.02	0.23	-0.10	0.43	**0.64**	-0.09	0.33	0.20	0.14	0.00	0.38	0.19	**0.53**	0.02	0.19	0.10	**1.00**			
U	0.21	-0.15	-0.09	-0.05	0.05	0.11	0.05	-0.17	-0.01	-0.19	-0.26	-0.28	-0.24	-0.10	0.36	-0.27	0.30	**0.51**	0.34	0.18	-0.15	-0.07	-0.07	0.05	-0.02	-0.01	0.10	**0.56**	0.46	-0.22	**0.56**	0.49	0.17	0.13	**0.70**	0.00	0.15	-0.02	-0.01	0.13	**0.66**	**1.00**		
Sn	-0.01	0.03	-0.04	-0.30	0.23	0.18	0.11	-0.04	0.04	0.16	-0.07	-0.14	-0.06	0.07	0.27	-0.18	0.43	**0.51**	0.42	0.16	-0.03	0.45	0.50	0.16	-0.10	**0.58**	-0.07	0.50	0.44	-0.18	0.47	0.18	0.21	0.10	**0.54**	0.47	**0.75**	-0.09	**0.62**	0.32	**0.55**	0.44	**1.00**	
Sb	-0.16	-0.01	0.07	-0.17	0.27	0.21	0.16	-0.07	0.12	0.25	0.13	0.22	0.02	0.09	0.34	0.06	0.14	0.16	0.11	-0.01	0.17	0.23	0.19	0.27	0.06	0.30	0.39	0.15	0.19	0.00	0.19	-0.21	0.00	0.37	-0.10	0.23	0.21	**0.58**	0.28	-0.03	0.07	-0.01	0.12	**1.00**

7.4 GROUPING OF VARIABLES BY CLUSTER ANALYSIS

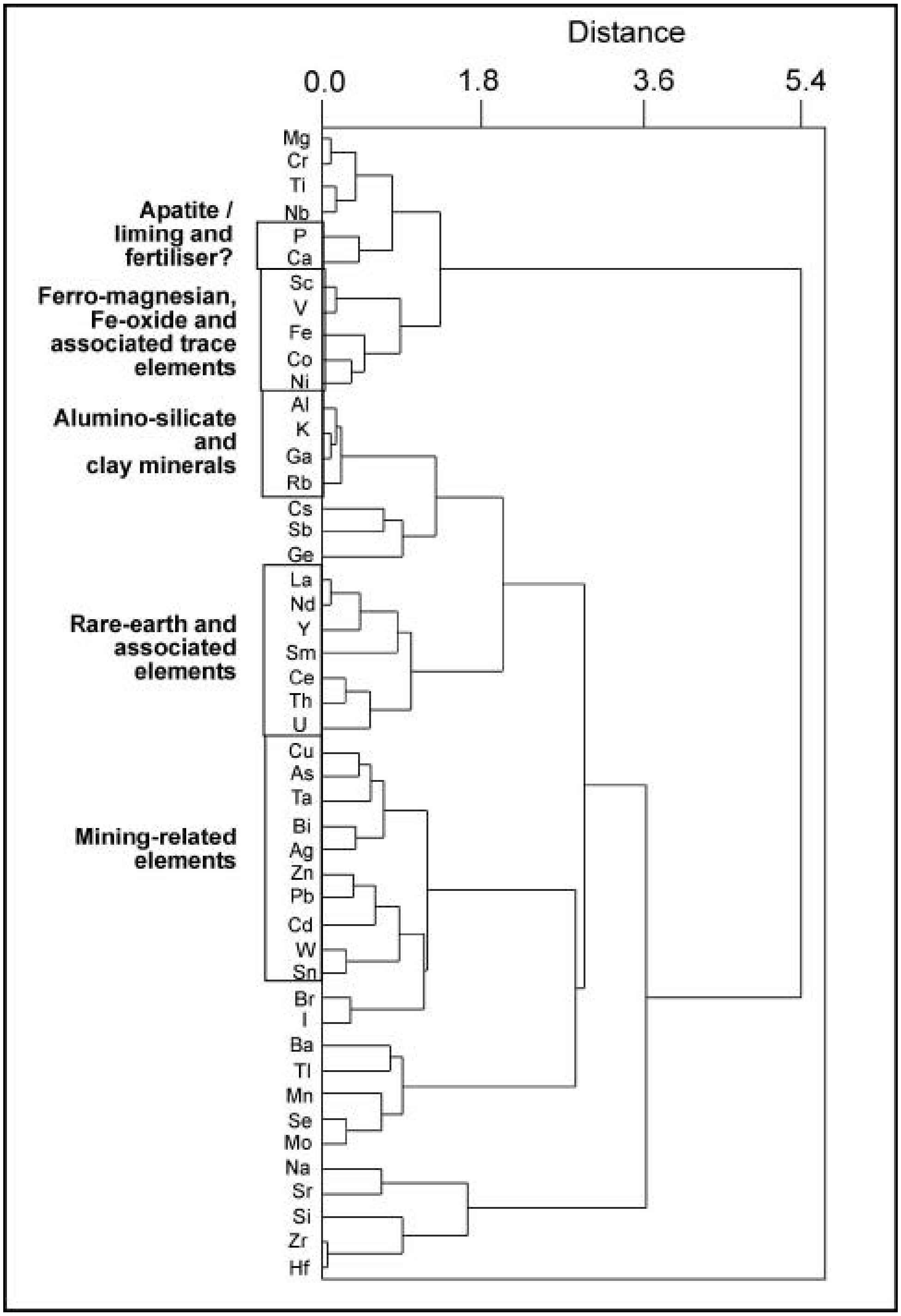

Figure 17 - Dendogram showing the clustering of total element concentrations in stream sediments.

7.5 BEDROCK GEOLOGY

7.5.1 Alumino-silicate and clay minerals

There are very strong relationships between **aluminium** (expressed as **Al_2O_3**), **potassium** (expressed as **K_2O**), **gallium (Ga)** and **rubidium (Rb) -** correlations are consistently high (r>0.8). Common host minerals for these elements include feldspars, micas and clay minerals. Concentrations are generally higher in sediments overlying the clay-rich argillaceous beds, south of the Crackington Formation. Areas of elevated concentration further north may reflect higher clay contents within particular sections of the Crackington Formation. The lowest levels of these elements generally overlie the Bude Formation, to the north. This lithology contains the highest ratio of sand to clay throughout the study area. A strong granite signature is evident for **Rb** in the stream sediments, with concentrations in excess of 238 mg/kg in the vicinity of the intrusions. Similar concentrations are also focused around the most Kit Hill/Gunnislake area (around the Devon Great Consols mine), suggesting a mining-related influence, which is also evident in the patterns of the other clay-related elements.

The trace elements **barium (Ba)** and **germanium (Ge)** have some positive correlations with the clay-related elements. The distribution of **Ge** does not, however, provide any clear patterns, due to a low range in sample concentrations (2.4 mg kg^{-1} at the 99th percentile). Concentrations of **Ba** are generally lower over the sand formations, with the exception of an enriched region (>700 mg/kg) within the Bude Formation. Very low concentrations of **Ba** (largely <300 mg/kg) surround the margins of the granite intrusions.

7.5.2 Ferromagnesian minerals and associated trace elements

The major element **magnesium** (expressed as **MgO**) is strongly associated with **titanium** (expressed as **TiO_2**), **chromium (Cr)**, **niobium (Nb)**, **scandium (Sc)** and **vanadium (V)**. These elements are derived from common ferromagnesian minerals, including pyroxene and mica and are generally more enriched within sediments overlying argillaceous beds in the southern part of the catchment. Lower concentrations, generally below the 75th percentile level, overlie the sand-rich Crackington and Bude Formations. With the exception of **MgO**, lower levels of these elements are observed over the Bude Formation, than the Crackington Formation. This may reflect a higher sand content in the Bude Formation. **Chromium**, **Sc** and **V** are all very low in concentration close to the granite intrusions.

The levels and distributions of the trace elements **Cr**, **Nb**, **Sc** and **V** strongly reflect patterns observed for topsoils in the area (section 8.5.2). Although the distributions are similar, **MgO** is more concentrated in the stream sediments than in the soils, while **TiO_2** is slightly more concentrated in the soils. At the 99th percentile, **MgO** levels are almost twice as high in the stream sediments (5.7%). The sediment concentrations of **TiO_2** are generally around 0.1% lower than the soil levels, in each percentile class. While **TiO_2** is a relatively immobile element, likely to accumulate in soils as they are weathered, **MgO** is highly mobile in the environment and may, therefore, be significantly leached from soils over time.

7.5.3 Rare earth and associated elements

There are strong geochemical associations in the stream sediments between the rare earth elements (REEs) **cerium (Ce)**, **lanthanum (La)** and **neodymium (Nd)**. The correlations between these elements are close (r>0.7); **La** and **Nd** are the most closely related (r=0.92). Correlations between these elements and the REE **samarium (Sm)** are significantly lower, however, **Sm** concentrations across the area are nearly an order of magnitude lower than those obtained for the other REEs. The highest concentrations of all the REEs are associated with the two granite intrusions and with a band of intense mine workings including the Devon Great Consols mine (Kit Hill/Gunnislake area). Lower values occur over the Bude Formation to the north of the catchment and an area of complex stratigraphy lying between the two granite bodies. The relative abundance of the REEs follows the order: **Ce**, **La**, **Nd**, **Sm**, with median concentrations of 83, 44, 39 and 7 mg/kg, respectively.

Yttrium (Y) has a strong geochemical association with the REEs, co-existing in host minerals such as monazite and bastnaesite. This is reflected in the similarities in the distribution of **Y** with **Ce**, **La** and **Nd**, with correlations of r=0.48, 0.6 and 0.64, respectively. The chemical properties of both **thorium (Th)** and **uranium (U)** are similar to the REEs and they also occur in common host minerals. Both elements have significant relationships with the REEs and the correlation between **Th** and **Ce** is particularly strong (r=0.82). The correlation between **U** and **Th** is also significant (r=0.66) and these elements provide strong granite signatures in the stream sediments. There is approximately a two-fold increase in **U** and **Th** concentrations in samples close to or overlying the granites, with respect to the median values for the area. In contrast to **Th** and the REEs, concentrations of **U** in sediments from the Kit Hill/Gunnislake area are generally low.

Positive correlations are also found between the REEs and **bismuth (Bi)**, **bromine (Br)** and **caesium (Cs)**. These relationships are most likely attributed to elevated concentrations of the elements around the granite intrusions and the heavily-mined region in the south of the catchment. A very strong distinction is apparent in the distribution for **Br**, dividing the sand-rich formations in the north of the area and the argillaceous, mineralised lithologies towards the south of the catchment. Concentrations of **Br** are above the 75th percentile (15 mg/kg) in the mineralised region, while low values are restricted to the Bude and Crackington Formations. This feature is not reflected in the REE distributions, where low concentrations occur in the mineralised region, between the granites, however, a distinction between sand and clay-rich lithologies is observed in the distribution of **Y**.

7.5.4 Other major and trace elements

The major elements **silicon** (expressed as $\mathbf{SiO_2}$) and **sodium** (expressed as $\mathbf{Na_2O}$), and the trace elements **hafnium (Hf)** and **zirconium (Zr)** form a distinctive group of elements, which have stronger affinities to the sand-rich lithologies of the Tamar Catchment. Silica ($\mathbf{SiO_2}$) constitutes the mineral quartz and increasing concentrations are therefore likely to reflect an increase in the sand content of the parent material. There is a strong geological control on the $\mathbf{SiO_2}$ content in stream sediments, evident in the banded changes in distribution from north to south. The lowest concentrations occur over the largely Devonian deposits in the far south of the catchment and around the two granite intrusions, on Dartmoor and Bodmin Moor, where sediments largely comprise less than 53% $\mathbf{SiO_2}$. Sediments overlying the Bude Formation, to the north, contain the highest proportion of $\mathbf{SiO_2}$ in the catchment, up to around 70%.

The geological influence on the distribution of $\mathbf{Na_2O}$ appears to be less significant than for $\mathbf{SiO_2}$, however, the lowest concentrations (<0.4%) generally occur to the south of the Crackington Formation. The highest concentrations occur in isolated regions in the southern half of the catchment, which include the two granite intrusions to the east and west.

The geochemical association of **Hf** and **Zr** in minerals such as zircon and baddeleyite is reflected by a strong correlation (r=0.91). These elements are again more enriched in sediments towards the north of the map, particularly over the Bude Formation, corresponding well with the distribution of $\mathbf{SiO_2}$ in this area. Unlike $\mathbf{SiO_2}$, **Hf** and **Zr** have significant granite signatures in the sediments, particularly in the Dartmoor area, where **Hf** exceeds 13 mg/kg and **Zr** concentrations exceed 500 mg/kg.

The highest concentrations of **strontium (Sr)** (>100 mg/kg) occur in a band across the argillaceous deposits, south of the Crackington Formation and in an area close to the northern margin of the Crackington Formation. Elevated levels are also found to the far south of the catchment. The lower concentrations (<60 mg/kg) are located to the far north, over the Bude Formation, to the far east and western margins of the area and over the most intensely-mined area around the Devon Great Consols mine in the south of the catchment.

Although **iron** ($\mathbf{Fe_2O_3}$) and **manganese (MnO)** do not have a strong positive correlation (r=0.29), these elements demonstrate common relationships with the trace elements **Co** and **Ni** (r>0.5). This may be related to very similar distributions of $\mathbf{Fe_2O_3}$ and **MnO** in the southern part of the catchment, where levels are generally within the higher range of the distributions. Concentrations of $\mathbf{Fe_2O_3}$ are lowest in sediments overlying the Bude Formation (generally <6%), while the lowest concentrations of **MnO** (below 0.1%) are largely associated with regions of the Crackington Formation. Low concentrations of $\mathbf{Fe_2O_3}$ are also associated with the granite intrusions. Although **MnO** concentrations decline slightly over the Bodmin Moor granite, the relationship is of relatively low significance.

The correlation between **cobalt (Co)** and **nickel (Ni)** is r=0.68; **Ni** also has significant positive relationships with **Cr** and **V**. The distributions of these elements are similar, with the lowest values overlying the Bude Formation in the north and the highest concentrations associated with the central region of the catchment, around and between the granite intrusions. **Nickel** levels are low over the granites, while a small area of low **Co** concentration is only apparent over the Bodmin Moor granite. Both Co and Ni are significantly more concentrated in the stream sediments than they are in the soils (section 8).

Positive correlations are found between **selenium (Se)**, **molybdenum (Mo)** and **thorium (Th)**. These elements are consistently elevated throughout the central belt of the catchment, particularly along the boundary between the Crackington Formation and the mineralised region of complex stratigraphy. Very low concentrations of **Se** (<0.2 mg/kg) occur over the Bodmin Moor granite.

7.6 MINING / MINERALISATION

Arsenic (As), **copper (Cu)**, **lead (Pb)**, **tantalum (Ta)**, **tin (Sn)**, **tungsten (W)** and **zinc (Zn)** are characterised by significantly elevated concentrations in the most intensely-mined area of the Tamar catchment, particularly around the Devon Great Consols mine. Concentrations of **As**, **Cu**, **Ta**, **W** and **Zn** are higher in the sediments than in the soils within this area, while concentrations elsewhere are relatively similar. At the 99th percentile **W** and **Zn** levels are four times higher in the sediments (142 mg/kg and 915 mg/kg, respectively). This suggests that a significant volume of mining/smelter contamination is entering the stream network (section 1.2.5). **Lead** is however present in lower concentrations in the stream sediments in this area, which suggests that this element is retained more strongly in the soil environment. The low solubility of **Pb** and the binding of **Pb** to organic matter inhibit its migration to surface and groundwater.

Over the remainder of the catchment, significant geological controls are apparent for most of these elements, with the lowest concentrations generally occurring over the Bude Formation, in the north of the area. Higher levels of **As**, **Cu**, **Pb**, **Sn** and **Zn** define the mineralised zone in the southern half of the catchment. Concentrations are also elevated around the two granite intrusions, and are above the 95th percentile for **As**, **Sn**, **Ta** and **W**. The strongest relationships observed between the mining-related elements are **As-Cu-Ta** (with correlations of r>0.9), **Pb-Zn** (r=0.79), **As-W** (r=0.86) and **Sn-W** (r=0.75).

7.7 LIMING AND FERTILISER APPLICATION

There is a close correlation (r=0.62) between **phosphorus** (expressed as **P_2O_5**) and **calcium** (expressed as **CaO**) which may in part reflect the erosion of soil from fields in which both agricultural lime ($CaCO_3$) and phosphorus fertilisers have been applied. However, it also reflects the natural association of Ca and P in the mineral apatite, present both in soils, and at elevated levels in stream sediment resulting from erosion and precipitation. These elements are generally present at higher concentrations in the southern half of the catchment, to the south of the Crackington Formation. Many of the highest concentrations of P in stream sediment (>0.5 % **P_2O_5**) may reflect point-sources of pollution, such as sewage treatment works or historical mining contamination.

8 Interpretation of topsoil geochemistry

8.1 SYNOPSIS OF TOPSOIL GEOCHEMISTRY

Topsoil geochemistry largely reflects the chemistry of the underlying parent material (bedrock geology or any superficial deposit) at a sampling site. Topographic influences can be significant in determining the degree of infiltration or waterlogging of the soil profile at a site, determining the magnitude of leaching of soluble elements from the soil profile. Historical land use can also have a significant impact on soil geochemistry, particularly if significant loads of mine waste or agricultural dressings (lime and fertiliser) have been applied.

In general, the soil geochemical data could be used to assess the suitability of land to be used for the application of sewage sludge with respect to permissible guideline values. However, the following three specific issues related to soil quality are of potential significance in the Tamar catchment:

8.1.1 Soil Guideline Value for arsenic (As) exceedance

Approximately 60% of the sites throughout the catchment had total soil **As** values above the recently published Soil Guideline Value for residential land use of 20 mg kg^{-1} (Department of the Environment Food and Rural Affairs and the Environment Agency, 2002). The highest values were in the south of the catchment in areas of intense former mining activity. This does not imply that soil in these areas pose a significant risk to human health, but that the first stage of the UK government's tiered approach to risk assessment has been passed, indicating that further assessments would be needed to determine whether there is the possibility of significant harm.

8.1.2 Agricultural cobalt (Co) and molybdenum (Mo) deficiency

Around 20% of the land in the catchment (generally soils derived from the Bude and Crackington Formations to the north) have **Co** concentrations below 5 mg/kg. It has been suggested that soils with total **Co** concentrations below this level may lead to **Co** deficiency in ruminant animals which graze grassland in these areas (Scottish Agricultural Colleges, 1992). However, the relationship between available and total **Co** is not simple, therefore further extraction tests would be required to determine whether the soil is likely to lead to deficiencies in grazing animals. Soils in parts of the north and south of the catchment have particularly low **Mo** concentrations (<0.35mg/kg), which in soils of pH values of 5.5 and below, as these are, may pose problems of **Mo** deficiency for certain crops (Williams, 1971). Further tests would be needed to determine the available **Mo** contents of these soils to establish whether **Mo** deficiency is likely.

8.1.3 Elevated levels of available 'Olsen' soil phosphorus

Around one third of the soils had 'excessive' **available P** contents for sites under grassland, which accounts for approximately two-thirds of land use across the catchment. Such elevated concentrations may result in greater losses of P to watercourses and problems associated with eutrophication.

8.2 PRESENTATION OF TOPSOIL GEOCHEMISTRY

Images showing the variation in the total concentration of each element determined are provided in Appendix C.

8.3 SUMMARY STATISTICS

Table 9 – Summary statistics for total soil element concentrations and other soil parameters (n=468).

Units are mg/kg unless otherwise stated.

Element / Parameter	Min	Max	Median	Mean	Std. Dev.	Skew	Detection Limit (mg/kg)	Lower Reporting Limit (%)	* Median E&W mg/kg
Ag	0.3	7.1	0.3	0.3	0.4	14.8	0.5		
Al2O3 (%)	6.2	22.5	16.4	16.3	2.4	-0.5			
As	6.8	15000	22.5	79.1	689	21.3	0.9		
Ba	132	856	433	441	97.6	0.6	2.9		121
Bi	0.2	43.5	0.5	0.8	2.3	14.1	0.3		
Br	6.8	184	25.4	27.2	15.0	3.8	3		
CaO (%)	0.0	5.6	0.4	0.4	0.3	8.6		0.05	
Cd	0.3	2.2	0.3	0.3	0.2	6.4	0.5		
Ce	23.0	255	77.5	77.6	15.2	5.2	3.2		
Co	-0.6	88.9	8.9	11.6	10.4	3.0			9.8
Cr	24.0	433	112	119	37.8	3.6			39.3
Cu	2.4	2655	29.8	45.3	130	17.5	0.9		18.1
Fe2O3 (%)	0.8	23.0	6.3	6.3	2.1	1.4		0.01	
Ga	5.8	27.2	17.5	17.8	3.5	0.2	0.3		
Ge	0.1	6.8	1.5	1.5	0.5	3.1	1		
Hf	1.1	15.2	5.8	5.9	1.4	0.7	1		
I	2.0	90.0	10.0	11.2	7.5	2.9			
K2O (%)	1.2	4.6	2.3	2.4	0.6	0.7		0.05	0.56
La	18.0	154	41.0	41.4	7.7	6.5	1.5		
MgO (%)	0.2	4.8	0.7	0.9	0.6	3.4		0.1	
MnO (%)	0.0	4.3	0.1	0.2	0.3	10.7		0.01	
Mo	0.2	12.0	0.9	1.3	1.3	2.5	0.3		
Na2O (%)	0.1	1.1	0.5	0.5	0.1	0.2		0.1	
Nb	9.5	104	16.5	17.7	5.9	7.8	0.9		
Nd	8.0	219	34.0	34.0	10.0	13.1	2.5		
Ni	1.4	137	19.8	26.2	19.4	2.5	0.9		22.6
Olsen_P	0.0	238	20.5	26.9	23.6	3.5			19
Organic C (%)	2.9	19.4	5.6	5.8	1.8	3.3			3.5
P2O5 (%)	0.1	1.0	0.3	0.3	0.1	1.2		0.05	0.18
Pb	13.8	532	35.5	49.1	47.4	5.6	1.2		40
pH (-log H+)	3.0	6.9	4.8	4.9	0.5	0.4			6
Rb	42.9	332	114	119	37.7	1.4	0.8		
Sb	0.5	24.6	2.3	3.5	3.3	2.5	1		
Sc	5.0	39.0	15.0	15.1	3.4	0.9	1		
Se	0.2	3.8	1.0	1.1	0.6	1.7	0.4		
SiO2 (%)	43.6	85.1	60.7	60.7	6.3	0.4			
Sm	2.0	48.0	7.0	7.0	3.6	3.7	1		
Sn	2.0	610	5.3	14.4	41.5	9.0	1		
Sr	18.8	651	74.6	77.4	33.1	11.3	0.8		27
Ta	0.1	19.8	1.1	1.3	1.2	7.8	0.2		
Th	4.0	49.0	11.0	11.1	2.6	6.3	0.4		
TiO2 (%)	0.3	2.4	1.0	1.0	0.2	2.6		0.01	
Tl	0.1	3.2	0.4	0.5	0.4	1.3	0.2		
U	0.3	7.7	2.8	2.9	1.0	0.9	0.5		
V	25.2	337	143	146	31.6	0.6	2.4		
W	0.1	160	3.2	4.7	10.5	9.4	0.2		
Y	9.7	70.2	26.3	26.2	3.9	3.7	0.8		
Zn	18.2	386	65.3	75.4	46.2	2.4	1		82
Zr	128	575	229	235	48.1	1.0	0.8		

* Median E&W – median element concentration or median value for this parameter reported in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992).

Table 10 - Correlation coefficients (r) between elements determined in topsoil samples (n=468).
Correlations greater than 0.5 in bold.

	pH	%C	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	MnO	Fe2O3	Sc	V	Cr	Co	Cs	Ba	La	Ce	Nd	Sm	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Hf	Ta	W	Tl	Pb	Bi	Th	U	Sn	Sb	I	*Olsen P
PH	**1.00**																																														
%C	-0.38	**1.00**																																														
Na2O	-0.07	-0.08	**1.00**																																													
MgO	0.04	0.15	-0.20	**1.00**																																												
Al2O3	0.10	-0.12	0.03	0.05	**1.00**																																											
SiO2	0.05	-0.34	-0.05	-0.49	-0.63	**1.00**																																										
P2O5	0.19	0.22	-0.23	0.49	0.02	-0.41	**1.00**																																									
K2O	0.06	0.09	-0.12	0.10	**0.71**	-0.56	0.24	**1.00**																																								
CaO	**0.51**	0.07	-0.02	0.27	-0.03	-0.22	0.44	0.04	**1.00**																																							
TiO2	0.00	0.08	-0.01	**0.68**	0.13	-0.46	0.25	-0.09	0.16	**1.00**																																						
MnO	0.01	0.01	-0.10	0.19	-0.01	-0.22	0.30	0.10	0.06	0.06	**1.00**																																					
Fe2O3	0.11	-0.02	-0.15	**0.52**	0.38	-0.69	0.37	0.37	0.18	0.49	0.31	**1.00**																																				
Sc	0.08	0.14	-0.17	**0.67**	**0.53**	-0.73	0.45	0.43	0.24	**0.65**	0.21	**0.72**	**1.00**																																			
V	0.10	0.09	-0.21	**0.53**	0.36	-0.50	0.43	0.23	0.19	**0.59**	0.23	**0.61**	**0.80**	**1.00**																																		
Cr	0.05	0.11	-0.14	**0.85**	0.19	-0.52	0.42	0.09	0.22	**0.73**	0.16	**0.56**	**0.73**	**0.69**	**1.00**																																	
Co	0.02	0.04	-0.04	**0.53**	0.10	-0.49	0.34	0.11	0.16	0.43	**0.60**	**0.66**	**0.53**	0.39	0.49	**1.00**																																
Cs	-0.09	0.23	-0.01	-0.03	0.29	-0.31	0.00	0.43	0.12	-0.07	-0.02	0.10	0.13	0.02	-0.04	0.06	**1.00**																															
Ba	0.10	-0.12	-0.20	0.01	**0.55**	-0.33	0.21	**0.51**	-0.01	-0.21	0.37	0.30	0.32	0.27	0.01	0.24	0.05	**1.00**																														
La	-0.01	0.22	0.01	-0.16	0.30	-0.17	-0.04	0.11	-0.14	-0.07	0.01	0.04	0.07	0.08	-0.07	-0.04	0.02	0.26	**1.00**																													
Ce	0.00	0.14	-0.06	-0.18	0.26	-0.15	-0.05	0.12	-0.07	-0.16	0.00	0.08	0.02	0.00	-0.14	-0.01	0.10	0.26	**0.81**	**1.00**																												
Nd	0.02	0.26	-0.03	-0.12	0.13	-0.09	-0.02	0.03	-0.07	-0.11	0.00	0.00	0.01	0.01	-0.10	-0.02	0.00	0.13	**0.87**	**0.78**	**1.00**																											
Sm	0.03	0.19	-0.01	-0.05	-0.03	-0.06	0.07	-0.02	0.01	-0.03	0.02	-0.02	-0.01	-0.04	-0.07	0.03	-0.03	0.04	0.45	0.47	**0.54**	**1.00**																										
Ni	0.07	0.12	-0.16	**0.84**	0.10	-0.52	0.49	0.16	0.21	**0.53**	0.49	**0.63**	**0.67**	**0.54**	**0.77**	**0.77**	0.06	0.23	-0.06	-0.08	-0.06	-0.01	**1.00**																									
Cu	-0.01	-0.01	-0.20	0.10	0.07	-0.18	0.13	0.17	0.14	-0.07	0.07	0.23	0.10	0.04	0.04	0.14	0.17	0.13	-0.04	0.40	0.04	-0.02	0.12	**1.00**																								
Zn	0.10	0.07	-0.16	0.46	0.36	-0.60	**0.60**	0.49	0.28	0.17	0.39	**0.57**	**0.55**	0.33	0.35	**0.56**	0.25	0.41	-0.03	0.05	-0.03	-0.01	**0.59**	0.32	**1.00**																							
Ga	0.07	0.02	-0.11	0.22	**0.85**	-0.69	0.20	**0.83**	0.07	0.16	0.12	**0.54**	**0.63**	0.48	0.28	0.22	0.43	**0.51**	0.20	0.23	0.06	-0.06	0.27	0.22	**0.52**	**1.00**																						
Ge	0.10	-0.04	-0.01	0.01	0.35	-0.26	0.15	0.36	0.11	-0.02	0.05	0.15	0.21	0.10	0.02	0.06	0.22	0.25	0.05	0.02	0.02	0.03	0.07	-0.01	0.39	0.41	**1.00**																					
As	-0.03	-0.01	-0.16	0.04	0.04	-0.12	0.03	0.11	0.11	-0.08	0.00	0.17	0.04	-0.01	-0.01	0.07	0.14	0.05	-0.05	0.42	0.04	-0.04	0.03	**0.94**	0.16	0.16	-0.07	**1.00**																				
Se	0.06	0.21	-0.33	0.09	-0.15	0.04	0.17	0.01	0.02	-0.06	0.18	0.22	0.17	0.37	0.11	0.16	-0.03	0.22	0.18	0.09	0.20	0.12	0.22	-0.05	0.04	0.00	-0.06	-0.08	**1.00**																			
Br	-0.16	**0.65**	-0.23	0.31	-0.10	-0.30	0.22	0.23	0.05	0.17	0.08	0.18	0.24	0.17	0.23	0.13	0.19	-0.15	0.07	0.06	0.17	0.12	0.21	0.11	0.12	0.16	-0.03	0.12	0.25	**1.00**																		
Rb	-0.01	0.07	-0.07	-0.05	**0.60**	-0.46	0.13	**0.90**	0.00	-0.23	0.04	0.23	0.24	0.09	-0.06	-0.01	**0.59**	0.38	0.04	0.08	-0.03	-0.05	0.00	0.20	0.41	**0.77**	0.37	0.13	-0.07	0.23	**1.00**																	
Sr	0.16	-0.14	0.17	0.00	0.33	-0.22	0.10	0.18	0.27	0.03	0.03	0.17	0.18	0.14	0.10	0.07	-0.02	0.23	0.19	0.18	0.09	-0.02	0.08	0.04	0.14	0.24	0.18	0.03	-0.07	-0.15	0.10	**1.00**																
Y	0.17	-0.09	-0.04	-0.21	0.10	0.10	-0.07	-0.10	-0.09	-0.08	0.04	0.00	-0.05	0.02	-0.15	-0.03	-0.18	0.14	**0.71**	**0.71**	**0.72**	0.38	-0.12	0.07	-0.07	0.01	0.01	0.08	0.17	-0.14	-0.20	0.05	**1.00**															
Zr	0.04	-0.29	0.17	-0.18	-0.47	0.47	-0.23	-0.58	-0.09	0.00	-0.21	-0.44	-0.52	-0.53	-0.23	-0.24	-0.27	-0.50	-0.19	-0.17	-0.15	-0.04	-0.30	-0.20	-0.38	-0.61	-0.27	-0.13	-0.34	-0.23	-0.52	-0.14	0.09	**1.00**														
Nb	0.05	0.03	-0.18	**0.51**	-0.11	-0.14	0.24	-0.10	0.11	**0.51**	0.16	0.27	0.27	0.28	0.40	0.30	0.00	-0.20	0.04	0.06	-0.01	-0.03	0.46	0.01	0.19	0.13	0.01	-0.02	0.02	0.13	-0.14	-0.09	0.20	0.20	**1.00**													
Mo	0.05	-0.01	-0.20	-0.11	-0.08	0.17	0.07	0.05	-0.06	-0.19	0.15	0.09	0.02	0.25	-0.04	0.00	-0.03	0.32	0.14	0.09	0.07	-0.01	0.02	0.02	-0.05	0.02	-0.07	-0.02	**0.59**	0.02	0.06	-0.01	0.15	-0.29	-0.08	**1.00**												
Hf	0.05	-0.29	0.12	-0.18	-0.33	0.33	-0.16	-0.43	-0.02	-0.02	-0.19	-0.32	-0.42	-0.42	-0.20	-0.22	-0.16	-0.39	-0.16	-0.07	-0.13	-0.04	-0.28	0.02	-0.25	-0.42	-0.20	0.06	-0.33	-0.20	-0.35	-0.09	0.11	**0.84**	0.19	-0.28	**1.00**											
Ta	-0.05	0.01	-0.23	0.26	0.05	-0.24	0.21	0.18	0.15	0.08	0.07	0.26	0.18	0.11	0.14	0.20	0.25	0.05	-0.10	0.28	-0.04	-0.06	0.24	**0.80**	0.36	0.28	0.05	**0.72**	-0.06	0.14	0.24	-0.04	0.02	-0.14	0.33	-0.07	0.09	**1.00**										
W	-0.06	0.05	-0.17	0.02	0.13	-0.15	0.09	0.24	0.06	-0.13	0.00	0.02	0.00	-0.10	-0.05	-0.02	0.31	0.08	-0.09	0.05	-0.06	-0.02	-0.01	0.32	0.31	0.20	0.08	0.24	-0.20	0.08	0.37	-0.03	-0.16	-0.08	-0.05	-0.03	0.01	0.28	**1.00**									
Tl	0.05	0.22	-0.05	-0.01	0.23	-0.13	0.08	0.32	0.08	-0.14	0.00	0.08	0.12	0.05	-0.04	0.05	0.26	0.25	0.11	0.09	0.11	0.01	0.07	0.00	0.24	0.25	0.19	-0.02	0.24	0.14	0.29	0.02	0.03	-0.29	-0.11	0.22	-0.28	-0.10	0.09	**1.00**								
Pb	0.05	0.04	-0.11	0.16	0.20	-0.26	0.34	0.36	0.15	-0.07	0.14	0.23	0.23	0.11	0.09	0.21	0.20	0.36	0.03	0.14	0.03	0.01	0.24	0.29	**0.66**	0.36	**0.52**	0.19	0.05	0.06	0.33	0.10	0.03	-0.28	0.06	-0.02	-0.15	0.28	0.19	0.29	**1.00**							
Bi	-0.03	-0.01	-0.10	0.00	0.13	-0.13	0.03	0.22	0.01	-0.05	0.00	0.03	0.06	-0.01	-0.01	0.00	0.37	0.06	-0.05	0.00	-0.05	0.04	0.01	0.19	0.17	0.25	0.12	0.10	-0.11	0.05	0.38	-0.05	-0.14	-0.09	0.02	0.19	-0.03	0.22	0.36	0.08	0.09	**1.00**						
Th	0.02	-0.10	-0.05	-0.17	0.44	-0.29	0.01	**0.54**	0.01	-0.28	-0.01	0.21	0.08	-0.01	-0.16	-0.04	0.33	0.31	0.14	0.47	0.08	-0.07	-0.10	**0.68**	0.26	**0.57**	0.19	**0.69**	-0.12	0.04	**0.61**	0.14	0.12	-0.29	-0.04	0.00	-0.06	**0.61**	0.26	0.04	0.30	0.17	**1.00**					
U	-0.01	0.10	-0.10	-0.19	0.02	0.08	0.11	0.25	-0.05	-0.33	0.08	-0.13	-0.07	0.07	-0.19	-0.14	0.22	0.21	0.19	0.11	0.14	0.03	-0.11	-0.04	0.01	0.15	0.07	-0.12	0.42	0.05	0.34	-0.04	0.09	-0.26	-0.02	0.46	-0.17	0.09	0.02	0.06	0.03	0.13	0.24	**1.00**				
SN	-0.04	0.04	-0.22	0.08	0.13	-0.24	0.18	0.29	0.19	-0.13	0.02	0.16	0.07	-0.05	-0.01	0.07	0.36	0.13	-0.12	0.25	-0.05	-0.03	0.07	**0.79**	0.45	0.29	0.13	**0.72**	-0.17	0.14	0.41	0.02	-0.11	-0.18	-0.03	-0.05	0.02	**0.67**	**0.72**	0.08	0.37	0.36	**0.59**	0.01	**1.00**			
SB	0.08	-0.06	-0.14	0.07	0.02	0.02	0.18	0.23	0.06	-0.11	0.37	0.21	0.16	0.25	0.11	0.22	0.13	0.31	0.02	0.15	0.02	-0.02	0.27	0.35	0.25	0.21	0.11	0.31	0.36	0.05	0.16	0.05	0.10	-0.35	0.06	0.38	-0.27	0.26	0.02	0.14	0.35	0.02	0.28	0.25	0.21	**1.00**		
I	0.02	0.40	-0.30	0.46	0.06	-0.45	0.44	0.29	0.12	0.28	0.26	0.40	0.46	0.35	0.39	0.38	0.07	0.09	0.24	0.14	0.33	0.26	0.44	0.02	0.37	0.28	0.13	-0.04	0.32	**0.73**	0.21	-0.06	0.07	-0.26	0.24	-0.02	-0.20	0.11	0.01	0.05	0.24	0.00	-0.02	0.07	0.04	0.12	**1.00**	
Olsen_P	0.23	-0.04	-0.21	0.13	0.05	-0.12	**0.68**	0.21	0.34	-0.09	0.11	0.13	0.14	0.11	0.09	0.09	0.03	0.21	-0.12	0.04	-0.08	-0.03	0.15	0.37	**0.51**	0.15	0.22	0.28	-0.01	0.00	0.17	0.08	-0.02	-0.16	-0.02	0.01	-0.05	0.31	0.15	0.14	0.40	0.06	0.25	0.05	0.38	0.18	0.08	**1.00**

*Olsen P refers to ‘available’ (Olsen) phosphorus

8.4 GROUPING OF VARIABLES BY CLUSTER ANALYSIS

The cluster analysis highlighted several groupings related to bedrock lithology (mineralogy), land-use/topography and mining-related activities (see Figure 18).

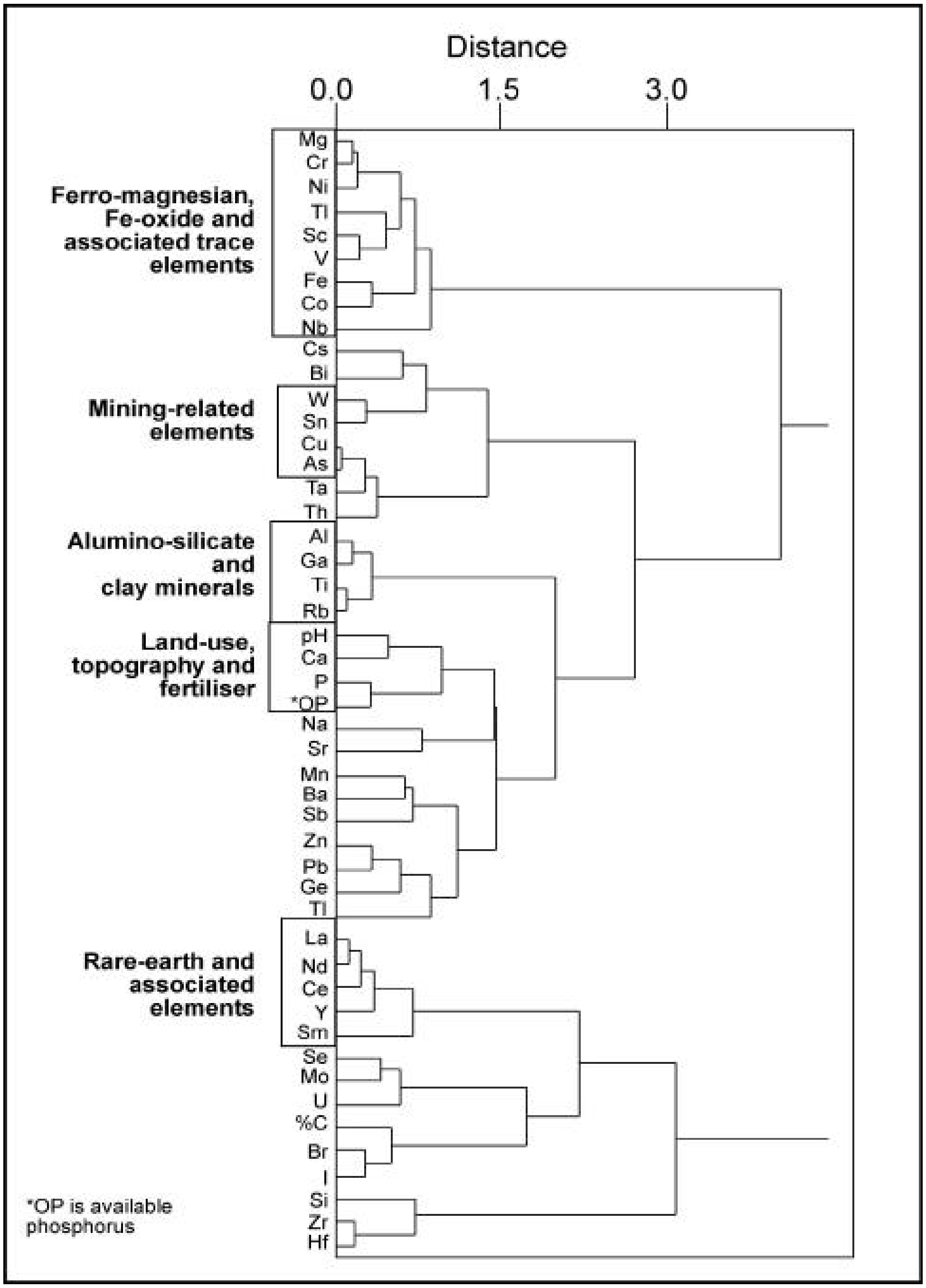

Figure 18 – Dendogram showing the clustering of total soil element concentrations and other soil parameters.

8.5 BEDROCK LITHOLOGY

8.5.1 Alumino-silicate and clay minerals

Silicon (Si) occurs in all silicates including quartz, feldspar minerals and clay minerals, typically comprising the vast majority of soil minerals. Where **Si** is abundant (and aluminium contents are lower on average) soils are of a coarse texture, having a larger proportion of sand. Soils in the southern parts of the Bude and

Crackington Formations have the highest **SiO_2** contents (>65%). Soils associated with the region of complex stratigraphy to the south of the Crackington Formation have higher **SiO_2** contents than soils further south (<54%) which are derived predominantly from Upper Devonian lithologies.

The spatial distribution of **aluminium (Al_2O_3)** and **potassium (K_2O)** is contrary to that of **SiO_2**, higher **Al** contents indicating finer textured soils with a larger proportion of clay minerals. **Potassium (K)** is a component of both **Al**-feldspar minerals and illite (clay), accounting for its close spatial association with **Al**. Both **rubidium (Rb)** which substitutes for **K** in silicates, and **gallium (Ga)** which occurs in feldspars and micas have similar distributions to **K** and **Al**. **Titanium (TiO_2)** tends to be associated with the fine soil fraction, accounting for its spatial distribution being contrary to that of **Si**, which is particularly clear in the region of complex stratigraphy to the south of the Crackington Formation.

8.5.2 Ferromagnesian minerals, Fe-oxides and associated trace elements

Iron (Fe) and **magnesium (Mg)** are associated geochemically as they occur in ferromagnesian minerals including olivine and mica. Their distributions throughout the catchment are relatively similar, with the highest values occurring in soils overlying outcrops of the Lower Carboniferous and Upper Devonian lithologies. The **Fe**-bearing ferromagnesian minerals are unstable in the soil environment, weathering to form **Fe**-oxyhydroxide minerals. A range of trace elements are strongly absorbed to these minerals including **nickel (Ni)** and **chromium** (**Cr)**, which accounts for their similarity with the distribution of **Fe**. There is a ten-fold variation in **Ni** concentrations throughout the catchment, the highest concentrations occurring in soils over the Upper Devonian and Lower Carboniferous Lithologies (>45 mg/kg).

Scandium (Sc), **cobalt (Co) and vanadium (V)** occur in ferromagnesian minerals such as pyroxenes, amphiboles and micas, accounting for the similarity in their distribution to **Fe** and **Mg**. A considerable area of the catchment has **Co** concentrations in topsoil of below 5 mg/kg, particularly those derived from the Bude and Crackington Formations in the north of the catchment – approximately 20% of the catchment area. It has been suggested that soils with total **Co** concentrations below this level may lead to **Co** deficiency in ruminant animals which graze grassland in such areas (Scottish Agricultural Colleges, 1992).

8.5.3 Rare-earth and associated elements

The geochemical association of **yttrium (Y)** with the rare earth elements (REEs) is reflected in the strong correlations that **yttrium** has with **lanthanum (La)**, **cerium (Ce)** and **neodymium (Nd)** (r=0.71, 0.71 and 0.72, respectively). The correlations between **La**, **Ce** and **Nd** are stronger, (r=0.78-0.87); however, the poorest relationships are associated with the REE **samarium (Sm)**. This element is present in significantly lower concentrations than **La**, **Ce**, **Nd** or **Y** across the catchment. Weaker correlations (r=0.38 to 0.54) are therefore unsurprising. The median values of all five elements are fairly consistent with estimated median concentrations for world soils (Reimann and de Caritat, 1998). The most abundant element is **Ce**, with a median of 78 mg/kg (the estimated world average is 65 mg/kg), followed by **La**, **Y**, **Nd** and finally **Sm**, which has a median of just 6.5 mg/kg (the estimated world average is 6.1 mg/kg).

There is a less than two-fold variation between the 5th and the 99th percentile, in the ranges of concentration for all the REEs and **yttrium**. Despite this small variation, geochemical signatures are apparent, with the exception of **Sm**. The lowest concentrations correspond with the granite outcrops and the mineralised zone between them (largely composed of argillaceous rocks and chert). Slightly elevated concentrations occur over the Bude and Crackington Formations (interbedded sandstones and argillaceous rocks) to the north, and the Upper Devonian/Lower Carboniferous argillaceous rocks at the southern extent of the catchment.

8.5.4 Other elements

Manganese oxide (MnO), **barium (Ba)**, **bismuth (Bi)**, **germanium (Ge)** and **thallium (Tl)** form a cluster on the dendogram (Figure 18) with the mining-related elements **Pb**, **W** and **Zn** (section 8.6). The former group is closely related to the clay size-fraction elements (**Al_2O_3**, **K_2O**, **Ga** and **Rb**). The distributions obtained for most of these elements are consistent with this relationship, with lower concentrations in soils derived from the sand-rich lithologies in the northern half of the catchment than those overlying argillaceous lithologies towards the south. Excluding the mining-related elements, the relationship between **Ba** and the clay-related elements is the strongest, with positive correlations (r>0.5) with **Al_2O_3**, **K_2O** and **Ga**.

Barium and **MnO** are the most closely related of the five elements (**MnO**, **Ba**, **Bi**, **Ge**, and **Tl**), with a correlation of 0.37. Topsoils of the Tamar catchment consistently have twice the average **Ba** content than for those in England and Wales (Table 9). **Barium** and **MnO** concentrations are elevated across the mineralised band between the two granite bodies, with relatively even distributions to the north, increasing slightly in soils overlying the Bude Formation in the far north of the area. The elevated levels of **Ba** and **MnO** (>500 mg/kg and >0.2%, respectively) extend to the far south of the catchment, across the most intensely mined region, however, low concentrations (<350 mg/kg) of **Ba** are associated with chert-rich lower Carboniferous rocks within the mineralised area. Lower concentrations of both elements are also associated with the granite intrusions (more significantly in the case of **Ba**).

The range in **Ge** concentrations across the catchment is very low, from 0.8 mg/kg at the 5th percentile, to 2.4 mg/kg at the 99th percentile. The top 1% of the samples in the distribution (the most enriched samples) are clustered towards the far south of catchment, in the area associated with the most intensive mining activities (Kit Hill/Gunnislake area). The remaining elements, **Bi** and **Tl** are again characterised by low ranges in concentration (4.15 mg/kg **Bi** and 1.4 mg/kg **Tl** at the 99th percentile). No significant patterns can be implied for **Tl**, however, the highest concentrations of **Bi** coincide with a band of intense mining around the Devon Great Consols mine. The lowest concentrations of **Bi** (<0.3 mg/kg) are almost entirely limited to the far west and northern parts of the catchment, overlying the Carboniferous sandstone formations. The distribution does not, however, follow any obvious geological boundaries and may not be significant.

Molybdenum (Mo), **selenium (Se) and uranium (U)** are associated geochemically in sandstones, but may also be present at elevated concentrations in fertilizers. Much of the catchment is comprised of sandstone bedrock and has been subject to the application of fertiliser, either of which may account for the similarities in their distributions (correlation coefficients of r=0.4-0.5). In each case, soils derived from the Bude Formation generally have low concentrations of **Mo** (<0.35 mg/kg) **Se** (<0.65 mg/kg) and **U** (<2 mg/kg). Soils in parts of the north and south of the catchment have particularly low **Mo** concentrations (<0.35 mg/kg), which in soils with pH values of 5.5 and below, as these are, may pose problems of **Mo** deficiency for certain crops ((Williams, 1971)). Further tests would be needed to determine the available **Mo** contents of these soils to establish whether **Mo** deficiency is likely. The highest concentrations of **Mo** (71.5 mg/kg) generally occur in the region of mineralisation across the middle of the catchment. Locally high **U** concentrations (75.5 mg/kg) occur over soils derived from a range of bedrock types: granite, the Crackington Formation and Lower Carboniferous deposits. The median **U** soil concentration in the Tamar catchment (2.8 mg/kg) is very similar to that estimated for soils worldwide (2.7 mg/kg; Reimann and Caritat, 1998).

The spatial distributions of **iodine (I)** and **bromine (Br)** are closely related to organic carbon content (%C – see Figure 18). Both are strongly absorbed to **Fe** and **Al** oxyhydroxides and organic matter, and are concentrated in dry and wet atmospheric deposition. This may, in part, account for their higher concentrations closer to the coasts at the north and south of the catchment. The mean **I** concentration (11 mg/kg) is similar to the mean reported for a range of soils in England and Wales (Whitehead, 1979) of 9.2 mg/kg.

The vast majority of the soil samples had **silver (Ag)** and **cadmium (Cd)** concentrations below their analytical detection limits of 0.5 mg/kg. Those samples with concentrations above this level were generally in the south of the catchment close to former mine shafts, suggesting the values may be elevated due to mining contamination.

8.6 MINING AND RELATED ACTIVITIES

Six elements, **arsenic (As)**, **copper (Cu)**, **lead (Pb)**, **tin (Sn)**, **tungsten (W)** and **zinc (Zn)** have been selected as elements which have strong associations with historical mining activities in the Tamar Valley. From this group of elements, three geochemical associations are apparent. **Arsenic** and **Cu** have extremely similar spatial distributions, with the strongest correlation observed for any of the elements (r=0.94). **Lead** and **Zn** also appear to be significantly related in these soils, with a correlation of r=0.66. The correlation between **Sn** and **W** is r=0.72, however, while **Sn** has strong relationships with **As** and **Cu** (r=0.72 and 0.79, respectively), **W** does not demonstrate any other close associations with elements in the topsoils. The observed relationships may be largely attributed to the dominant mineral-bearing phases of these elements in the underlying bedrock. **Copper** and **As** were major commodities of the Tamar Valley and were extracted from loads rich in chalcopyrite ($CuFeS_2$) and arsenopyrite (AsFeS). **Lead** and **Zn** also commonly co-exist in mineral deposits, largely in the form of galena (PbS) and sphalerite (ZnS). **Tin** and **W**, by contrast, are not chalcophilic elements; the main host minerals for **Sn** are cassiterite (SnO_2) and stannite (Cu_2FeSnS_4); while the main hosts for **W** are scheelite ($CaWO_4$) and wolframite ($(Fe,Mn)WO_4$).

The highest concentrations of **As**, **Cu, Sn** and **W** are found in the area around the Devon Great Consols mine, in the southern Tamar Valley. The band of enrichment observed on the images overlies argillaceous rocks of Upper Devonian/Carboniferous age and represents the most intensely mined region of the catchment. This suggests that the very high concentrations in this area are partly related to the nature of bedrock mineralisation, and to an increased volume of disturbed ground, mine waste and pollution derived from smelting activities. **Lead** and **Zn** enrichment continues to the south of the Devon Great Consols mine and **Pb** is significantly more enriched towards the far south of the catchment. This is reflected in the past mining activities; the area was worked for **Pb**, **Zn**, **Ag** and fluorite (CaF_2).

To the north of the mineralised zone, concentrations of **As** and **Cu** are largely below the median values for the catchment, 21.9 mg/kg and 28.7 mg/kg, respectively. These concentrations do not appear to be significantly elevated with respect to typical values for UK soils. The average **Cu** content for soils of England and Wales is 18.1 mg/kg (see Table 9). The average **As** concentration in soils from a large survey of north-east England was 13 mg/kg (British Geological Survey, in preparation). The lowest levels of **As** and **Cu** occur in soils overlying the Bude Formation to the north. Although ‘available’ **Cu** provides a more accurate measure of likely **Cu** deficiency in soil than total **Cu**, it has been suggested that cultivated soils containing less than 2 mg/kg total **Cu** may, over time, give rise to deficiencies in plants (Caldwell, 1971). A number of samples overlying the Bude Formation fall close to this level and the lowest concentrations of the dataset, 2.4 mg/kg and 3.3 mg/kg are associated with the granite intrusions. In the southern part of the map, the range in **As** concentration is very high, increasing to around 300 mg/kg. The soil guideline value (SGV) for residential land use is 20 mg/kg (Department of the Environment Food and Rural Affairs and the Environment Agency, 2002). At the 99th percentile, the concentration of **As** in the Tamar catchment is 307 mg/kg, demonstrating a combination of naturally elevated values (related to mineralisation) and significant levels of mining-related contamination. **Copper** is a less toxic element than **As** and is significantly less enriched in the most contaminated area, with a concentration of 175.2 mg/kg at the 99th percentile.

Lead and **Zn** distributions are generally even to the north of the mineralised zone. The higher concentrations (above the 50th percentile) are again concentrated in the southern part of the area, corresponding with the mineralised region. The average **Pb** concentration in the Tamar soils is 49 mg/kg, somewhat higher than the average value of 40 mg/kg for England and Wales (see Table 9). The average concentration of **Zn** (75 mg/kg) is somewhat lower than the England and Wales average of 82 mg/kg. The soils of the Tamar do not therefore seem to have been significantly affected by sources of **Pb** or **Zn** contamination other than mining related pollution, which is largely restricted to the most southerly part of the catchment. Although the highest **Pb** levels measured do not represent significant levels of contamination (202 mg/kg at the 99th percentile) this element can become more soluble at lower pH values, particularly below pH 5 (Martinez and Motto, 2000). The Tamar soils generally have low pH (pH 5-6) across the whole area. **Lead** uptake to plants may therefore be of concern, especially in the southern half of the catchment.

Soil **Sn** concentrations are also elevated in the southern half of the catchment, across the mineralised zone. In the Kit Hill/Gunnislake area (around the Devon Great Consols mine), concentrations exceed 89 mg/kg. This is nearly a twenty-fold increase with respect to the median concentration of 4.7 mg/kg. **Tin** levels reach around 30 mg/kg over, and in close proximity to, the granite intrusions. Concentrations in the northern half of the catchment are largely between 3 mg/kg and 4 mg/kg, with the lowest values occurring over the Bude Formation. This is consistent with the world average estimate of 4 mg/kg (Reimann and de Caritat, 1998).

North of the Kit Hill/Gunnislake area, the concentrations of **W** generally fall within a narrow range of about 4 mg/kg. The distribution is relatively even and does not demonstrate a strong relationship with the underlying geology. There is, however, one additional area of noticeable enrichment, overlying the edge of the Bodmin Moor granite, although concentrations do not exceed about 8 mg/kg in this area. The estimated world average for **W** in soils is 1.5 mg/kg (Reimann and de Caritat, 1998). Around 75% of the samples in the Tamar catchment contain higher levels of **W**, with a median of 3.2 mg/kg.

8.7 AGRICULTURE / LAND USE / TOPOGRAPHY

There is more than a three-fold variation in **total P** (phosphorus) content in soils throughout the catchment which reflects both the bedrock P content and that applied as fertilizer. There is considerable variation in soils overlying the Bude and Crackington Formations (<0.14% to >0.36%). **Total P** contents are generally higher in the south of the catchment (>0.3%) which is probably due to the higher P content of bedrock. Median **total P** contents are higher in the Tamar catchment (0.29%) than for the rest of England and Wales (0.18% - cf Table 9). The variable with the closest correlation to **total P** is **available P** (r=0.68). The determination of **available P** (using the Olsen method) is widely accepted as an indicator of soil P fertility. There is more than a ten-fold variation in **available P** contents in soils throughout the catchment, reflecting variations in fertilizer P additions, the initial soil content and soil mineralogy. (Different soils have different mineral compositions which will vary the quantity of P ‘fixed’ by the soil and its availability). Table 11 shows the P index of the soils in the catchment based on their available P content. **Available P** should strictly be measured on soils between a depth of 0-7.5 cm; in this study the samples were collected across the depth range 0-15cm, which would tend to underestimate the **available P** at the shallower depth. Despite this, around one third of the soils had ‘excessive’ **available P** contents for grassland, which accounts for approximately two-thirds of land use at the soil sample sites. Land use has a clear influence on **available P** contents, arable sites having higher mean **available P** values (39 mg/kg) than the other land uses (Table 12). Such elevated concentrations may result in greater losses of P to watercourses. Median **available P** in the Tamar catchment (20.5 mg/kg) is similar to that throughout England and Wales (19 mg/kg).

Table 11 – Comparison of available soil P concentrations with published values for the status of grassland*

P index	Olsen-P concentration (mg/kg)	Proportion of Tamar topsoil samples in class (%)	Status (for grassland)
0	0-9	10.7	Deficient
1	10-15	25.6	Low
2	16-25	26.5	Adequate
3	26-45	23.3	Excessive
4+	>46	13.5	Excessive

* after MAFF (2000).

Soil **pH** is dependent on the capacity of the soil to buffer external inputs of, or internally generated, acidity (H^+). Carbonate minerals and the base cations (Mg^{2+} and Ca^{2+}) are effective buffers of acidity, but are often leached from the soil profile by rainfall. Soils in the Tamar catchment generally have naturally low carbonate contents, hence the median **soil pH** of 4.8 is lower than the median valves for the rest of England and Wales (pH 6). The lower **soil pH** values (< 4.5) occur at the highest altitudes on the sides of Bodmin Moor and Dartmoor where the soils have greater organic matter contents, leading to leaching of organic acids. Variations in the carbonate content of bedrock and the application of agricultural lime (calcium carbonate) are the most likely causes of **soil pH** variation throughout the rest of the catchment. Arable soils throughout the catchment have mean **pH** values 0.5 units higher than grassland sites (Table 12). Soils with relatively acid **pH** (<5) are more likely to leach heavy metals (Pb, Cu, Zn) from their profiles than more neutral soils.

Soil **organic carbon** (**C**) contents reflect the variations in land use and topography across the catchment. The highest **organic C** contents occur in upland areas (>400m above sea level) on Dartmoor and Bodmin Moor. Throughout the rest of the catchment, agriculture is most likely the dominant influence on **organic C** content, grazing sites having higher values (4.7 – 4.9%) than arable sites (4.5%).

Table 12 – Mean values of agricultural and land-use related parameters in topsoil.

Land Use	Number of Sites	Land use (%)	Mean soil pH	Mean organic C content (%)	Mean P_2O_5(%)	Mean Olsen P (mg/kg)
Arable	51	10.9	5.4	4.5	0.31	39
Pasture	309	66.0	4.9	5.8	0.31	26
Rough Grazing	81	17.3	4.7	6.3	0.32	25

9 Relating the geochemical data to environmental issues

9.1 REACTIVE PHOSPHORUS IN STREAM WATER (EUTROPHICATION)

The Environment Agency has established reactive phosphorus (RP<0.45) standards for riverine SACs in England and Wales for specific geological and river classifications. The Tamar catchment falls predominantly into class B (see Table 1 below). The *standard* figure is intended to represent the phosphorus concentration that relates to an acceptably low human influence and above which adverse ecological changes are likely. The *threshold* figure indicates the phosphorus concentration above which no further ecological response might be expected (see Table 2).

Table 13 - Environment Agency geological classification for phosphorus standards in riverine SACs.

A. Hard upland geologies (all land over 330m)	Igneous, plus Cambrian to Devonian series and Carboniferous. Low porosity, poor geology with hill farming and v. low population density
B. Other Cambrian – Devonian, and Carboniferous	Hard mudstones, sandstones, limestones. Improved pasture plus some arable, low population density

Table 14 - Phosphorus values assigned to river types (reactive phosphorus, RP(<0.45) mg/l).

Geological class	1. Headwaters	2. River	3. Large river
A			
Natural	Undetectable	20	20
Standard	**20**	**20**	**60**
Threshold	*40*	*60*	*100*
B			
Natural	20	20	30
Standard	**60**	**60**	**100**
Threshold	*100*	*100*	*100*

By comparing data on discharge at the catchment gauging station at Gunnislake for the month of September with historical data, it is clear that flow conditions during sampling were:

- relatively consistent across the sampling period (range 2.7 to 3.9 m^3/s compared to an annual mean flow of around 26 m^3/s), and therefore
- approximate to baseflow conditions.

The small variation in discharge suggests that hydrological conditions were unlikely to have a significant impact on **RP(<0.45)** concentrations *between* sites during the sampling period. The Agency 'standard' for headwater streams is 60 µg **RP(<0.45)** l^{-1}, and the threshold figure is 100 µg **RP(<0.45)** l^{-1} (for a catchment with the geological characteristics of the Tamar). Around 10 % of the headwater streams had **RP(<0.45)** concentrations above the 60 µg P l^{-1} *standard*, whilst 5 % of sites had values exceeding the 100 µg **RP(<0.45)** l^{-1} threshold figure (see Appendix A). The distribution of **RP(<0.45)** in the catchment indicates several significant point sources of phosphorus pollution, particularly in the north and west of the catchment, some of which may warrant further investigation.

Based on a series of assumptions it was possible to estimate the relative importance of the most significant sources of P pollution. In these calculations we assumed that:

1. the ratio of the sub-catchment to total Tamar catchment *area* (pC) is equivalent to the ratio of sub-catchment to the total Tamar catchment *discharge* (pQ*)*
2. the TP(<0.45) and RP(<0.45) load of the stream could be estimated by multiplying the above ratio (pC) by the discharge at the Gunnislake gauging station at the time the stream sample was collected and the concentration of the appropriate P fraction

By undertaking the above calculation for all the first-order and a large proportion of the second-order streams (which had no first order streams that had been sampled within their catchment), it was possible to estimate the **TP(<0.45)** and **RP(<0.45)** loads to the stream system draining 42% of the catchment area.

The outcome of these calculations showed that 5% (or 17) of the 361 streams accounted for 50% of the **RP(<0.45)** load to the catchment system. In addition, that 10% (or 36) of these streams accounted for 50% of the **TP(<0.45)** load to the catchment system. These calculations demonstrate the importance of the concentrated sources of P to the total P load of the Tamar catchment.

9.2 HUMAN HEALTH RISK ASSESSMENT - ARSENIC IN TOPSOIL

Guidance has recently been published by the UK government on the assessment of risks to human health from land contamination, including SGV's (soil guideline values) for a range of inorganic contaminants. The intervention value (SGV) for residential areas and allotments for arsenic (As) is 20 mg kg^{-1} (Department of the Environment Food and Rural Affairs and the Environment Agency, 2002). The tiered risk analysis approach advocated in UK guidance suggests that further site-specific studies should be undertaken when a statistically derived upper mean value at a site exceeds the guideline value for specific land use types. Data on arsenic in topsoil indicates that the SGV is exceeded across much of the catchment area, including residential districts (see Appendix C). This does not imply that soil in these areas pose a significant risk to human health, but that considerable effort may be needed in undertaking risk assessments to determine whether there is the possibility of significant harm.

The SGV's are based on the assumption that 100% of the ingested arsenic is taken up by the human systemic circulation. However, if arsenic is bound to the soil in a non-reactive form which is not available for absorption in the human gut, the actual bioaccessibility, and therefore exposure, may be greatly reduced. Hence, assuming 100% bioavailability may overestimate the risk to human health from soil arsenic. To assess the fraction of arsenic in the soil that is likely to be 'bioaccessible', and hence improve human health risk assessment, extraction tests can be applied to soil samples that mimic the conditions in the human gastro-intestinal tract (Ruby et al., 1996). This test tube (*in vitro*) method mimics the pH and Eh (oxidising/reducing conditions) in the human stomach and small intestine, and the residence times of ingested material. The stomach phase of the test is acidic (pH 2.5), whilst the intestinal phase is neutral (pH 7). The concentration of arsenic in the test solution as a proportion of its concentration in the soil is used to estimate bioaccessibility (as operationally defined by the method).

Studies undertaken by the British Geological Survey and Environment Agency using this test on several soil types throughout the UK have shown that the majority have values of less than 20% As bioaccessibility (Environment Agency, 2003). This has significant implications for the assessment of risk and the area of land in the Tamar catchment which might be considered to pose a threat to human health. Given certain assumptions on exposure, if the soil at a site contains on average 100 mg/kg arsenic, of which only 20% is bioaccessible, one could argue that the exposure would be equivalent to the SGV of 20 mg/kg. Soils with arsenic contents of between 20 and 100 mg/kg could, with the application of a bioaccessibility test, be shown to lead to exposure less than that assumed in the SGV. To illustrate this Figure 19 and Figure 20 show the probability of exceeding these two thresholds (20 and 100 mg/kg, respectively) in soils throughout the Tamar catchment. These interpolated images were prepared using a method called disjunctive kriging (Webster and Oliver, 2001), one of the methods commonly used in geostatistics.

Figure 20 shows that the area in which probabilities of exceeding 100 mg/kg are high comprises a relatively small part of the total catchment. For much of the rest of the area, soil arsenic concentrations are likely to be below 100 mg/kg, and application of bioaccessibility tests are likely to indicate in most cases that exposure to soil arsenic equates to less than that represented by the SGV.

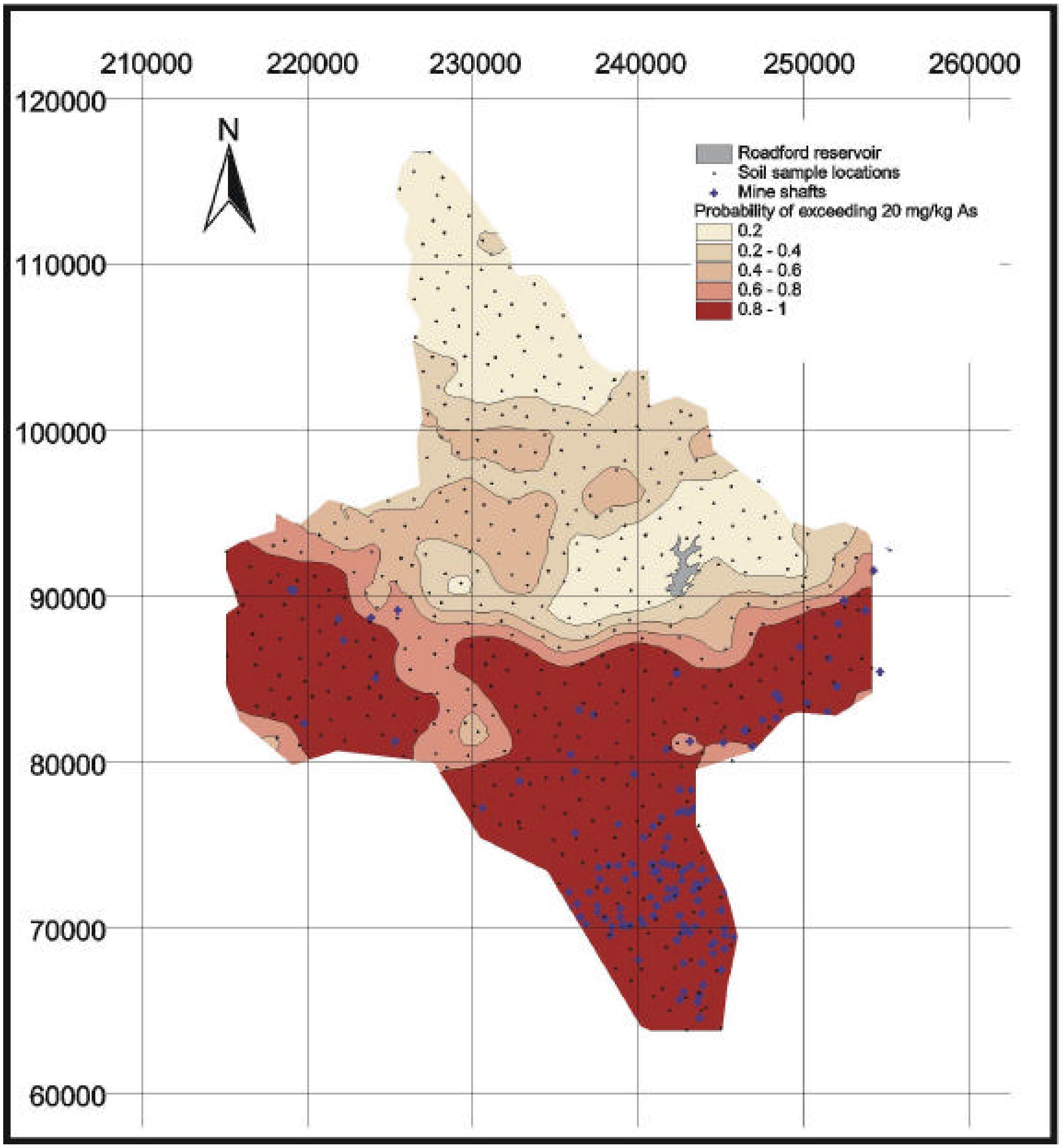

Figure 19 - Probability of exceeding 20 mg/kg Soil Guideline Value for arsenic concentration in topsoil.

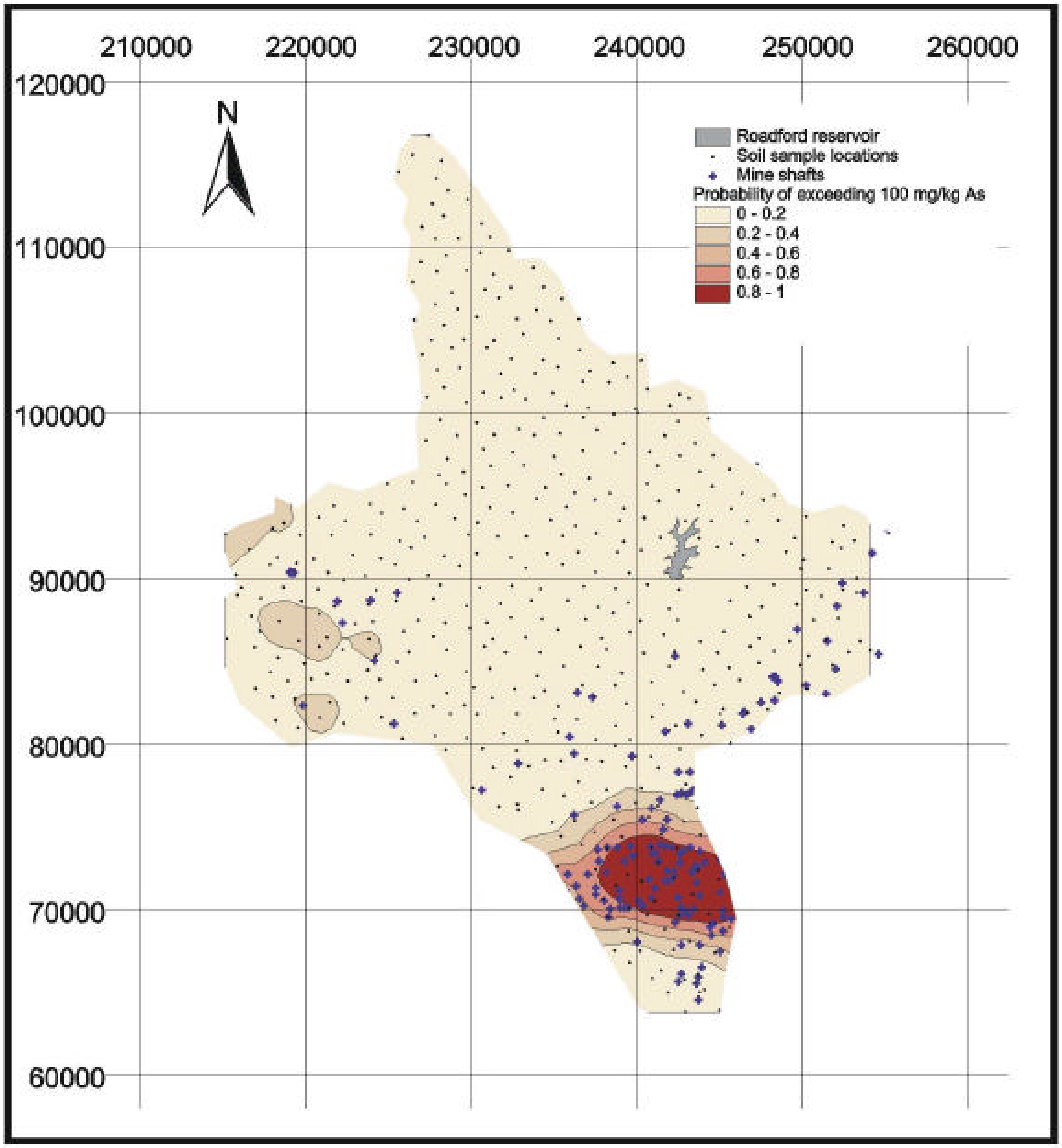

Figure 20 – Probability of exceeding 100 mg/kg total arsenic concentration in topsoil

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Appendix A – Element distributions in stream water of the Tamar catchment (spatial and temporal)

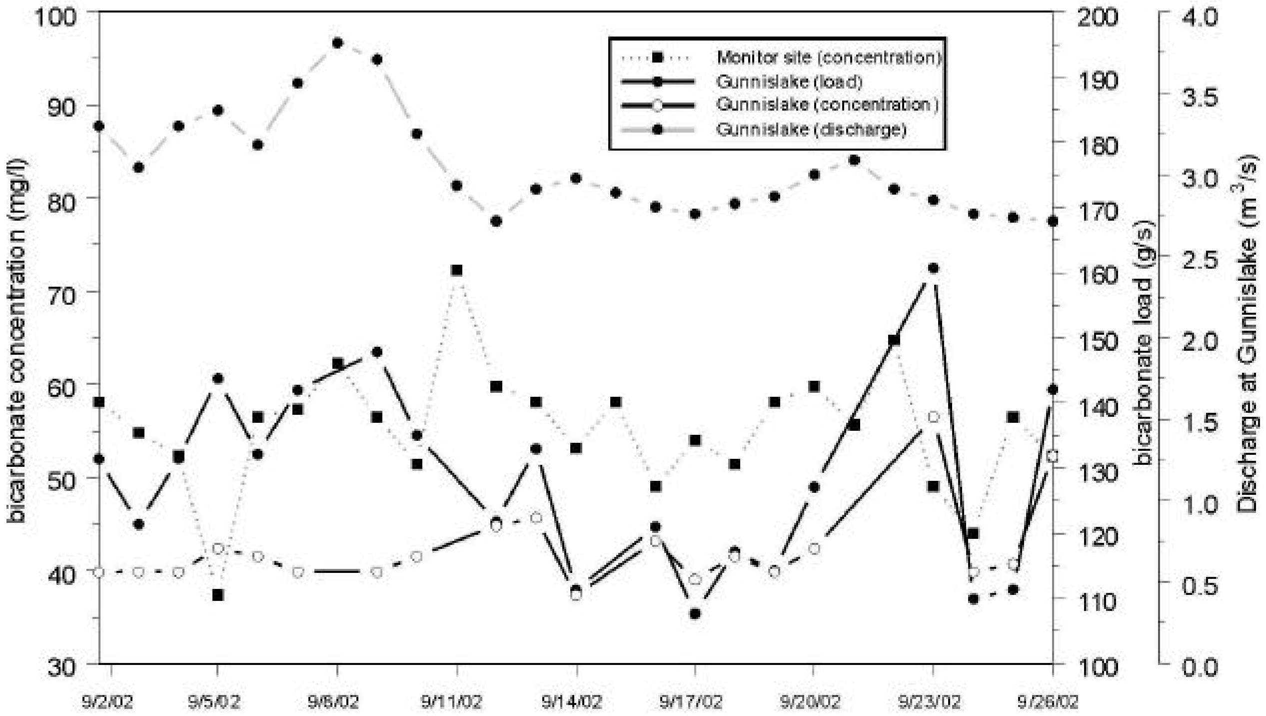
The images presented in this appendix are the outcome of a geochemical survey of the Tamar catchment undertaken in September 2002. The methods adopted in the survey (sampling, analysis and data presentation) are described in the main report entitled 'Geochemical survey of the Tamar catchment (south-west England)'.

Full bibliographic reference:

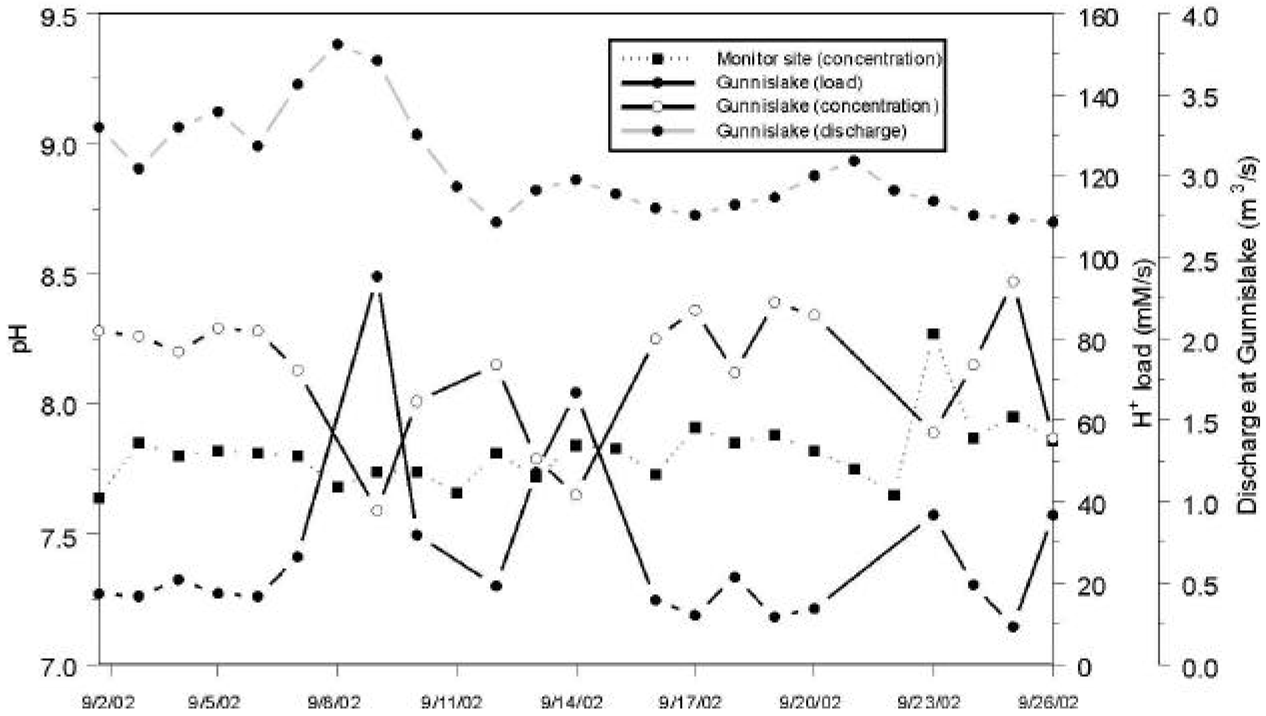
RAWLINS, B. G., O'DONNELL, K. AND INGHAM, M. 2003. Geochemical survey of the Tamar catchment (south-west England). *British Geological Survey Report*, CR/03/027. 232pp.

Part I – Temporal variations in selected stream water chemistry parameters at the Tamar catchment gauging station (Gunnislake) and the monitor site (South Petherwin) throughout September 2002.

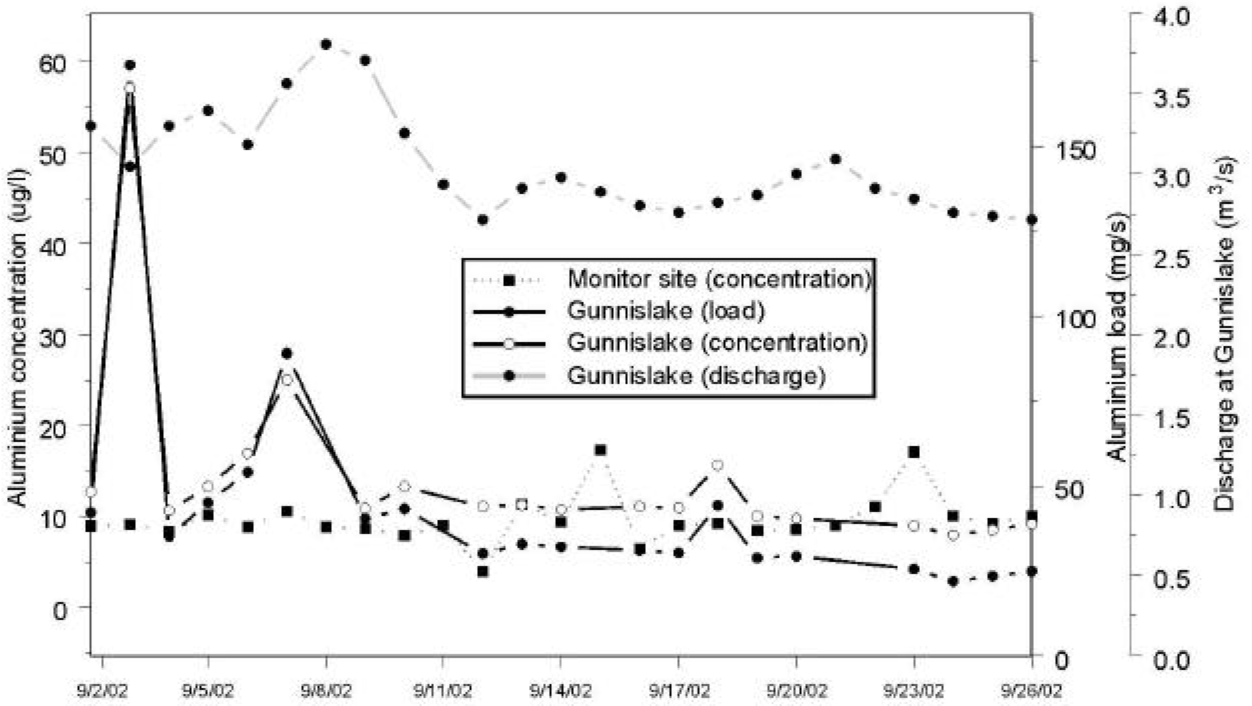
Temporal variations in bicarbonate concentration, load and flow



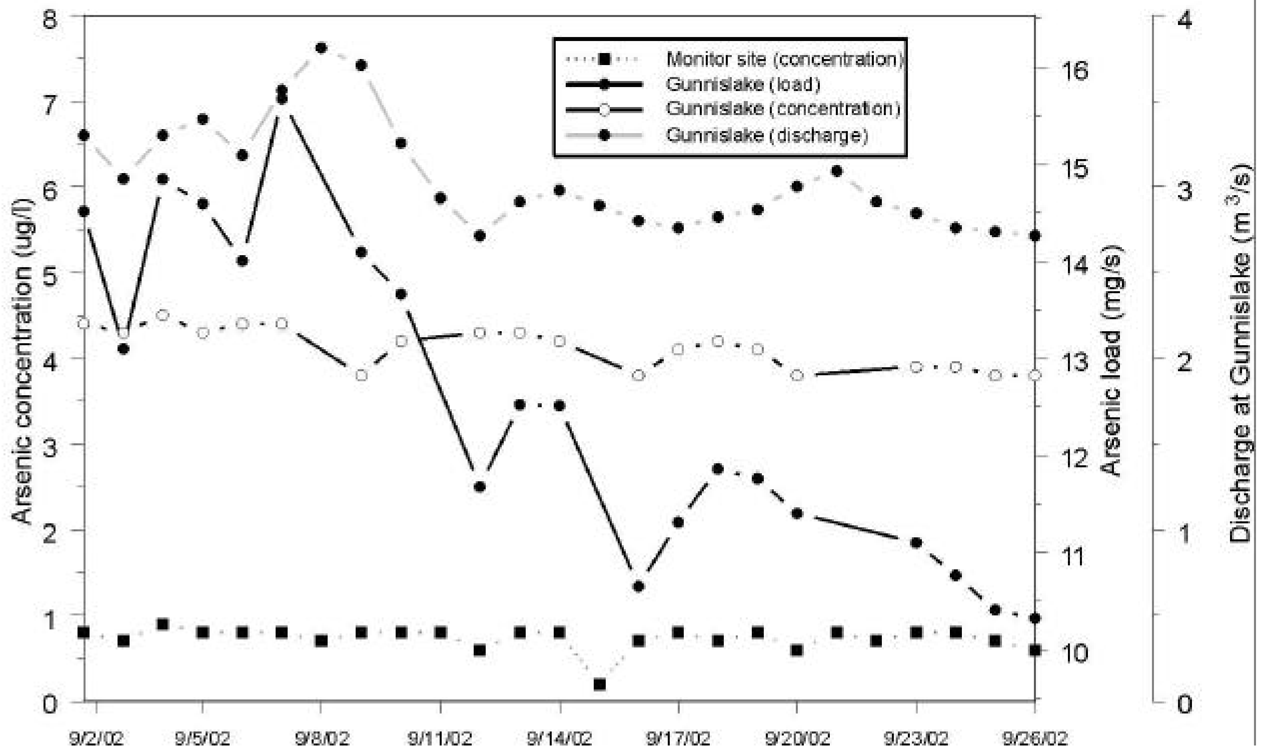
Temporal variations in pH, H$^+$ ion load and flow



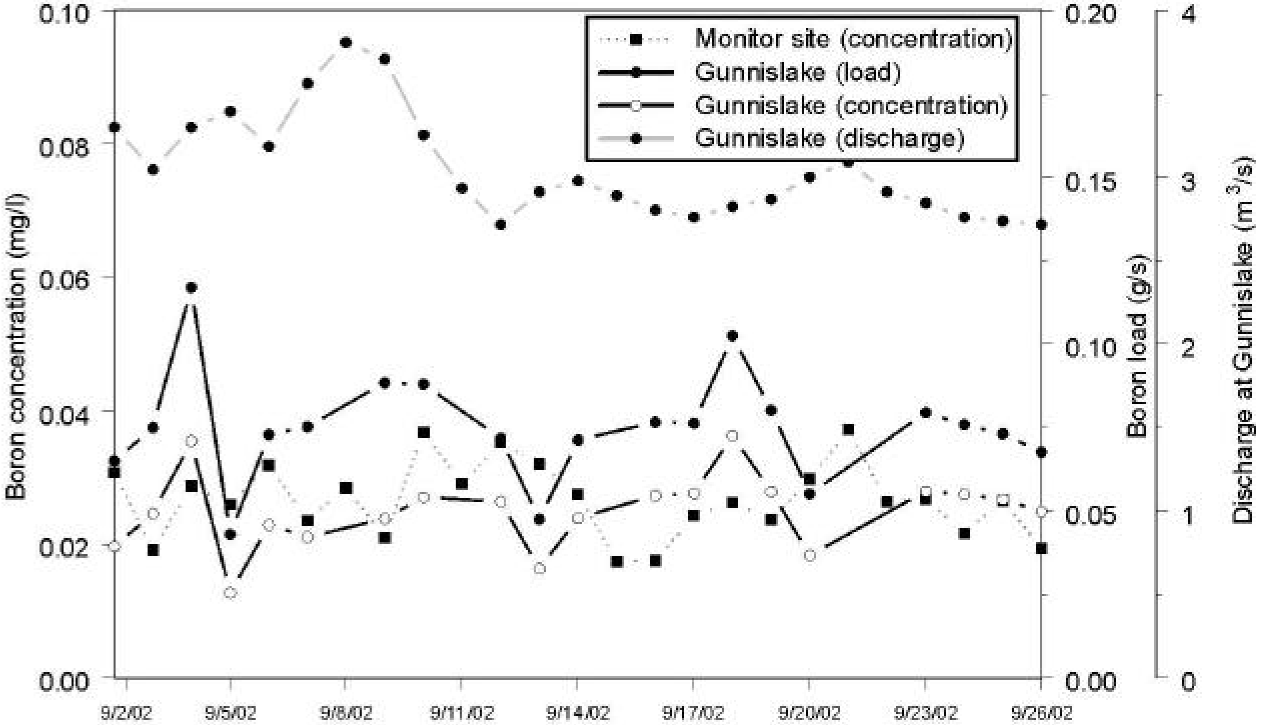
Temporal variations in aluminium (Al) concentrations, load and flow



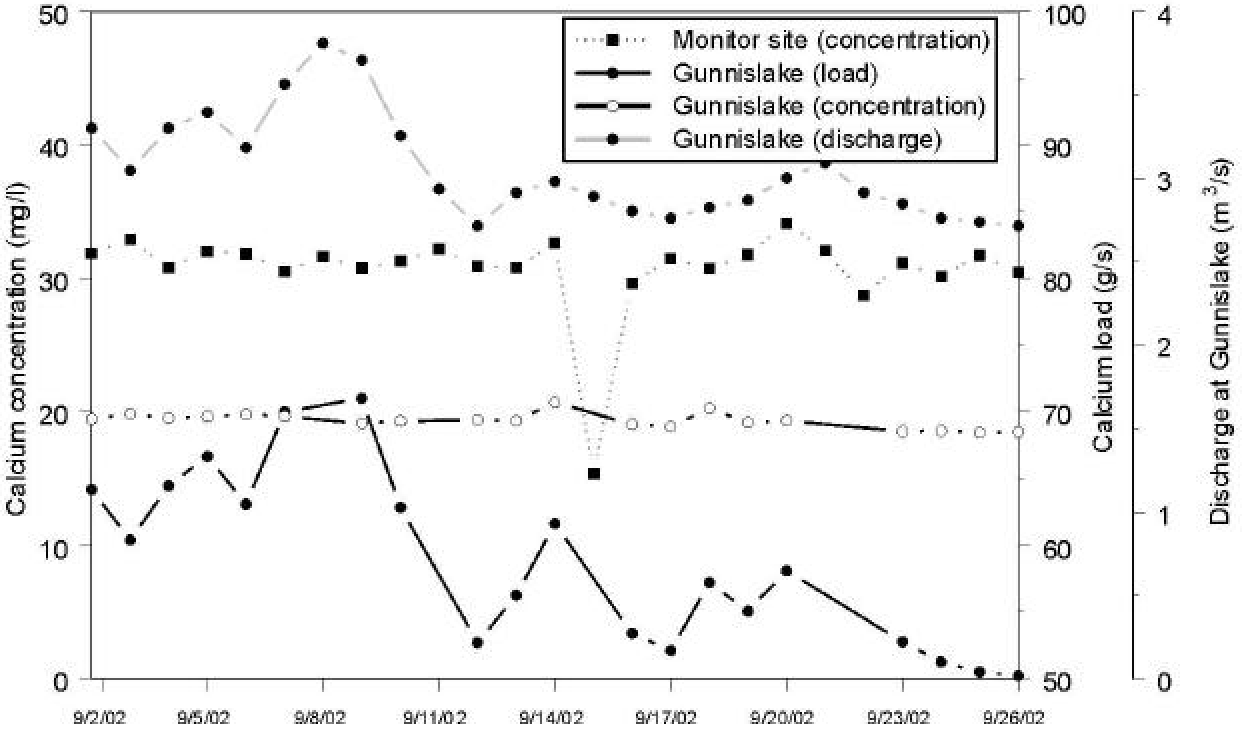
Temporal variations in arsenic (As) concentrations, load and flow



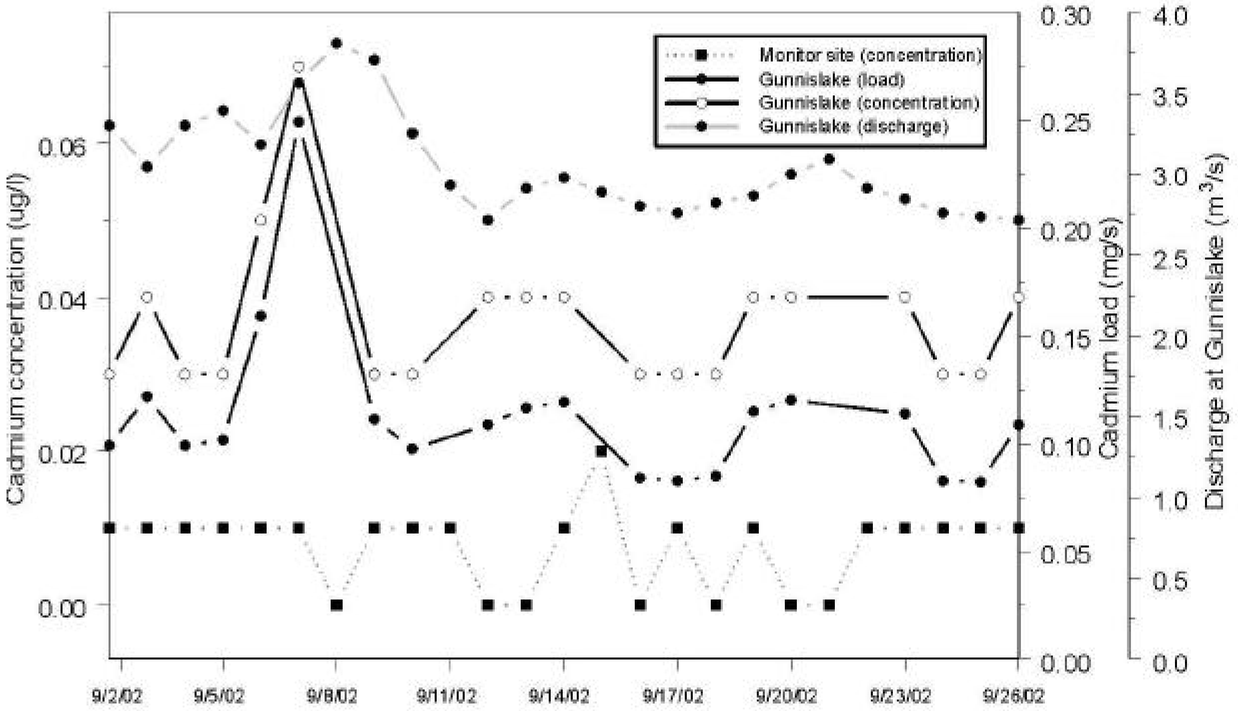
Temporal variations in boron (B) concentrations, load and flow



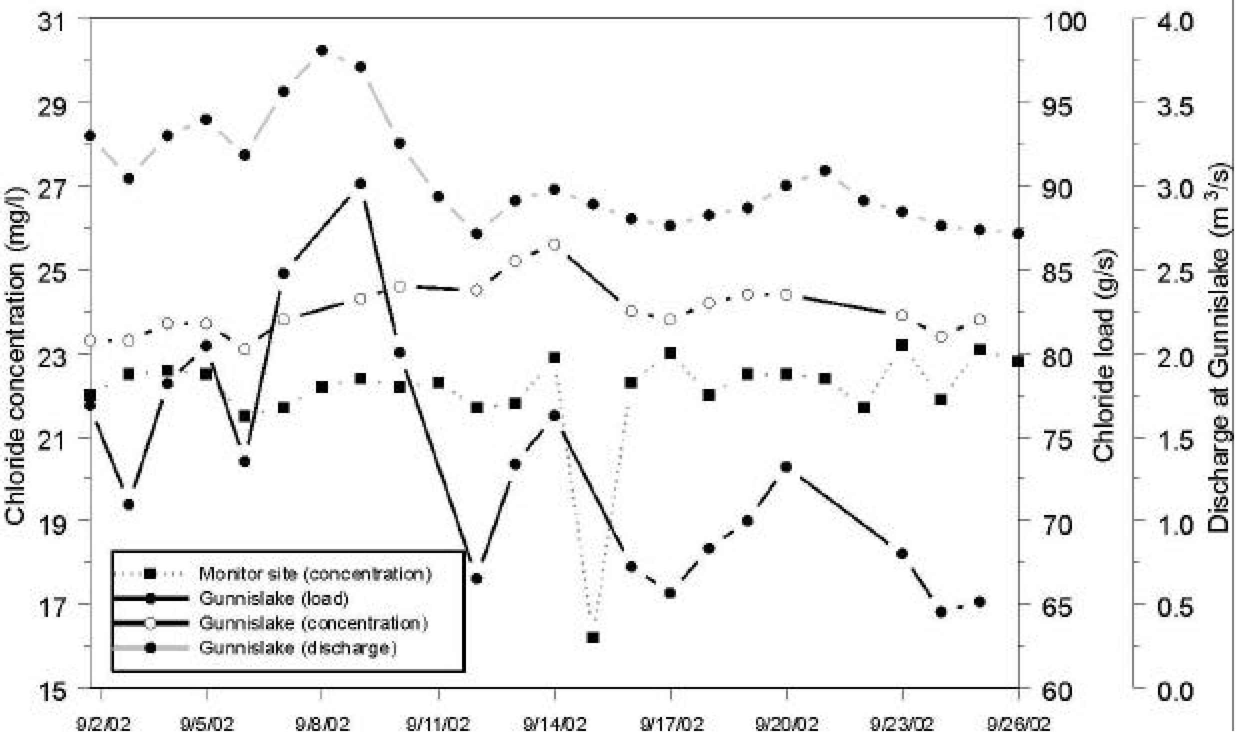
Temporal variations in calcium (Ca) concentrations, load and flow



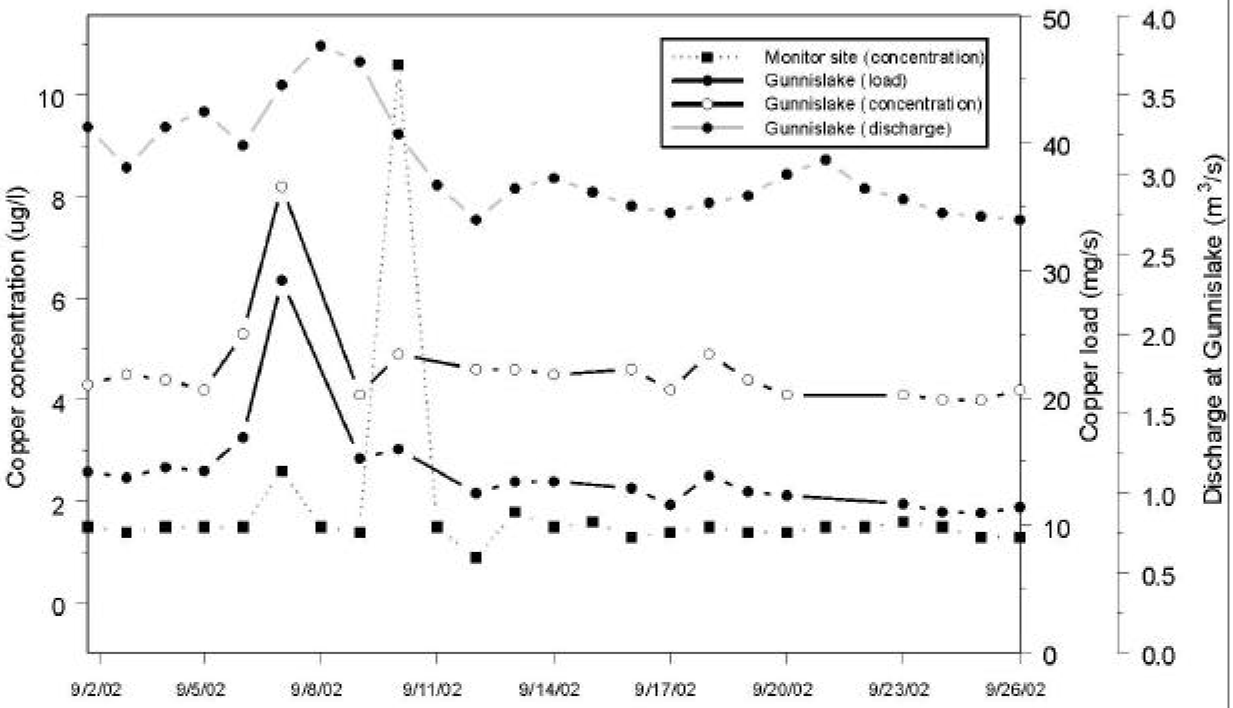
Temporal variations in cadmium (Cd) concentrations, load and flow



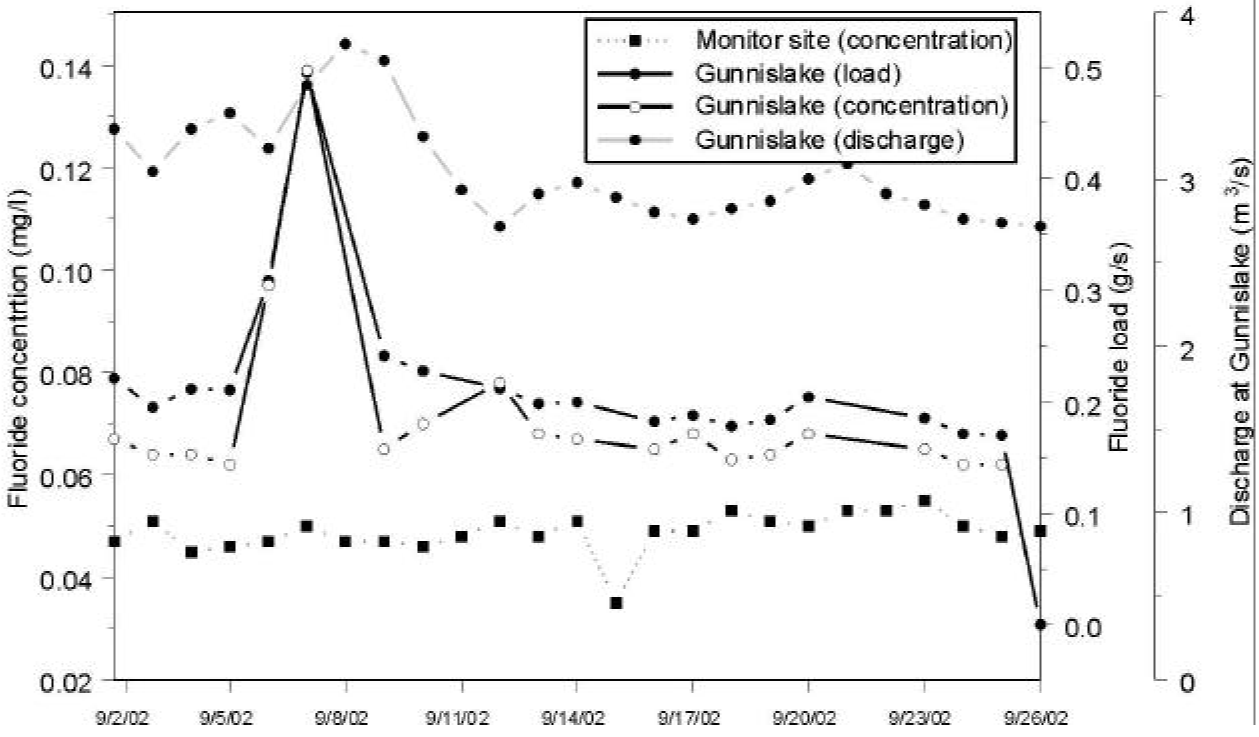
Temporal variations in chloride (Cl^-) concentrations, load and flow



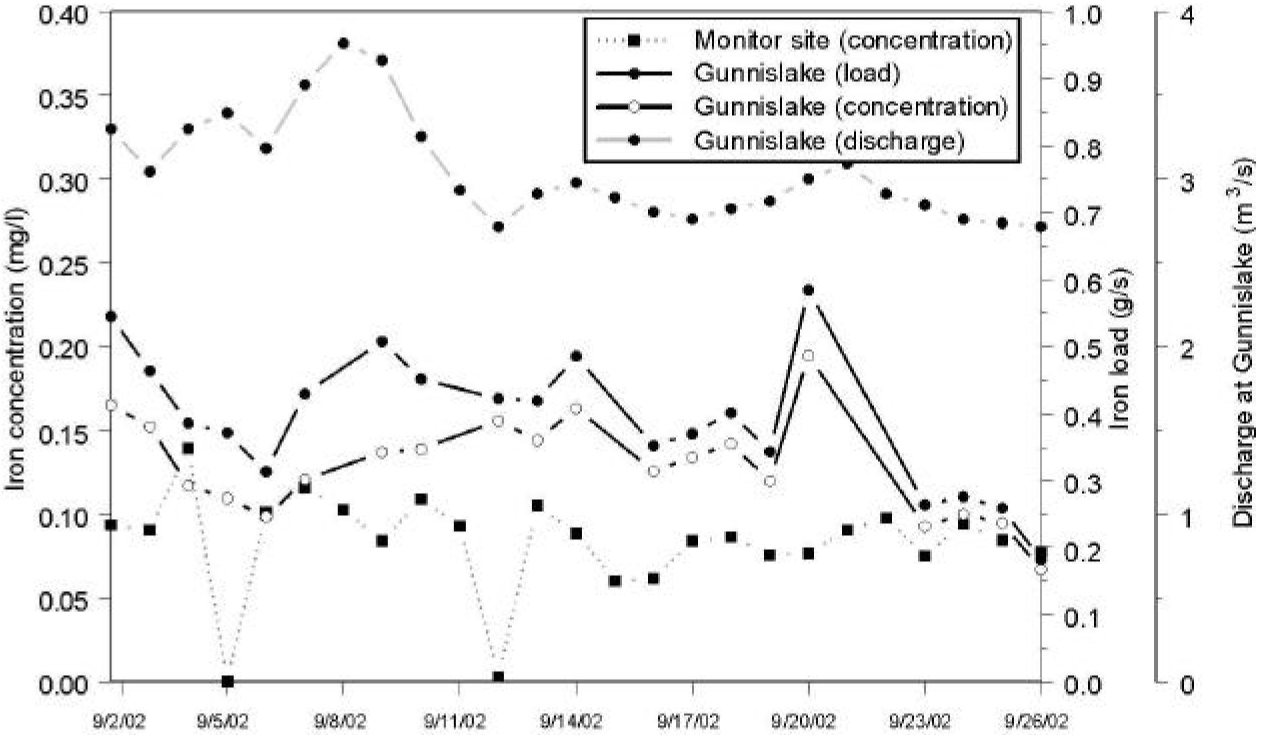
Temporal variations in copper (Cu) concentrations, load and flow



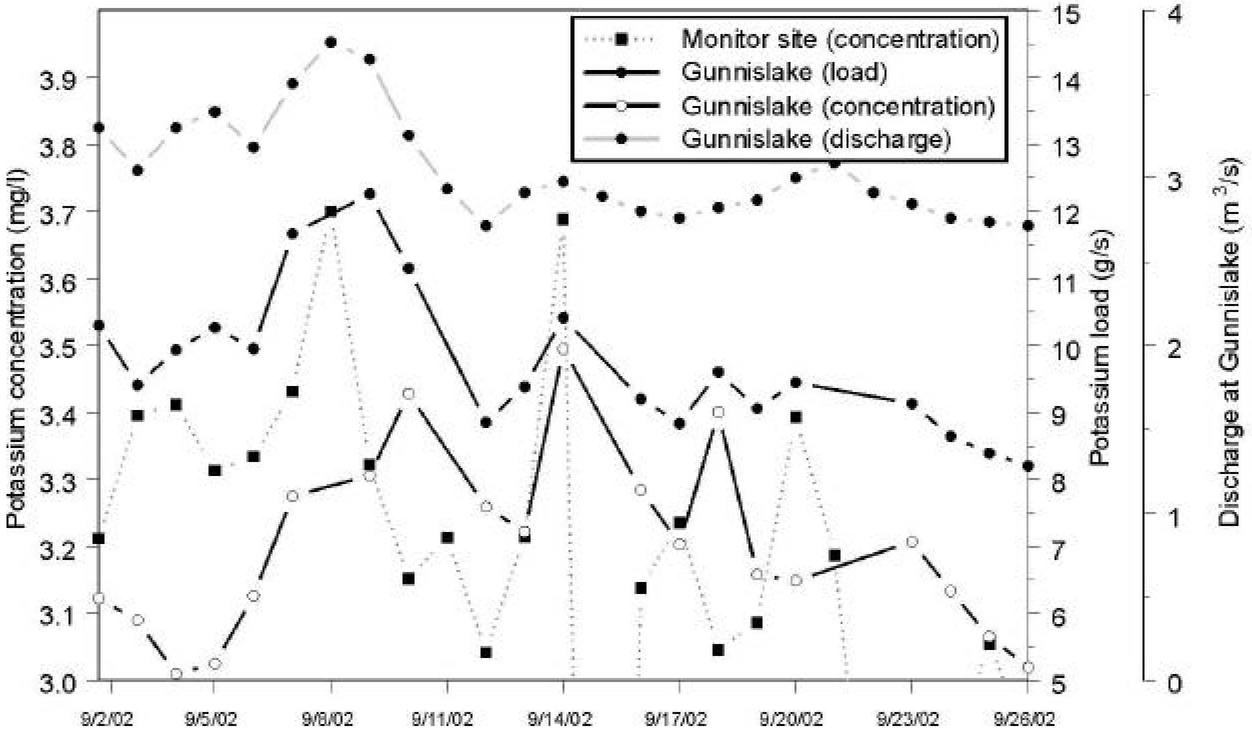
Temporal variations in fluoride (F^-) concentrations, load and flow

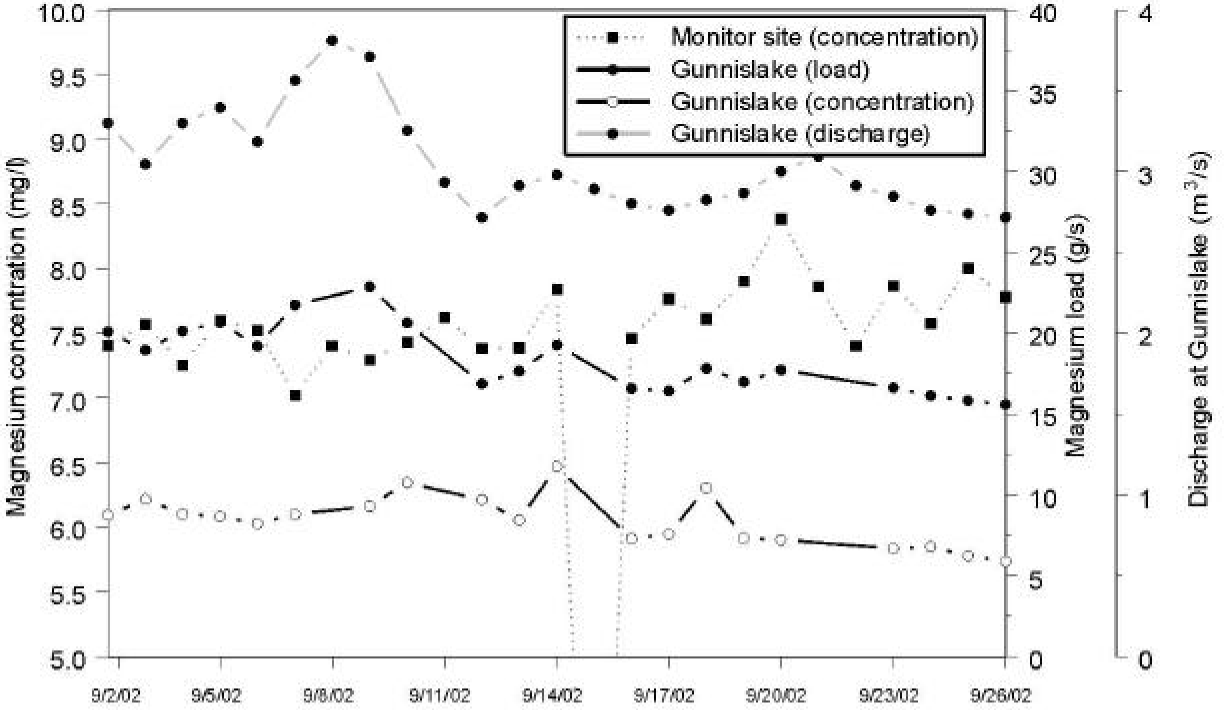


Temporal variations in iron (Fe) concentrations, load and flow

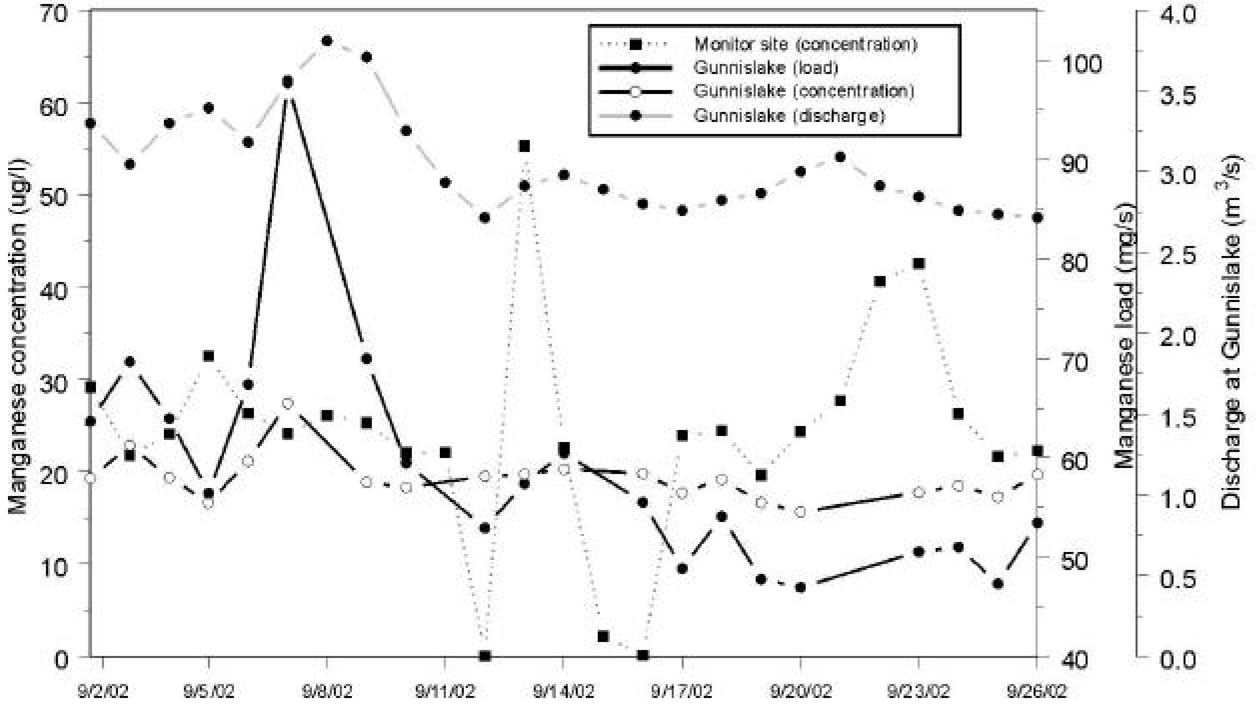


Temporal variations in potassium (K) concentrations, load and flow



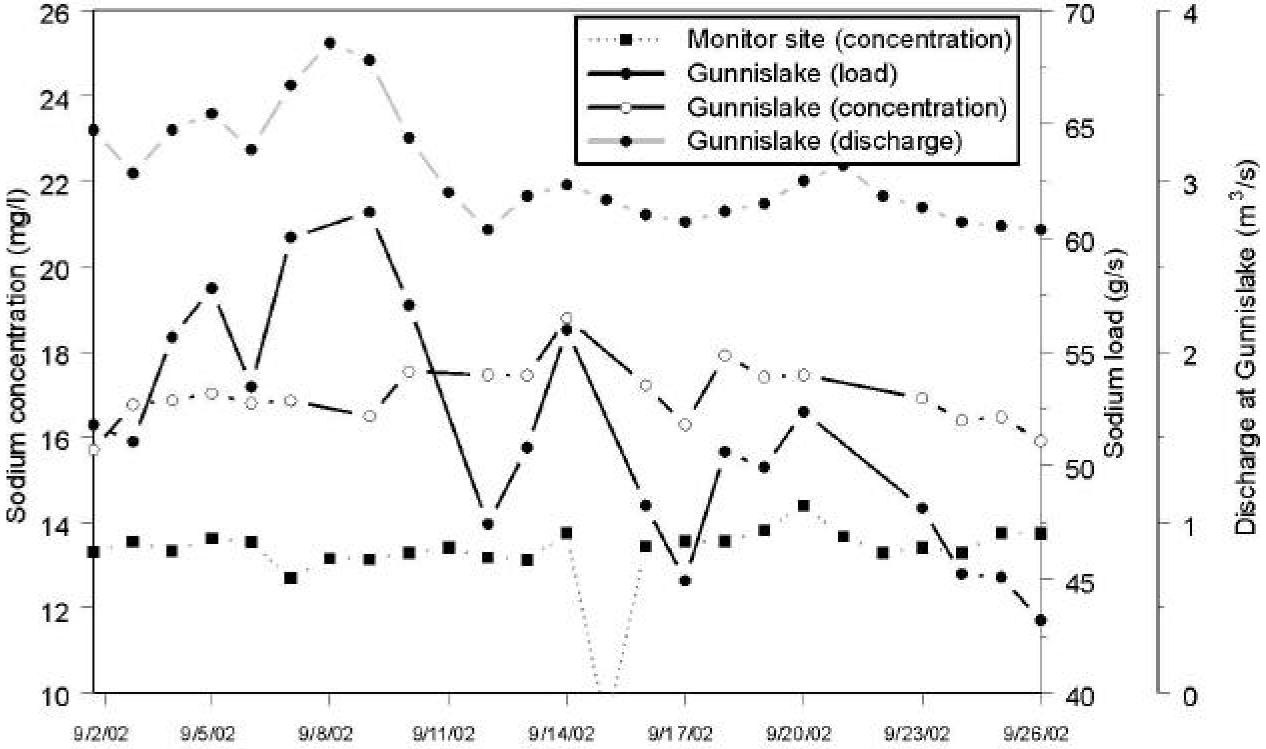


Temporal variations in magnesium (Mg) concentrations, load and flow

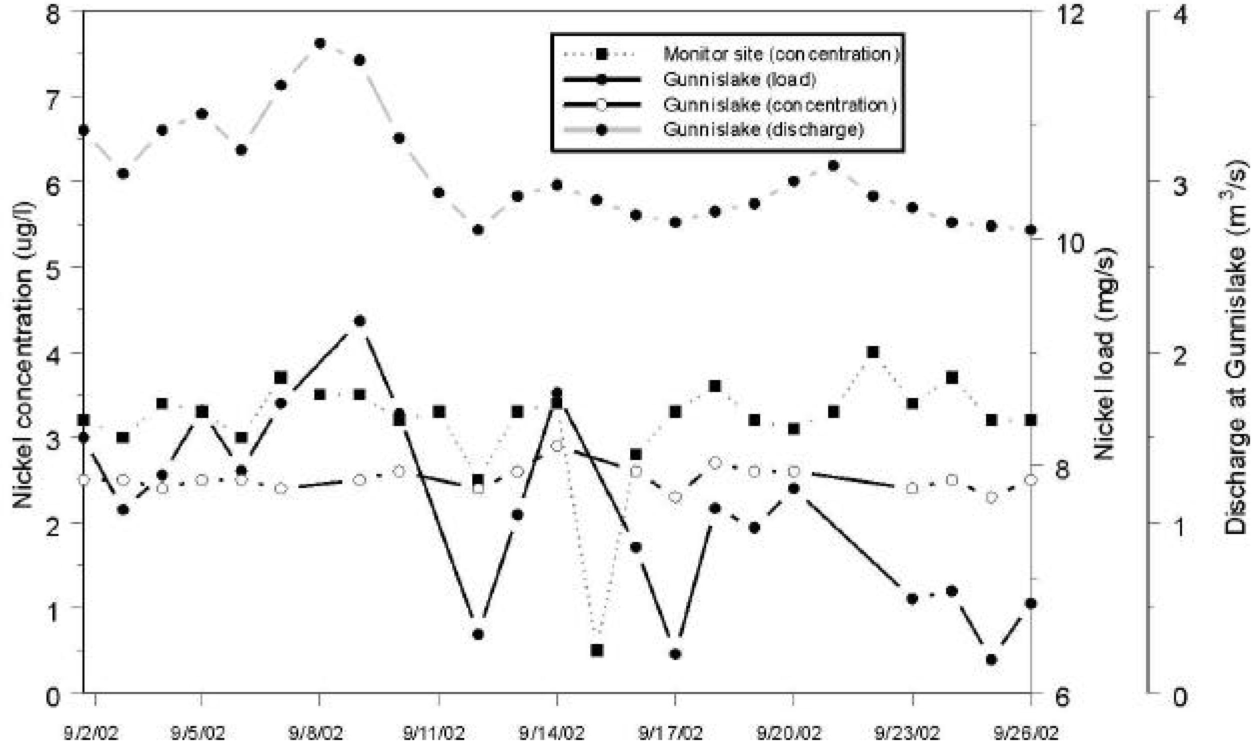


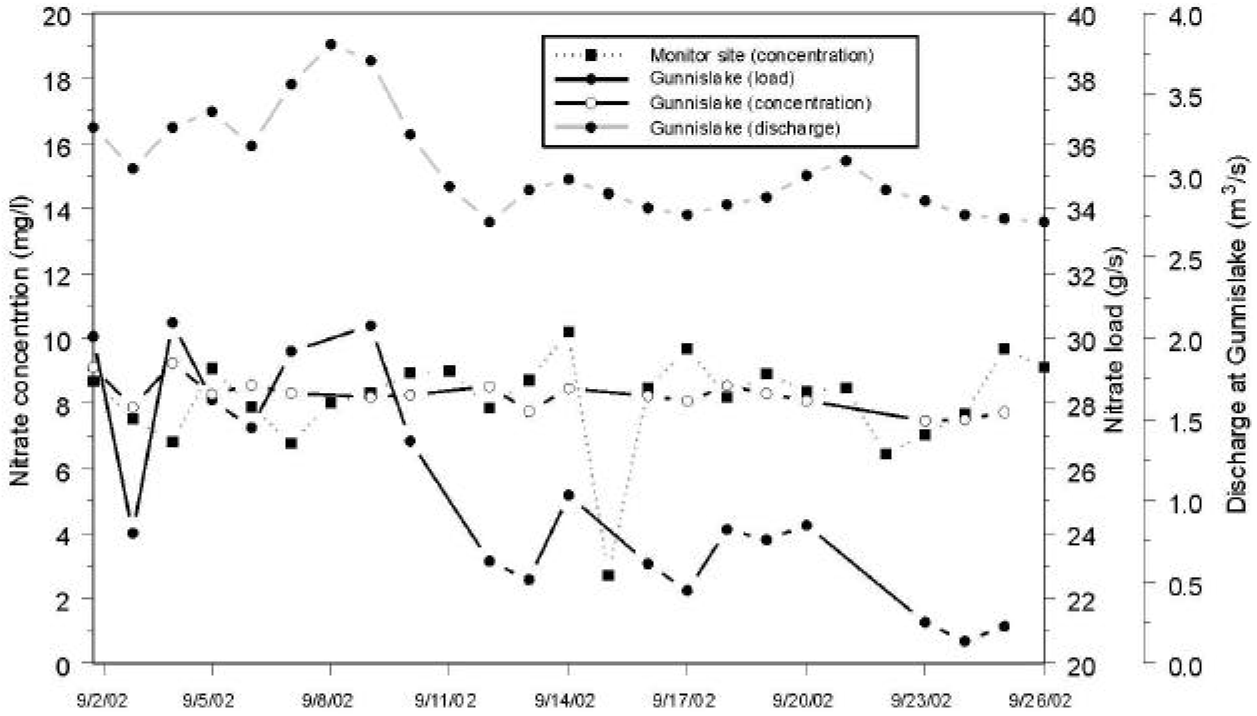
Temporal variations in manganese (Mn) concentrations, discharge and flow

Temporal variations in sodium (Na) concentrations, load and flow

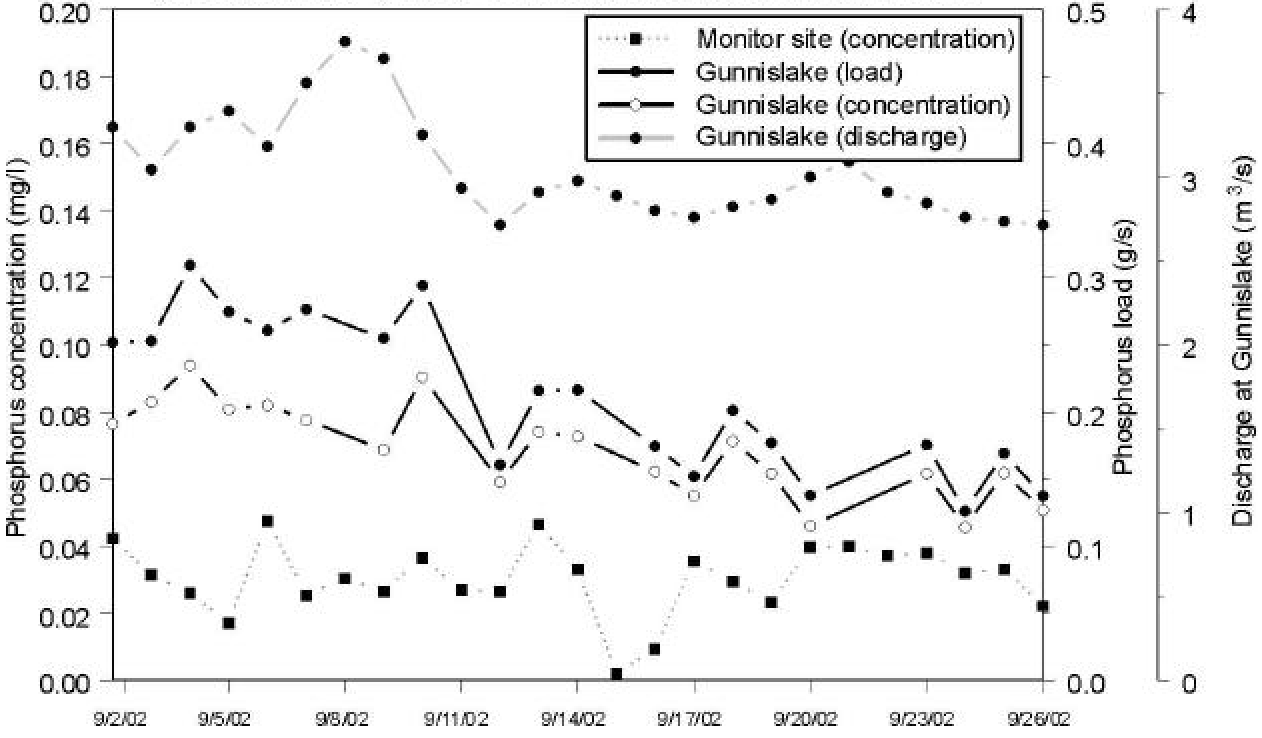


Temporal variations in nickel (Ni) concentrations, discharge and flow

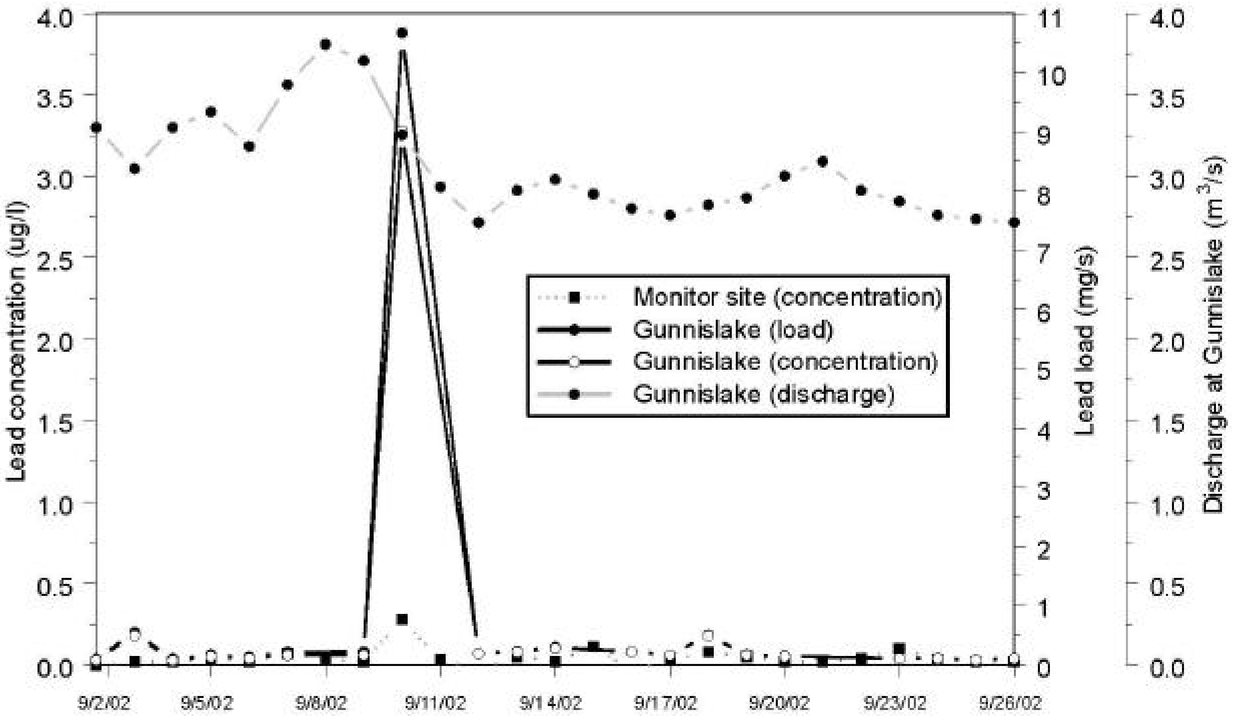


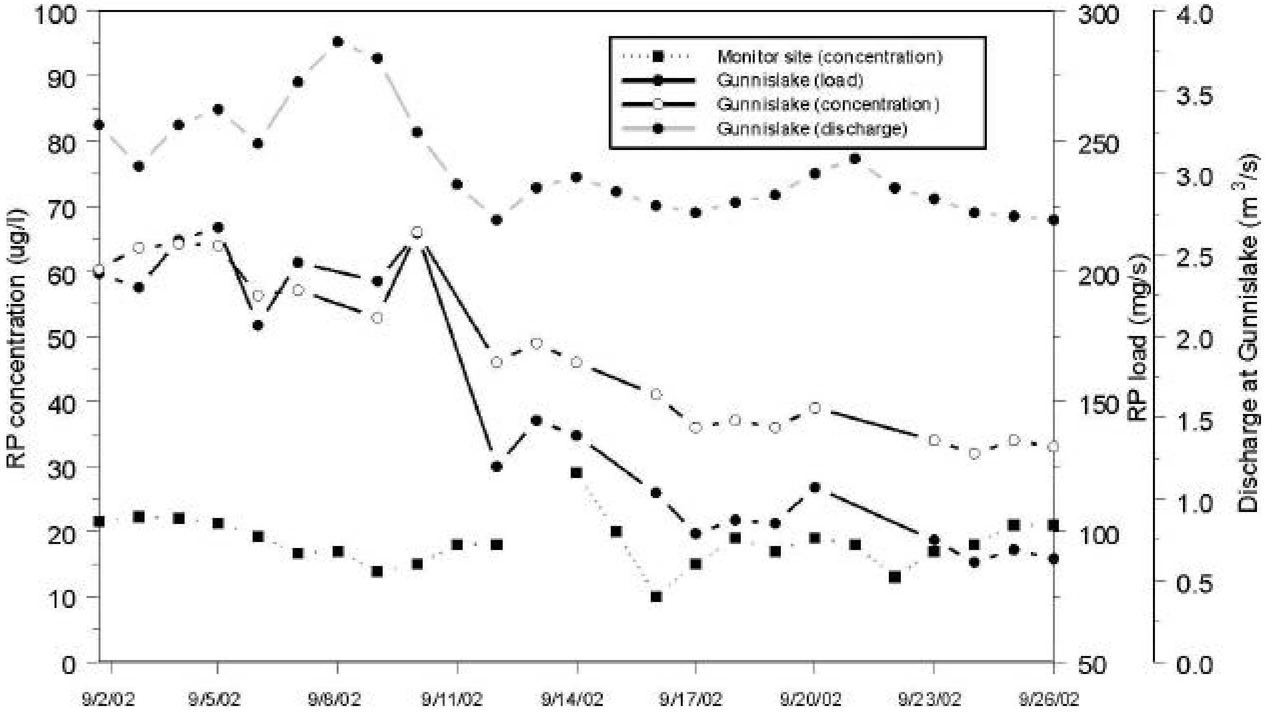


Temporal variations in nitrate (NO3-) concentrations, load and flow

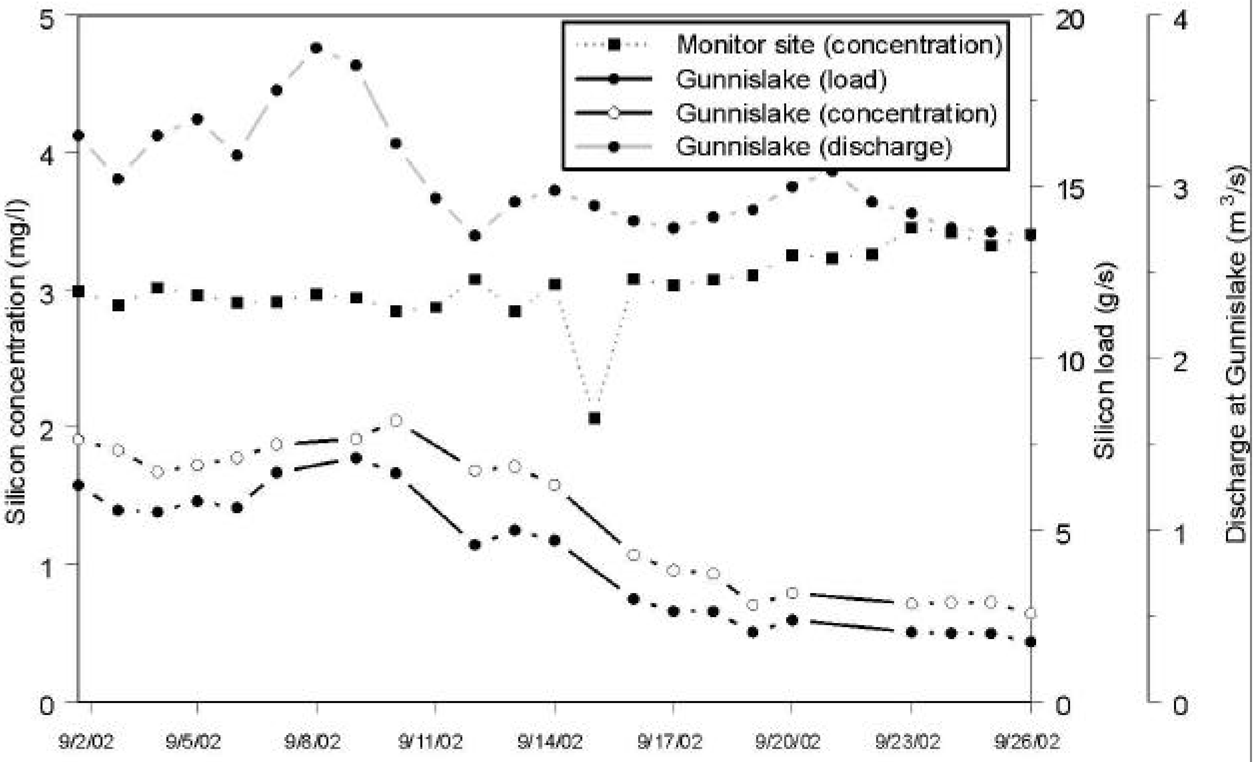


Temporal variations in total dissolved phosphorus (TDP) concentrations, load and flow

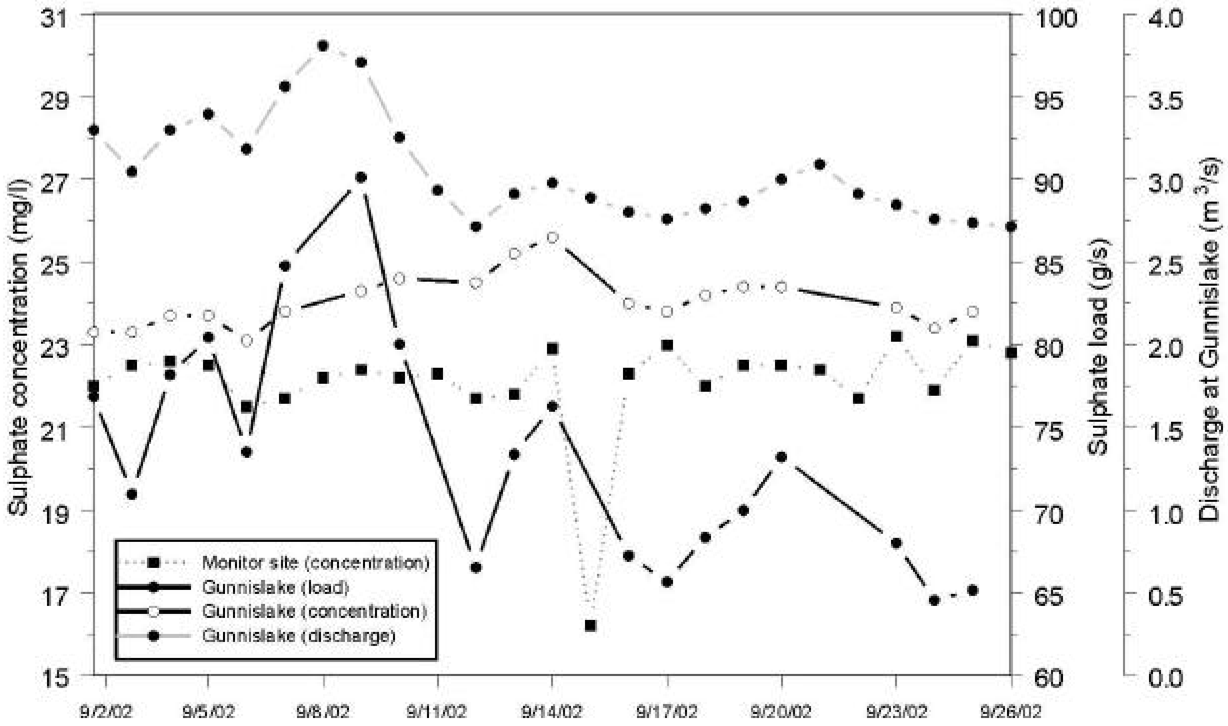

Temporal variations in lead (Pb) concentrations, load and flow


Temporal variations in dissolved reactive phosphorus (DRP) concentrations, load and flow

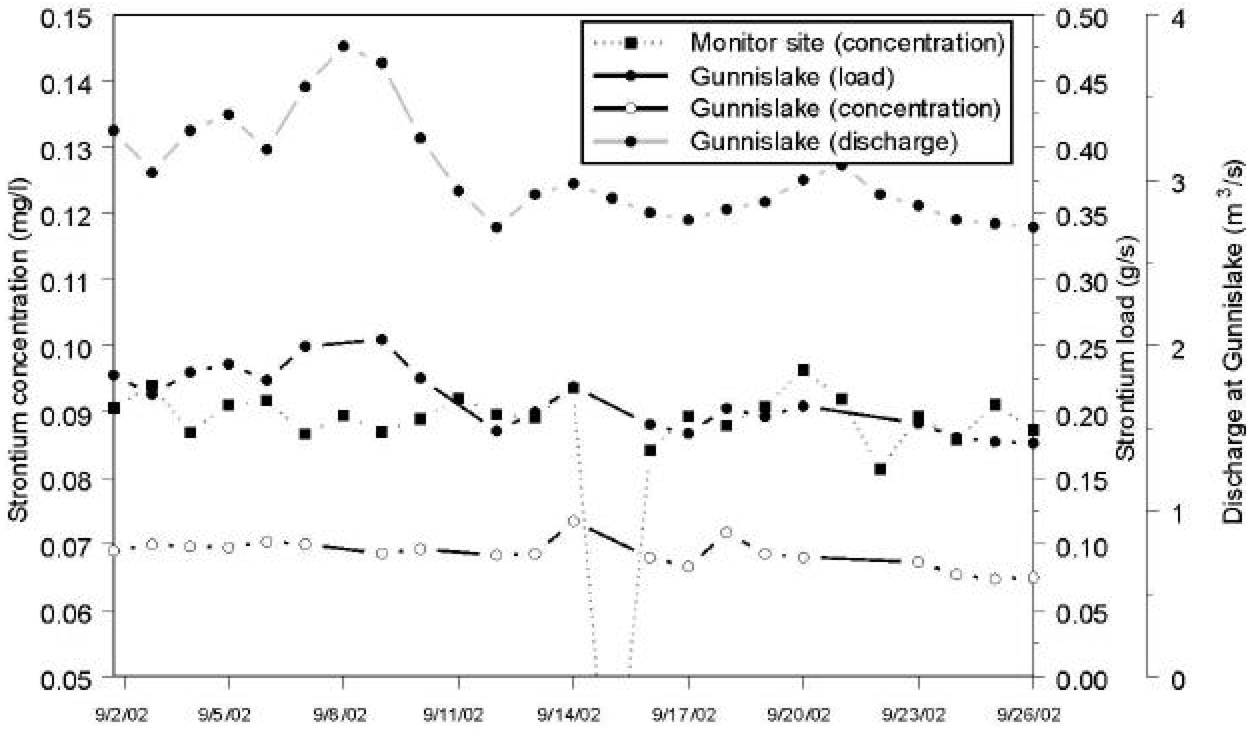
Temporal variations in silicon (Si) concentrations, load and flow



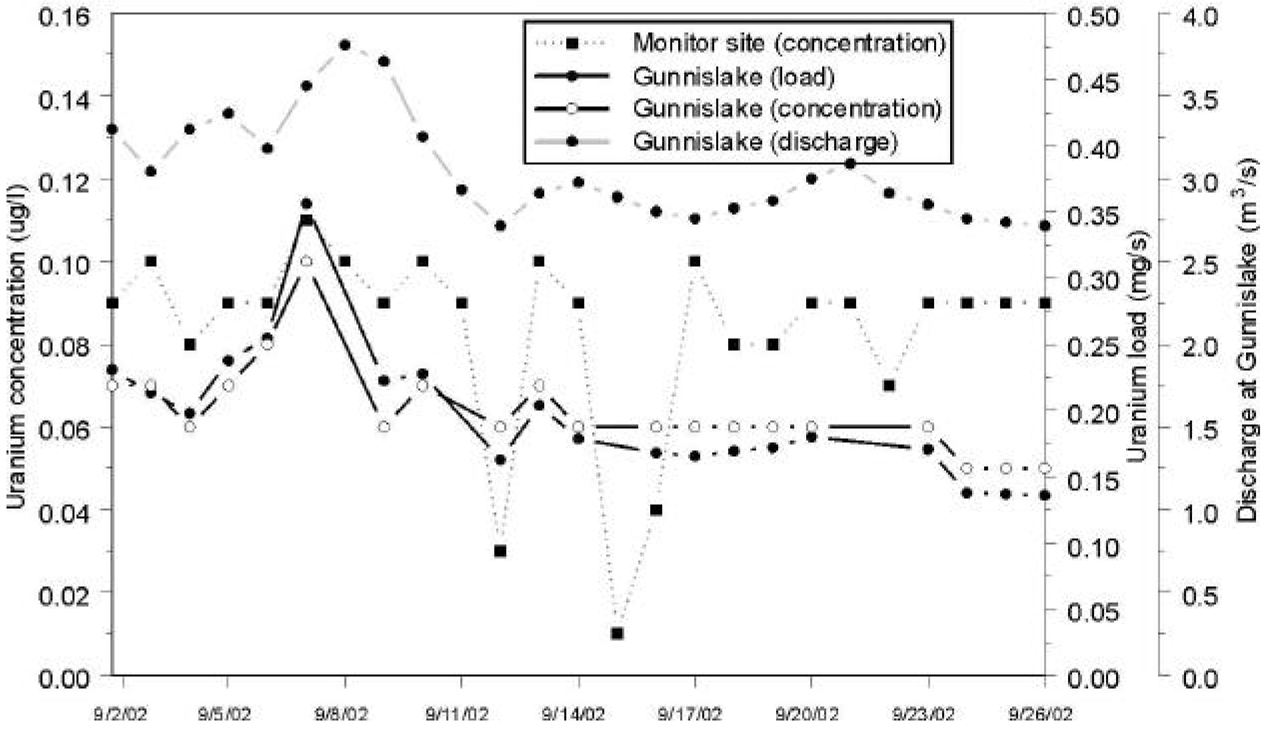
Temporal variations in sulphate (SO_4^{2-}) concentrations, load and flow



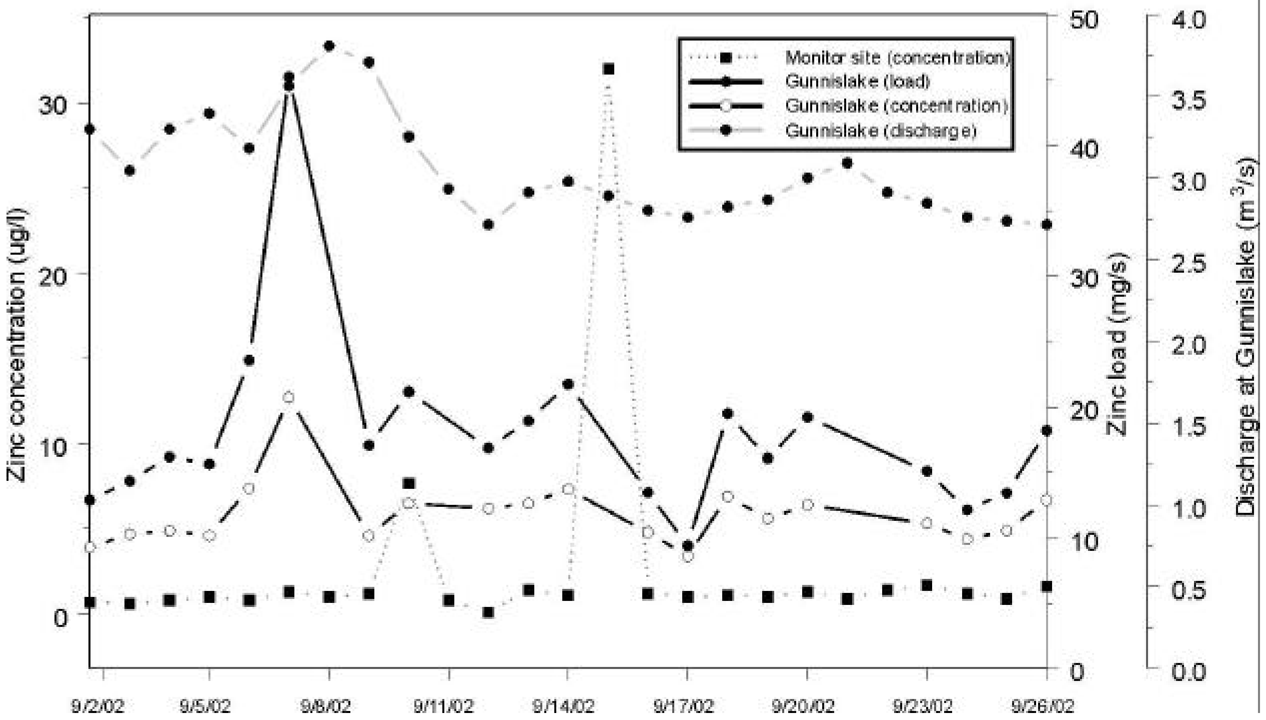
Temporal variations in strontium (Sr) concentrations, load and flow



Temporal variations in uranium (U) concentrations, discharge and flow

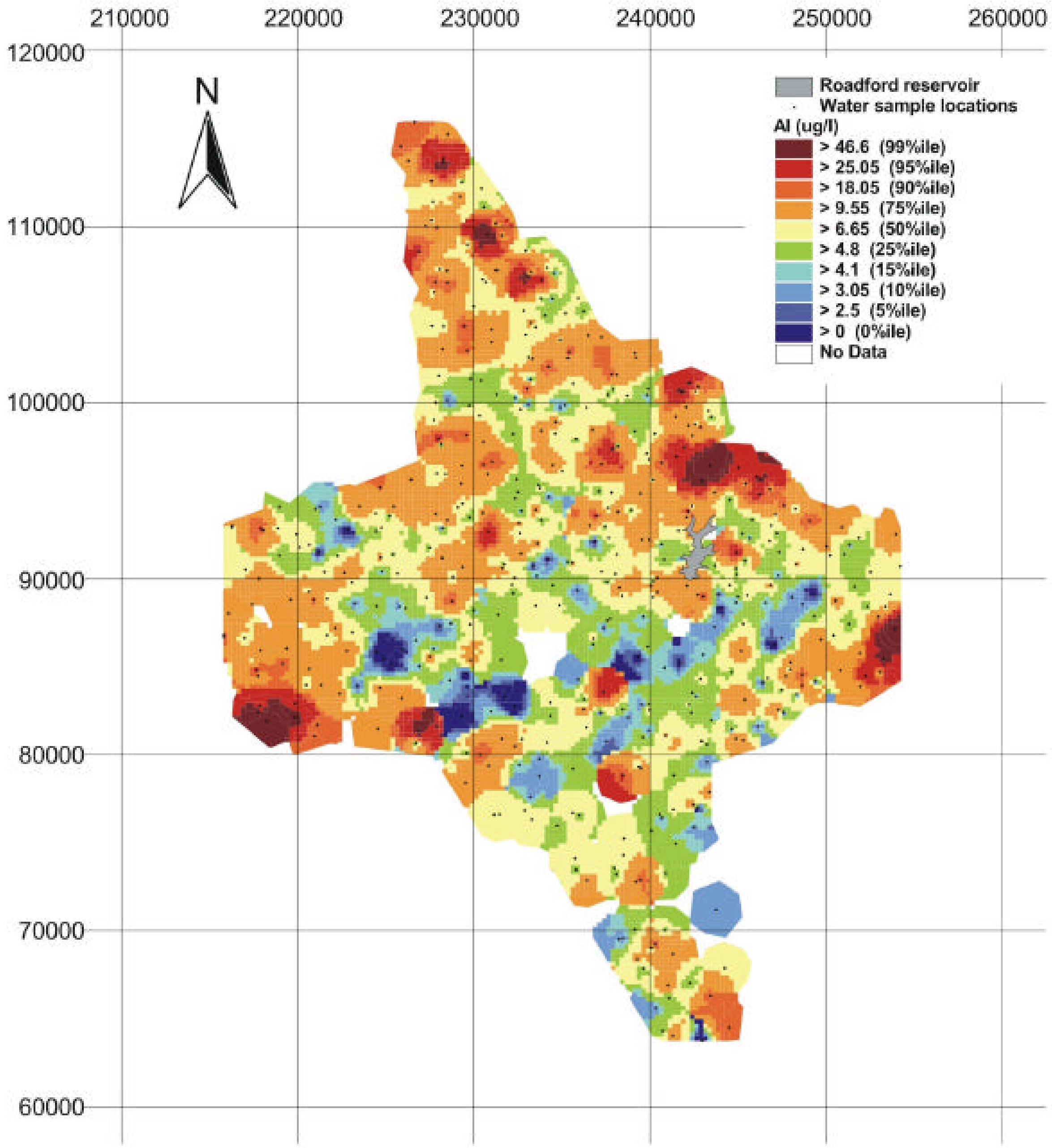


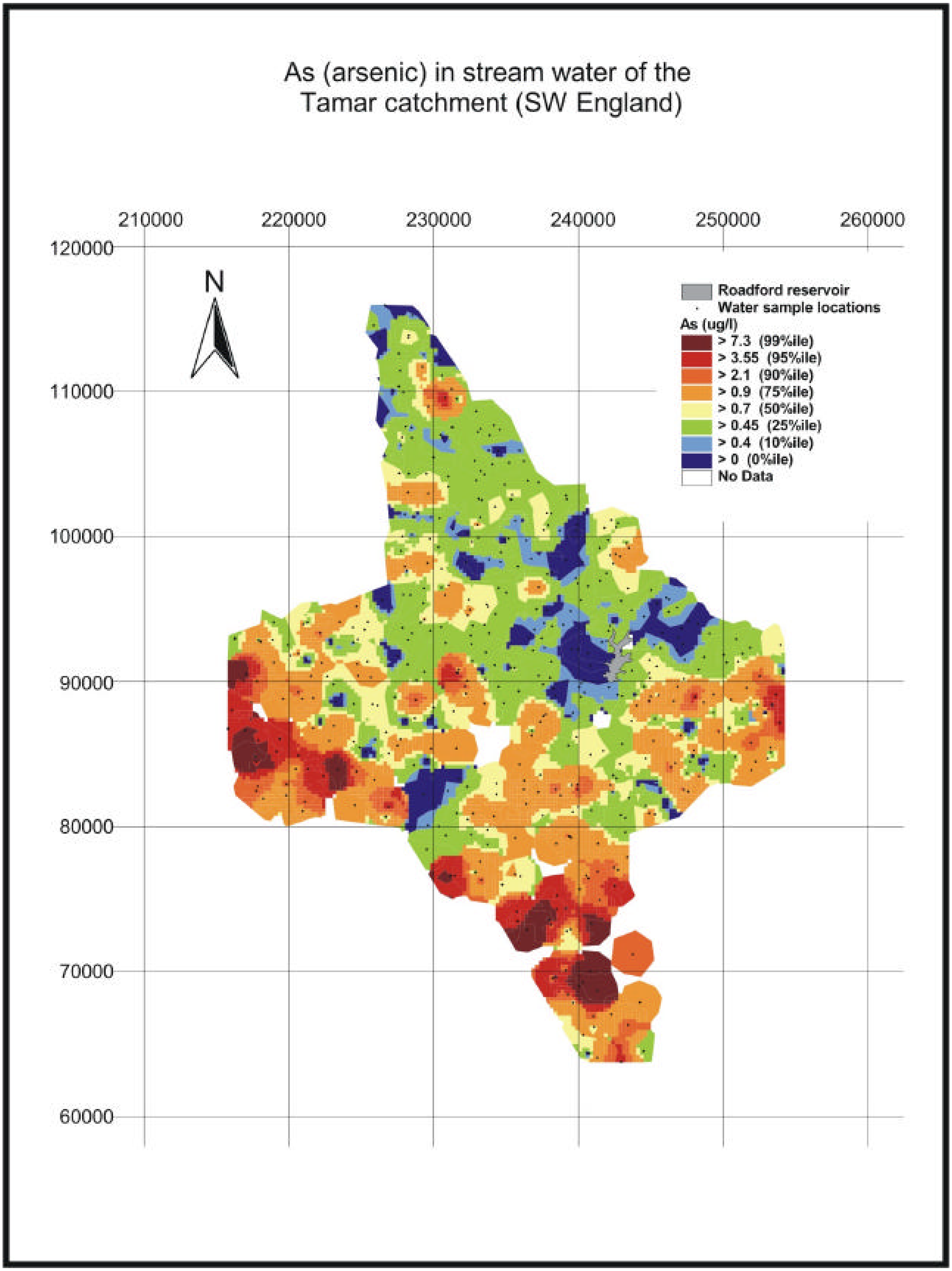
Temporal variations in zinc (Zn) concentrations, load and flow



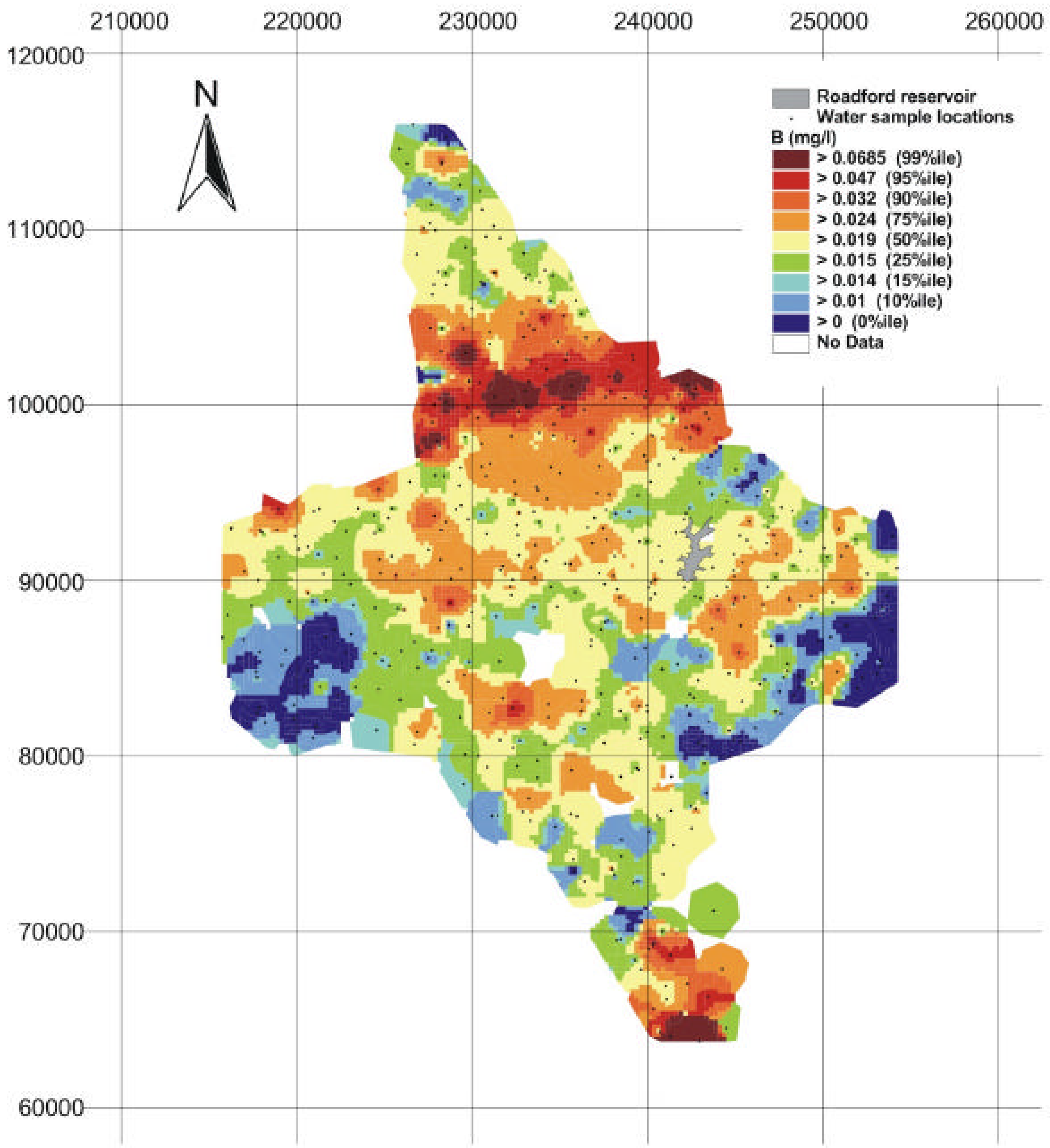
Part II: Spatial variation in stream water chemistry throughout the Tamar catchment

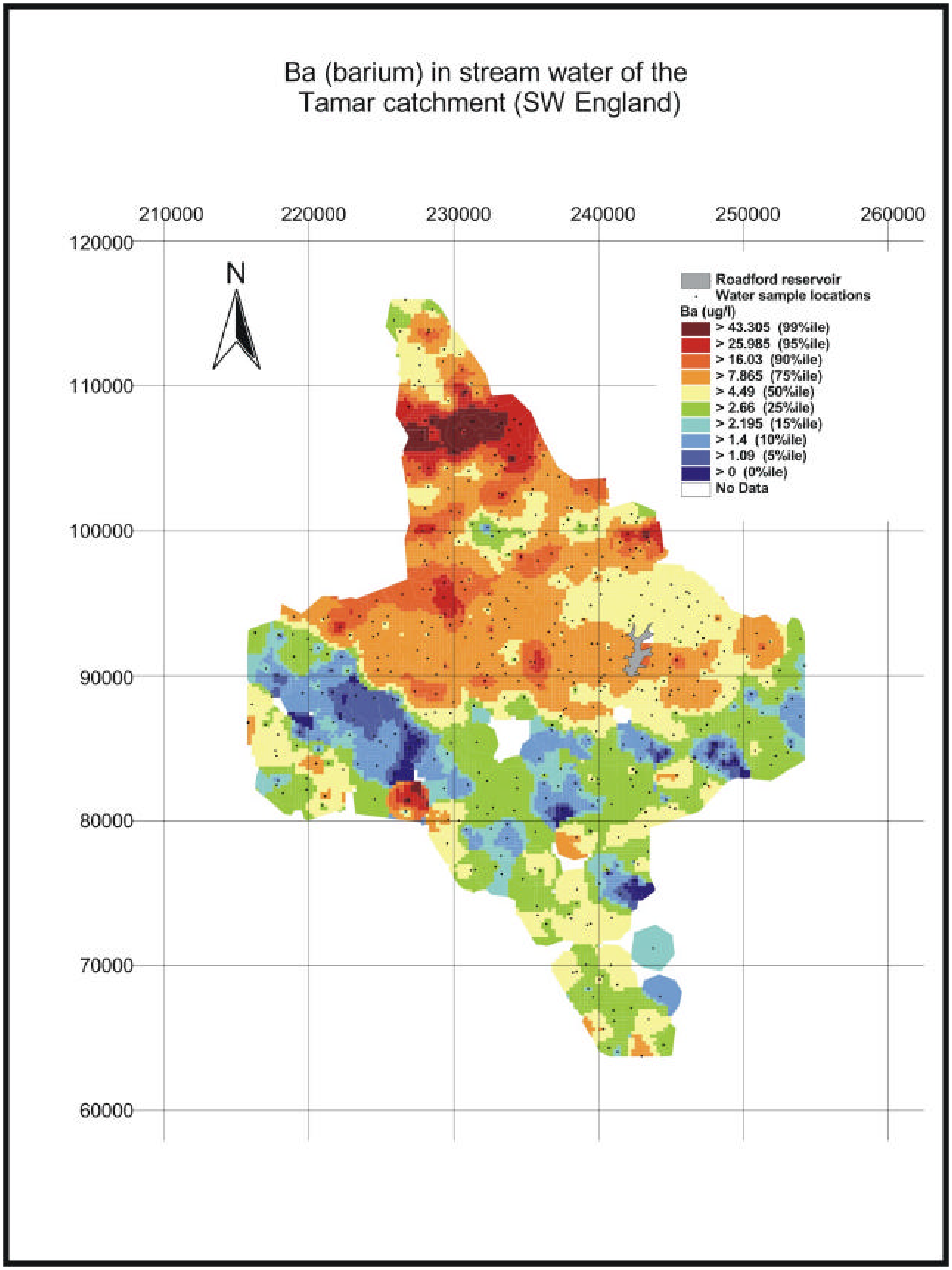
Al (aluminium) in stream water of the Tamar catchment (SW England)



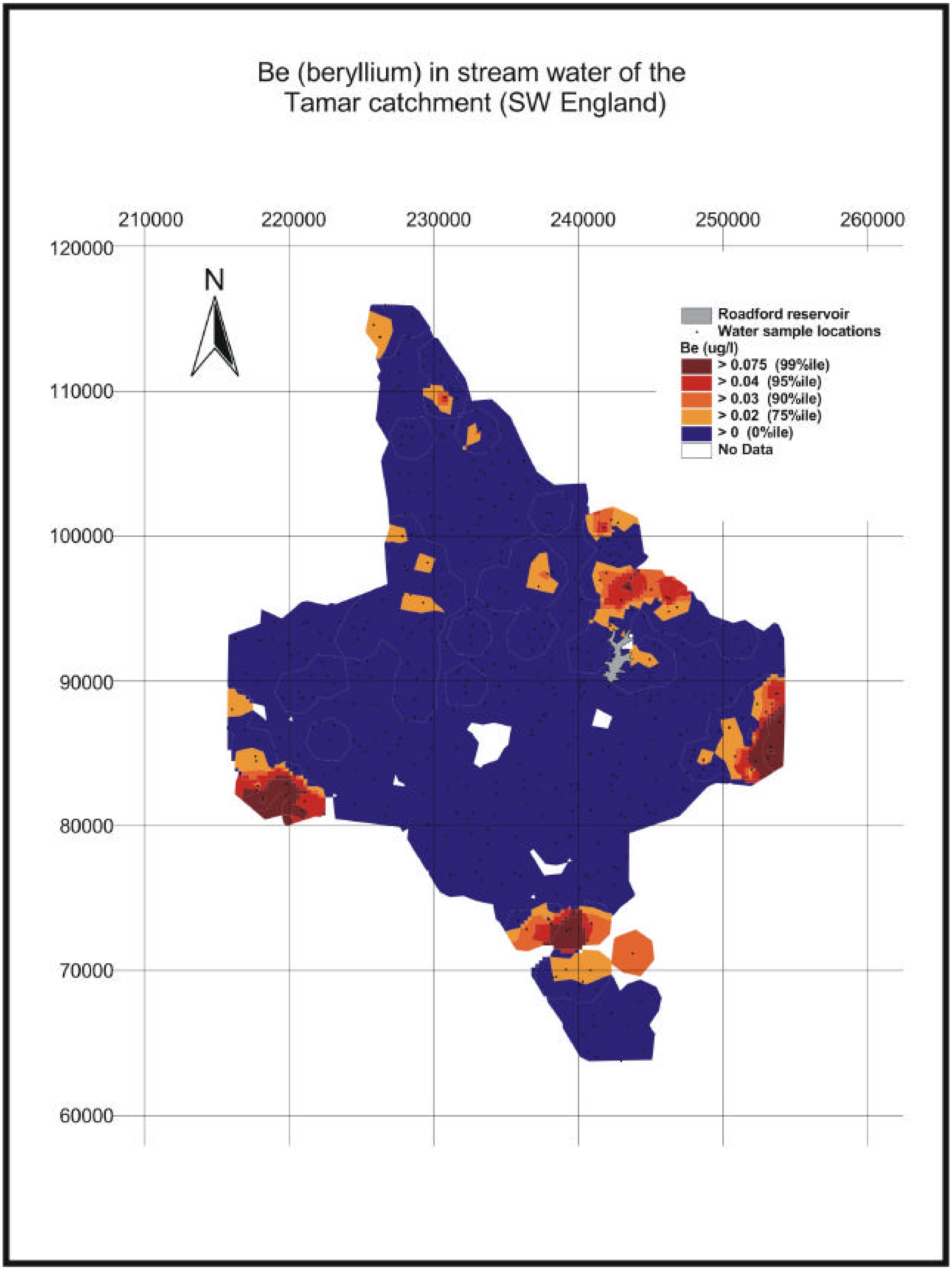

As (arsenic) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
As (ug/l)
> 7.3 (99%ile)
> 3.55 (95%ile)
> 2.1 (90%ile)
> 0.9 (75%ile)
> 0.7 (50%ile)
> 0.45 (25%ile)
> 0.4 (10%ile)
> 0 (0%ile)
No Data

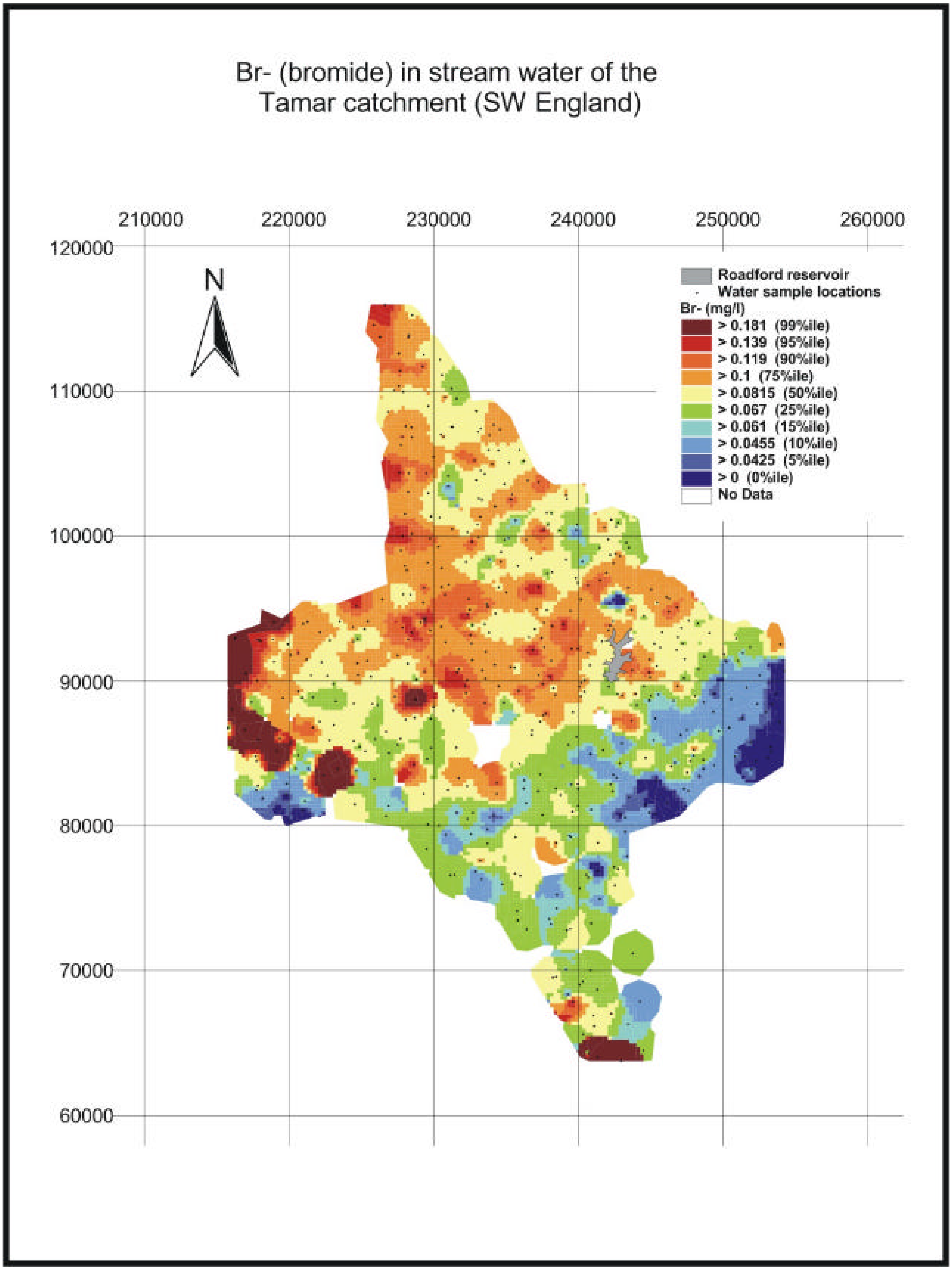
B (boron) in stream water of the Tamar catchment (SW England)

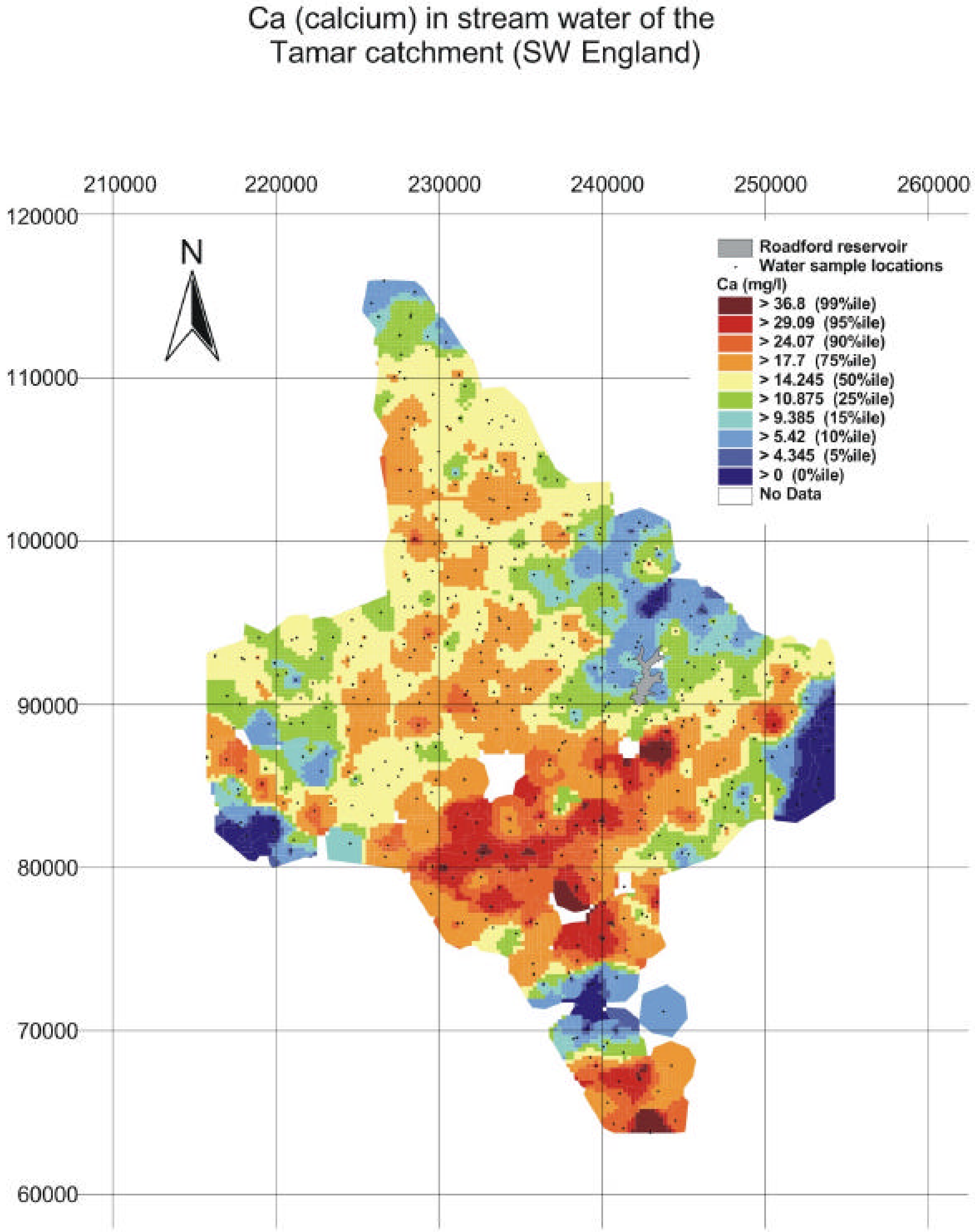




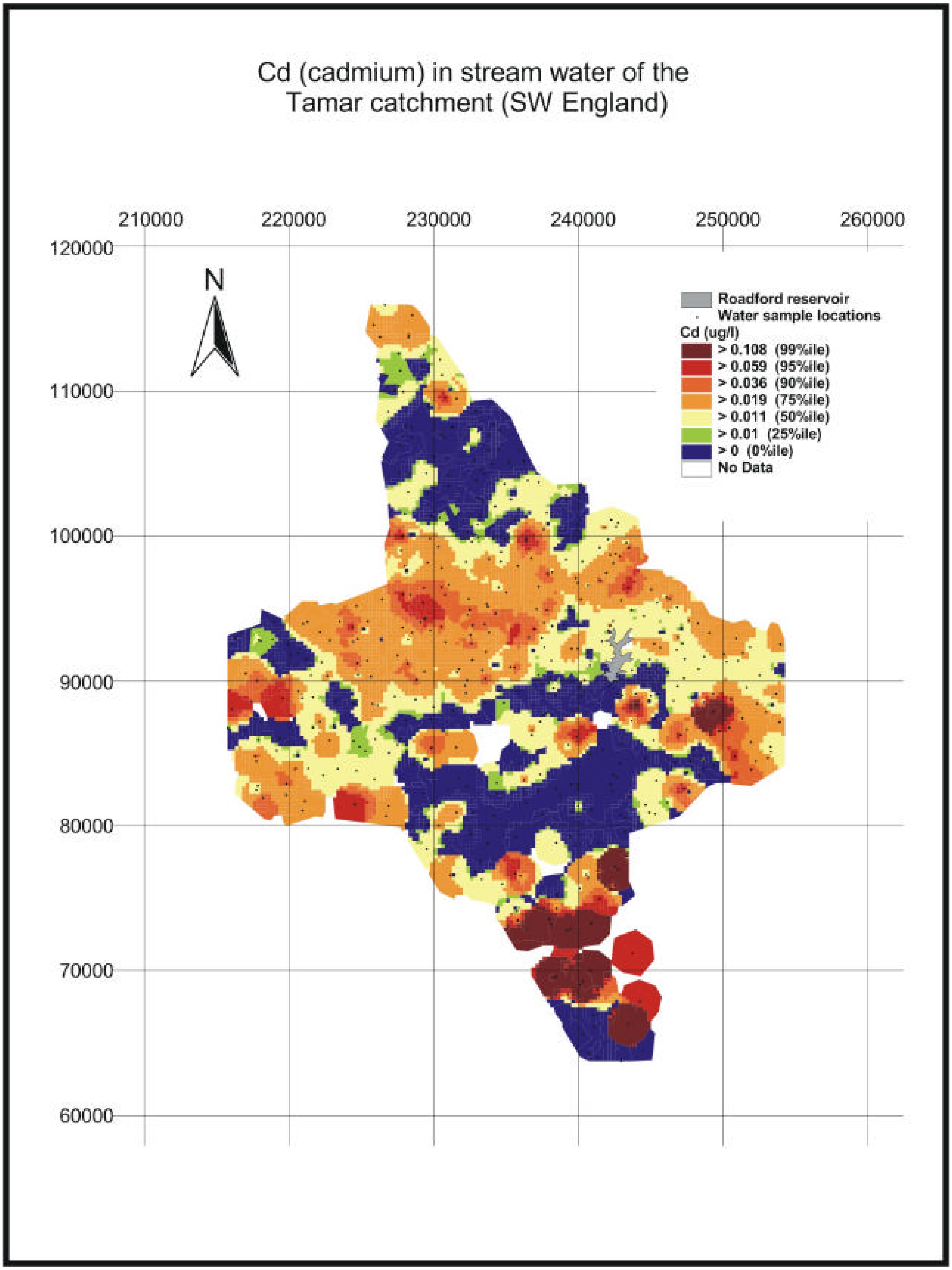
Ba (barium) in stream water of the Tamar catchment (SW England)


Be (beryllium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Be (ug/l)
> 0.075 (99%ile)
> 0.04 (95%ile)
> 0.03 (90%ile)
> 0.02 (75%ile)
> 0 (0%ile)
No Data

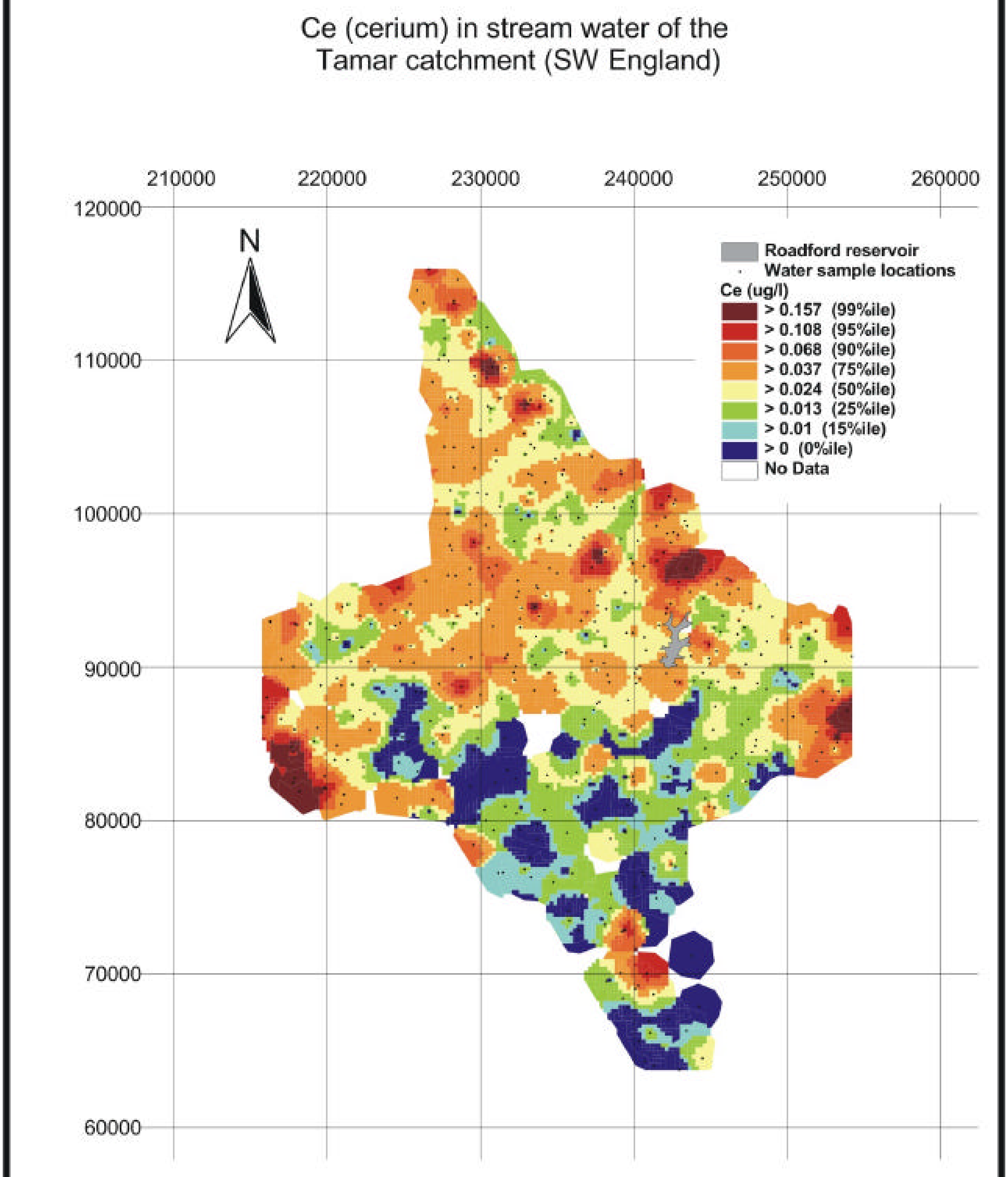

Br- (bromide) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Br- (mg/l)
> 0.181 (99%ile)
> 0.139 (95%ile)
> 0.119 (90%ile)
> 0.1 (75%ile)
> 0.0815 (50%ile)
> 0.067 (25%ile)
> 0.061 (15%ile)
> 0.0455 (10%ile)
> 0.0425 (5%ile)
> 0 (0%ile)
No Data

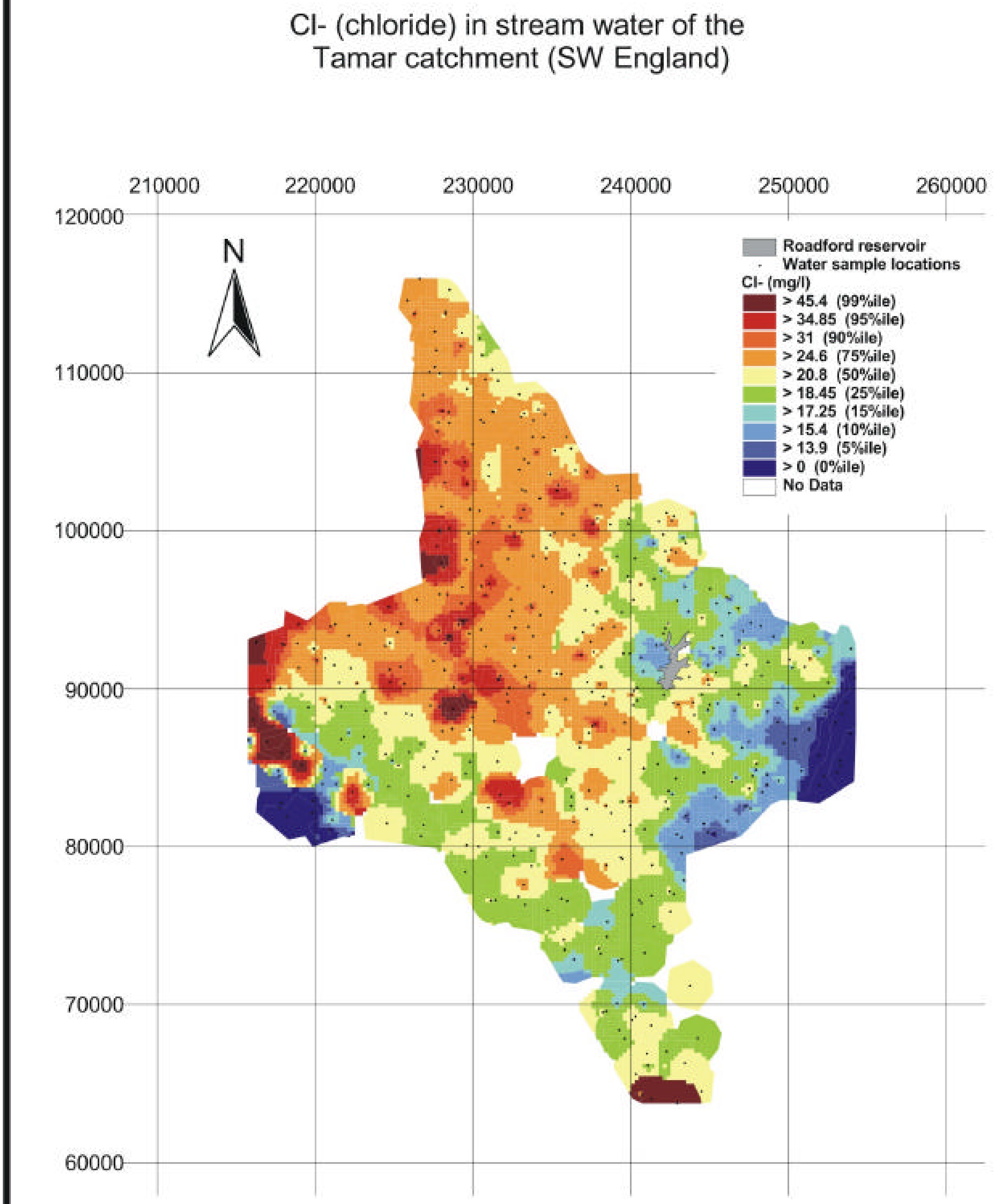


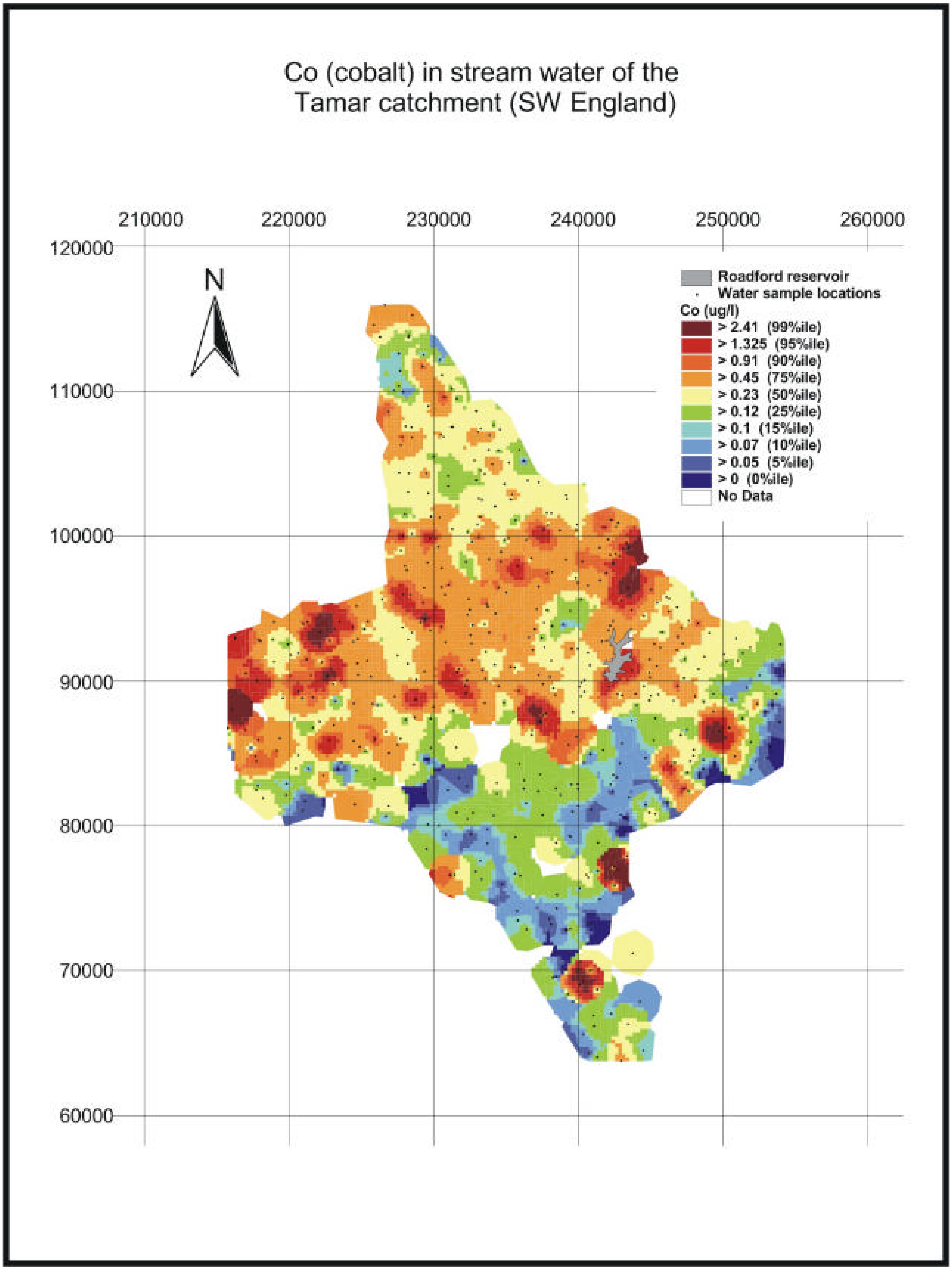
Ca (calcium) in stream water of the Tamar catchment (SW England)

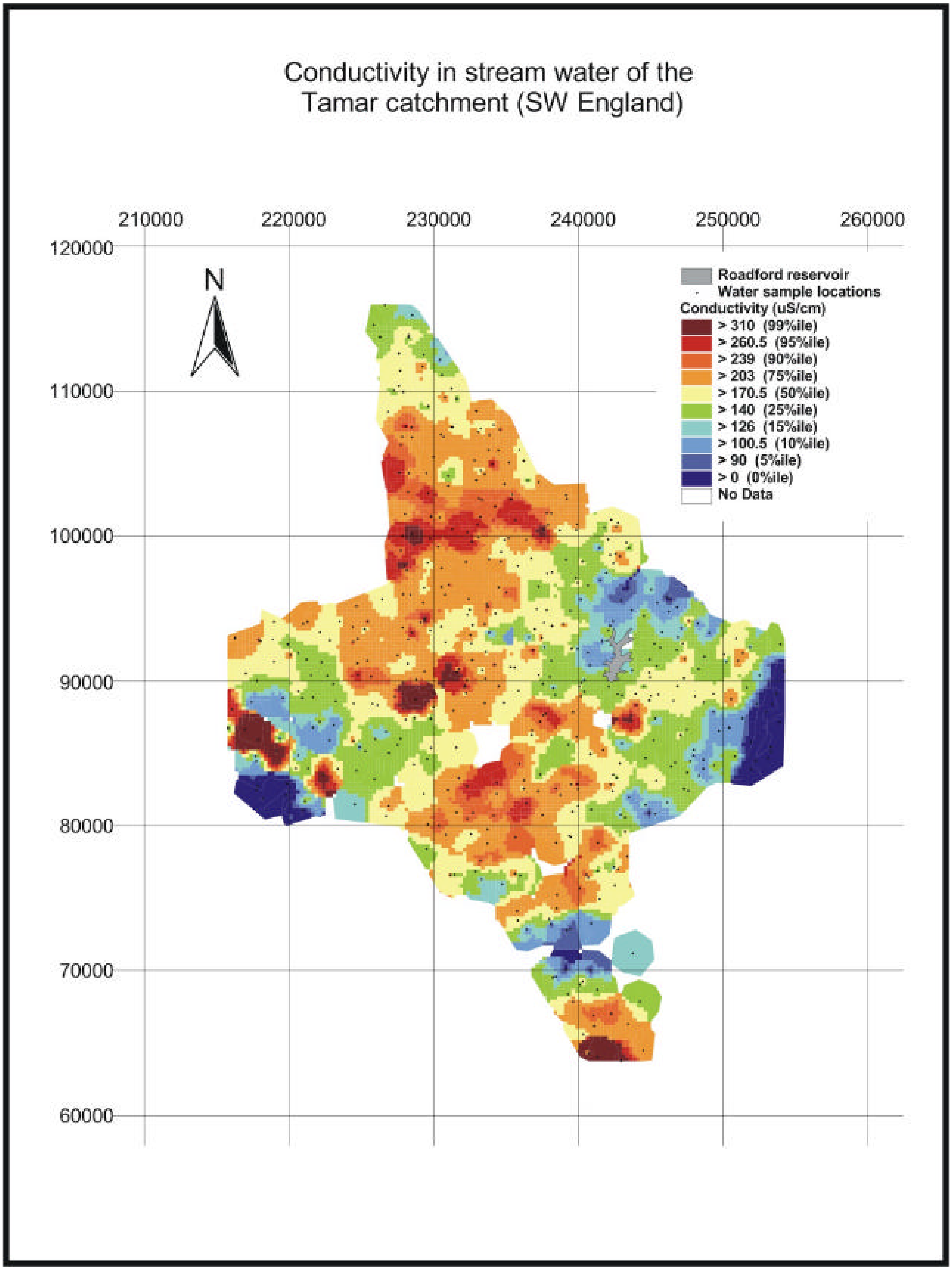


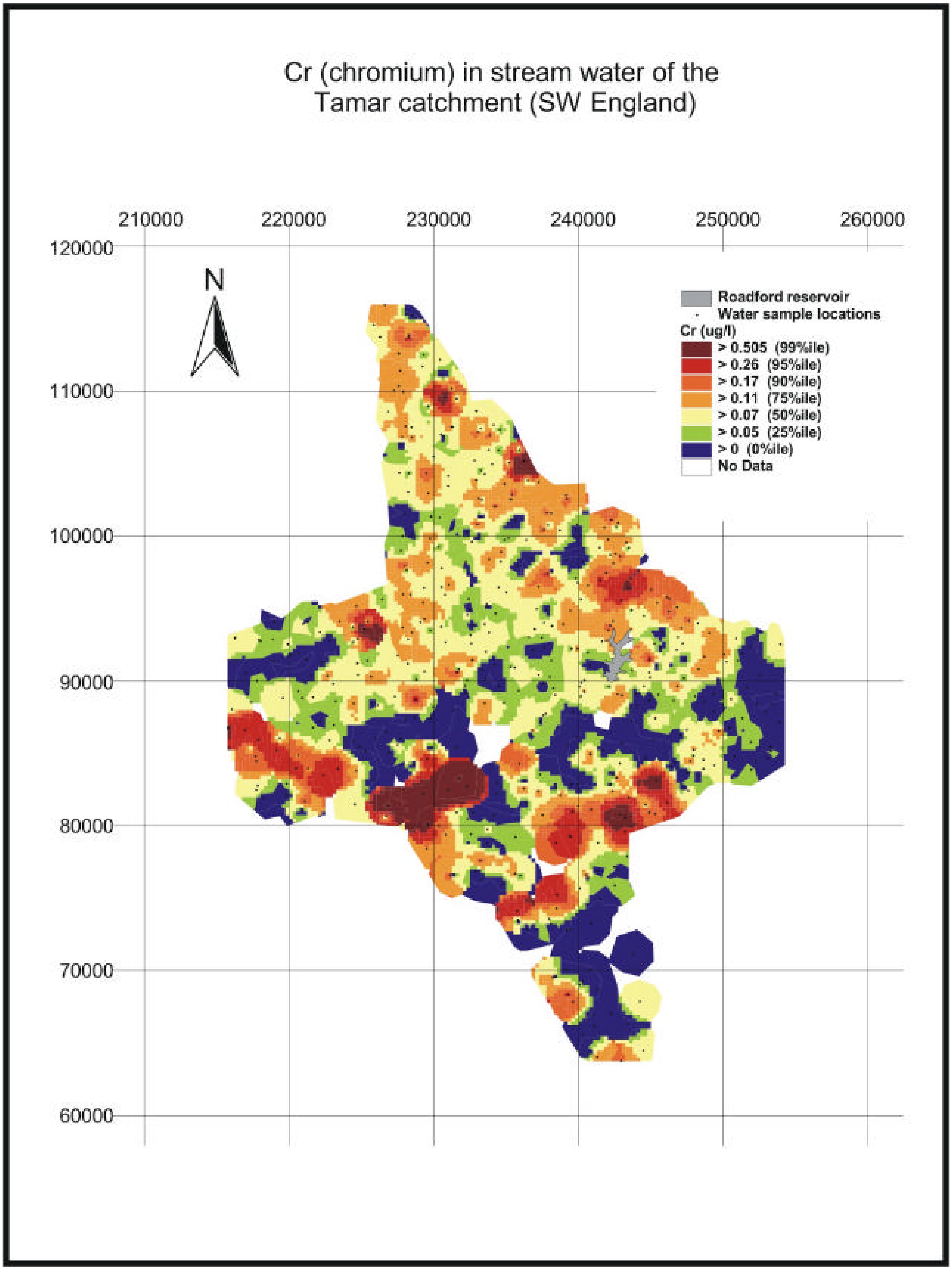
Cd (cadmium) in stream water of the Tamar catchment (SW England)

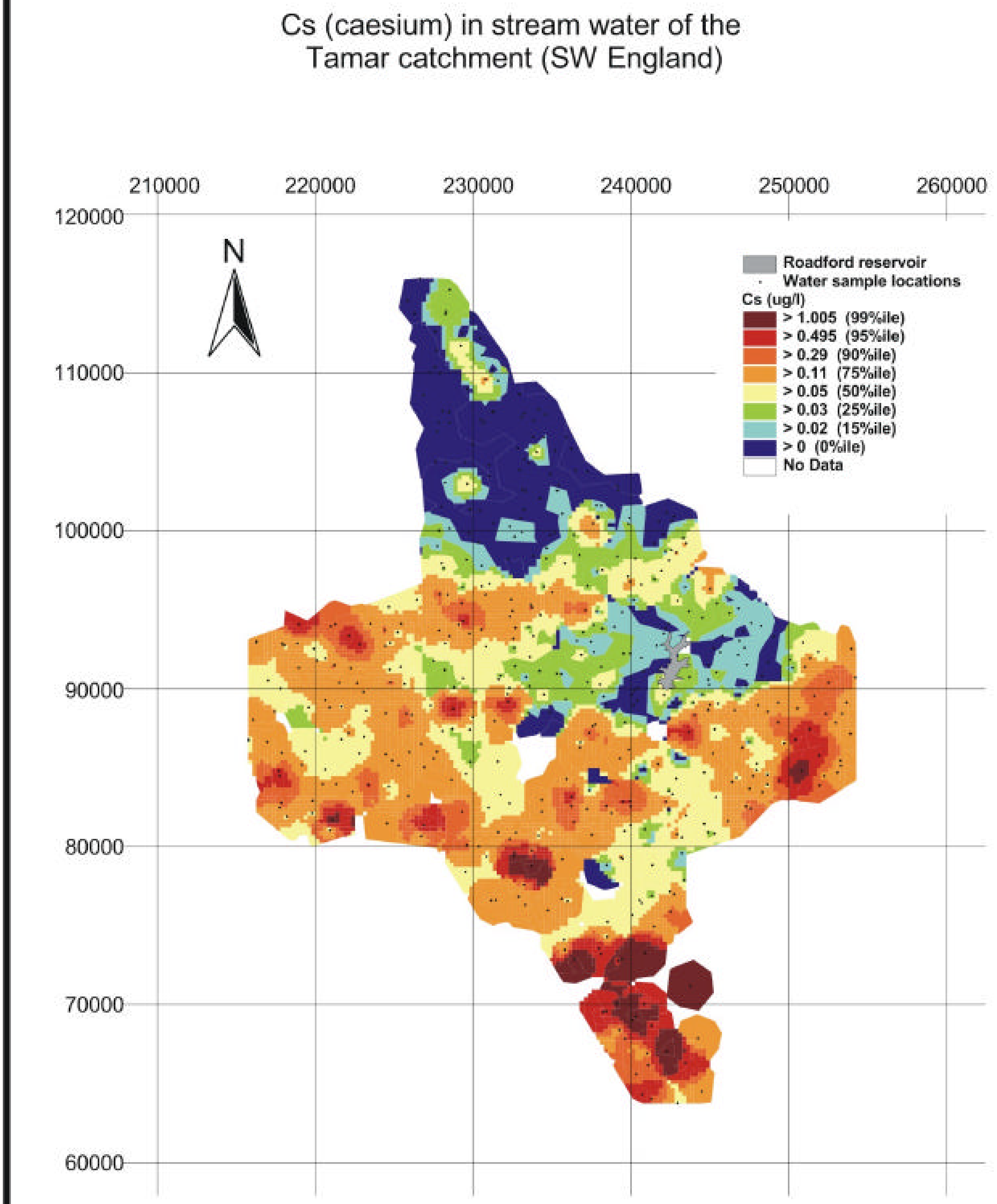

Ce (cerium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Ce (ug/l)
> 0.157 (99%ile)
> 0.108 (95%ile)
> 0.068 (90%ile)
> 0.037 (75%ile)
> 0.024 (50%ile)
> 0.013 (25%ile)
> 0.01 (15%ile)
> 0 (0%ile)
No Data


Cl- (chloride) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Cl- (mg/l)
> 45.4 (99%ile)
> 34.85 (95%ile)
> 31 (90%ile)
> 24.6 (75%ile)
> 20.8 (50%ile)
> 18.45 (25%ile)
> 17.25 (15%ile)
> 15.4 (10%ile)
> 13.9 (5%ile)
> 0 (0%ile)
No Data

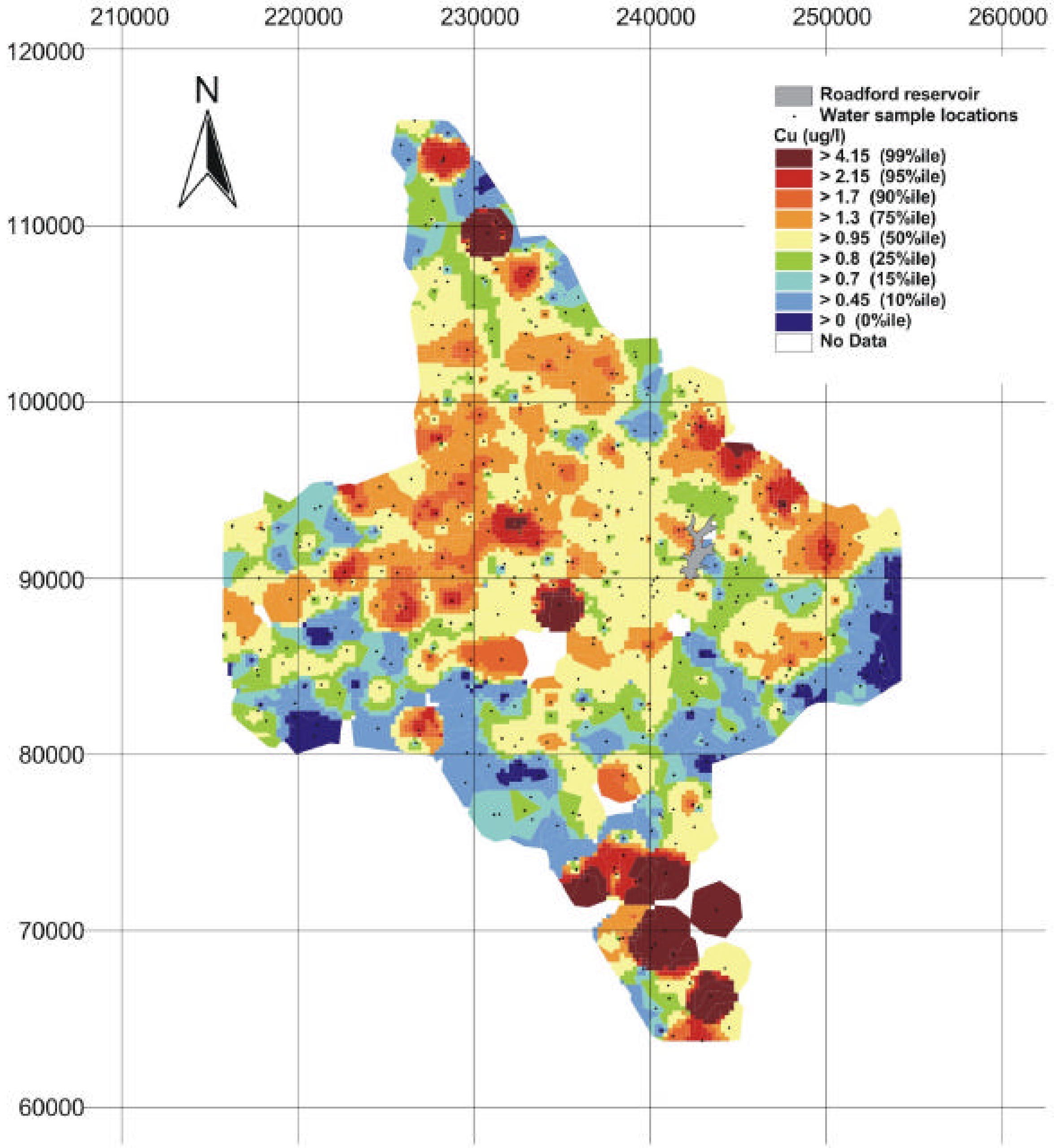

Co (cobalt) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Co (ug/l)
> 2.41 (99%ile)
> 1.325 (95%ile)
> 0.91 (90%ile)
> 0.45 (75%ile)
> 0.23 (50%ile)
> 0.12 (25%ile)
> 0.1 (15%ile)
> 0.07 (10%ile)
> 0.05 (5%ile)
> 0 (0%ile)
No Data

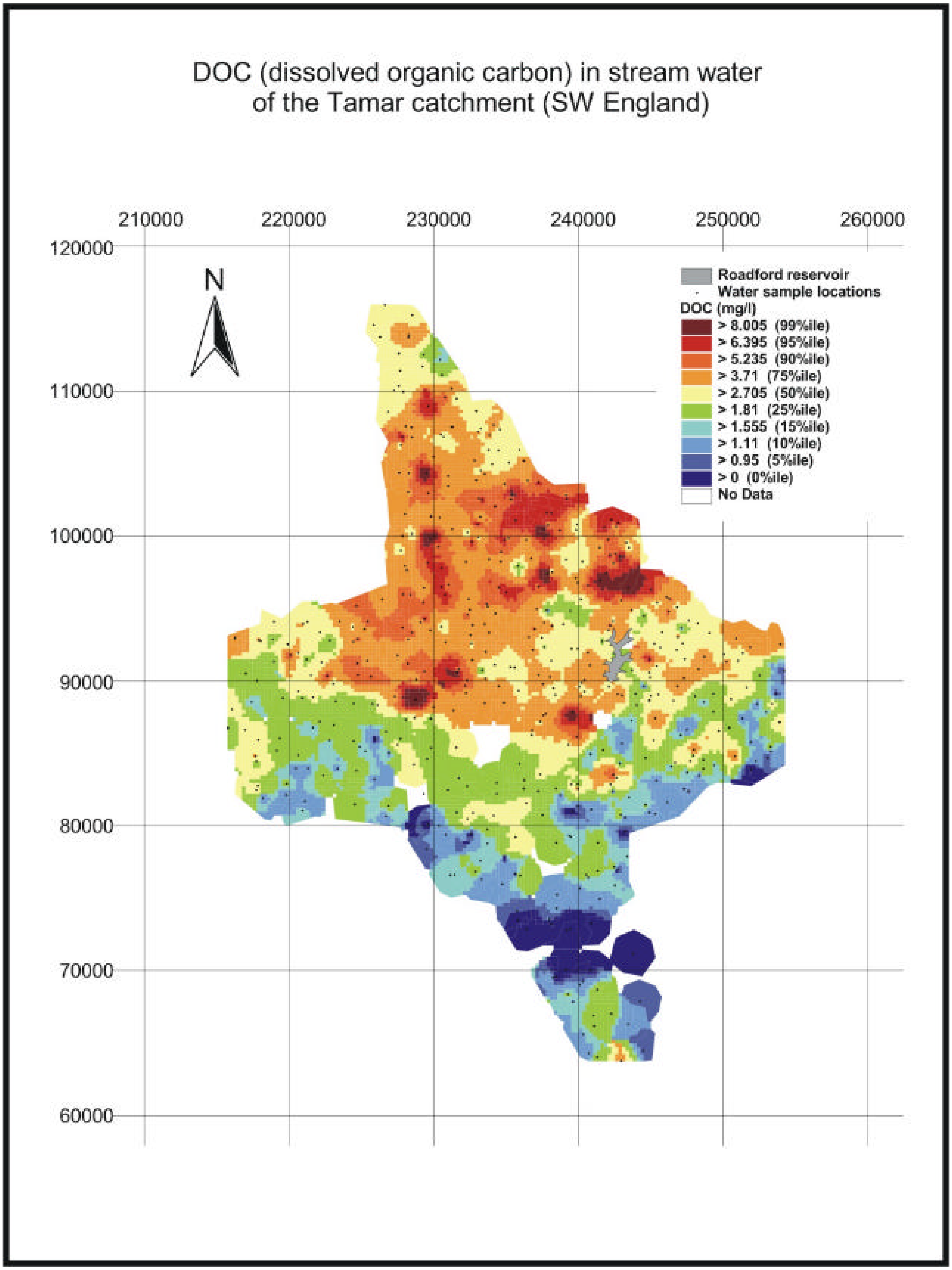

Conductivity in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Conductivity (uS/cm)
> 310 (99%ile)
> 260.5 (95%ile)
> 239 (90%ile)
> 203 (75%ile)
> 170.5 (50%ile)
> 140 (25%ile)
> 126 (15%ile)
> 100.5 (10%ile)
> 90 (5%ile)
> 0 (0%ile)
No Data

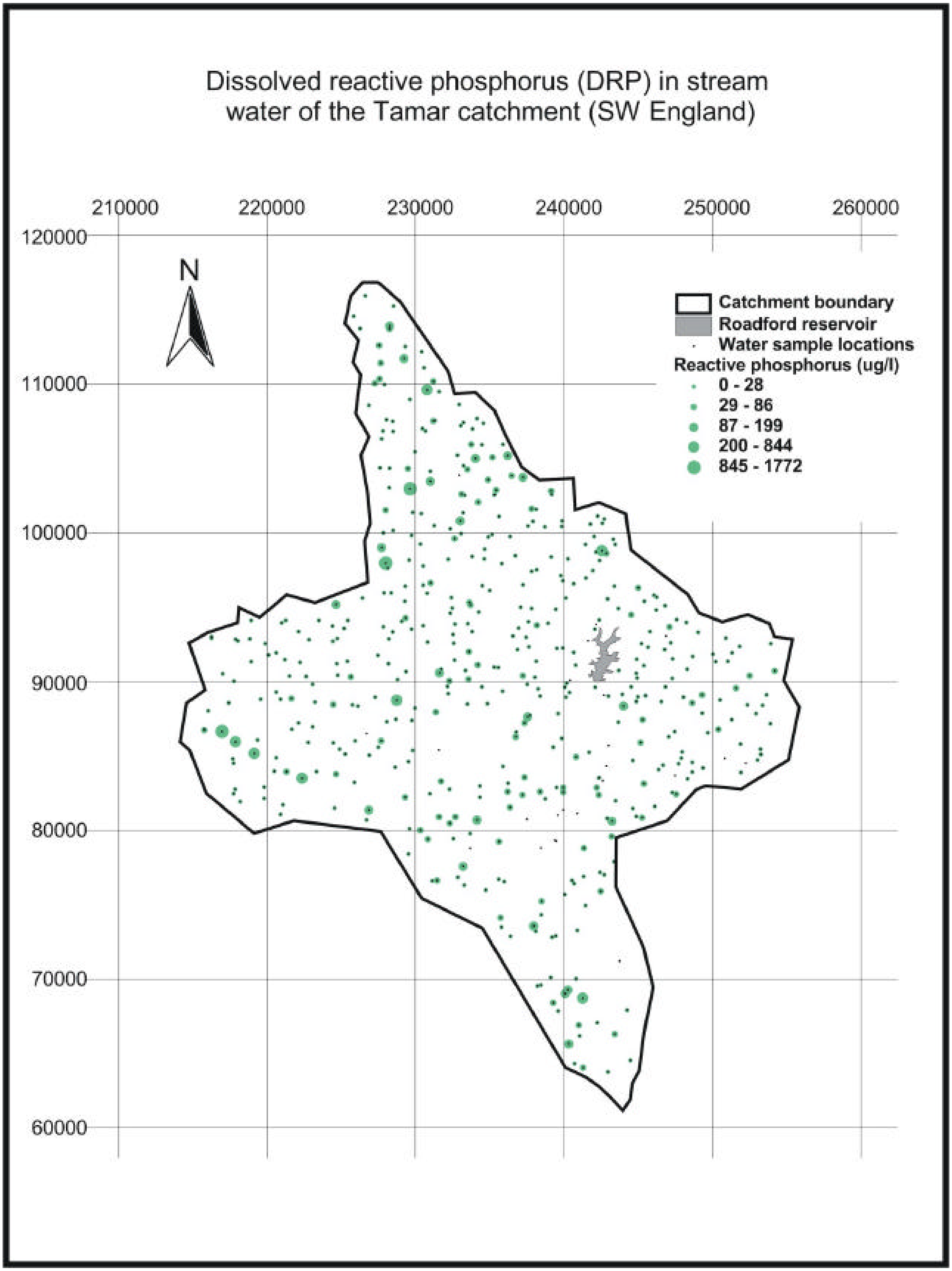

Cr (chromium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Cr (ug/l)
> 0.505 (99%ile)
> 0.26 (95%ile)
> 0.17 (90%ile)
> 0.11 (75%ile)
> 0.07 (50%ile)
> 0.05 (25%ile)
> 0 (0%ile)
No Data

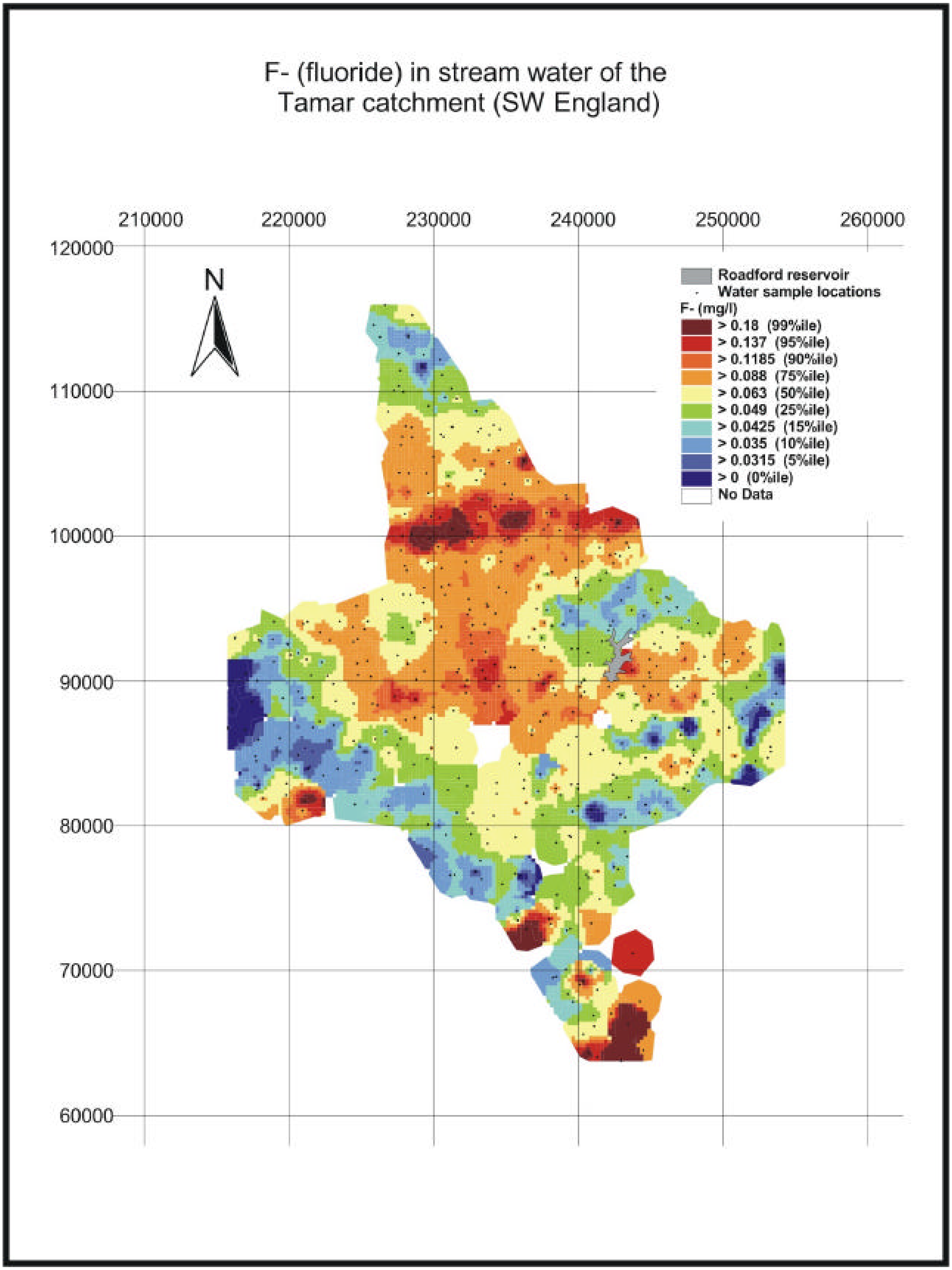

Cs (caesium) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Cs (ug/l)
> 1.005 (99%ile)
> 0.495 (95%ile)
> 0.29 (90%ile)
> 0.11 (75%ile)
> 0.05 (50%ile)
> 0.03 (25%ile)
> 0.02 (15%ile)
> 0 (0%ile)
No Data

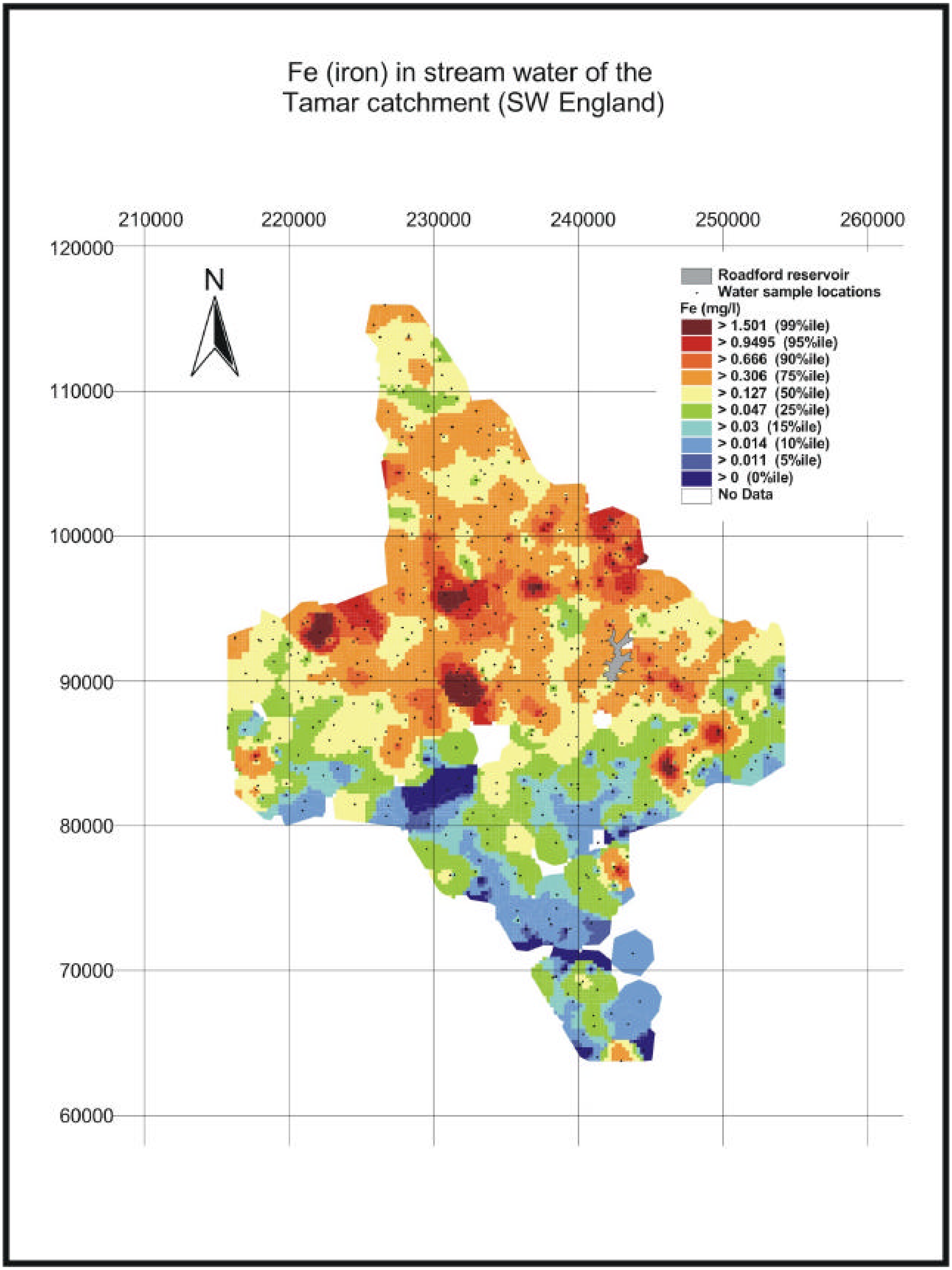
Cu (copper) in stream water of the Tamar catchment (SW England)

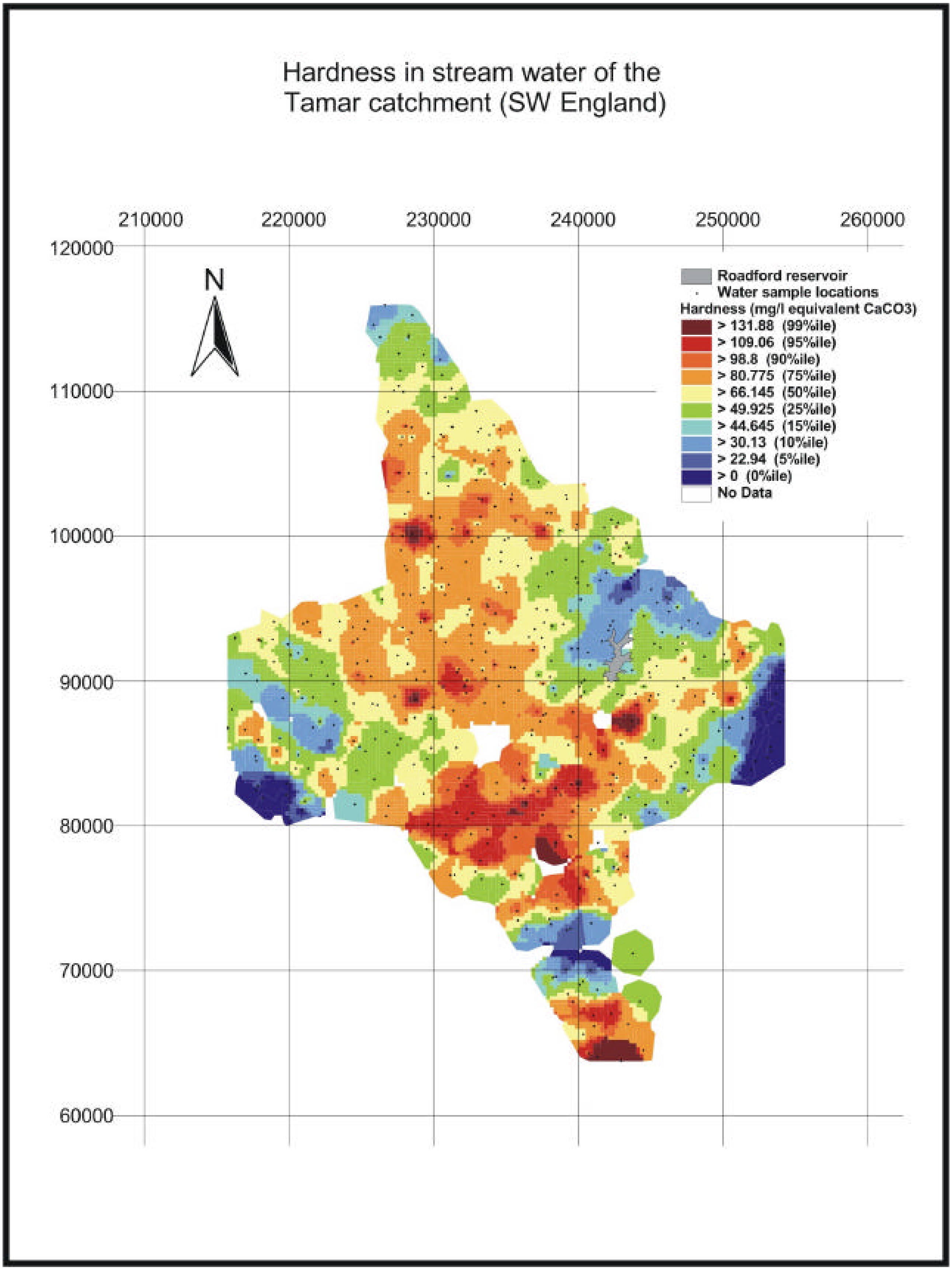


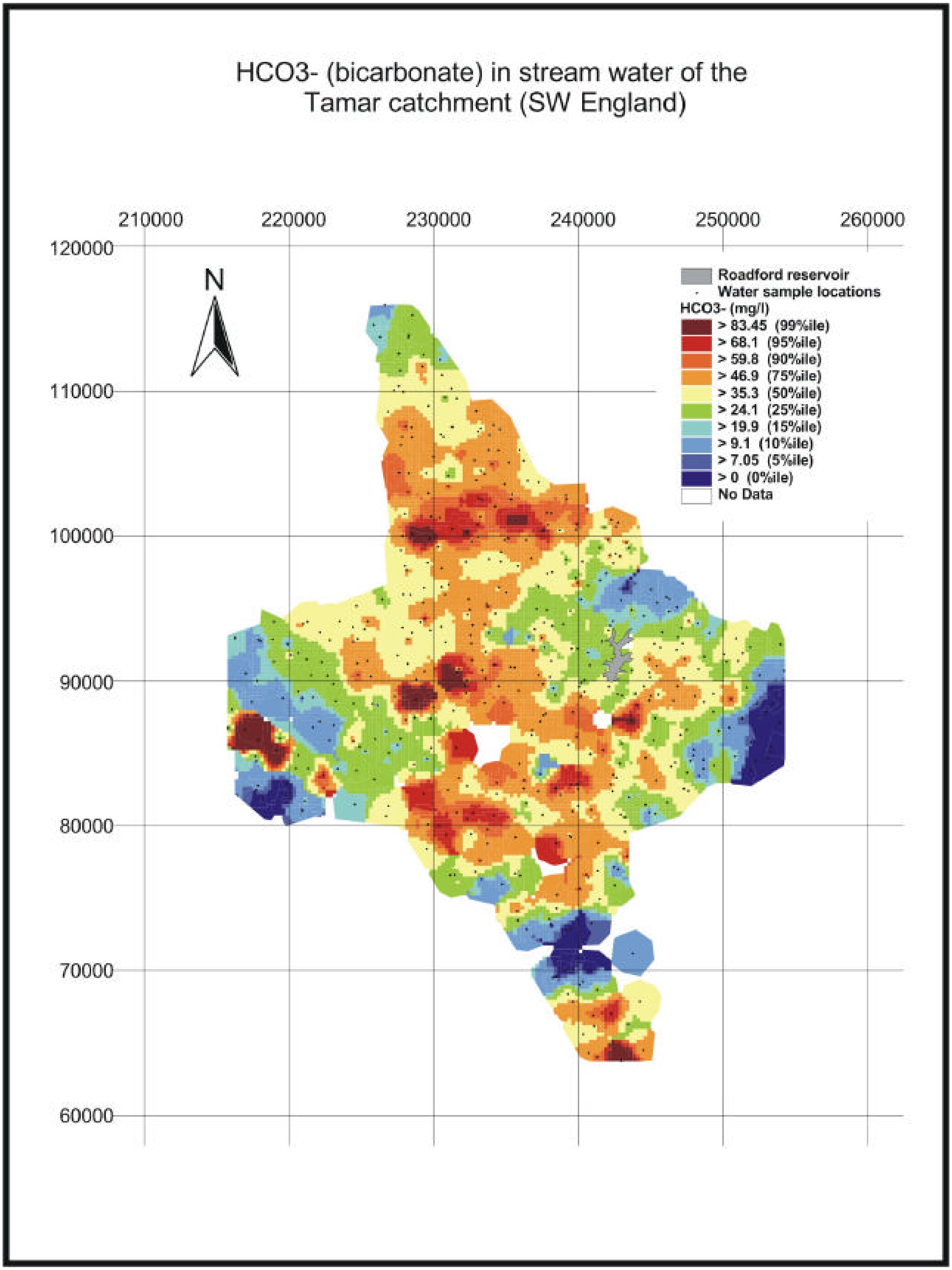

DOC (dissolved organic carbon) in stream water
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
DOC (mg/l)
> 8.005 (99%ile)
> 6.395 (95%ile)
> 5.235 (90%ile)
> 3.71 (75%ile)
> 2.705 (50%ile)
> 1.81 (25%ile)
> 1.555 (15%ile)
> 1.11 (10%ile)
> 0.95 (5%ile)
> 0 (0%ile)
No Data

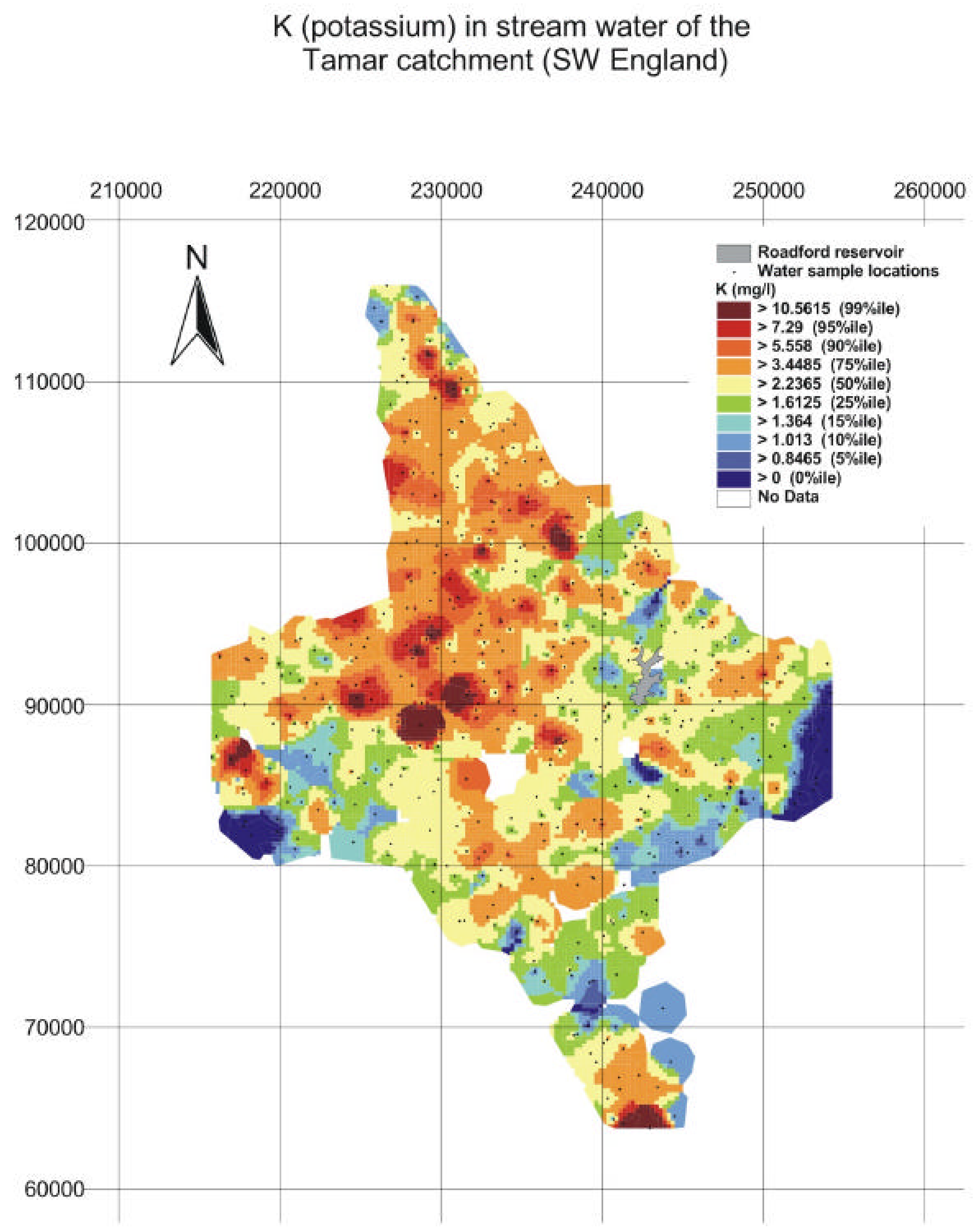

Dissolved reactive phosphorus (DRP) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Catchment boundary
Roadford reservoir
Water sample locations
Reactive phosphorus (ug/l)
0 - 28
29 - 86
87 - 199
200 - 844
845 - 1772


F- (fluoride) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
F- (mg/l)
> 0.18 (99%ile)
> 0.137 (95%ile)
> 0.1185 (90%ile)
> 0.088 (75%ile)
> 0.063 (50%ile)
> 0.049 (25%ile)
> 0.0425 (15%ile)
> 0.035 (10%ile)
> 0.0315 (5%ile)
> 0 (0%ile)
No Data

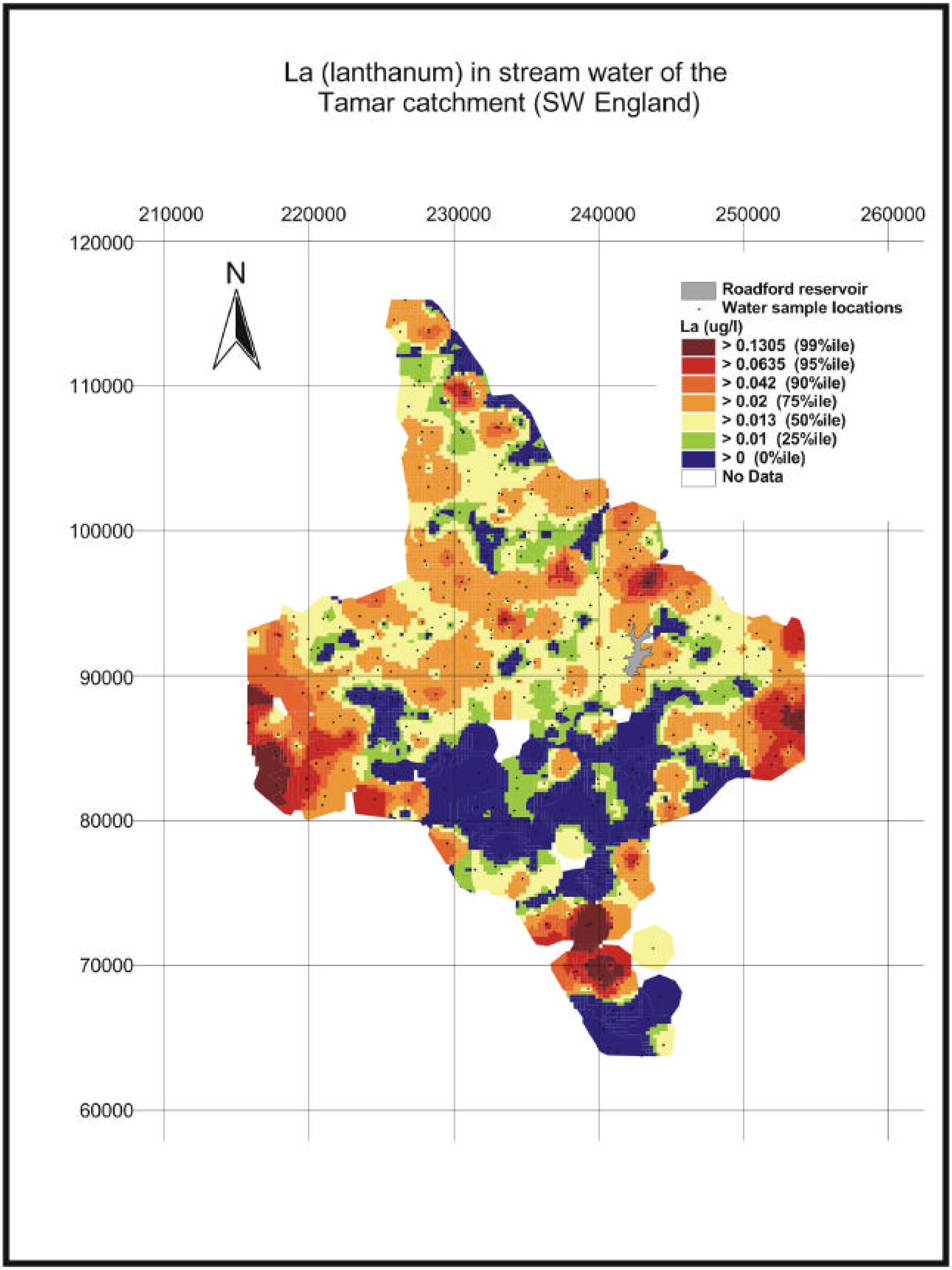

Fe (iron) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Fe (mg/l)
> 1.501 (99%ile)
> 0.9495 (95%ile)
> 0.666 (90%ile)
> 0.306 (75%ile)
> 0.127 (50%ile)
> 0.047 (25%ile)
> 0.03 (15%ile)
> 0.014 (10%ile)
> 0.011 (5%ile)
> 0 (0%ile)
No Data

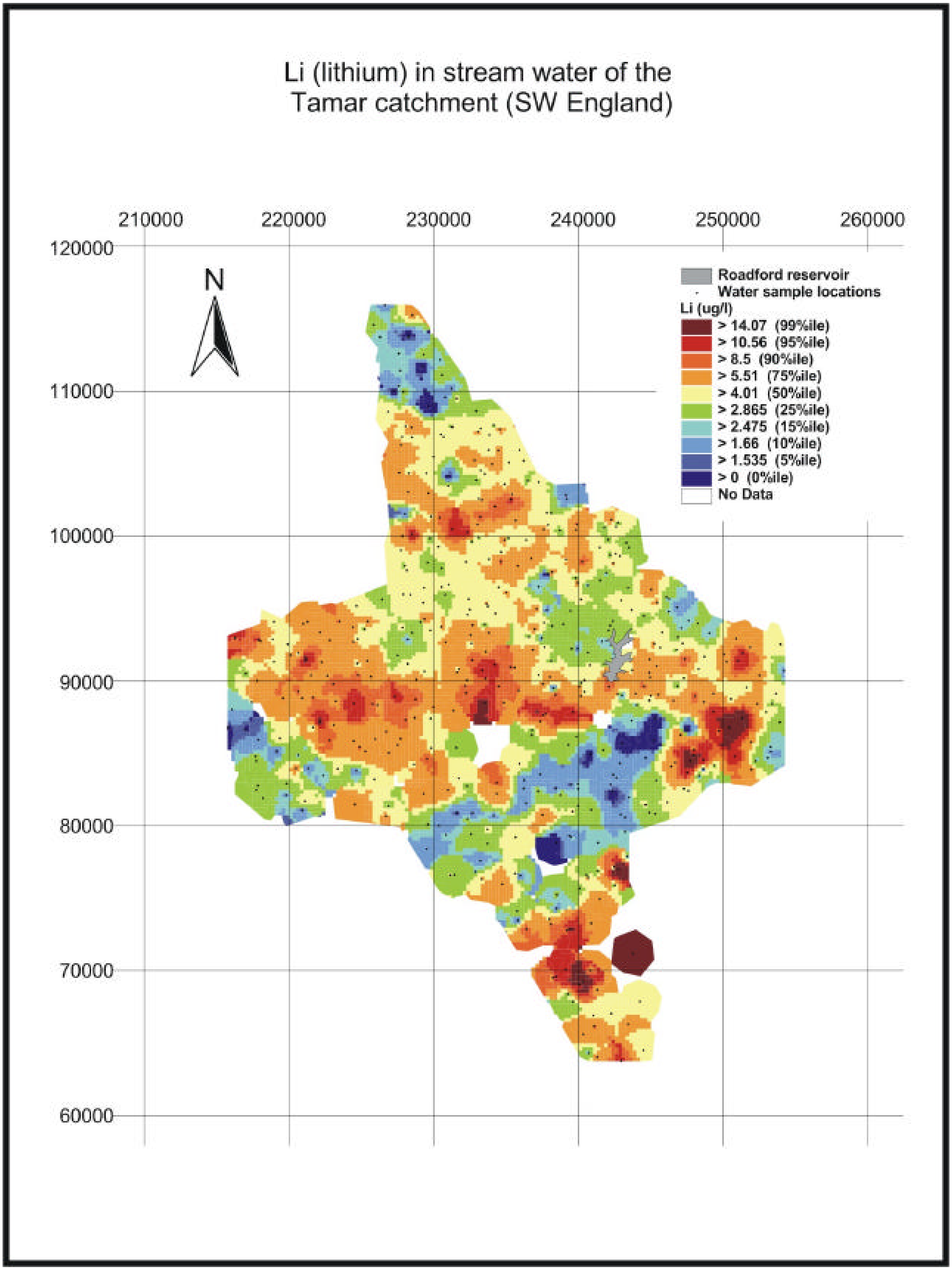

Hardness in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Hardness (mg/l equivalent CaCO3)
> 131.88 (99%ile)
> 109.06 (95%ile)
> 98.8 (90%ile)
> 80.775 (75%ile)
> 66.145 (50%ile)
> 49.925 (25%ile)
> 44.645 (15%ile)
> 30.13 (10%ile)
> 22.94 (5%ile)
> 0 (0%ile)
No Data

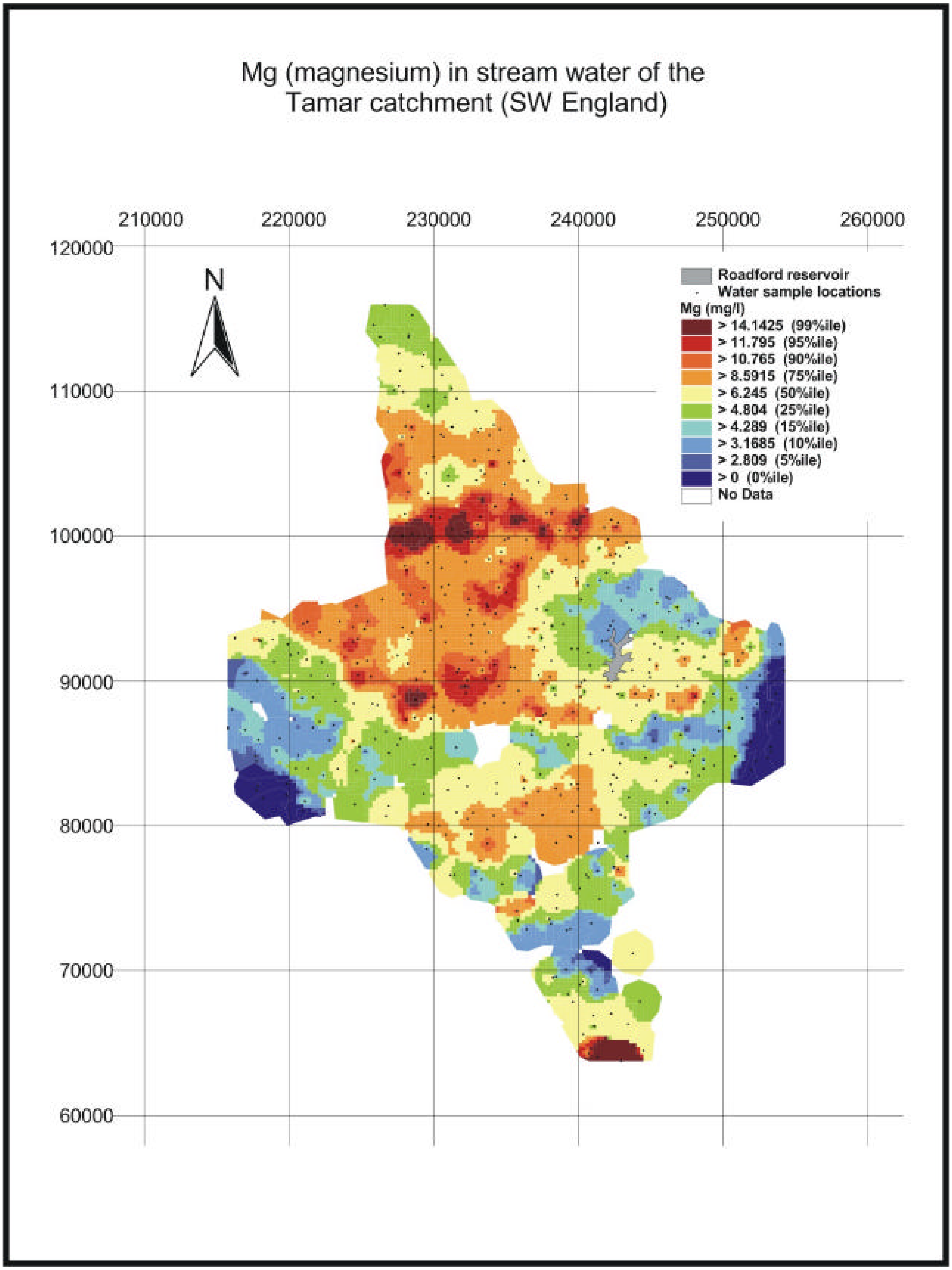

HCO3- (bicarbonate) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
HCO3- (mg/l)
> 83.45 (99%ile)
> 68.1 (95%ile)
> 59.8 (90%ile)
> 46.9 (75%ile)
> 35.3 (50%ile)
> 24.1 (25%ile)
> 19.9 (15%ile)
> 9.1 (10%ile)
> 7.05 (5%ile)
> 0 (0%ile)
No Data

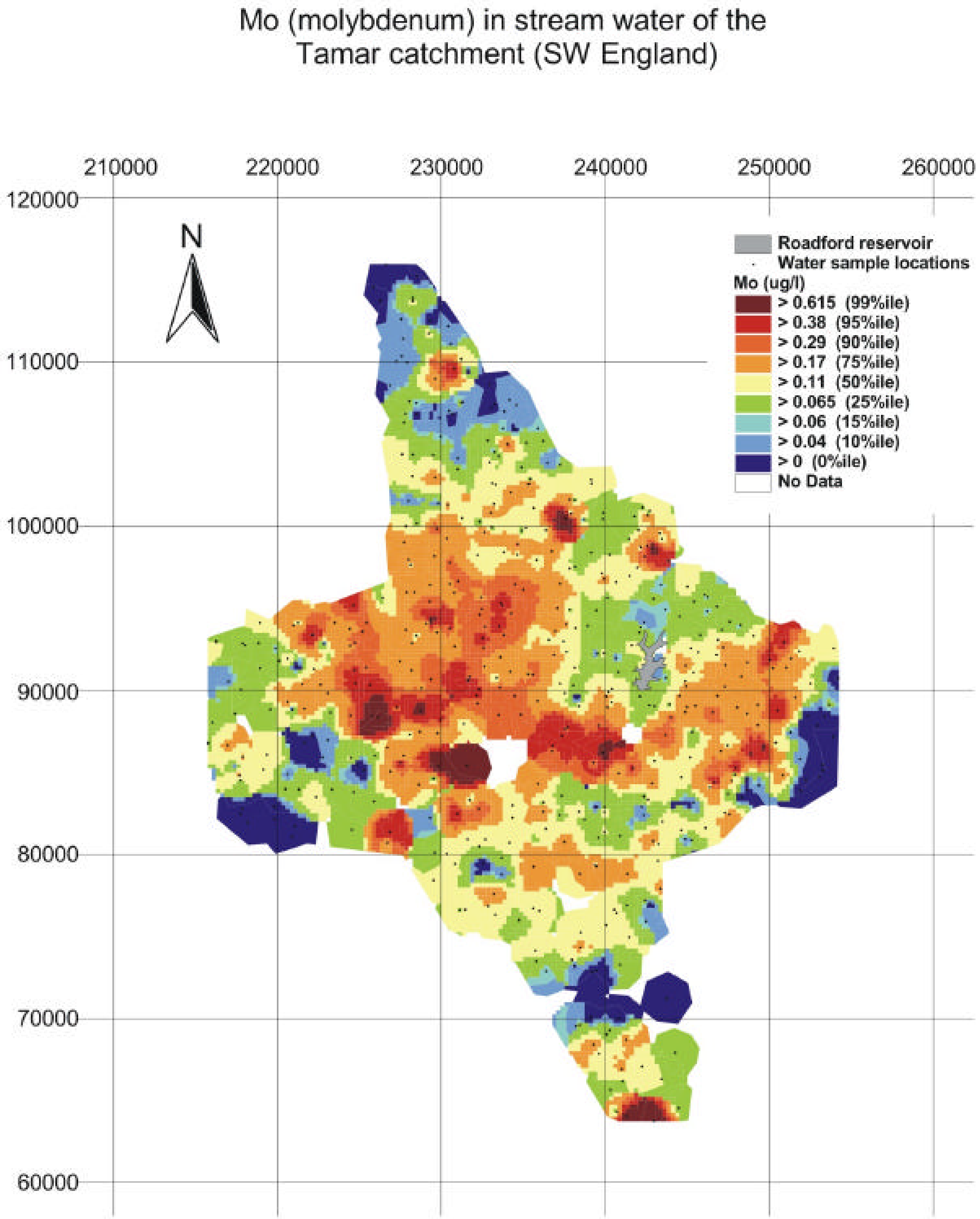


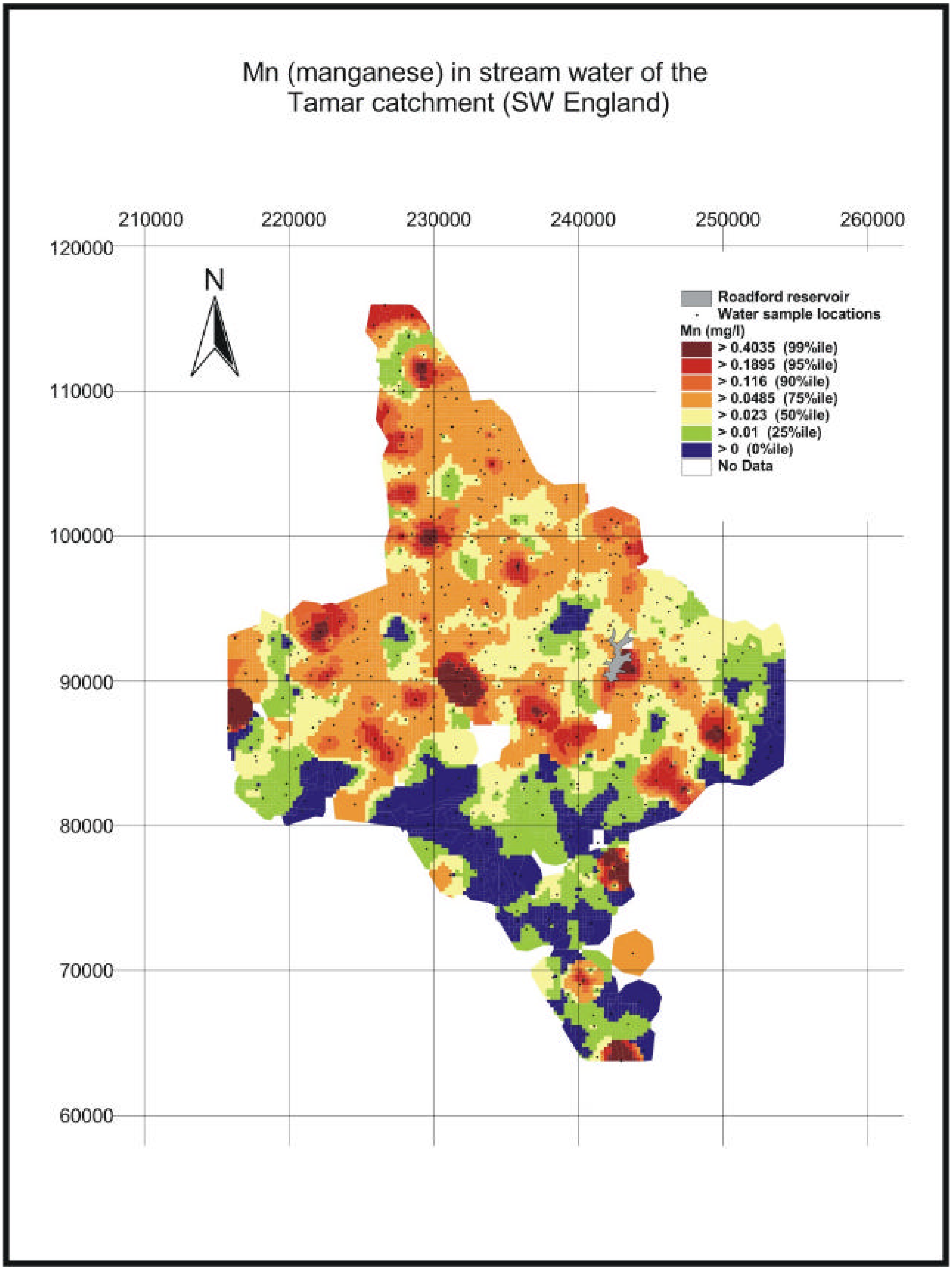
K (potassium) in stream water of the Tamar catchment (SW England)

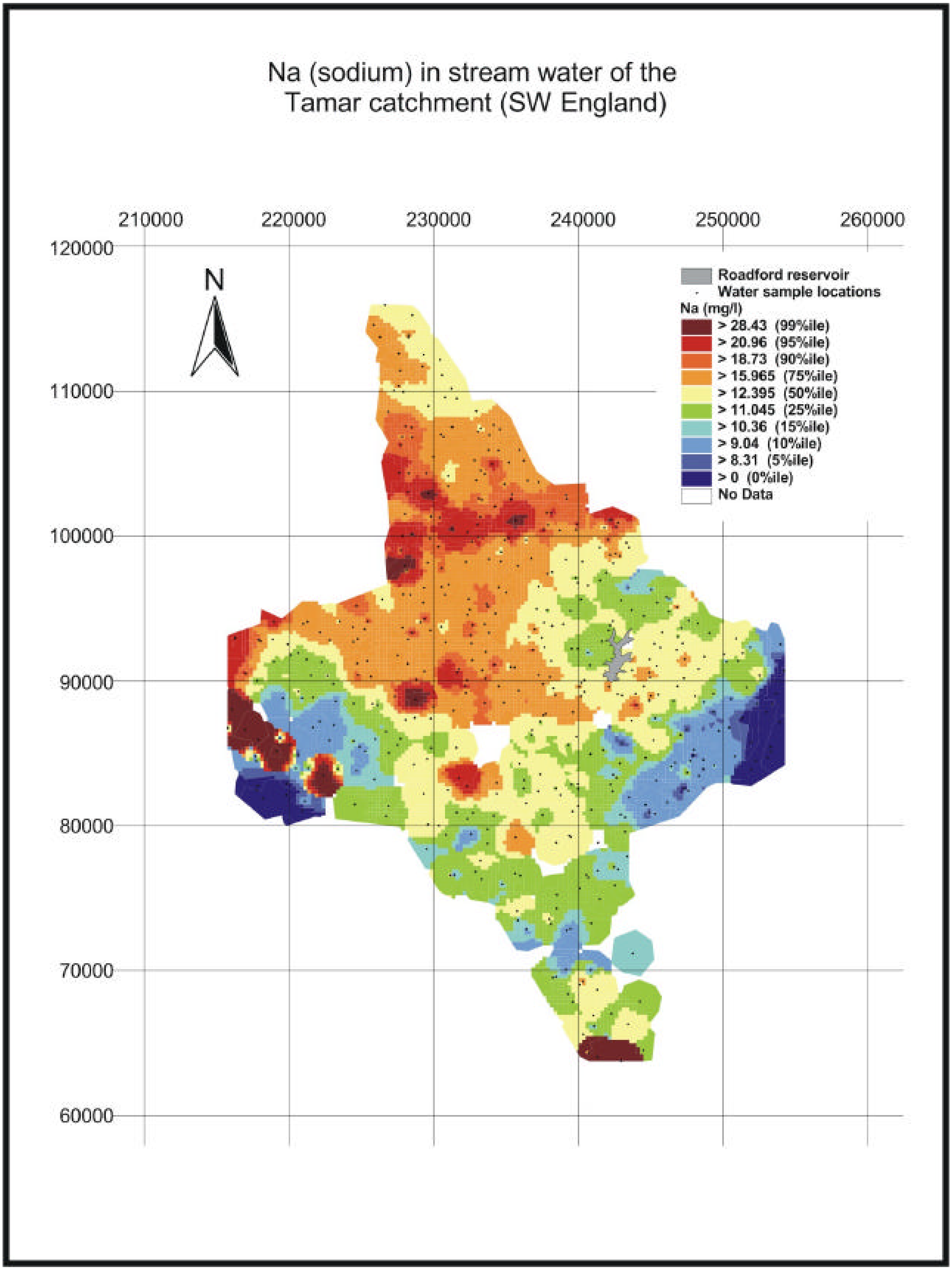

La (lanthanum) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
La (ug/l)
> 0.1305 (99%ile)
> 0.0635 (95%ile)
> 0.042 (90%ile)
> 0.02 (75%ile)
> 0.013 (50%ile)
> 0.01 (25%ile)
> 0 (0%ile)
No Data

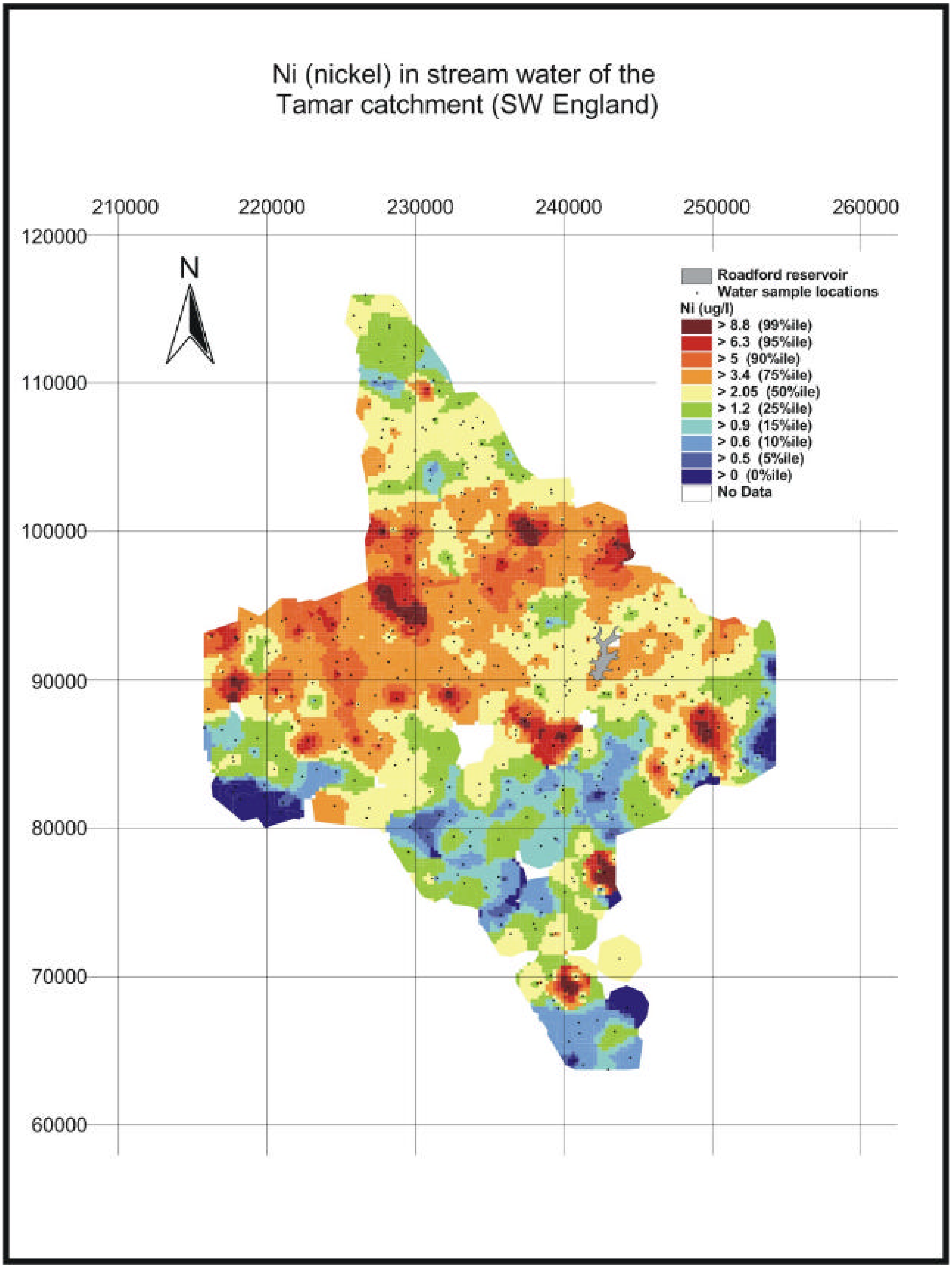

Li (lithium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Li (ug/l)
> 14.07 (99%ile)
> 10.56 (95%ile)
> 8.5 (90%ile)
> 5.51 (75%ile)
> 4.01 (50%ile)
> 2.865 (25%ile)
> 2.475 (15%ile)
> 1.66 (10%ile)
> 1.535 (5%ile)
> 0 (0%ile)
No Data

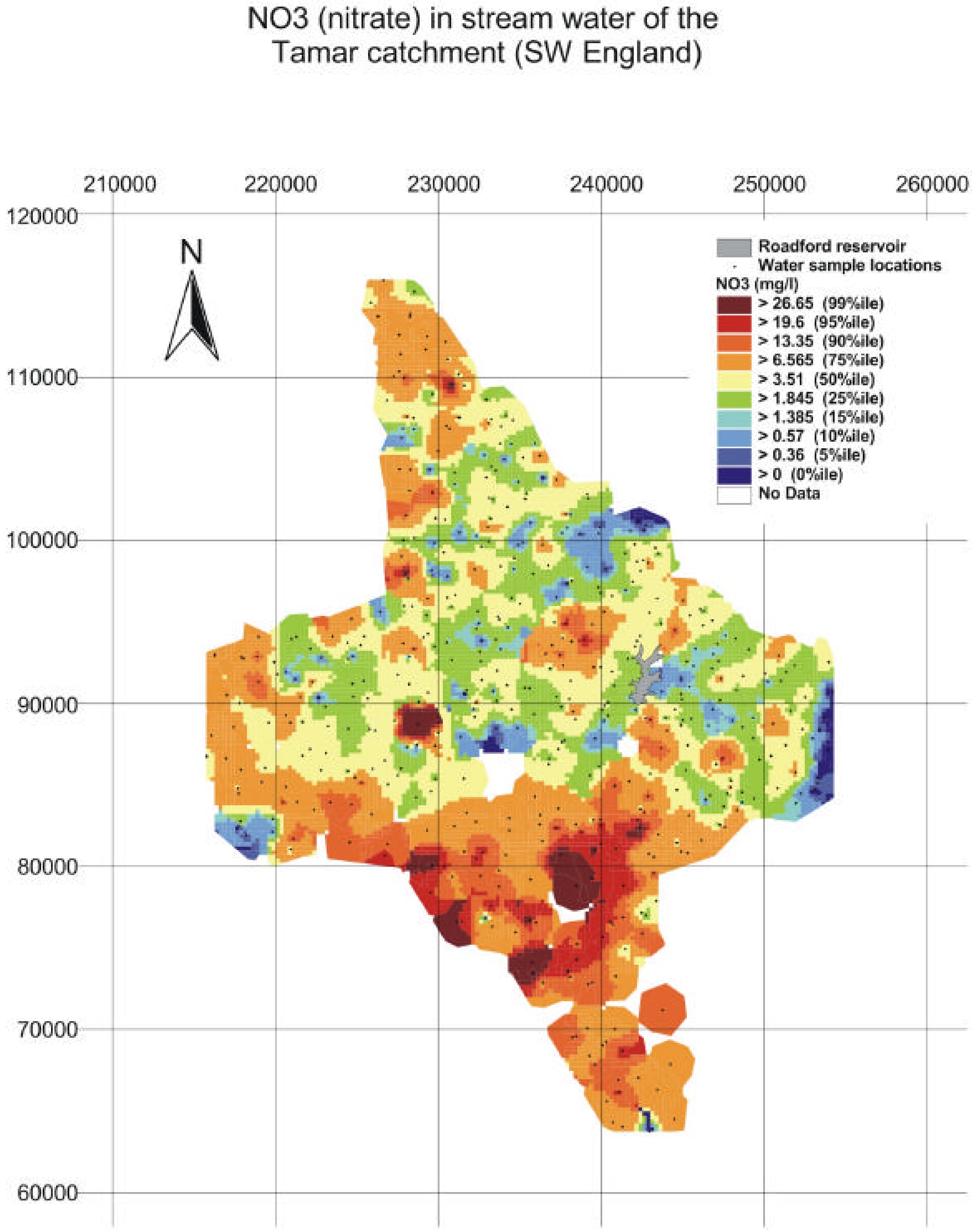

Mg (magnesium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Mg (mg/l)
> 14.1425 (99%ile)
> 11.795 (95%ile)
> 10.765 (90%ile)
> 8.5915 (75%ile)
> 6.245 (50%ile)
> 4.804 (25%ile)
> 4.289 (15%ile)
> 3.1685 (10%ile)
> 2.809 (5%ile)
> 0 (0%ile)
No Data

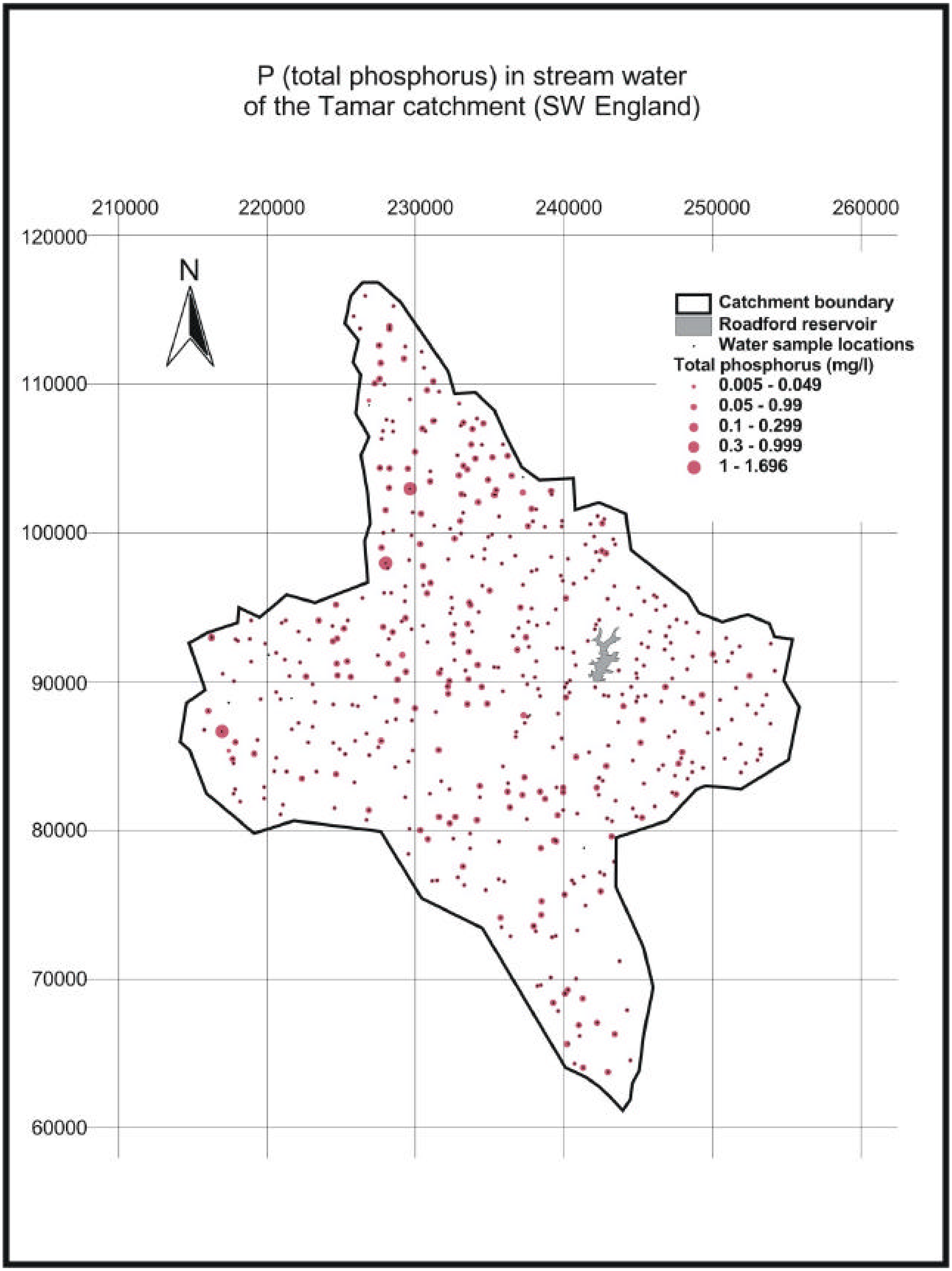

Mo (molybdenum) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Mo (ug/l)
> 0.615 (99%ile)
> 0.38 (95%ile)
> 0.29 (90%ile)
> 0.17 (75%ile)
> 0.11 (50%ile)
> 0.065 (25%ile)
> 0.06 (15%ile)
> 0.04 (10%ile)
> 0 (0%ile)
No Data

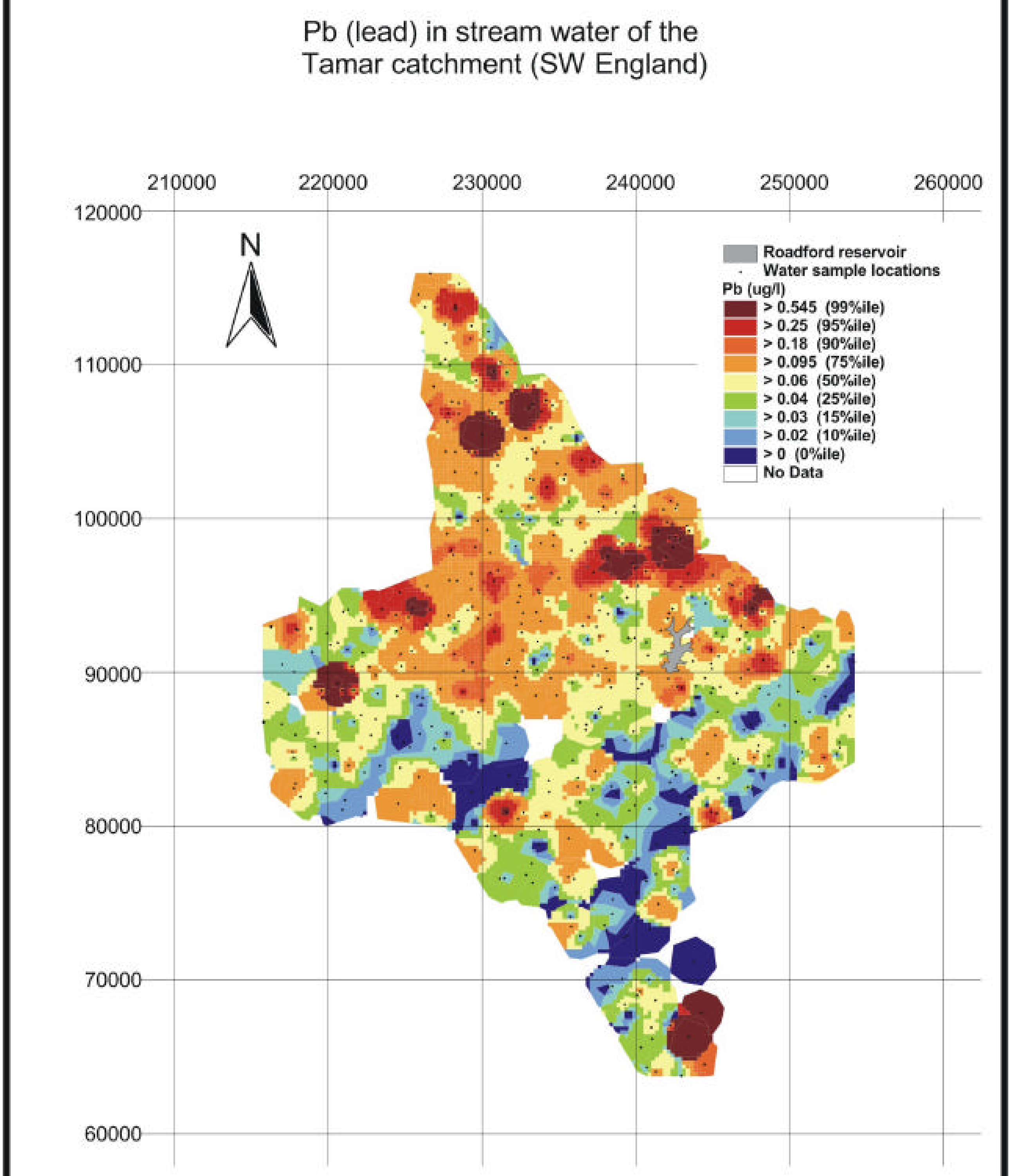

Mn (manganese) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Mn (mg/l)
> 0.4035 (99%ile)
> 0.1895 (95%ile)
> 0.116 (90%ile)
> 0.0485 (75%ile)
> 0.023 (50%ile)
> 0.01 (25%ile)
> 0 (0%ile)
No Data

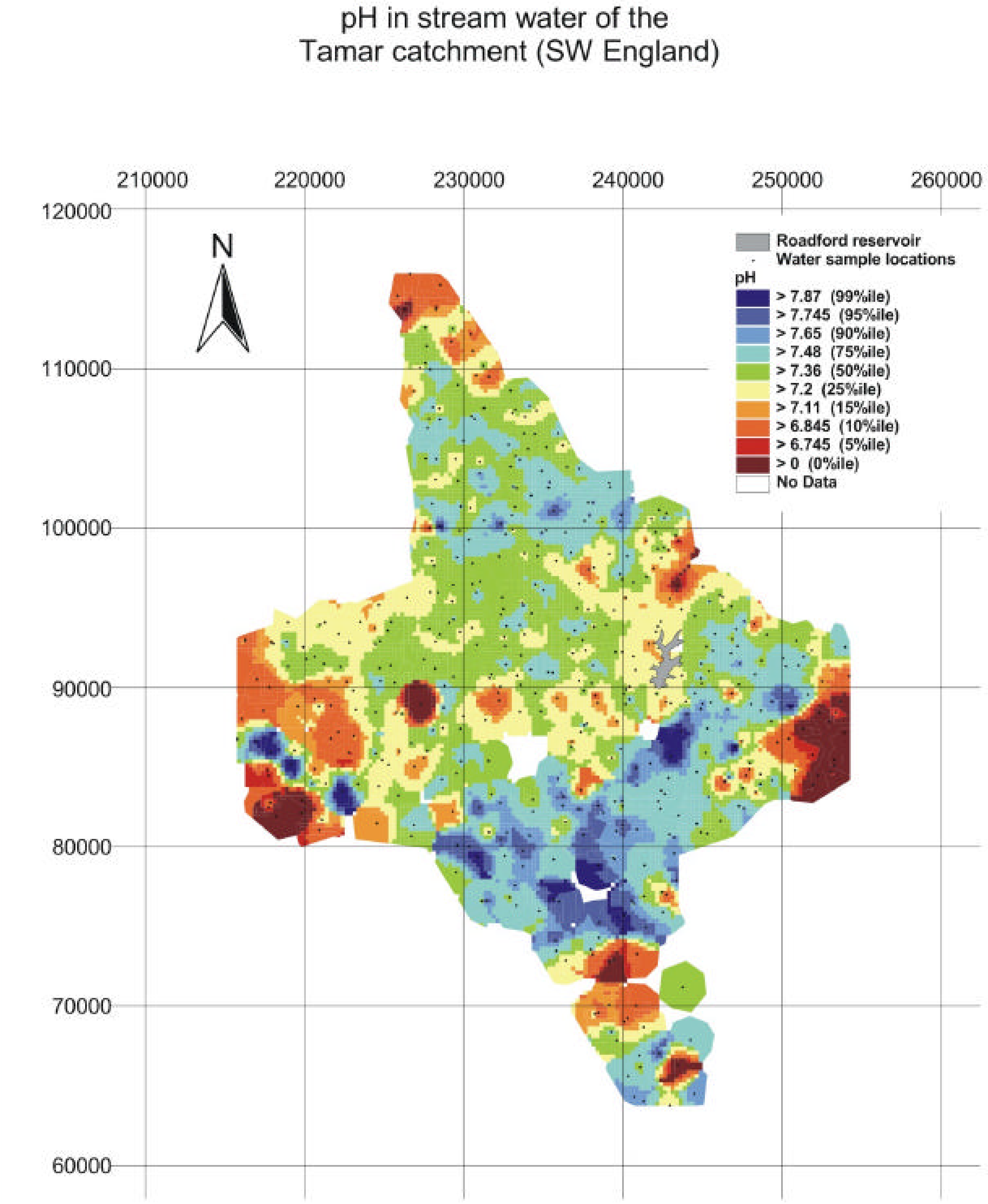

Na (sodium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Na (mg/l)
> 28.43 (99%ile)
> 20.96 (95%ile)
> 18.73 (90%ile)
> 15.965 (75%ile)
> 12.395 (50%ile)
> 11.045 (25%ile)
> 10.36 (15%ile)
> 9.04 (10%ile)
> 8.31 (5%ile)
> 0 (0%ile)
No Data

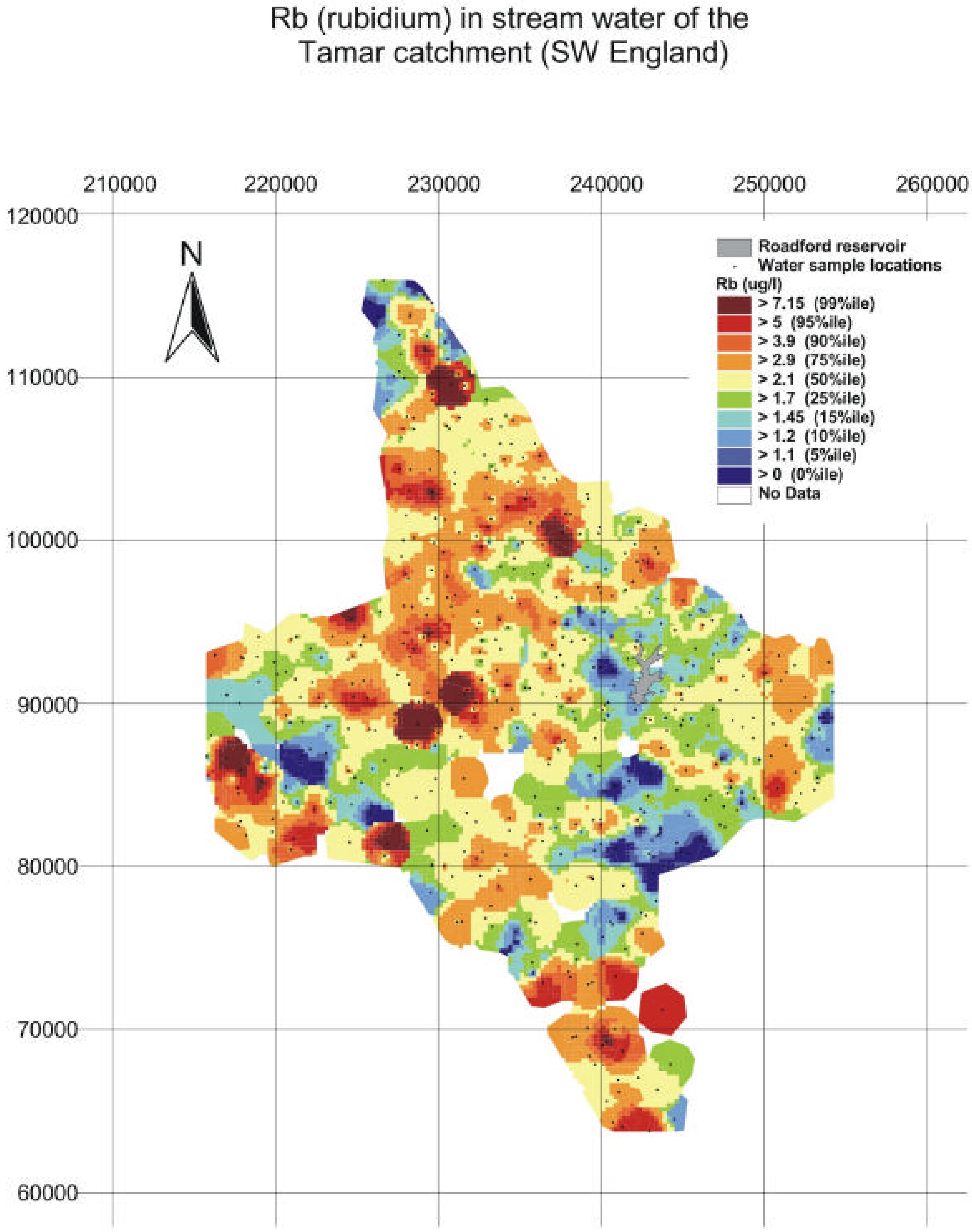

Ni (nickel) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Ni (ug/l)
> 8.8 (99%ile)
> 6.3 (95%ile)
> 5 (90%ile)
> 3.4 (75%ile)
> 2.05 (50%ile)
> 1.2 (25%ile)
> 0.9 (15%ile)
> 0.6 (10%ile)
> 0.5 (5%ile)
> 0 (0%ile)
No Data

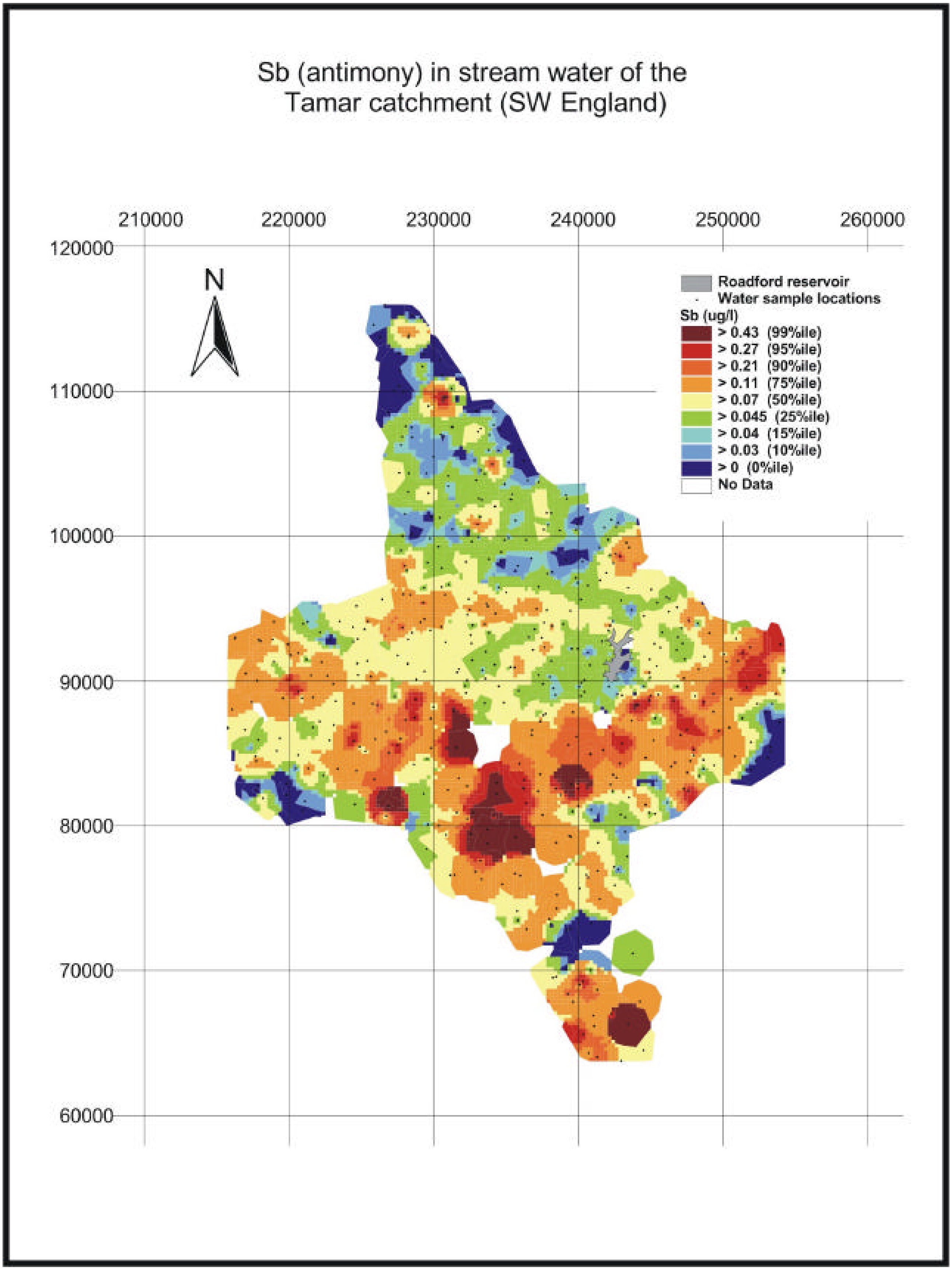

NO3 (nitrate) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
NO3 (mg/l)
> 26.65 (99%ile)
> 19.6 (95%ile)
> 13.35 (90%ile)
> 6.565 (75%ile)
> 3.51 (50%ile)
> 1.845 (25%ile)
> 1.385 (15%ile)
> 0.57 (10%ile)
> 0.36 (5%ile)
> 0 (0%ile)
No Data

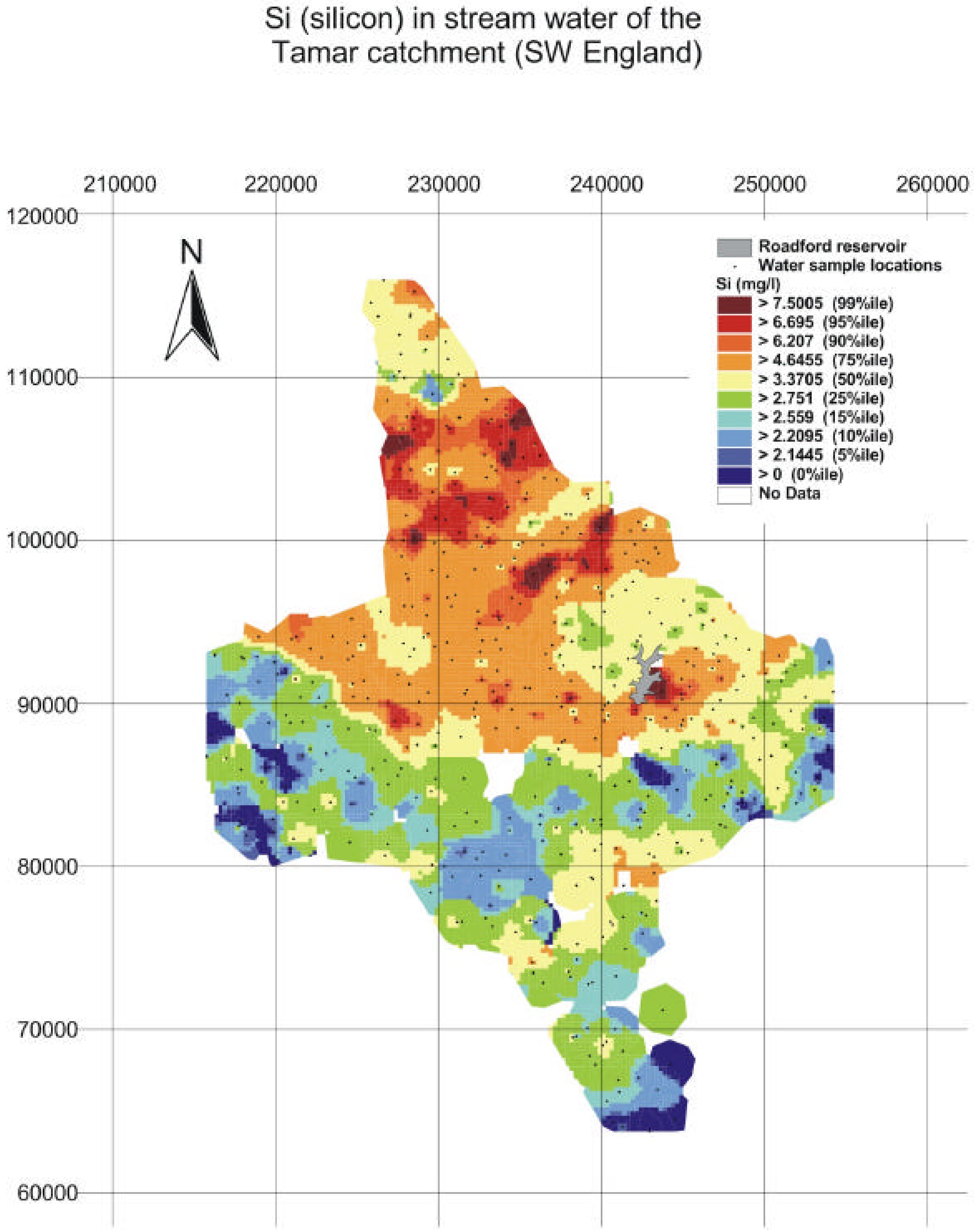

P (total phosphorus) in stream water
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Catchment boundary
Roadford reservoir
Water sample locations
Total phosphorus (mg/l)
0.005 - 0.049
0.05 - 0.99
0.1 - 0.299
0.3 - 0.999
1 - 1.696


Pb (lead) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Pb (ug/l)
> 0.545 (99%ile)
> 0.25 (95%ile)
> 0.18 (90%ile)
> 0.095 (75%ile)
> 0.06 (50%ile)
> 0.04 (25%ile)
> 0.03 (15%ile)
> 0.02 (10%ile)
> 0 (0%ile)
No Data

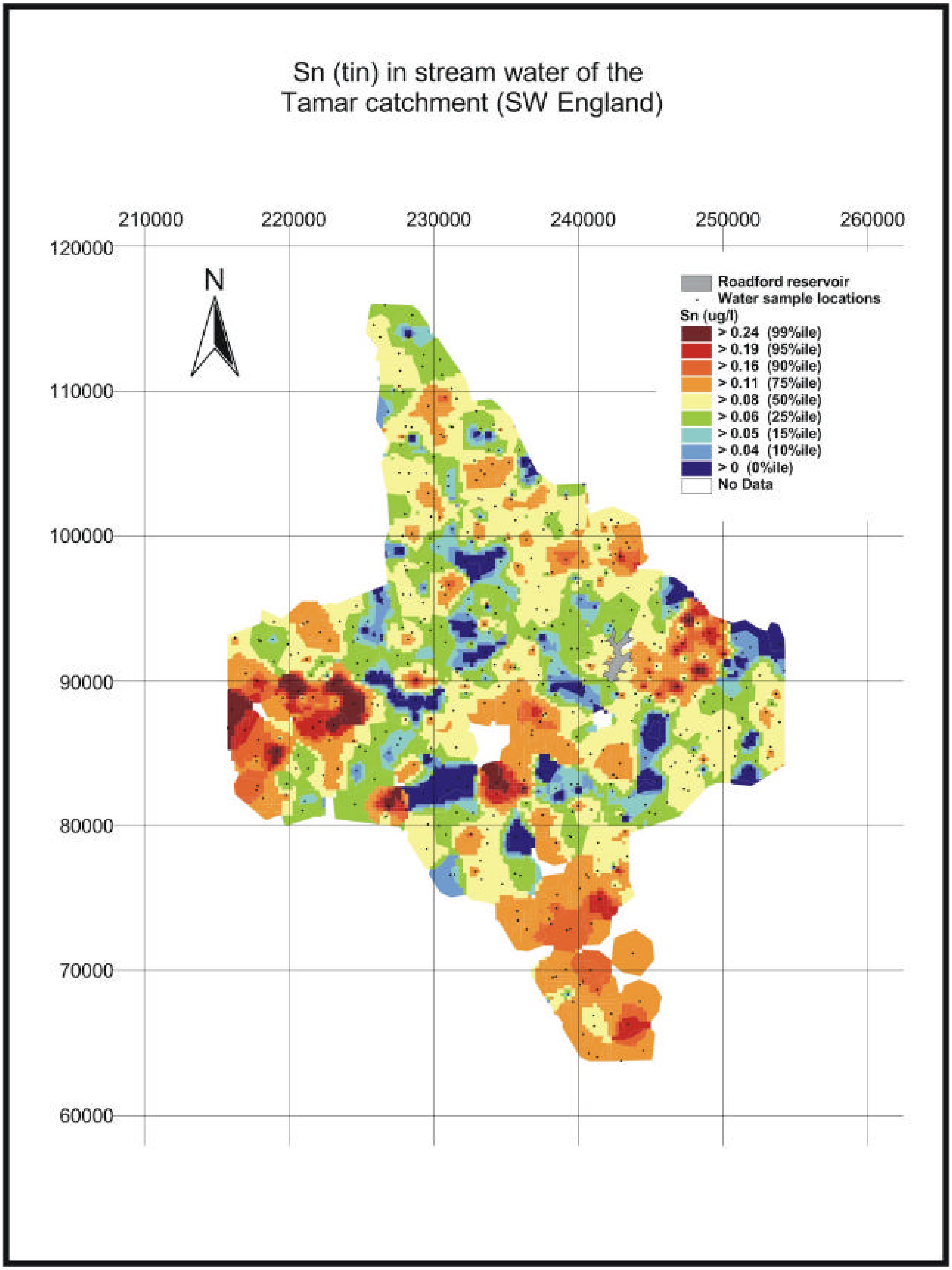

pH in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
pH
> 7.87 (99%ile)
> 7.745 (95%ile)
> 7.65 (90%ile)
> 7.48 (75%ile)
> 7.36 (50%ile)
> 7.2 (25%ile)
> 7.11 (15%ile)
> 6.845 (10%ile)
> 6.745 (5%ile)
> 0 (0%ile)
No Data

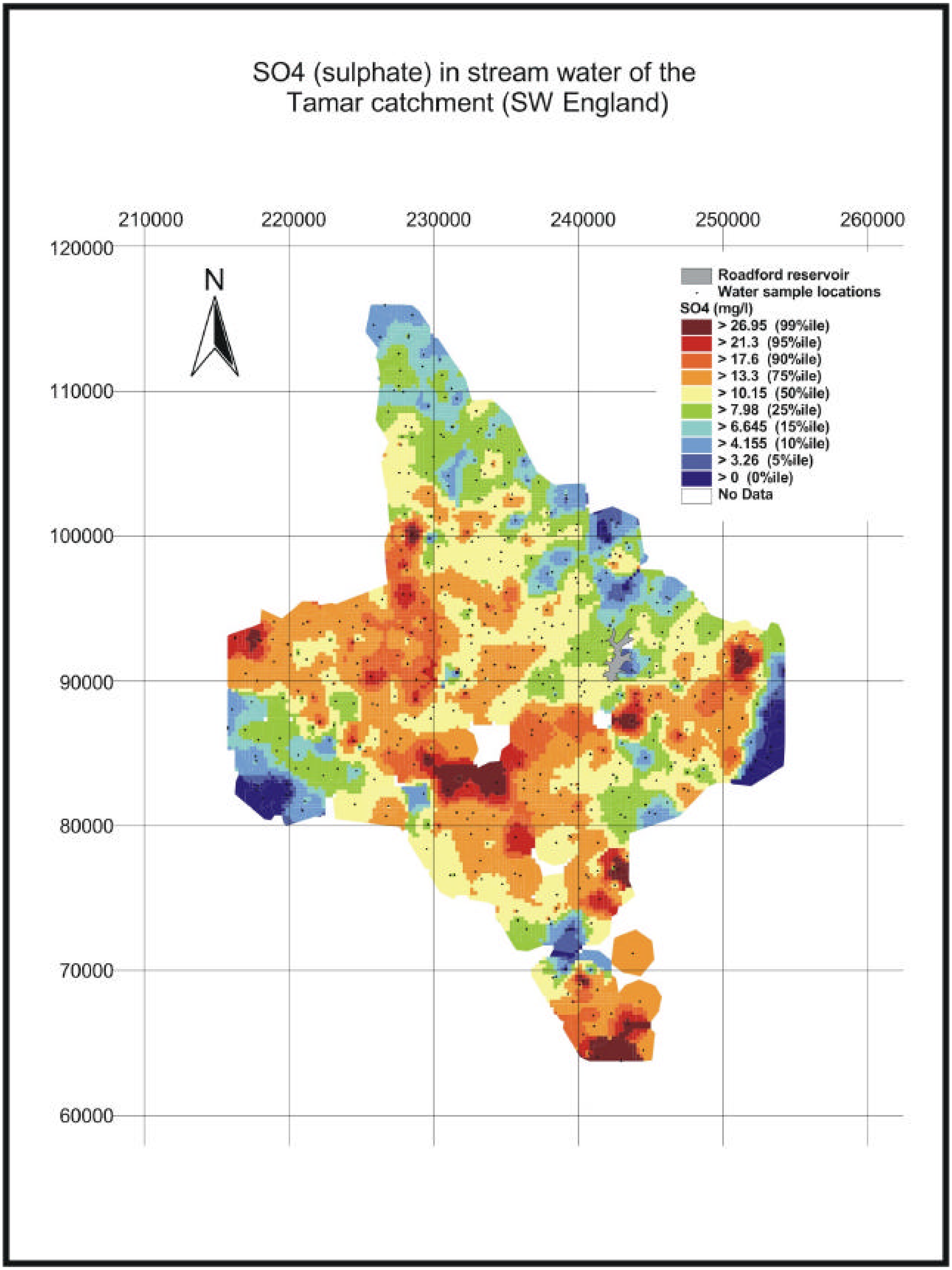

Rb (rubidium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Rb (ug/l)
> 7.15 (99%ile)
> 5 (95%ile)
> 3.9 (90%ile)
> 2.9 (75%ile)
> 2.1 (50%ile)
> 1.7 (25%ile)
> 1.45 (15%ile)
> 1.2 (10%ile)
> 1.1 (5%ile)
> 0 (0%ile)
No Data

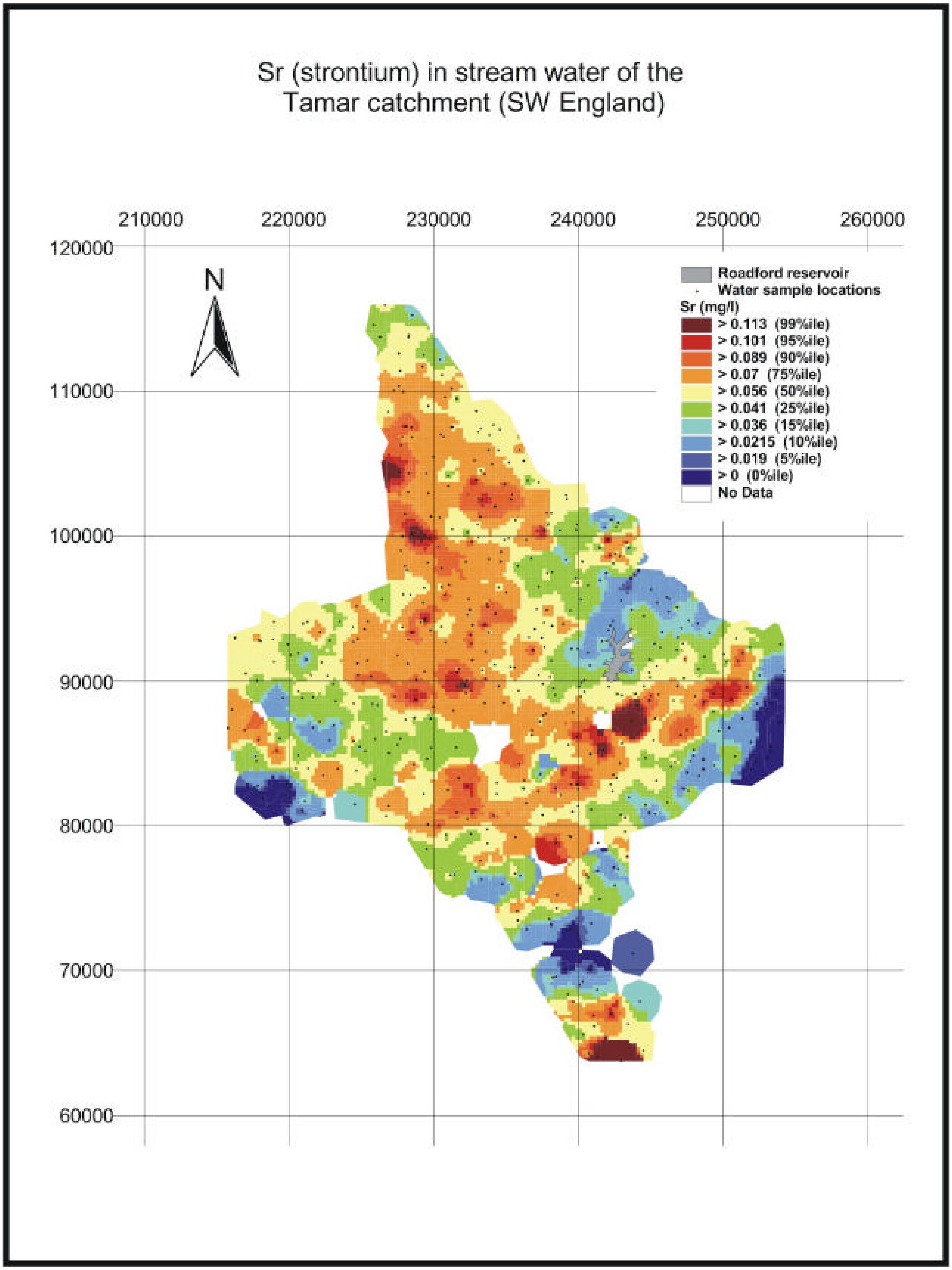

Sb (antimony) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Sb (ug/l)
> 0.43 (99%ile)
> 0.27 (95%ile)
> 0.21 (90%ile)
> 0.11 (75%ile)
> 0.07 (50%ile)
> 0.045 (25%ile)
> 0.04 (15%ile)
> 0.03 (10%ile)
> 0 (0%ile)
No Data

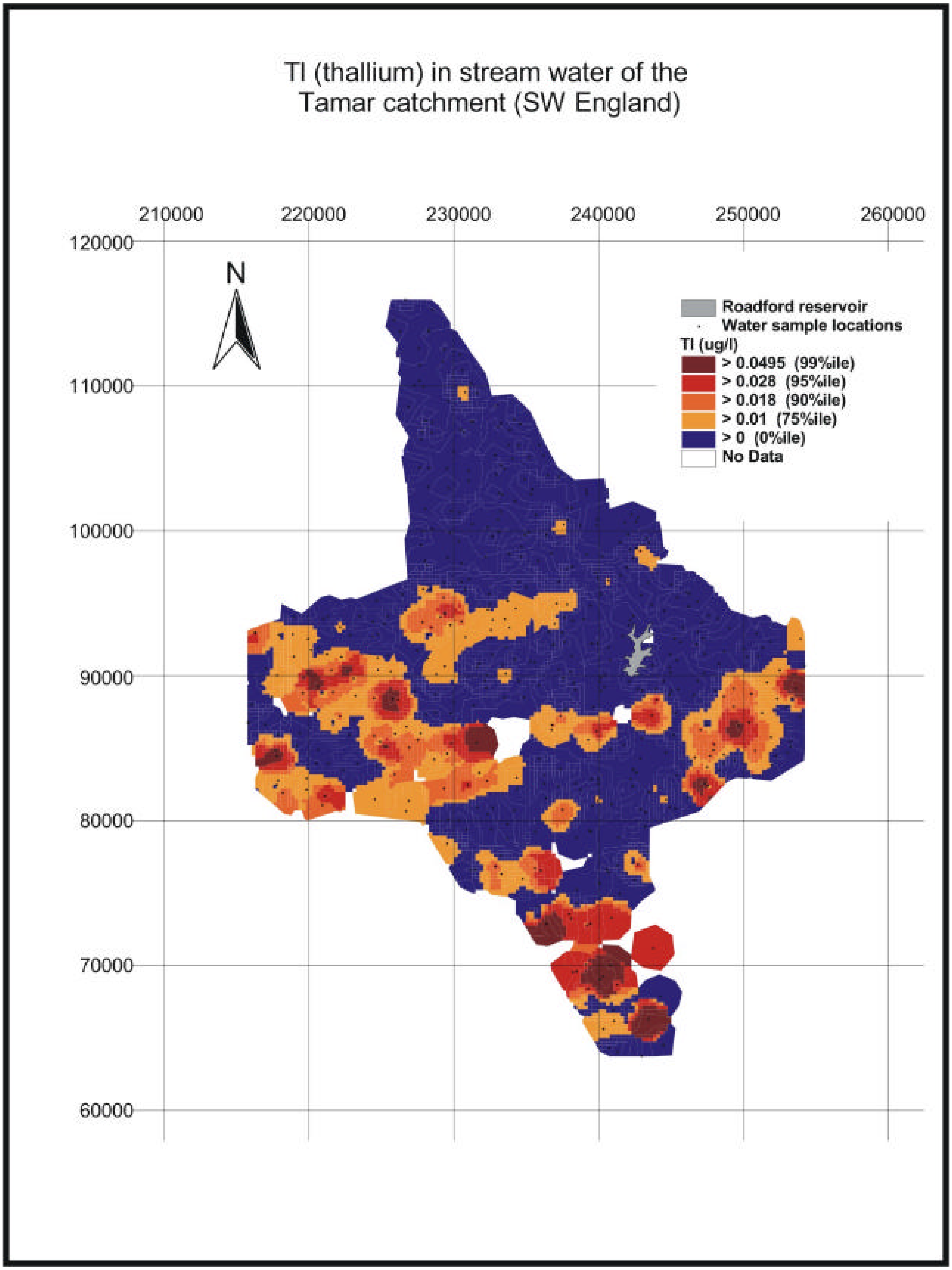


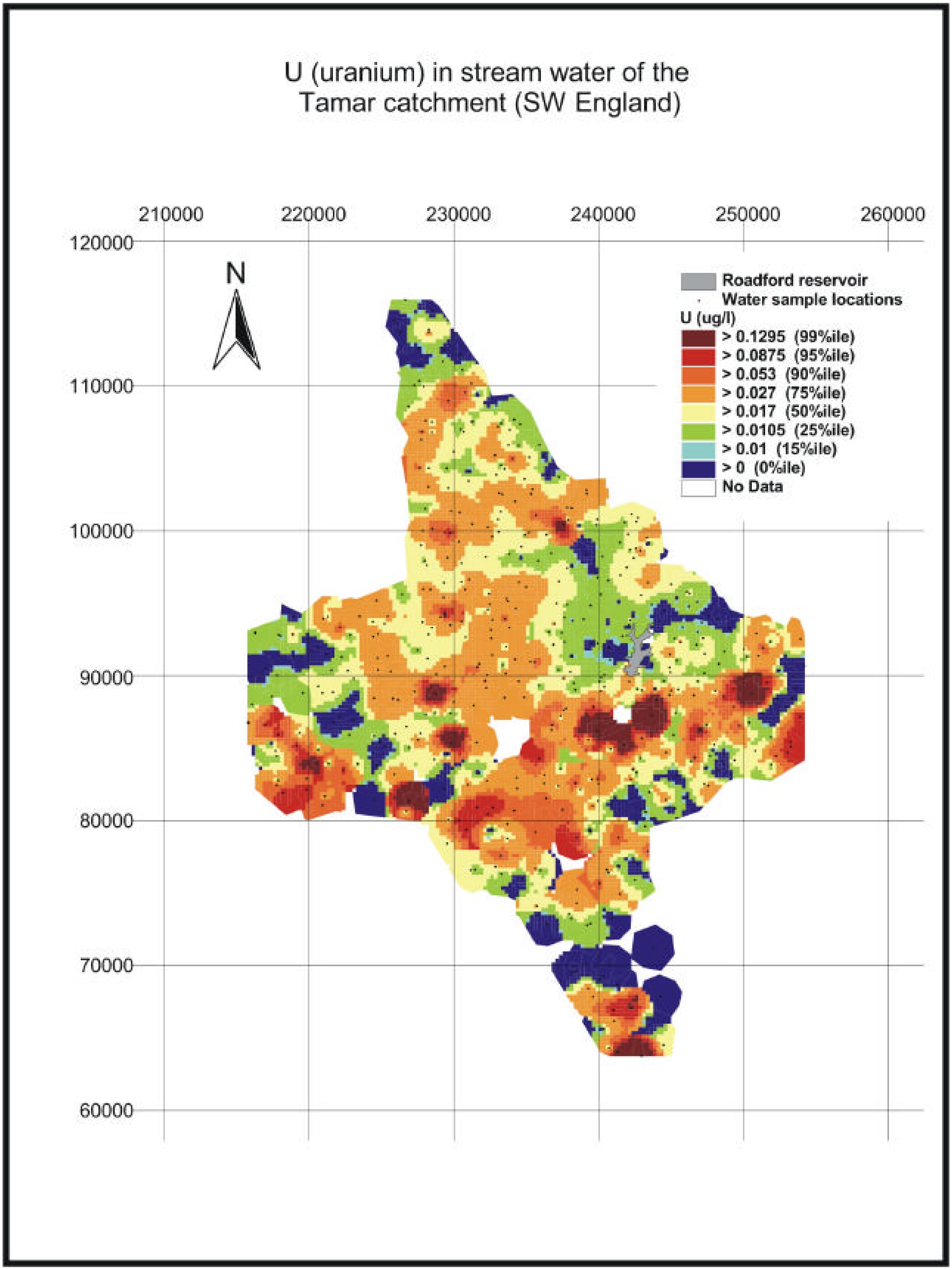
Si (silicon) in stream water of the Tamar catchment (SW England)

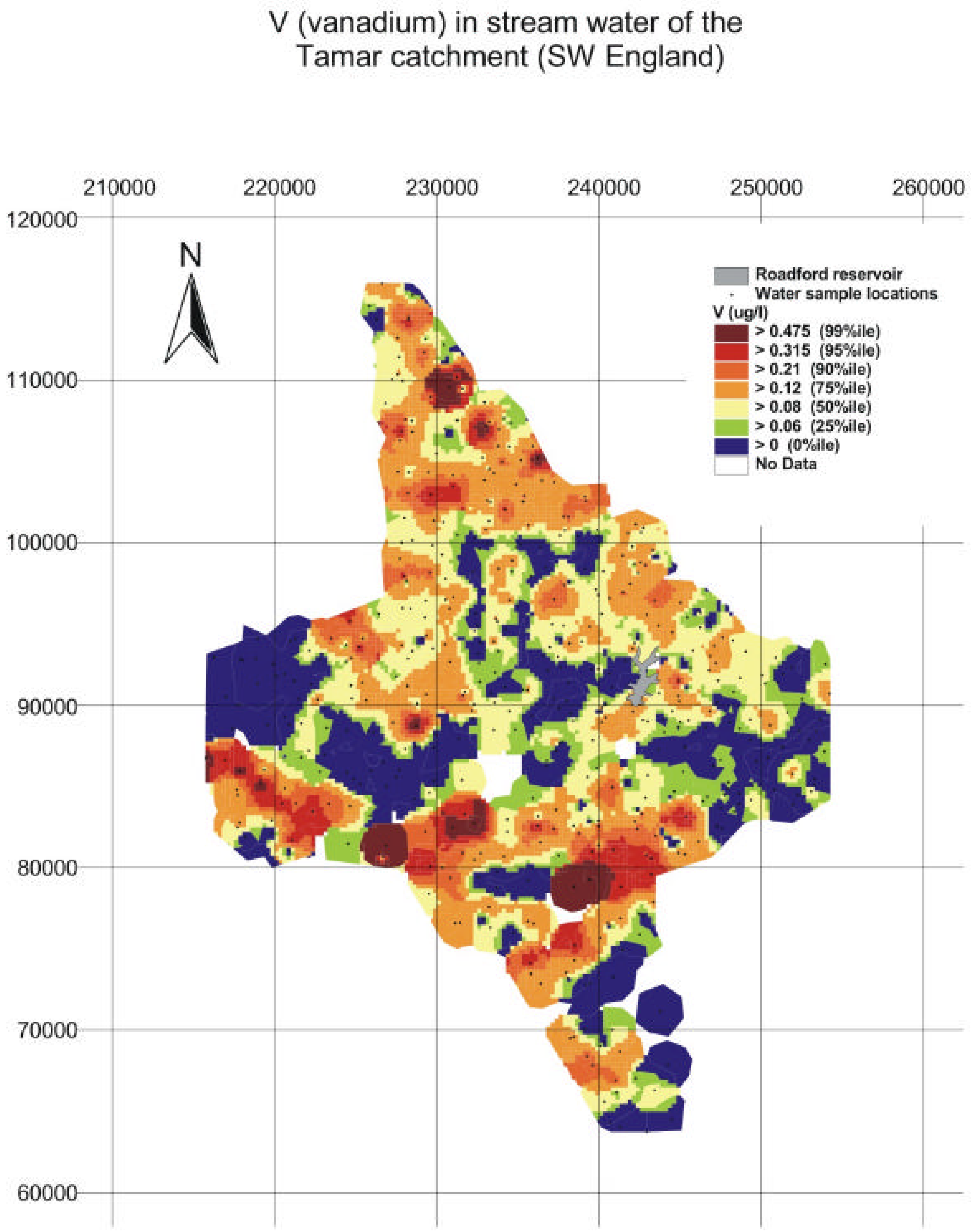

Sn (tin) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Sn (ug/l)
> 0.24 (99%ile)
> 0.19 (95%ile)
> 0.16 (90%ile)
> 0.11 (75%ile)
> 0.08 (50%ile)
> 0.06 (25%ile)
> 0.05 (15%ile)
> 0.04 (10%ile)
> 0 (0%ile)
No Data

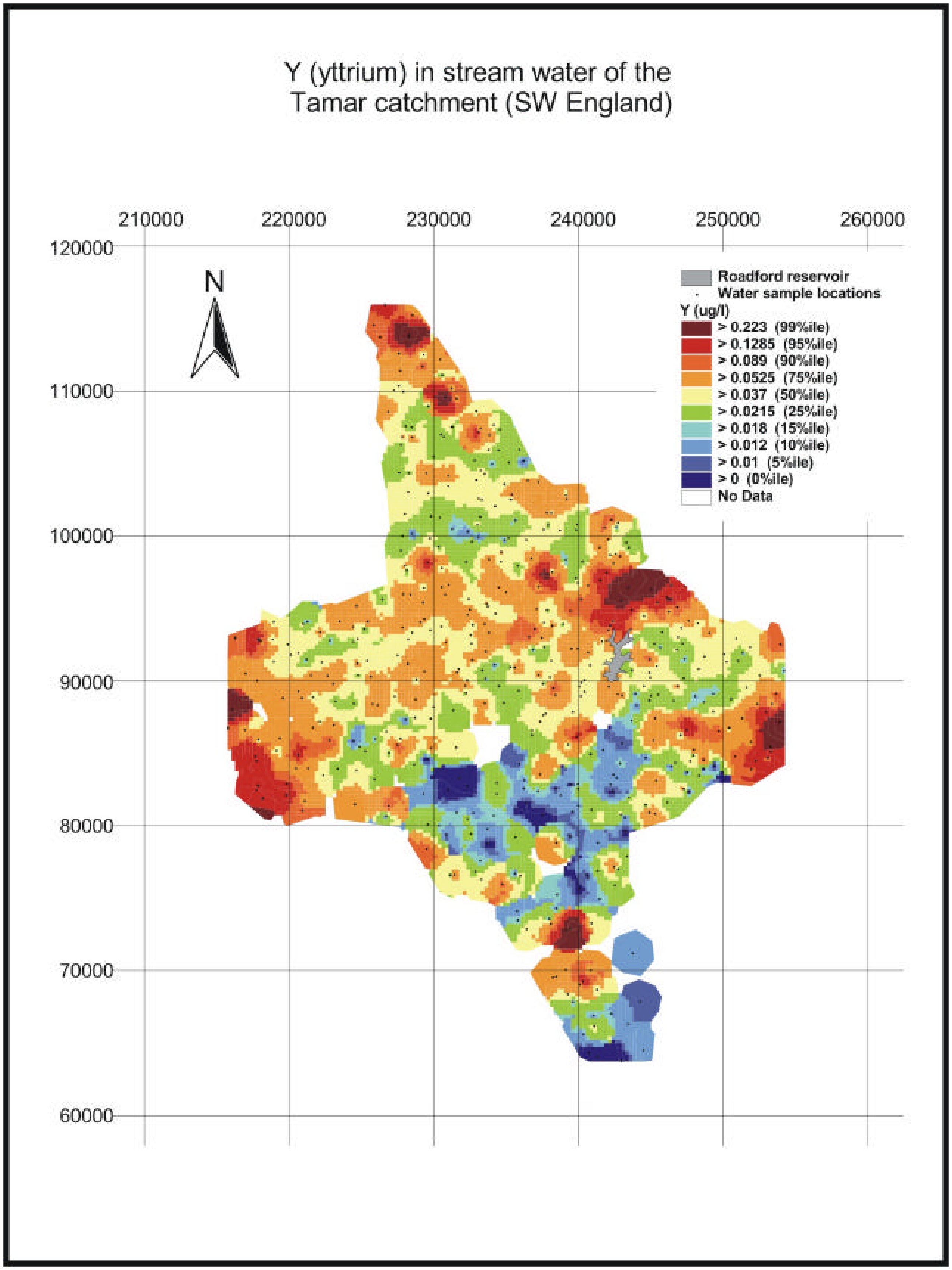

SO4 (sulphate) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
SO4 (mg/l)
> 26.95 (99%ile)
> 21.3 (95%ile)
> 17.6 (90%ile)
> 13.3 (75%ile)
> 10.15 (50%ile)
> 7.98 (25%ile)
> 6.645 (15%ile)
> 4.155 (10%ile)
> 3.26 (5%ile)
> 0 (0%ile)
No Data

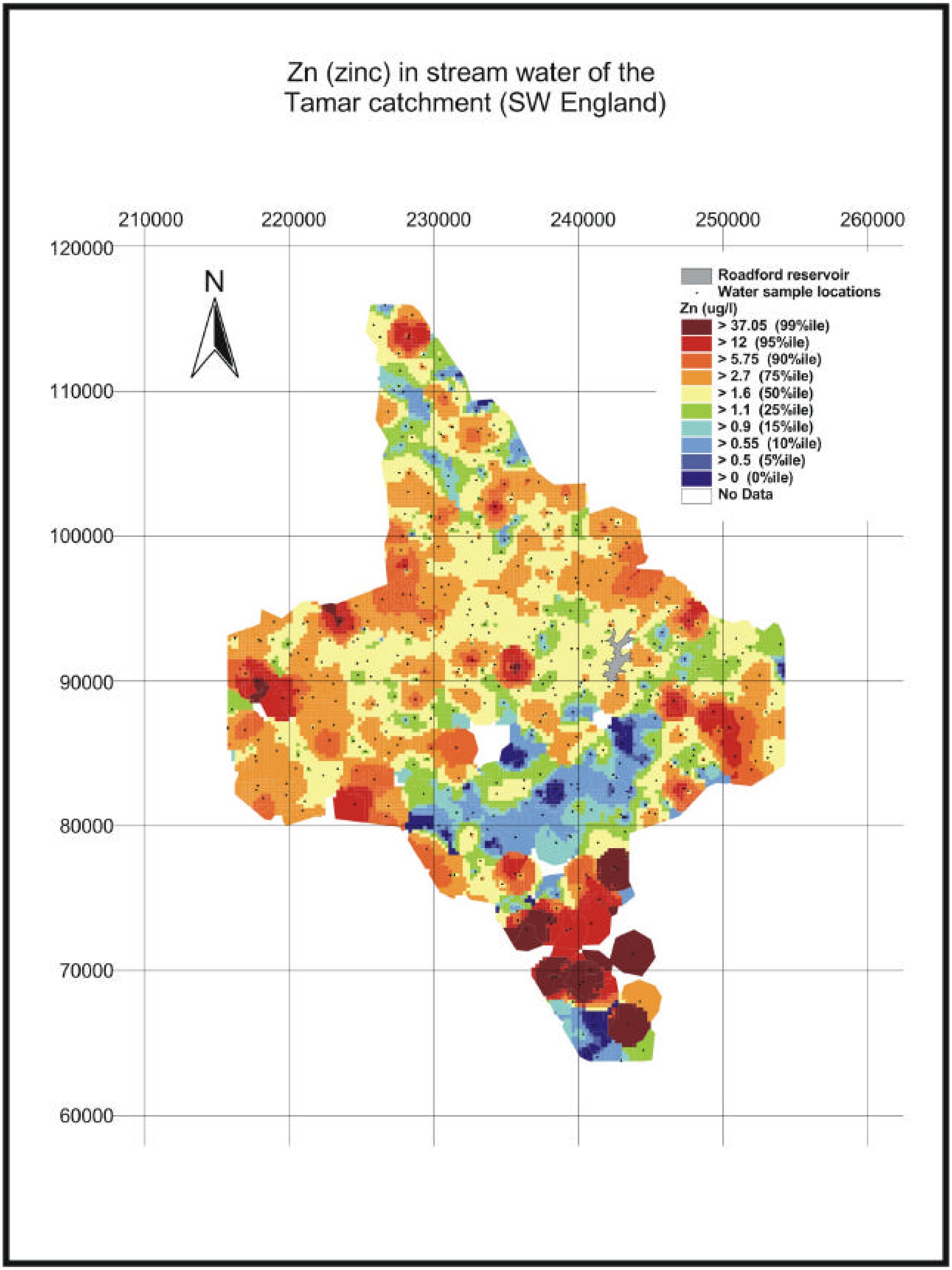

Sr (strontium) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Sr (mg/l)
> 0.113 (99%ile)
> 0.101 (95%ile)
> 0.089 (90%ile)
> 0.07 (75%ile)
> 0.056 (50%ile)
> 0.041 (25%ile)
> 0.036 (15%ile)
> 0.0215 (10%ile)
> 0.019 (5%ile)
> 0 (0%ile)
No Data

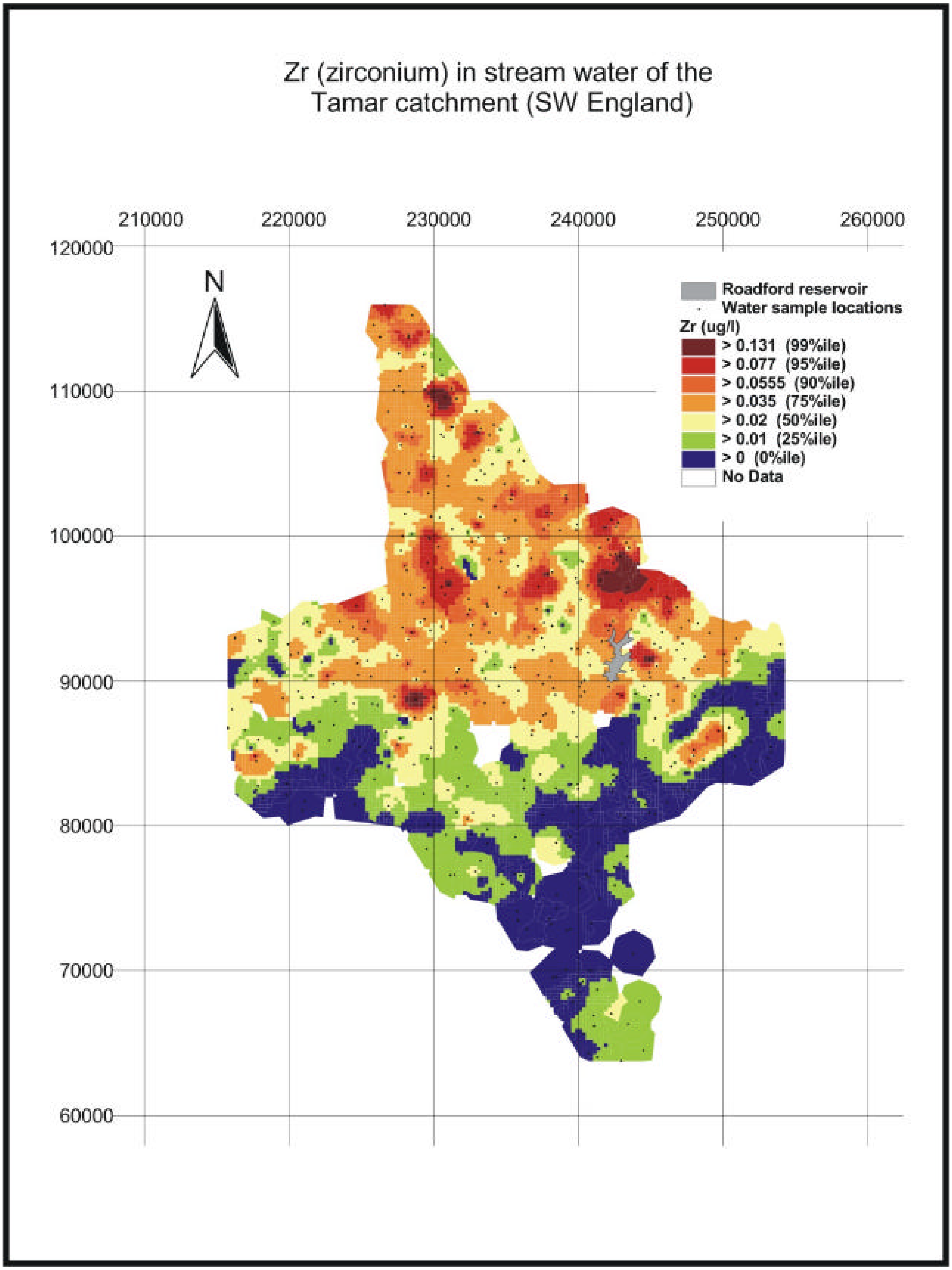

Tl (thallium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Tl (ug/l)
> 0.0495 (99%ile)
> 0.028 (95%ile)
> 0.018 (90%ile)
> 0.01 (75%ile)
> 0 (0%ile)
No Data


U (uranium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
U (ug/l)
> 0.1295 (99%ile)
> 0.0875 (95%ile)
> 0.053 (90%ile)
> 0.027 (75%ile)
> 0.017 (50%ile)
> 0.0105 (25%ile)
> 0.01 (15%ile)
> 0 (0%ile)
No Data


V (vanadium) in stream water of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
V (ug/l)
> 0.475 (99%ile)
> 0.315 (95%ile)
> 0.21 (90%ile)
> 0.12 (75%ile)
> 0.08 (50%ile)
> 0.06 (25%ile)
> 0 (0%ile)
No Data


Y (yttrium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Y (ug/l)
> 0.223 (99%ile)
> 0.1285 (95%ile)
> 0.089 (90%ile)
> 0.0525 (75%ile)
> 0.037 (50%ile)
> 0.0215 (25%ile)
> 0.018 (15%ile)
> 0.012 (10%ile)
> 0.01 (5%ile)
> 0 (0%ile)
No Data


Zn (zinc) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Zn (ug/l)
> 37.05 (99%ile)
> 12 (95%ile)
> 5.75 (90%ile)
> 2.7 (75%ile)
> 1.6 (50%ile)
> 1.1 (25%ile)
> 0.9 (15%ile)
> 0.55 (10%ile)
> 0.5 (5%ile)
> 0 (0%ile)
No Data

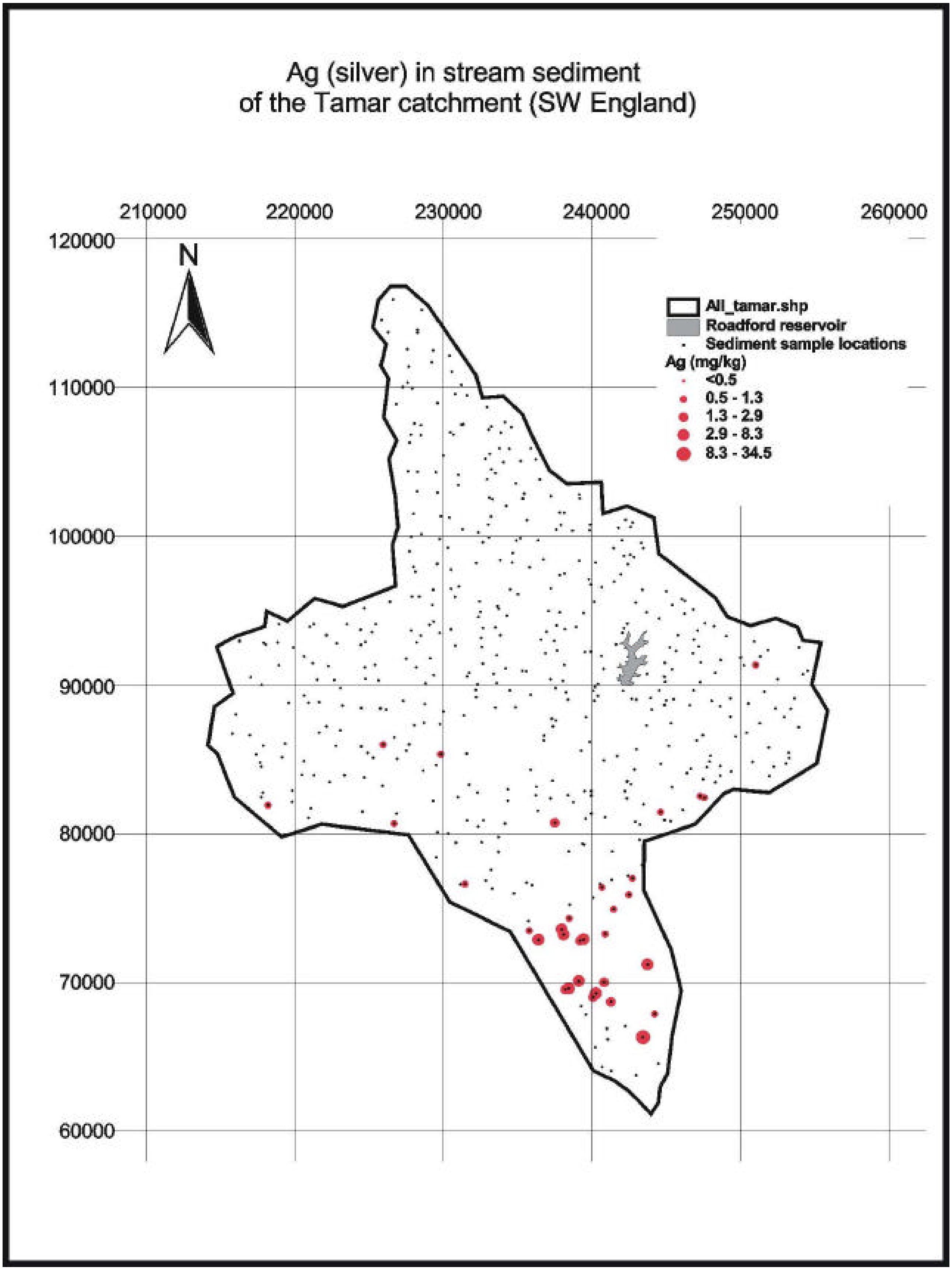

Zr (zirconium) in stream water of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Water sample locations
Zr (ug/l)
> 0.131 (99%ile)
> 0.077 (95%ile)
> 0.0555 (90%ile)
> 0.035 (75%ile)
> 0.02 (50%ile)
> 0.01 (25%ile)
> 0 (0%ile)
No Data

Appendix B – Element distributions in stream sediment of the Tamar catchment

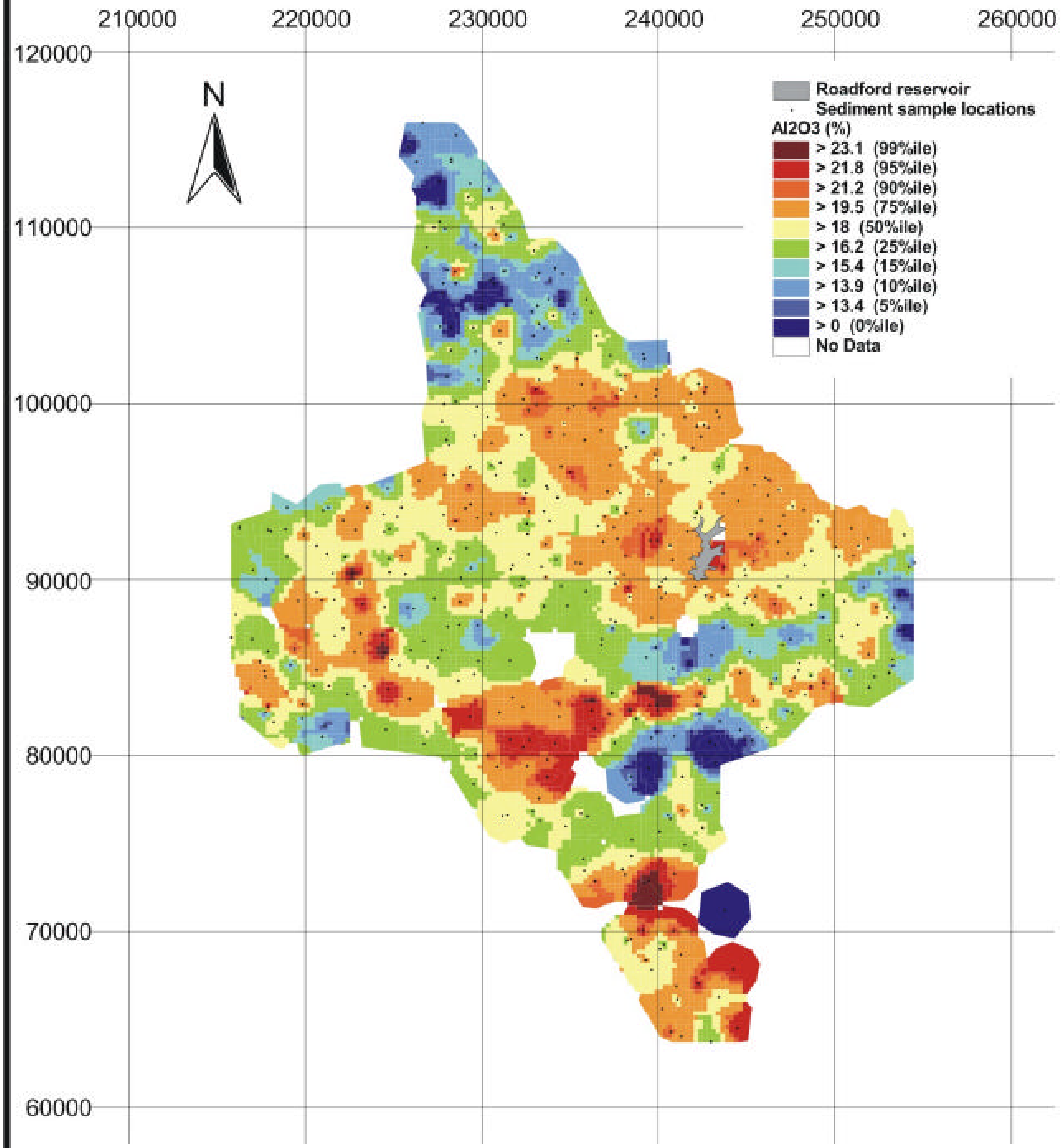
The images presented in this appendix are the outcome of a geochemical survey of the Tamar catchment undertaken in September 2002. The methods adopted in the survey (sampling, analysis and data presentation) are described in the main report entitled 'Geochemical survey of the Tamar catchment (south-west England)'.

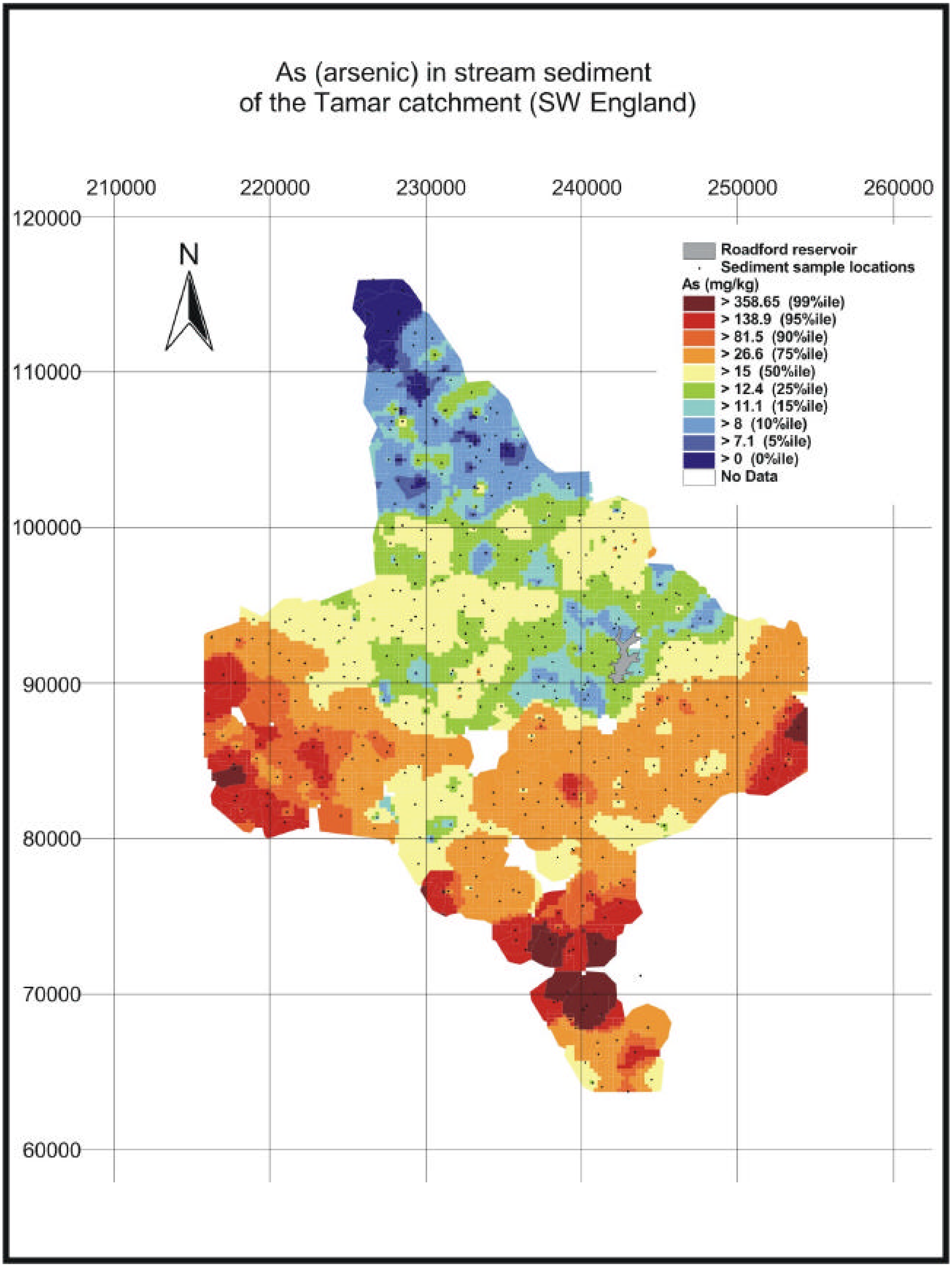
Full bibliographic reference:

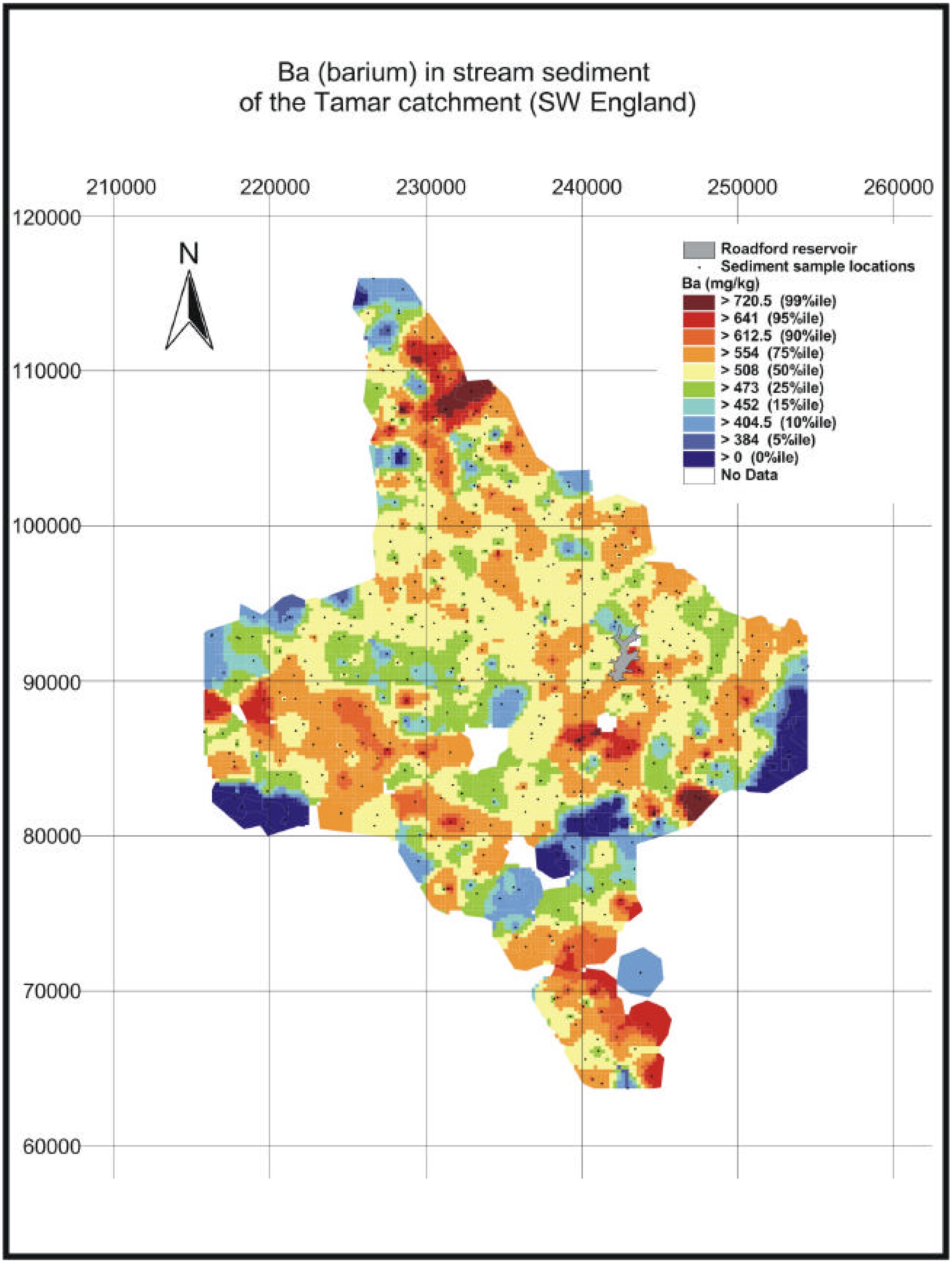
RAWLINS, B. G., O'DONNELL, K. AND INGHAM, M.2003. Geochemical survey of the Tamar catchment (south-west England). *British Geological Survey Report*, CR/03/027. 232pp.

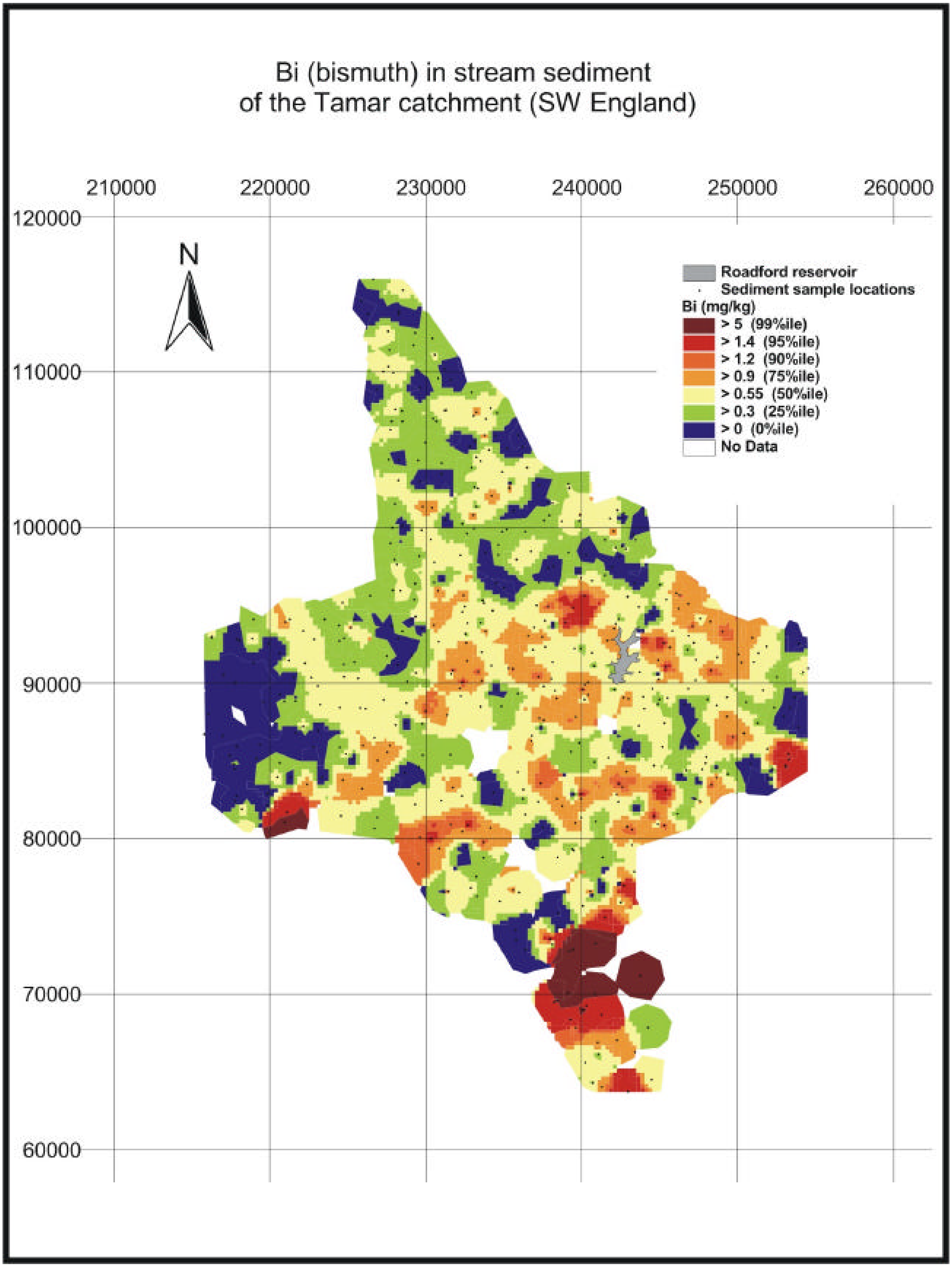

Ag (silver) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
All_tamar.shp
Roadford reservoir
Sediment sample locations
Ag (mg/kg)
<0.5
0.5 - 1.3
1.3 - 2.9
2.9 - 8.3
8.3 - 34.5

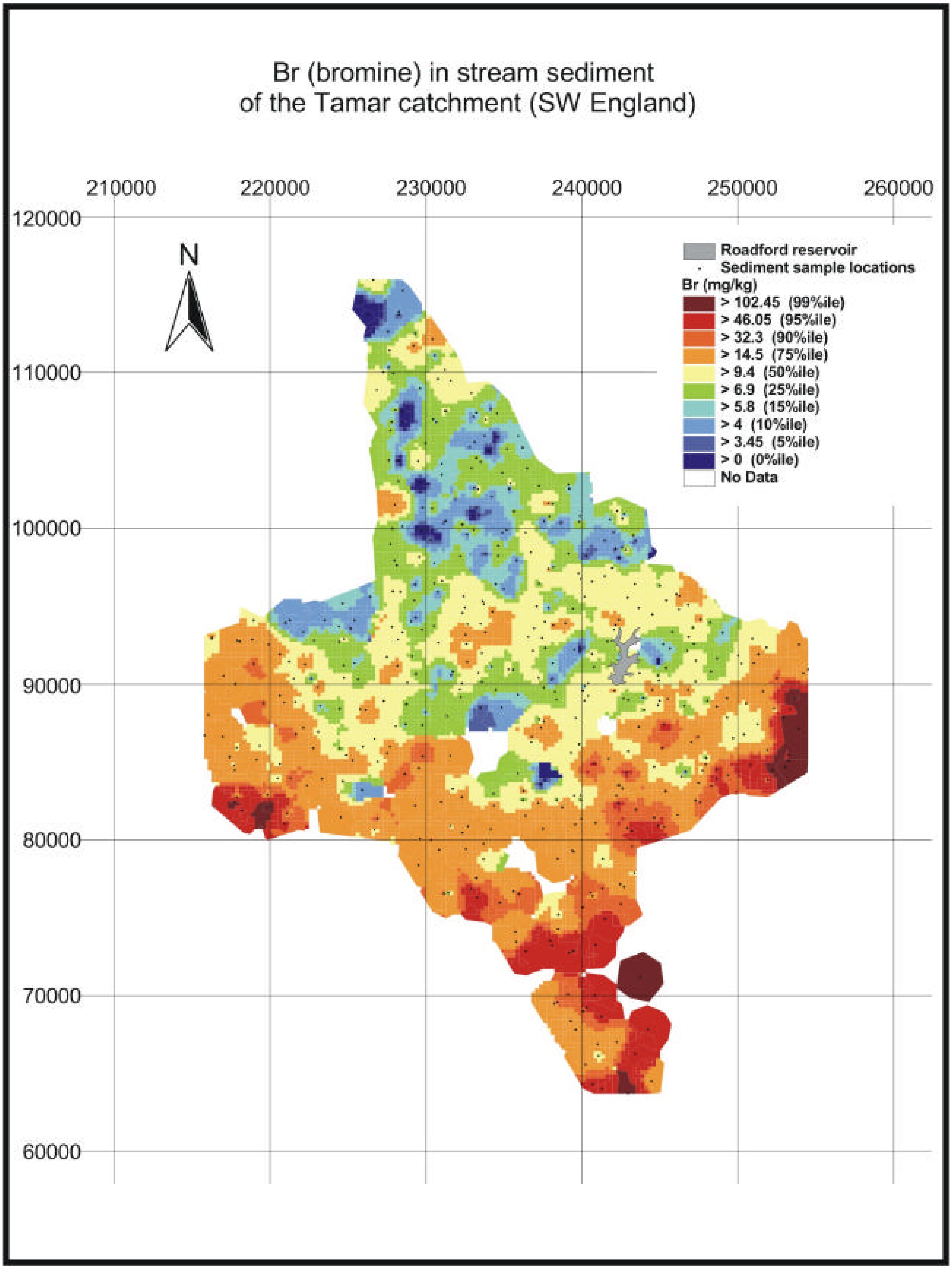
Al2O3 (aluminium oxide) in stream sediment
of the Tamar catchment (SW England)

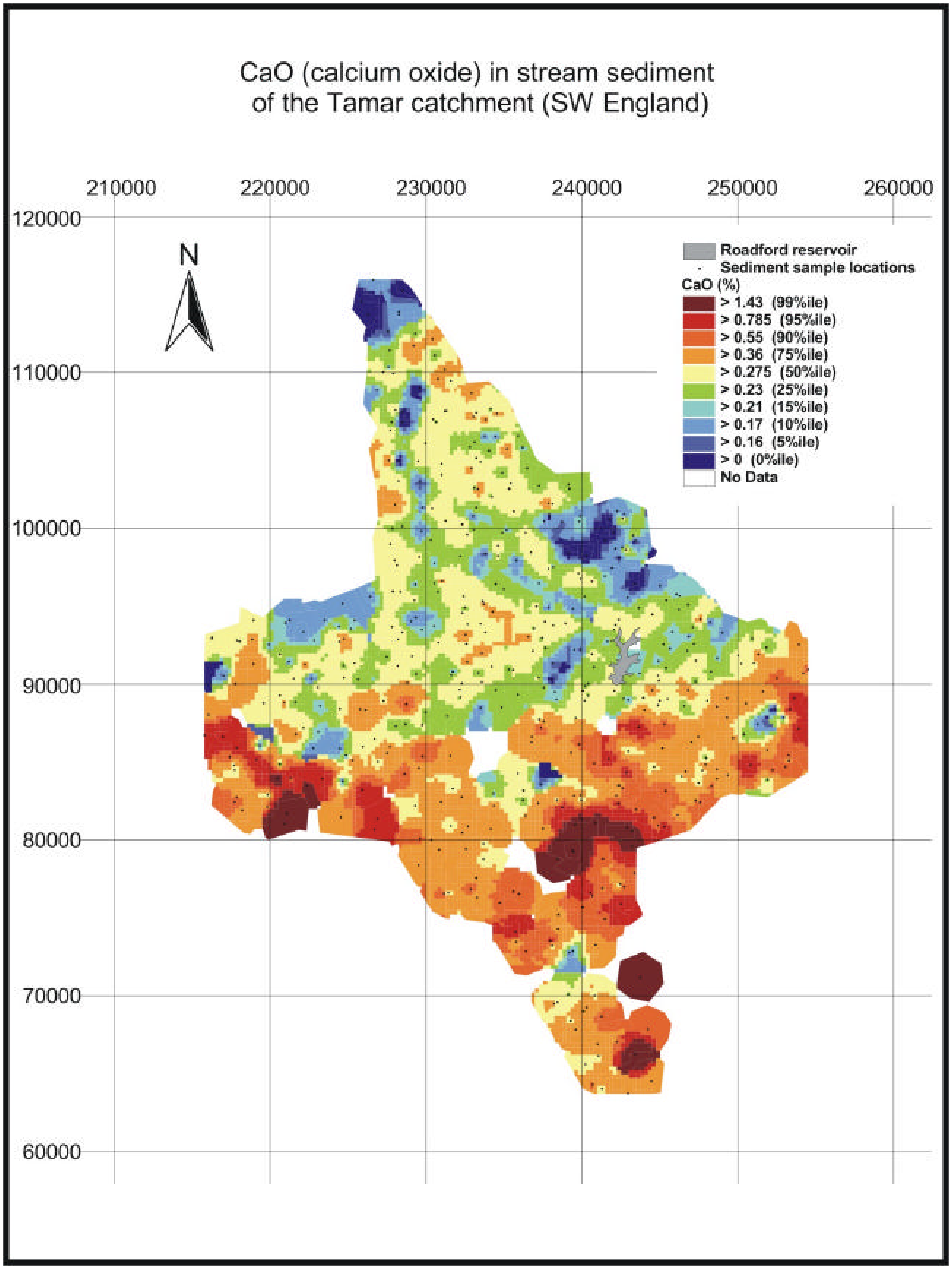


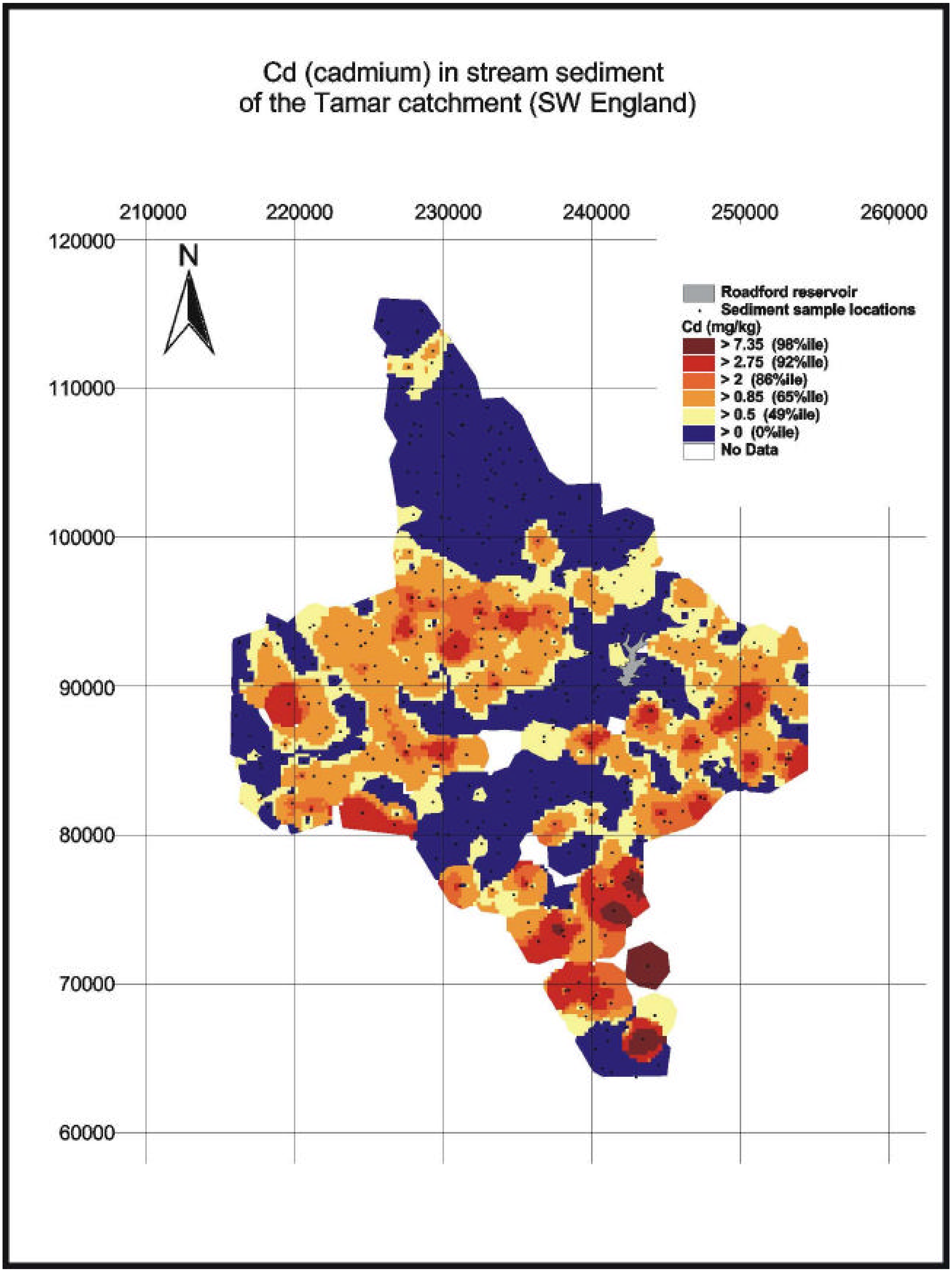

As (arsenic) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
As (mg/kg)
> 358.65 (99%ile)
> 138.9 (95%ile)
> 81.5 (90%ile)
> 26.6 (75%ile)
> 15 (50%ile)
> 12.4 (25%ile)
> 11.1 (15%ile)
> 8 (10%ile)
> 7.1 (5%ile)
> 0 (0%ile)
No Data


Ba (barium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Ba (mg/kg)
> 720.5 (99%ile)
> 641 (95%ile)
> 612.5 (90%ile)
> 554 (75%ile)
> 508 (50%ile)
> 473 (25%ile)
> 452 (15%ile)
> 404.5 (10%ile)
> 384 (5%ile)
> 0 (0%ile)
No Data

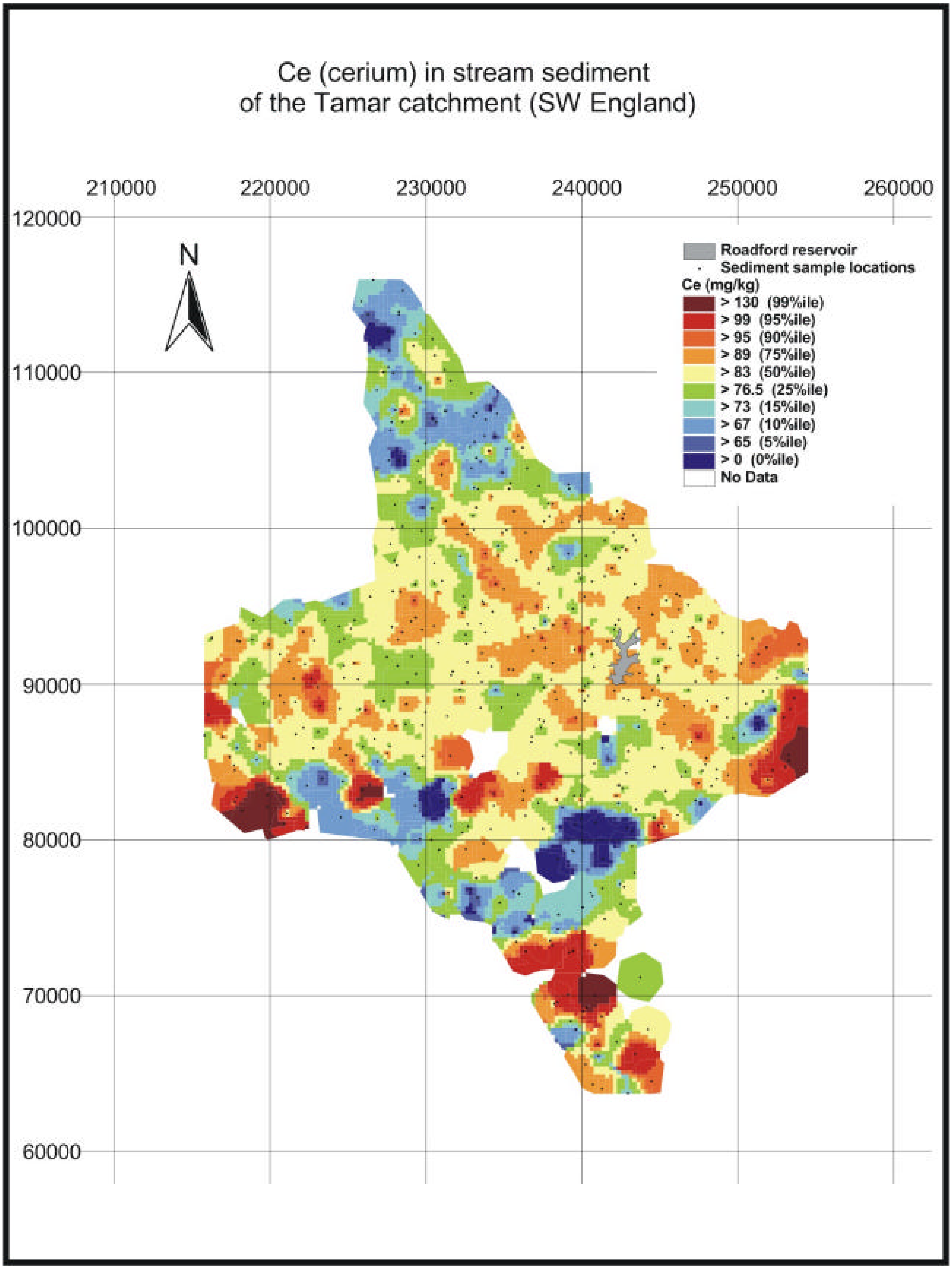

Bi (bismuth) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Bi (mg/kg)
> 5 (99%ile)
> 1.4 (95%ile)
> 1.2 (90%ile)
> 0.9 (75%ile)
> 0.55 (50%ile)
> 0.3 (25%ile)
> 0 (0%ile)
No Data

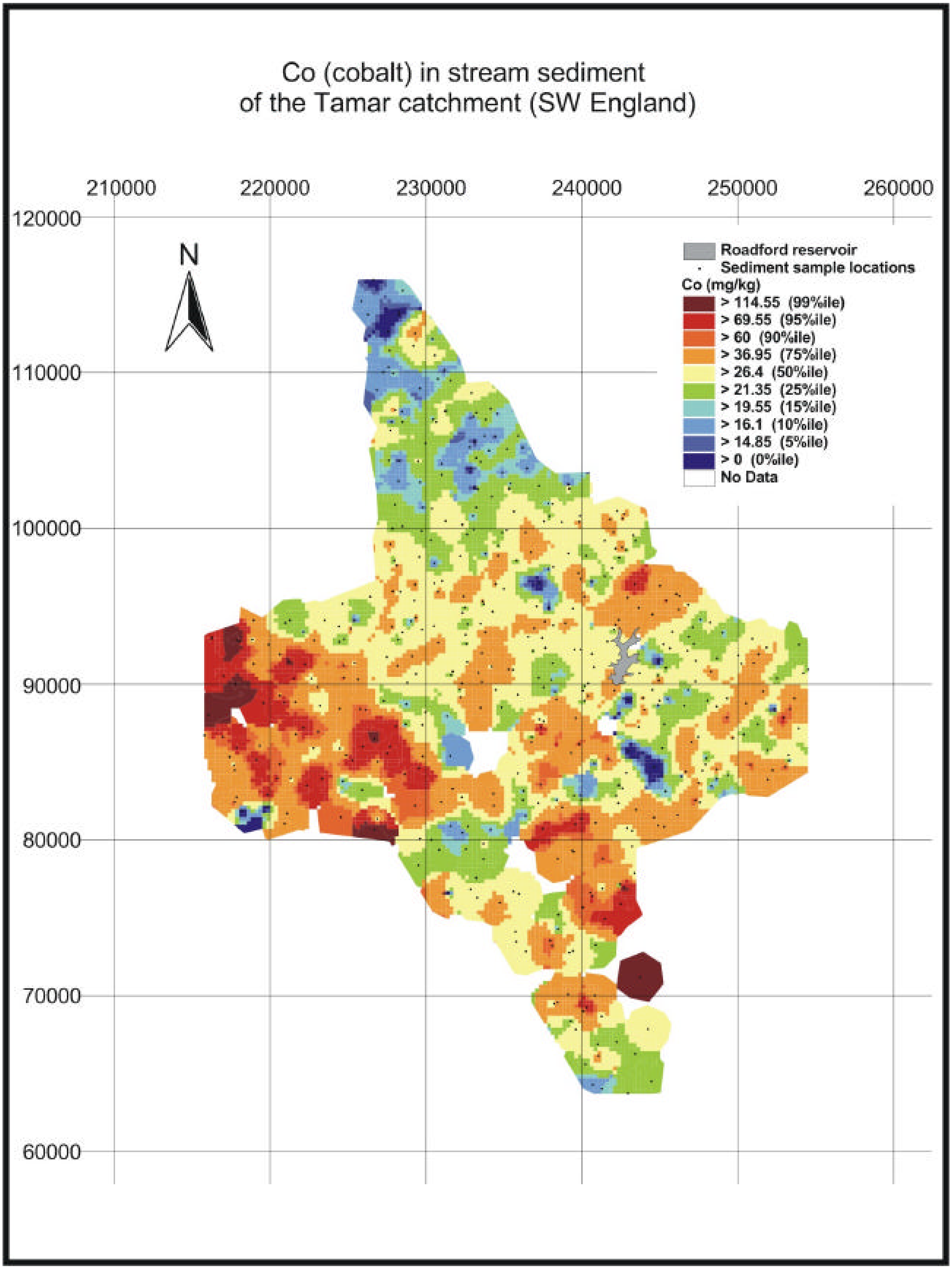

Br (bromine) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Br (mg/kg)
> 102.45 (99%ile)
> 46.05 (95%ile)
> 32.3 (90%ile)
> 14.5 (75%ile)
> 9.4 (50%ile)
> 6.9 (25%ile)
> 5.8 (15%ile)
> 4 (10%ile)
> 3.45 (5%ile)
> 0 (0%ile)
No Data


CaO (calcium oxide) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
CaO (%)
> 1.43 (99%ile)
> 0.785 (95%ile)
> 0.55 (90%ile)
> 0.36 (75%ile)
> 0.275 (50%ile)
> 0.23 (25%ile)
> 0.21 (15%ile)
> 0.17 (10%ile)
> 0.16 (5%ile)
> 0 (0%ile)
No Data

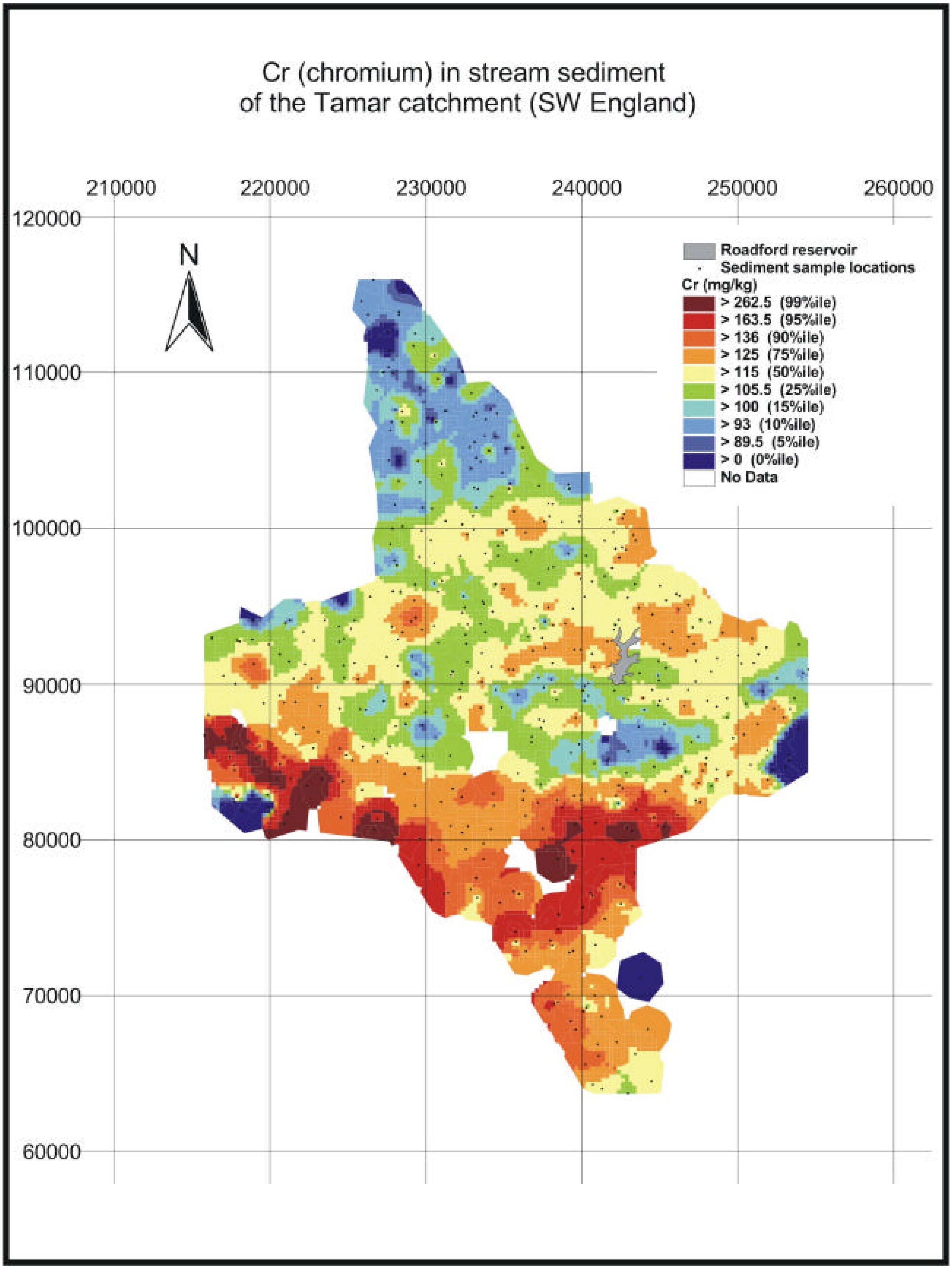


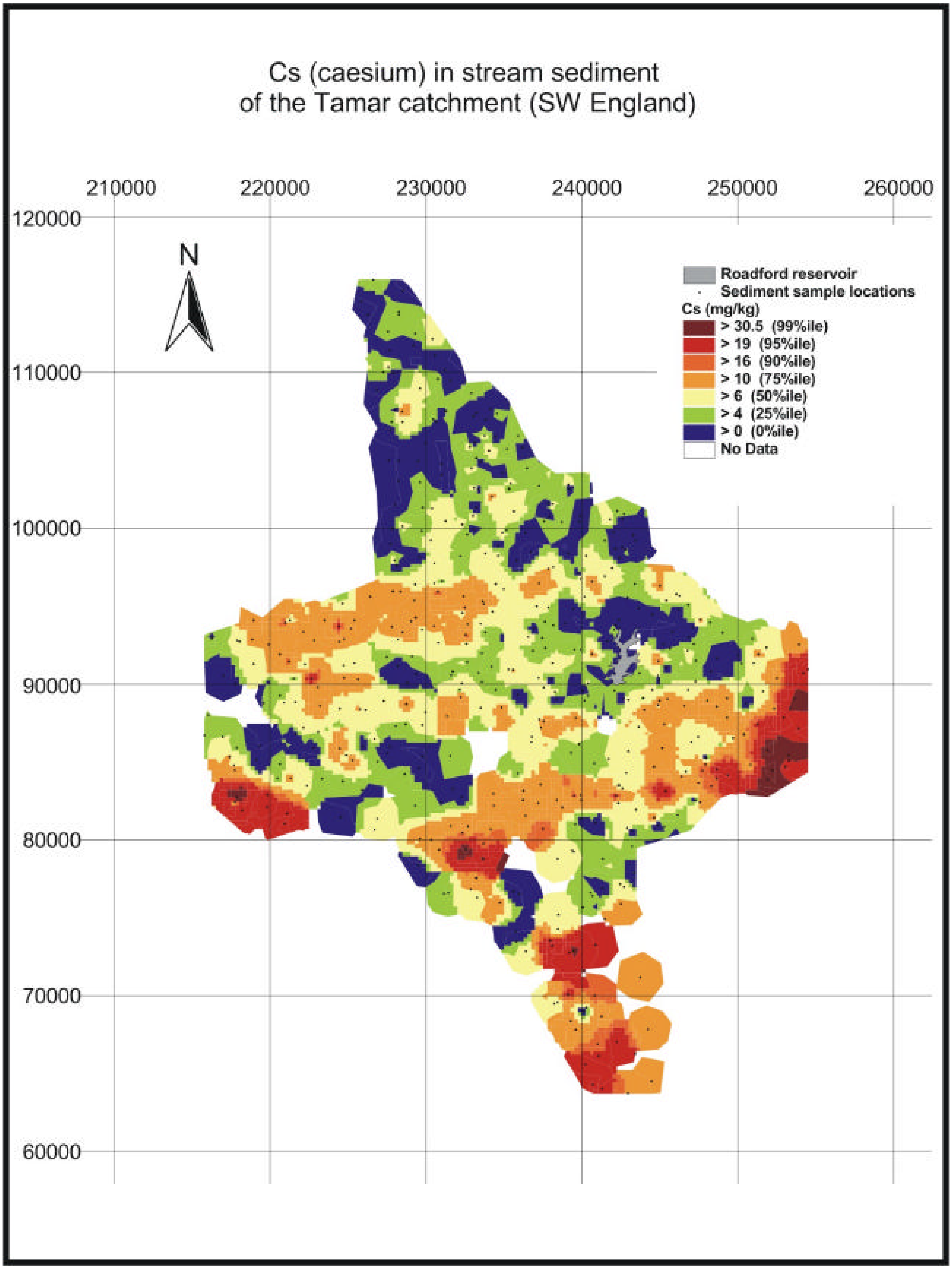
Cd (cadmium) in stream sediment
of the Tamar catchment (SW England)

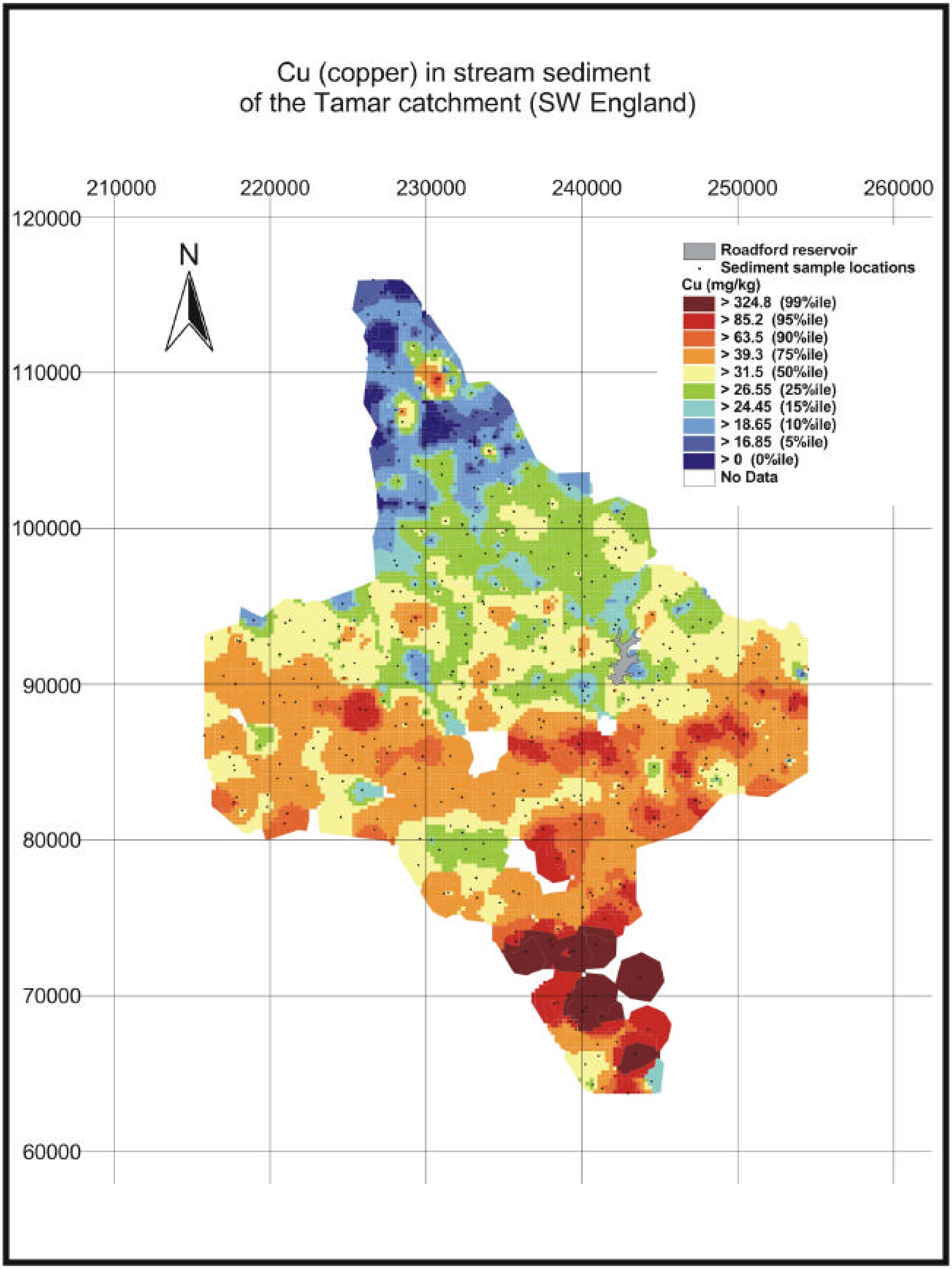

Ce (cerium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Ce (mg/kg)
> 130 (99%ile)
> 99 (95%ile)
> 95 (90%ile)
> 89 (75%ile)
> 83 (50%ile)
> 76.5 (25%ile)
> 73 (15%ile)
> 67 (10%ile)
> 65 (5%ile)
> 0 (0%ile)
No Data

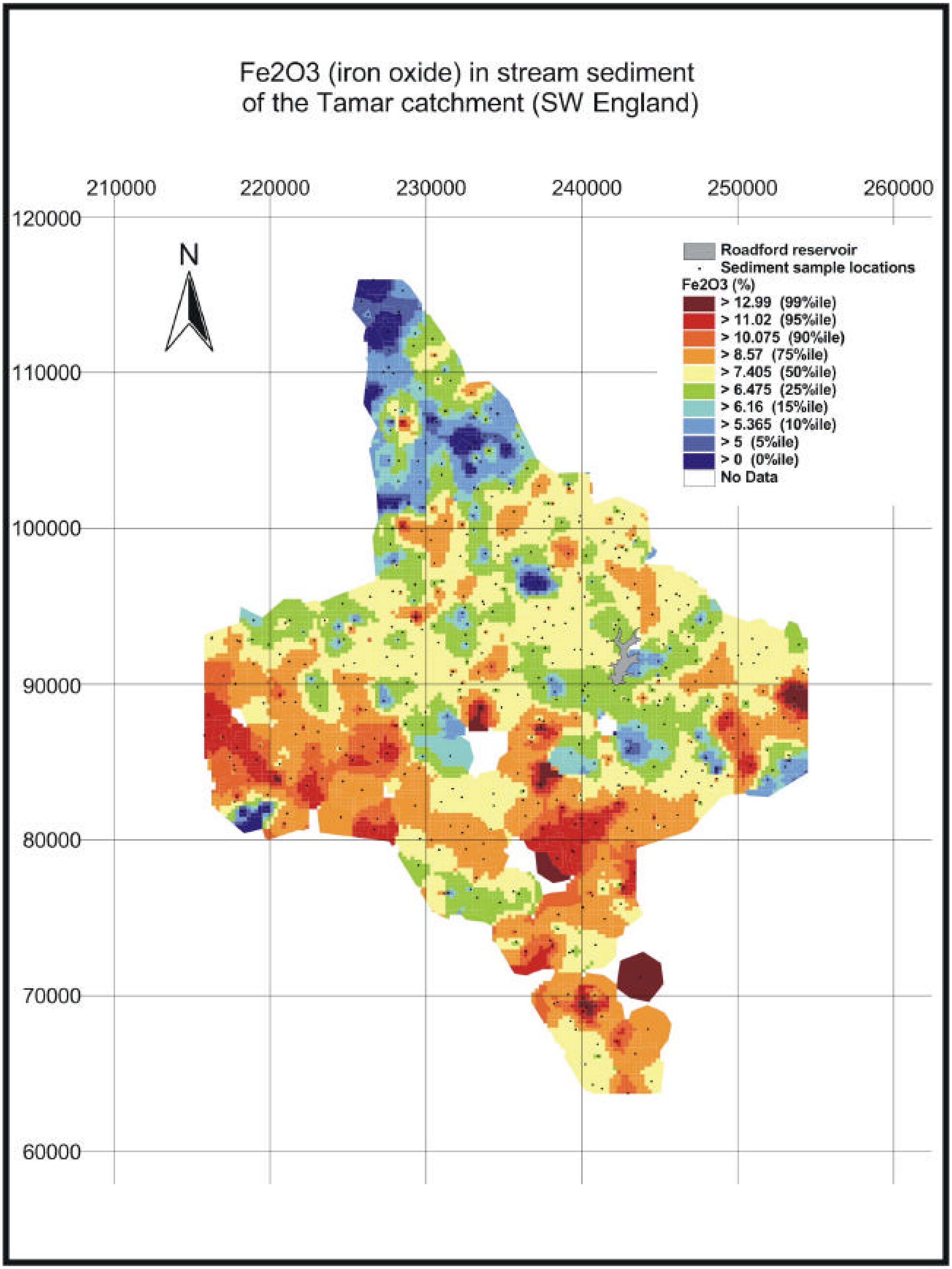


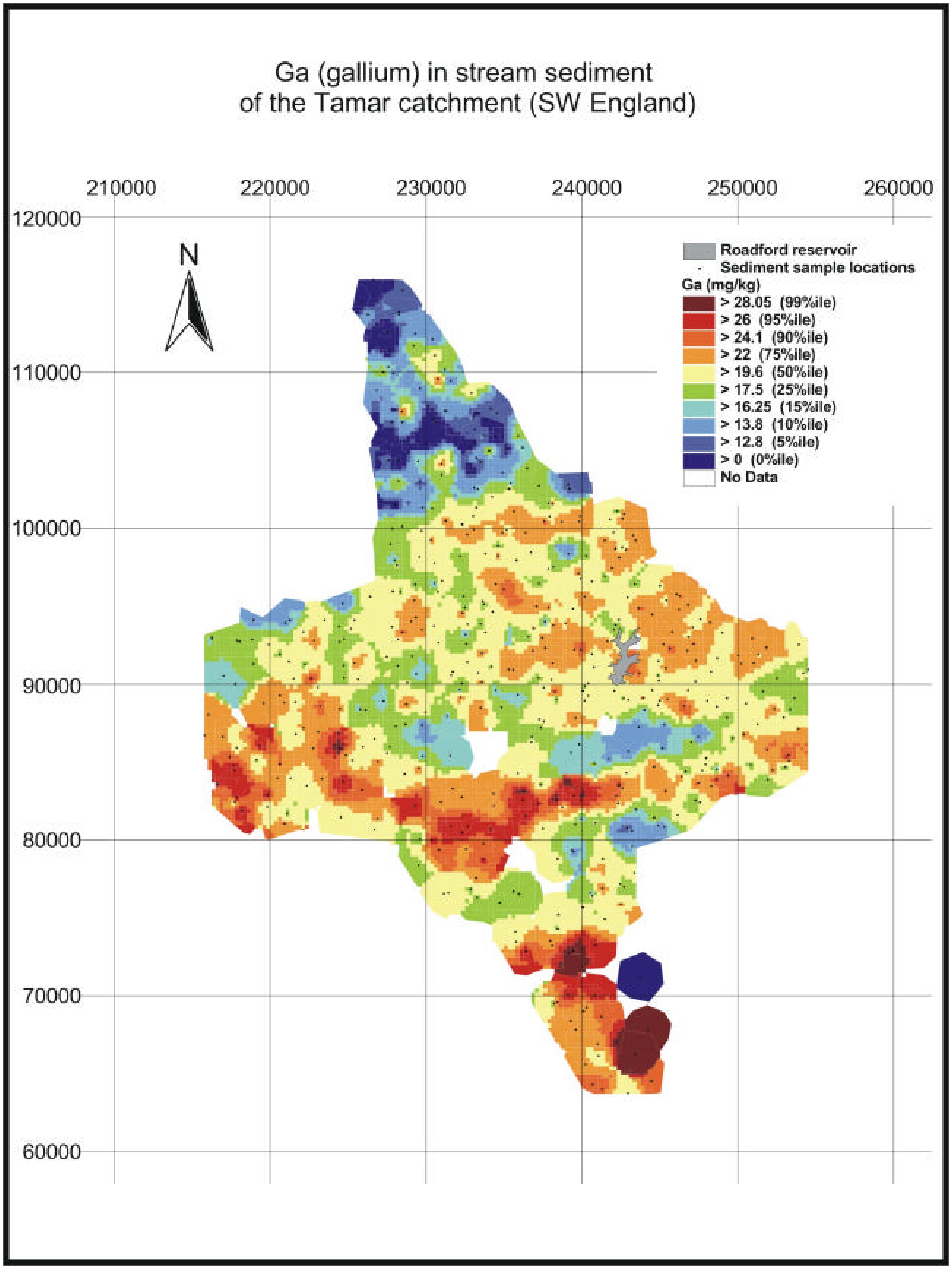
Co (cobalt) in stream sediment
of the Tamar catchment (SW England)

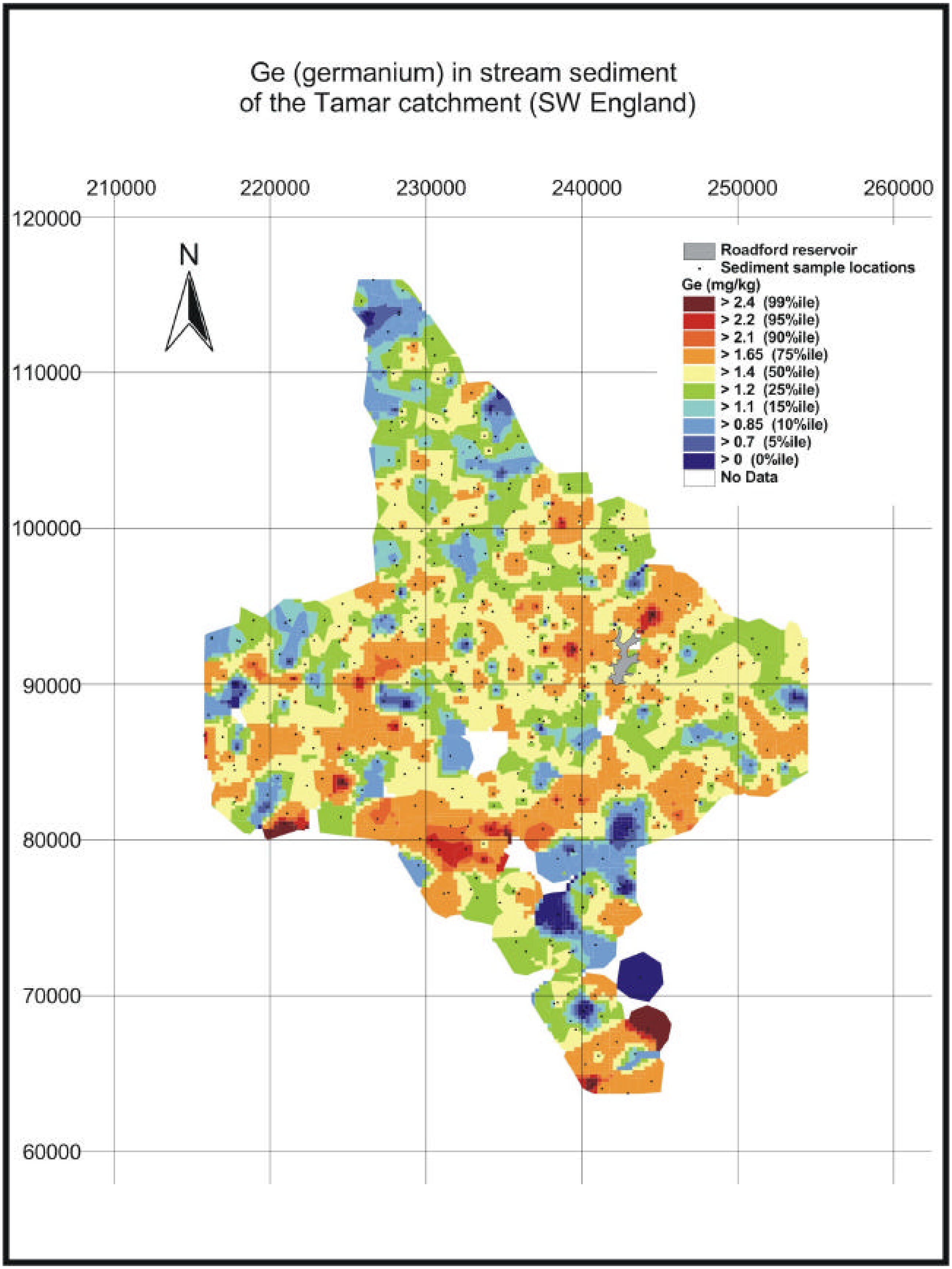

Cr (chromium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Cr (mg/kg)
> 262.5 (99%ile)
> 163.5 (95%ile)
> 136 (90%ile)
> 125 (75%ile)
> 115 (50%ile)
> 105.5 (25%ile)
> 100 (15%ile)
> 93 (10%ile)
> 89.5 (5%ile)
> 0 (0%ile)
No Data

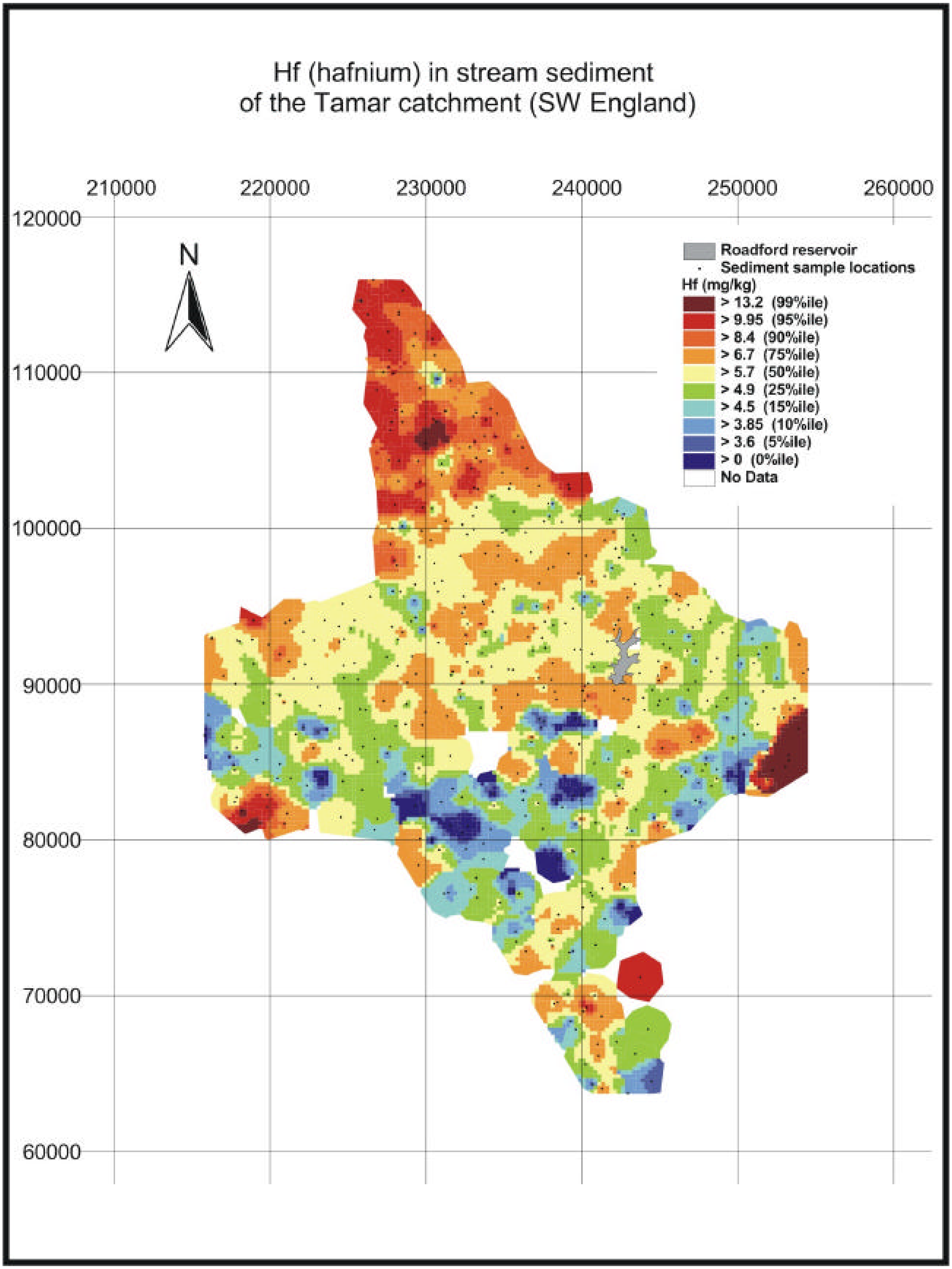

Cs (caesium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Cs (mg/kg)
> 30.5 (99%ile)
> 19 (95%ile)
> 16 (90%ile)
> 10 (75%ile)
> 6 (50%ile)
> 4 (25%ile)
> 0 (0%ile)
No Data


Cu (copper) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Cu (mg/kg)
> 324.8 (99%ile)
> 85.2 (95%ile)
> 63.5 (90%ile)
> 39.3 (75%ile)
> 31.5 (50%ile)
> 26.55 (25%ile)
> 24.45 (15%ile)
> 18.65 (10%ile)
> 16.85 (5%ile)
> 0 (0%ile)
No Data

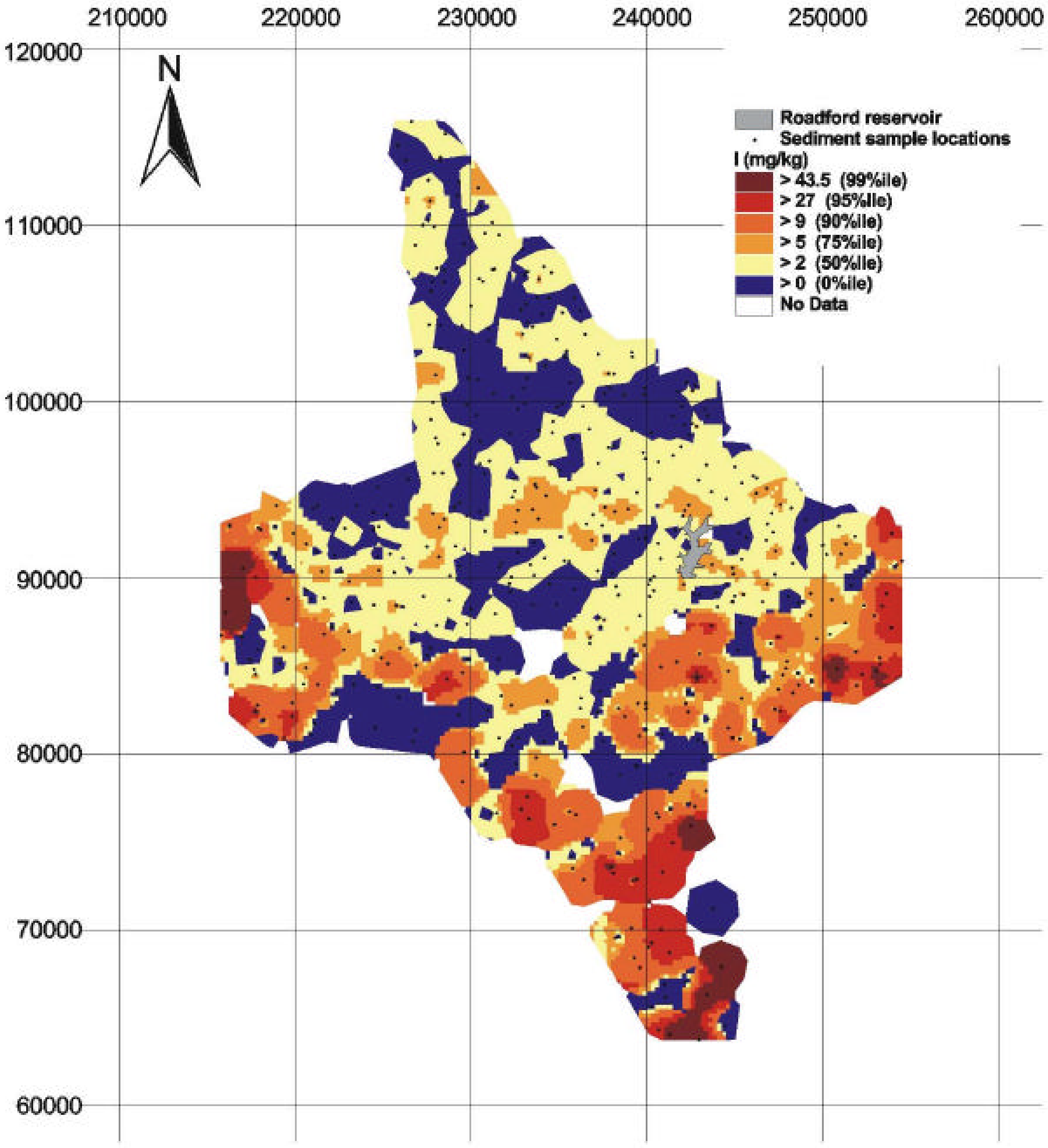

Fe2O3 (iron oxide) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Fe2O3 (%)
> 12.99 (99%ile)
> 11.02 (95%ile)
> 10.075 (90%ile)
> 8.57 (75%ile)
> 7.405 (50%ile)
> 6.475 (25%ile)
> 6.16 (15%ile)
> 5.365 (10%ile)
> 5 (5%ile)
> 0 (0%ile)
No Data


Ga (gallium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Ga (mg/kg)
> 28.05 (99%ile)
> 26 (95%ile)
> 24.1 (90%ile)
> 22 (75%ile)
> 19.6 (50%ile)
> 17.5 (25%ile)
> 16.25 (15%ile)
> 13.8 (10%ile)
> 12.8 (5%ile)
> 0 (0%ile)
No Data

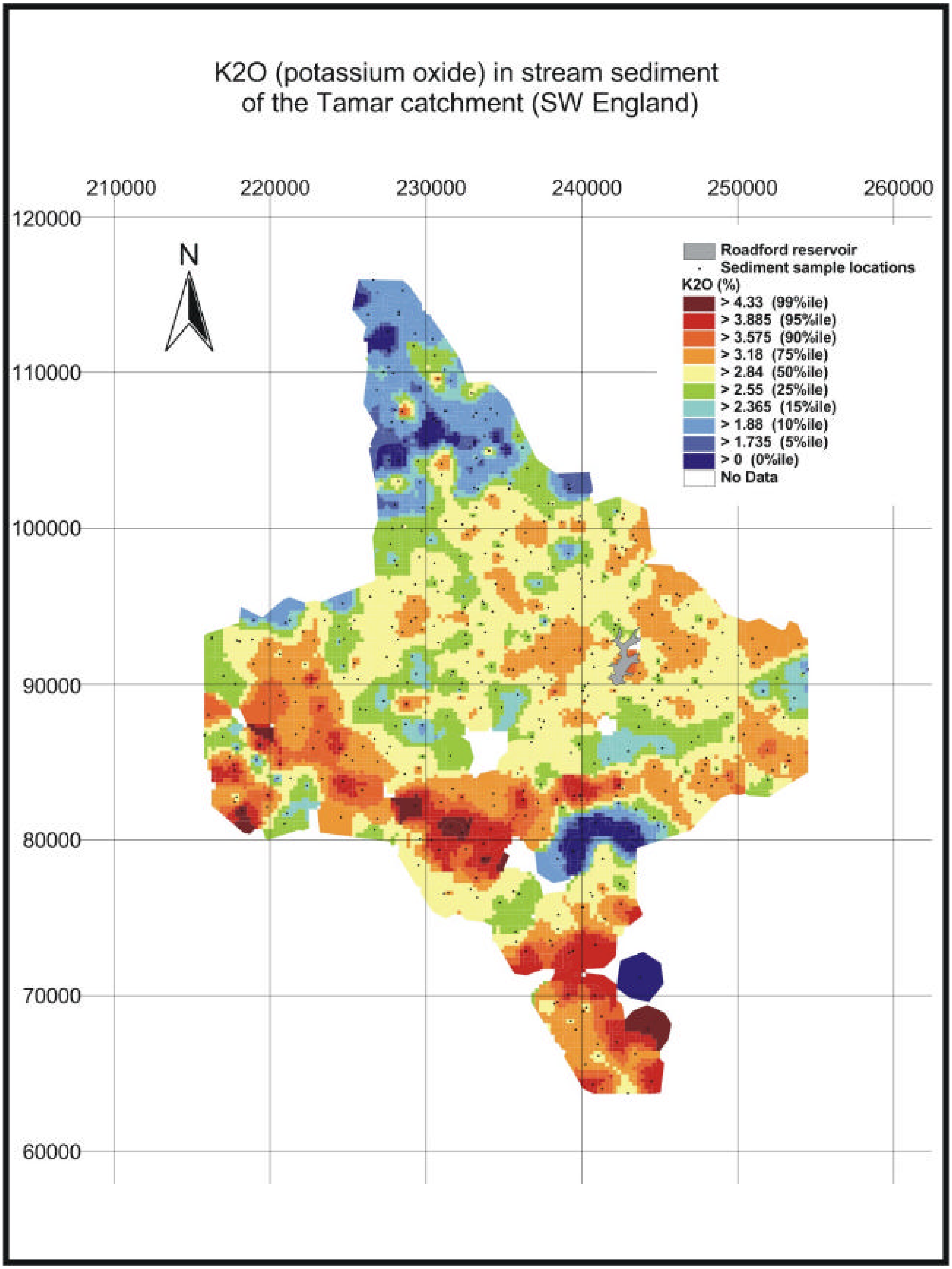

Ge (germanium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Ge (mg/kg)
> 2.4 (99%ile)
> 2.2 (95%ile)
> 2.1 (90%ile)
> 1.65 (75%ile)
> 1.4 (50%ile)
> 1.2 (25%ile)
> 1.1 (15%ile)
> 0.85 (10%ile)
> 0.7 (5%ile)
> 0 (0%ile)
No Data

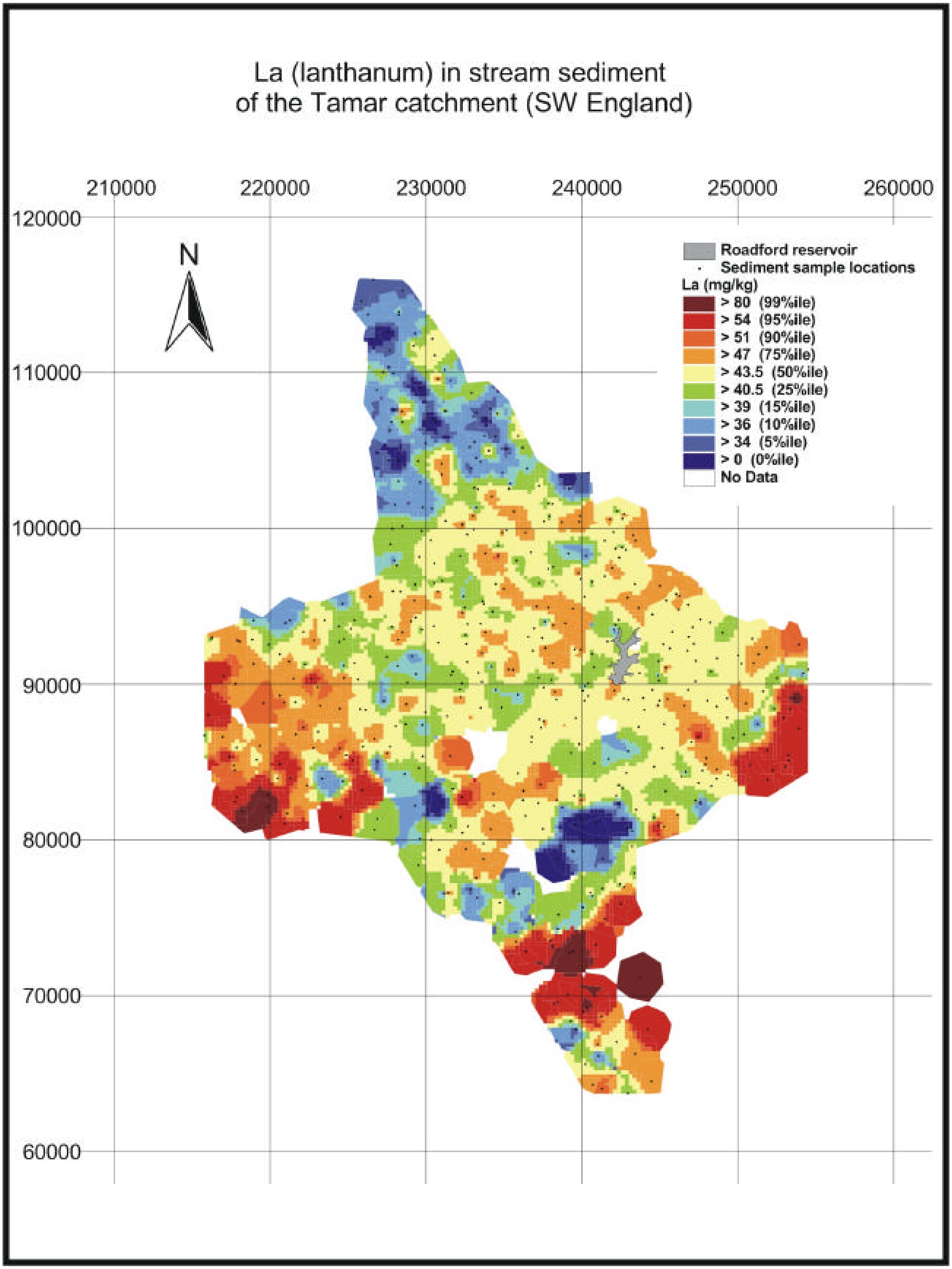


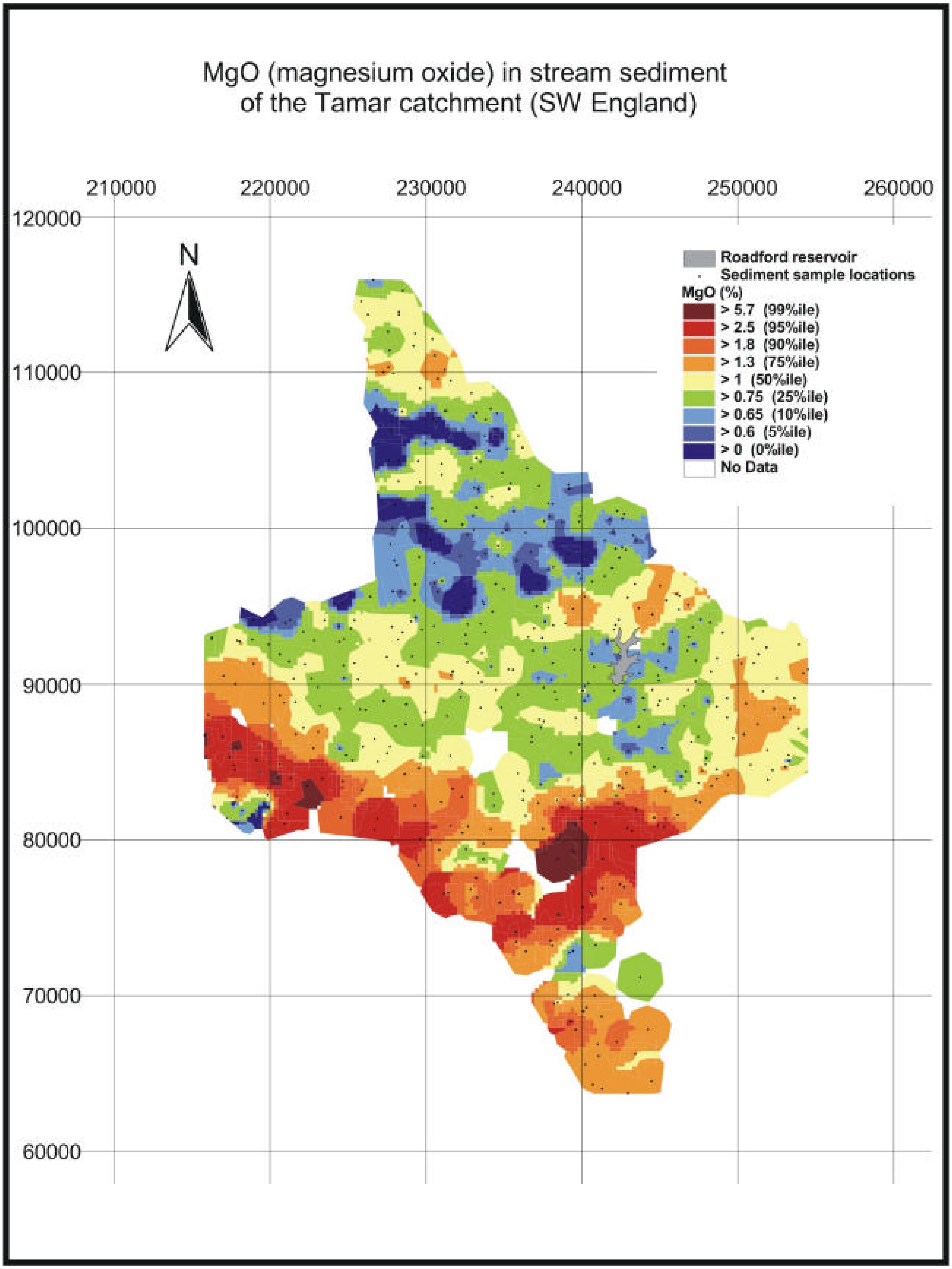
Hf (hafnium) in stream sediment of the Tamar catchment (SW England)

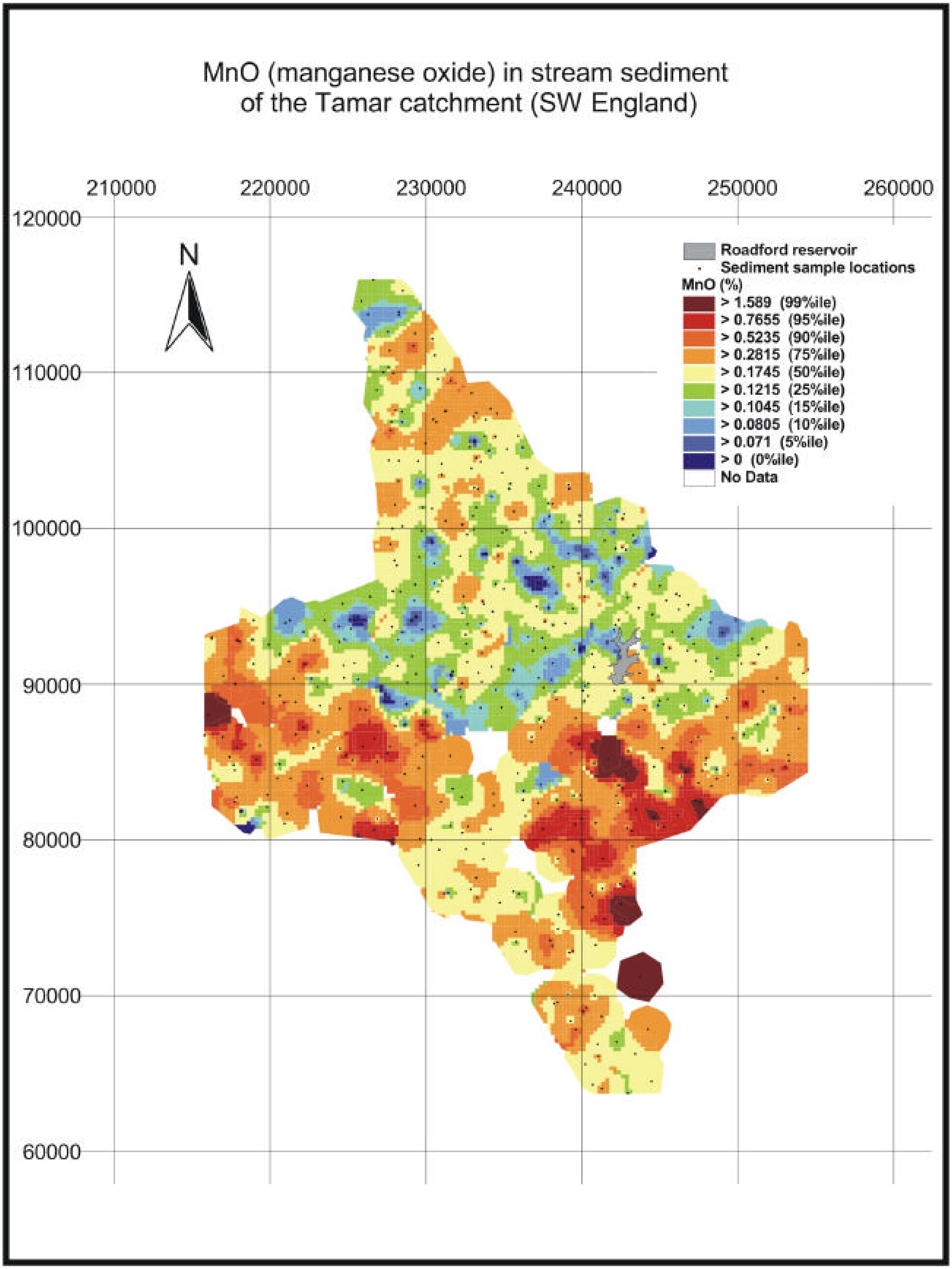


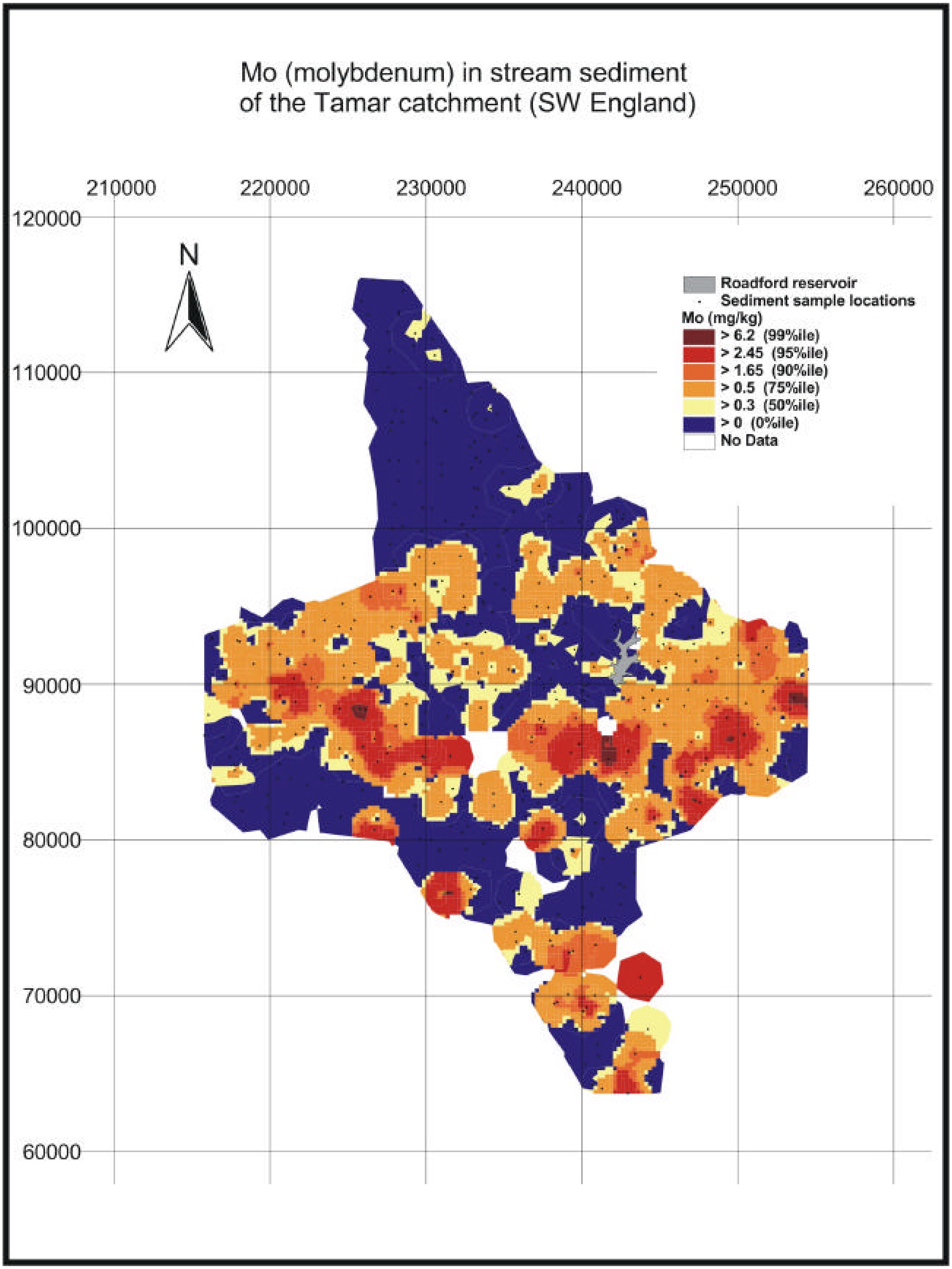
I (iodine) in stream sediment
of the Tamar catchment (SW England)

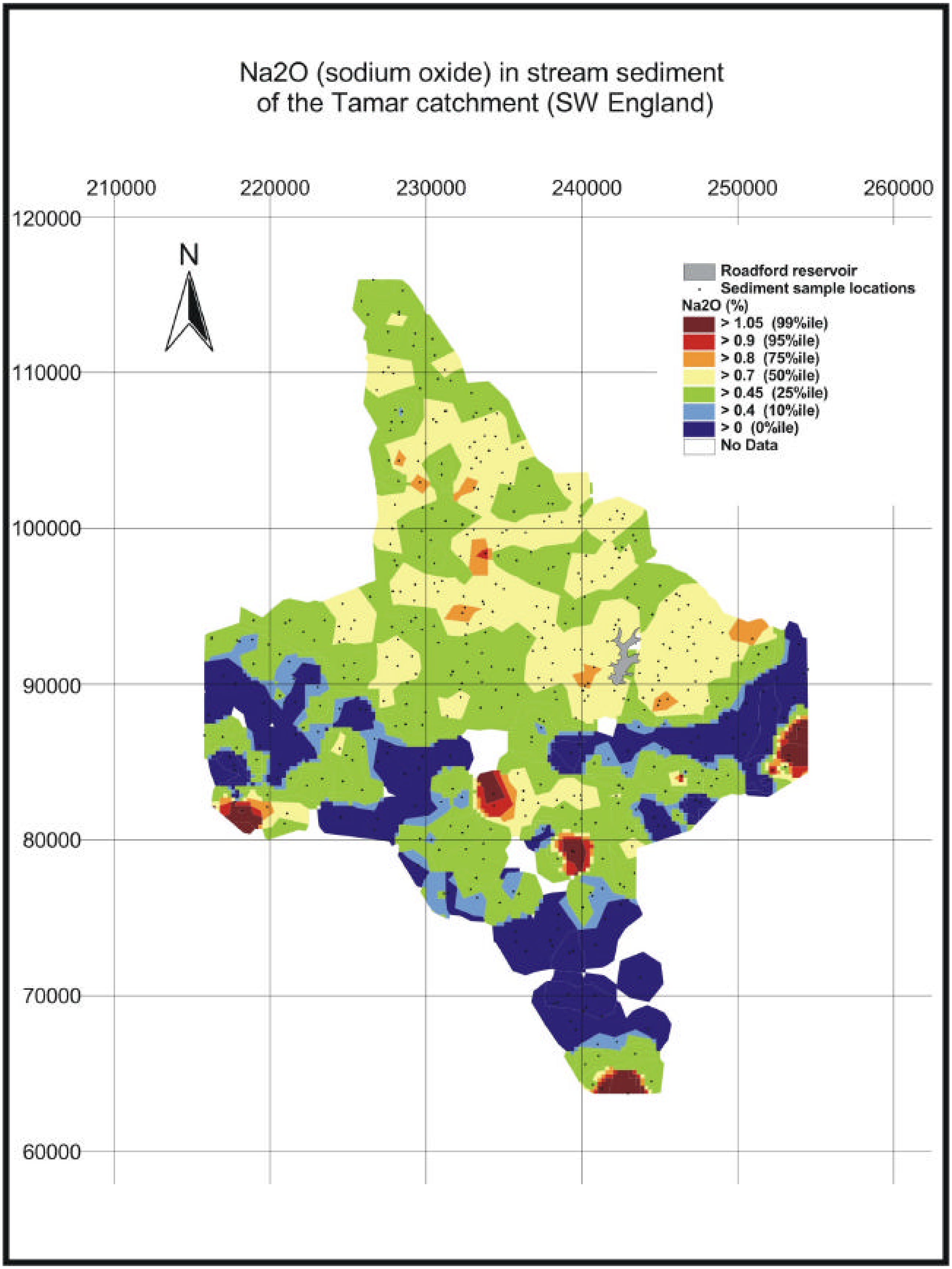

K2O (potassium oxide) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
K2O (%)
> 4.33 (99%ile)
> 3.885 (95%ile)
> 3.575 (90%ile)
> 3.18 (75%ile)
> 2.84 (50%ile)
> 2.55 (25%ile)
> 2.365 (15%ile)
> 1.88 (10%ile)
> 1.735 (5%ile)
> 0 (0%ile)
No Data

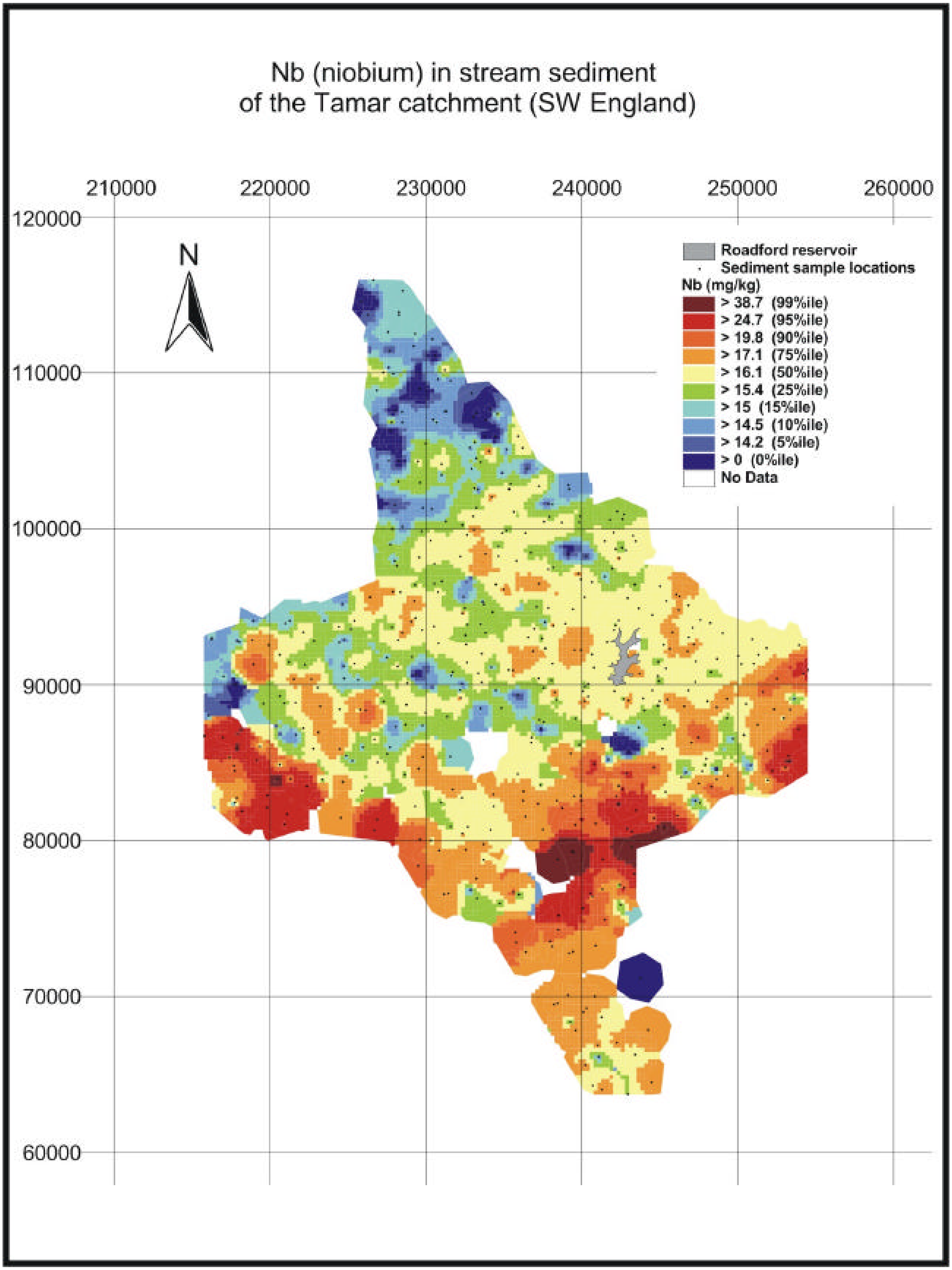

La (lanthanum) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
La (mg/kg)
> 80 (99%ile)
> 54 (95%ile)
> 51 (90%ile)
> 47 (75%ile)
> 43.5 (50%ile)
> 40.5 (25%ile)
> 39 (15%ile)
> 36 (10%ile)
> 34 (5%ile)
> 0 (0%ile)
No Data

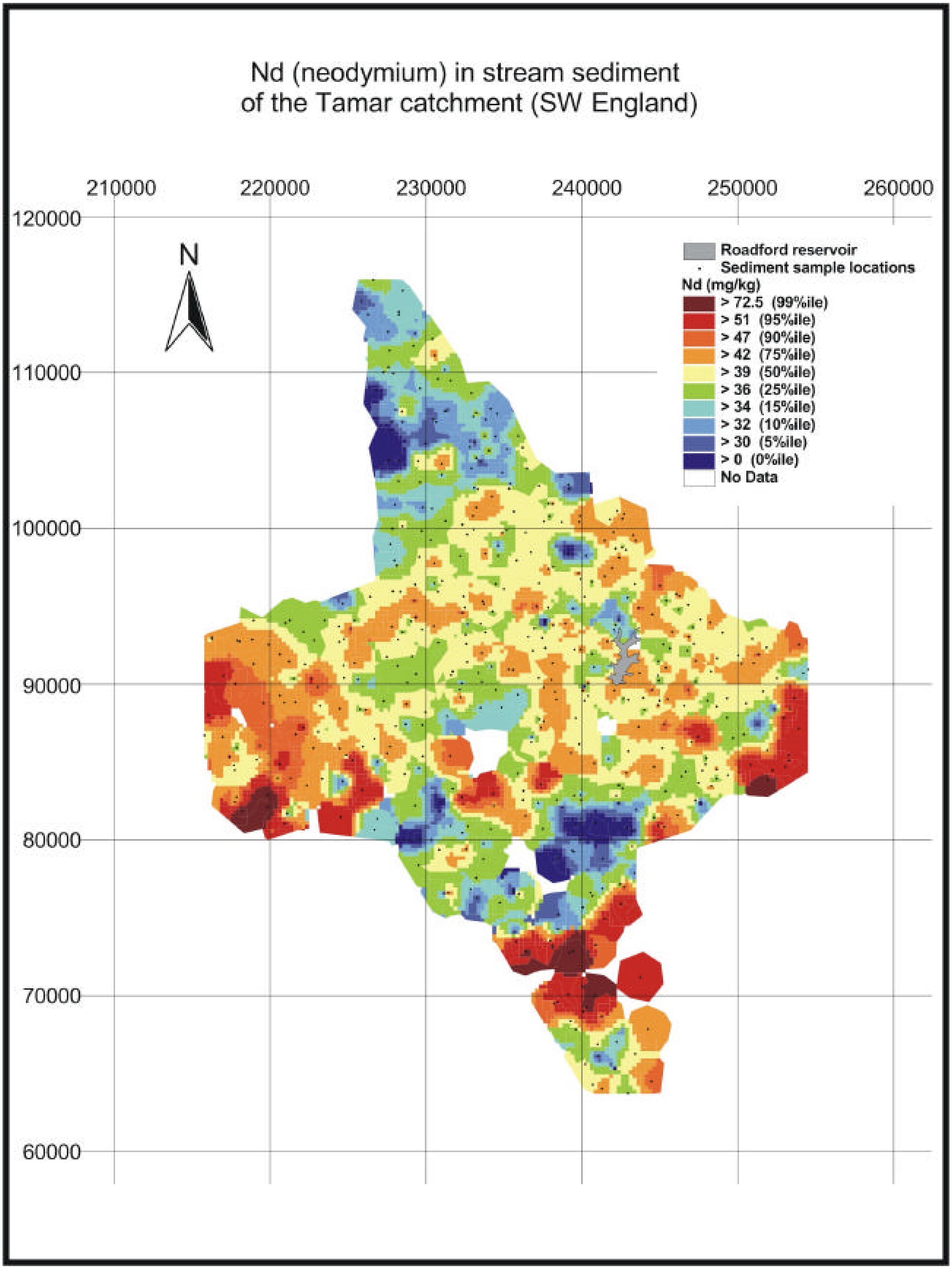

MgO (magnesium oxide) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
MgO (%)
> 5.7 (99%ile)
> 2.5 (95%ile)
> 1.8 (90%ile)
> 1.3 (75%ile)
> 1 (50%ile)
> 0.75 (25%ile)
> 0.65 (10%ile)
> 0.6 (5%ile)
> 0 (0%ile)
No Data

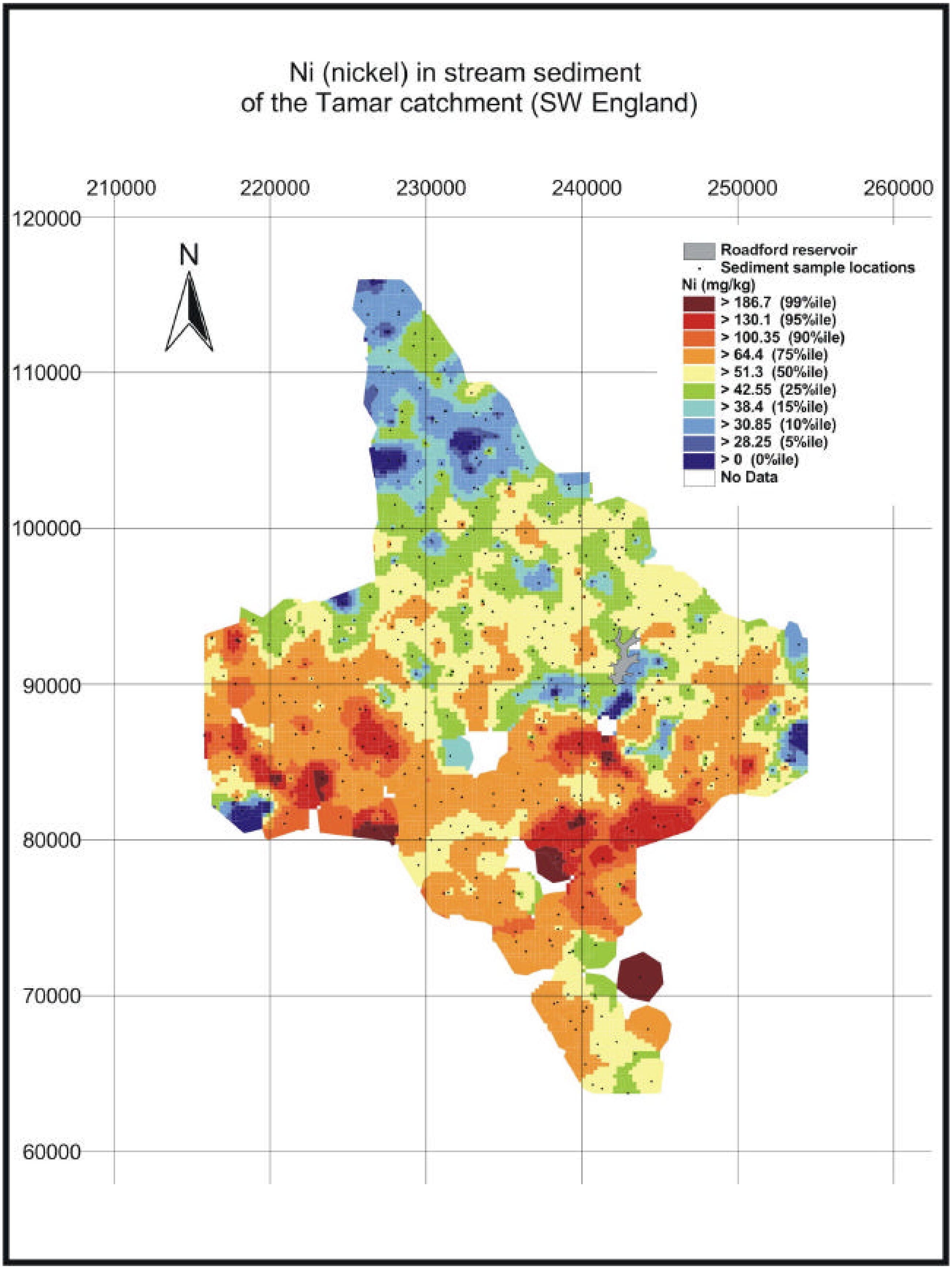

MnO (manganese oxide) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
MnO (%)
> 1.589 (99%ile)
> 0.7655 (95%ile)
> 0.5235 (90%ile)
> 0.2815 (75%ile)
> 0.1745 (50%ile)
> 0.1215 (25%ile)
> 0.1045 (15%ile)
> 0.0805 (10%ile)
> 0.071 (5%ile)
> 0 (0%ile)
No Data

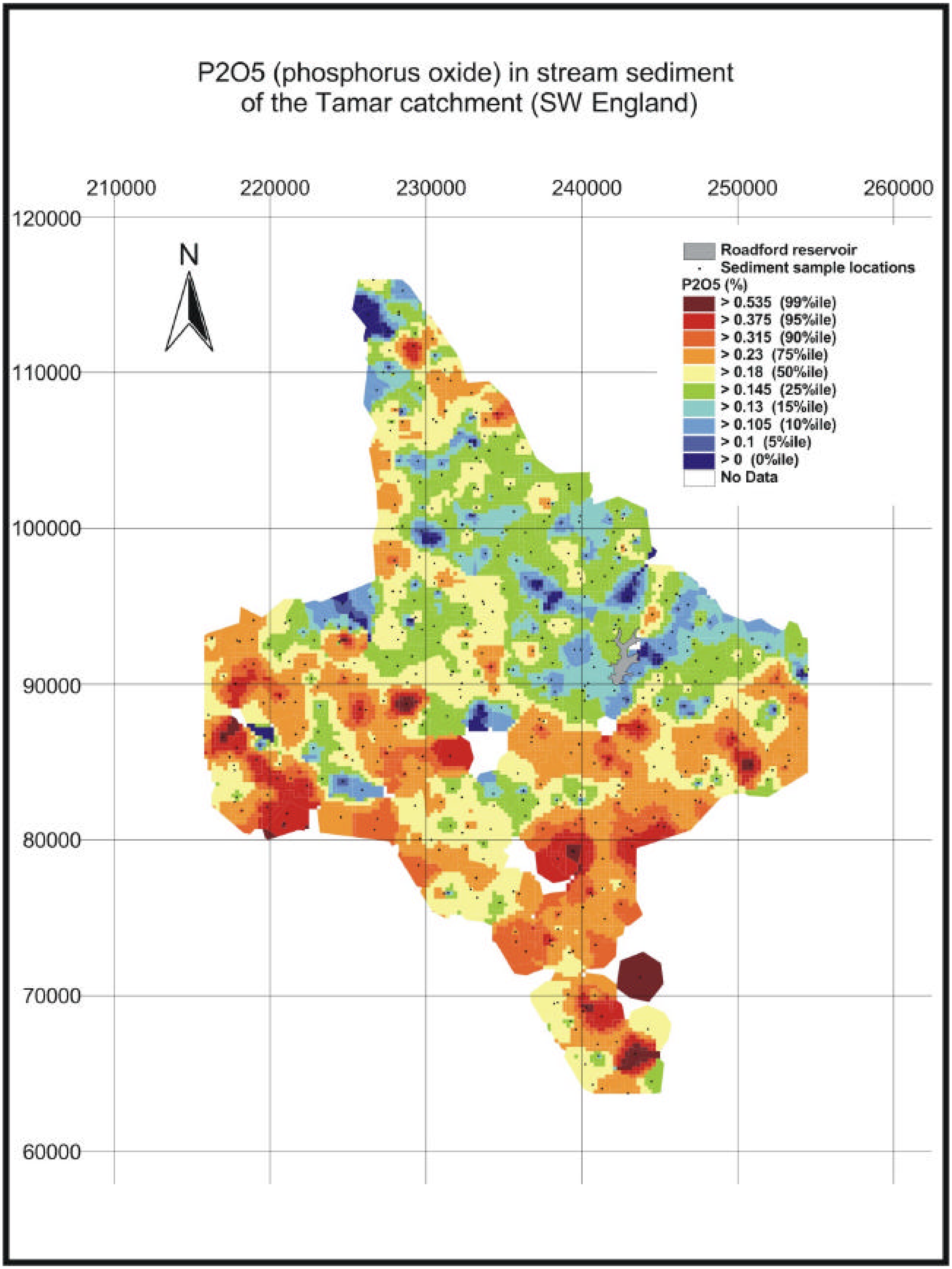

Mo (molybdenum) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Mo (mg/kg)
> 6.2 (99%ile)
> 2.45 (95%ile)
> 1.65 (90%ile)
> 0.5 (75%ile)
> 0.3 (50%ile)
> 0 (0%ile)
No Data

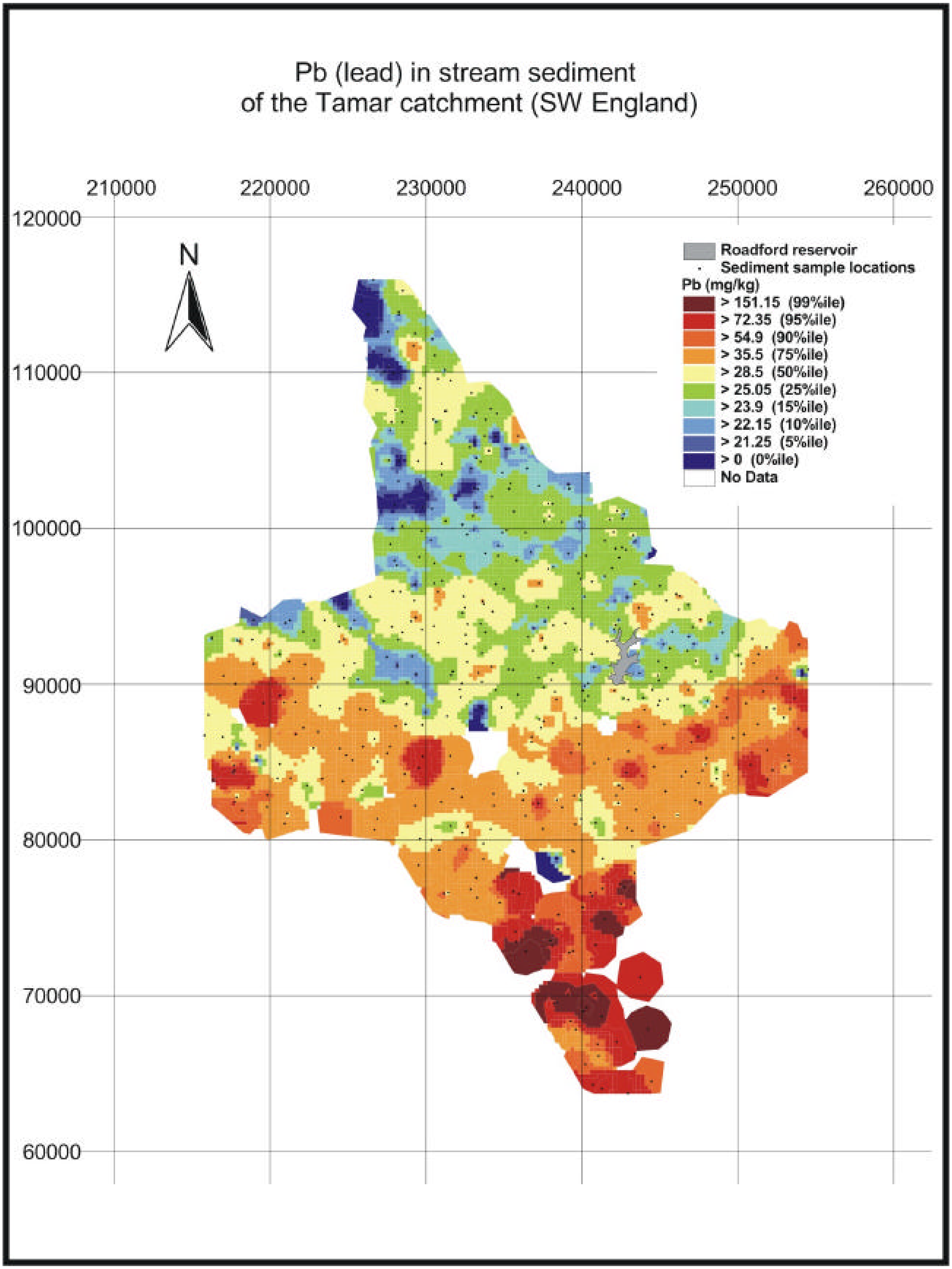

Na2O (sodium oxide) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Na2O (%)
> 1.05 (99%ile)
> 0.9 (95%ile)
> 0.8 (75%ile)
> 0.7 (50%ile)
> 0.45 (25%ile)
> 0.4 (10%ile)
> 0 (0%ile)
No Data


Nb (niobium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Nb (mg/kg)
> 38.7 (99%ile)
> 24.7 (95%ile)
> 19.8 (90%ile)
> 17.1 (75%ile)
> 16.1 (50%ile)
> 15.4 (25%ile)
> 15 (15%ile)
> 14.5 (10%ile)
> 14.2 (5%ile)
> 0 (0%ile)
No Data

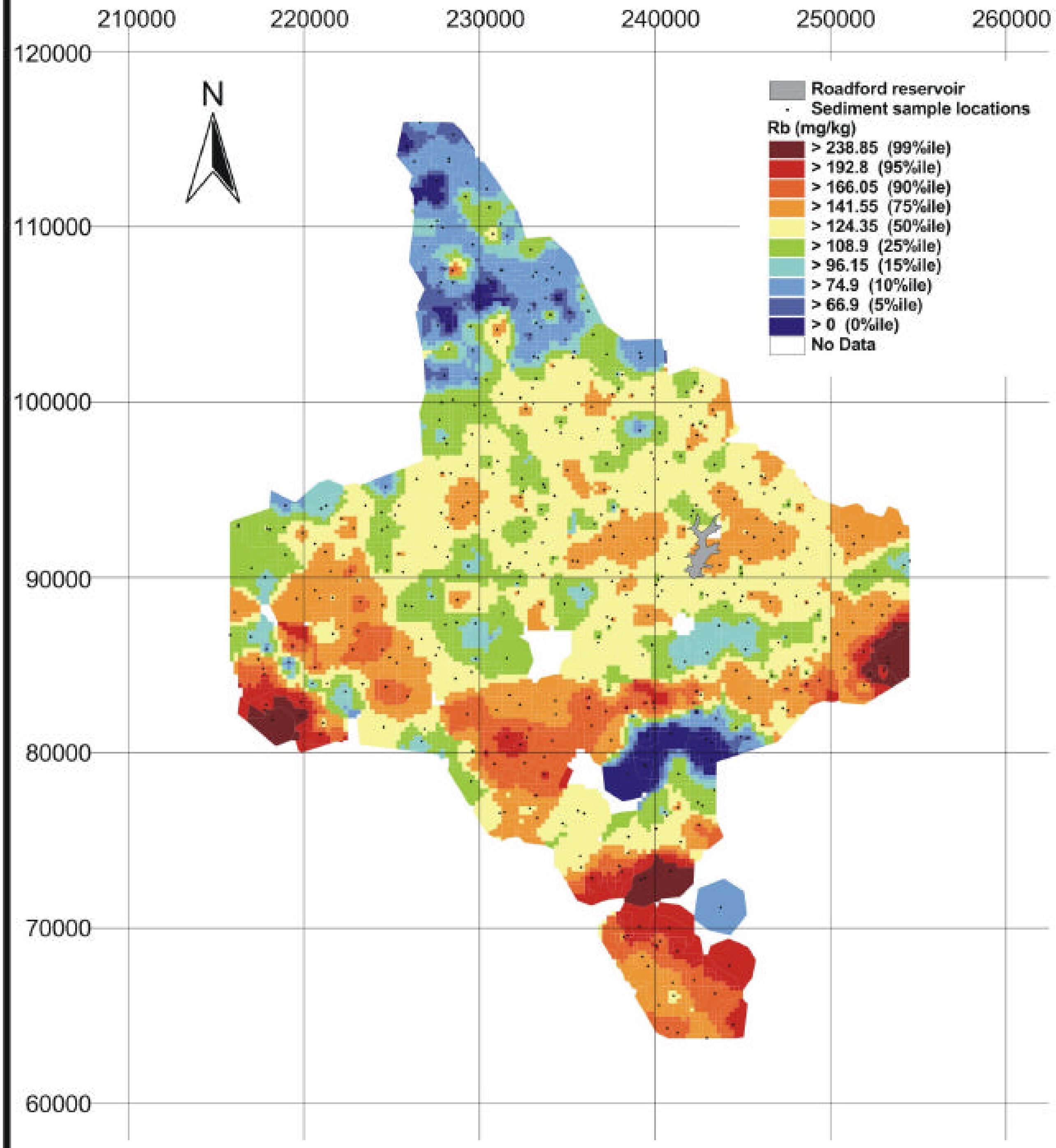

Nd (neodymium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Nd (mg/kg)
> 72.5 (99%ile)
> 51 (95%ile)
> 47 (90%ile)
> 42 (75%ile)
> 39 (50%ile)
> 36 (25%ile)
> 34 (15%ile)
> 32 (10%ile)
> 30 (5%ile)
> 0 (0%ile)
No Data


Ni (nickel) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Ni (mg/kg)
> 186.7 (99%ile)
> 130.1 (95%ile)
> 100.35 (90%ile)
> 64.4 (75%ile)
> 51.3 (50%ile)
> 42.55 (25%ile)
> 38.4 (15%ile)
> 30.85 (10%ile)
> 28.25 (5%ile)
> 0 (0%ile)
No Data

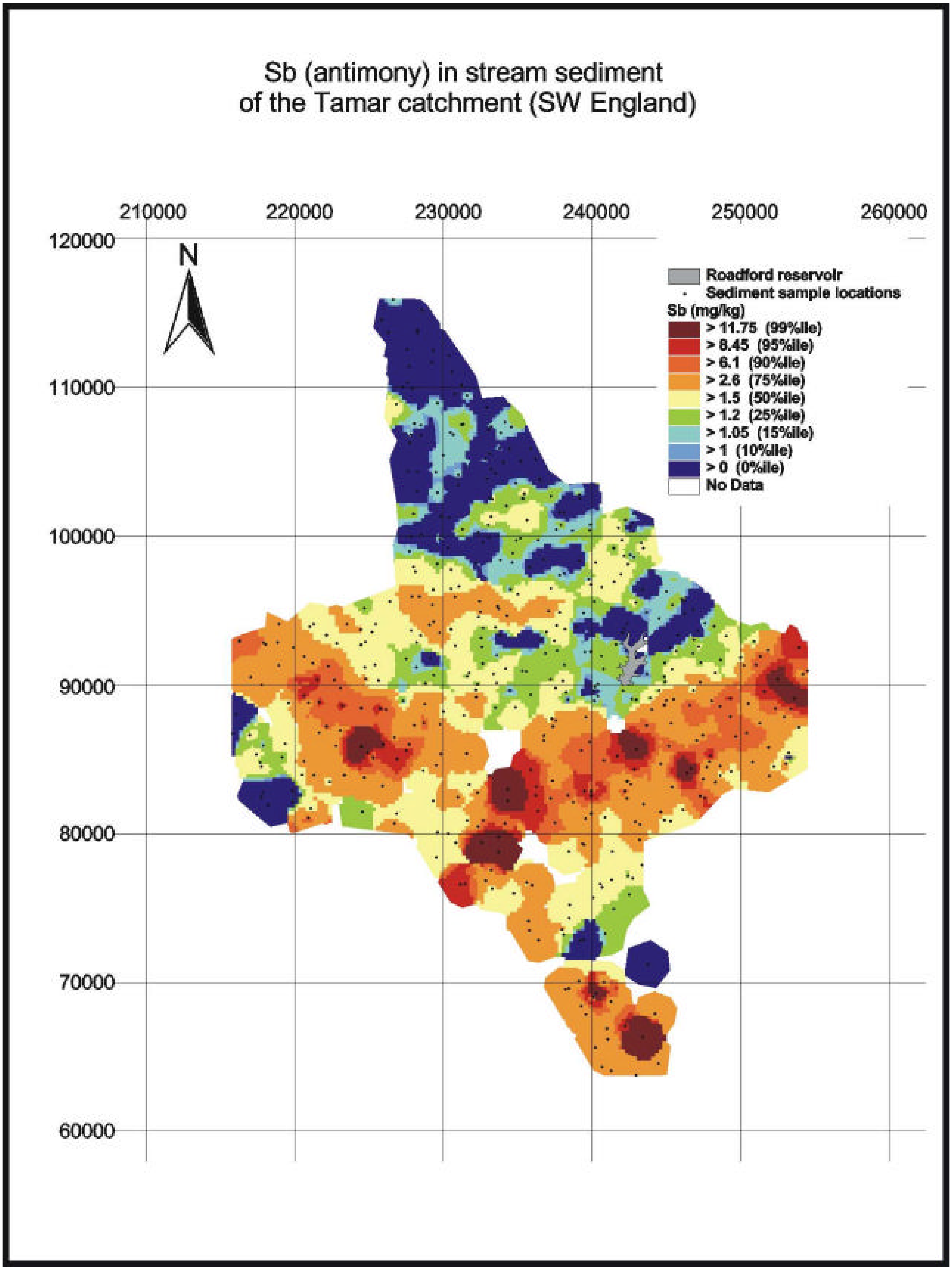

P2O5 (phosphorus oxide) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
P2O5 (%)
> 0.535 (99%ile)
> 0.375 (95%ile)
> 0.315 (90%ile)
> 0.23 (75%ile)
> 0.18 (50%ile)
> 0.145 (25%ile)
> 0.13 (15%ile)
> 0.105 (10%ile)
> 0.1 (5%ile)
> 0 (0%ile)
No Data



Pb (lead) in stream sediment
of the Tamar catchment (SW England)

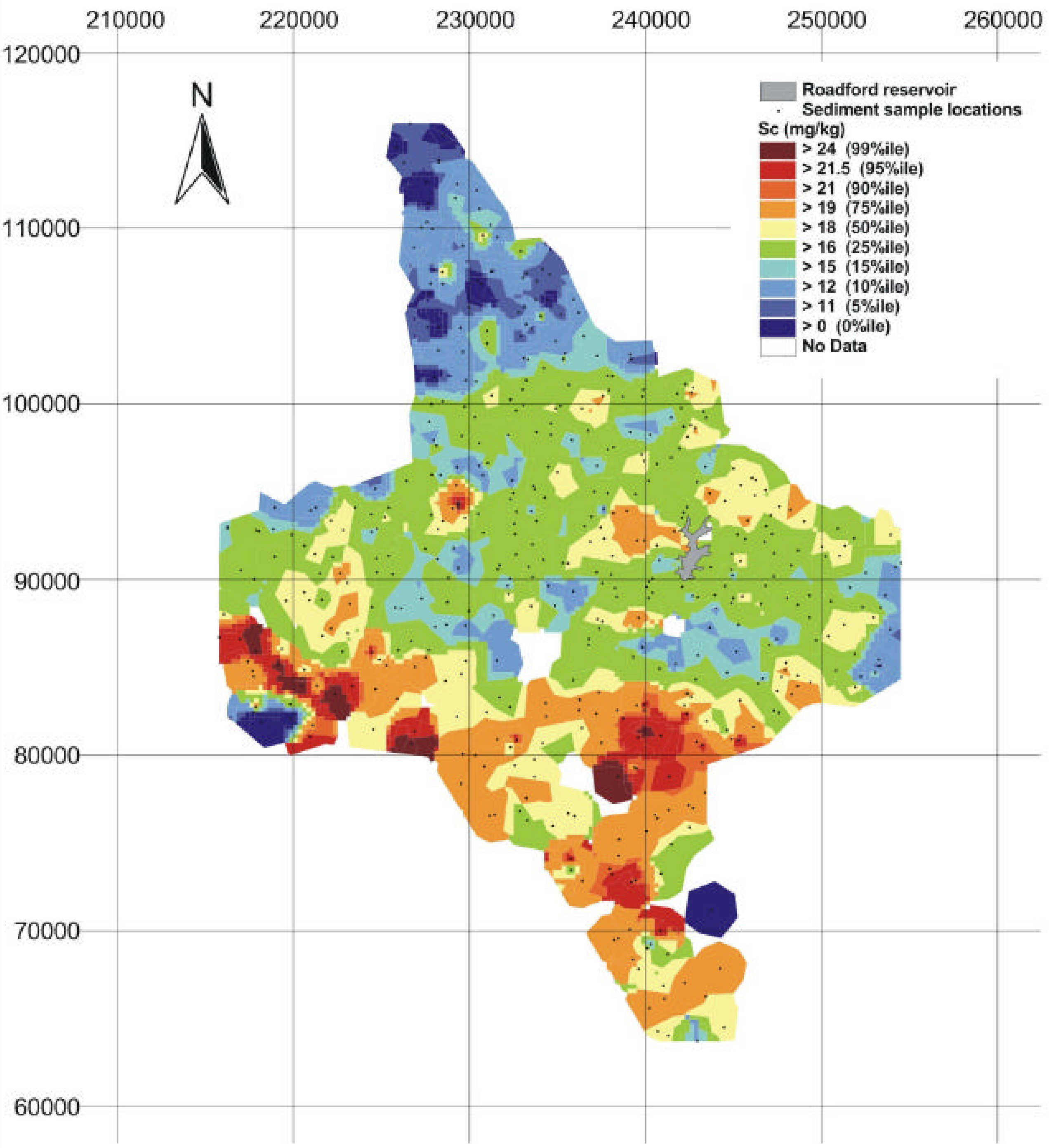


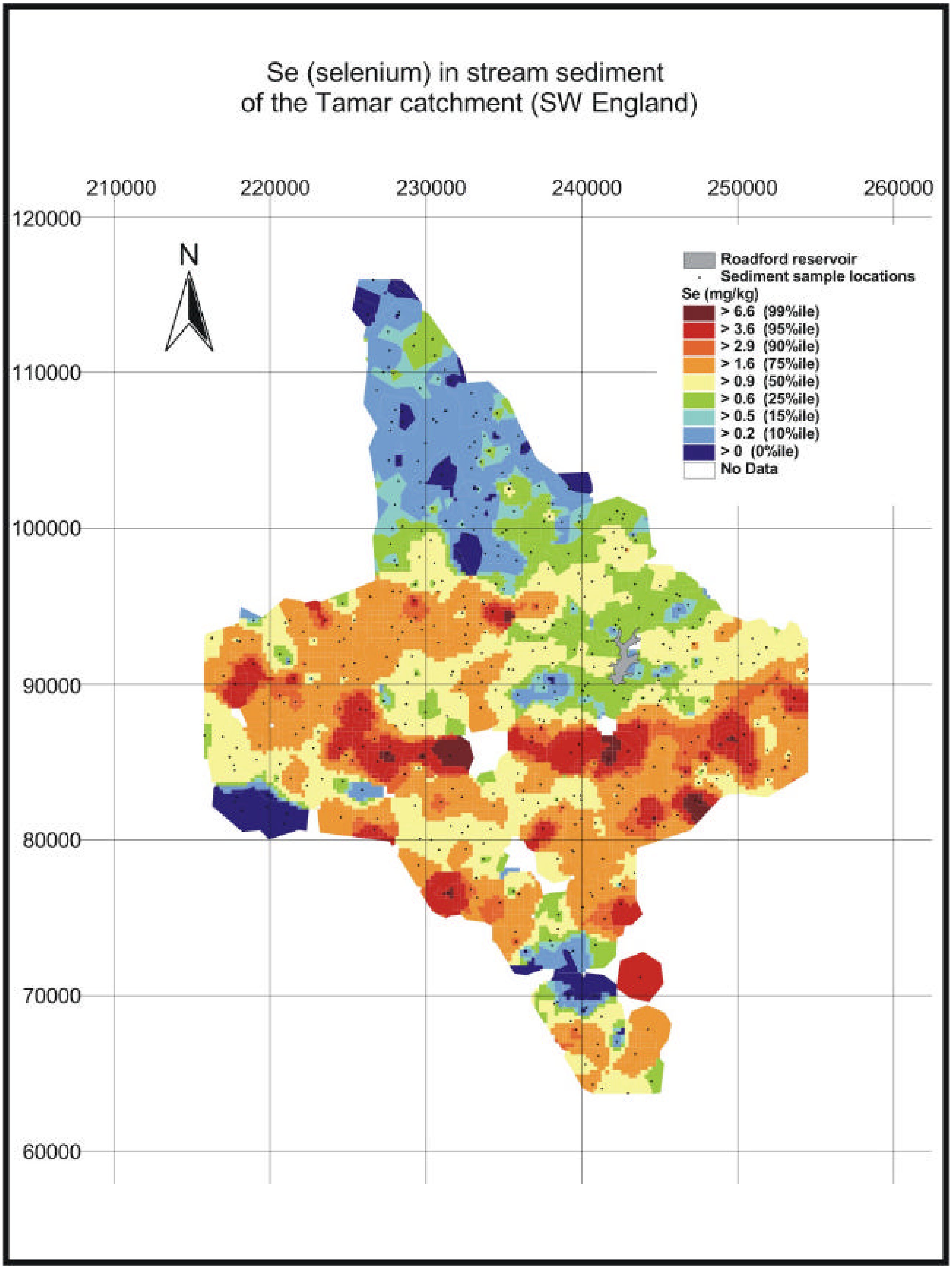
Rb (rubidium) in stream sediment
of the Tamar catchment (SW England)

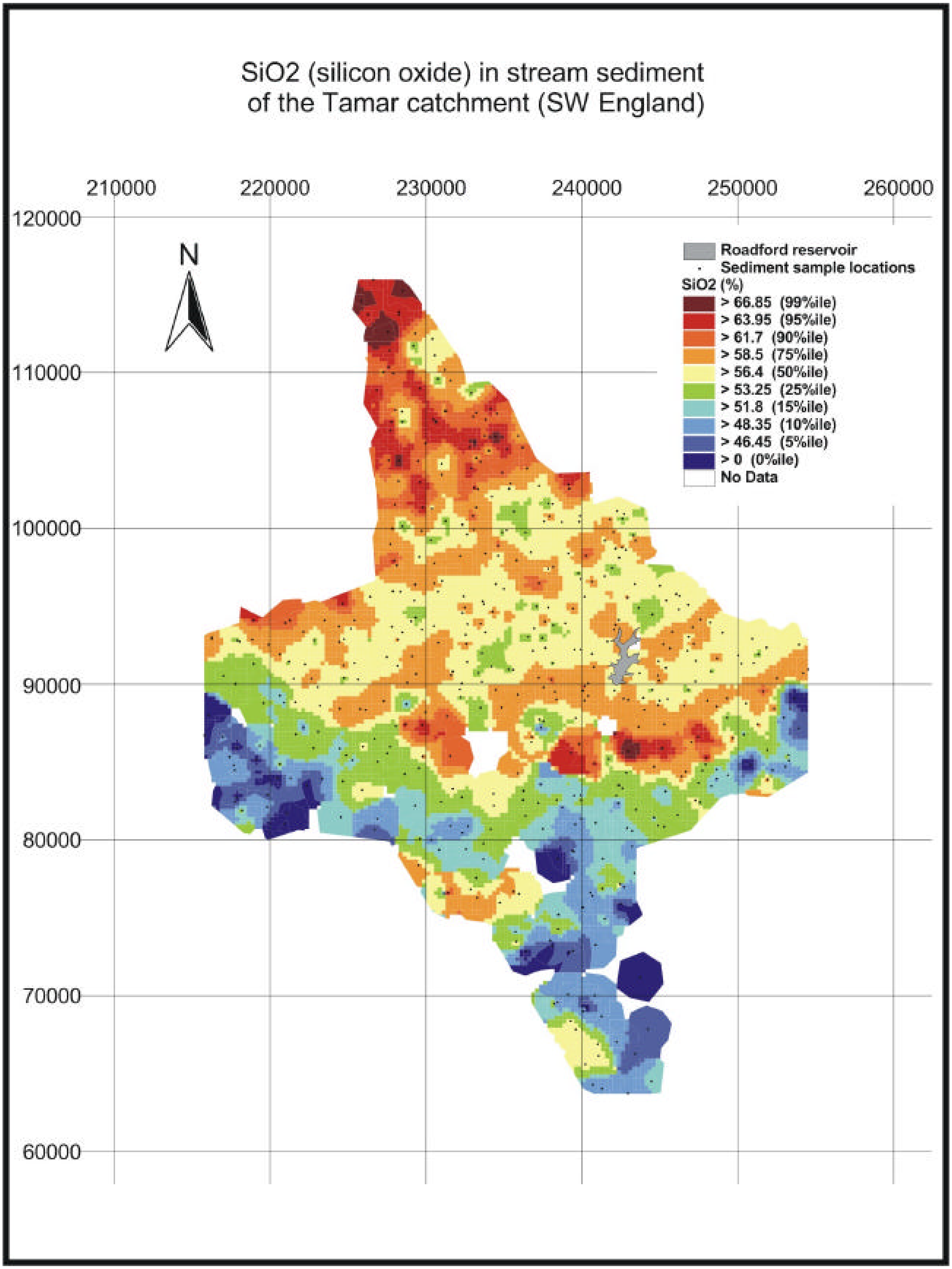


Sb (antimony) in stream sediment
of the Tamar catchment (SW England)

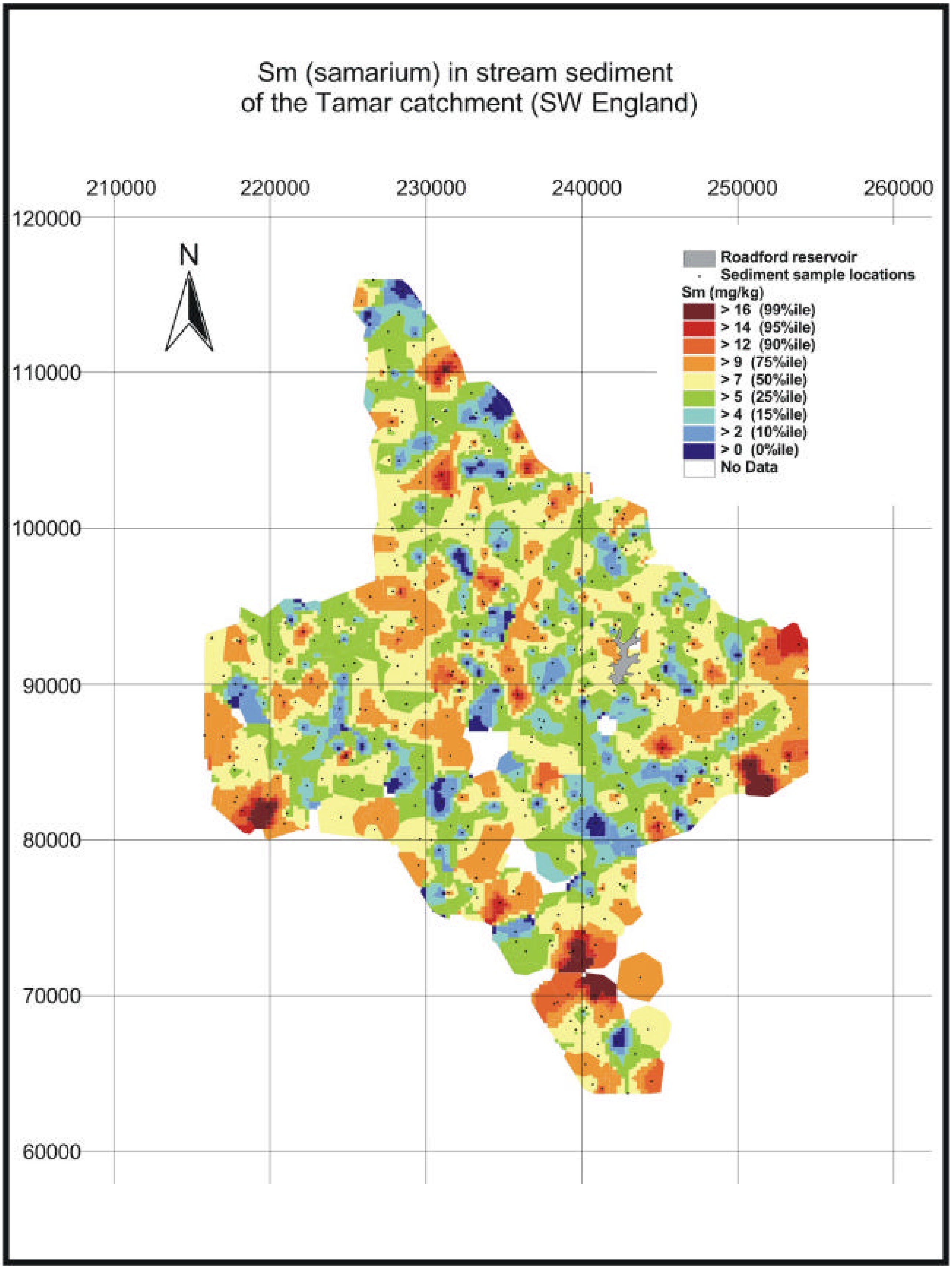
Sc (scandium) in stream sediment
of the Tamar catchment (SW England)

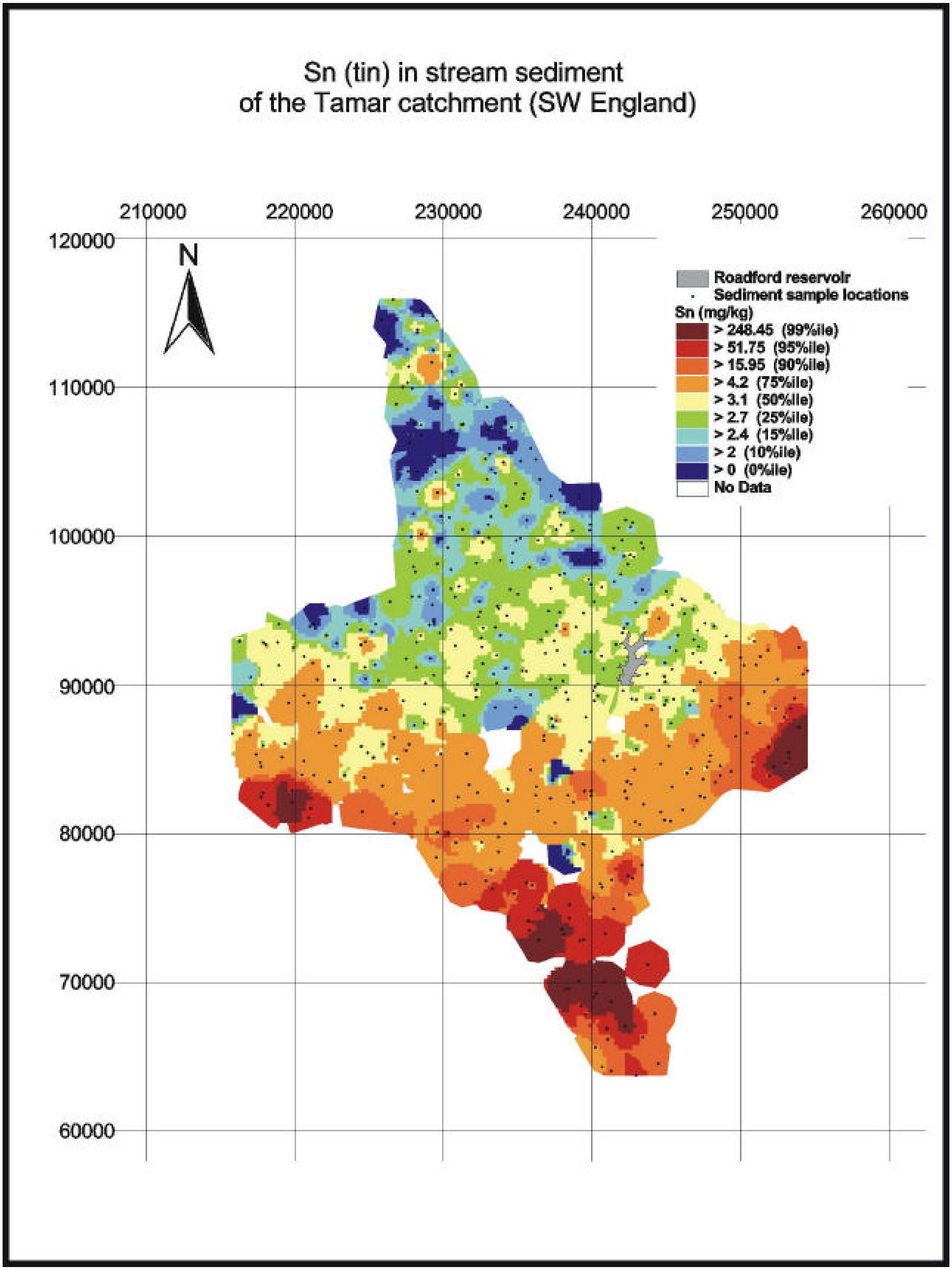


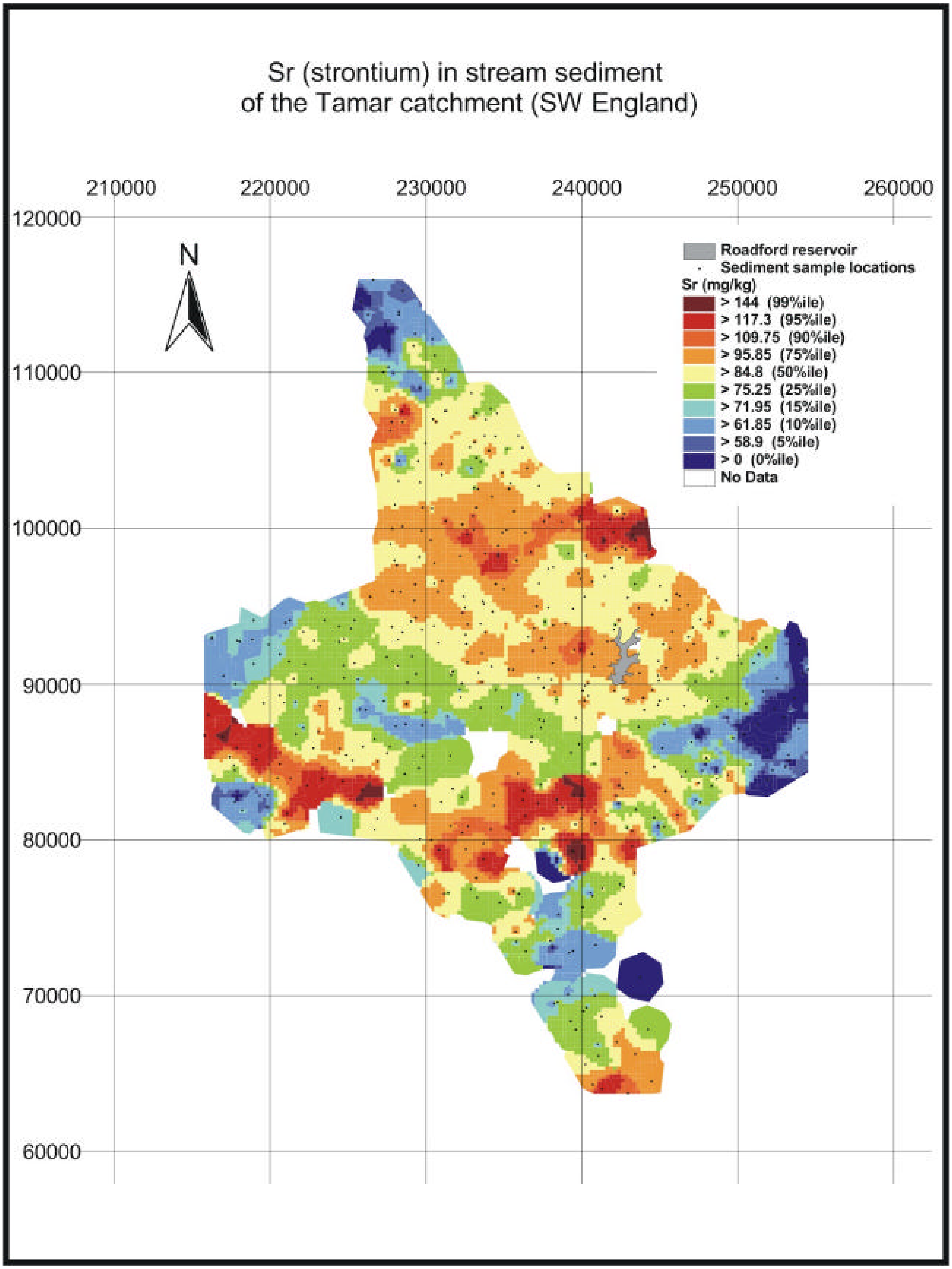

Se (selenium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Se (mg/kg)
> 6.6 (99%ile)
> 3.6 (95%ile)
> 2.9 (90%ile)
> 1.6 (75%ile)
> 0.9 (50%ile)
> 0.6 (25%ile)
> 0.5 (15%ile)
> 0.2 (10%ile)
> 0 (0%ile)
No Data

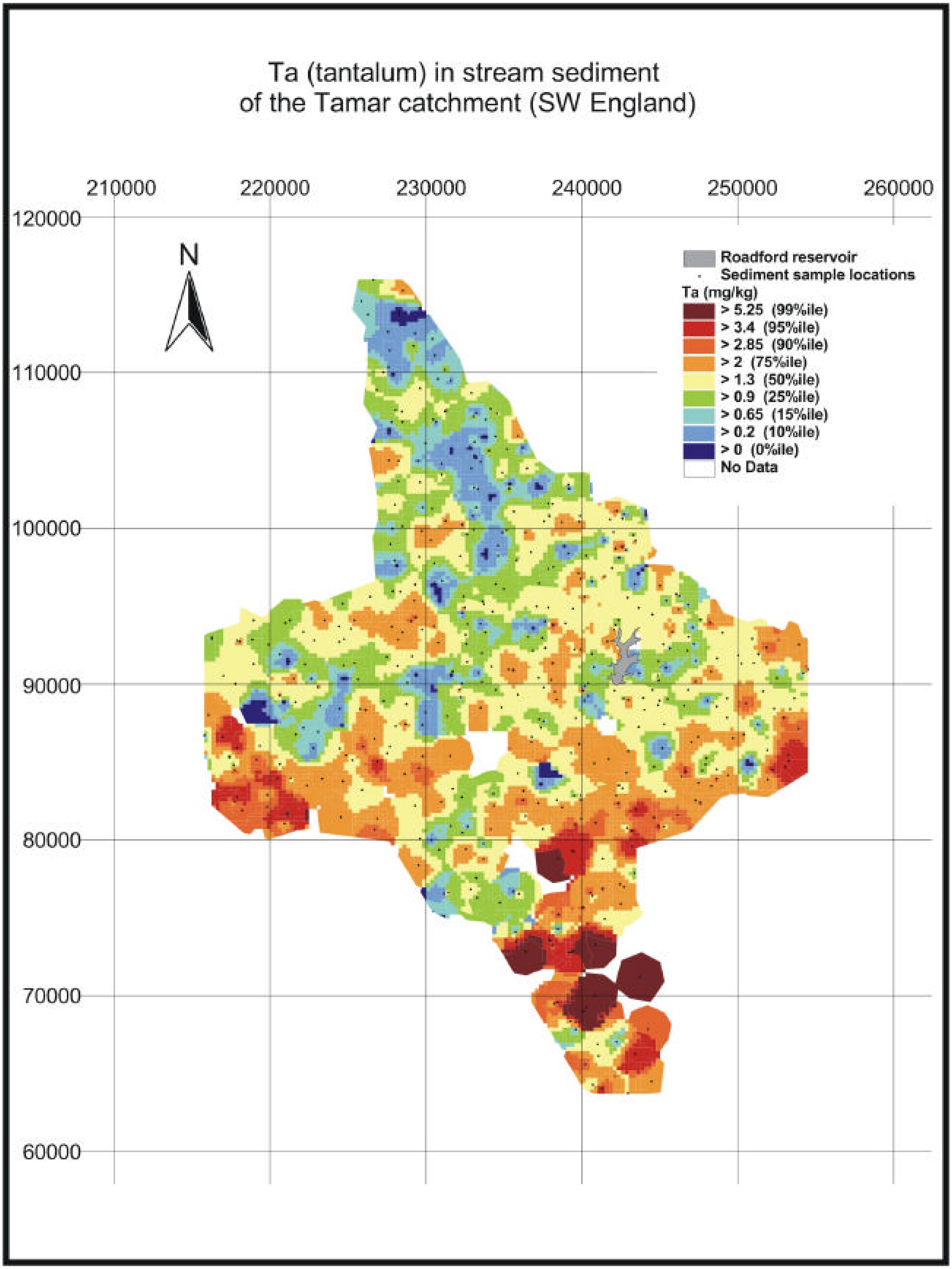


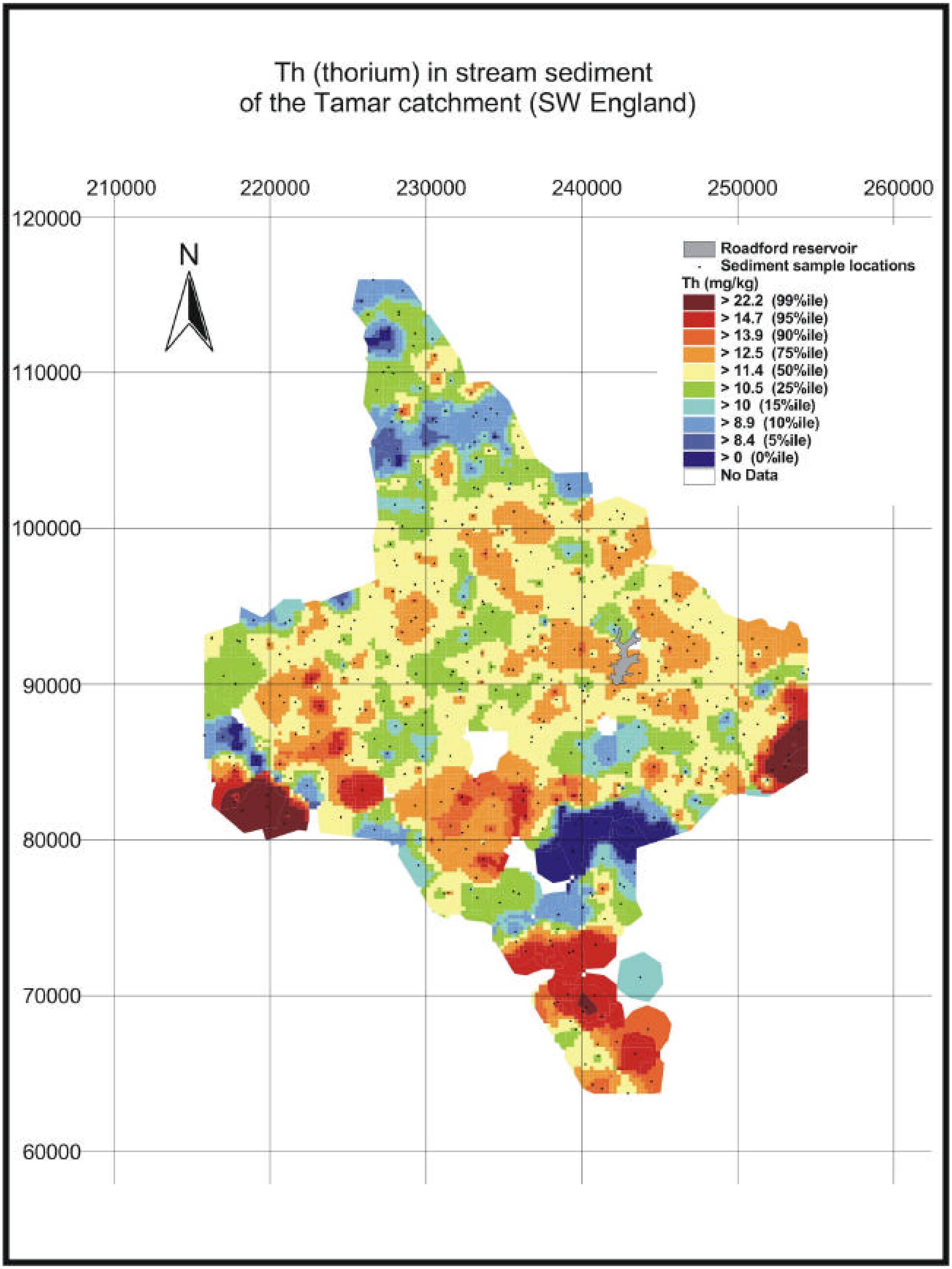
SiO2 (silicon oxide) in stream sediment of the Tamar catchment (SW England)

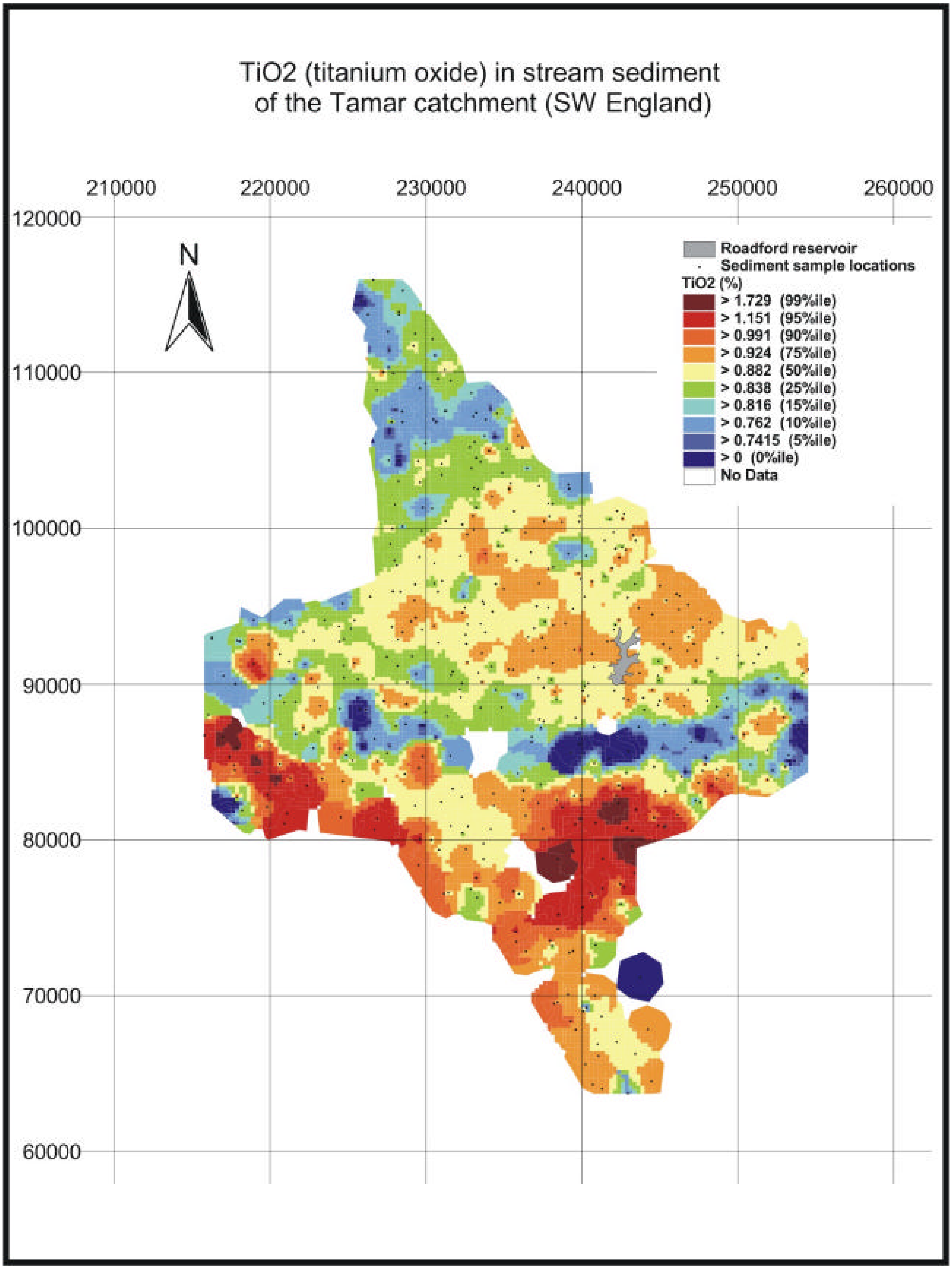

Sm (samarium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Sm (mg/kg)
> 16 (99%ile)
> 14 (95%ile)
> 12 (90%ile)
> 9 (75%ile)
> 7 (50%ile)
> 5 (25%ile)
> 4 (15%ile)
> 2 (10%ile)
> 0 (0%ile)
No Data


Sn (tin) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Sn (mg/kg)
> 248.45 (99%ile)
> 51.75 (95%ile)
> 15.95 (90%ile)
> 4.2 (75%ile)
> 3.1 (50%ile)
> 2.7 (25%ile)
> 2.4 (15%ile)
> 2 (10%ile)
> 0 (0%ile)
No Data

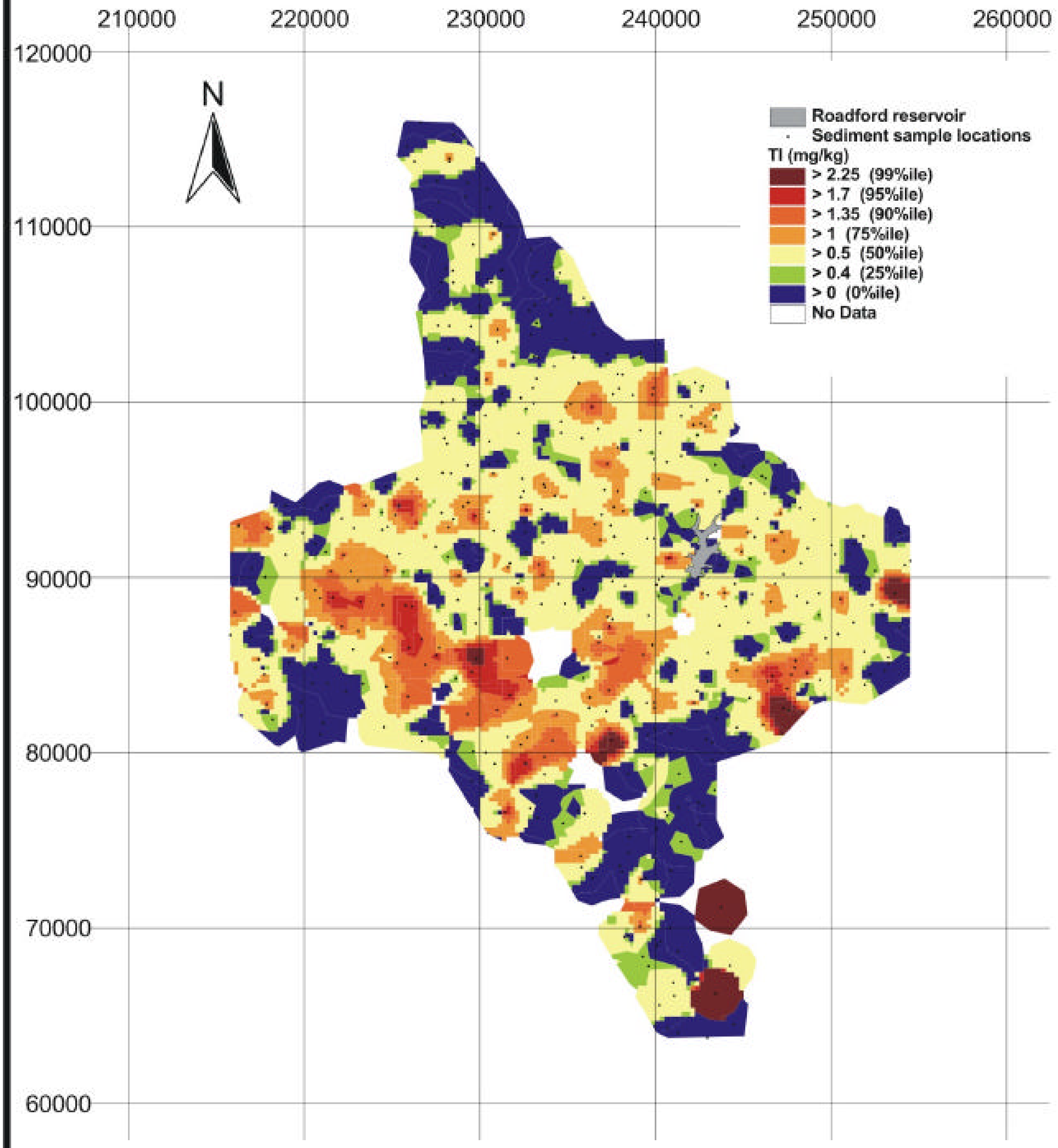

Sr (strontium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Sr (mg/kg)
> 144 (99%ile)
> 117.3 (95%ile)
> 109.75 (90%ile)
> 95.85 (75%ile)
> 84.8 (50%ile)
> 75.25 (25%ile)
> 71.95 (15%ile)
> 61.85 (10%ile)
> 58.9 (5%ile)
> 0 (0%ile)
No Data

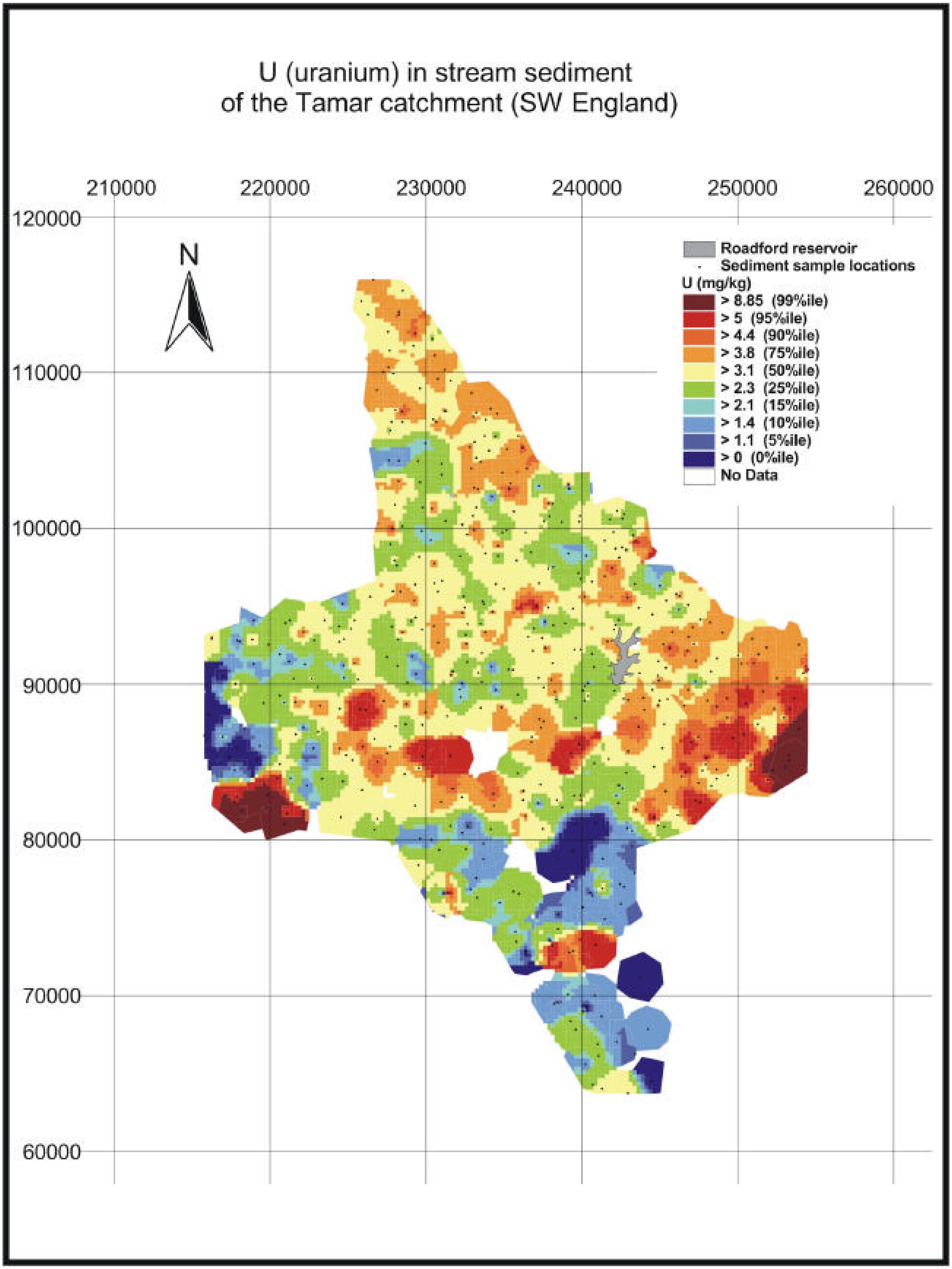

Ta (tantalum) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Ta (mg/kg)
> 5.25 (99%ile)
> 3.4 (95%ile)
> 2.85 (90%ile)
> 2 (75%ile)
> 1.3 (50%ile)
> 0.9 (25%ile)
> 0.65 (15%ile)
> 0.2 (10%ile)
> 0 (0%ile)
No Data

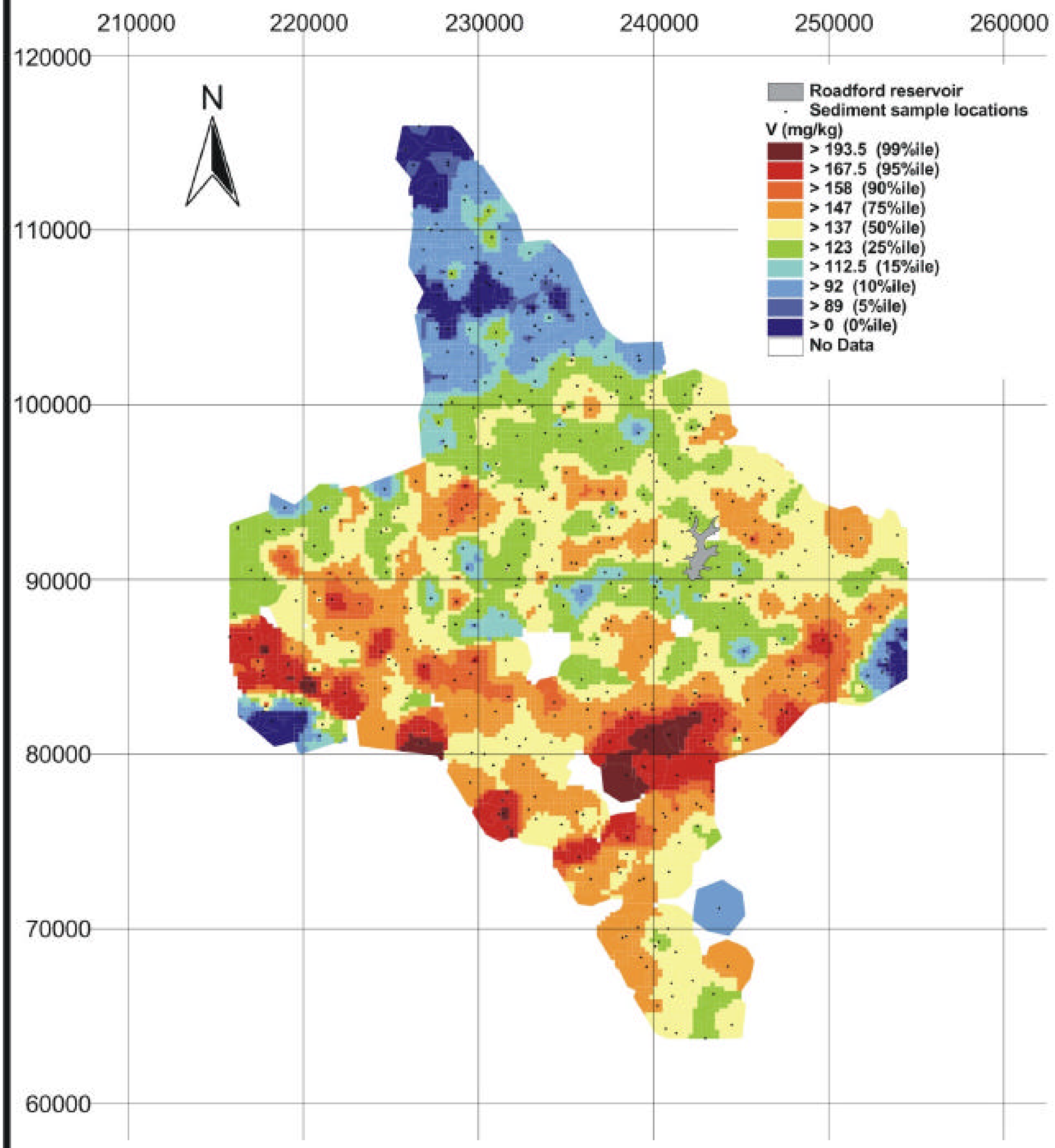

Th (thorium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Th (mg/kg)
> 22.2 (99%ile)
> 14.7 (95%ile)
> 13.9 (90%ile)
> 12.5 (75%ile)
> 11.4 (50%ile)
> 10.5 (25%ile)
> 10 (15%ile)
> 8.9 (10%ile)
> 8.4 (5%ile)
> 0 (0%ile)
No Data


TiO2 (titanium oxide) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
TiO2 (%)
> 1.729 (99%ile)
> 1.151 (95%ile)
> 0.991 (90%ile)
> 0.924 (75%ile)
> 0.882 (50%ile)
> 0.838 (25%ile)
> 0.816 (15%ile)
> 0.762 (10%ile)
> 0.7415 (5%ile)
> 0 (0%ile)
No Data

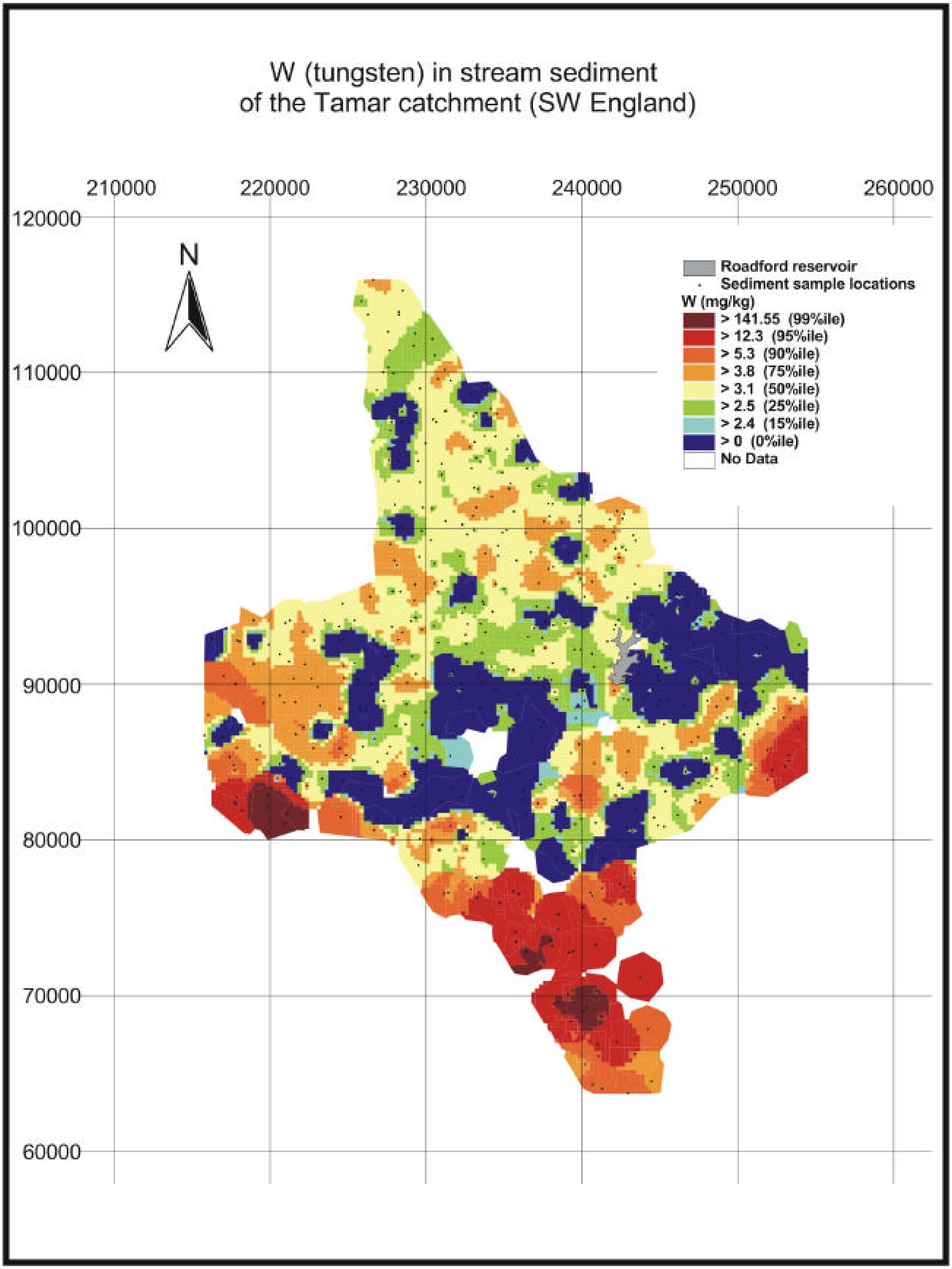
Tl (thallium) in stream sediment
of the Tamar catchment (SW England)

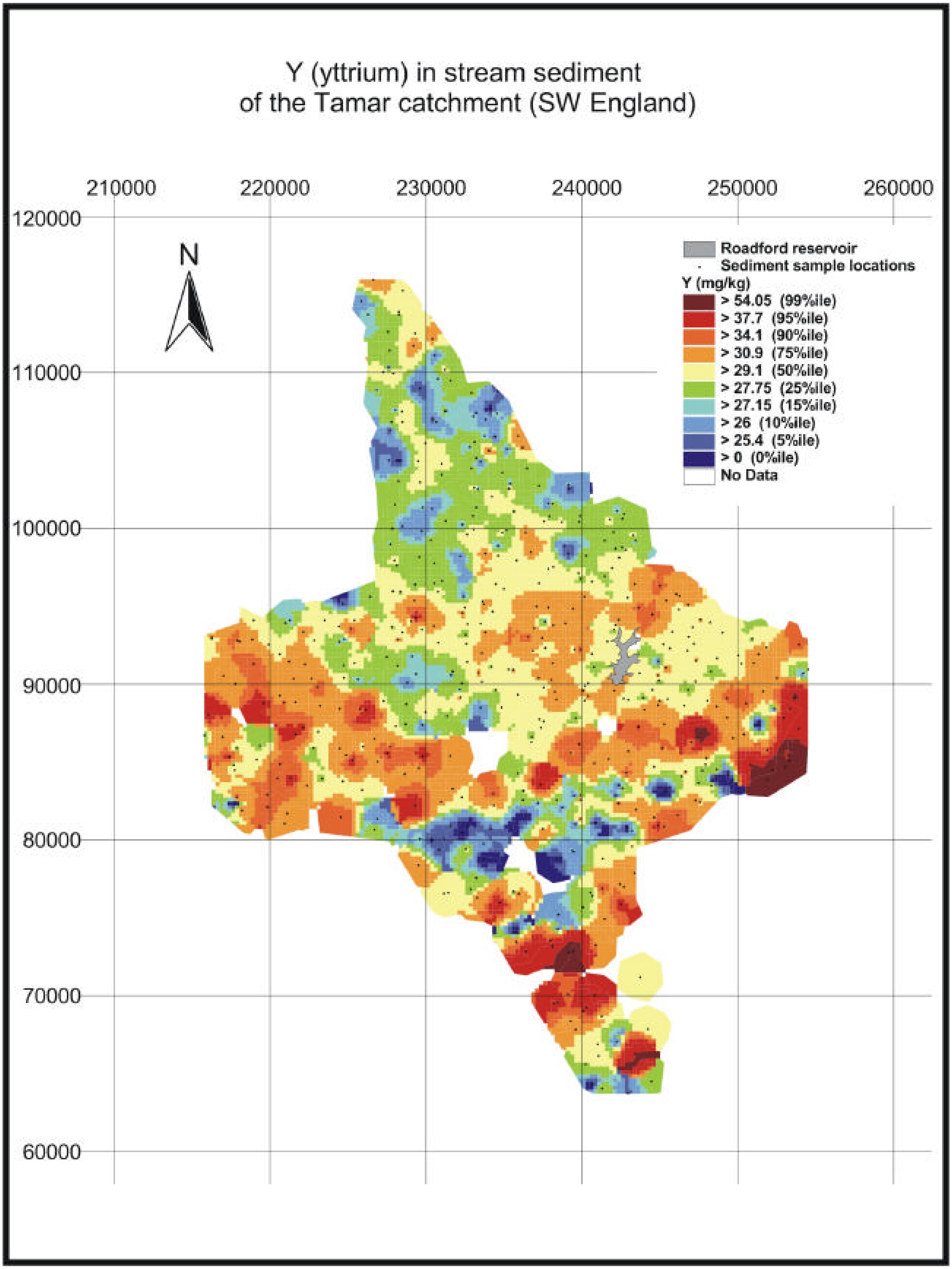


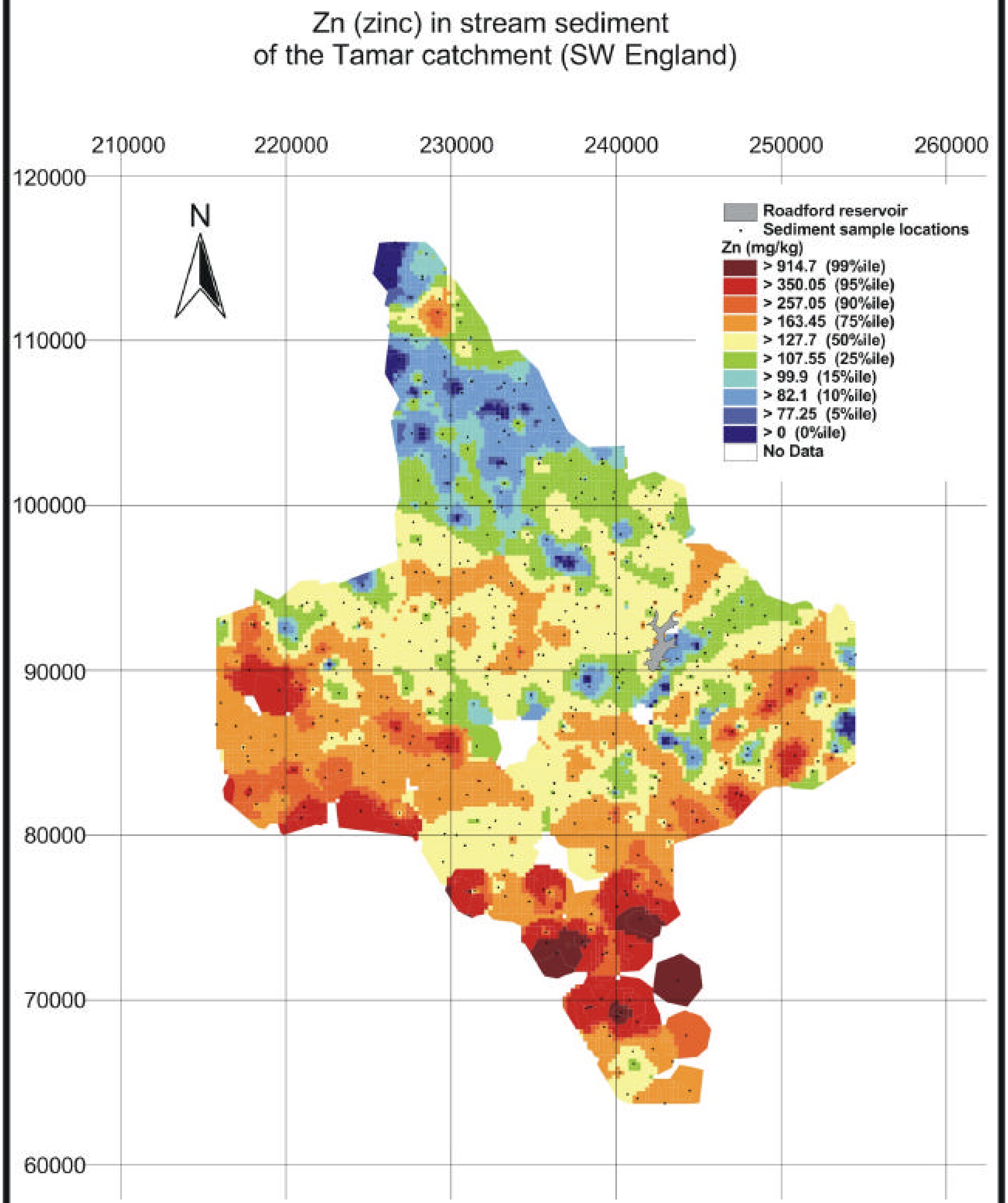

U (uranium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
U (mg/kg)
> 8.85 (99%ile)
> 5 (95%ile)
> 4.4 (90%ile)
> 3.8 (75%ile)
> 3.1 (50%ile)
> 2.3 (25%ile)
> 2.1 (15%ile)
> 1.4 (10%ile)
> 1.1 (5%ile)
> 0 (0%ile)
No Data

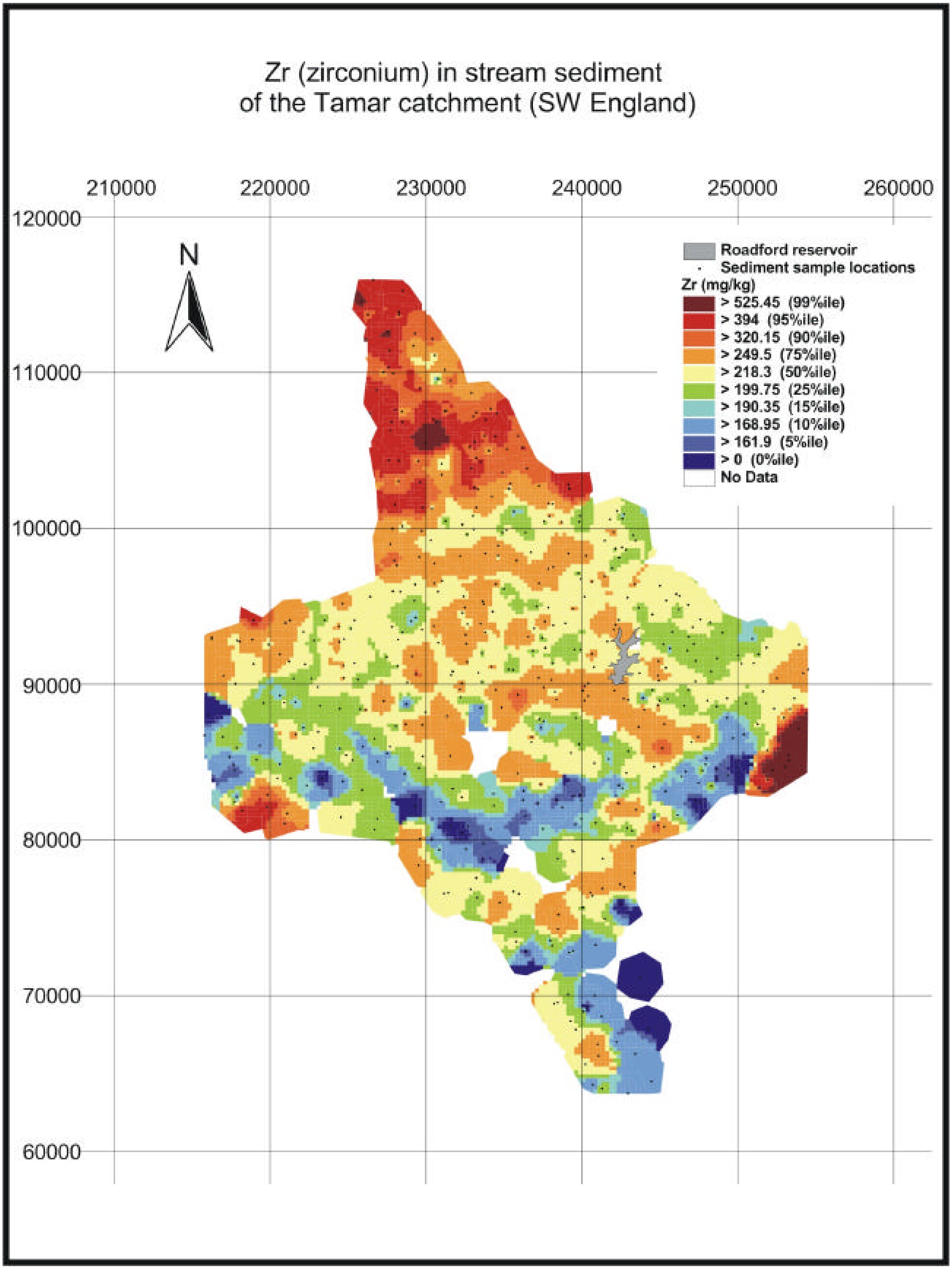


V (vanadium) in stream sediment
of the Tamar catchment (SW England)


W (tungsten) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
W (mg/kg)
> 141.55 (99%ile)
> 12.3 (95%ile)
> 5.3 (90%ile)
> 3.8 (75%ile)
> 3.1 (50%ile)
> 2.5 (25%ile)
> 2.4 (15%ile)
> 0 (0%ile)
No Data


Y (yttrium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Y (mg/kg)
> 54.05 (99%ile)
> 37.7 (95%ile)
> 34.1 (90%ile)
> 30.9 (75%ile)
> 29.1 (50%ile)
> 27.75 (25%ile)
> 27.15 (15%ile)
> 26 (10%ile)
> 25.4 (5%ile)
> 0 (0%ile)
No Data


Zn (zinc) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Zn (mg/kg)
> 914.7 (99%ile)
> 350.05 (95%ile)
> 257.05 (90%ile)
> 163.45 (75%ile)
> 127.7 (50%ile)
> 107.55 (25%ile)
> 99.9 (15%ile)
> 82.1 (10%ile)
> 77.25 (5%ile)
> 0 (0%ile)
No Data

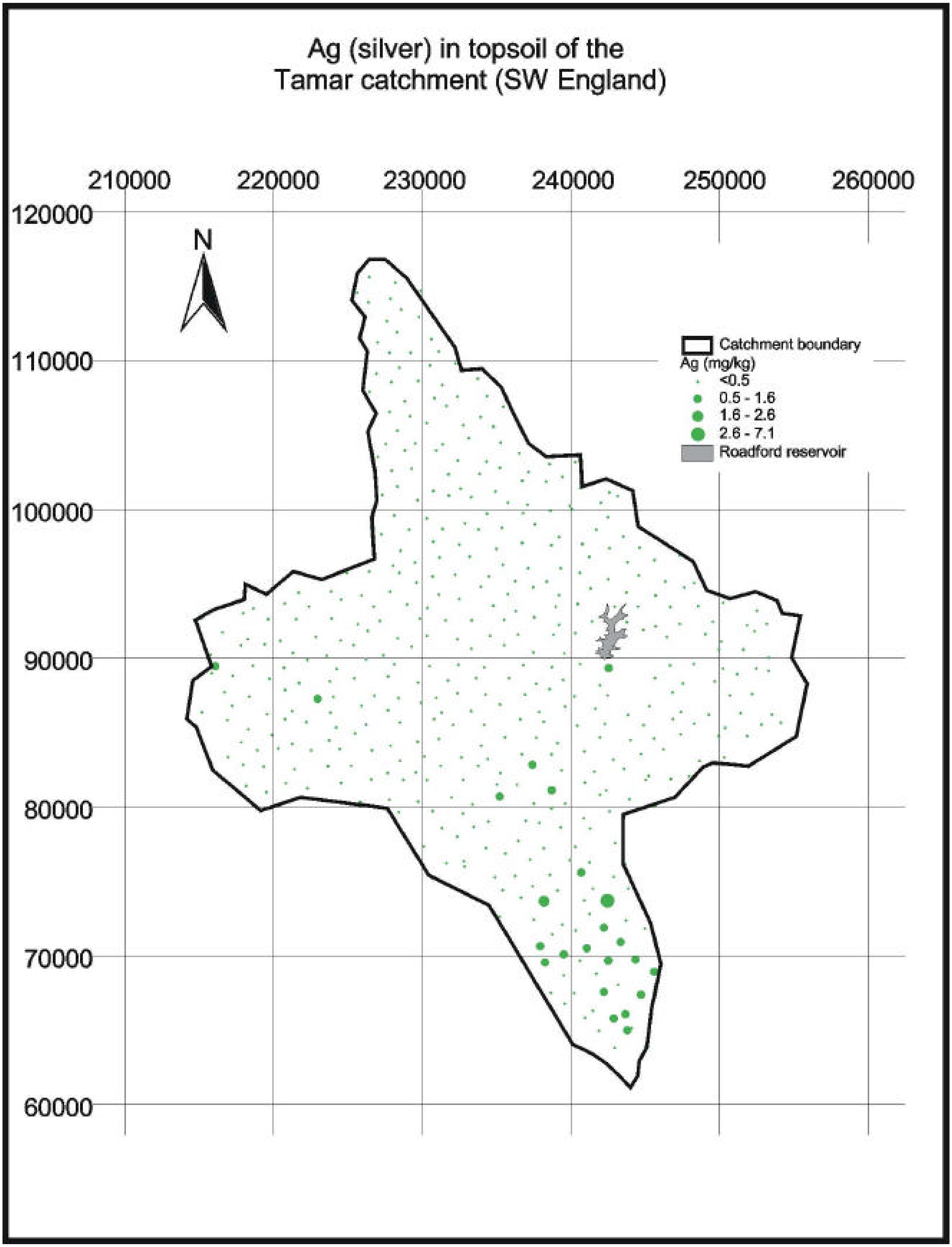

Zr (zirconium) in stream sediment
of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Sediment sample locations
Zr (mg/kg)
> 525.45 (99%ile)
> 394 (95%ile)
> 320.15 (90%ile)
> 249.5 (75%ile)
> 218.3 (50%ile)
> 199.75 (25%ile)
> 190.35 (15%ile)
> 168.95 (10%ile)
> 161.9 (5%ile)
> 0 (0%ile)
No Data

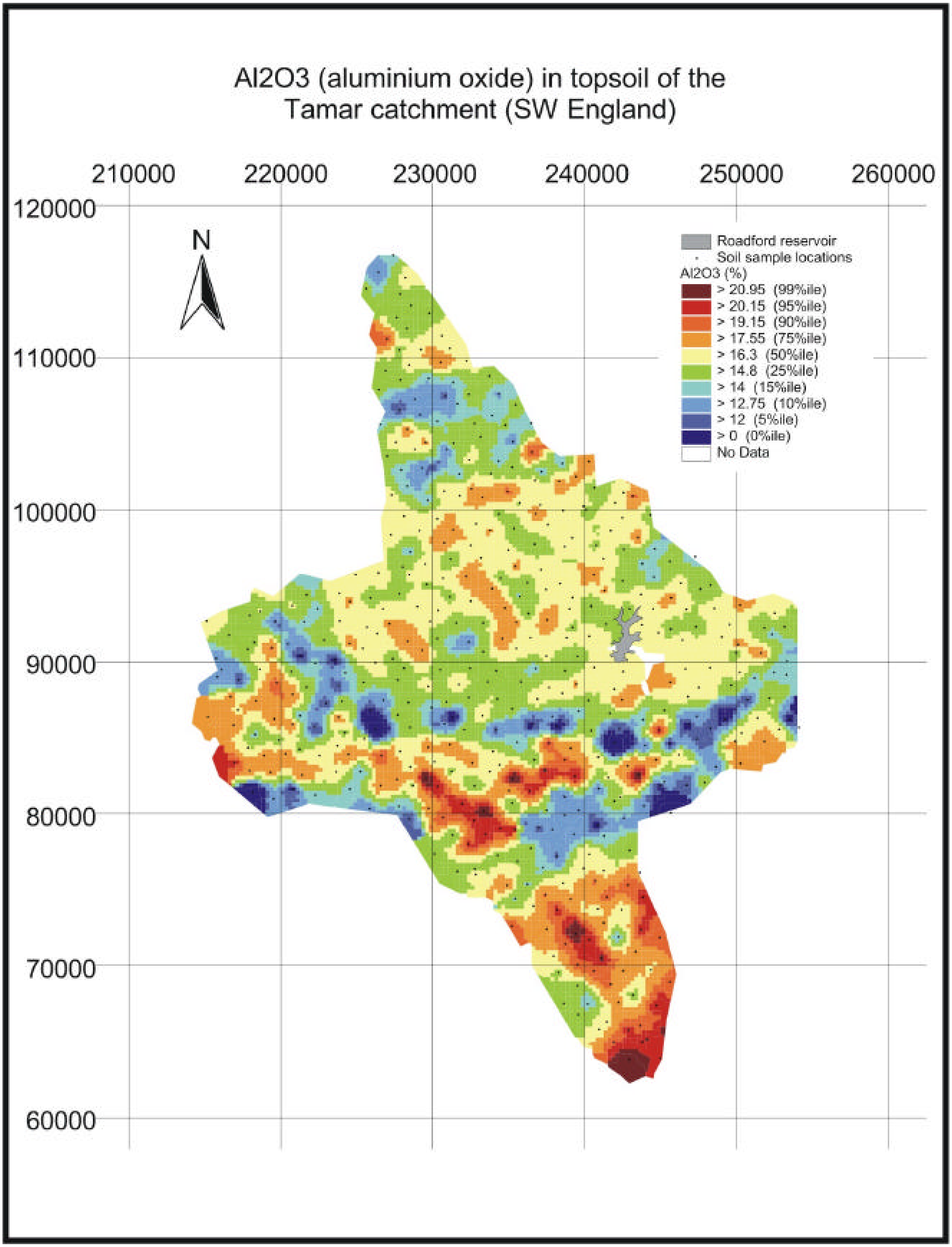
Appendix C – Element distributions in topsoil of the Tamar catchment

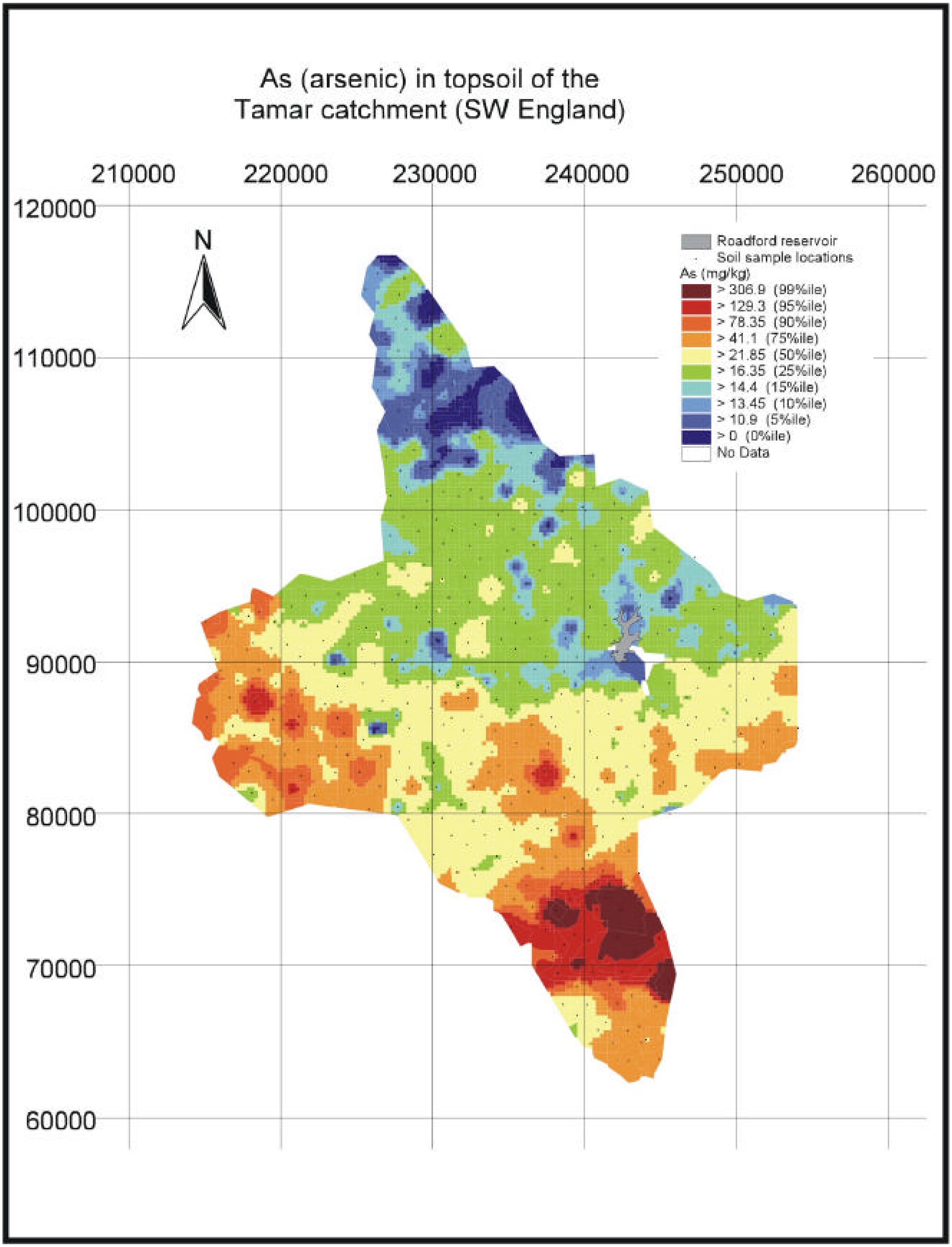
The images presented in this appendix are the outcome of a geochemical survey of the Tamar catchment undertaken in September 2002. The methods adopted in the survey (sampling, analysis and data presentation) are described in the main report entitled ‘Geochemical survey of the Tamar catchment (south-west England)’.

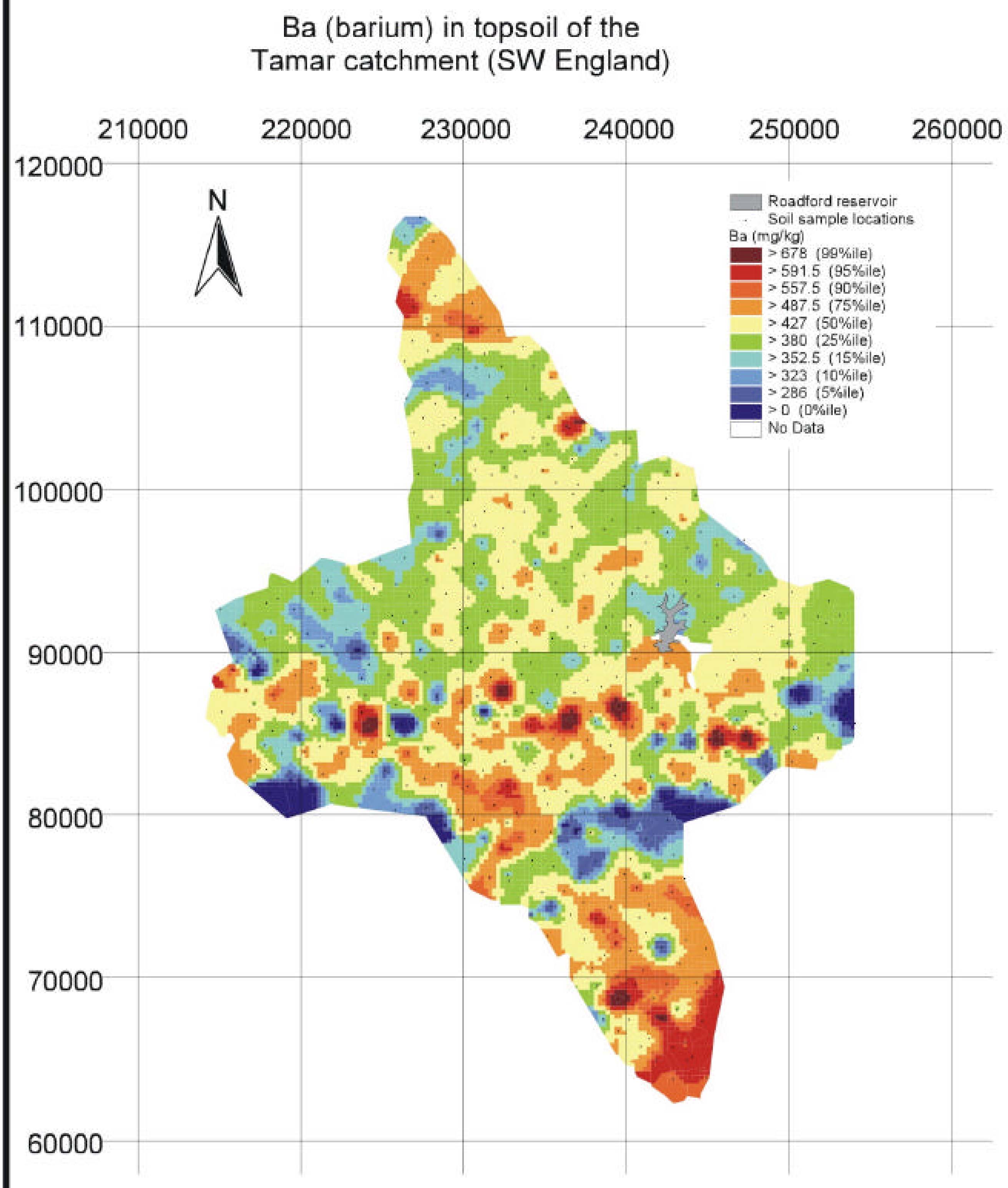
Full bibliographic reference:

RAWLINS, B. G., O'DONNELL, K. AND INGHAM, M. 2003. Geochemical survey of the Tamar catchment (south-west England). *British Geological Survey Report*, CR/03/027. 232pp.

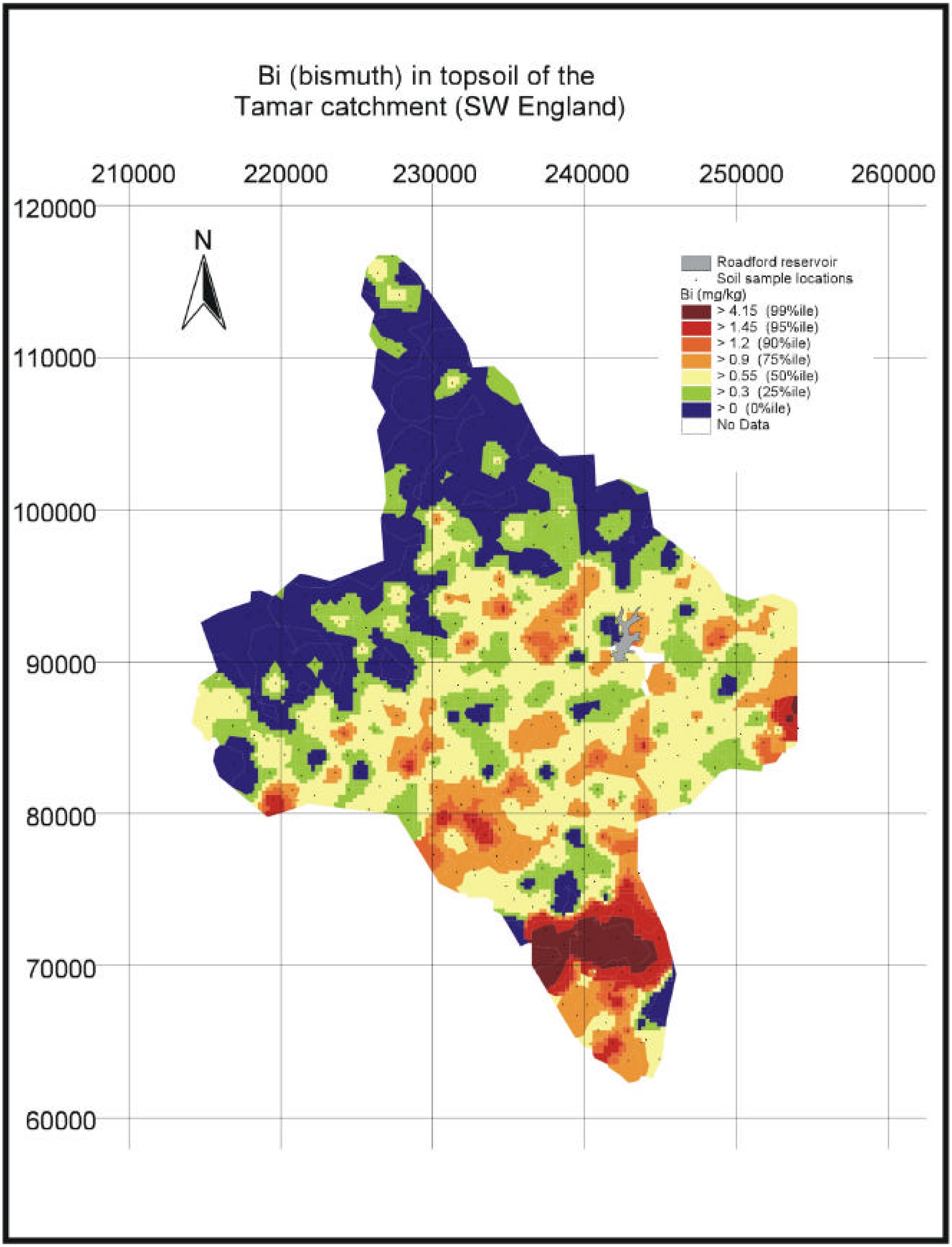

Ag (silver) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Catchment boundary
Ag (mg/kg)
<0.5
0.5 - 1.6
1.6 - 2.6
2.6 - 7.1
Roadford reservoir


Al2O3 (aluminium oxide) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Al2O3 (%)
> 20.95 (99%ile)
> 20.15 (95%ile)
> 19.15 (90%ile)
> 17.55 (75%ile)
> 16.3 (50%ile)
> 14.8 (25%ile)
> 14 (15%ile)
> 12.75 (10%ile)
> 12 (5%ile)
> 0 (0%ile)
No Data

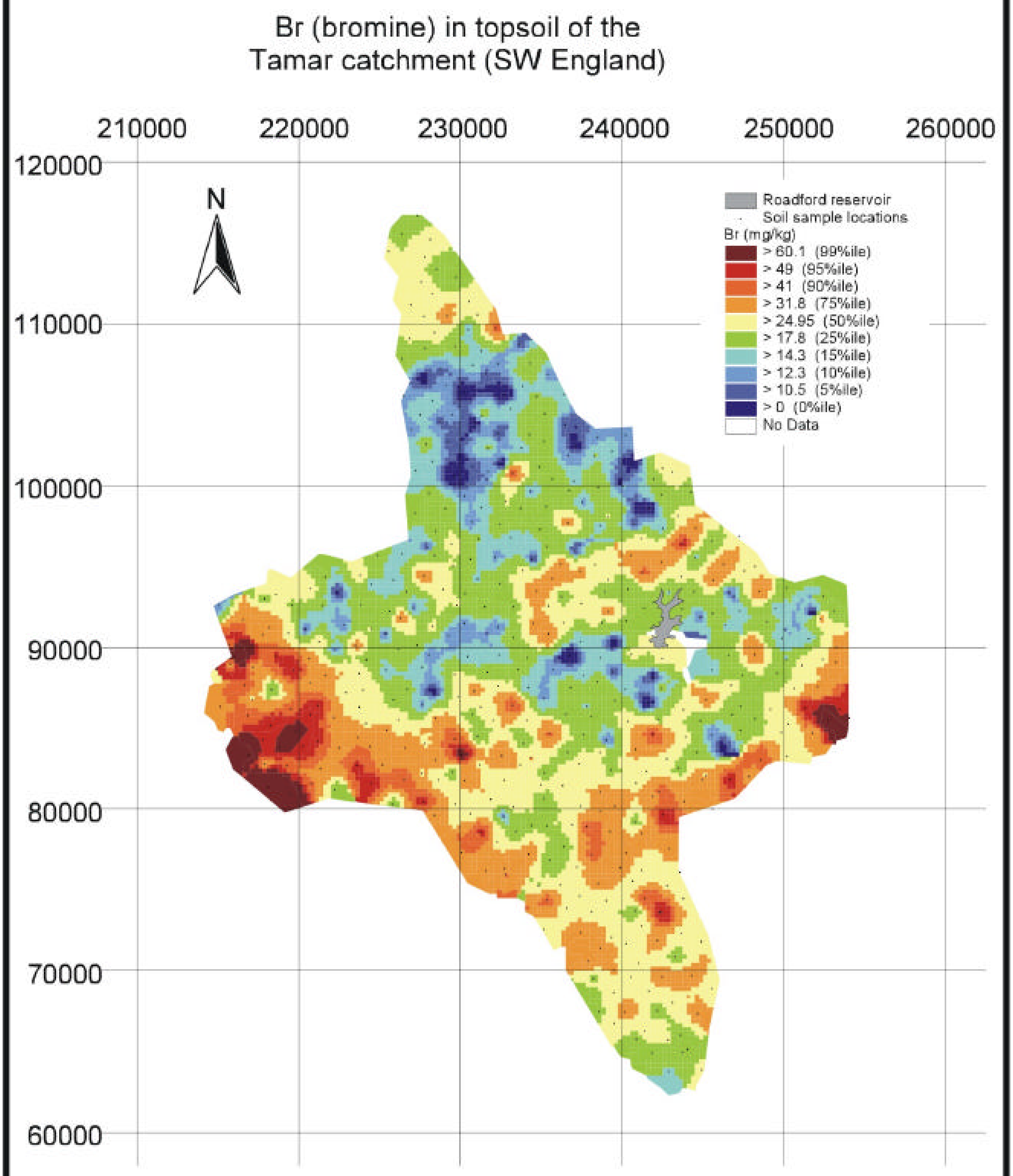

As (arsenic) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
As (mg/kg)
> 306.9 (99%ile)
> 129.3 (95%ile)
> 78.35 (90%ile)
> 41.1 (75%ile)
> 21.85 (50%ile)
> 16.35 (25%ile)
> 14.4 (15%ile)
> 13.45 (10%ile)
> 10.9 (5%ile)
> 0 (0%ile)
No Data

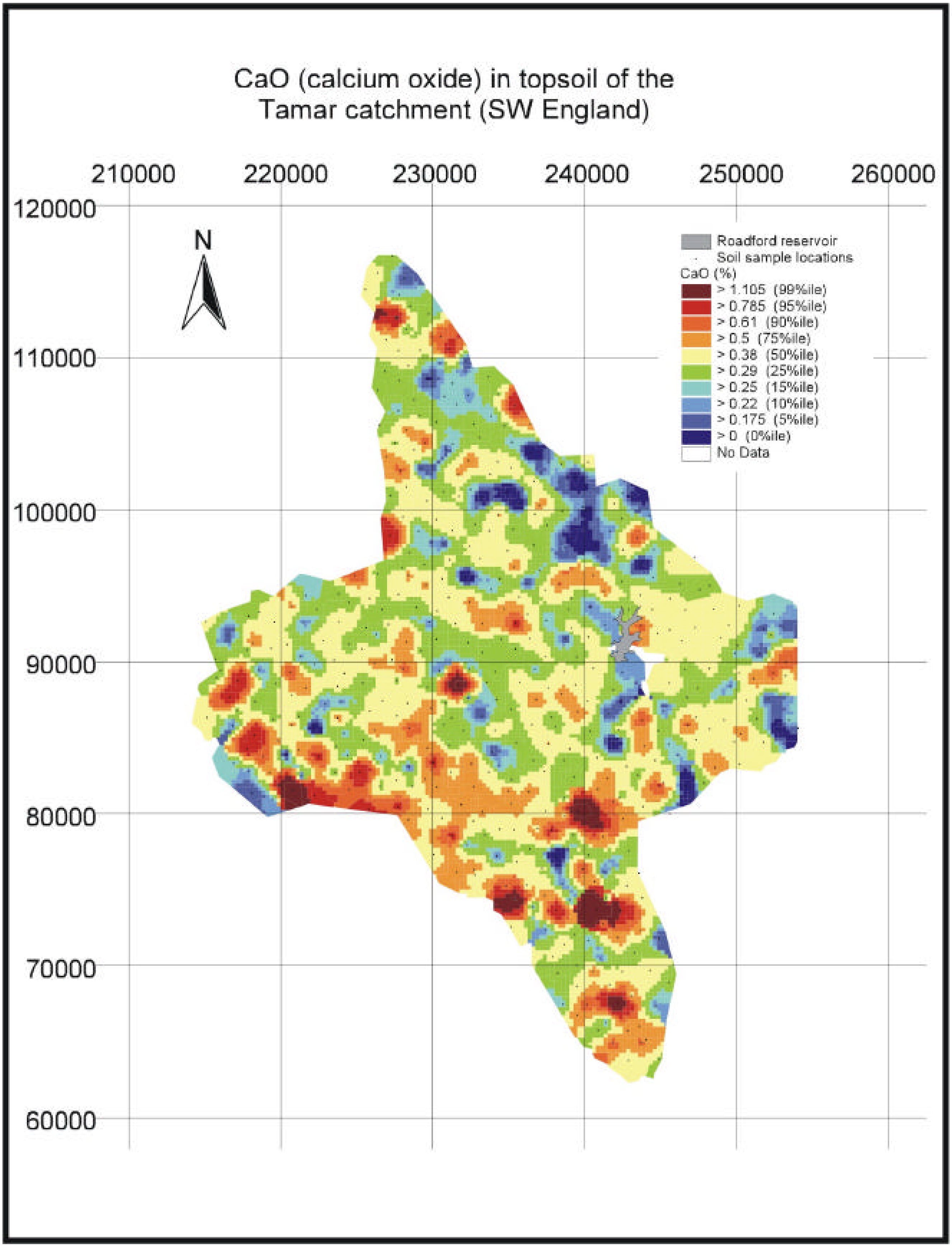


Ba (barium) in topsoil of the Tamar catchment (SW England)

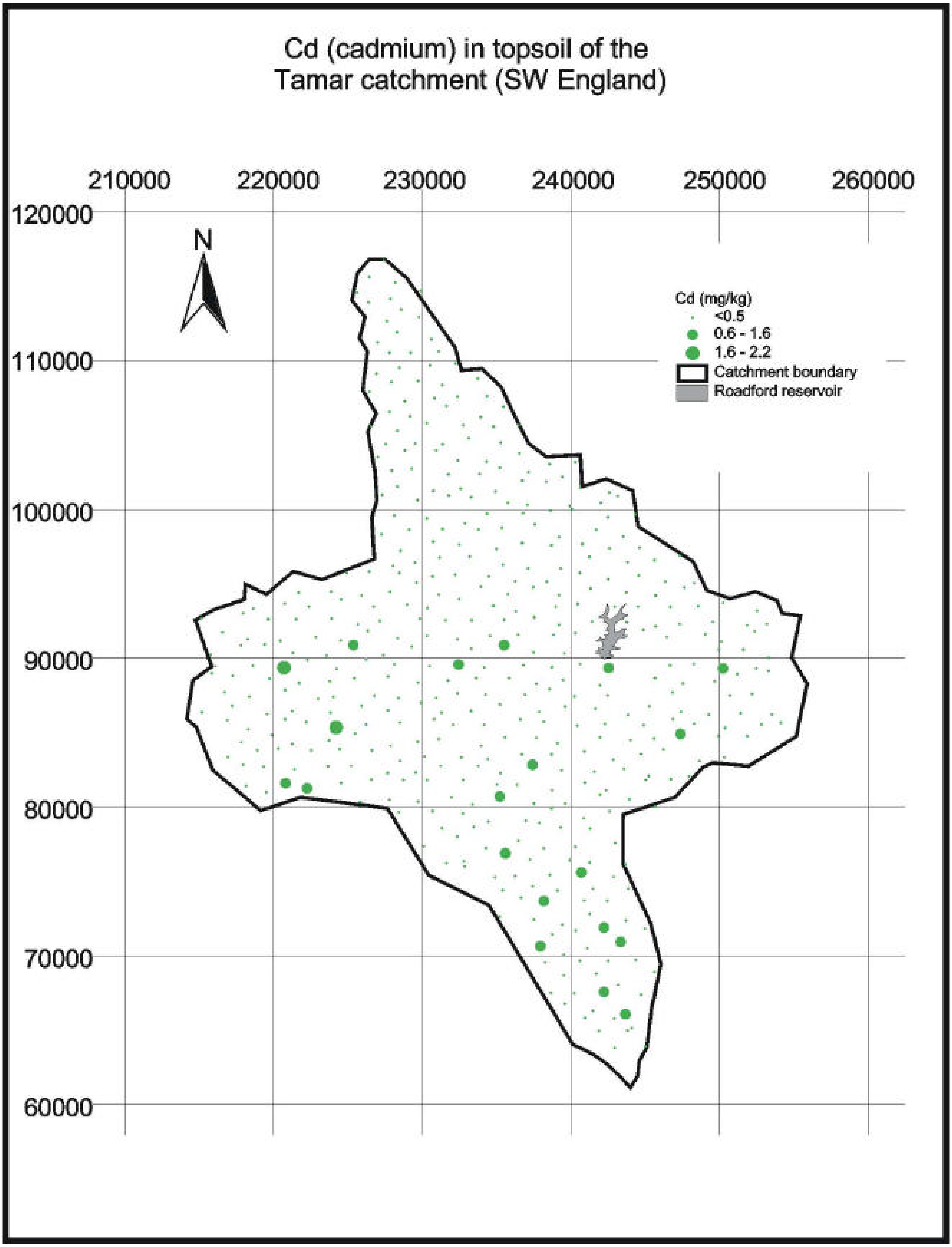


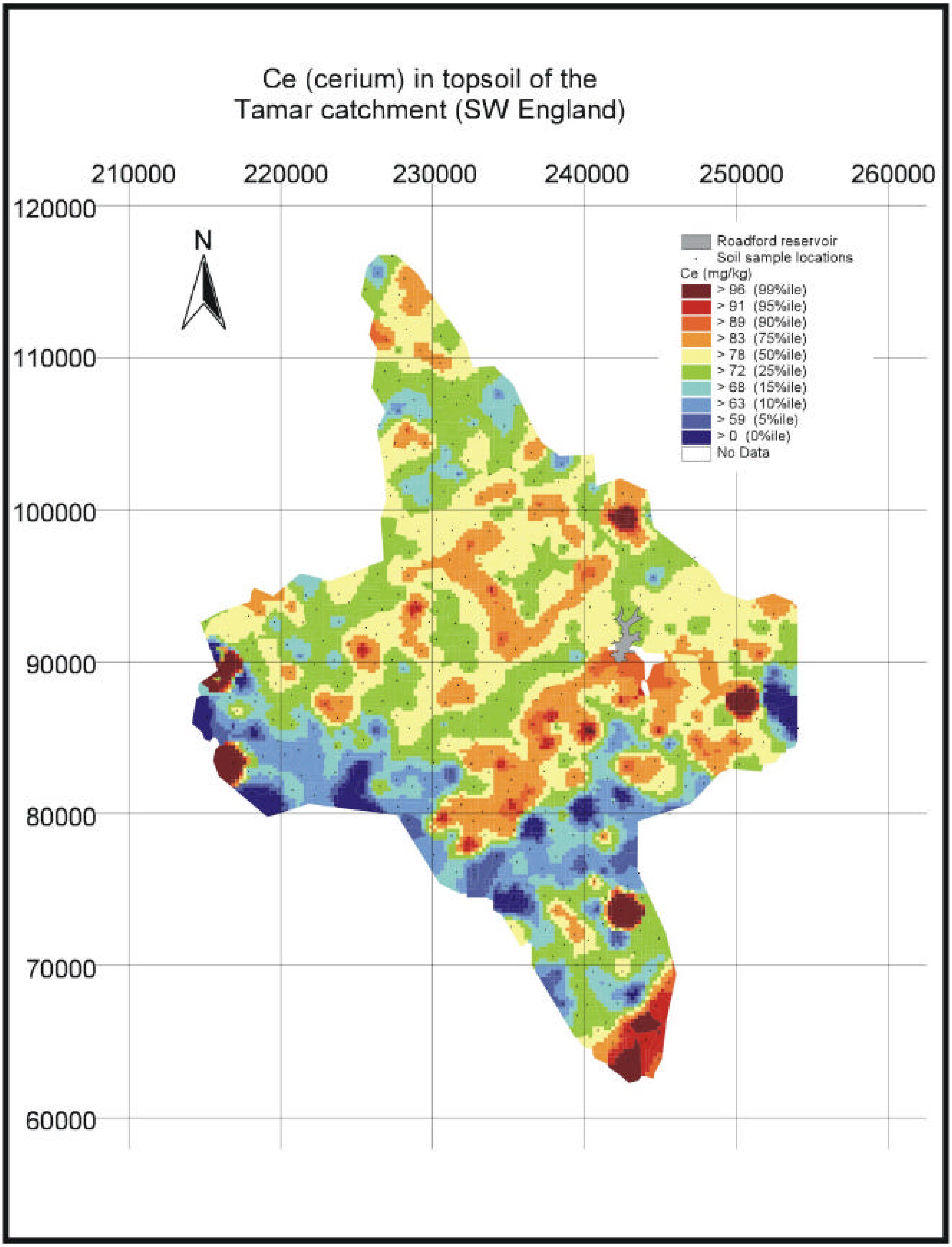
Bi (bismuth) in topsoil of the
Tamar catchment (SW England)

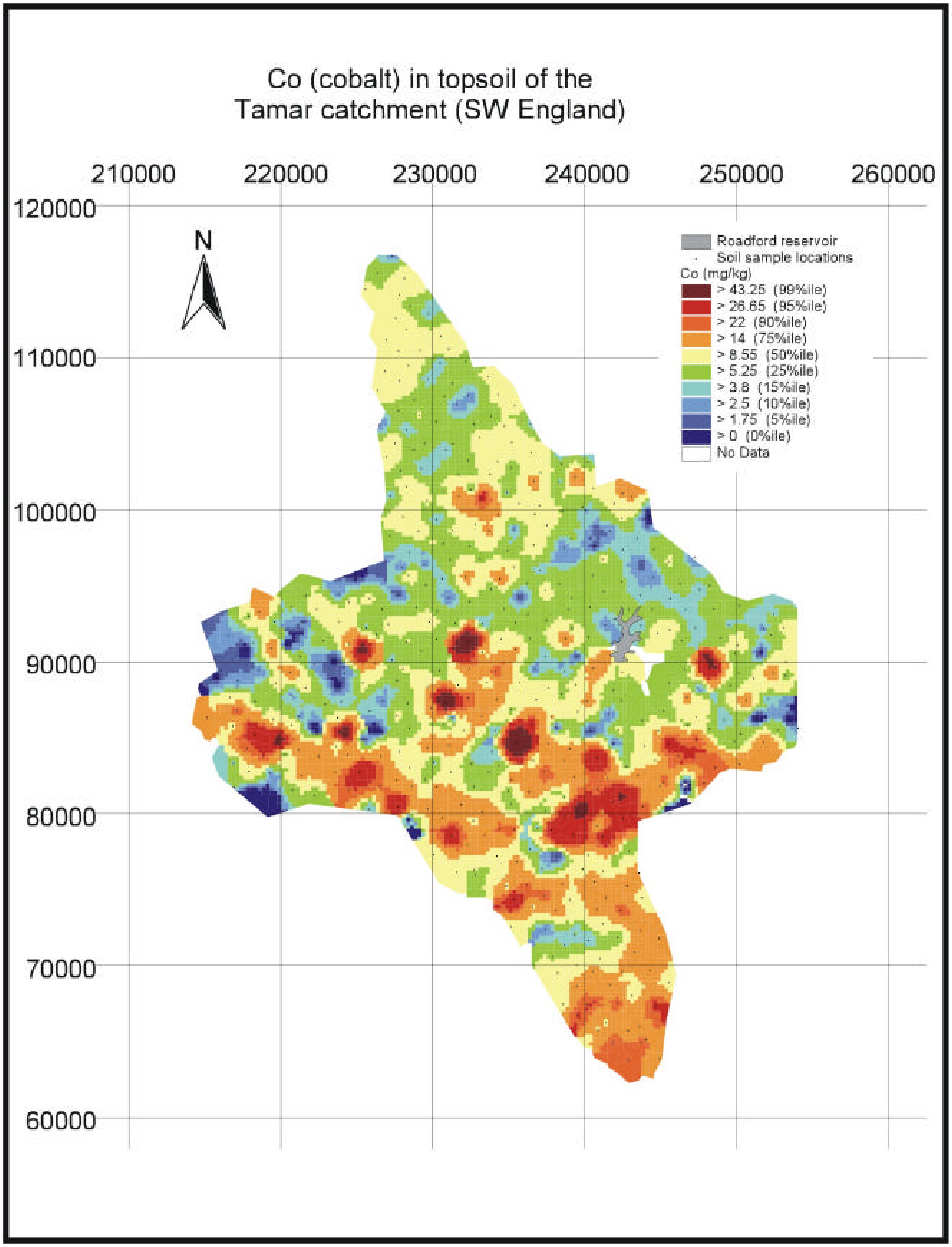

Br (bromine) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Br (mg/kg)
> 60.1 (99%ile)
> 49 (95%ile)
> 41 (90%ile)
> 31.8 (75%ile)
> 24.95 (50%ile)
> 17.8 (25%ile)
> 14.3 (15%ile)
> 12.3 (10%ile)
> 10.5 (5%ile)
> 0 (0%ile)
No Data

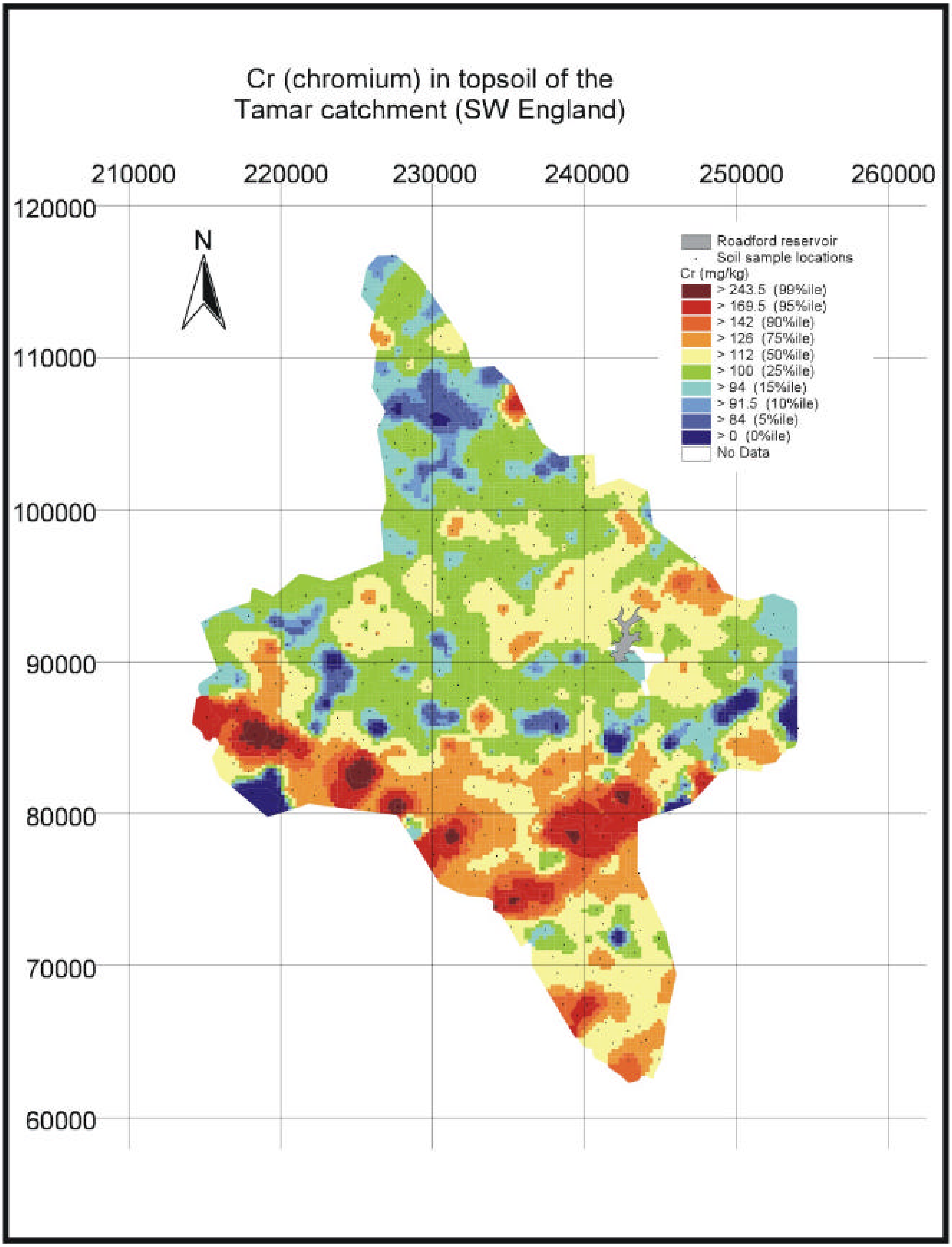


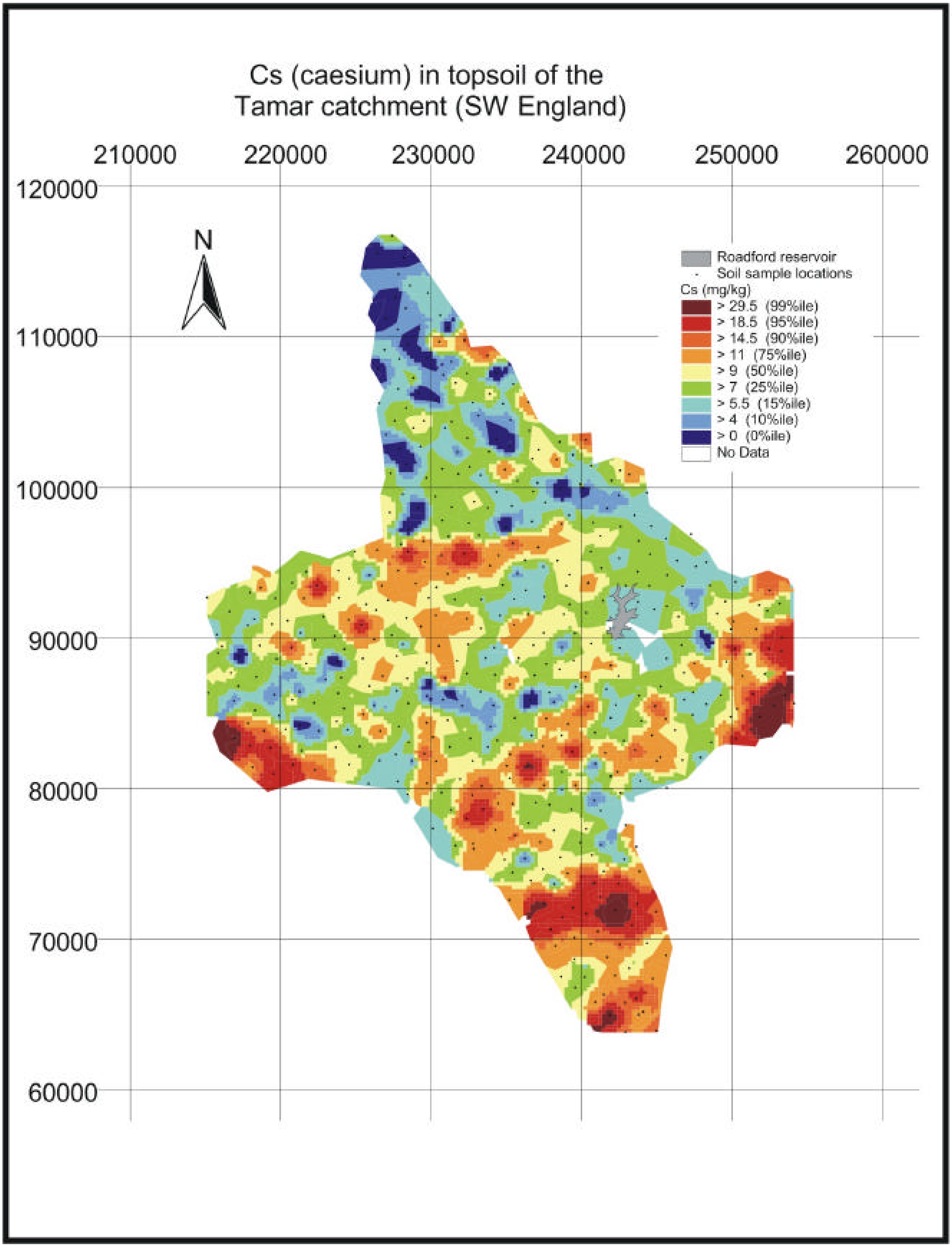
CaO (calcium oxide) in topsoil of the Tamar catchment (SW England)

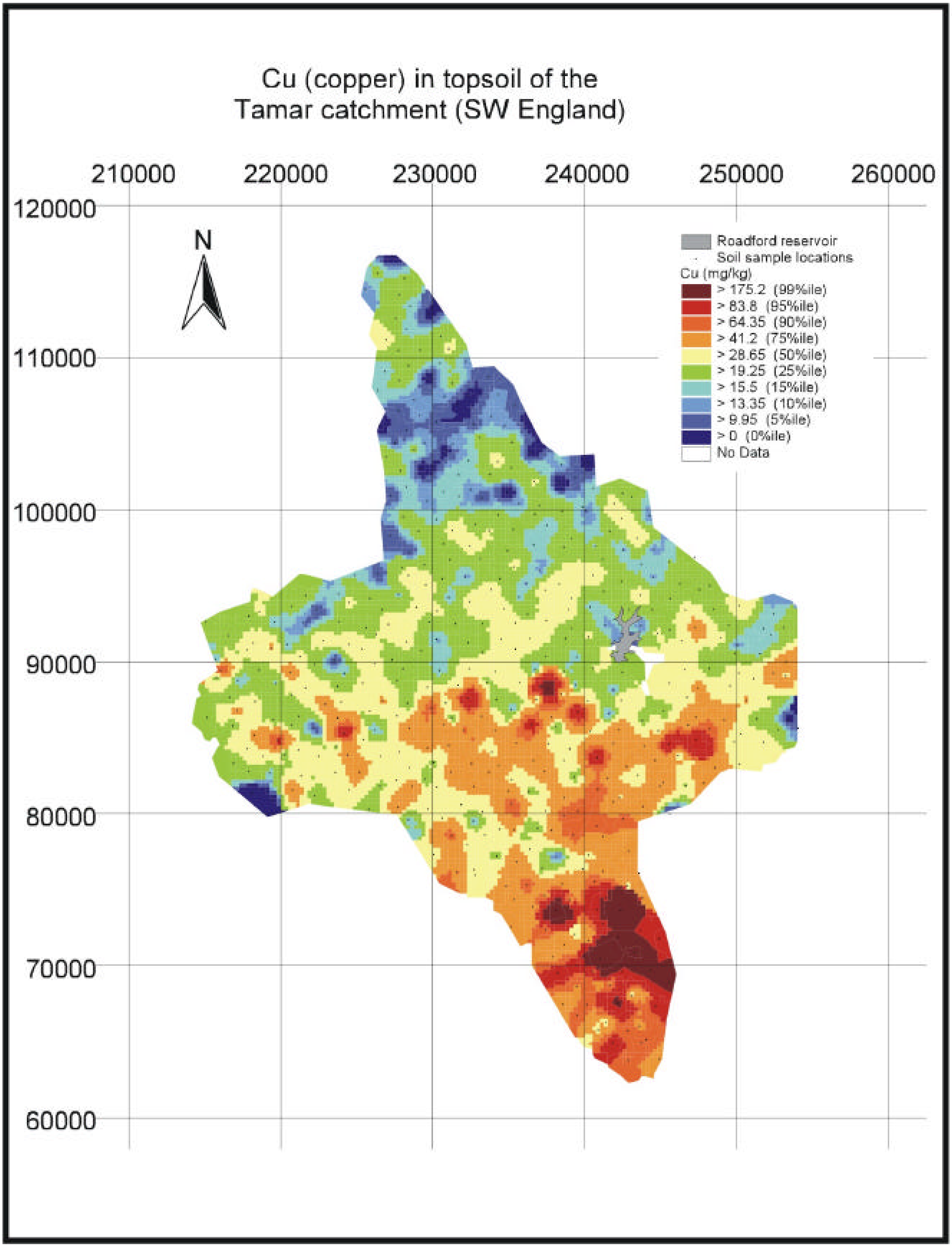

Cd (cadmium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Cd (mg/kg)
<0.5
0.6 - 1.6
1.6 - 2.2
Catchment boundary
Roadford reservoir

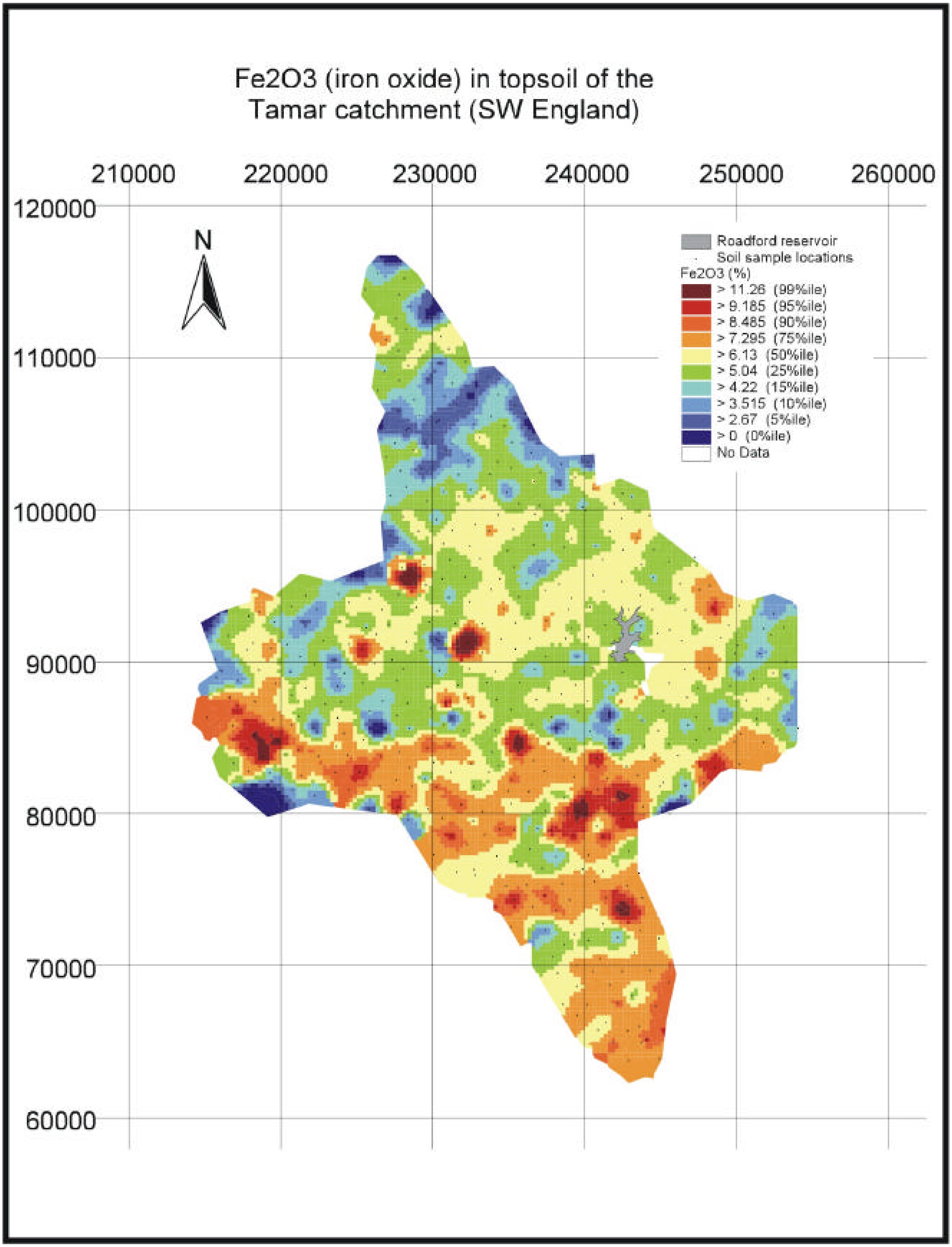

Ce (cerium) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Ce (mg/kg)
> 96 (99%ile)
> 91 (95%ile)
> 89 (90%ile)
> 83 (75%ile)
> 78 (50%ile)
> 72 (25%ile)
> 68 (15%ile)
> 63 (10%ile)
> 59 (5%ile)
> 0 (0%ile)
No Data

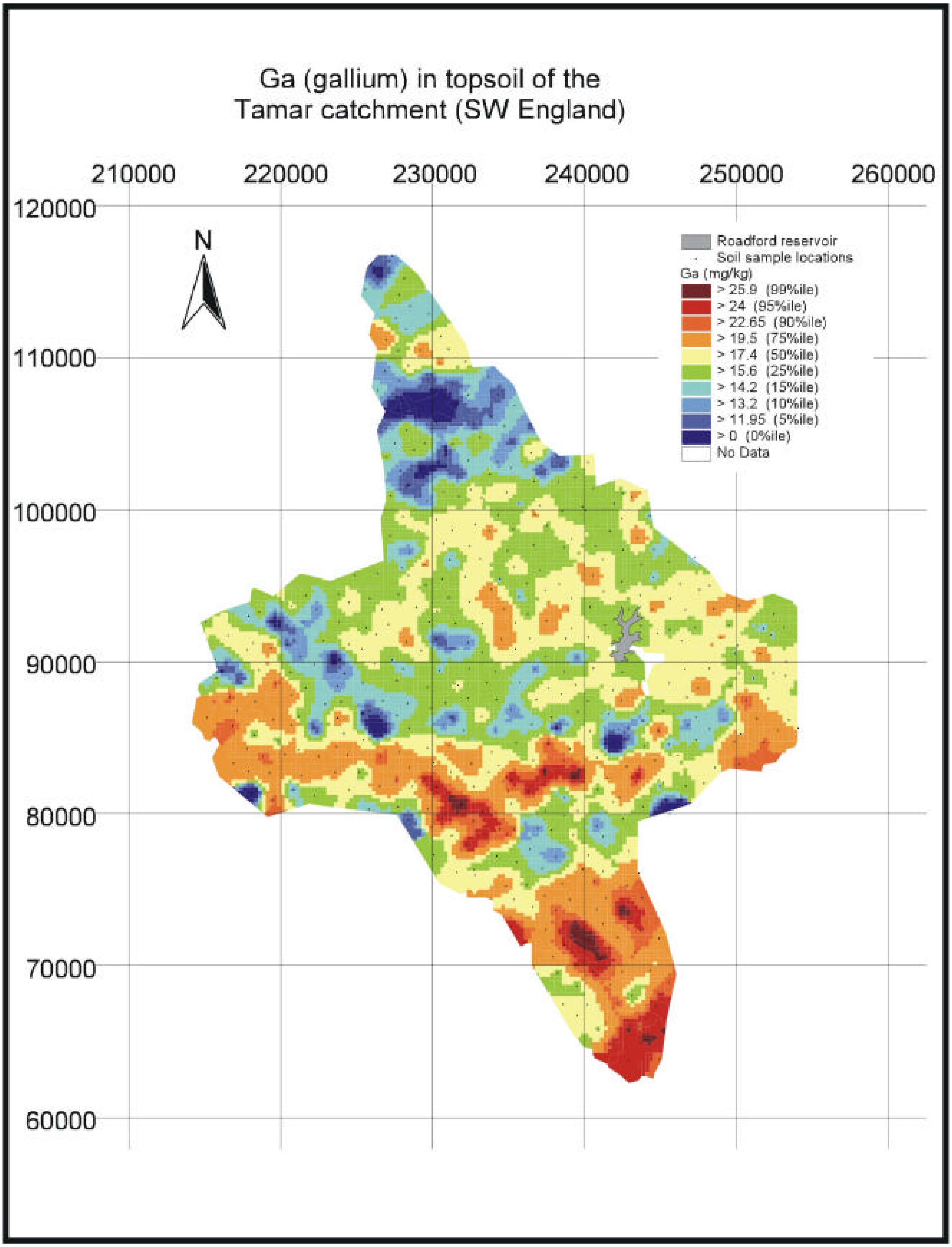

Co (cobalt) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Co (mg/kg)
> 43.25 (99%ile)
> 26.65 (95%ile)
> 22 (90%ile)
> 14 (75%ile)
> 8.55 (50%ile)
> 5.25 (25%ile)
> 3.8 (15%ile)
> 2.5 (10%ile)
> 1.75 (5%ile)
> 0 (0%ile)
No Data

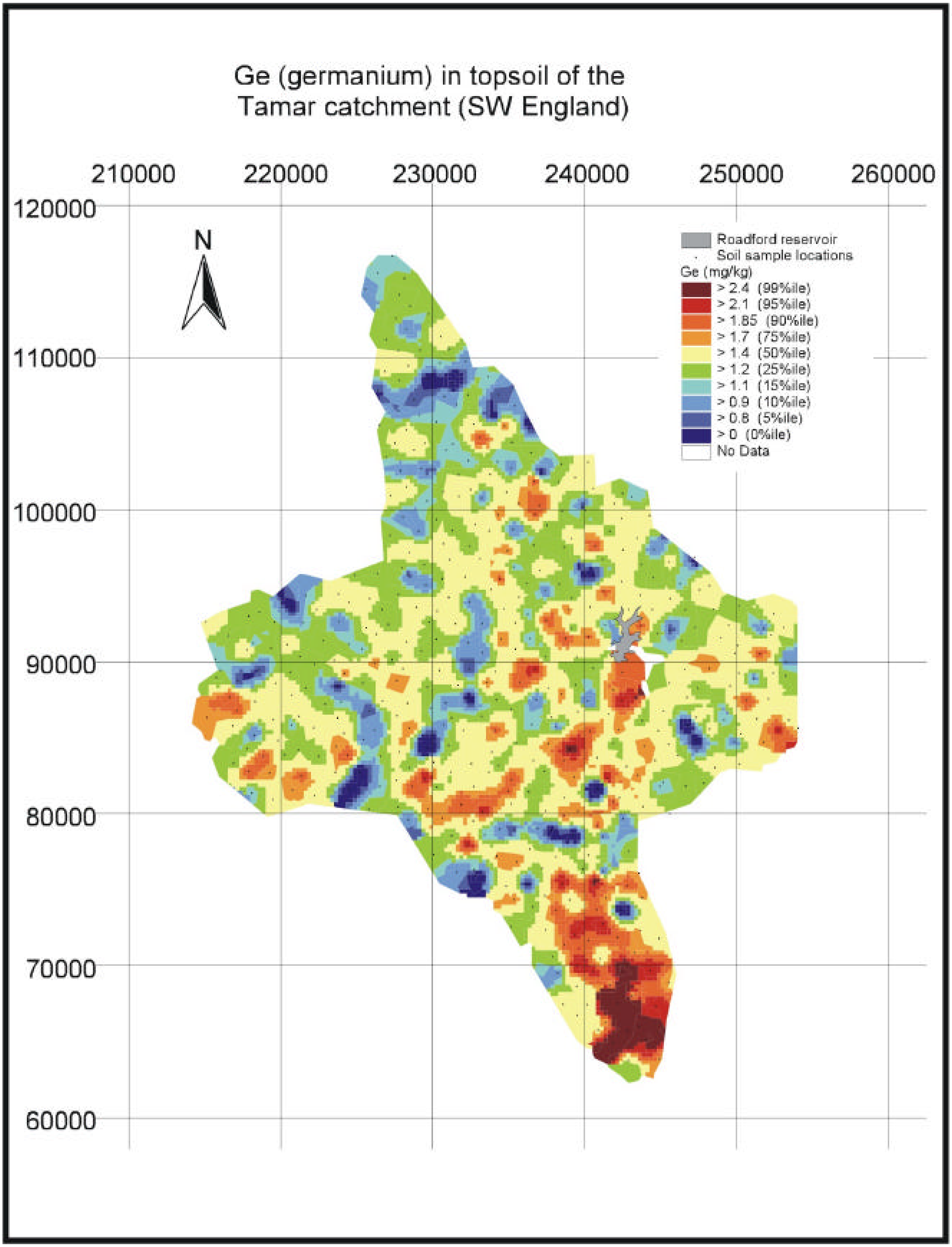

Cr (chromium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Cr (mg/kg)
> 243.5 (99%ile)
> 169.5 (95%ile)
> 142 (90%ile)
> 126 (75%ile)
> 112 (50%ile)
> 100 (25%ile)
> 94 (15%ile)
> 91.5 (10%ile)
> 84 (5%ile)
> 0 (0%ile)
No Data

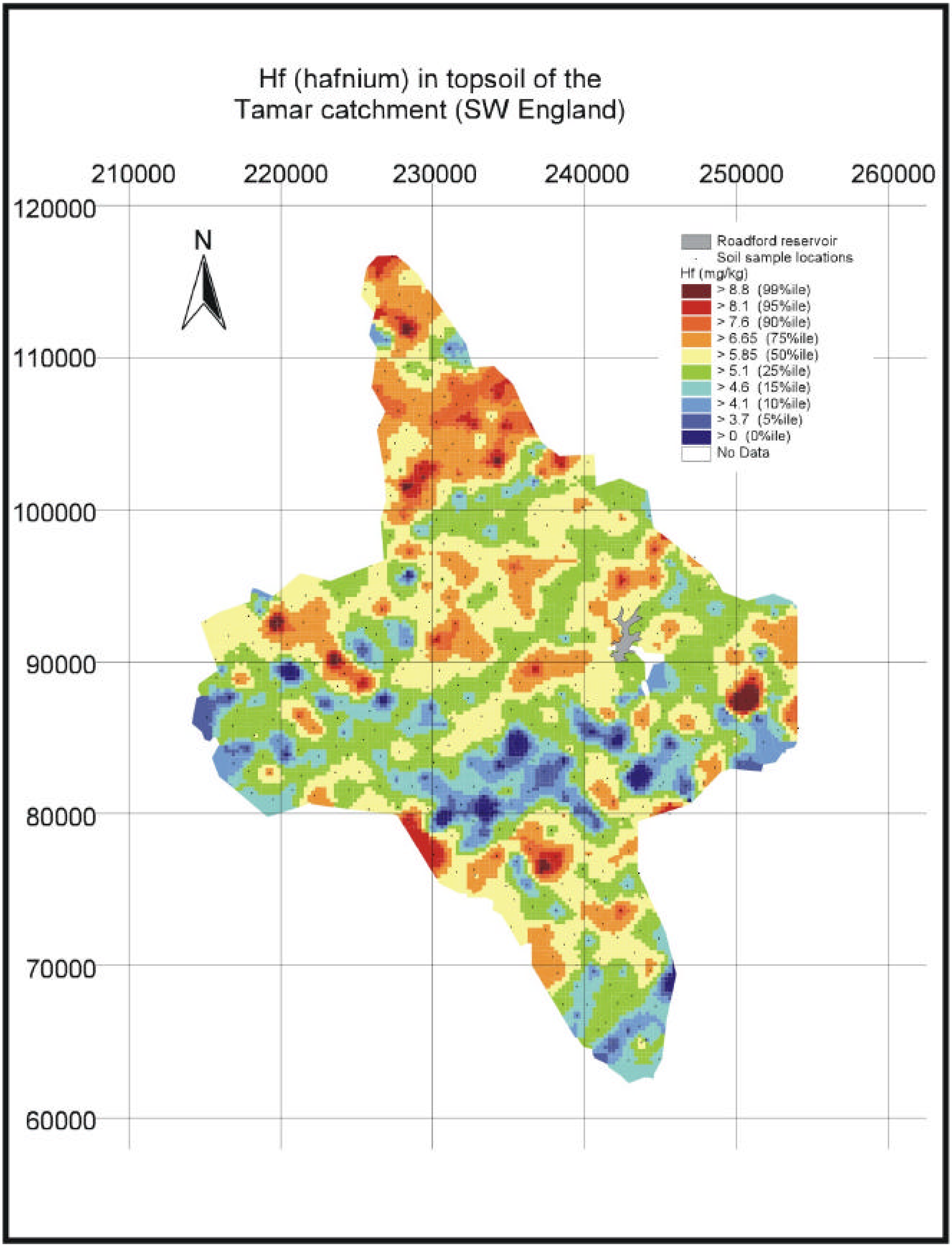

Cs (caesium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Cs (mg/kg)
> 29.5 (99%ile)
> 18.5 (95%ile)
> 14.5 (90%ile)
> 11 (75%ile)
> 9 (50%ile)
> 7 (25%ile)
> 5.5 (15%ile)
> 4 (10%ile)
> 0 (0%ile)
No Data


Cu (copper) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Cu (mg/kg)
> 175.2 (99%ile)
> 83.8 (95%ile)
> 64.35 (90%ile)
> 41.2 (75%ile)
> 28.65 (50%ile)
> 19.25 (25%ile)
> 15.5 (15%ile)
> 13.35 (10%ile)
> 9.95 (5%ile)
> 0 (0%ile)
No Data

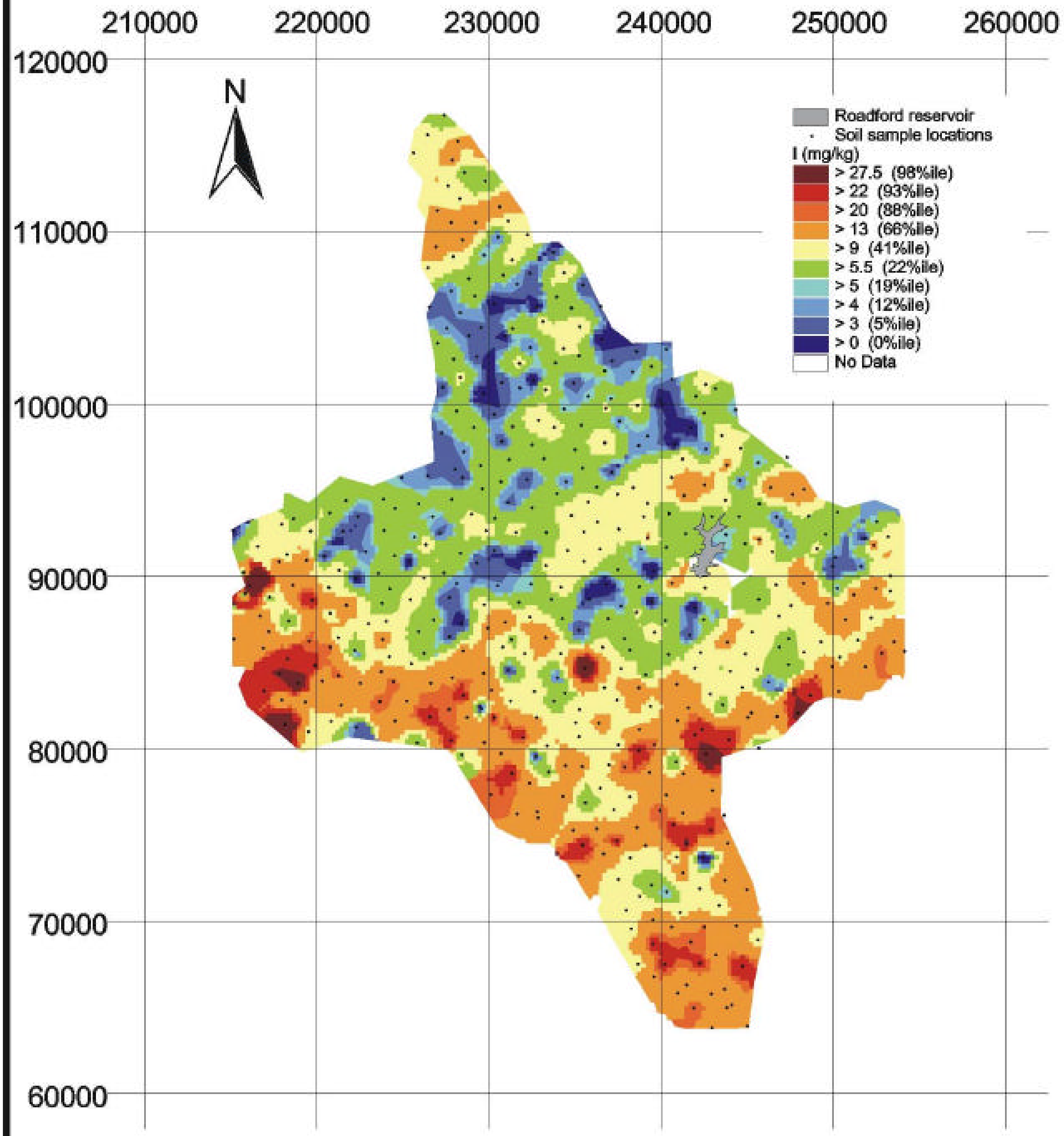

Fe2O3 (iron oxide) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Fe2O3 (%)
> 11.26 (99%ile)
> 9.185 (95%ile)
> 8.485 (90%ile)
> 7.295 (75%ile)
> 6.13 (50%ile)
> 5.04 (25%ile)
> 4.22 (15%ile)
> 3.515 (10%ile)
> 2.67 (5%ile)
> 0 (0%ile)
No Data

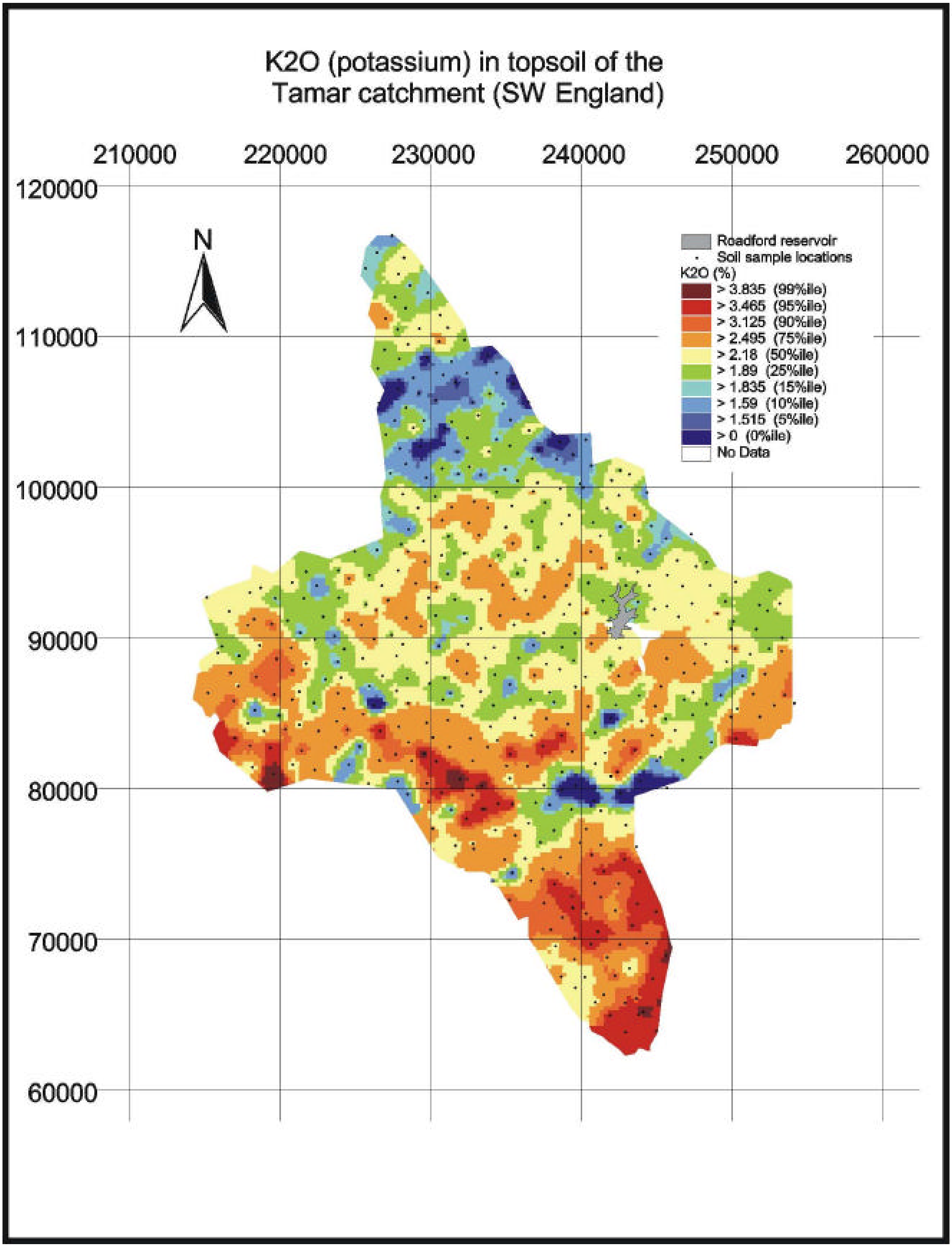

Ga (gallium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Ga (mg/kg)
> 25.9 (99%ile)
> 24 (95%ile)
> 22.65 (90%ile)
> 19.5 (75%ile)
> 17.4 (50%ile)
> 15.6 (25%ile)
> 14.2 (15%ile)
> 13.2 (10%ile)
> 11.95 (5%ile)
> 0 (0%ile)
No Data

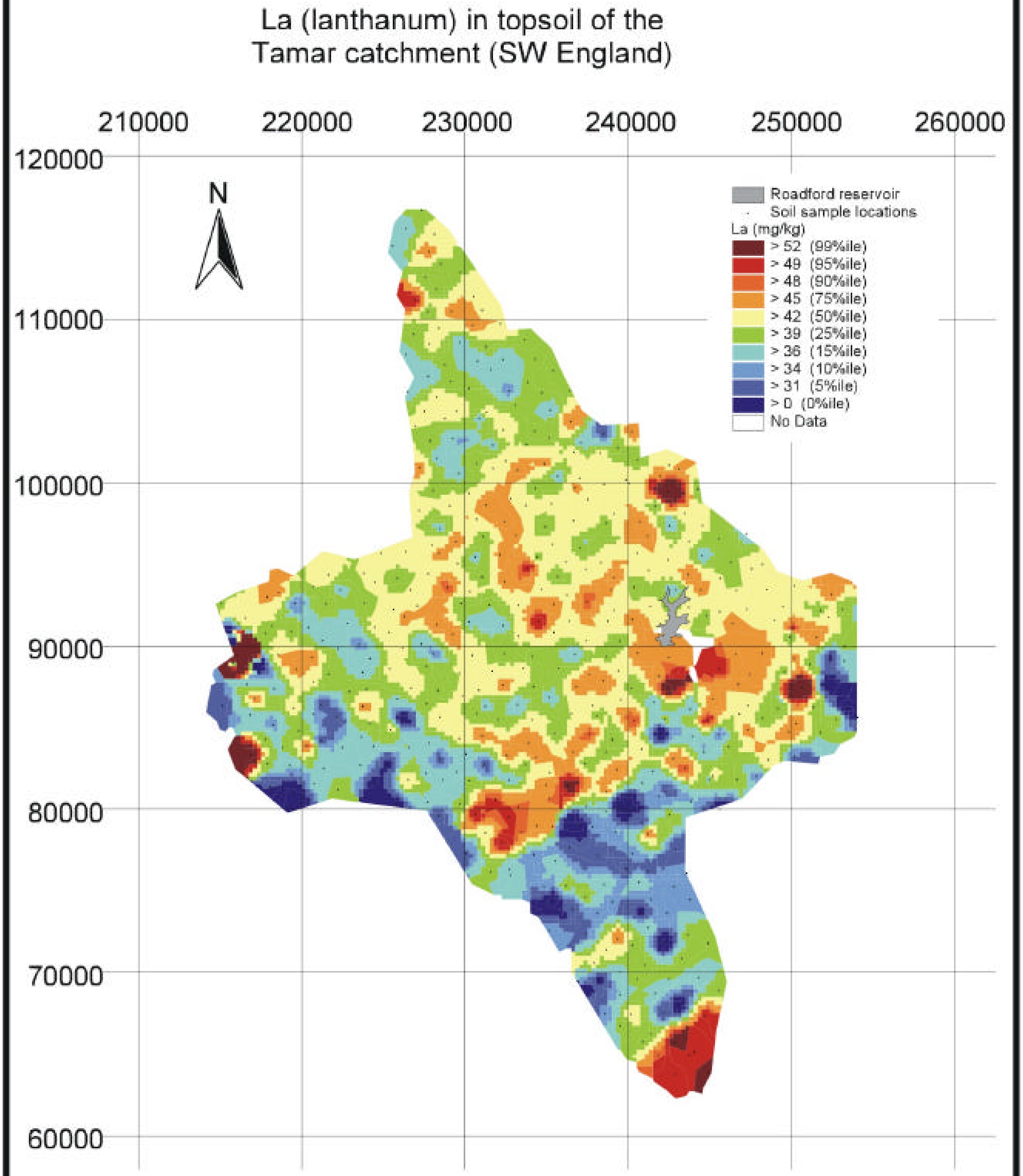

Ge (germanium) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Ge (mg/kg)
> 2.4 (99%ile)
> 2.1 (95%ile)
> 1.85 (90%ile)
> 1.7 (75%ile)
> 1.4 (50%ile)
> 1.2 (25%ile)
> 1.1 (15%ile)
> 0.9 (10%ile)
> 0.8 (5%ile)
> 0 (0%ile)
No Data

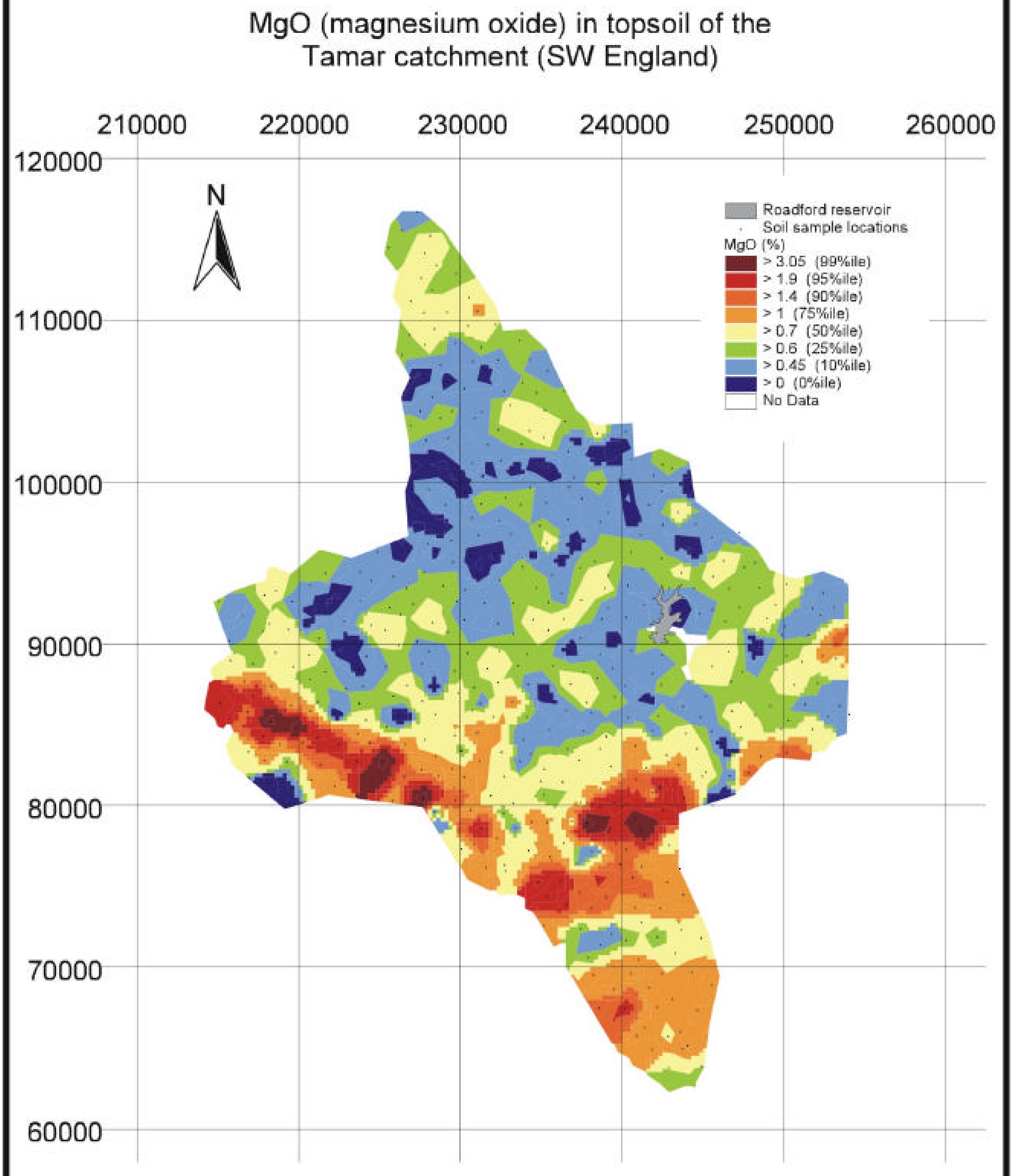

Hf (hafnium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Hf (mg/kg)
> 8.8 (99%ile)
> 8.1 (95%ile)
> 7.6 (90%ile)
> 6.65 (75%ile)
> 5.85 (50%ile)
> 5.1 (25%ile)
> 4.6 (15%ile)
> 4.1 (10%ile)
> 3.7 (5%ile)
> 0 (0%ile)
No Data

I (iodine) in topsoil of the
Tamar catchment (SW England)

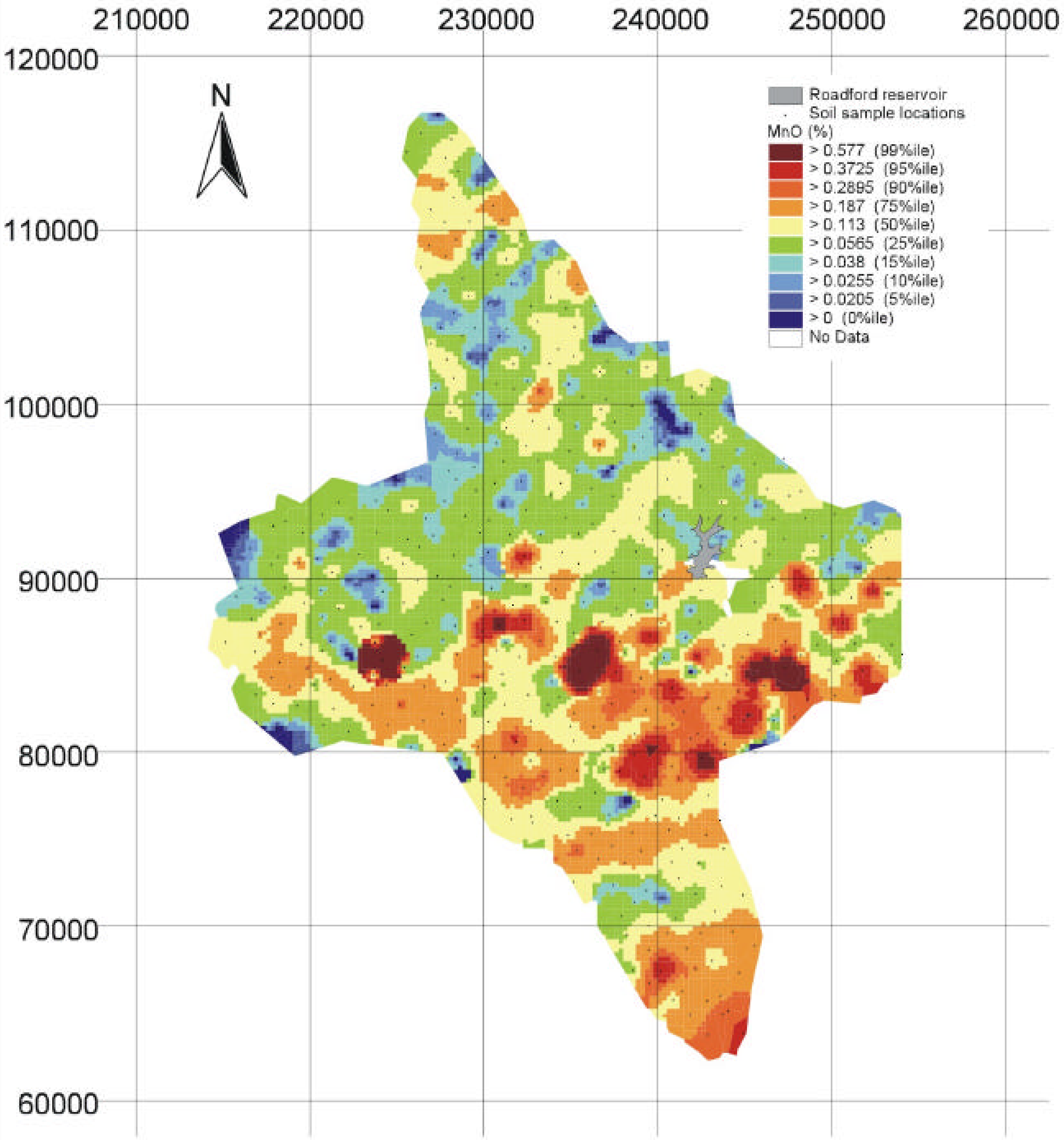


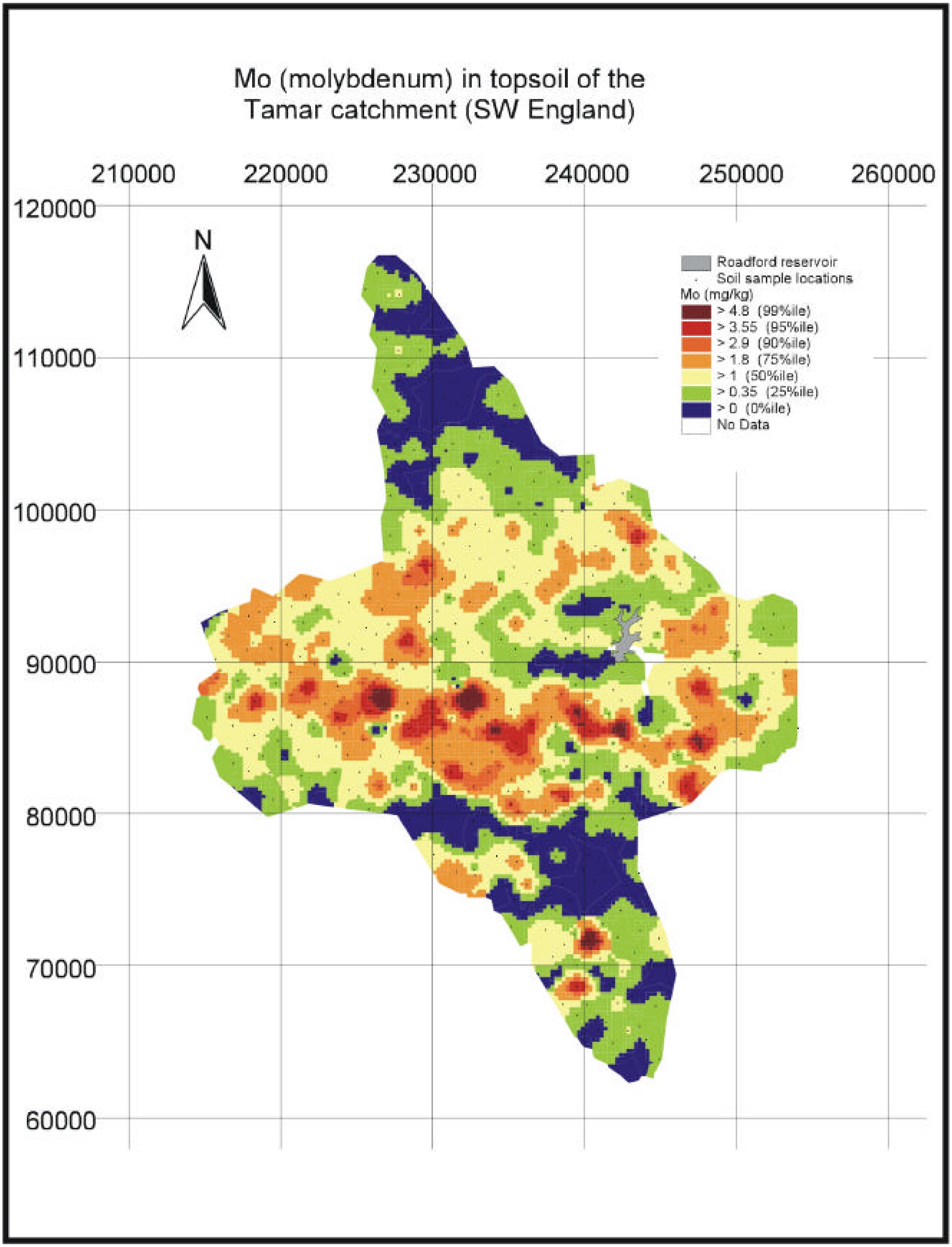

K2O (potassium) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
K2O (%)
> 3.835 (99%ile)
> 3.465 (95%ile)
> 3.125 (90%ile)
> 2.495 (75%ile)
> 2.18 (50%ile)
> 1.89 (25%ile)
> 1.835 (15%ile)
> 1.59 (10%ile)
> 1.515 (5%ile)
> 0 (0%ile)
No Data

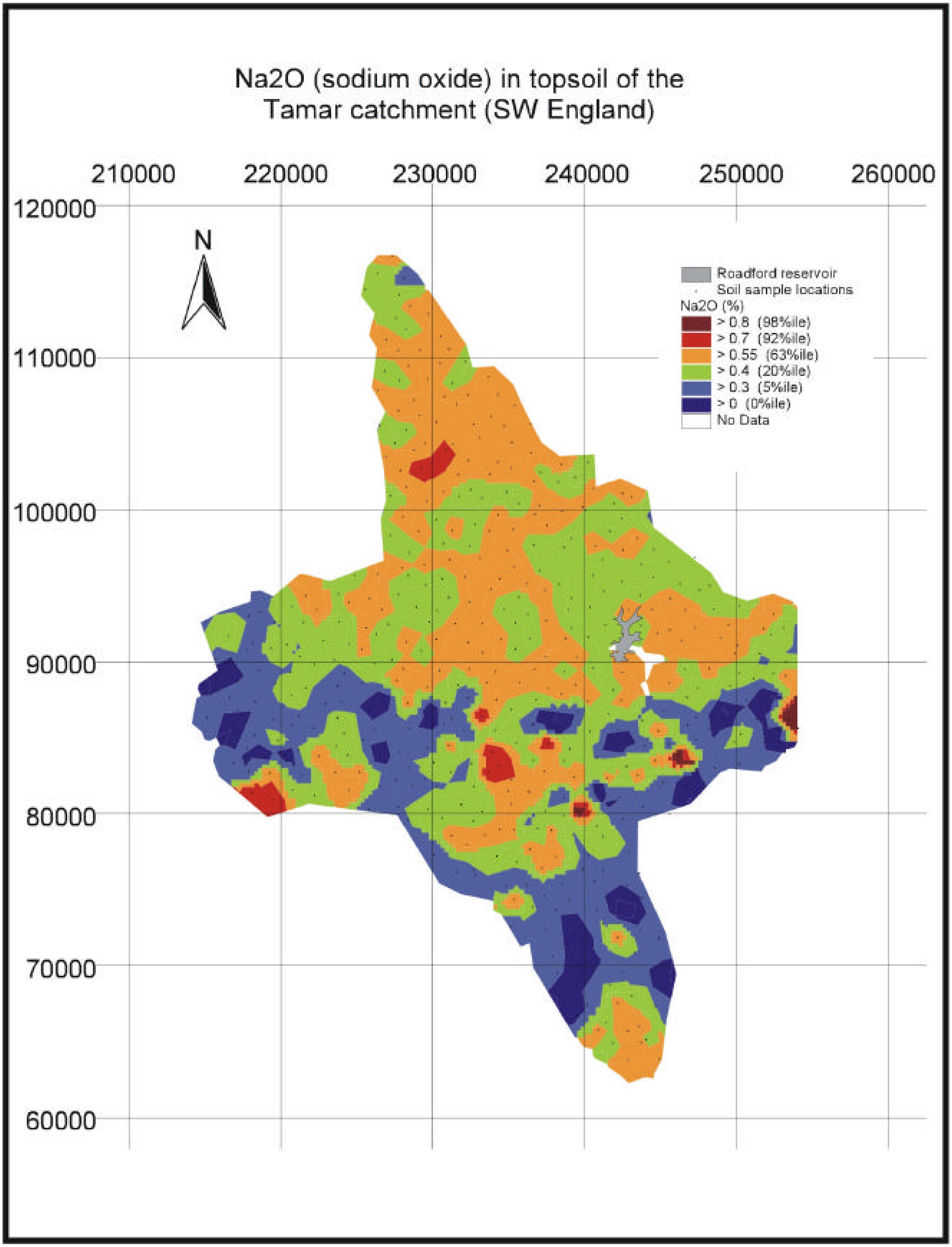

La (lanthanum) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
La (mg/kg)
> 52 (99%ile)
> 49 (95%ile)
> 48 (90%ile)
> 45 (75%ile)
> 42 (50%ile)
> 39 (25%ile)
> 36 (15%ile)
> 34 (10%ile)
> 31 (5%ile)
> 0 (0%ile)
No Data


MgO (magnesium oxide) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
MgO (%)
> 3.05 (99%ile)
> 1.9 (95%ile)
> 1.4 (90%ile)
> 1 (75%ile)
> 0.7 (50%ile)
> 0.6 (25%ile)
> 0.45 (10%ile)
> 0 (0%ile)
No Data

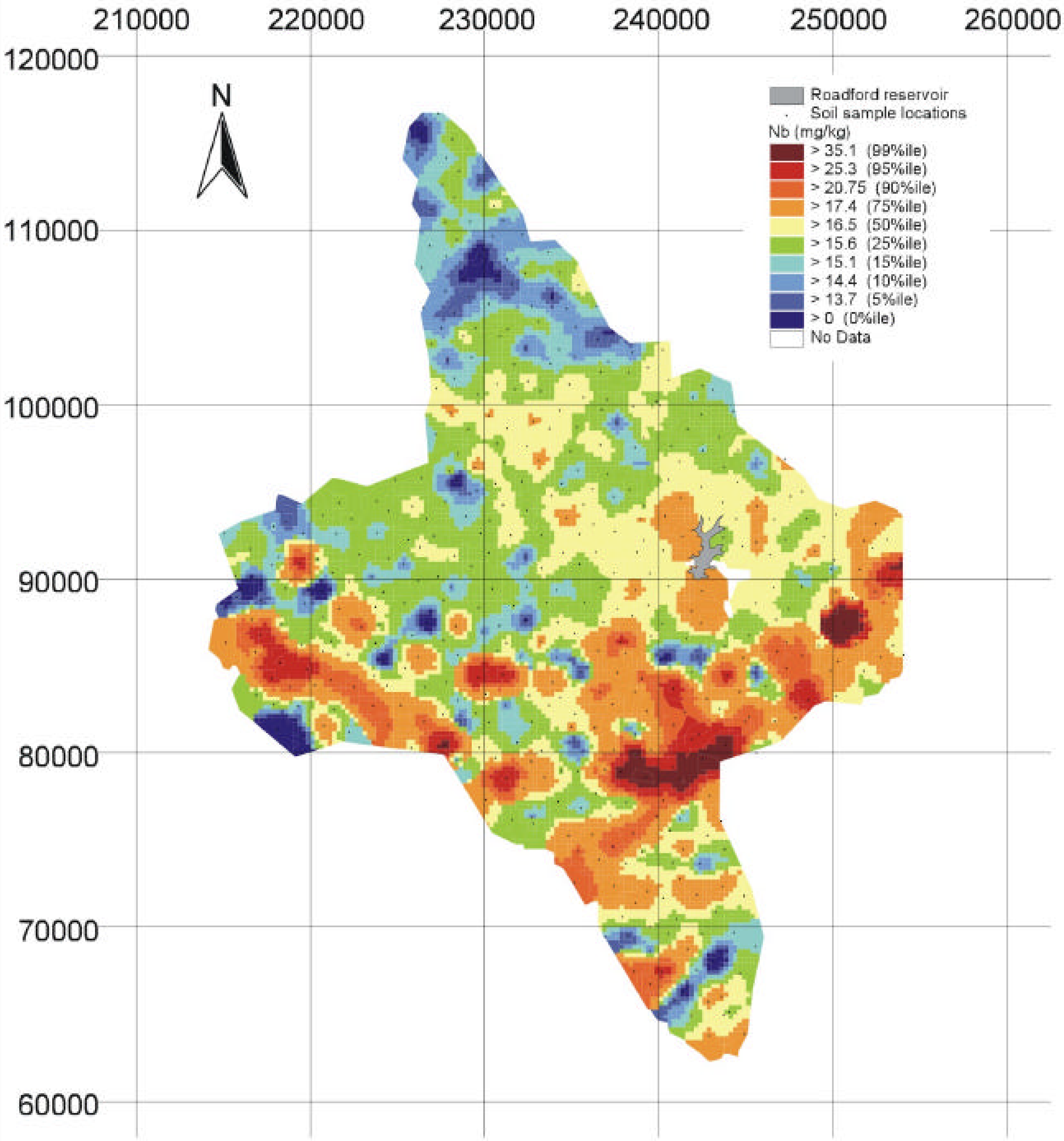
MnO (manganese oxide) in topsoil of the Tamar catchment (SW England)

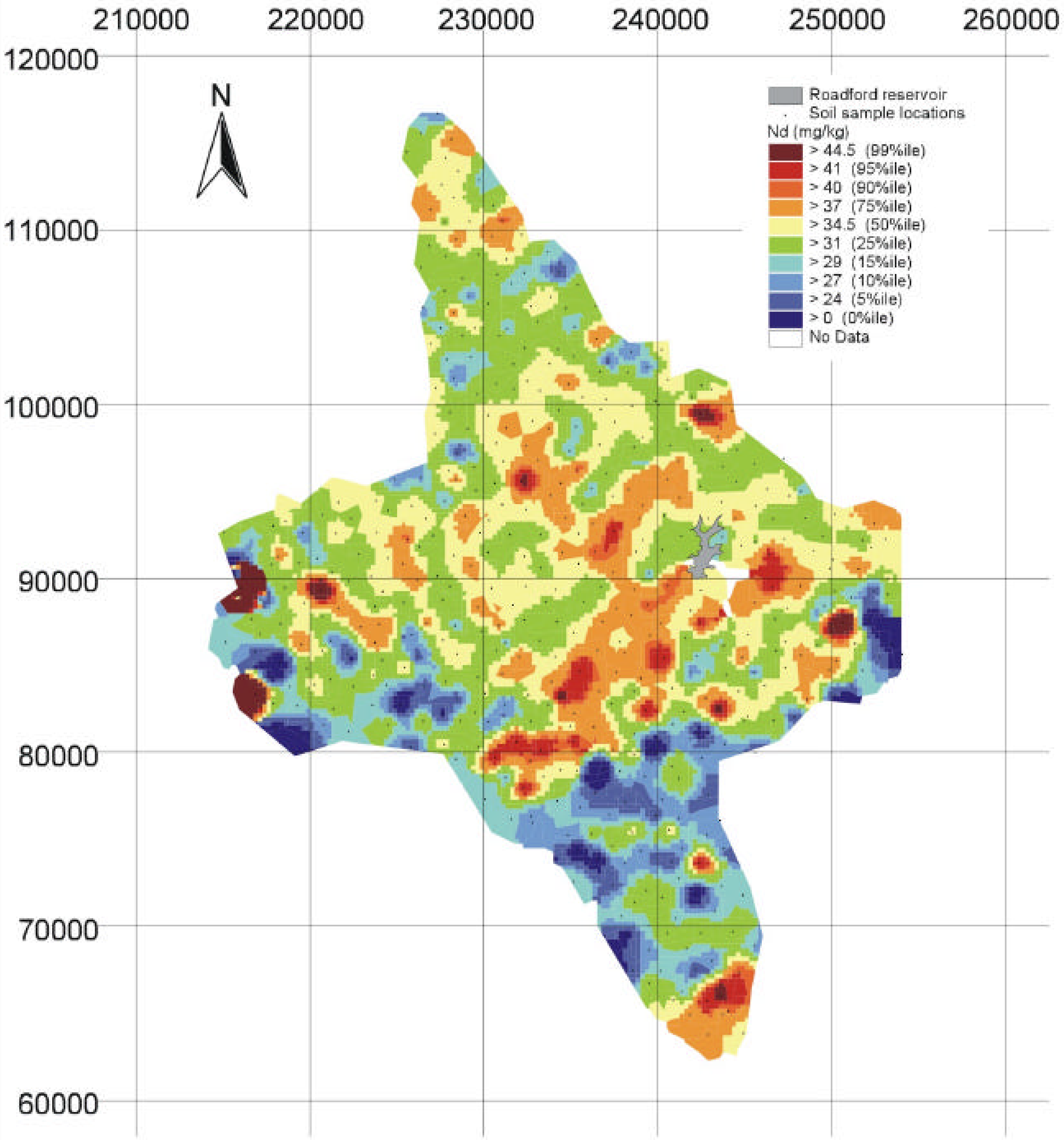



Mo (molybdenum) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Mo (mg/kg)
> 4.8 (99%ile)
> 3.55 (95%ile)
> 2.9 (90%ile)
> 1.8 (75%ile)
> 1 (50%ile)
> 0.35 (25%ile)
> 0 (0%ile)
No Data

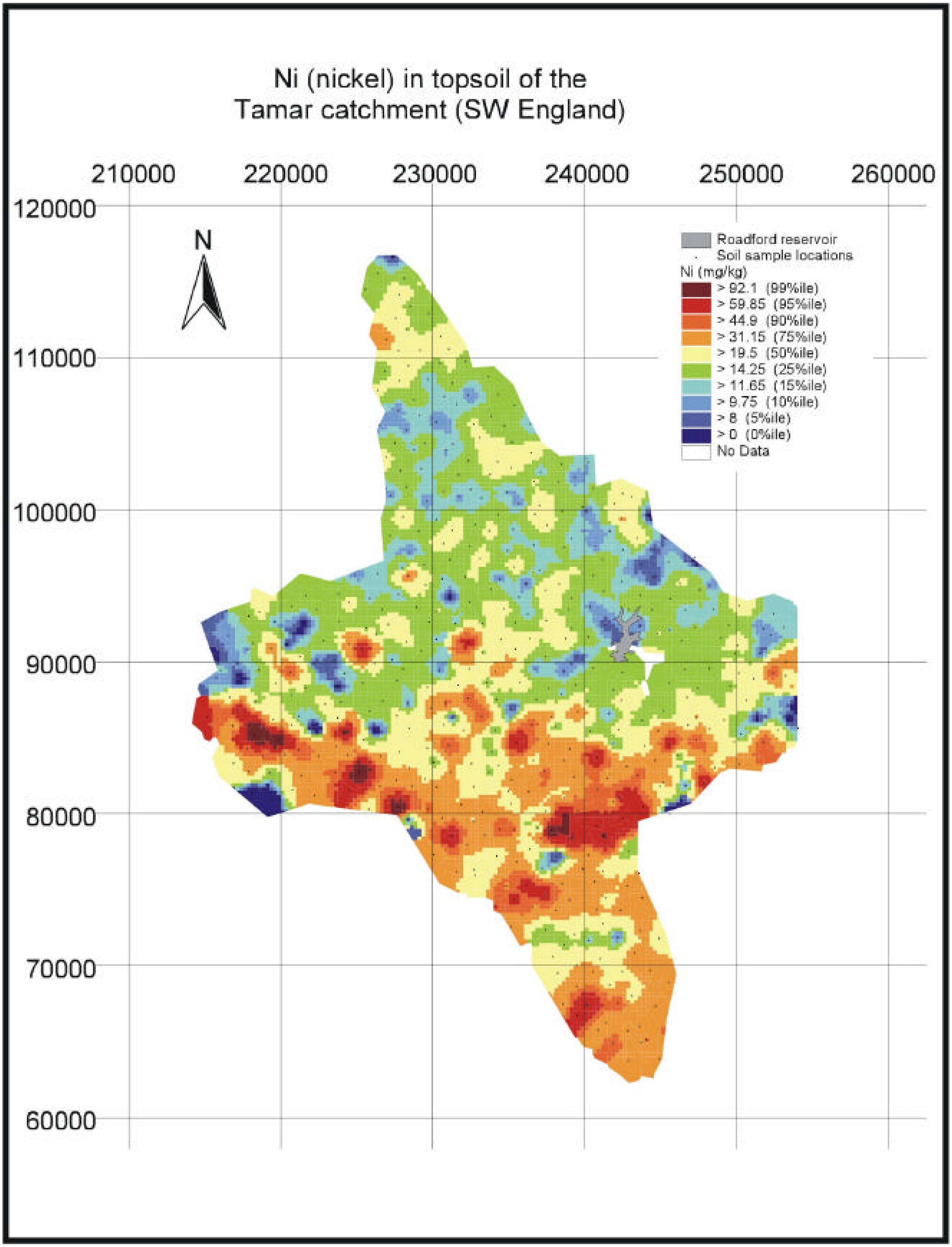

Na2O (sodium oxide) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Na2O (%)
> 0.8 (98%ile)
> 0.7 (92%ile)
> 0.55 (63%ile)
> 0.4 (20%ile)
> 0.3 (5%ile)
> 0 (0%ile)
No Data

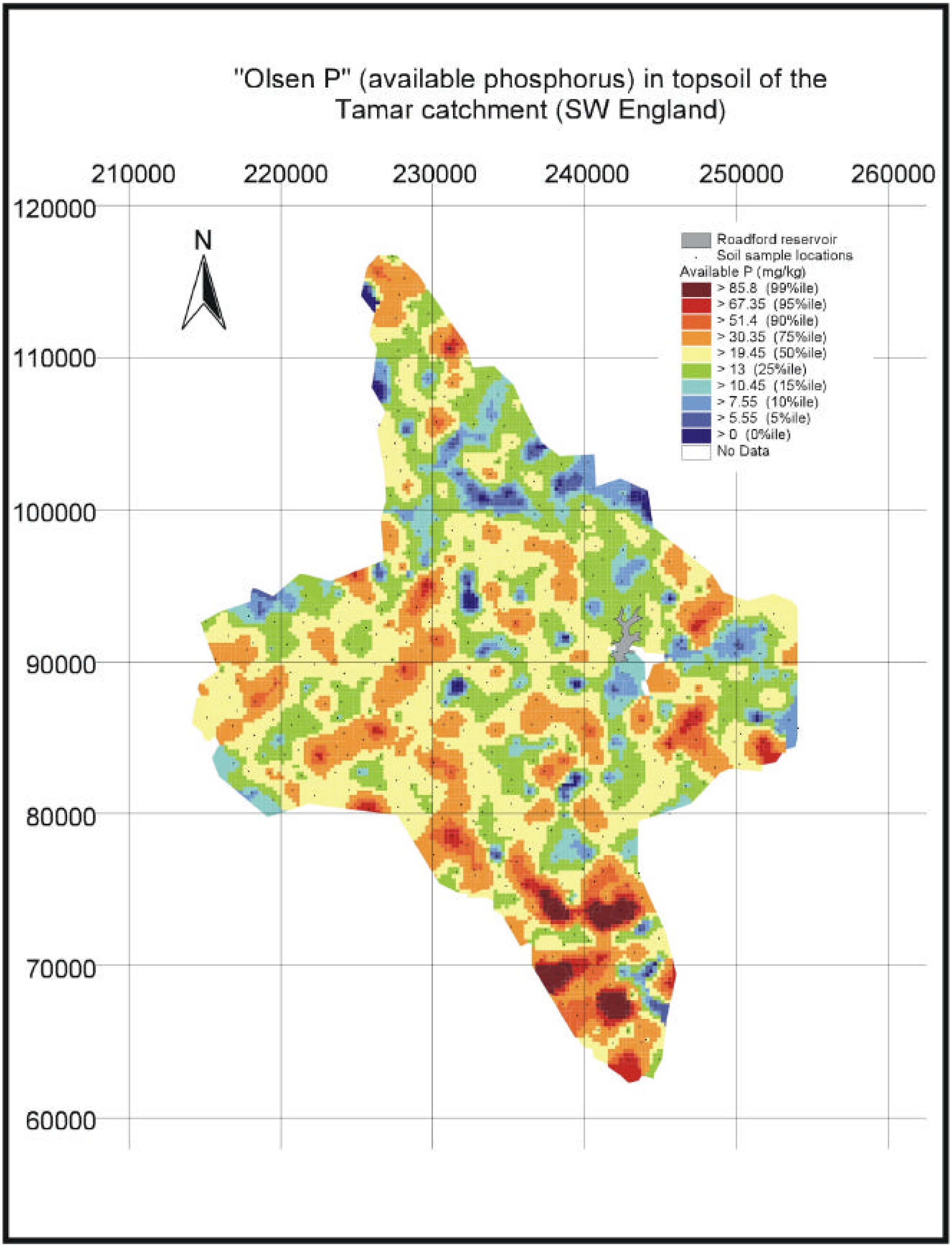
Nb (niobium) in topsoil of the Tamar catchment (SW England)



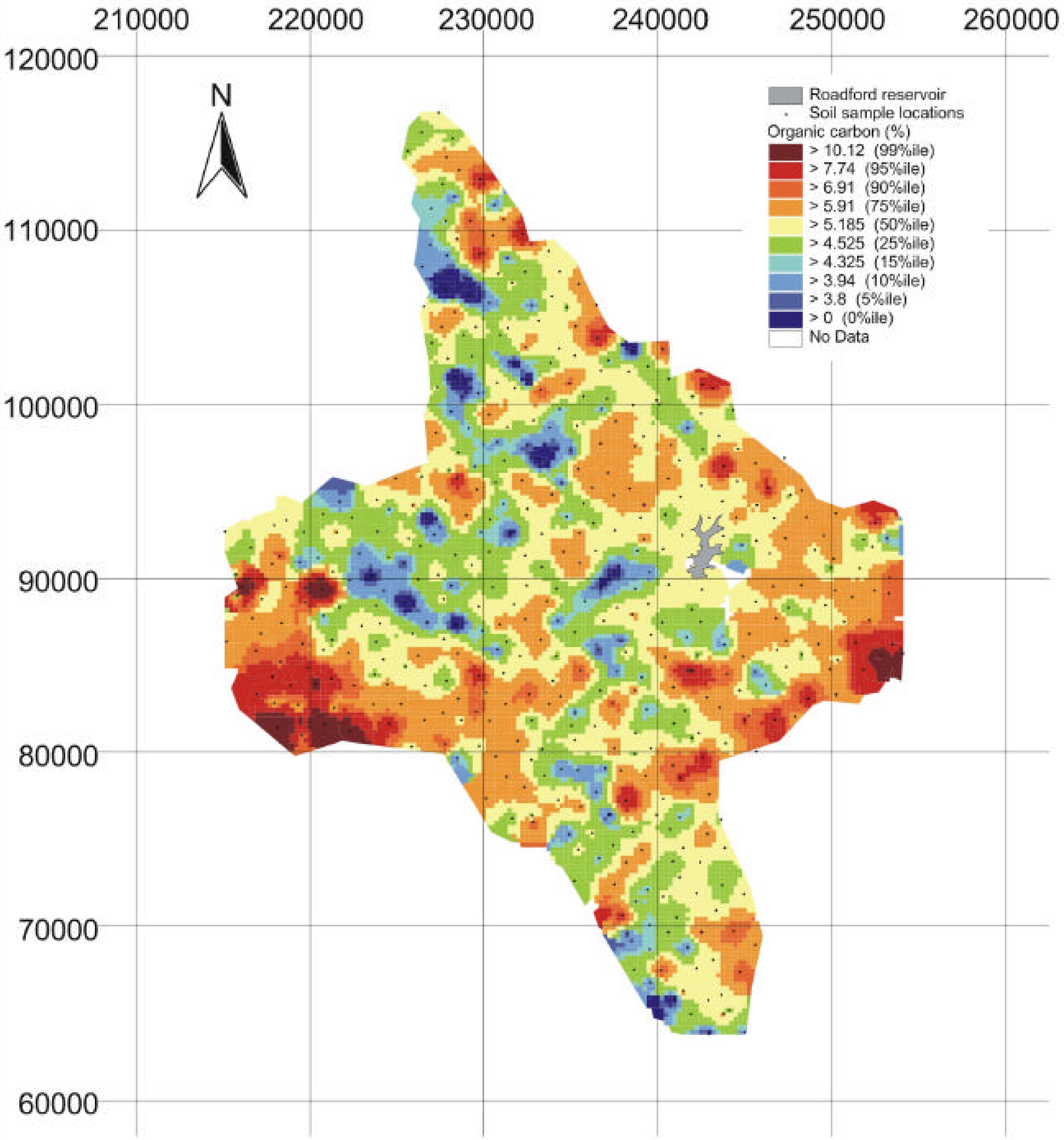


Nd (neodymium) in topsoil of the Tamar catchment (SW England)

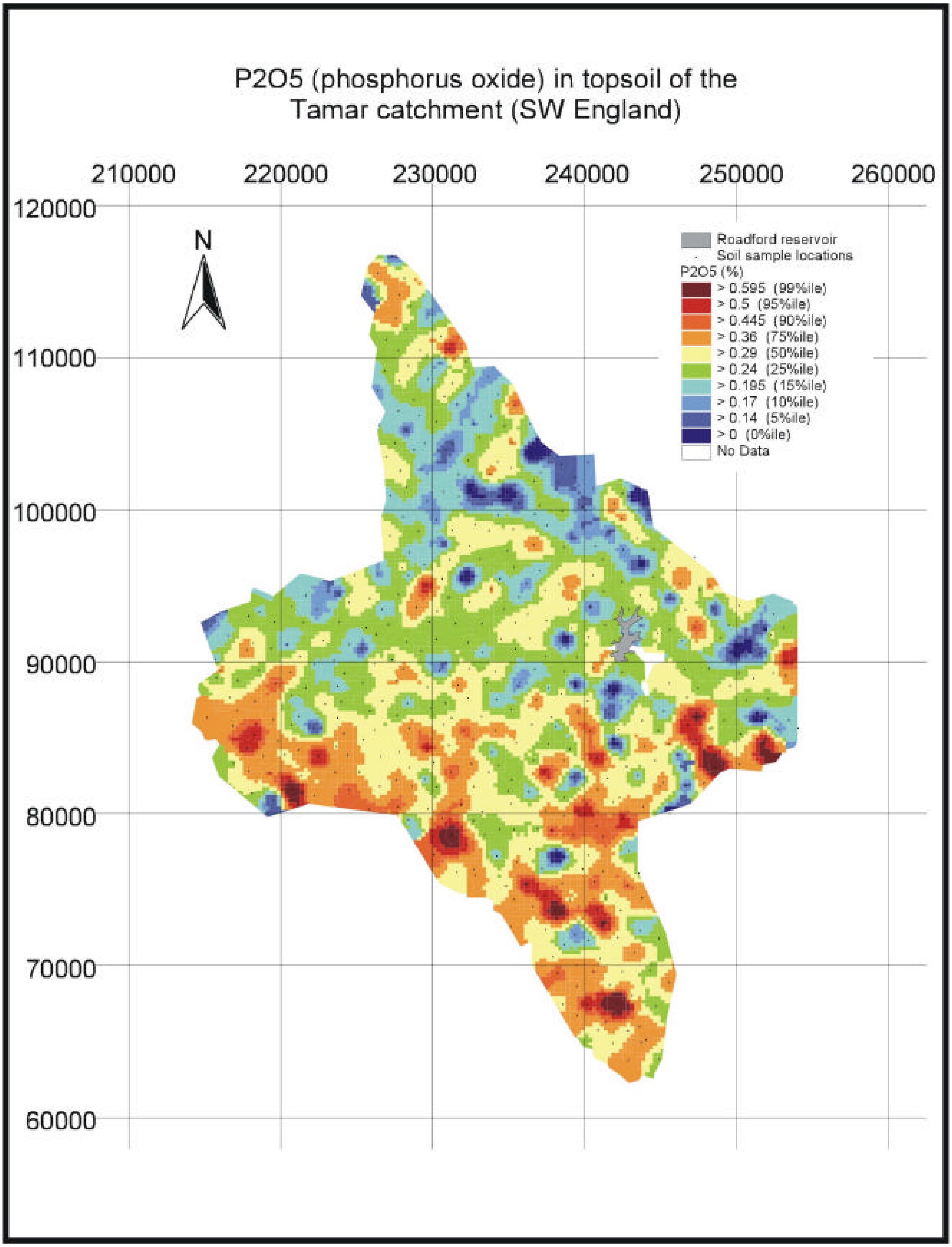

Ni (nickel) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Ni (mg/kg)
> 92.1 (99%ile)
> 59.85 (95%ile)
> 44.9 (90%ile)
> 31.15 (75%ile)
> 19.5 (50%ile)
> 14.25 (25%ile)
> 11.65 (15%ile)
> 9.75 (10%ile)
> 8 (5%ile)
> 0 (0%ile)
No Data

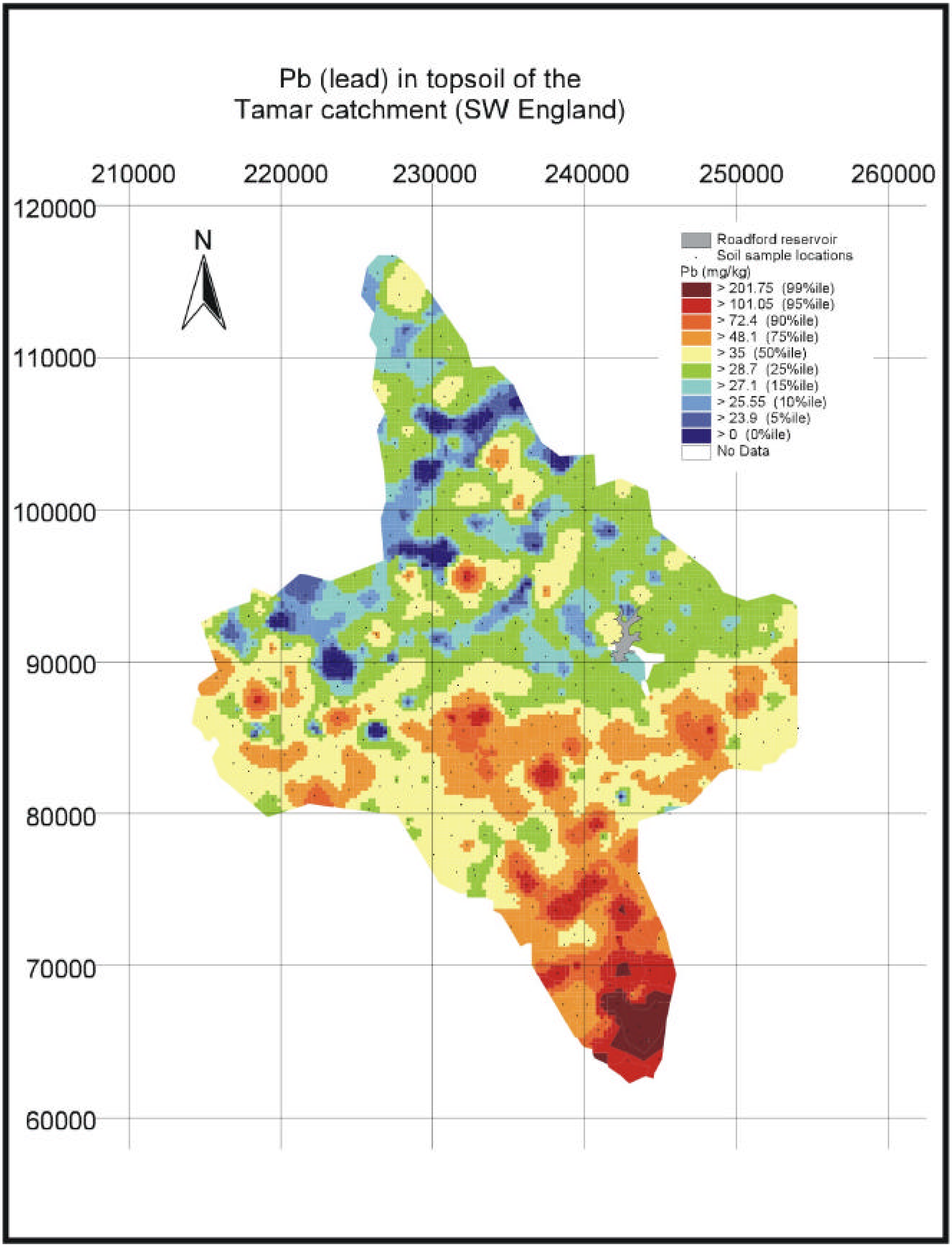


"Olsen P" (available phosphorus) in topsoil of the Tamar catchment (SW England)

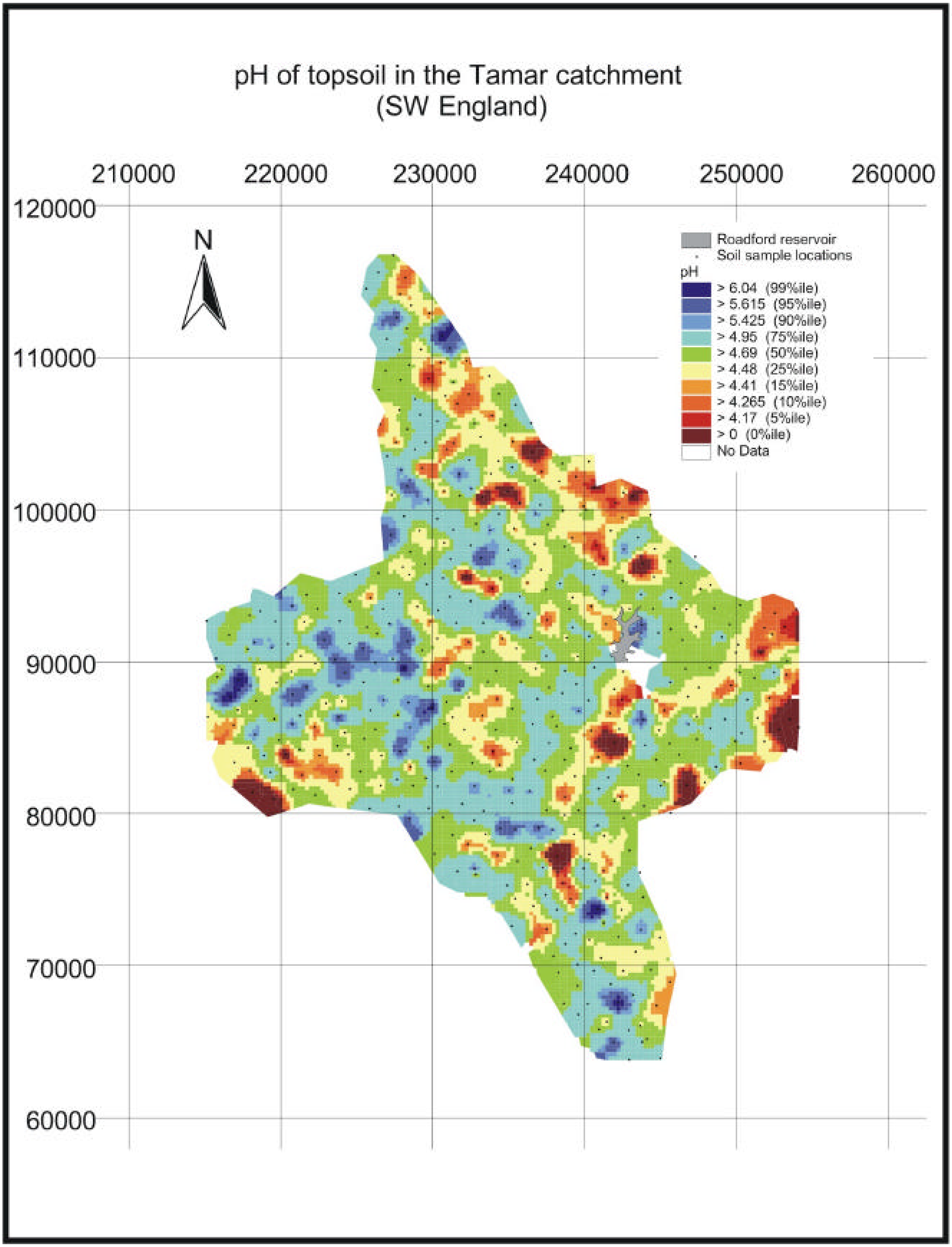


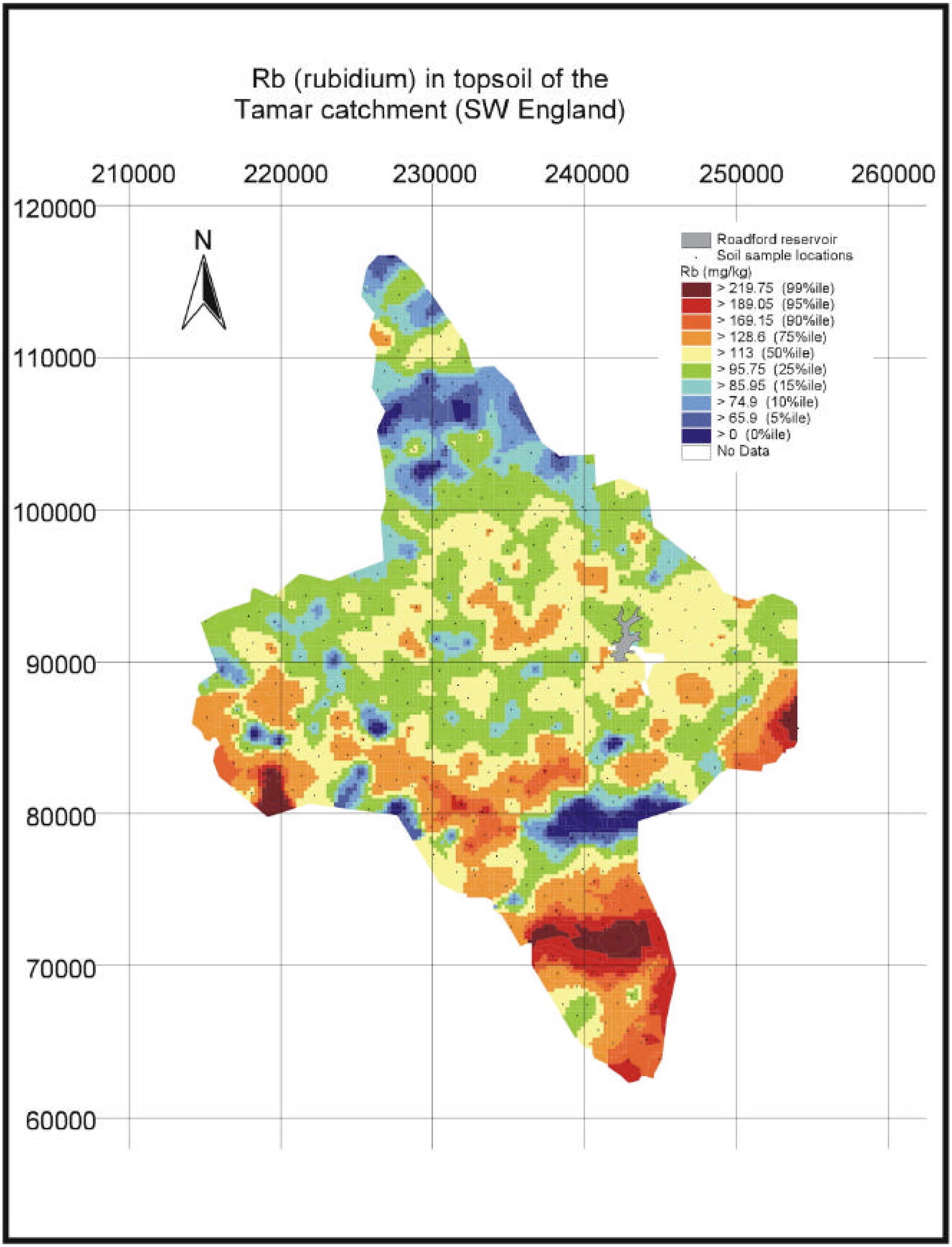
Organic carbon content (%) in topsoil of the Tamar catchment (SW England)

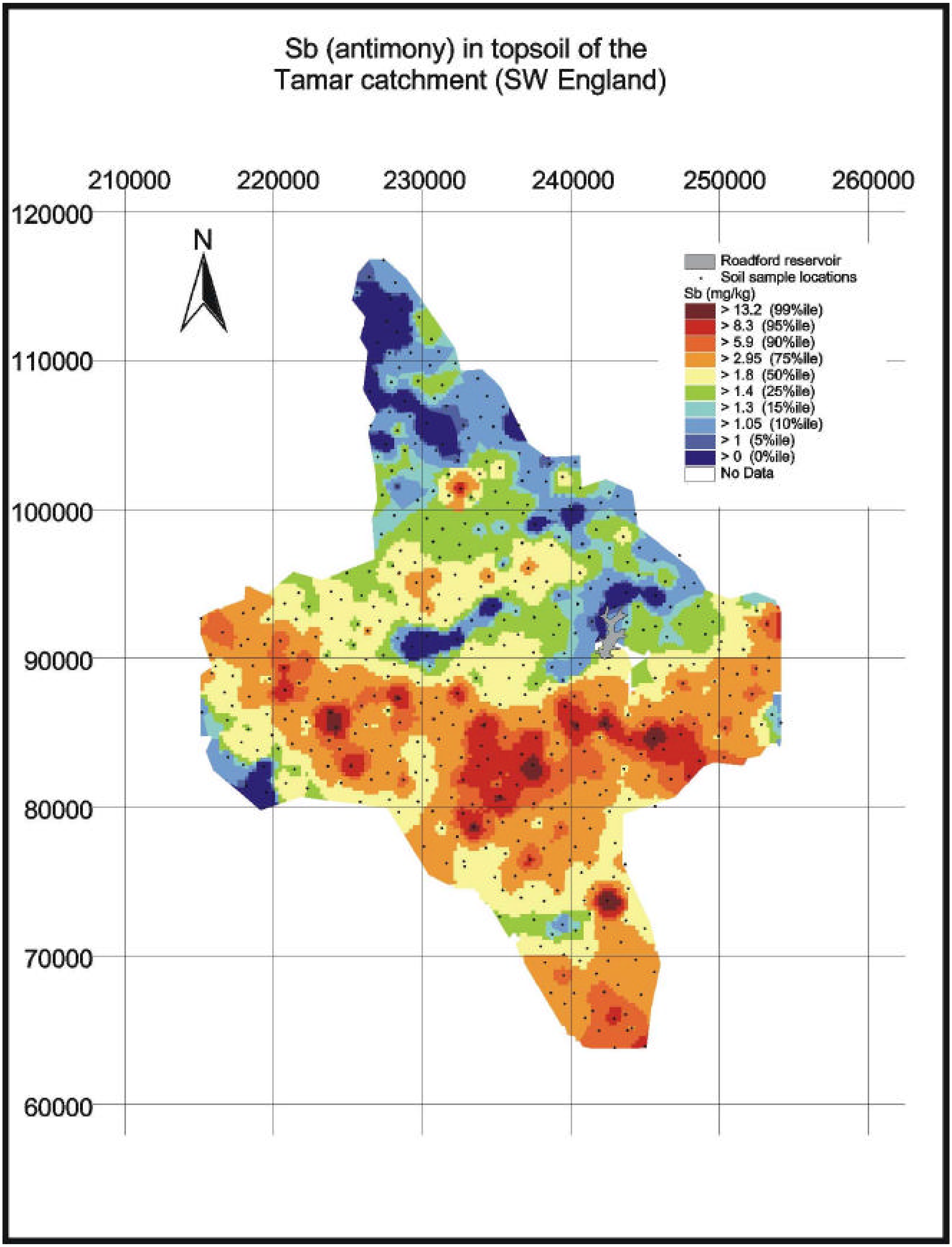

P2O5 (phosphorus oxide) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
P2O5 (%)
> 0.595 (99%ile)
> 0.5 (95%ile)
> 0.445 (90%ile)
> 0.36 (75%ile)
> 0.29 (50%ile)
> 0.24 (25%ile)
> 0.195 (15%ile)
> 0.17 (10%ile)
> 0.14 (5%ile)
> 0 (0%ile)
No Data

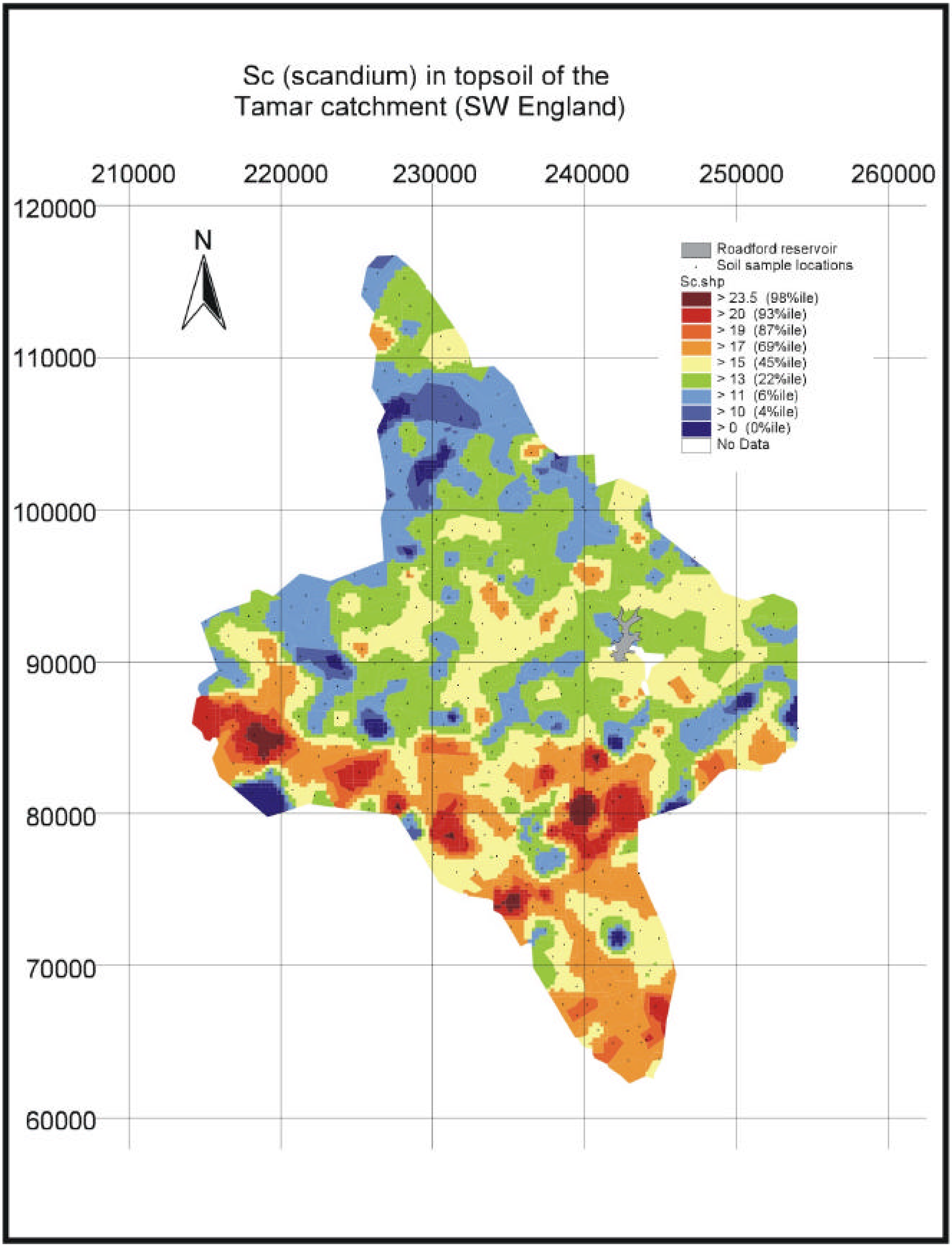


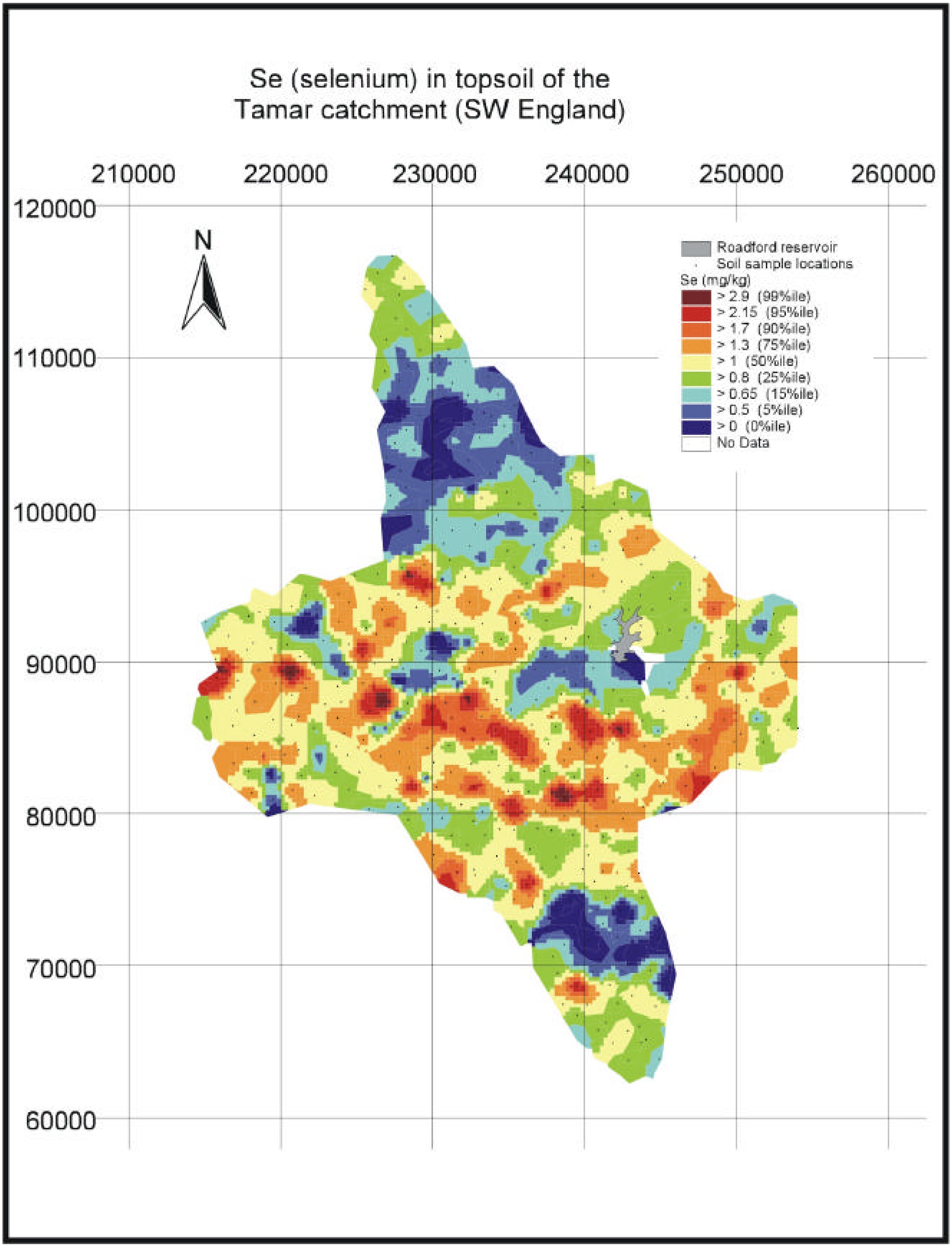
Pb (lead) in topsoil of the Tamar catchment (SW England)

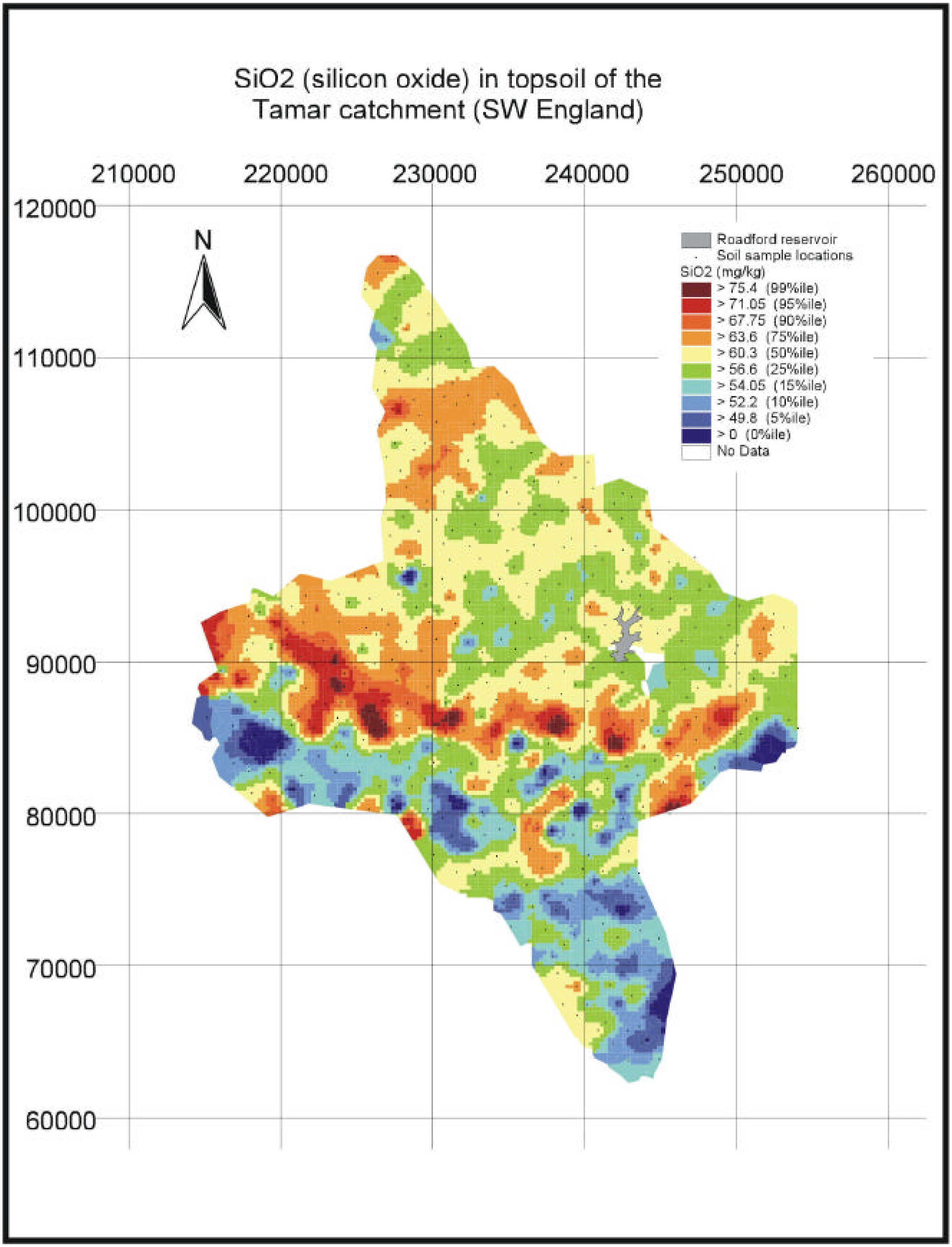

pH of topsoil in the Tamar catchment
(SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
pH
> 6.04 (99%ile)
> 5.615 (95%ile)
> 5.425 (90%ile)
> 4.95 (75%ile)
> 4.69 (50%ile)
> 4.48 (25%ile)
> 4.41 (15%ile)
> 4.265 (10%ile)
> 4.17 (5%ile)
> 0 (0%ile)
No Data

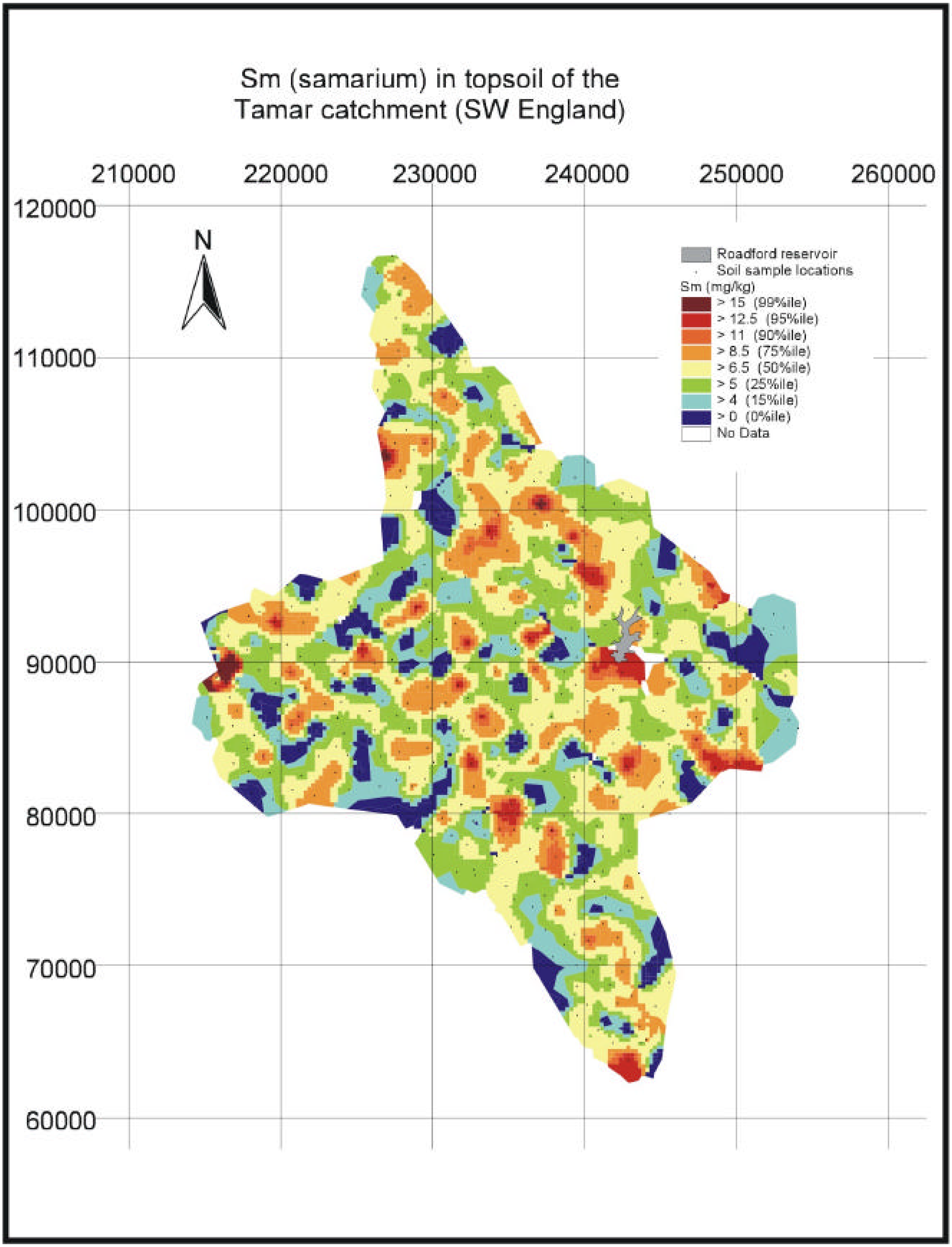

Rb (rubidium) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Rb (mg/kg)
> 219.75 (99%ile)
> 189.05 (95%ile)
> 169.15 (90%ile)
> 128.6 (75%ile)
> 113 (50%ile)
> 95.75 (25%ile)
> 85.95 (15%ile)
> 74.9 (10%ile)
> 65.9 (5%ile)
> 0 (0%ile)
No Data

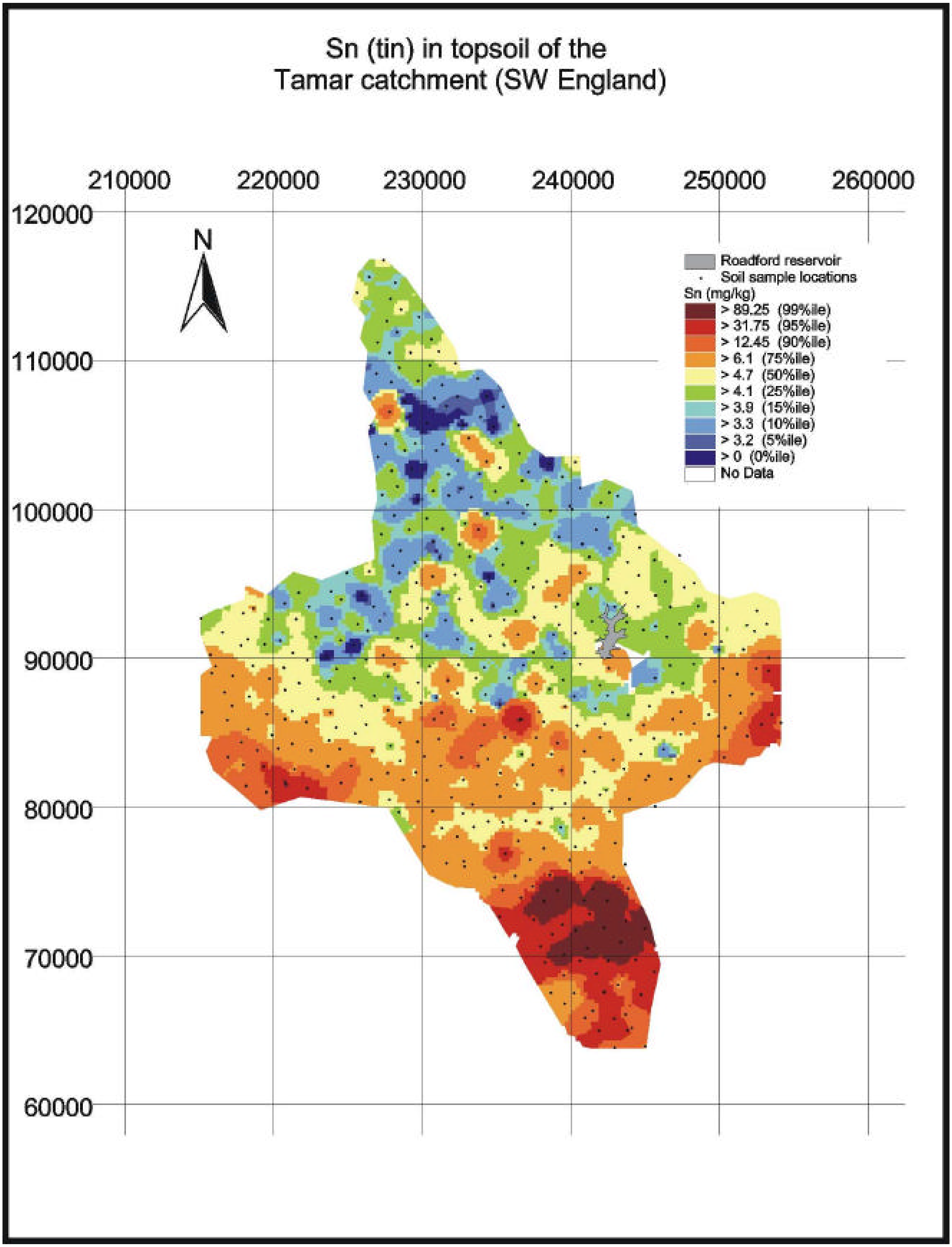

Sb (antimony) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Sb (mg/kg)
> 13.2 (99%ile)
> 8.3 (95%ile)
> 5.9 (90%ile)
> 2.95 (75%ile)
> 1.8 (50%ile)
> 1.4 (25%ile)
> 1.3 (15%ile)
> 1.05 (10%ile)
> 1 (5%ile)
> 0 (0%ile)
No Data


Sc (scandium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Sc.shp
> 23.5 (98%ile)
> 20 (93%ile)
> 19 (87%ile)
> 17 (69%ile)
> 15 (45%ile)
> 13 (22%ile)
> 11 (6%ile)
> 10 (4%ile)
> 0 (0%ile)
No Data

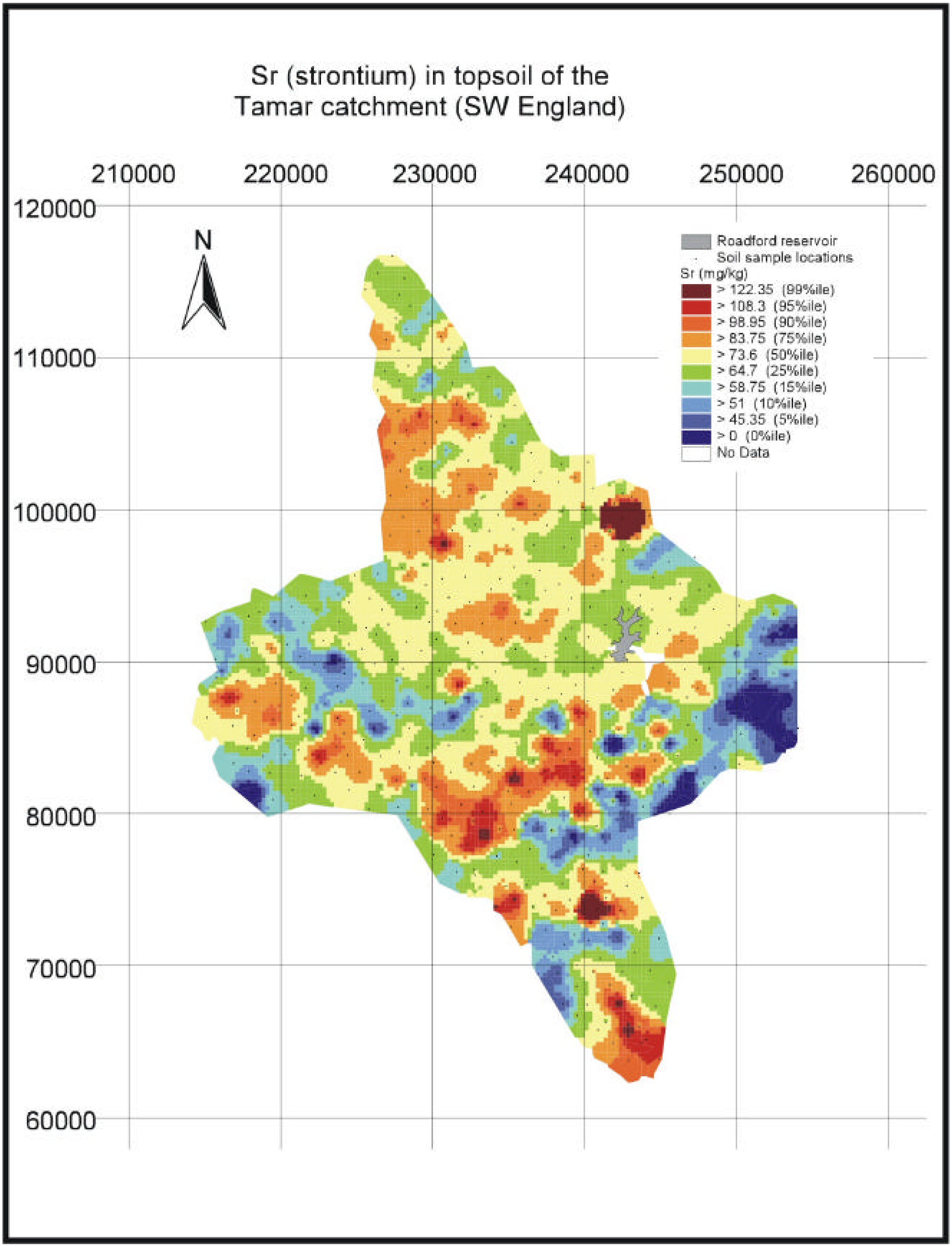

Se (selenium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Se (mg/kg)
> 2.9 (99%ile)
> 2.15 (95%ile)
> 1.7 (90%ile)
> 1.3 (75%ile)
> 1 (50%ile)
> 0.8 (25%ile)
> 0.65 (15%ile)
> 0.5 (5%ile)
> 0 (0%ile)
No Data

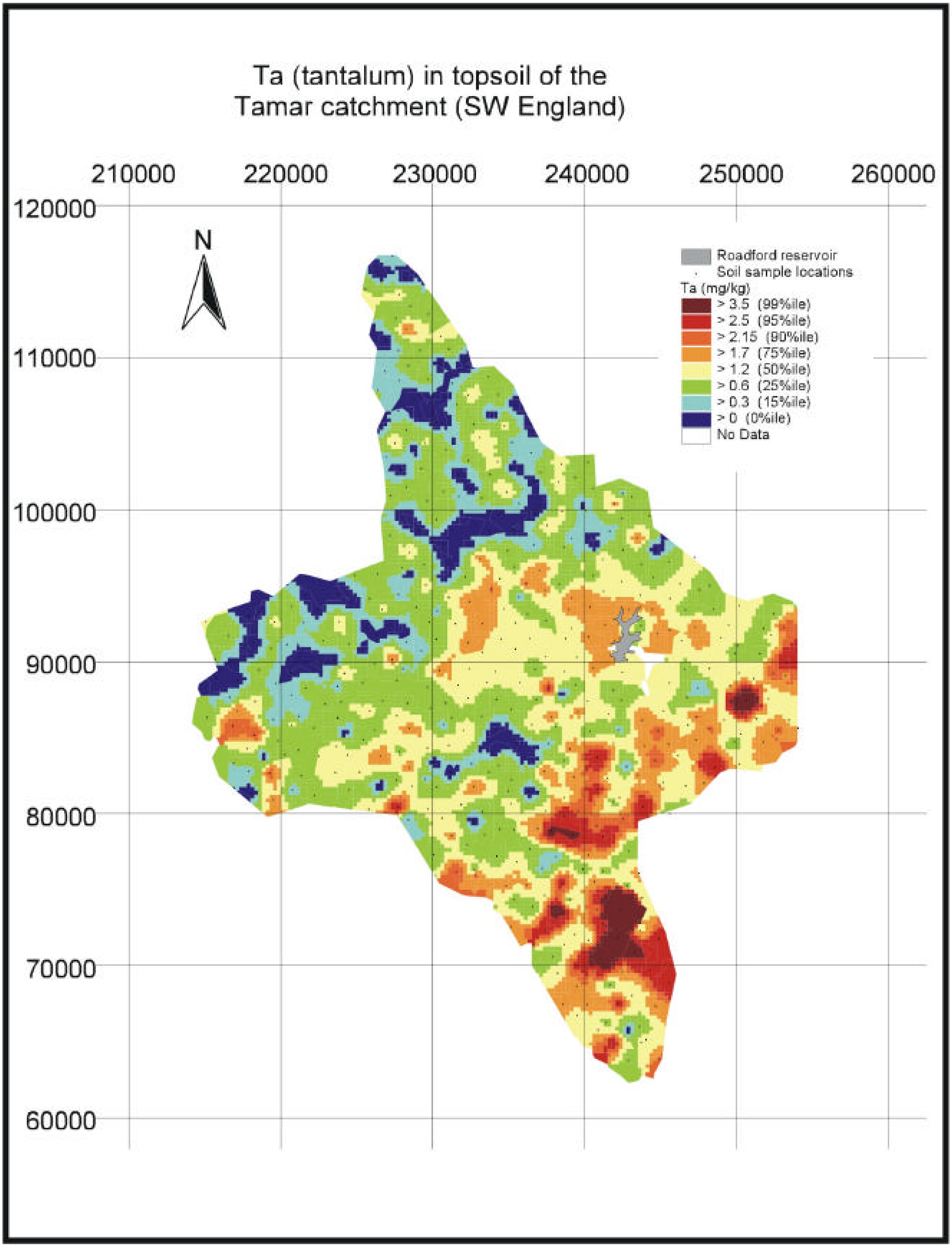

SiO2 (silicon oxide) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
SiO2 (mg/kg)
> 75.4 (99%ile)
> 71.05 (95%ile)
> 67.75 (90%ile)
> 63.6 (75%ile)
> 60.3 (50%ile)
> 56.6 (25%ile)
> 54.05 (15%ile)
> 52.2 (10%ile)
> 49.8 (5%ile)
> 0 (0%ile)
No Data

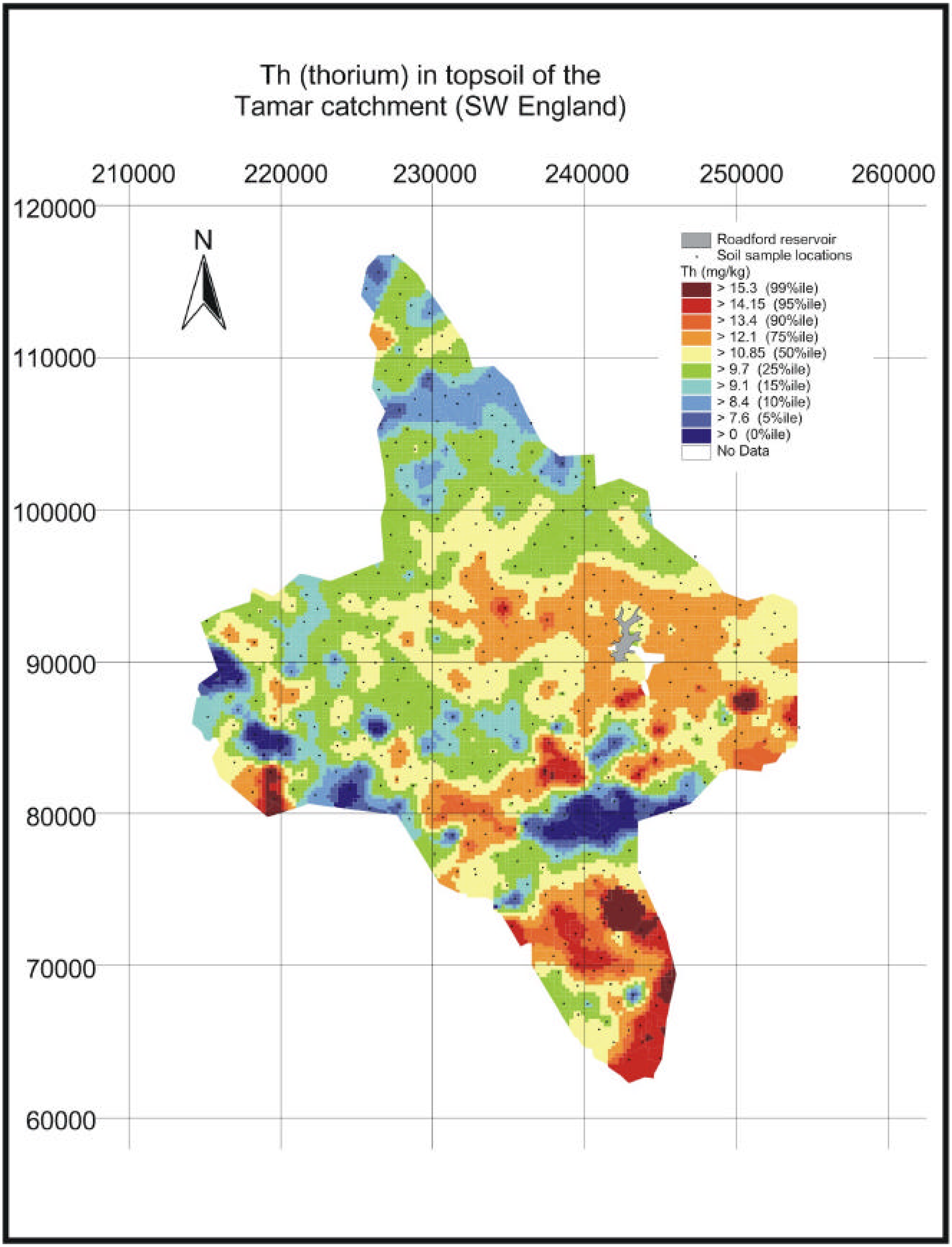

Sm (samarium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Sm (mg/kg)
> 15 (99%ile)
> 12.5 (95%ile)
> 11 (90%ile)
> 8.5 (75%ile)
> 6.5 (50%ile)
> 5 (25%ile)
> 4 (15%ile)
> 0 (0%ile)
No Data

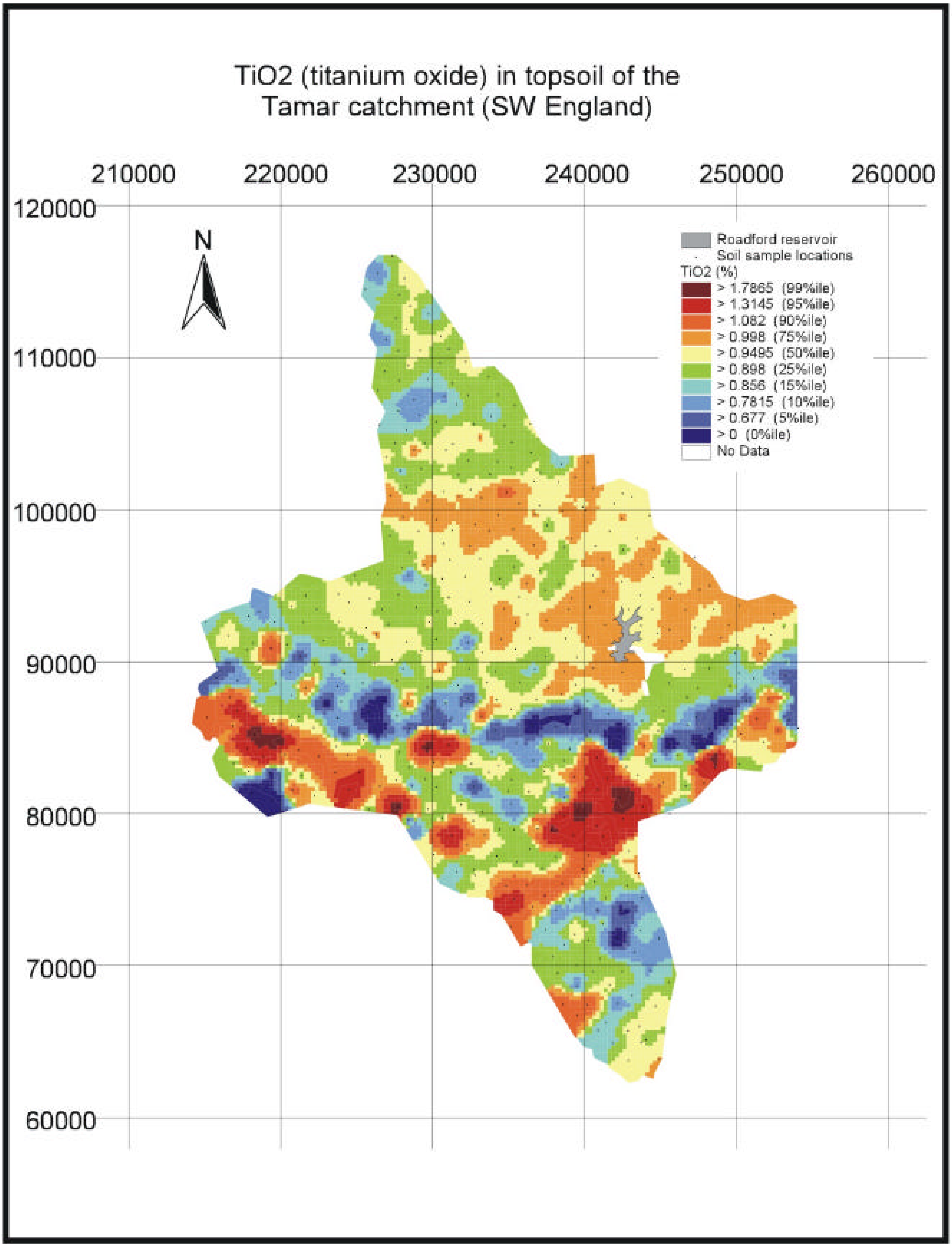


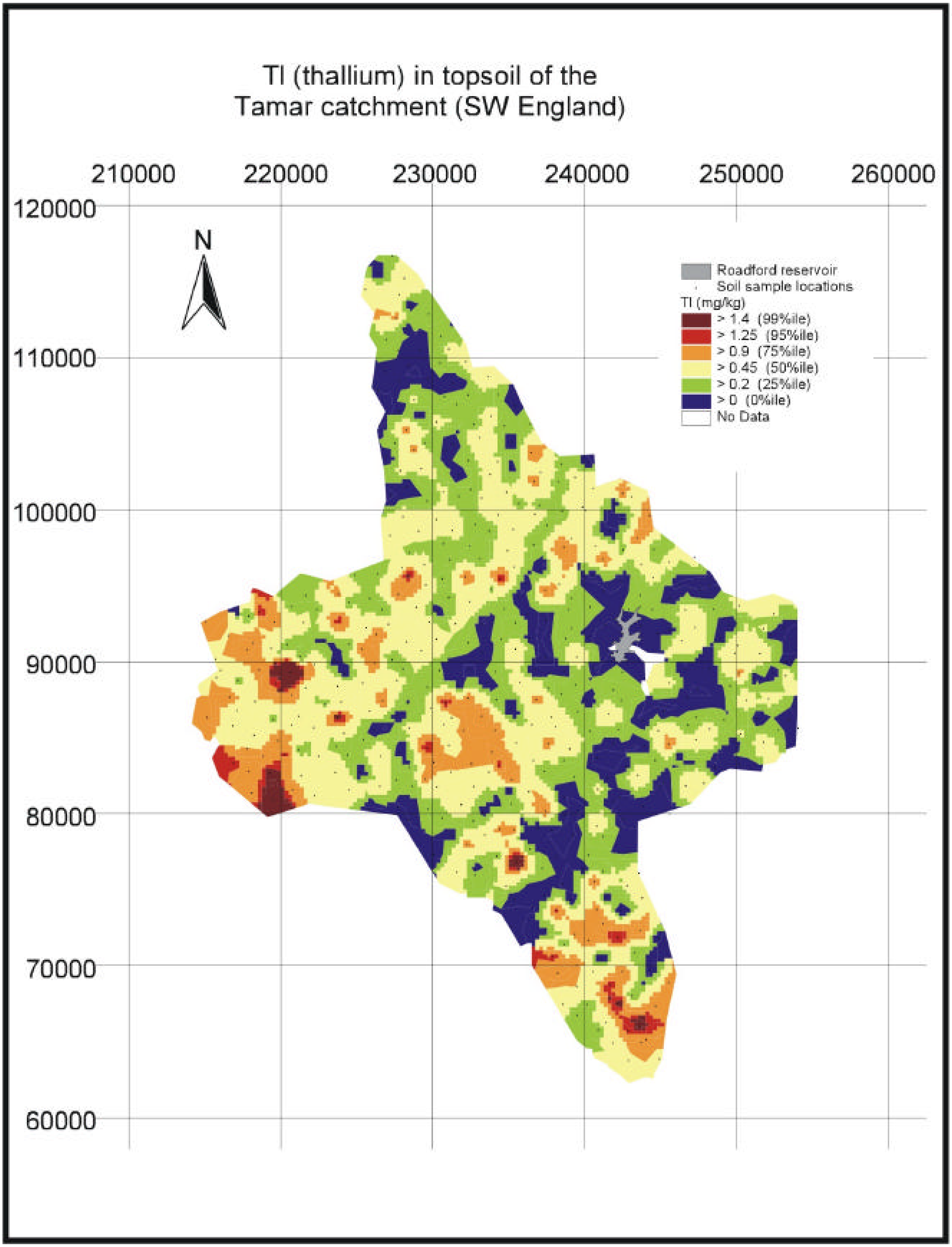
Sn (tin) in topsoil of the Tamar catchment (SW England)

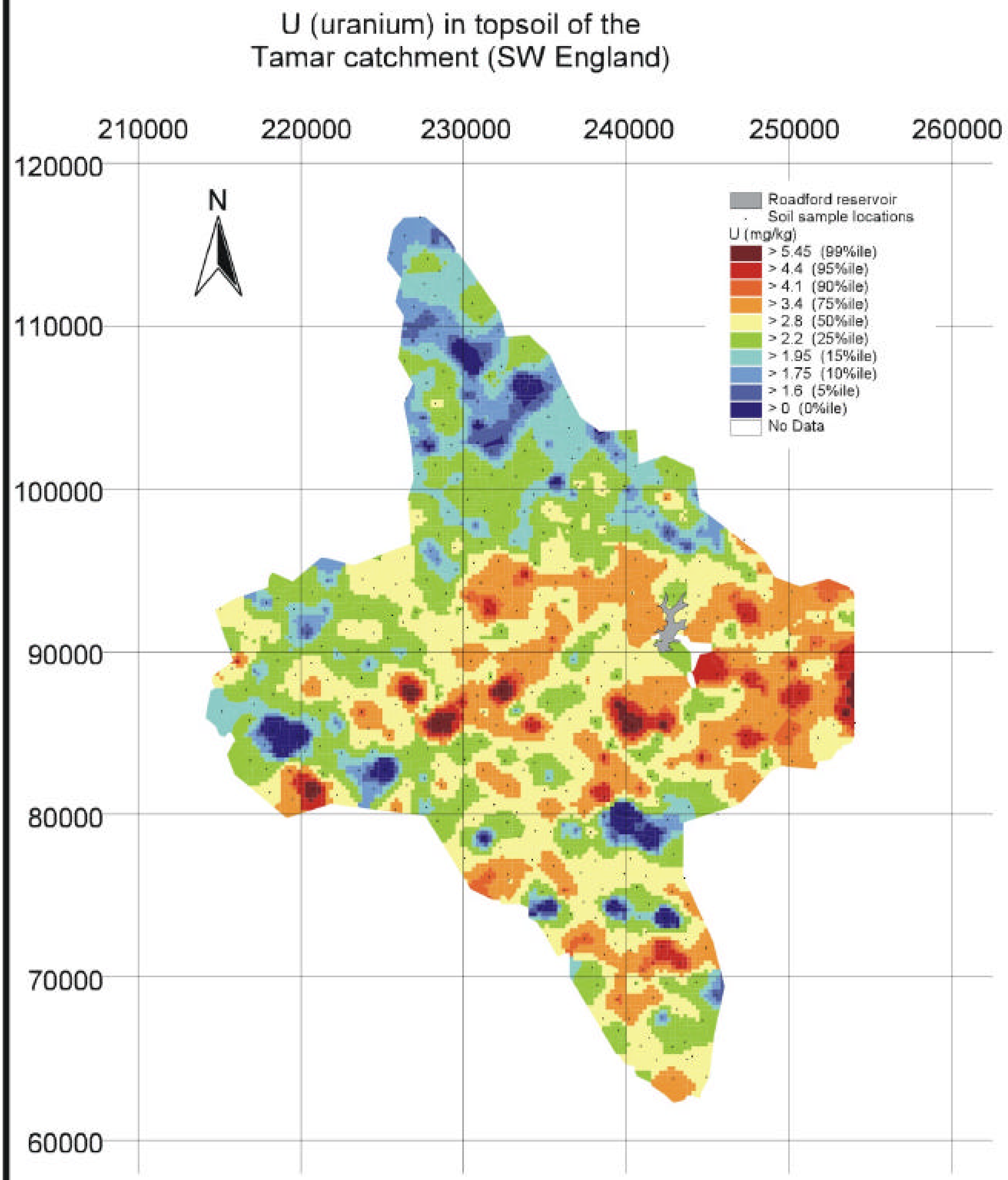

Sr (strontium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Sr (mg/kg)
> 122.35 (99%ile)
> 108.3 (95%ile)
> 98.95 (90%ile)
> 83.75 (75%ile)
> 73.6 (50%ile)
> 64.7 (25%ile)
> 58.75 (15%ile)
> 51 (10%ile)
> 45.35 (5%ile)
> 0 (0%ile)
No Data


Ta (tantalum) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Ta (mg/kg)
> 3.5 (99%ile)
> 2.5 (95%ile)
> 2.15 (90%ile)
> 1.7 (75%ile)
> 1.2 (50%ile)
> 0.6 (25%ile)
> 0.3 (15%ile)
> 0 (0%ile)
No Data

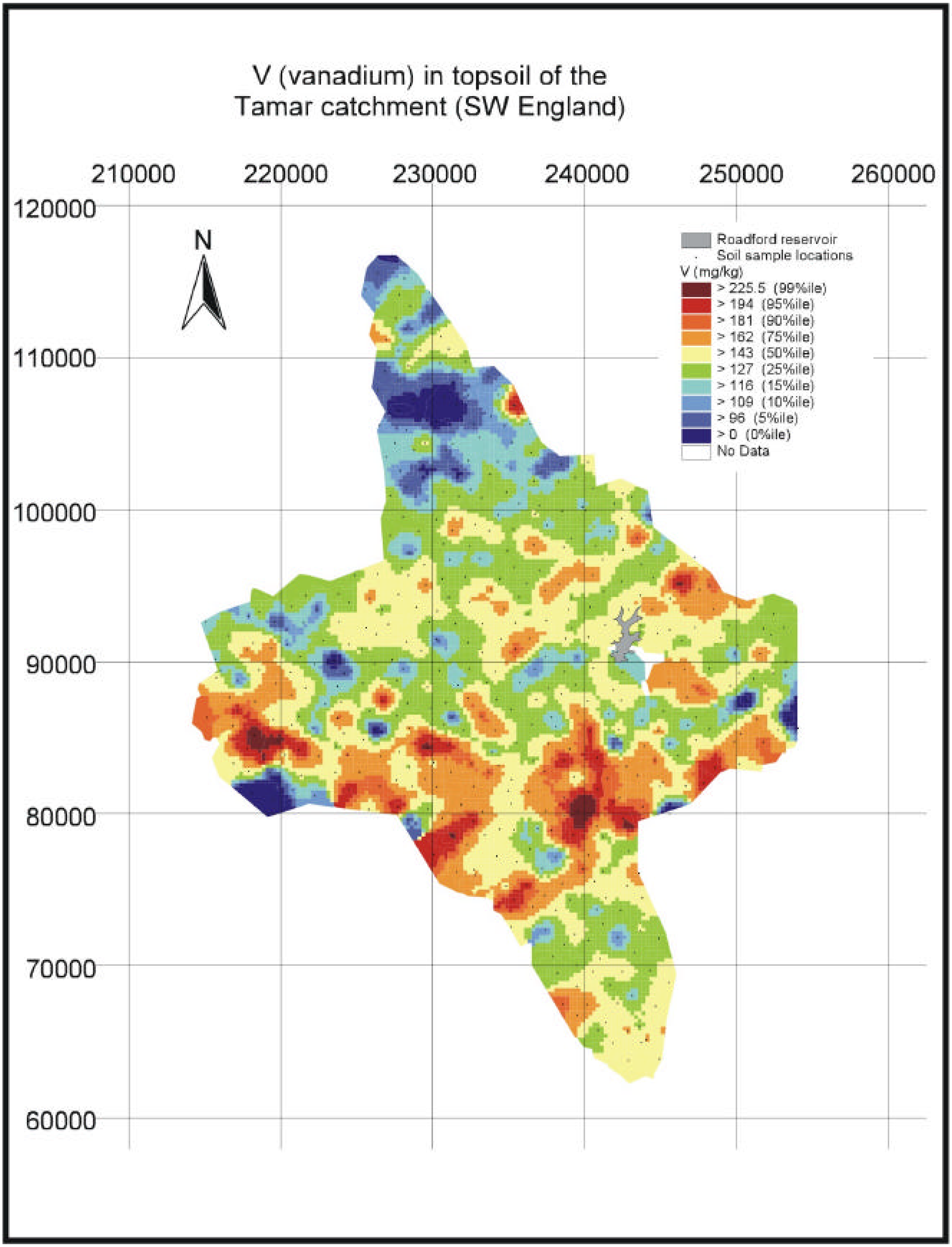

Th (thorium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Th (mg/kg)
> 15.3 (99%ile)
> 14.15 (95%ile)
> 13.4 (90%ile)
> 12.1 (75%ile)
> 10.85 (50%ile)
> 9.7 (25%ile)
> 9.1 (15%ile)
> 8.4 (10%ile)
> 7.6 (5%ile)
> 0 (0%ile)
No Data

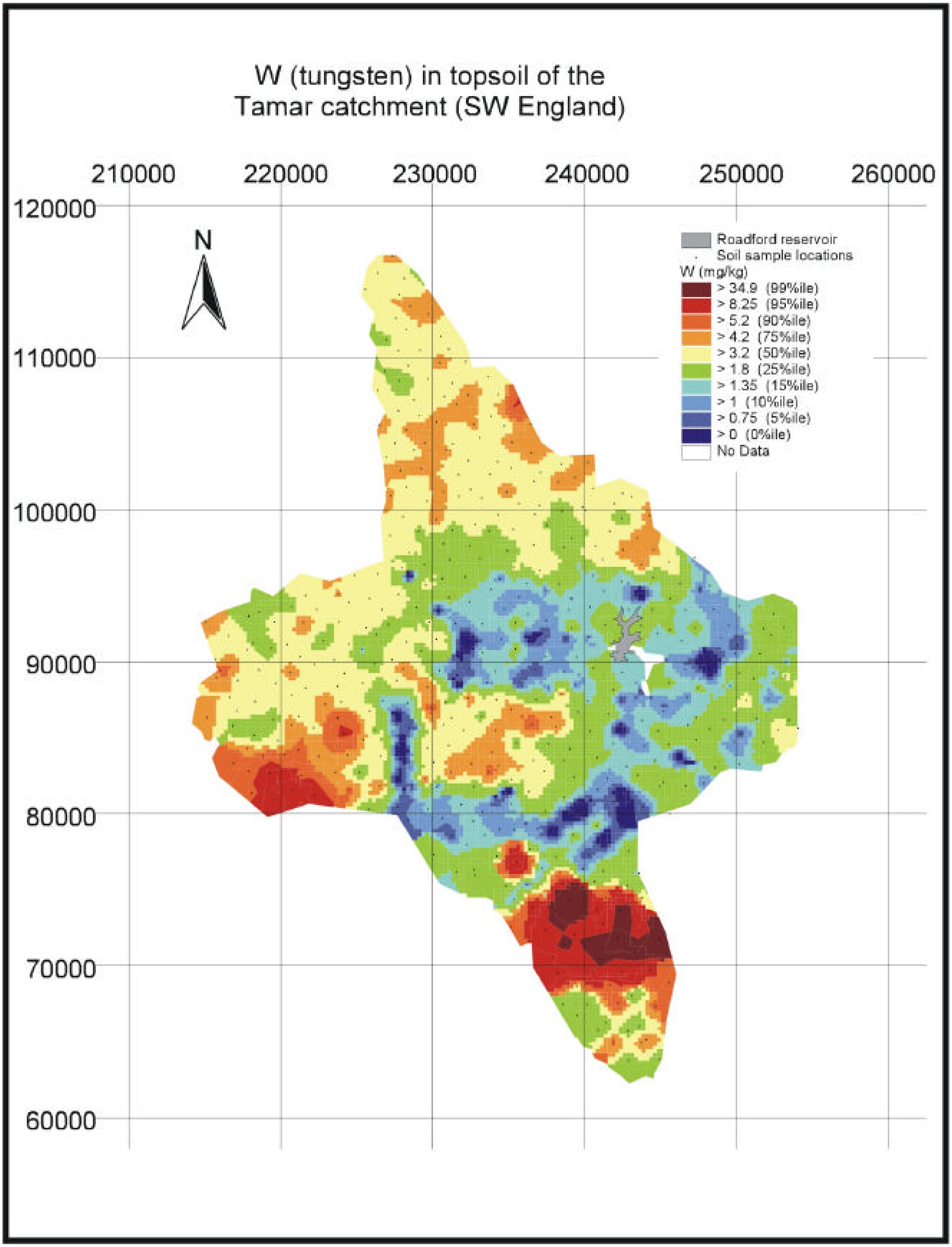

TiO2 (titanium oxide) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
TiO2 (%)
> 1.7865 (99%ile)
> 1.3145 (95%ile)
> 1.082 (90%ile)
> 0.998 (75%ile)
> 0.9495 (50%ile)
> 0.898 (25%ile)
> 0.856 (15%ile)
> 0.7815 (10%ile)
> 0.677 (5%ile)
> 0 (0%ile)
No Data

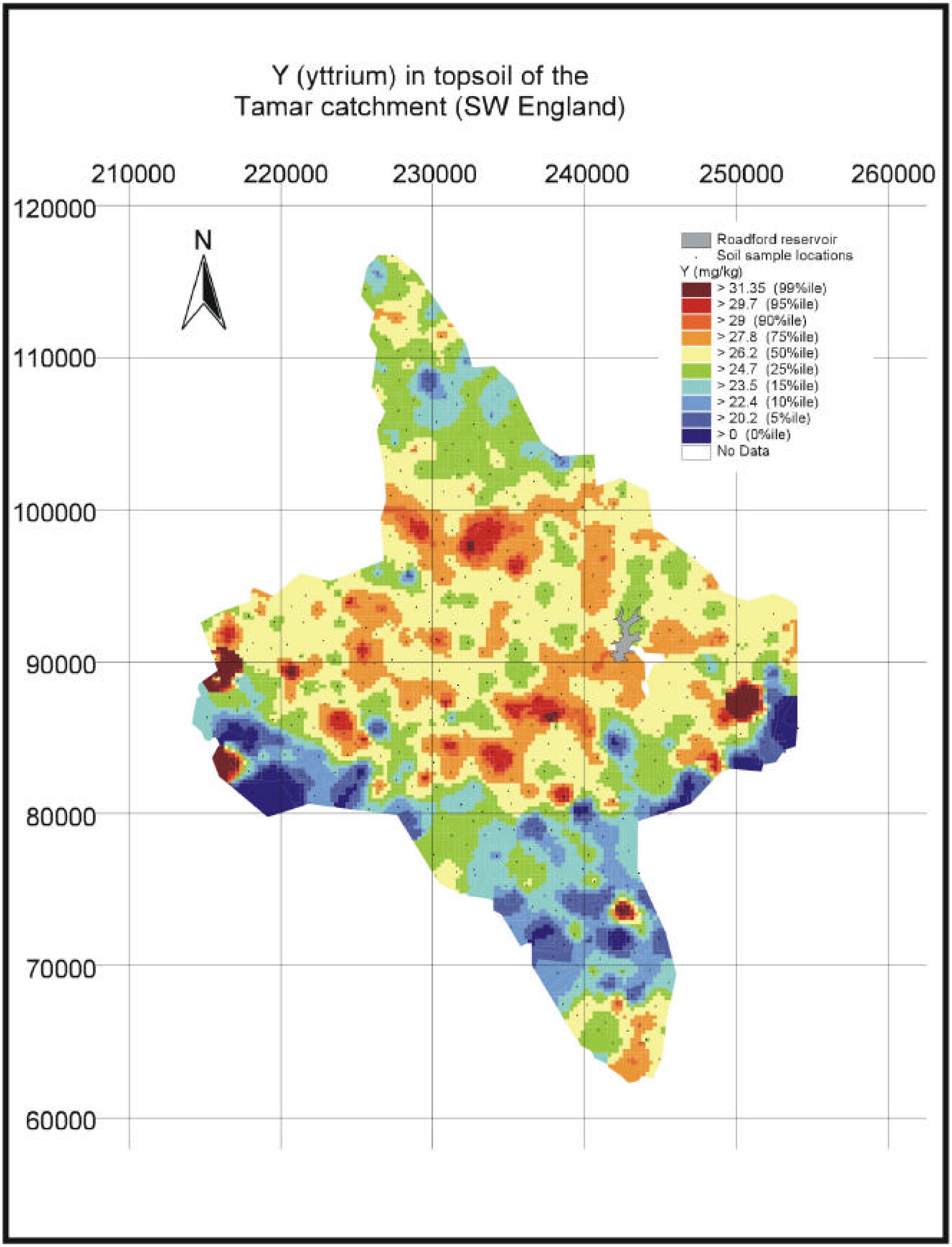

Tl (thallium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Tl (mg/kg)
> 1.4 (99%ile)
> 1.25 (95%ile)
> 0.9 (75%ile)
> 0.45 (50%ile)
> 0.2 (25%ile)
> 0 (0%ile)
No Data

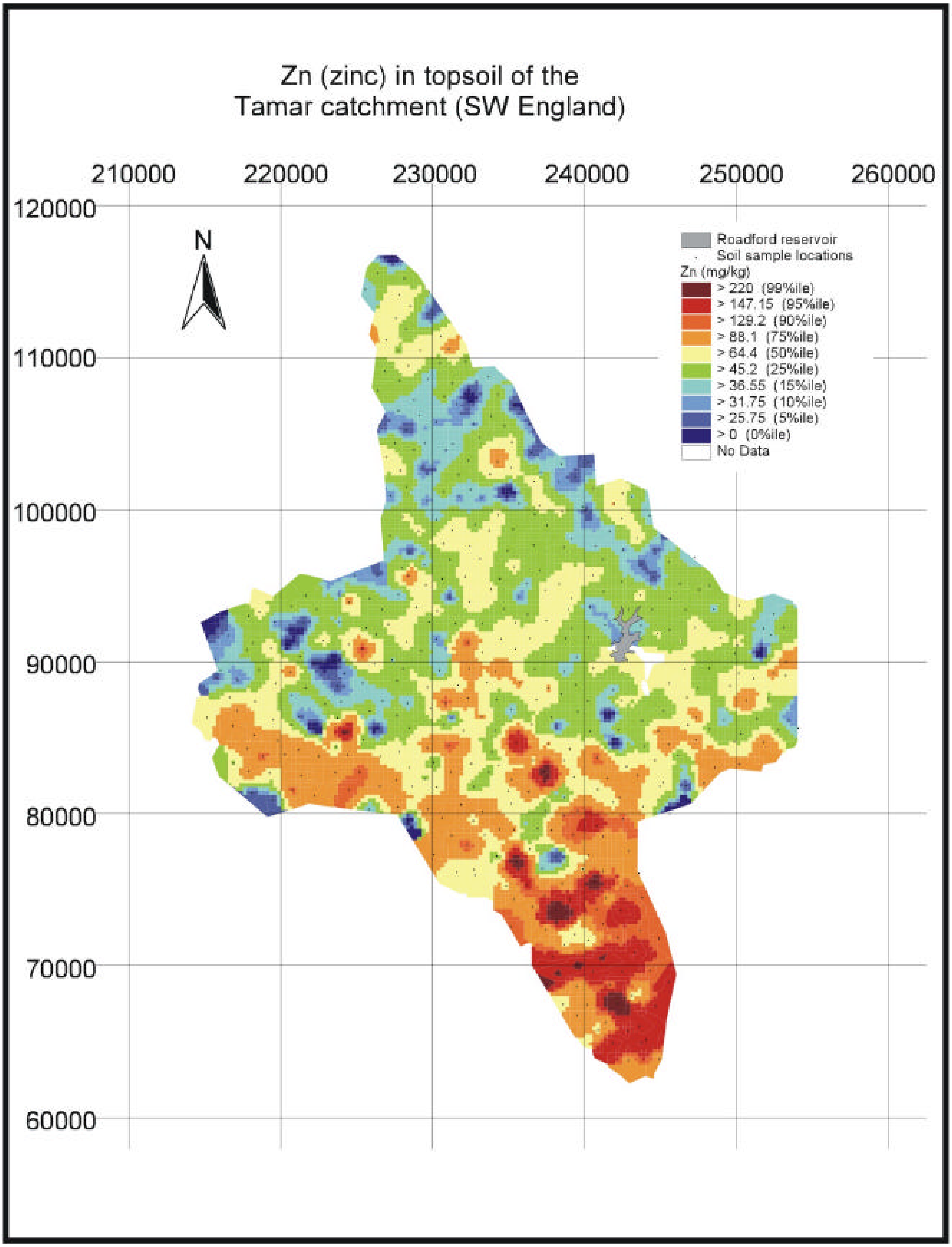


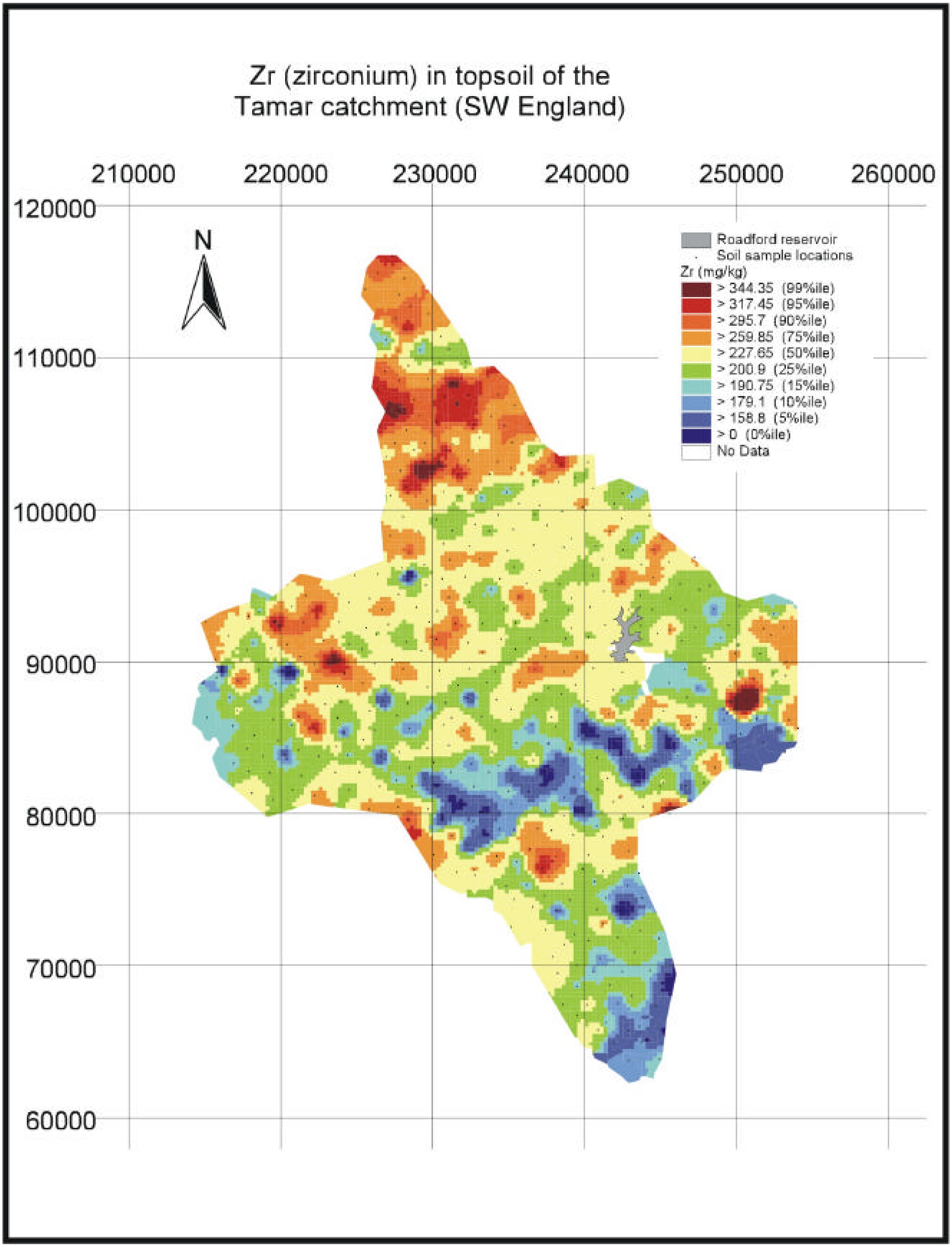
U (uranium) in topsoil of the Tamar catchment (SW England)


V (vanadium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
V (mg/kg)
> 225.5 (99%ile)
> 194 (95%ile)
> 181 (90%ile)
> 162 (75%ile)
> 143 (50%ile)
> 127 (25%ile)
> 116 (15%ile)
> 109 (10%ile)
> 96 (5%ile)
> 0 (0%ile)
No Data


W (tungsten) in topsoil of the Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
W (mg/kg)
> 34.9 (99%ile)
> 8.25 (95%ile)
> 5.2 (90%ile)
> 4.2 (75%ile)
> 3.2 (50%ile)
> 1.8 (25%ile)
> 1.35 (15%ile)
> 1 (10%ile)
> 0.75 (5%ile)
> 0 (0%ile)
No Data


Y (yttrium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Y (mg/kg)
> 31.35 (99%ile)
> 29.7 (95%ile)
> 29 (90%ile)
> 27.8 (75%ile)
> 26.2 (50%ile)
> 24.7 (25%ile)
> 23.5 (15%ile)
> 22.4 (10%ile)
> 20.2 (5%ile)
> 0 (0%ile)
No Data


Zn (zinc) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Zn (mg/kg)
> 220 (99%ile)
> 147.15 (95%ile)
> 129.2 (90%ile)
> 88.1 (75%ile)
> 64.4 (50%ile)
> 45.2 (25%ile)
> 36.55 (15%ile)
> 31.75 (10%ile)
> 25.75 (5%ile)
> 0 (0%ile)
No Data


Zr (zirconium) in topsoil of the
Tamar catchment (SW England)
210000
220000
230000
240000
250000
260000
120000
110000
100000
90000
80000
70000
60000
N
Roadford reservoir
Soil sample locations
Zr (mg/kg)
> 344.35 (99%ile)
> 317.45 (95%ile)
> 295.7 (90%ile)
> 259.85 (75%ile)
> 227.65 (50%ile)
> 200.9 (25%ile)
> 190.75 (15%ile)
> 179.1 (10%ile)
> 158.8 (5%ile)
> 0 (0%ile)
No Data