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Stream sediment geochemical atlas of the United Kingdom

Geoanalytics and Modelling programme

Open Report OR/18/048

About this atlas

This atlas has been published as an ‘interactive pdf document’, which features several functions that allow the reader to access and display different geochemical maps and information in various ways:

- clickable buttons, which toggle between two styles of stream sediment geochemical map for each chemical element
- clickable buttons on each element information page, which toggle between different views showing: 1) a reference geology map (which can be enlarged to a full page) and a boxplot of the data distribution over different geological units for that element; 2) a histogram, a table of summary statistics, and a hyperlinked map showing areas covered by the British Geological Survey’s (BGS) previously published Regional Geochemistry Atlases.
- By clicking on the hyperlinked map, the reader can readily access previously published maps and information in the BGS Regional Geochemistry Atlases. The hyperlinks embedded in the map navigate to the BGS publications portal on the World Wide Web, and when activated will open the selected atlas in your default web browser at the relevant page. N.B. some of the early Regional Geochemistry Atlases did not include information for all of the elements presented here; therefore, hyperlinks are not included in all cases.

In addition, the report contains the following links:

- from the table of contents to each principal section heading, figures and tables
- from each page number back to the contents page
- from the periodic table of the elements in Figure 1 to the relevant section for each element

This atlas is designed to be read in two-page view using Adobe pdf software (e.g. Adobe Reader, Adobe Acrobat).

BRITISH GEOLOGICAL SURVEY

GEOANALYTICS AND MODELLING PROGRAMME

OPEN REPORT OR/18/048

Stream sediment geochemical atlas of the United Kingdom

Everett P A, Lister T R, Fordyce F M, Ferreira A M P J, Donald A W, Gowing C J B and Lawley R S.

Editor

Palumbo-Roe, B.

Contributors

G-BASE, TellusNI and Analytical Chemistry Teams

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The river Clyde

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BRITISH GEOLOGICAL SURVEY

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The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as basic research projects. It also undertakes programmes of technical aid in geology in developing countries.

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British Geological Survey offices

BGS Central Enquiries Desk

Tel 0115 936 3143 Fax 0115 936 3276
email enquiries@bgs.ac.uk

Environmental Science Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3241 Fax 0115 936 3488
email sales@bgs.ac.uk

The Lyell Centre, Research Avenue South, Edinburgh
EH14 4AP

Tel 0131 667 1000 Fax 0131 668 2683
email scotsales@bgs.ac.uk

Natural History Museum, Cromwell Road, London SW7 5BD

Tel 020 7589 4090 Fax 020 7584 8270
Tel 020 7942 5344/45
email bgslondon@bgs.ac.uk

Cardiff University, Main Building, Park Place, Cardiff CF10 3AT

Tel 029 2167 4280 Fax 029 2052 1963

Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB

Tel 01491 838800 Fax 01491 692345

Geological Survey of Northern Ireland, Dundonald House, Upper Newtownards Road, Ballymiscaw, Belfast, BT4 3SB

Tel 028 9038 8462 Fax 028 9038 8461
email: gsni@economy-ni.gov.uk
www.bgs.ac.uk/gsni/

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500 Fax 01793 411501
www.nerc.ac.uk

UK Research and Innovation, Polaris House, Swindon SN2 1FL

Tel 01793 444000
www.ukri.org

Website www.bgs.ac.uk
Shop online at www.geologyshop.com

G-BASE, TellusNI and Analytical Chemistry Teams

G-BASE Project & Management	
Baldock	Dr J. W.
Bateson	Mr J. H.
Bowie	Dr S. H. U.
Cave	Dr M. R.
Dunkley	Dr P. N.
Flight	Ms D. M. A.
Howard	Dr A. S.
Johnson	Dr C. C.
Klinck	Dr B. A.
Lawley	Mr R. S.
Lee	Dr M. K.
Morgan	Dr D. J.
Parrish	Prof R. R.
Petterson	Dr M. G.
Plant	Prof J. A.
Reeves	Dr H. J.
Royse	Dr K. R.
Scheib	Ms C. E.
Simpson	Prof P. R.
Smith	Dr B.
Wragg	Dr J.

G-BASE Project Team	
Ander	Dr E. L.
Bearcock	Dr J. M.
Breward	Dr N.
Brown	Mr M. J.
Brown	Mrs A. J.
Durham	Mr J. J.
Everett	Mr P.
Ferguson	Mr A. J.
Ferreira	Mr A. M. P. J
Fordyce	Ms F. M.
Forrest	Mr M. D.
Freestone	Ms S. E.
Green	Mr P. M.
Greenbaum	Dr D.
Harvey	Mrs J. M.
Haslam	Dr H. W.
Henney	Dr P. J.
Hutchins	Dr M. G.
Jones	Mr R. C.
Kirkwood	Mr C. W.
Knights	Ms K. V.
Lister	Mr T. R.
Mackenzie	Mr A. C.
Markle	Mr C. I.
Mills	Ms A. J.
Mogdridge	Mr R.T.
Nice	Mrs S. E.
O'Donnell	Ms K. E.
Ostle	Mr D.
Rawlins	Dr B. G.
Scheib	Mr A. J.
Shenton	Mrs T.
Smith	Mr R.T.
Stevenson	Mr A.G.
Strutt	Mr M. H.
Wiggans	Mr G. N.
Williams	Ms R. A. C.
Williams	Dr T. M.

TELLUSNI Project Team	
Cowan	Dr M. T.
Earls	Mr G.
Young	Dr M. E.
Patton	Mr M. A. G.
Smyth	Dr D.
Donald	Mr A. W.
van Dam	Mr C.

Analytical Team	
Miles	Mr D. L.
Milne	Dr C. J.
Fortey	Dr N. J.
Reeder	Mr S.
Watts	Dr M. J.
Allen	Mr M. A.
Ault	Ms L.
Barker	Mr K.
Blackwell	Mr P. A.
Bradley	Mr A. D.
Breward	Mrs K. M.
Carter	Mr S. J.
Chenery	Dr S. R. N.
Cook	Ms J. M.
Date	Dr A. R.
Eatherington	Mr N. D.
Gowing	Dr C. J. B.
Green	Mrs K. A.
Hobbs	Ms S. F.
Holmes	Mr K. A.
Ingham	Mr M. N.
Moore	Mr P. J.
Murphy	Mr H. A.
Robinson	Mr J. J.
Tait	Mr B. A. R.
Waine	Ms E.
Windmill	Mrs V.A.
Wheeler	Mr J.

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Dedication

Without the dedication and determination of Professor Jane Plant CBE, it is debatable whether this baseline geochemical dataset for the UK would exist. An internationally renowned scientist, Jane pioneered the G-BASE methodology and led the programme until her appointment as BGS Chief Scientist in 2002. The G-BASE principles and methodologies have been adopted in many parts of the world and Jane was instrumental in co-leading the International Union of Geological Sciences Global Geochemical Baselines Project for several years. The authors and contributors wish to dedicate this publication to the achievements and memory of Jane.

Professor Jane Plant CBE 1945-2016

Foreword

Founded in 1835, the British Geological Survey (BGS) is the world's oldest national geological survey and the United Kingdom's premier centre for earth science information and expertise. The BGS provides expert services and impartial advice in all areas of geoscience. Our client base is drawn from the public and private sectors both in the UK and internationally.

Our innovative digital data products aim to help describe the ground surface, and what's beneath, across the United Kingdom (UK). These digital products are based on the outputs of the BGS's survey and research programmes and our substantial national data holdings. These data, coupled with our in-house geoscientific knowledge, are combined to provide products relevant to a wide range of users in central and local government, the insurance and housing industry, engineering and environmental business, the research community and the British public.

This atlas represents the first publication of complete national maps from the Geochemical Baseline Survey of the Environment (G-BASE) and the Geological Survey of Northern Ireland's TellusNI projects. The aim of these projects was to conduct a national geochemical survey of the UK in order to improve understanding of our geology, mineral resources and environment and to provide quantitative evidence, against which to gauge future environmental change. It is a milestone publication, representing 45 years of work, to characterise the chemical quality of the UK surface environment. In terms of sample density, it represents one of the most detailed datasets of its kind internationally.

The data presented here are the analyses of up to 111,000 sediment samples, collected from first and second order (i.e. small) streams across the UK, at an average density of 1 sample per 2.5km^2. Sampling began in northern Scotland in 1968 and was completed in 2013, in south-east England. The fine grain-size fraction (<150 µm) of the sediment samples was analysed to determine the total concentration of a range of naturally occurring inorganic chemical elements, 18 of which are included in this atlas. Throughout the lifetime of the G-BASE and TellusNI projects, strict quality control procedures have been in place at all stages from sample collection to analytical data reporting. Analytical data have been closely monitored to ensure continuity during numerous field campaigns and between different analytical methods. All data have been conditioned with respect to certified reference materials in order to provide both accurate and precise element concentrations with a high degree of confidence.

Stream sediment is largely composed of weathered material derived from the underlying bedrock. Hence, the results of the surveys show that regional variations in stream sediment chemistry across the UK closely reflect that of the underlying rock strata and that geology exerts the primary control on the distribution of most elements. Land use, soil type and secondary weathering processes also influence stream sediment chemistry, particularly where acid conditions prevail in peatland and in coniferous forests. Acid conditions enhance the mobility of many metal elements, which are subsequently sorbed to organic matter and iron and manganese oxyhydroxides in the stream sediment, resulting in enrichment. In addition, human impacts on stream sediment chemistry are evident. Stream sediment acts as a sink for materials generated from activities such as mining, industrialisation, urbanisation and agriculture and these elevate the concentrations of elements in sediment at a more local level. For the first time, this atlas provides an overview of stream sediment quality for inorganic chemistry across the UK, showing both the natural geological variability in element distributions, and human impacts. This landmark dataset has applications to sustainable resource management, environmental protection and to understanding geological/Earth-system processes. It aims to support UK sustainability and development, as defined under guidance such as Agenda 21 of the United Nations Earth Summit (UN 1992) and the European Union Water Framework Directive (CEC 2000).

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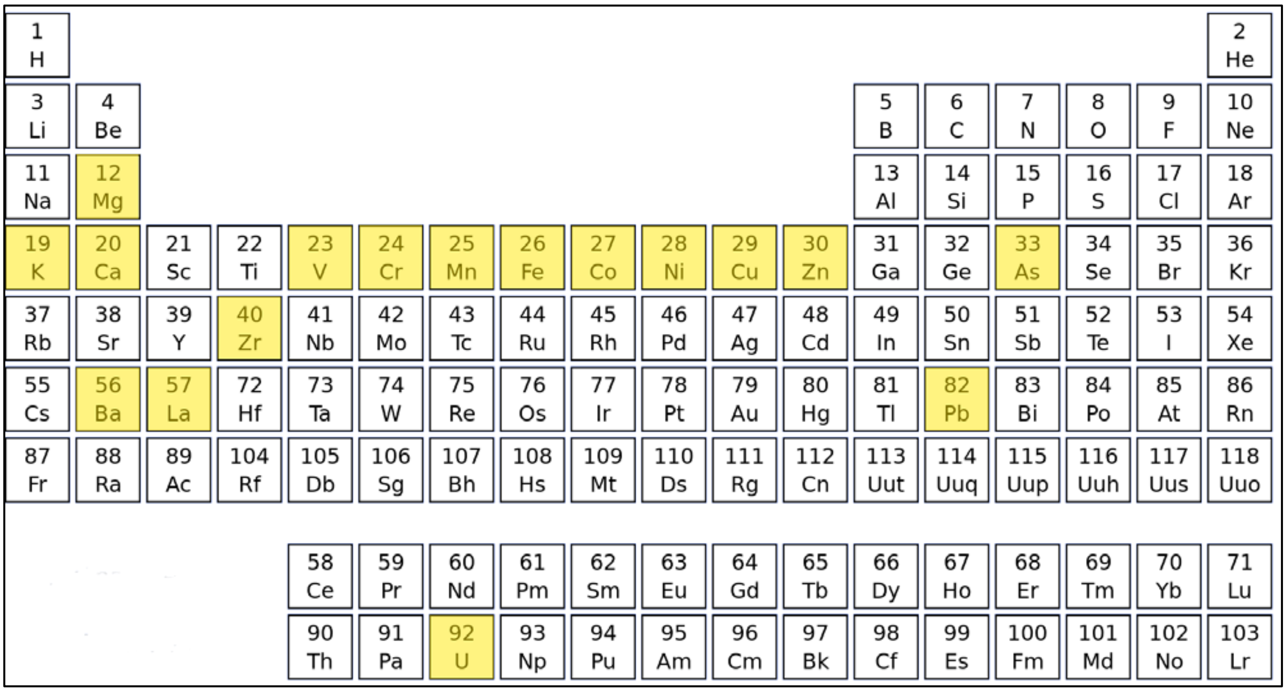
Introduction

Stream sediment largely comprises weathered fragments and mineral grains derived from the underlying bedrock and superficial deposits in the stream catchment area. As such, the chemical composition of the sediment typically reflects the nature of the underlying rocks. Stream sediment also acts as a sink for pollutants that may be attributed to human activity such as mining, heavy industry and agricultural practices. Therefore, stream sediment is a useful sample medium that provides a 'natural average' of material in a catchment that can be used to document the chemical quality of the surface environment (Johnson et al. 2008).

The geochemistry of stream sediments can provide invaluable insight into the distribution of different naturally occurring elements at the Earth's surface, as an aid to mineral resource management, environmental protection and geological/Earth-system process understanding (Plant 1983). Hence, many national geochemical surveys around the world collect and analyse stream sediment samples (Darnley et al. 1995). These include the British Geological Survey's Geochemical Baseline Survey (G-BASE) of Great Britain (Johnson et al. 2005) and the Geological Survey of Northern Ireland (GSNI) Tellus Geochemical Survey of Northern Ireland (Young and Donald 2013; Young et al. 2016).

The results of the G-BASE and TellusNI stream sediment chemical analyses are reported here as the Stream Sediment Geochemical Atlas of the UK. Geochemical maps and data are presented for 18 elements commonly occurring on the Earth's surface for which data were available across the UK landmass. These include arsenic (As), barium (Ba), calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), lanthanum (La), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), rubidium (Rb), uranium (U), vanadium (V), zinc (Zn) and zirconium (Zr) (Figure 1). Concentrations of Ca, Fe, Mg, Mn and K are presented as weight percent of oxides – CaO, Fe_2O_3, MgO, MnO and K_2O, whereas concentrations of the other elements are presented in mg/kg.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 1. The Periodic Table of the Elements. The 18 elements presented in this Atlas are highlighted. Each highlighted element symbol contains a link, which navigates to the section wherein geochemical maps and information are presented for that element. Source: Wikimedia Commons**.**

The history of the G-BASE and TellusNI projects

In 1968, the Institute of Geological Sciences (IGS) (now the British Geological Survey [BGS]) began a regional geochemical sampling programme in the northern Highlands of Scotland. This work was aimed at producing maps to show the distribution of trace elements in stream sediment for mineral resource management. Prior to this, earlier geochemical studies were mainly involved with uranium reconnaissance work, a programme supported by the UK Atomic Energy Authority (1967 – 1972). The establishment of a Geochemistry Division on 1st August 1967 must be seen as the step that initiated the regional geochemical mapping programme. Funded by the Department of Trade and Industry (DTI) in the early 1970s, the project was originally known as the Regional Geochemical Reconnaissance Programme (RGRP) and was closely associated with the work of the Mineral Reconnaissance Programme (MRP), also funded by the DTI. The earliest samples are from the Sutherland Atlas area, and were collected in the summer of 1968 as part of the ongoing uranium reconnaissance work. The first systematic sampling for regional geochemistry began in Orkney and Shetland in 1970. The work has progressed southwards from northern Scotland until completion in south-east England in 2013.

A further reorganisation of the IGS saw the creation of a Special Surveys Division in 1977, and the RGRP became a major project within the Metalliferous Minerals and Applied Geochemistry Unit. Work on the Orkney and Shetland geochemical atlases commenced in 1974 and the Regional Geochemical Atlas of Shetland became the first in the series to be published, in 1978. Between 1975 and 1990, the work continued to be funded by the DTI. After 1990 however, funding came from the Department of Education and Science and subsequently from the Office of Science and Technology. In more recent years, the project has been supported by the Department for Business, Energy and Industrial Strategy (BEIS) via the Natural Environment Research Council (NERC). The project was renamed the Geochemical Survey Programme (GSP) in 1988, and again in 1994 as the Geochemical Baseline Survey of the Environment (G-BASE). Few BGS projects have produced such a wealth of external peer reviewed publications, a fact that has established BGS's regional geochemical mapping expertise in high regard worldwide. Geochemists who have worked on this project have become key figures in the development of international geochemical projects and working groups. Many geological organisations around the world have adopted and adapted the G-BASE methodology for their own national geochemical surveys.

Samples of stream sediment were collected over the whole of Northern Ireland during two discrete time periods. BGS G-BASE staff collected 2908 samples from western Northern Ireland between 1994 and 1996, on behalf of the Department of Economic Development (NI) and the Department of Environment (NI). Sampling of the eastern counties was undertaken by the GSNI and the BGS G-BASE staff under the TellusNI project in 2005 and 2006, when a further 2966 stream sediment samples were collected on behalf of the Department of Enterprise, Trade and Investment (NI).

The methods used for sample collection in TellusNI followed the protocols set out by the G-BASE programme, which were also recommended as international standards for geochemical mapping (Darnley et al., 1995). Therefore, the geochemical data for both TellusNI and G-BASE conform to the standards set by the International Geological Correlation Programme (IGCP) 259 for the preparation of internationally compatible regional geochemical maps.

The regional geochemical atlases published by BGS, IGS and GSNI for the UK serve as definitive accounts of the stream sediment baseline geochemistry of each atlas area and document the methods and rationale employed throughout the development and re-organisation of the programme. Accordingly, the reader is directed to the regional geochemical atlases to explore these in more detail. Bibliographic information and details of the area covered by each atlas are presented in Figure 2 and Table 1; Figure 1 also contains hyperlinks to the BGS online publications portal from where the atlases can be accessed.

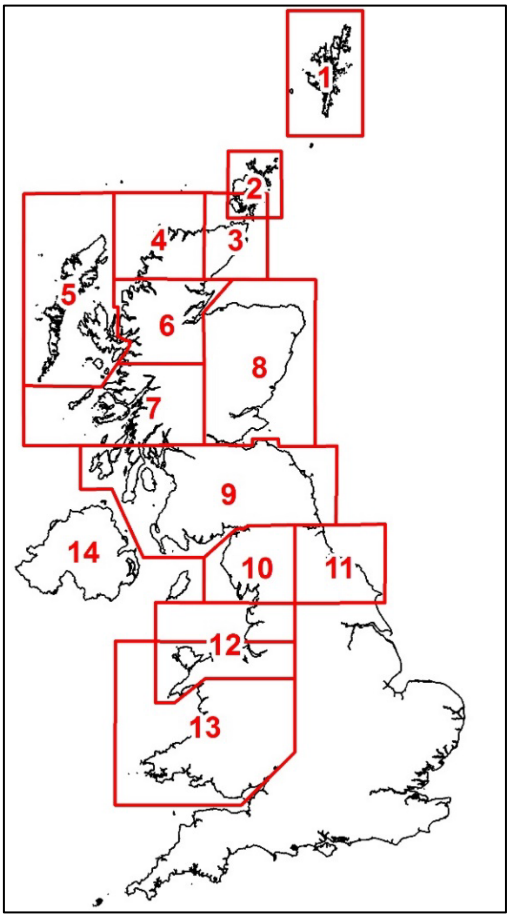


Figure 2. Areas of the UK covered by previously published Regional Geochemical Atlases. The numbers identifying each area correspond to the bibliographic information for each atlas in Table 1.

Table 1. Bibliographic information for previously published Regional Geochemical Atlases of the UK.

Number	Year	Publisher *	Author/ Editor	Title
1	1978b	IGS	IGS	Regional geochemical atlas: Shetland
2	1978a	IGS	IGS	Regional geochemical atlas: Orkney
3	1979	IGS	IGS	Regional geochemical atlas: south Orkney and Caithness
4	1982	IGS	IGS	Regional geochemical atlas: Sutherland
5	1983	IGS	IGS	Regional geochemical atlas: The Hebrides
6	1987	BGS	BGS	Regional geochemical atlas: Great Glen
7	1990	BGS	BGS	Regional geochemical atlas: Argyll
8	1992a	BGS	BGS	Regional geochemistry of the East Grampian area
9	1992b	BGS	BGS	Regional geochemistry of the Lake District and adjacent areas
10	1993	BGS	BGS	Regional geochemistry of Southern Scotland and part of Northern England
11	1996a	BGS	BGS	Regional geochemistry of north-east England
12	1997	BGS	BGS	Regional geochemistry of parts of north-west England and North Wales
13	2000	BGS	BGS	Regional geochemistry of Wales and part of west-central England: Stream sediment and soil
14	2013	GSNI	Young and Donald	A guide to the Tellus data

* IGS: Institute of Geological Sciences; BGS: British Geological Survey; GSNI: Geological Survey of Northern Ireland. The number in the first column corresponds to that used to identify the area covered by each atlas in Figure 2.

Sampling and sample preparation

Sampling was carried out annually from 1968 until 2013 (with the exception of 2001, due to restrictions imposed by foot and mouth disease), generally between the months of June to September when stream base-flow conditions prevailed. Samples were collected by teams of student ‘Voluntary Workers’, who were trained and supervised in the field by experienced full-time members of BGS staff.

Full details of the stream sediment sampling methodology can be found in the G-BASE Field Procedures Manual (Johnson 2005).

Samples of sediment were collected from the active channel of small first and second order streams at a sample density of approximately 1 every 2.5km^2.

During the period from 1968 – 1974, samples were wet sieved at site to a size of <2mm (Plant 1971). Approximately 2kg of <2mm material was collected from each sample site. The <2mm samples were dried at ~80^{o}C in drying cabinets before being sieved to a size fraction of <150µm. The fine fraction material was then ground in mechanical agate mortars until 95% of the material was finer than 100µm.

From 1975, the sampling procedure was adapted (Plant and Moore 1979) to accommodate sieving of the stream sediment at site to <150µm, using a system devised by B A Toms (Dept. of Chemistry, University of Birmingham) (Figure 3). After sieving the sediment to <150µm, the fine material was dried at a field laboratory at ~95^{o}C in drying cabinets (1975 – 1985). From 1986, the <150µm size fraction of stream sediment material was freeze dried at a field laboratory, following initial air drying at < 30 °C to avoid the volatilisation of mercury (Hg) and selenium (Se) at the field base. After drying, the <150µm material was disaggregated and a sub-sample ground in a planetary ball mill until 95% of the material was finer than 53µm. Splits were then taken for analysis.

Figure 3. Sieving a stream sediment sample at site.

Analysis

A variety of analytical methods have been utilised throughout the duration of the project. The number of reported analytes has also changed. Details of the different analytical methodologies can be found by referring to the appropriate volume(s) of the published BGS 1:250k Regional Geochemical Atlas Series (see Table 1). Table 2 lists the different methods of analysis and the corresponding number of analyses by each method, and the maps in Figure 4 outline the spatial distribution of samples analysed by each analytical method. Additional ICP-MS analysis of samples from the earliest atlas areas was completed in 2002, to supplement the data with an expanded range of analytes.

The average Lower Limit of Detection (LLD) for each element was calculated and is provided in Table 3. For direct-reading optical emission spectrometry (DR-OES) and x-ray fluorescence spectrometry (XRF), 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 detection limit.

Table 2. Methods of stream sediment analysis and number of analyses by method.

Element	DNA	AAS	ICP-MS	DR-OES	XRF	TOTAL
Arsenic (As)		23011	10525		54276	87812
Barium (Ba)				65156	45533	110689
Calcium (Ca)			2902	61169	45524	109595
Chromium (Cr)				65184	45442	110626
Cobalt (Co)				65143	45533	110676
Copper (Cu)		3851		61300	45539	110690
Iron (Fe)				65035	45545	110580
Lanthanum (La)			2985	61173	45517	109675
Lead (Pb)		3853		61387	45554	110794
Magnesium (Mg)			2913	61265	45429	109607
Manganese (Mn)				65146	45540	110686
Nickel (Ni)				65162	45539	110701
Potassium (K)			2928	61265	45429	109622
Rubidium (Rb)			2898	61173	45521	109592
Uranium (U)	64703				45478	110181
Vanadium (V)				64932	45542	110474
Zinc (Zn)		3854		61331	45552	110737
Zirconium (Zr)				65106	45536	110642

DNA – Delayed neutron activation

AAS – Atomic absorption spectrophotometry

ICP-MS – Inductively coupled plasma mass spectrometry

DR-OES – Direct-reading optical emission spectroscopy

XRF – X-ray fluorescence

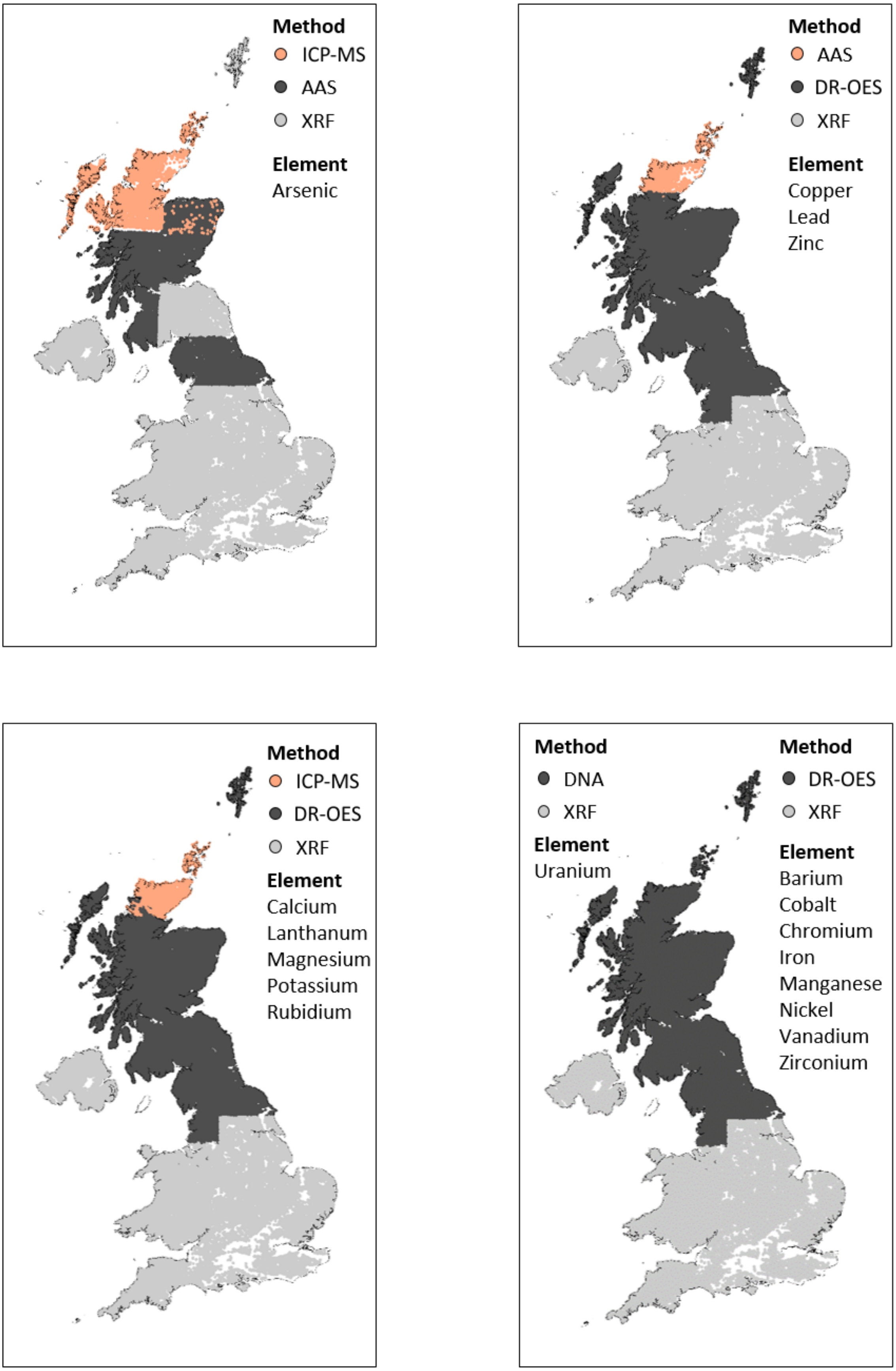


Figure 4. Maps showing the spatial distribution of the analytical methods utilised and corresponding elements analysed.

Table 3. Average Lower Limits of Detection (LLD) for the different analytical methods utilised.

Element	Units	DNA	AAS	ICP-MS	DR-OES	XRF
Arsenic (As)	mg/kg		5	1.0	n/a	0.9
Barium (Ba)	wt %				32	1
Calcium (CaO)	wt %			0.01	0.2	0.04
Chromium (Cr)	mg/kg				5	3
Cobalt (Co)	mg/kg				2	1.5
Copper (Cu)	mg/kg		5		3	1.3
Iron (Fe_2O_3)	wt %				0.2	0.01
Lanthanum (La)	mg/kg			1	15	1
Lead (Pb)	mg/kg		10		10	1.3
Magnesium (MgO)	wt %			0.01	0.2	0.18
Manganese (MnO)	wt %				0.01	0.004
Nickel (Ni)	mg/kg				5	1.3
Potassium (K_2O)	wt %			0.01	0.1	0.01
Rubidium (Rb)	mg/kg			2	1	1
Uranium (U)	mg/kg	0.2				0.5
Vanadium (V)	mg/kg				9	3
Zinc (Zn)	mg/kg		10		10	1.3
Zirconium (Zr)	mg/kg				30	1

With the exception of ICP-MS, which analyses a liquid solution of the sample following fusion with a lithium borate flux and acid digestion, therefore measuring what are considered to be ‘pseudo-total’ element concentrations, all the analytical methods utilised by the GBASE and TELLUS projects analyse the solid sample material directly; hence, they report ‘total’ element concentrations. In order to incorporate ICP-MS data for As, Ca, K, La, Mg, Mn and Rb, 242 samples of a selection of secondary reference materials (SRM) routinely analysed within batches of GBASE samples were also submitted along with the field samples for ICP-MS analysis. For As, a simple linear regression based on the analysis of the incorporated SRMs was used to calculate a ‘conditioning’ factor to align the ICP-MS data with that of the other analytical methods. For the remaining five elements with data generated by ICP-MS analysis, conditioning factors based on comparative percentile distributions (5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 95%) over like lithologies were applied to align the data with the other analytical methods.

Quality control

Strict quality control procedures have been in place throughout all stages of the national geochemical mapping projects; from sample site selection, sample collection, sample preparation and analysis to the continual monitoring of the analytical data generated by the laboratories.

Samplers worked in pairs, but were interchanged daily to reduce the likelihood of sampling bias being introduced by the use of individual procedures. As far as possible, samples were collected upstream of any potential source of contamination, such as habitation, industrial activity or road/track crossings. Systematic error in field sampling and analysis was monitored using a method of randomised sample site numbers (Plant 1973).

A site duplicate sample was routinely collected within each batch of 100 field samples in order to apportion different components of associated variance. The duplicate samples were subsequently split in the laboratory to yield four replicates for chemical analysis. A random nested model of analysis of variance (ANOVA) was used to calculate between site (representing the natural distribution of elements in stream sediments), between sample (representing the within-site variability as well as any variability introduced as a result of sample collection) and residual (representing any inhomogeneities introduced during sample preparation, sub-sampling and analysis) components of variance (Table 4). The ANOVA was generated using up to 483 replicate sets; 271 sets analysed by DR-OES and 212 sets analysed by XRF. Sub-sample splits were not routinely analysed by AAS, ICP-MS and DNA.

The results of the ANOVA demonstrate the validity of the sample collection, sample preparation and analysis methods with over 80% of the variance attributable to genuine spatial differences between sites.

Table 4. Analysis of variance (ANOVA) of UK stream sediment sample replicates.

Element	Between Site %	Between Sample %	Residual %
Arsenic (As)	91.61	5.52	2.87
Barium (Ba)	92.58	3.53	3.89
Calcium (CaO)	96.24	2.41	1.35
Chromium (Cr)	91.70	4.12	4.18
Cobalt (Co)	90.25	6.91	2.84
Copper (Cu)	86.02	5.76	8.21
Iron (Fe_2O_3)	82.32	9.79	7.89
Lanthanum (La)	91.63	4.59	3.78
Lead (Pb)	91.35	4.57	4.08
Magnesium (MgO)	92.50	2.86	4.65
Manganese (MnO)	91.76	6.86	1.39
Nickel (Ni)	89.26	6.37	4.38
Potassium (K_2O)	92.10	3.78	4.12
Rubidium (Rb)	92.54	4.79	2.66
Uranium (U)	81.91	2.62	15.46
Vanadium (V)	89.24	4.90	5.85
Zinc (Zn)	89.42	4.80	5.78
Zirconium (Zr)	87.19	7.23	5.59

Long-term analytical drift between batches of samples was monitored by the analyses of a series of secondary reference materials (SRM), representing ranges of concentrations for each element. The SRMs included several bulk stream sediment samples collected over representative rock types. At least two SRMs were analysed at random within each batch of 100 field samples. Accuracy of the data was assured by the analysis of a number of certified reference materials (CRM) within larger batches (approx. 600) of field samples (Tables 5-8). With the change of analytical methodology to XRF, four different CRMs were routinely analysed before and after every batch of 500 field samples, namely:

1	GSD-7	Bulk stream sediment	National Research Centre for CRMs, China
2	GSS-1	Bulk soil	National Research Centre for CRMs, China
3	LKSD-1	Bulk lake sediment	CANMET, Canada
4	LKSD-4	Bulk lake sediment	CANMET, Canada

The CRM results demonstrate good accuracy of the analytical methods.

Time versus concentration plots for each of these reference samples were prepared. Tolerance limits arbitrarily set at the mean ± 2σ were used to assess data quality. Simple arithmetic correlations were applied to normalise the data to correct for systematic drift (Lister and Johnson, 2005).

Table 5. Results of repeated XRF analyses of CRM GSD-7.

GSD-7 (n=69)	Units	Accredited Value (± Std Deviation)	Minimum	Maximum	Mean	Std Deviation
Arsenic (As)	mg/kg	84 (± 9)	80.7	85.7	83.3	1.1
Barium (Ba)	mg/kg	720 (± 20)	714	762	741.6	11.42
Calcium (CaO)	wt %	1.67 (± 0.07)	1.56	1.86	1.63	0.04
Chromium (Cr)	mg/kg	122 (± 10)	113.9	131.8	122.2	5.02
Cobalt (Co)	mg/kg	21 (± 3)	19	23.1	21.1	0.97
Copper (Cu)	mg/kg	38 (± 2)	34.3	39	36.7	0.83
Iron (Fe_2O_3)	wt %	6.51 (± 0.13)	6.4	6.74	6.53	0.08
Lanthanum (La)	mg/kg	45 (± 6)	43	47	45.1	0.97
Lead (Pb)	mg/kg	350 (± 26)	349	369.3	359.9	4.58
Magnesium (MgO)	wt %	3.08 (± 0.13)	4	4.9	4.43	0.26
Manganese (MnO)	wt %	0.089 (± 0.006)	0.089	0.099	0.093	0.002
Nickel (Ni)	mg/kg	53 (± 5)	52.5	57.7	55.1	1.22
Potassium (K_2O)	wt %	3.54 (± 0.12)	3.51	3.8	3.64	0.08
Rubidium (Rb)	mg/kg	147 (± 11)	142	149.1	146.4	1.77
Uranium (U)	mg/kg	3.5 (± 0.5)	2.3	4	3	0.31
Vanadium (V)	mg/kg	96 (± 9)	85.5	96.2	92.2	2.41
Zinc (Zn)	mg/kg	238 (± 19)	239.8	253.5	245.8	2.77
Zirconium (Zr)	mg/kg	162 (± 13)	151.1	161.1	155.3	1.92

The accredited value and accompanying standard deviation are those quoted in the CRM's certificate, and are derived from measurements by the certifying labs. The minimum, maximum, mean and standard deviation given in the following columns correspond to BGS repeat analyses of the CRM.

Table 6. Results of repeated XRF analyses of CRM GSS-1.

GSS-1 (n=69)	**Units**	**Accredited Value (± Std Deviation)**	**Minimum**	**Maximum**	**Mean**	**Std Deviation**
Arsenic (As)	mg/kg	33.5 (± 1.7)	33.9	37	35.8	0.66
Barium (Ba)	mg/kg	590 (± 15)	563	599	575.6	11.31
Calcium (CaO)	wt %	1.72 (± 0.03)	1.62	1.79	1.74	0.04
Chromium (Cr)	mg/kg	62 (± 2)	55.3	114.8	63.3	10.7
Cobalt (Co)	mg/kg	14.2 (± 0.4)	12.8	16.1	14.3	0.83
Copper (Cu)	mg/kg	21 (± 0.6)	18.7	21	19.8	0.63
Iron (Fe_2O_3)	wt %	5.19 (± 0.4)	5.08	5.43	5.25	0.07
Lanthanum (La)	mg/kg	34 (± 1)	31	35	32.7	0.92
Lead (Pb)	mg/kg	98 (± 3)	94.1	100.4	97.1	1.35
Magnesium (MgO)	wt %	1.81 (± 0.04)	2.1	2.4	2.23	0.11
Manganese (MnO)	wt %	0.227 (± 0.003)	0.226	0.251	0.239	0.006
Nickel (Ni)	mg/kg	20.4 (± 0.6)	19.1	22.8	20.9	0.68
Potassium (K_2O)	wt %	2.59 (± 0.02)	2.44	2.67	2.56	0.06
Rubidium (Rb)	mg/kg	140 (± 3)	135.7	142.3	138.4	1.51
Uranium (U)	mg/kg	3.3 (± 0.3)	2.7	4.2	3.5	0.37
Vanadium (V)	mg/kg	86 (± 2)	73.9	84.7	81.1	2.29
Zinc (Zn)	mg/kg	680 (± 11)	653.7	687.5	673.5	7.14
Zirconium (Zr)	mg/kg	245 (± 6)	243.3	253.7	248.6	2.2

The accredited value and accompanying standard deviation are those quoted in the CRM’s certificate, and are derived from measurements by the certifying labs. The minimum, maximum, mean and standard deviation given in the following columns correspond to BGS repeat analyses of the CRM.

Table 7. Results of repeated XRF analyses of CRM LKSD-1.

LKSD-1 (n=73)	Units	Provisional Value	Minimum	Maximum	Mean	Std Deviation
Arsenic (As)	mg/kg	40	33.6	37.1	35.1	0.79
Barium (Ba)	mg/kg	430	381	402	393.3	4.01
Calcium (CaO)	wt %	10.8	11.2	13.31	12.24	0.49
Chromium (Cr)	mg/kg	31	22.4	44.6	30.2	6.11
Cobalt (Co)	mg/kg	11	9.5	12.8	11.3	0.86
Copper (Cu)	mg/kg	44	38.2	44.7	40.2	1.16
Iron (Fe_2O_3)	wt %	4.1	3.85	4.16	4	0.06
Lanthanum (La)	mg/kg	16	13	15	14.1	0.59
Lead (Pb)	mg/kg	82	76.5	86.1	81.7	2.52
Magnesium (MgO)	wt %	1.7	1.5	1.9	1.76	0.1
Manganese (MnO)	wt %	0.1	0.087	0.095	0.092	0.002
Nickel (Ni)	mg/kg	16	14.4	18.3	15.9	0.83
Potassium (K_2O)	wt %	1.1	0.92	1.08	1.02	0.04
Rubidium (Rb)	mg/kg	24	21.3	24.1	22.6	0.53
Uranium (U)	mg/kg	9.7	9.1	10.8	8.4	0.35
Vanadium (V)	mg/kg	50	44.6	51.9	47.4	1.43
Zinc (Zn)	mg/kg	331	311.2	327.2	320.2	3.48
Zirconium (Zr)	mg/kg	134	119.4	139.4	130.9	4.23

The provisional value is that quoted in the CRM’s certificate, and is derived from measurements by the certifying labs. The minimum, maximum, mean and standard deviation given in the following columns correspond to BGS repeat analyses of the CRM.

Table 8. Results of repeated XRF analyses of CRM LKSD-4.

LKSD-4 (n=73)	Units	Provisional Value	Minimum	Maximum	Mean	Std Deviation
Arsenic (As)	mg/kg	16	14.9	18.1	16.6	0.59
Barium (Ba)	mg/kg	330	251	277	265	6.33
Calcium (CaO)	wt %	1.8	1.67	1.9	1.79	0.06
Chromium (Cr)	mg/kg	33	25.3	32.1	30.1	1.37
Cobalt (Co)	mg/kg	11	10.3	14.2	11.5	0.72
Copper (Cu)	mg/kg	31	27.1	31.2	29.3	0.95
Iron (Fe_2O_3)	wt %	4.1	3.98	4.31	4.15	0.09
Lanthanum (La)	mg/kg	26	19	23	21.1	0.83
Lead (Pb)	mg/kg	91	91.5	98.8	95.3	1.71
Magnesium (MgO)	wt %	0.9	0.9	1.1	1.02	0.06
Manganese (MnO)	wt %	0.1	0.063	0.071	0.067	0.002
Nickel (Ni)	mg/kg	31	31.6	35.8	33.4	0.94
Potassium (K_2O)	wt %	0.8	0.7	0.8	0.75	0.02
Rubidium (Rb)	mg/kg	28	23.3	26.4	24.7	0.67
Uranium (U)	mg/kg	31	29.5	32.2	26.3	0.73
Vanadium (V)	mg/kg	49	41	47.6	45	1.29
Zinc (Zn)	mg/kg	194	185.4	199.8	191.7	3.85
Zirconium (Zr)	mg/kg	105	94.1	102.8	98.7	2.47

The provisional value is that quoted in the CRM's certificate, and is derived from measurements by the certifying labs. The minimum, maximum, mean and standard deviation given in the following columns correspond to BGS repeat analyses of the CRM.

Data presentation

The geochemical data for each of the 18 elements included in this atlas are presented by means of: (i) a table of statistics; (ii) a histogram; (iii) a series of boxplots; and (iv) single element geochemical maps, which appear on each element description page in the Stream Sediment Geochemistry section of this atlas. All of these components have been produced using the R programming language and free software environment for statistical computing and graphics (R Core Team 2014).

The tables of statistics compare the data distribution of each element to median element concentrations in European stream sediments from the Forum of European Geological Surveys (FOREGS) Geochemical Atlas of Europe (De Vos and Tarvainen 2006).

To create the boxplots, each stream sediment sample was categorised according to the underlying bedrock geology using the geological classification scheme shown in Table 10. This allows the variation of the element concentrations in stream sediment over different parent material lithologies to be readily compared. The boxes show the 25th, 50th and 75th percentiles, and the whiskers the lower (Q1 − 1.5 × IQR) and upper limits (Q3 + 1.5 × IQR) of the data distribution; Q1 (1st quartile) and Q3 (3rd quartile) correspond to the 25th and the 75th percentile respectively, and IQR is the inter-quartile range. Samples not included between the whiskers are individually represented with a dot as outliers, and the box includes a notch around the median, which is a guide as to whether the difference between the medians in each category (i.e. between each geological unit) is statistically significant (if so, the respective notches do not overlap).

The boxplots, tables of statistics and histograms were generated using a purpose-built R script including basic R functions and graphics (R Core Team 2014) and the *StatDA* R package (Filzmoser, 2015).

The single element geochemical maps display the spatial variation in element concentrations in stream sediments across the United Kingdom. To produce these maps, interpolation to convert the original stream sediment geochemistry point sample data into a continuous surface covering the whole area of the UK was performed using a set of purpose-built R scripts that mainly use functions provided in the *sp* (Pebesma and Bivand, 2005; Bivand et al., 2013) and *gstat* (Pebesma, 2004; Graler et al, 2016) R packages.

To produce the continuous surface, the map area was split into a series of grid cells, with a cell size representing 500 x 500 m on the ground. Interpolation to estimate the predicted mean concentration of the element in stream sediments within each grid cell was then derived using ordinary kriging of the nearest 9 samples. Ordinary kriging is a geostatistical method that attempts to provide optimal unbiased predictions according to the spatial autocorrelation of the input data. For these maps, the input data are the point-sampled element concentrations.

Ordinary kriging makes use of a variogram (a model of the spatial autocorrelation within the data) in order to optimise the weights given to surrounding sample points when interpolating concentrations to new locations, i.e. the cell centres of the output grid. As an example, Figure 5 shows the variogram for potassium in UK stream sediments. It shows that the semi-variance (a measure of the difference between values) increases with the distance between sample sites.

While semi-variance is at its lowest at zero distance (i.e. neighbouring samples are more similar than distant samples), semi-variance is still non-zero. This difference in values even at the finest scales is known as the nugget effect. For the UK stream sediment dataset this nugget effect is handled as measurement error, in order to produce a non-exact interpolation (in which the surface does not pass precisely through the data points) to prevent overfitting to noise/outliers.

The location of the nearest 9 samples are within the spatial auto-correlation range, and their weights determined after fitting a *Matern* variogram model to the experimental variogram of the element being mapped (Figure 5, Table 9). A different set of model parameters were applied to each element; these are documented in Table 9.

Spatial anisotropy of the data was not taken into account during variogram modelling. By using a geostatistical interpolation approach, the final output map is expected to provide an optimal unbiased estimation on the nodes of the grid.

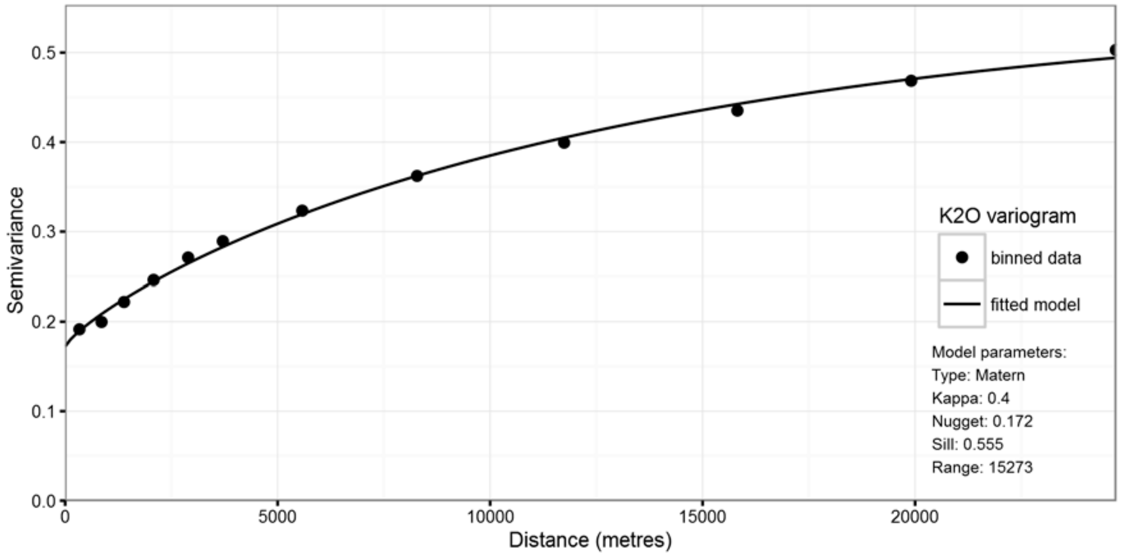


Figure 5. Example variogram of K_2O concentrations in UK stream sediments.

For the purposes of creating the grids, data from Northern Ireland have been re-projected into the British National Grid co-ordinate system. Baseline stream sediment data are not presented for the area within the boundary of the Greater London Authority as no surface drainage sampling was carried out in this area. The surface soil geochemistry of London is documented by the British Geological Survey's London Earth Project (BGS 2011) and also shown in the London Region Atlas of Topsoil Geochemistry (Ferreira et al., 2017).

Two types of single element geochemical map for each element were prepared, one which uses a colour classified image and the other which uses a histogram equalised (continuous scale) image scheme. Each type of map provides a different way to visualise the data, but both are based on the same interpolated data surface. For the colour classified (percentile classified) maps, percentiles of the real data distribution for each element are used to derive the classes applied to the interpolated data surface, as shown in the legend of each map. The histogram equalised maps apply a continuously variable monochrome colour scheme, whereby colour intensity is scaled according to population density across the entire data distribution of the values assigned to all cells within the interpolated surface (this is displayed in the legend using a coloured histogram). Therefore, the maximum value shown in the legend of the continuous scale map refers to that of the interpolated data surface and not to the maximum value of the real point data. For the purpose of generating interpolated geochemical images, the lowest quoted LLD in Table 3 has been applied in order to minimise the number of sub-detection data values incorporated in each individual element map.

In the digital version of this atlas, the reader can toggle between the percentile classified and continuous scale maps by means of the clickable buttons appearing below the maps.

Table 9. Ordinary kriging model parameters applied to map interpolation

Element/analyte	Units	Model Type	Kappa	Nugget	Sill	Range
Arsenic (As)	mg/kg	Matern	0.05	6350	8704	60577
Barium (Ba)	mg/kg	Matern	0.05	471157	879293	238239
Calcium (CaO)	wt %	Matern	0.15	0.267	4.68	33874
Chromium (Cr)	mg/kg	Matern	1	12467	20808	1901
Cobalt (Co)	mg/kg	Matern	1	607	791	2566
Copper (Cu)	mg/kg	Matern	1	5007	5662	3770
Iron (Fe_2O_3)	wt %	Matern	0.5	5.33	8.25	5770
Lanthanum (La)	mg/kg	Matern	1	189	309	3816
Lead (Pb)	mg/kg	Matern	0.2	57649	326166	4643
Magnesium (MgO)	wt %	Matern	0.15	0.215	1.23	9880
Manganese (MnO)	wt %	Matern	1	0.726	0.913	1533
Nickel (Ni)	mg/kg	Matern	0.5	2154	2154	27382
Potassium (K_2O)	wt %	Matern	0.4	0.172	0.555	15280
Rubidium (Rb)	mg/kg	Matern	0.5	293	1153	14521
Uranium (U)	mg/kg	Matern	1	175	306	1323
Vanadium (V)	mg/kg	Matern	0.4	1161	2750	12742
Zinc (Zn)	mg/kg	Matern	0.25	13304	52545	4723
Zirconium (Zr)	mg/kg	Matern	0.2	52286	135833	35529

Reference maps

Variations in baseline stream sediment element concentrations are influenced and controlled by a combination of the underlying bedrock geology, superficial deposits, mineralisation, anthropogenic activity (particularly mining and metalworking in the case of metallic elements) and surficial environmental factors (especially stream water acidity; i.e. pH). To better demonstrate the influence of these factors on stream sediment geochemistry, and to aid descriptions in the following section, a series of five reference maps are provided in this section.

Topographic map

A topographic map of the UK, showing places mentioned in the text is presented in Figure 6. The majority of upland areas in the UK are confined to Scotland, Northern Ireland, Wales and northern England, whereas much of eastern England and central-southern England are lower lying.

Figure 6. Topographic map of the UK. Selected towns, cities and localities referred to in this atlas are labelled. The inset map shows the extent of each of the UK's four constituent countries. Map data sourced from ESRI ArcGIS online resources under licence agreement E204CW 10/12/2018; source: US National Park Service, 'World physical map'. Contains Ordnance Survey data licence number [100021290 EUL]

Bedrock geology

Bedrock geology has a primary influence on the geochemistry of stream sediment. For the purposes of this interactive atlas, the bedrock geology of the UK has been simplified into major units based on the 1: 625 000 BGS DiGMap® dataset (Figure 7).

These major units are lithologically heterogeneous and consist of several significant lithostratigraphic divisions; some of which display a distinct geochemical pattern in the element distribution maps. Further detail on some significant lithostratigraphic divisions that are incorporated within each major unit is provided in Table 10. The 1:625 000 geology of the UK is fully described by Stone (2008) for Scotland, Northern Ireland and Northern England and Jackson (2008) for the rest of England and Wales. The reader is referred to these documents and the BGS Lexicon of named rock units (BGS 2018a) and digital geological maps (BGS 2018b) for further information on the geology and spatial extent of each of the UK's constituent bedrock units.

In summary, the bedrock geology of the UK is varied and complex. It ranges in age from the Archean to the Quaternary. The oldest rocks of Archean to Neoproterozoic age are dominantly found in the north and west, in Scotland, Northern Ireland and Wales and comprise crystalline metamorphic assemblages of gneiss, psammite, pelite, quartzite and schist. These are overlain by a varied sequence of sedimentary rocks, that broadly young towards the south-east of England. Into both these sequences, igneous intrusions and volcanic extrusive rocks of various ages have been emplaced.

Sedimentary Rocks

Neoproterozoic and Cambrian sediments are characterised by sandstone, quartzite and limestone sequences in the north-west of Scotland and by volcaniclastic conglomerates, mudstones and slates in north Wales. Ordovician sediments in central and southern Scotland, Northern Ireland, the Lake District and Wales (see Figure 6 for locations) comprise turbiditic sandstone, conglomerate, marine limestone and mudstone sequences, often interleaved with volcaniclastic deposits. The Silurian sediments of Northern Ireland, Wales, the Lake District and southern Scotland (see Figure 6 for locations) represent extensive sequences of conglomerate, wacke sandstone, siltstone, limestone and mudstone, much of which was laid down in a marine turbiditic setting.

By contrast, sedimentary rocks of Devonian age largely comprise fluvial, aeolian and lacustrine sandstones, mudstones and conglomerates, with the exception of south-west England, where there is transgression to a fully marine facies. Carboniferous sediments underlie large areas of central Scotland, Northern Ireland, north and central England, south-west England and Wales. These comprise shallow marine, fluvial and deltaic cyclical sequences of sandstone, limestone, mudstone, shale and coal deposits. Aeolian and fluvial sandstones, conglomerates and mudstones deposited in an arid environment dominate the Permian and Triassic sedimentary sequences that are limited in outcrop in Scotland and Northern Ireland, but that underlie extensive areas of England and the Welsh borders.

A marine transgression marks the end of the Triassic period, resulting in extensive sequences of limestone, mudstone, clay, siltstone, sandstone and ironstone, largely laid down in sub-tropical shallow seas during the Jurassic period over much of central, southern and eastern England, with sporadic outcrops in Wales, Scotland and Northern Ireland. During the Cretaceous period, the Wealden Group comprises fluvial and lagoonal sandstones and mudstones before a return to shallow marine deposition of sandstone, mudstone and clay strata of the Greensand and Gault Formations and extensive deposition of chalk in the upper Cretaceous period. The outcrop of Cretaceous strata are limited in their spatial extent in Northern Ireland and Scotland, but underlie large areas of eastern and southern England. Similarly, Paleogene, Neogene and Quaternary sediments comprising sandy limestone, sand and clay deposits of marine, estuarine and deltaic origin with abundant fossils and flints are largely confined to Southern England, but minor outcrops of lacustrine and fluvial clays and sands are present in Northern Ireland and the north-east of Scotland.

Igneous Rocks

Some of the oldest igneous rocks in the UK are located on the islands of north-west Scotland, where Paleoproterozoic granites and pegmatites were intruded into the Archean gneisses of the Outer Hebrides (see Figure 6 for locations). Minor outcrops of Neoproterozoic predominately felsic intrusions are found in north and south-west Wales as well as volcanic rocks comprising sequences of mafic, andesitic and felsic lavas and tuffs. During the Caledonian Orogeny (early Ordovician to early Devonian), mafic, ultramafic and largely granitic igneous bodies were emplaced in Northern Ireland, northern England and in Scotland, largely to the north of the Highland Boundary Fault and to the south of the Southern Uplands Fault. This period and beyond to the late Devonian was characterised by extensive volcanism in north Wales (mafic lava and tuffs), south-west Wales (andesitic lavas), south-west England (lavas, tuffs and ophiolite), the Lake District (basaltic, andesitic, rhyolitic lavas and pyroclastic rocks), western mainland Scotland (basalt, andesite, trachyte, rhyolite and volcanoclastic rocks), the Midland Valley of Scotland (largely mafic lavas with andesite) and the border region between Scotland and England (andesitic to trachytic lavas) (see Figure 6 and Figure 7 for locations). Similarly, volcanic activity during the Carboniferous era resulted in the emplacement of granites in south-west England and of largely mafic intrusions in northern England, as well as extensive areas of predominately-basaltic lavas in the Midland Valley of Scotland. By contrast, very minor outcrops of basaltic lava are reported in south-west Scotland during the Permian era. The most recent significant period of volcanic activity in the UK was during the Cretaceous period, associated with the opening of the Atlantic Ocean. This resulted in extensive areas of largely mafic lava in Northern Ireland and the west coast of Scotland, including those of the islands of Mull and Skye. The central volcanic complexes associated with this volcanism range in composition from gabbroic (e.g. Skye) to granite (e.g. islands of Arran and Mull) (see Figure 6 for locations).

Table 10. Index of lithostratigraphic units (groups and formations) included in major geological units

Sedimentary Rocks			
Major Geological Units		**Constituent Lithostratigraphic Units**	
		Code	**Name**
Neogene and Quaternary	Undifferentiated	NEOQ	Neogene and Quaternary Rocks (Undifferentiated)
Palaeogene	Undifferentiated	SOLT	Solent Group
		LNG	Lough Neagh Clays Group
		THAM	Thames Group
		BRBA	Bracklesham Group and Barton Group (Undifferentiated)
		TAB	Thanet Formation
		LMBE	Lambeth Group
Cretaceous	Chalk Group	WHCK	White Chalk Subgroup
		GYCK	Grey Chalk Subgroup
	Gault Formation and Upper Greensand Formation	GUGS	Gault Formation and Upper Greensand Formation (Undifferentiated)
		LGS	Lower Greensand Group
	Wealden Group	W	Wealden Group
Jurassic	Upper	PB	Purbeck Group
		PL	Portland Group
		WWAK	West Walton Formation, Ampthill Clay Formation and Kimmeridge Clay Formation (Undifferentiated)
		CR	Corallian Group
		KLOX	Kellaways Formation and Oxford Clay Formation (Undifferentiated)
	Middle	RAG	Ravenscar Group
		GOG	Great Oolite Group
		INO	Inferior Oolite Group
	Lower (Lias)	LI	Lias Group
Permian and Triassic	Undifferentiated	RBAY	Red Bay Formation
		NRS	New Red Sandstone Supergroup
		SSG	Sherwood Sandstone Group
		ZG	Zechstein Group
		APY	Appleby Group
		BELF	Belfast Group
		ENLE	Enler Group
		STEW	Stewartry Group
		MMG	Mercia Mudstone Group
Carboniferous	Undifferentiated	SLI	Slievebane Group
		BHCR	Bowland High Group and Craven Group (Undifferentiated)
		CKN	Clackmannan Group
		HOWY	Holsworthy Group
		TEVY	Teign Valley Group
		LEG	Leitrim Group
		KILS	Kilskeery Group
		ARMA	Armagh Group
		SYG	Strathclyde Group

Simplified Geological Units		Constituent Lithostratigraphic Units	
		Code	**Name**
Carboniferous	Undifferentiated	TYRO	Tyrone Group
		INV	Inverclyde Group
		BDR	Border Group
		HOLY	Holywood Group
		OWSA	Owenkillew Sandstone Group
		OMSG	Omagh Sandstone Group
		ROEV	Roe Valley Group
		MG	Millstone Grit Group
		WAWK	Warwickshire Group
		YORE	Yoredale Group
	Coal Measures Groups	PUCM	Pennine Upper Coal Measures Formation
		PCM	Pennine Coal Measures Group
		PSMCM	Pennine Middle Coal Measures Formation and South Wales Middle Coal Measures Formation (Undifferentiated)
		PSLCM	Pennine Lower Coal Measures Formation and South Wales Lower Coal Measures Formation (Undifferentiated)
		SWUCM	South Wales Upper Coal Measures Formation
		CM	Coal Measures Group [Northern Ireland]
		CMSC	Scottish Coal Measures Group
Devonian	Undifferentiated	SHG	Stonehaven Group
		UORS	Upper Old Red Sandstone
		SAG	Stratheden Group
		FIN	Fintona Group
		SHAN	Shanmullagh Formation
		MOR	Middle Old Red Sandstone (Undifferentiated)
		LORS	Lower Old Red Sandstone
		SEG	Strathmore Group
		CSSL	Cross Slieve Group
		ATGK	Arbuthnott-Garvock Group
		LNK	Lanark Group
		REST	Reston Group
		ORS	Old Red Sandstone Supergroup
		DRCR	Dunnottar-Crawton Group
Silurian	Silurian rocks (undifferentiated)	SILU	Silurian Rocks (Undifferentiated)
	Pridoli and Ludlow	PRID	Pridoli Rocks (Undifferentiated)
		LUDL	Ludlow Rocks (Undifferentiated)
	Wenlock and Llandovery	WEN	Wenlock Rocks (Undifferentiated)
		HWK	Hawick Group
		RCN	Riccarton Group
		GALA	Gala Group
		LDVY	Llandovery Rocks (Undifferentiated)
Ordovician	Undifferentiated	SHGN	Shinnel Formation and Glenlee Formation (Undifferentiated)
		ASHL	Ashgill Rocks (Undifferentiated)
		LHG	Leadhills Supergroup

Simplified Geological Units		**Constituent Lithostratigraphic Units**	
		Code	**Name**
Ordovician	Undifferentiated	PPGW	Portpatrick Formation and Glenwhargen Formation (Undifferentiated)
		KKF	Kirkcolm Formation
		TAP	Tappins Group
		CARA	Caradoc Rocks (Undifferentiated)
		BKGA	Blackcraig Formation and Galdenoch Formation (Undifferentiated)
		LLVN	Llanvirn Rocks (Undifferentiated)
		ARNG	Arenig Rocks (Undifferentiated)
		TREM	Tremadoc Rocks (Undifferentiated)
Neoproterozoic and Cambrian	Undifferentiated	UC	Upper Cambrian, Including Tremadoc
		MC	Middle Cambrian
		LRC	Lower Cambrian Rocks (Undifferentiated)
		ARDV	Ardvreck Group
		DNG	Durness Group
		TC	Torridon Group
		TB	Sleat Group
		TA	Stoer Group
Neoproterozoic and Cambrian	Undifferentiated	MSC	Strathy Complex
		UMAZ	Unnamed Metamorphic Rocks, Neoproterozoic
		UC	Upper Cambrian, Including Tremadoc
		UMSAZ	Unnamed Metasedimentary Rocks, Neoproterozoic
Metamorphic rocks			
Neoproterozoic and Cambrian	Southern Highland Group and Trossachs Group (Dalradian)	HBX	Highland Border Complex
		SOHI	Southern Highland Group
	Appin Group and Argyll Group (Dalradian)	APP	Appin Group
		ARGY	Argyll Group
	Grampian Group (Dalradian)	GRAM	Grampian Group
	Moine and Badenoch Supergroups	LEIL	Loch Eil Group
		MORR	Morar Group
		GLEN	Glenfinnan Group
		M	Moine Supergroup
Archean and early Proterozoic	Undifferentiated	L	Lewisian Complex
		LMR	Loch Maree Group
		QYFH	Queyfirth Group
Igneous Rocks			
Archean to Palaeogene	Felsic igneous intrusions	N/A	Various
	Volcanic rocks and mafic igneous intrusions	N/A	Various

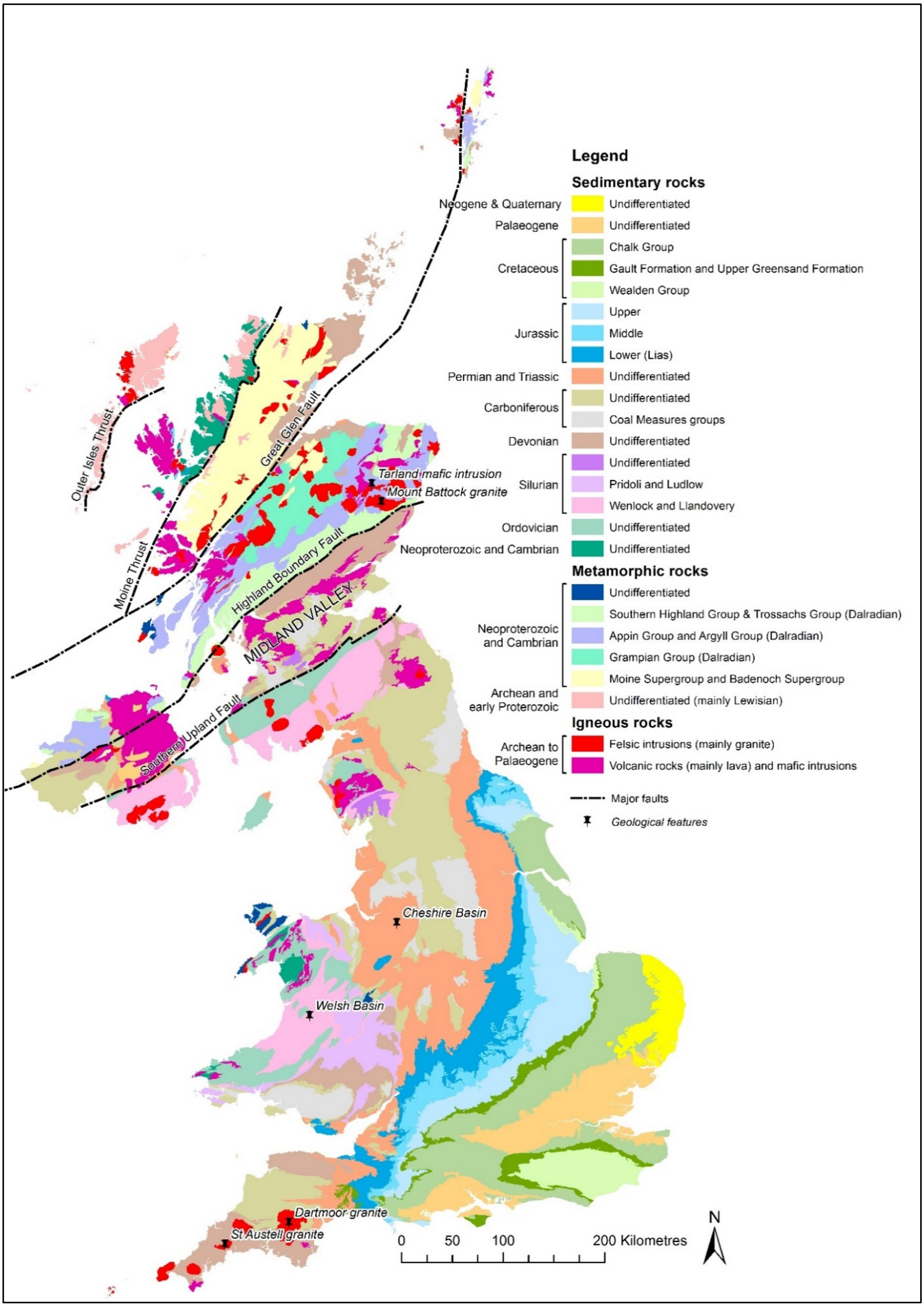


Figure 7. Simplified bedrock geology of the UK, showing the locations of major faults and geological features referred to in this atlas. Geological mapping based on BGS 1:625 000 DiGMap® data.

Superficial geology

Over much of the UK, the solid bedrock is covered in more recent unconsolidated superficial deposits, which exert a primary influence on stream sediment geochemistry. A map of the UK's superficial deposits is shown in Figure 8. These are described in Stone (2008) and McMillan et al. (2005). In summary, the deposits date from the Quaternary (circa 2.6 million years ago) to the present day. Whilst some of these deposits were formed in situ from the weathering of the underlying bedrock, most of them comprise material that has been transported by ice-sheets and meltwaters during an 'ice age' in north-west Europe that lasted from the Quaternary until c. 10,500 years ago. As the glaciers and ice-sheets advanced and retreated, they deposited large quantities of till over much of the UK, with the exception of southern England. Glaciofluvial sands and gravels were laid down over much of the UK also, washed out by vast meltwaters once the ice began to melt. In more recent times, extensive peat deposits have developed in upland areas and lowland fens in Scotland, Northern Ireland, Wales, northern England, south-west England and eastern England. River Terrace and alluvial sand and gravel deposits are associated with most of the UKs major river basins (Stone 2008; McMillan et al., 2005)

Metalliferous mineralisation and mining

Some geological units and features are enriched in certain elements, due to the processes of mineralisation, which have, in several parts of the UK, produced significant mineral deposits.

Metalliferous mineralisation, in particular, can have a distinct geochemical signature resulting in elevated concentrations of metal elements in environmental media such as stream sediments that are derived from the weathering of these rocks. The sensitivity of stream sediments for metallic elements makes them an excellent sample media for mineral reconnaissance, which was one of the original purposes of the G-BASE survey alongside determining a geochemical baseline for the UK. Metalliferous mineralisation has a substantial influence on the distribution of elements such as As, Ba, Cu, Fe, Pb and Zn with anomalous concentrations evident in stream sediments from orefields and mining districts in the UK.

Information on the main mineral occurrences and orefields/mining districts across the UK is outlined in Figure 9, based on the 'Metallogenic Map of Britain and Ireland' (BGS 1996b).

Metalliferous mining in the UK has been ongoing since pre Roman times, and the country possesses a diverse variety of mineral resources. These have been described in Colman and Cooper (2000) for Great Britain, and Arthurs and Earls (2004) for Northern Ireland.

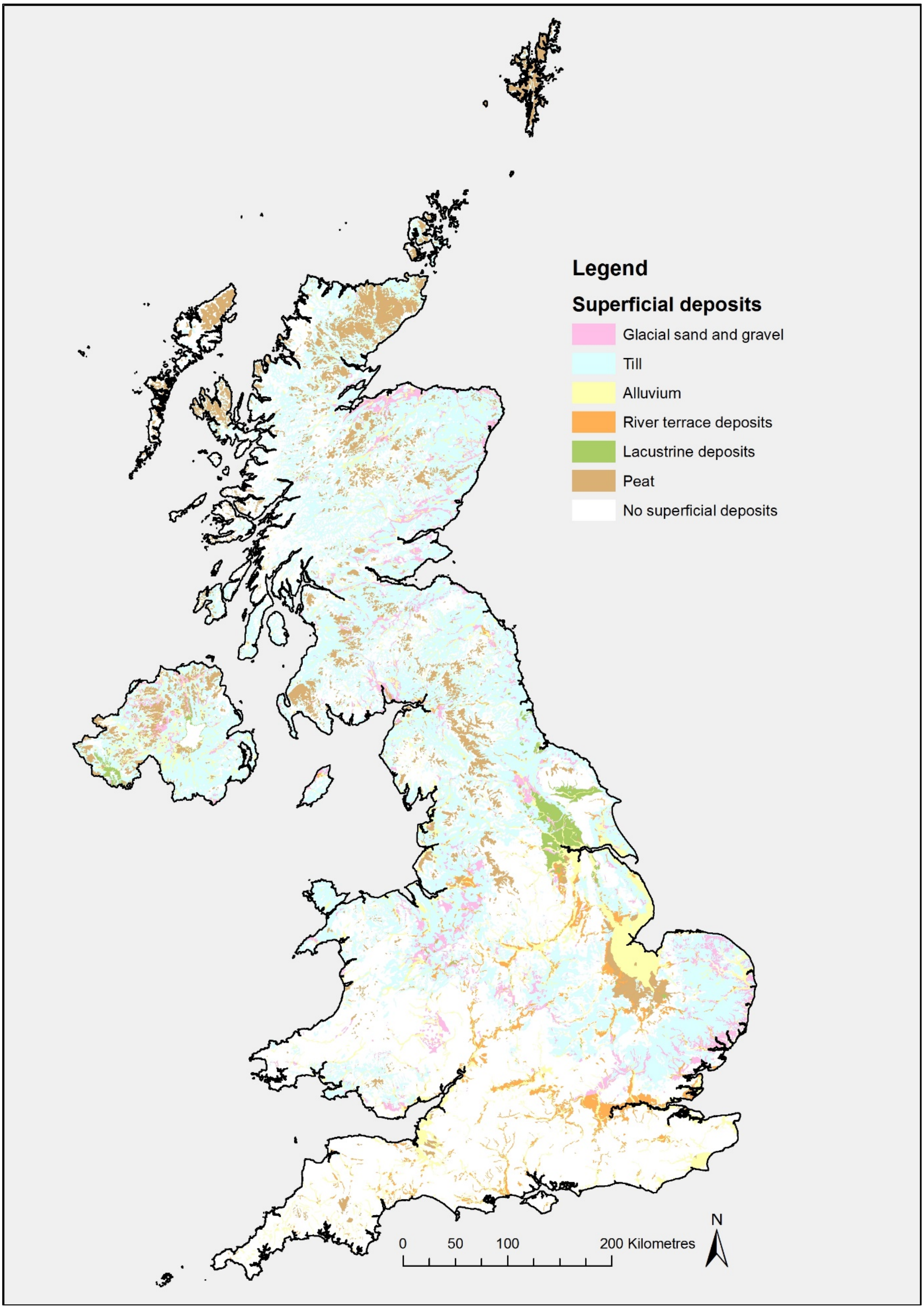


Figure 8. Superficial geology of the UK. Mapping for Great Britain is based on BGS 1:625 000 DiGMap® data; mapping for Northern Ireland is based on GSNI 1:250K Geology data under UK Open Government Licence; http://www.nationalarchives.gov.uk/doc/open-government-licence/version/3/

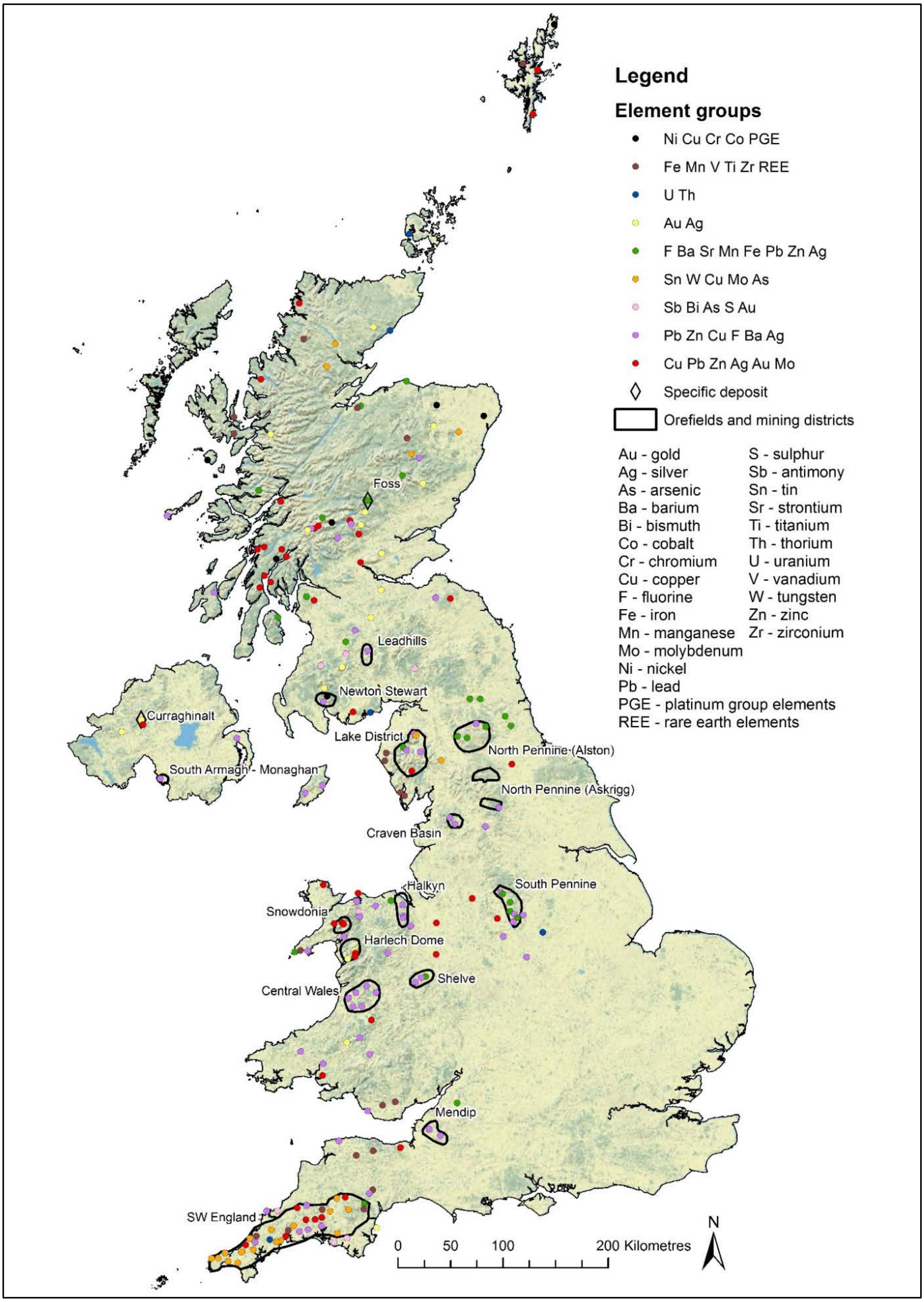


Figure 9. Map of metalliferous mineralisation, orefields and mining districts of the UK. Mineral occurrences are indicated by dots coloured according to the group of elements associated with the mineralisation. The information on mineral occurrences and orefields/mining districts is based on the 'Metallogenic Map of Britain and Ireland' (BGS 1996b). Map data sourced from ESRI ArcGIS online resources under licence agreement E204CW 10/12/2018; source: US National Park Service, 'World physical map'.

Stream water acidity

Stream water samples were collected at the same location as the stream sediment samples during the G-BASE and TELLUSNI geochemical surveys. A map showing the pH of stream waters is presented in Figure 10. Stream water acidity exerts an important control on the dissolution and mobility of many elements in stream sediment and water. In particular, the majority of metal elements tend to be more mobile under acid conditions (Hem 1992; BGS 2000). In addition, the precipitation of Mn and Fe oxyhydroxides in stream sediments is favoured under higher Eh and increasing pH conditions in stream water. This affects not only the spatial distribution of these elements, but of several important trace metals also, including Ag, As, Cd, Co, Pb and Ba, that sorb and coprecipitate with Fe and Mn oxyhydroxides (McKnight and Bencala 1990; Williams 1991; BGS 2000).

The acidity of water is a function of the activity of free hydrogen ions [H^+], with a range from 1 (strongly acid) through 7 (neutral) to 14 (strongly alkaline). Most natural waters fall in the pH range 5 to 9, although drainage from peat bogs and mines may be considerably more acid. Important controls on stream water pH include the pH of rainwater, the abundance of base cations (and other neutralising components) in the bedrock, soil and stream sediment, the ease of release of these cations and their mobility through soil and vegetation. Land use can be an important influence on stream water acidity. The use of lime and other fertilisers in agriculture can raise the pH, whereas coniferous forest plantations lower the pH by reducing the buffering capacity of the soil. Short-term variations in stream water pH are likely as a result of changing flow conditions and seasonal factors, such as faster biochemical reactions in summer than in winter (BGS 1999).

Distribution

Stream water pH for the UK ranges from 1.6 – 12.10 with a median value of 7.4. Lower values (< 6.9) tend to be concentrated in the north and west, whereas much of central and southern England is characterised by circum-neutral to alkaline pH stream waters (> pH 7.4). This distribution largely reflects the major controls that geology, soil type, rainfall, elevation and land use have on stream water pH. Acid conditions are associated with underlying Archean – Carboniferous hard crystalline rock types (metamorphic, metasediments and granites) in the north and west of Scotland, west and south of Northern Ireland, west Wales, the Scotland-England border area, the Lake District and the south-west of England, reflecting the low weathering rates and poor buffering capacity of these lithologies (see Figure 6 for locations). In addition, many of these areas form upland regions with higher rainfall and extensive peat soil, resulting in greater dominance of humic and fulvic acids in stream waters and commensurate low pH (< 6.1) (BGS 1990; BGS 1992a+b; BGS 1993; BGS 1999; Young and Donald 2013). Similarly, moorland peat soils developed over Carboniferous lithologies in central Scotland, south Wales and in the Pennines, Peak District, North York Moors and south-west England result in low pH stream water. Low-lying fenland peat soils account for the lower stream water pH values around Scunthorpe and The Fens in eastern England, the west coast of the Scotland-England border, and on the south-England coast. Large-scale coniferous forestry plantations contribute also to the acid stream water conditions in south-west Scotland, north and south Wales and at Kielder Forest in northern England (BGS, 1993; BGS 1999). In addition to upland peat soils, acid mine drainage in the coal fields of south Wales to the east of Swansea and to the north of Sunderland in the north of England also contribute to lower pH stream waters (< 6.1) in these regions. Similarly, the former world's largest copper mine on the island of Anglesey has very low pH values (< 3.5) as a result of acid mine drainage (see Figure 6 and Figure 7 for locations).

Over the rest of the sedimentary Carboniferous-Neogene geological sequence of central Scotland, the Welsh-English border, Northern Ireland and England, stream water pH values are largely neutral – alkaline (7.4 – 12.10) reflecting the calcareous nature of much of the underlying stratigraphic sequence that includes calcareous sandstones, marls, limestone and chalk. These areas are dominated by arable land and fertiliser inputs may contribute to the higher stream water pH in these areas (BGS 1999; Young and Donald 2013).

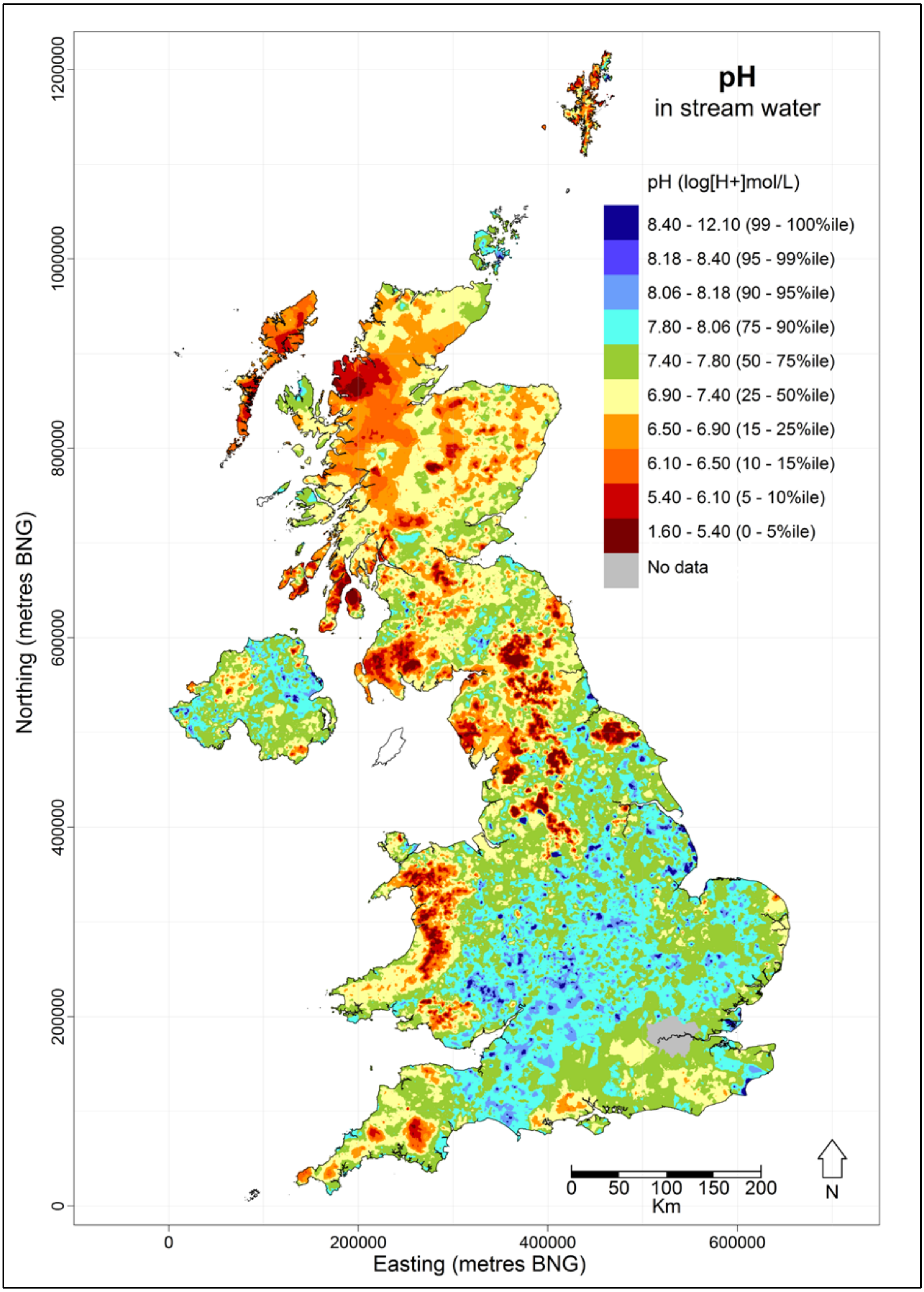


Figure 10. Map of stream water acidity across the UK.

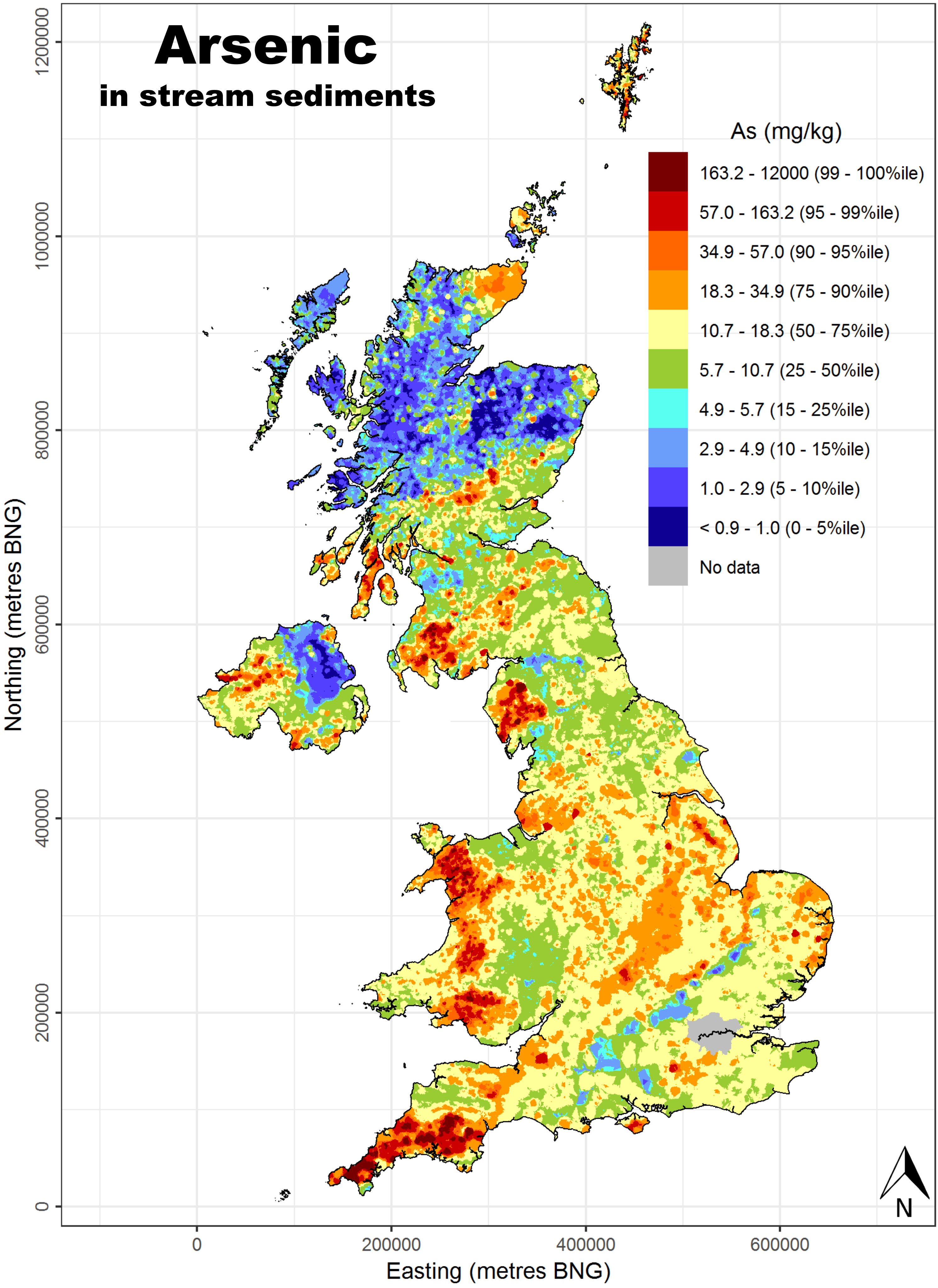
Stream sediment geochemistry

This section contains maps and statistical plots with accompanying descriptions of the distribution of each element in stream sediments across the UK. The environmental behaviour of each of the elements in stream sediments is described in the Appendix.

Table 11 summarises the range in concentrations reported for each element in the UK stream sediment dataset.

Table 11. Summary statistics for element concentrations determined in UK stream sediments

Element	Units	Minimum	Maximum	Median	Mean	Number
Arsenic (As)	mg/kg	<0.9	12,000	10.7	20.0	87812
Barium (Ba)	mg/kg	<1	147,300	533	629	110689
Calcium (CaO)	wt %	0.02	61.39	1.04	2.04	109595
Chromium (Cr)	mg/kg	<3	14,588	96	127	110626
Cobalt (Co)	mg/kg	<1.5	1,926	21.2	28.0	110676
Copper (Cu)	mg/kg	<1.3	12,000	21.6	28.4	110690
Iron (Fe_2O_3)	wt %	0.41	87.6	6.45	7.06	110580
Lanthanum (La)	mg/kg	<1	778.6	42.3	44.7	109675
Lead (Pb)	mg/kg	<1.3	22,982	33.8	79.6	110794
Magnesium (MgO)	wt %	0.15	27.96	1.50	1.88	109607
Manganese (MnO)	wt %	<0.004	30.511	0.181	0.406	110686
Nickel (Ni)	mg/kg	<1.3	4,966	36.8	45.4	110701
Potassium (K_2O)	wt %	<0.01	9.16	2.46	2.50	109622
Rubidium (Rb)	mg/kg	<1	916	83	87	109592
Uranium (U)	mg/kg	0.2	3,294	2.8	4.0	110181
Vanadium (V)	mg/kg	<3	2,106	104	114	110474
Zinc (Zn)	mg/kg	<1.3	20,000	111	154	110737
Zirconium (Zr)	mg/kg	<1	13,600	383	491	110642



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Distribution

Sediment As concentrations range from <0.9 to 12000 mg/kg, with a median concentration of 10.7 mg/kg. The distribution of As throughout the UK shows clearly identifiable regional patterns, which appear to be controlled predominantly by lithological variation and, secondly, by fluid movement including hydrothermal mineralisation processes in the underlying bedrock.

The lowest (< 2.9 mg/kg) sediment As concentrations occur in northern Scotland over the Archean and early Proterozoic Lewisian gneiss, the metamorphic rocks of the Moine, Badenoch, Appin, Argyll, and Grampian groups/supergroups, and over the Palaeogene lavas of Northern Ireland, the Isle of Skye, and Isle of Mull. Low values are observed also over the Chalk groups in southern England.

The highest (> 163.2 mg/kg) As concentrations are generally observed in sediments collected over sedimentary and metasedimentary country rocks surrounding intrusive and extrusive igneous bodies; for example those found in south-west Scotland, and across the orefields of the Lake District, Harlech Dome in north Wales and south-west England, where primary As enrichment is associated with sulphide mineralisation and historic mining; elevated sediment As is strongly linked to primary mineralised anomalies of Cu, Pb, and Zn.

A distinct NE-SW trending boundary between generally low (< 5.7 mg/kg) and moderate to high (10.7 – 163.2 mg/kg) As concentrations coincides with the boundary between the Argyll Group and the Southern Highland Group rocks in Scotland, reflecting sulphide mineralisation in the latter (Plant 1989). Elevated As concentrations associated with sulphide mineralisation also occur over the Coal Measures of south Wales.

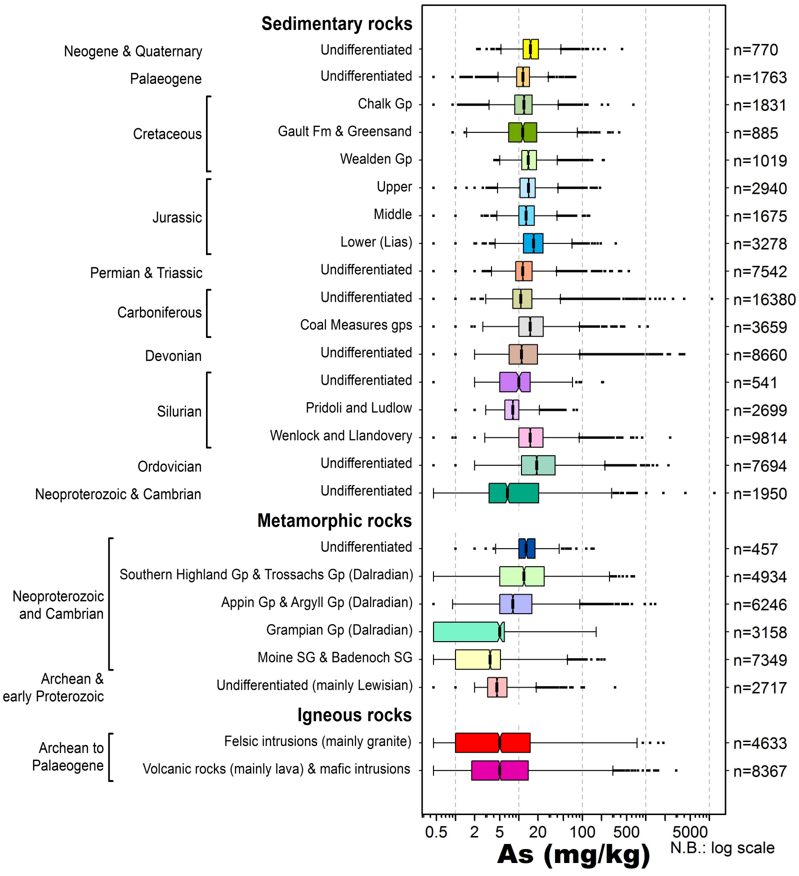
Secondary As enrichment due to co-precipitation of As with oxyhydroxides of Fe and Mn, which are often abundant in stream sediments, is another controlling influence on As distribution; Fe and Mn in stream sediment show a strong spatial association with high concentrations of As. For example, co-precipitation of As with Fe and Mn is the main source of sediment As enrichment over the Welsh Basin (BGS 2000).

Geological control of sediment As enrichment can be seen over clay-ironstone formations within the Cretaceous, evident as a NW-SE trending feature to the south east of Scunthorpe; similarly, across ferruginous sands of the Upper and Lower Greensand units on the Isle of Wight. A widespread area of moderate-high (20 – 60 mg/kg) As concentrations over Lower Jurassic (Lias) rocks in central England is attributable to the As-rich ironstone sedimentary rocks within this geological unit.

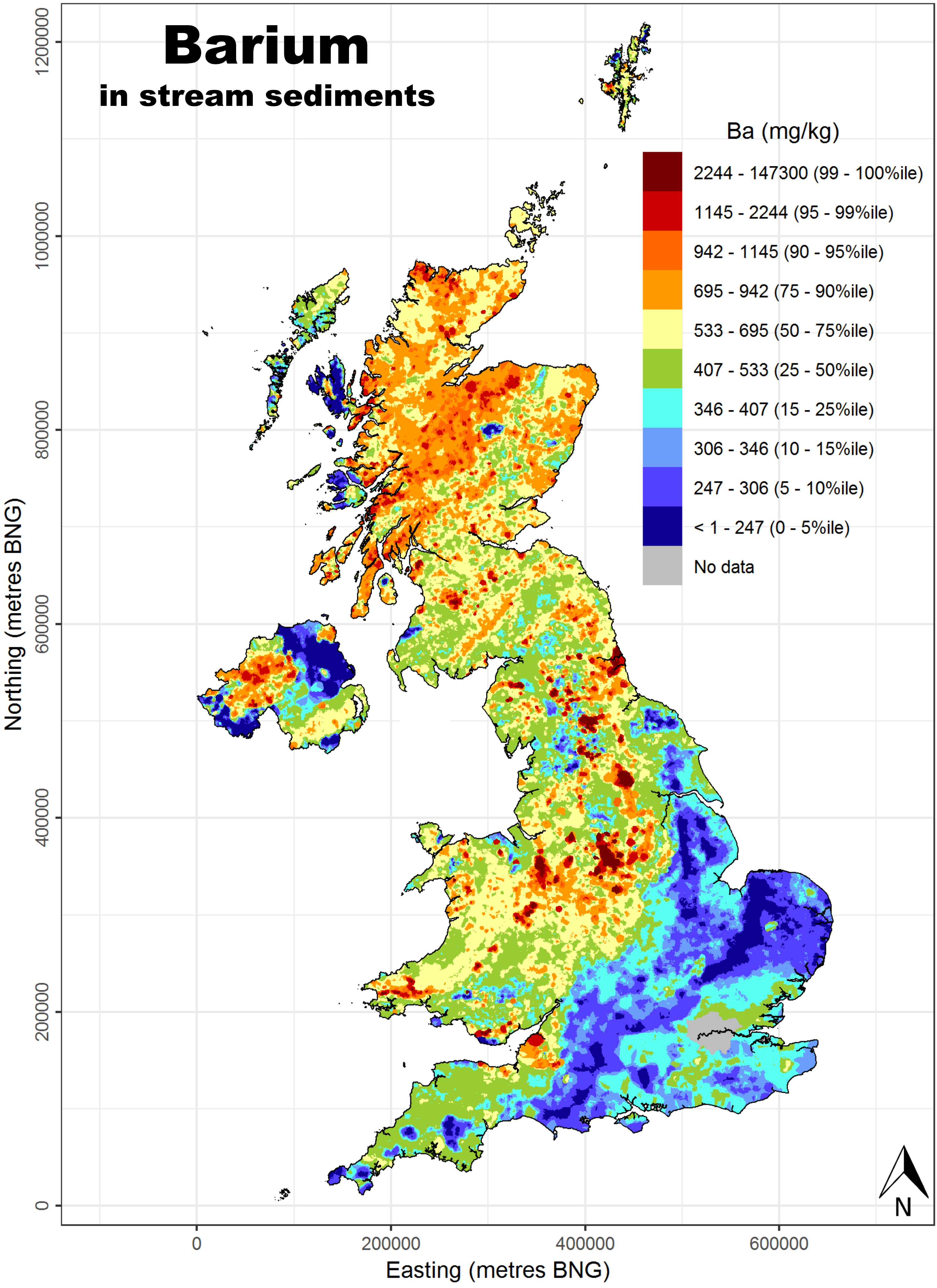
Other than the likelihood of wind-borne dispersion of As-rich smoke/fumes from sulphide-rich coal burning and historic smelting sites (e.g. Swansea, in south Wales), and that associated with metalliferous mining, there is little evidence of any substantial or widespread influence of anthropogenic activity on As distribution in stream sediments, although minor, localised anomalies that can be attributed to point contamination are present.

Full page maps

Legend and Boxplot



Show geology map **More (...)**



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Distribution

Sediment Ba concentrations range from <1 to 147300 mg/kg, with a median concentration of 533 mg/kg. The distribution of Ba over much of the UK shows similarities to that of K_2O in areas where lithological controls dominate, principally the variation in content of K-feldspars and micas in underlying sedimentary and metasedimentary rocks. The occurrence of barite mineralisation is also an influencing factor.

The lowest concentrations of Ba (<247 mg/kg) occur over Palaeogene lavas in Northern Ireland, granite intrusions in south-west England, and a number of granitic bodies in Scotland. Almost all of the samples over the Jurassic – Quaternary rocks of eastern and south-east England yield very low Ba concentrations, the exceptions being those over the Palaeogene succession and the Cretaceous Wealden Group, which have low to moderate (306 – 533 mg/kg) Ba concentrations, possibly derived from slight Ba enrichment in clay-rich strata of the underlying geological units. The strong relationship between Ba and K_2O in sediment is clearly evident in this part of the UK.

Moderate – high (>533 mg/kg) Ba concentrations dominate sediments in the north and north-west of Scotland, reflecting the composition of the K-feldspar-rich metasedimentary rocks of the underlying Moine, Badenoch, Grampian, Southern Highlands and Trossachs groups/supergroups. The slightly lower Ba concentrations over the Argyll and Appin groups in the Scottish Highlands are most likely attributable to a reduction in the volume of quartzo-feldspathic material present within this bedrock unit, as a result of a transition in depositional environment (Plant et al. 1984).

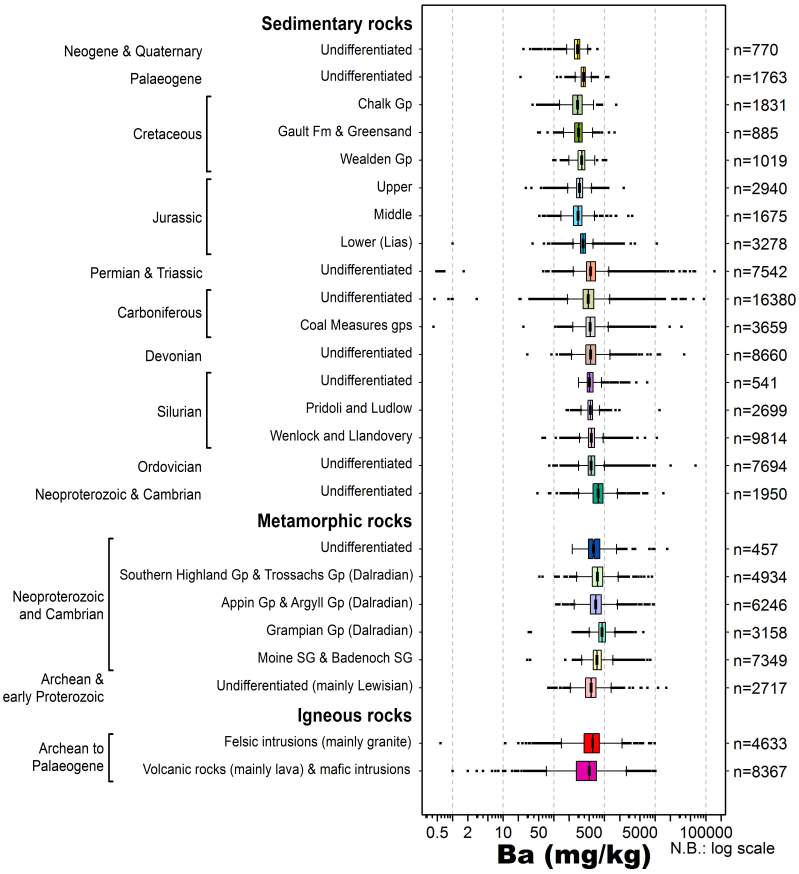
The highest Ba concentrations in UK sediments are associated with barite mineralisation, most notably around the South Pennine orefield. Indeed, the single highest value of 147,300 mg/kg (14.73%) Ba is located in this area. Other clusters of very high Ba are reported over the Mendip Hills orefield, and to the north-east of Leeds; the former is a site of historic mining for lead and iron ores, and the latter is associated with a localised occurrence of nodular barites that has been observed within magnesian limestone strata of the Permian Cadeby Formation (Edwards et al., 1950).

Enhanced Ba concentrations associated with gold and silver mineralisation occur over metasedimentary rocks of the Dalradian Supergroup, both in Scotland (e.g. Foss) and Northern Ireland (e.g. Curraghinalt). The Foss mine works a stratabound exhalative deposit with resources of several million tonnes of high-grade barite (Colman and Cooper 2000).

Anthropogenic contamination of Ba is not commonly apparent in the UK stream sediment data, however, Ba enrichment in gangue material resulting from metalliferous mining (e.g. Pb and Zn) has been observed in stream sediments in north-east England (BGS 1996).

Full page maps

Legend and Boxplot



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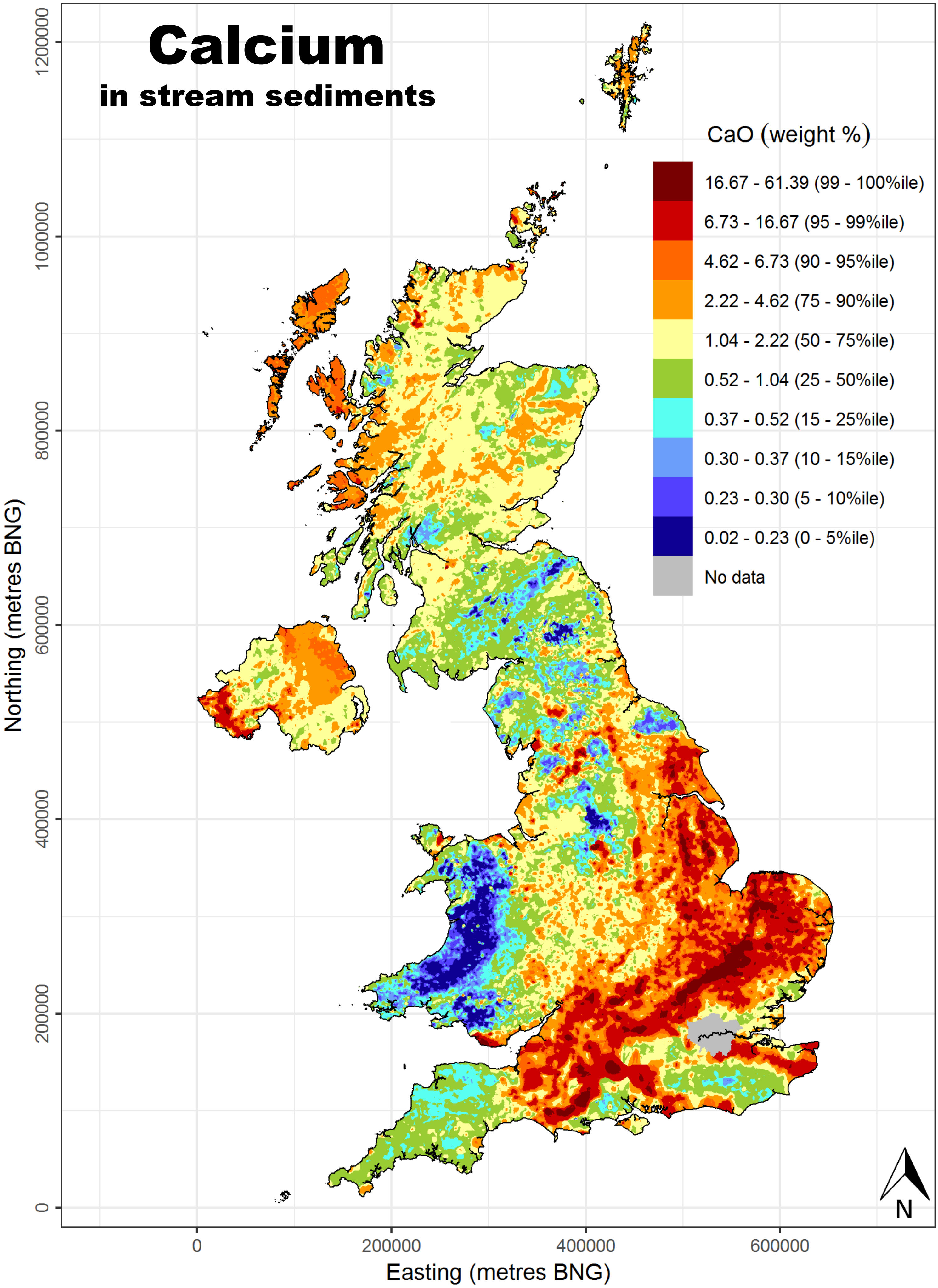

Calcium

in stream sediments

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Distribution

Sediment Ca concentrations are expressed as calcium oxide (CaO), and range from 0.02 to 61.39 wt%, with a median value 1.04 wt%. CaO concentrations strongly reflect the composition of underlying bedrock, and in particular, the distribution of Ca-bearing minerals, especially carbonates, sulphates, plagioclase feldspar, amphiboles, and pyroxenes.

The lowest concentrations of CaO (< 0.3 wt%) occur over Silurian and Ordovician rocks of west Wales, especially those of the Llandovery and Ashgill series. A NE-SW trending area of low CaO over Silurian/ Ordovician sedimentary rocks in southern Scotland corresponds with depleted concentrations of Ni and Cr in stream sediment, suggesting a change in rock-sediment provenance to one of a more mafic-deficient source in the underlying strata (BGS 1993).

Low CaO concentrations are also evident in a number of other areas underlain by sedimentary rocks that are mudstone/siltstone/sandstone dominant, e.g. the Upper Coal Measures Formation in south Wales, Carboniferous age rocks of central and northern England, and parts of the Jurassic succession in north-east England. In some parts of the UK (including the North York Moors, Kielder Forest, and Peak District, for example), the dissolution of Ca-bearing minerals in very acidic (pH <5.0) stream waters (see Figure 10) is likely to be an additional factor that contributes to low CaO concentrations. Sediments with low to moderate (< 1.04 wt%) CaO concentrations are otherwise typical over the Devonian and Carboniferous sedimentary rocks of south-west England, and the early Cretaceous Wealden Group rocks of south-east England.

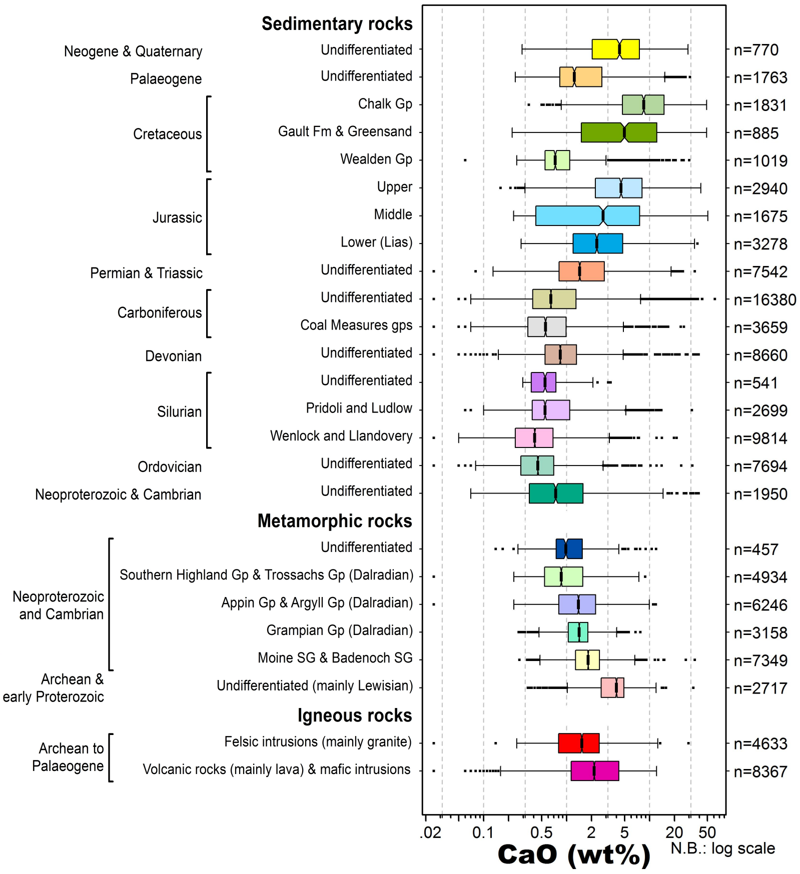
Moderate to slightly enhanced CaO sediment concentrations (0.52 – 4.62 wt%) dominate the landscape of central and northern Scotland; values over Devonian sedimentary rocks are indistinguishable from the adjacent metamorphic rocks, indicating local derivation of Ca. Concentrations in the range 2.22 – 6.73 wt% are uniform across the Lewisian rocks of the Outer Hebrides, and the Palaeogene lavas of the Inner Hebrides and Northern Ireland. A similar range of concentrations is observed over Permian, Triassic and Lower Jurassic rocks in central England and east Wales; higher (> 6.73 wt%) CaO sediment concentrations occur over limestone dominant strata.

The highest (> 16.67 wt%) sediment CaO concentrations within the UK are located over carbonate lithologies, particularly those of the Chalk groups; concentrations of CaO up to 49.0 wt% are reported from the Grey Chalk around Cambridge. The limestone and chalk units exhibit extremely close lithological control of CaO distribution in stream sediments throughout the UK.

Locally elevated CaO concentrations found throughout the low-calcium domains may reflect anthropogenic activity, particularly the practice of soil improvement through lime addition to agricultural land, which might affect the drainage system.

Full page maps

Legend and Boxplot



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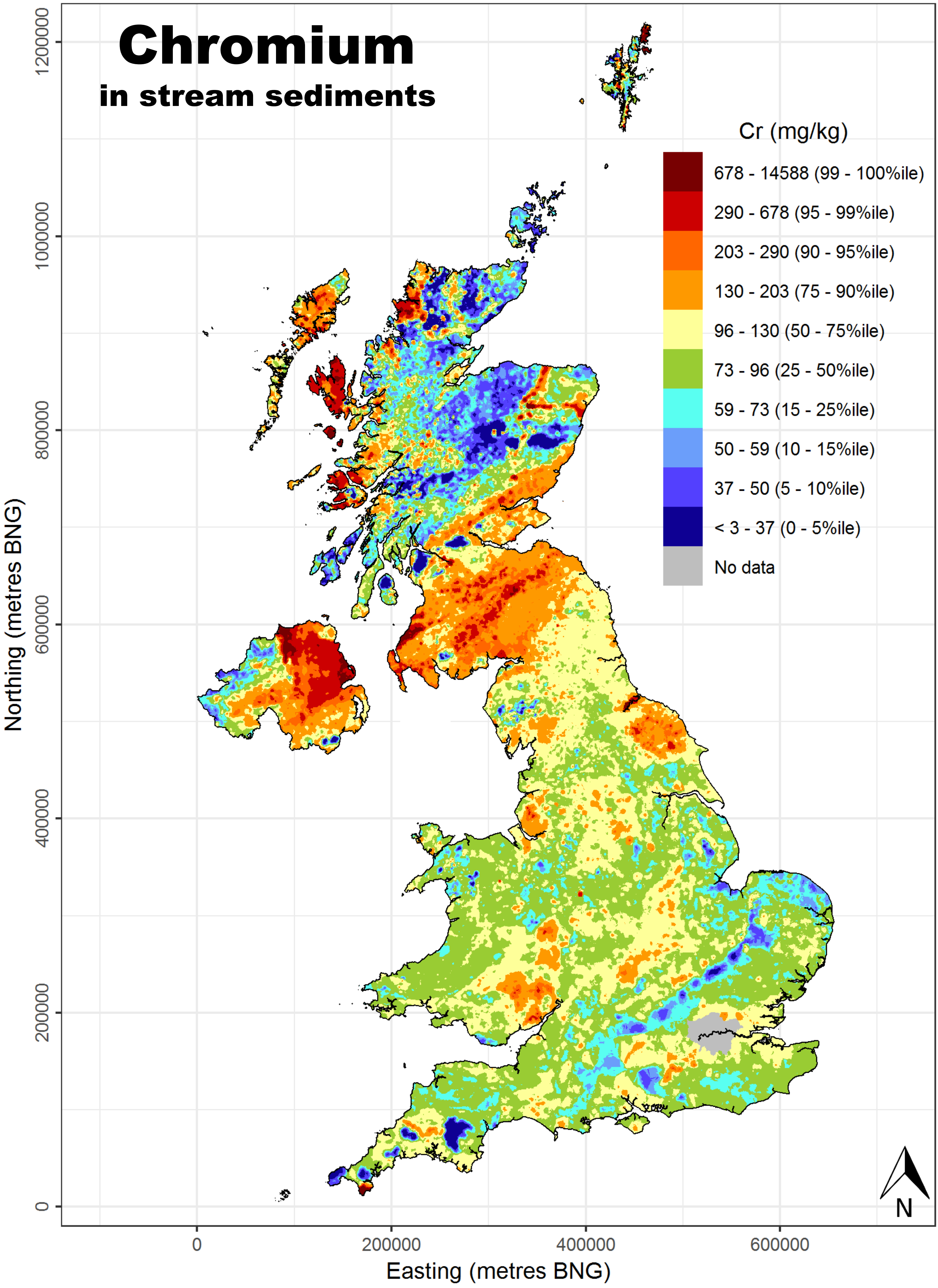

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Distribution

Sediment Cr concentrations range from < 3 mg/kg to 14588 mg/kg, with a median concentration of 96 mg/kg. The distribution of Cr throughout the UK shows clear similarities with that of Ni and V, as all are elements with mafic affinity (De Vos and Tarvainen 2006); the lowest and highest concentrations are therefore typically associated with felsic and mafic igneous rocks respectively.

Accordingly, the lowest Cr concentrations (< 37 mg/kg) are reported from samples collected over evolved felsic igneous intrusions, such as the granite plutons between Aberdeen and the Cairngorm Mountains in Scotland, evolved granites in south-west England and the Palaeogene granites of the Mourne Mountains in Northern Ireland. The metamorphic terrains of northern Scotland exhibit relatively low Cr concentrations, and similarly low concentrations are reported over Dalradian rocks in Northern Ireland. Prominent low Cr anomalies in the Renfrewshire Hills and Campsie Fells of the Scottish Midland Valley relate to intermediate volcanic rocks within the Clyde Plateau Volcanic Formation; this volcanic formation is however compositionally diverse, many parts of it being comparatively mafic.

The Grey Chalk Subgroup of south-east England produces a closely defined low Cr feature. Chromium concentrations in the range 59 – 130 mg/kg otherwise prevail in sediments collected across the majority of the Carboniferous-Quaternary sedimentary rock succession of England and Wales, with comparatively little lithological variation or constraint from west to east, the only other notable exception being higher concentrations over the Lower-Middle Jurassic. This is particularly noticeable at the North York Moors, but can be followed along their outcrop down through central England. This corresponds with to elevated sediment Cr and Fe values, reflecting the presence of ironstones in these bedrock units.

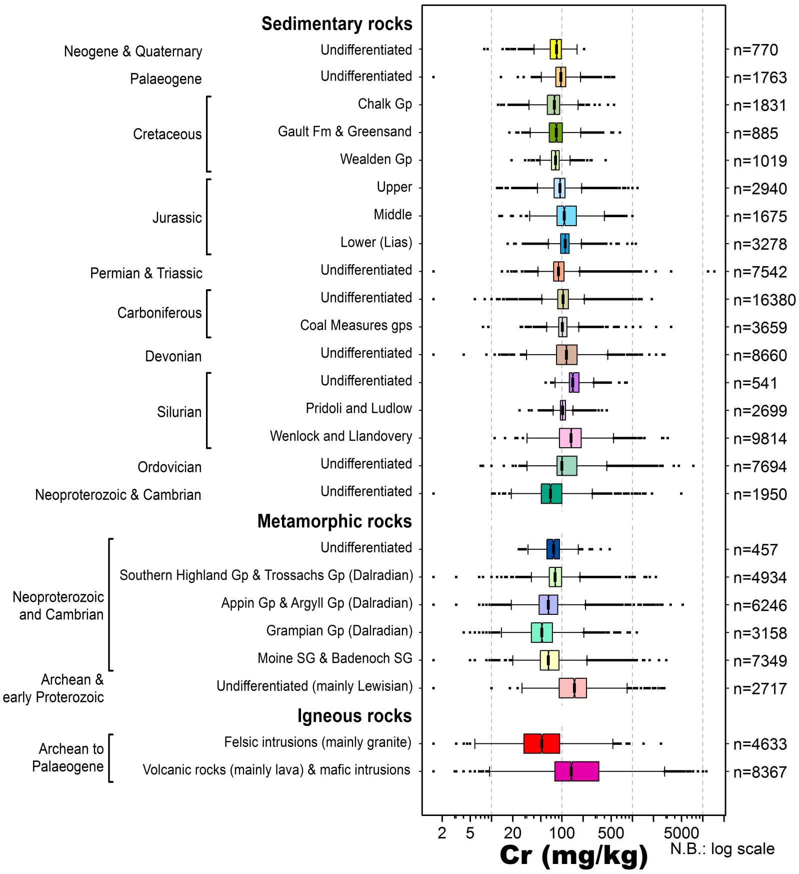
High (130 – 290 mg/kg) Cr concentrations are seen over much of the northern part of the Midland Valley of Scotland, and to the south of the Southern Uplands fault in southern Scotland. In both cases, an increase in the spinel content of underlying Devonian sedimentary rocks (Midland Valley) and Silurian greywacke (southern Scotland) is considered to be the cause of Cr enrichment in stream sediments (BGS, 1993; Stone et al. 1991). Similar concentrations are seen over corresponding sedimentary rock sequences in Northern Ireland and the Devonian in east Wales. Over Lewisian rocks of the Outer Hebrides and North-west Scotland, high concentrations reflect the presence of amphibolite within the gneiss bedrock.

The highest (>290 mg/kg) concentrations of sediment Cr are associated with mafic and ultramafic igneous rocks, both intrusive and extrusive. This is clearly evidenced over the Palaeogene lavas of Northern Ireland and the Inner Hebrides. Very high Cr is also observed over mafic/ultramafic intrusions in north-east Scotland, and the ophiolite complexes at Ballantrae in south-west Scotland, the Lizard in south-west England and those of the northern Shetland Isles of Unst and Fetlar.

The single highest value of Cr (14,589 mg/kg) is reported from the site of a former chromite processing plant near Middlesbrough, and gives rise to a small-scale locally derived anthropogenic anomaly.

Full page maps

Legend and Boxplot



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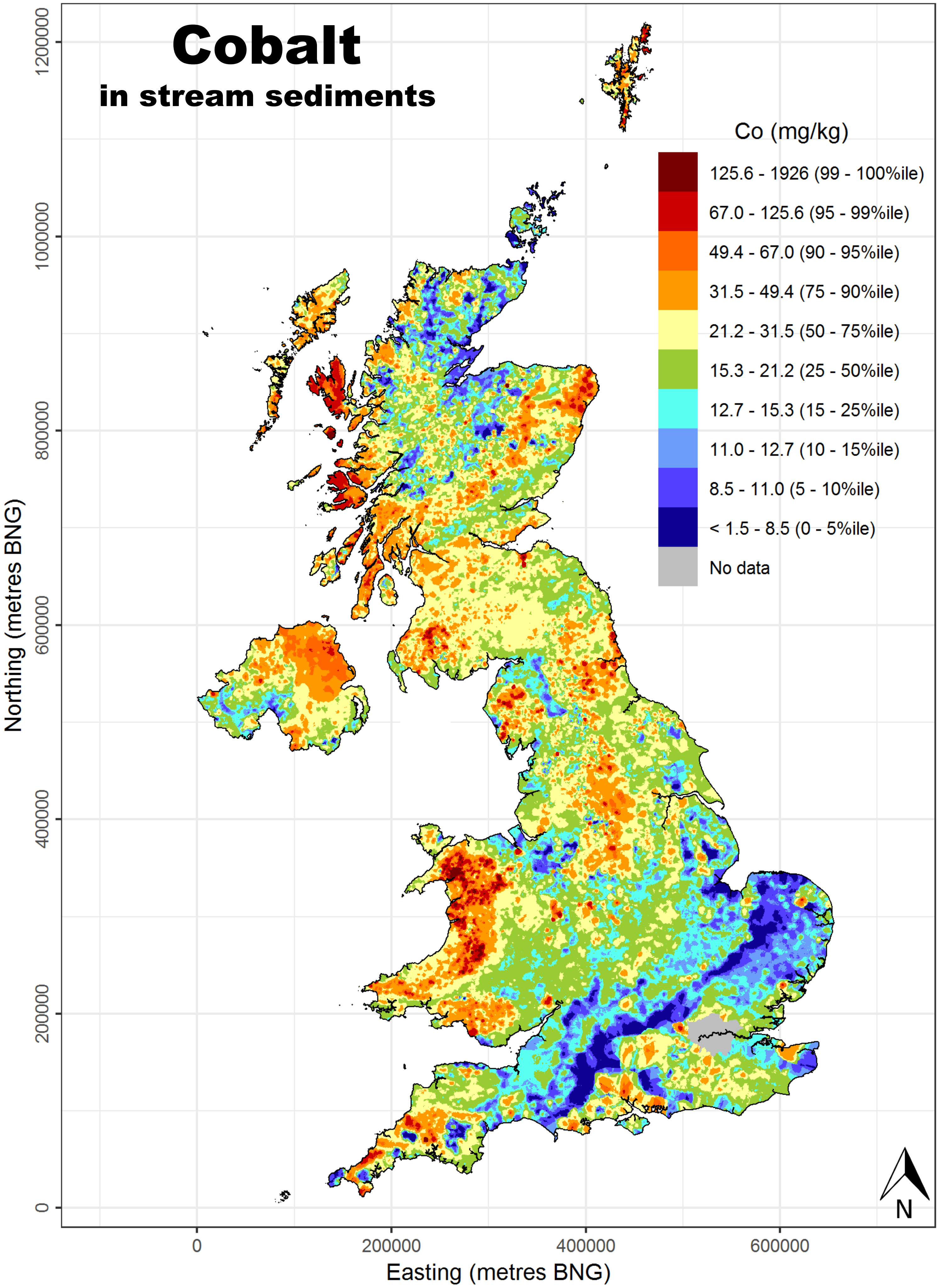

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Distribution

Sediment Co concentrations range from < 1.5 to 1,926 mg/kg, with a median concentration of 21.2 mg/kg. The distribution of Co throughout the UK shows a strong spatial relationship with iron (and to a slightly lesser extent manganese), which is likely to result from sorption of Co by secondary hydrous Fe and Mn oxides in stream sediments, which have a particularly strong sorption affinity for cobalt (De Vos and Tarvainen 2006). The general distribution of Co also shows similarities to other elements of mafic affinity, such as Ni and V.

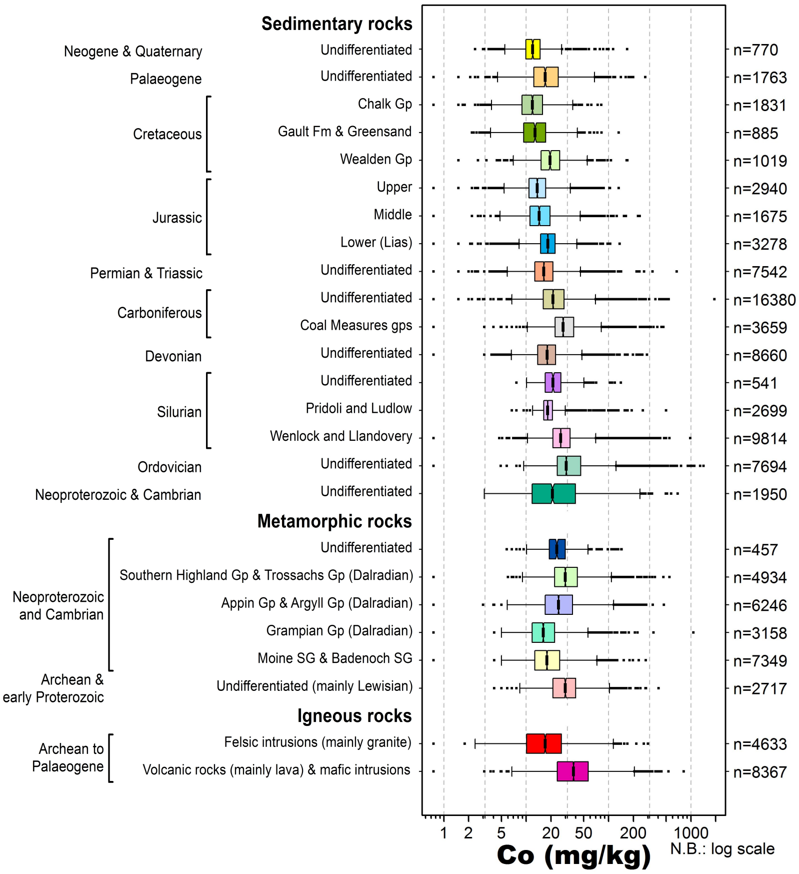
The lowest (<12.7 mg/kg) concentrations of Co occur over carbonate-rich lithologies, most notably the Grey and White Chalk Subgroups of south-east England. Very low concentrations are also evident over the Palaeogene granites of south-west England. Other areas of low Co concentration include those underlain by sedimentary rocks of Permian and Triassic age in south-west and north-west England, Triassic rocks of the Cheshire Basin (and other parts of central England), and sandstone strata within the Devonian of northern Scotland. A number of late Silurian – early Devonian granites in north-central Scotland also yield low sediment Co concentrations.

Over much of north-east and central England, central and east Wales, and south-east England, underlying sedimentary rocks of Silurian – mid Jurassic age give rise to low to moderate Co stream sediment concentrations predominantly in the range 12.7 – 21.2 mg/kg. Similar concentrations are reported over Devonian sedimentary rocks immediately south of the Highland Boundary Fault in Scotland, with Co concentrations of the metamorphic Southern Highland Group and Argyll and Appin Groups north being noticeably enhanced. These rock units are also clearly distinguished from the remainder of the Neoproterozoic and Cambrian metamorphic rocks of Northern Ireland and Scotland by significantly more elevated values, as previously detailed by Plant (1984). Similarly enhanced (21.2 – 49.4 mg/kg) Co concentrations are typical of sediments collected over the metamorphic rocks of the Shetland Islands and those of the Lewisian Complex in the Outer Hebrides and north-west Scotland, reflecting the presence of mafic sequences in these metamorphic terrains. Sediments over the Coal Measures in central Scotland, north-east England, the Pennines and south Wales, the Carboniferous and Devonian basins of south-west England, and the early Cretaceous and Palaeogene successions of south and south-east England all yield Co concentrations in the same range (21.2 – 49.4 mg/kg).

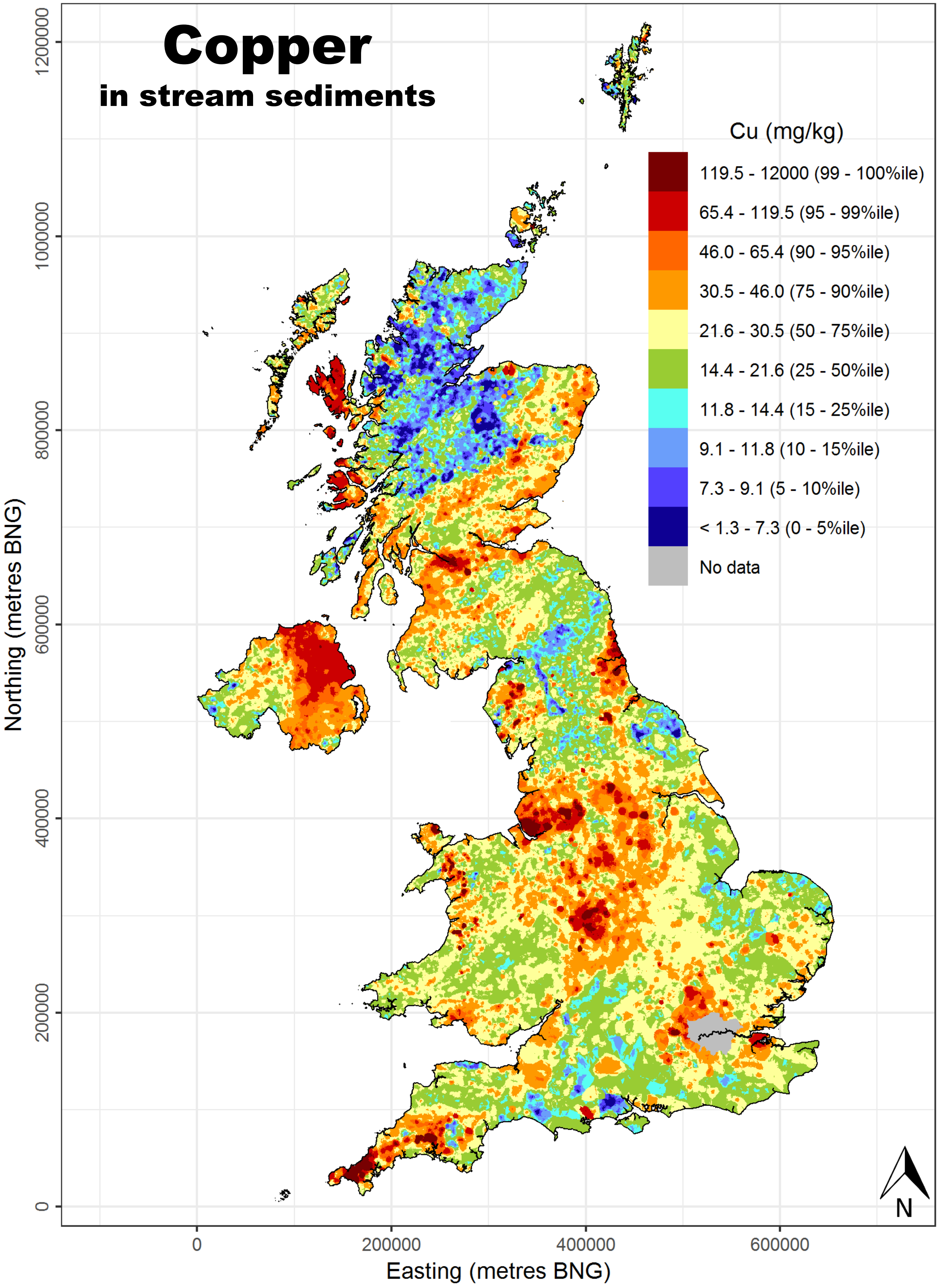
High to very high (>49.4mg/kg) Co concentrations are associated with mafic intrusive rocks of Unst and Fetlar (Shetland Islands), and the Palaeogene lavas of the Inner Hebrides and Northern Ireland. High to very high concentrations of Co across much of west Wales are observed. These are coincident with high levels of MnO and Fe_2O_3; an indication that Co enrichment is due to the presence of secondary Fe and Mn oxides. The highest Co concentration reported occurs in south-west England and is associated with enhanced antimony (Sb), As, Cu, Pb, silver (Ag), tin (Sn), tungsten (W) and Zn, all of which suggest a mineralised source within this region of historic ore mining.

Full page maps

Legend and Boxplot



Show geology map **More (...)**



Toggle map symbology: Percentile classified Continuous scale

Distribution

Sediment Cu concentrations range from < 1.3 to 12000 mg/kg, with a median value of 21.6 mg/kg. Copper distribution is partly controlled by lithology, but importantly, strongly enhanced Cu levels are associated with metalliferous mineralisation (often coinciding with enhanced Pb and Zn) and anthropogenic contamination.

Low Cu concentrations (<14.4 mg/kg) occur in northern Scotland over the Grampian Group and Moine Supergroup, and can be related to the predominantly quartzo-feldspathic lithologies of these bedrock units. In contrast, elevated (>30.5 mg/kg) Cu concentrations over parts of the Southern Highland Group and Appin and Argyll Groups are evidence for a substantial addition of Cu to the upper crust within the Dalradian rift system (Plant et al. 1984). Over parts of the Dalradian of north-east Scotland, the presence of generally sub-economic mineralisation has resulted in numerous localised high-Cu anomalies (BGS 1992a).

Generally moderate to low (<21.6 mg/kg) Cu is seen over felsic igneous intrusions. Several of these (e.g. those in southern Scotland, and most notably south-west England) appear associated with higher Cu (>65.4 mg/kg), but this is related to intrusion-related hydrothermal mineralisation, not the lithology of the intrusions.

Elevated (>30.5 mg/kg) Cu is observed over the Carboniferous Coal Measures Groups in the Midland Valley of Scotland, north-east England, central England and south Wales. This can be attributed to the coals and black shales present in these lithologically variable bedrock units. Mining of these strata may have caused further dispersion of Cu in the environment, contaminating stream sediments. Over Permian and Triassic sedimentary rocks, in places (e.g. the Cheshire Basin), elevated Cu coinciding with elevated Ba concentrations may be explained by the presence of red-bed Ba-Cu mineralisation (Plant et al. 2000).

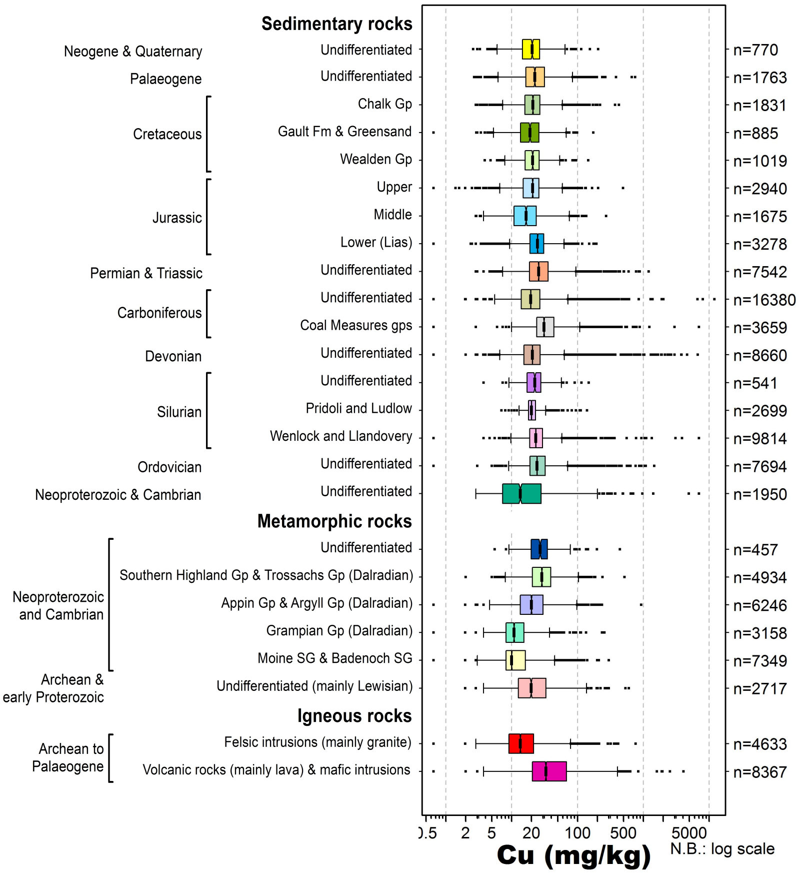
High Cu concentrations (>65.4 mg/kg) are observed over volcanic and mafic igneous rocks such as those in Northern Ireland, the islands of Skye and Mull, the Midland Valley of Scotland and the Lake District. These rock types are commonly enriched in Cu, due to its tendency to be incorporated as a trace element in the minerals biotite, pyroxene and amphibole, which characterise these lithologies.

High-Cu anomalies (>65.4 mg/kg) related to mineralisation are observed over the orefields/mining districts of the Peak District, Lake District, Snowdonia, south-west England, central Wales and on the island of Anglesey in North Wales, where Europe's (and probably the world's) largest copper mine was active in the late 18th century (Cooper et al. 1989). Extensive mining of copper ore has doubtless enhanced its dispersion into the environment in these areas.

Anthropogenic contamination has an important influence on the distribution of Cu in stream sediments. Many of the UK's most heavily urbanised and industrialised areas, including Leeds, Bristol, Swansea, Liverpool, Manchester, the outskirts of London, and particularly Glasgow and Birmingham (which both have a history of coal mining and metal working and extraction), are associated with high sediment Cu concentrations that locally overwhelm the geological signature.

Full page maps

Legend and Boxplot



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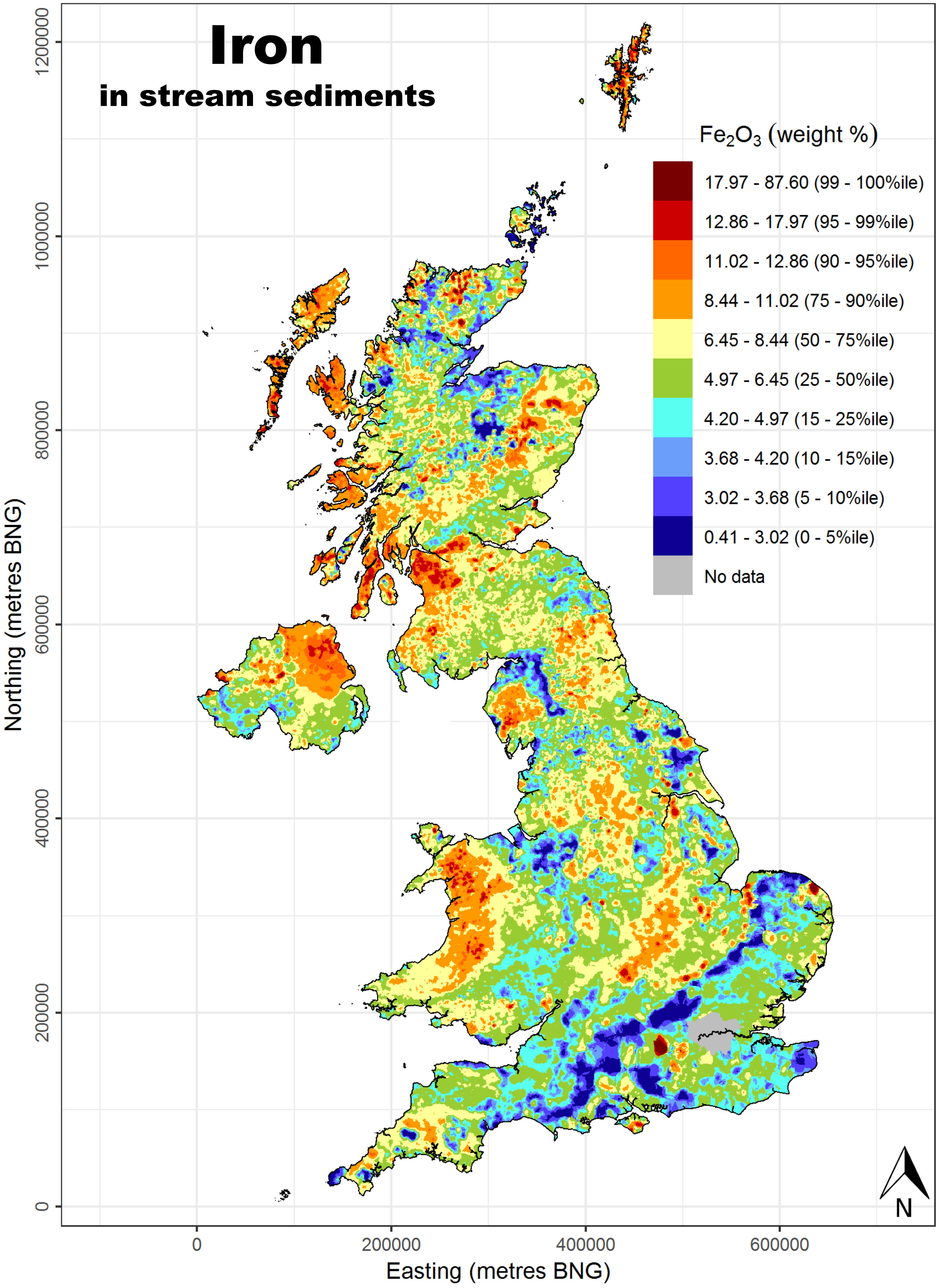
Iron

in stream sediments



Toggle map symbology: **Percentile classified** **Continuous scale**

Distribution

Sediment Fe concentrations are expressed as iron oxide (Fe_2O_3), and range from 0.41 to 87.6 wt%, with a median value of 6.45 wt%. The distribution of Fe is controlled not only by the underlying bedrock, but also by acid drainage, mineralisation associated with metal (Pb, Zn) and coal mining, and the formation of secondary ferric oxides.

Consistently low concentrations (<4.2 wt%) are reported over carbonate-rich strata, exemplified by the Chalk Group in south-east England, which shows extremely close lithological control of sediment Fe_2O_3. Low concentrations are also exhibited over Jurassic oolitic limestone strata between Thirsk and Scarborough in northern England, over Devonian sandstones of northern Scotland and the Orkney Islands, and over the Permian and Triassic rocks of the Cheshire Basin and north-west England. Felsic igneous intrusions generally produce low Fe_2O_3 in sediments (for example, over a number of granites in south-west England and northern Scotland), although slight enrichment is evident where secondary Fe oxides have formed over acidic, peaty ground, for example, on Dartmoor.

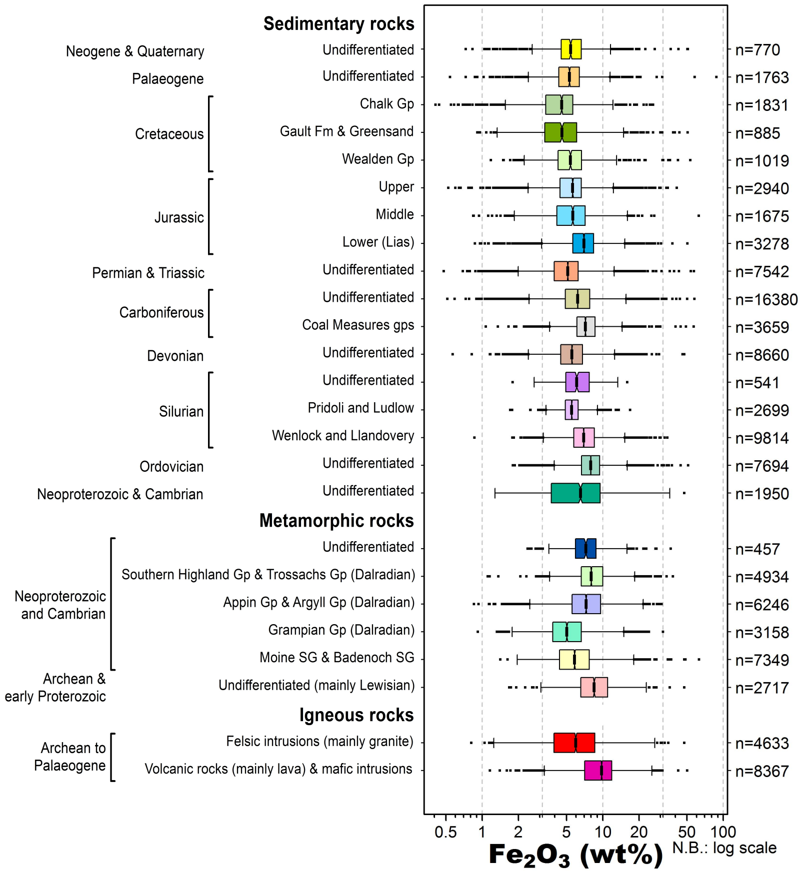
Much of the Silurian, Devonian, Triassic and Middle and Upper Jurassic sedimentary rock sequences display overlying stream sediment Fe_2O_3 concentrations in the range 4.97 wt% - 8.44 wt%, with very little differentiation between lithological units. A similar range of concentrations is seen over the Carboniferous basins of south-west England; however, some lithological contrast can be discerned in these areas. Exceptionally, sediments over Silurian rocks of west Wales display elevated Fe_2O_3 (up to 25 wt%). Iron enhancement in this area is coincident with high concentrations of MnO and low stream water pH, indicative of the formation of secondary Fe oxides. Most of the Neoproterozoic and Cambrian metamorphic rocks of Northern Ireland and Scotland are related to low Fe_2O_3 in stream sediments, but the Southern Highland Group in Scotland can be distinguished by significantly more elevated values (up to 11.02 wt%), due to the presence of epidiorites, green beds and tholeiitic extrusive rocks (BGS 1992a) within this predominantly metasedimentary, but lithologically diverse sequence.

Moderate to high (4.97 wt% - 11.02 wt%) Fe_2O_3 concentrations over the Carboniferous Coal Measures in central Wales, central and northern England reflect the presence of Fe held in pyrite within coal and organic-rich horizons, and the surface dispersion of mining waste. Sediments over Lower and Middle Jurassic rocks in central England are conspicuously elevated in Fe_2O_3 coinciding with higher Cr and Ni, reflecting the presence of sedimentary ironstone in the geological sequence; a clear high Fe_2O_3 anomaly near Scunthorpe can be attributed to historical mining of the ironstone.

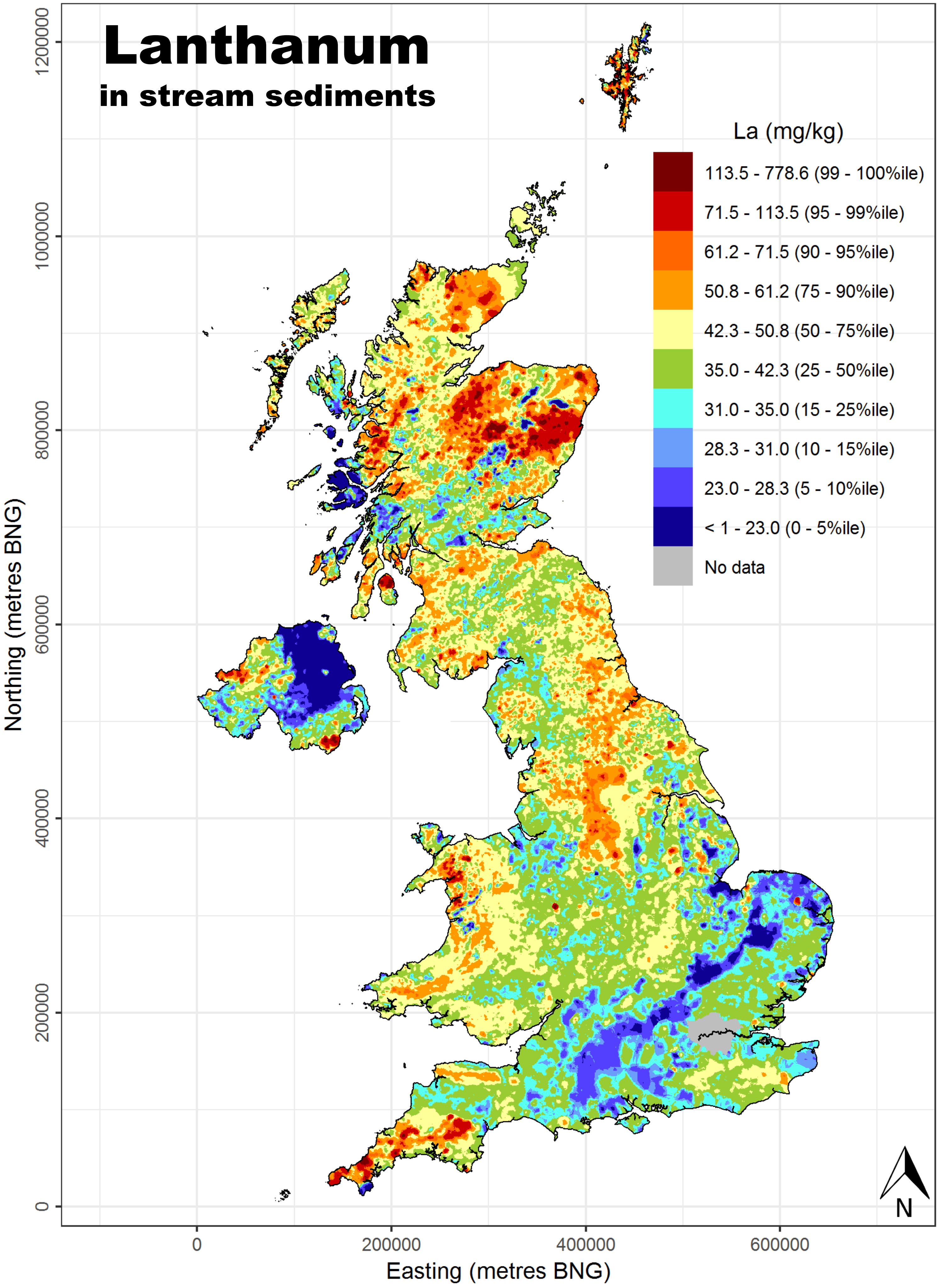
High to very high Fe concentrations (> 11.02 wt%) occur in sediments over Palaeogene lavas of the Inner Hebrides and Northern Ireland, as well as over the outcrop of Carboniferous lavas that surround Glasgow, reflecting bedrock composition (BGS 1993; Young and Donald 2013). Sediments over mafic rocks of Ordovician to Silurian age in the Lake District and Snowdonia are similarly high in Fe_2O_3.

Full page maps

Legend and Boxplot



Show geology map **More (...)**



Toggle map symbology: **Percentile classified** **Continuous scale**

Distribution

Sediment La concentrations range from <1 to 778.6 mg/kg, with a median of 42.3 mg/kg. The distribution of La is influenced primarily by lithological and sedimentological controls, such as the tendency for La to occur in resistate minerals, but it also appears to show some enhancement in association with metalliferous mineralisation. Lanthanum enrichment in stream sediments as a result of anthropogenic contamination is not a significant feature of the national dataset.

Very low sediment La concentrations (<28.3 mg/kg) characterise the underlying Palaeogene volcanic rocks and mafic igneous intrusions of Northern Ireland and the Inner Hebrides in Scotland. This is explained by La fractionation out of the mafic melts that formed these rocks, and the corresponding La concentration into the more evolved magmas that produced the genetically-related Palaeogene granites.

Similarly low La concentrations are observed over Cretaceous chalk units in south east England. In west Wales, low La concentrations over Ashgill rocks within the Ordovician sequence are explained by La being hosted by coarse monazite in stream sediments of this area, the coarse grain size meaning little of the element remains in the sampled <150µm fraction (BGS 2000; Smith et al. 1994). Over the remainder of the UK's sedimentary bedrock, La levels display some lithological control, particularly enrichment over sandstone-dominated Carboniferous and Devonian units in Scotland and northern England. The close relationship of higher La with higher K_2O and lower Zr over the Wenlock, Llandovery and Ordovician successions of Wales indicates that this La enrichment is likely to be related to alkali feldspar content.

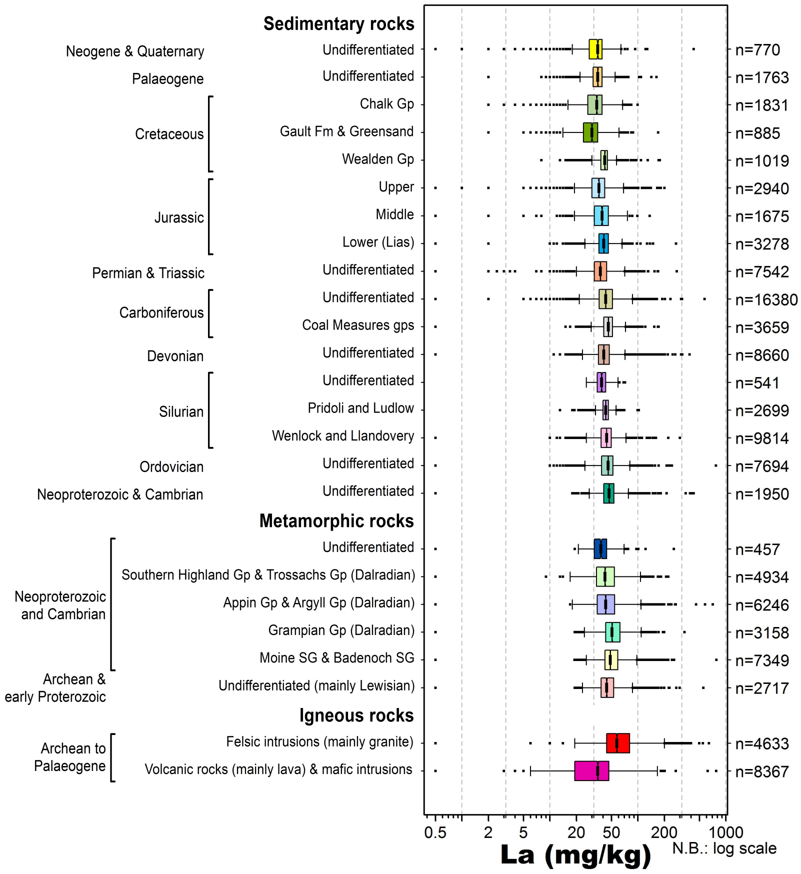
Moderately high levels of La (>50.8 mg/kg) occur in sediments collected over parts of the Moine/Badenoch Supergroups and Grampian Group. In many locations, the primary reason for this enrichment is enigmatic, but commonly high La corresponds with high Zr concentrations, suggesting that local physical concentration of resistate minerals in present-day drainage channels is responsible. A similar pattern of La enrichment in the Lake District is partly attributable to the same process (BGS1992b), in which topography plays a role.

Lanthanum concentrations are generally high (>61.2 mg/kg) in sediments over felsic igneous intrusions. La is typically enriched in felsic igneous rocks, as it is an incompatible element that concentrates in the melt phase as magmas evolve through partial melting and fractional crystallisation (White 2013). Variability in La concentrations in sediments collected over different felsic intrusions can therefore be explained by the type and degree of magmatic evolution they have experienced. For example, very high La concentrations (>71.5 mg/kg) are seen over the granites of south-west England, the Palaeogene granites of the Isles of Arran and Skye in Scotland, and the Mourne Mountains in Northern Ireland, all of which are highly-evolved.

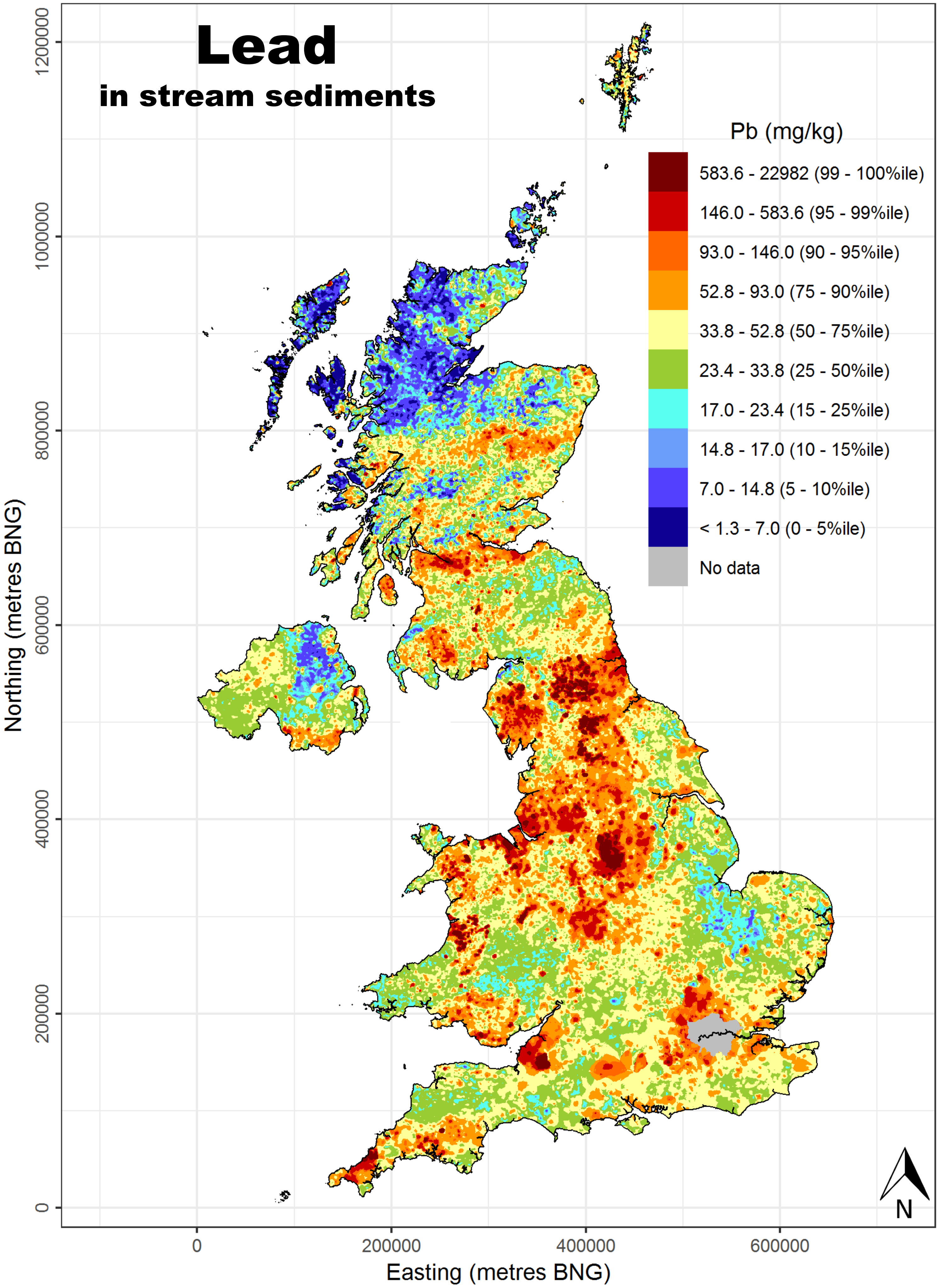
Some high-La anomalies (such as that nearby St Agnes) in south-west England do not directly overlie the La-rich granites. This is instead explained by the circulation of alkaline hydrothermal fluids that produced extensive metalliferous mineralisation in this area. High La-anomalies at Snowdonia, the Harlech dome in north-west Wales, and possibly the South Pennine Orefield, can also be related to mineralisation processes.

Full page maps

Legend and Boxplot



Show geology map **More (...)**



Toggle map symbology: **Percentile classified** **Continuous scale**

Distribution

Sediment Pb concentrations range between <1.3 and 22,982 mg/kg, with a median value of 33.8 mg/kg. The distribution of Pb is controlled by a combination of the underlying bedrock composition, metalliferous mineralisation and anthropogenic factors, which gives rise to the positively skewed data distribution. The amount of K-feldspar in the underlying bedrock is interpreted to be one of the main lithological influences.

The lowest Pb concentrations (< 17 mg/kg) are observed over the Lewisian and Moine rocks of north-west Scotland and the Outer Hebrides, and the Palaeogene lavas of the Inner Hebrides and Northern Ireland. Very low Pb concentrations are also observed over mafic igneous rocks of north-east Scotland and around other smaller mafic bodies throughout the UK. Low to moderate (7.0 – 33.8 mg/kg) concentrations of Pb are evident over The Fens and the Lincolnshire Marshes, where Upper Jurassic sedimentary rocks form the bedrock. Pb concentrations in stream sediments across most of the sedimentary bedrock (with the exception of the Carboniferous Coal Measures) are moderate to slightly elevated (23.4 – 52.8 mg/kg). However, the natural background concentrations are overprinted in many areas by the effects of metalliferous mining and anthropogenic sources related to heavy industry and urbanisation.

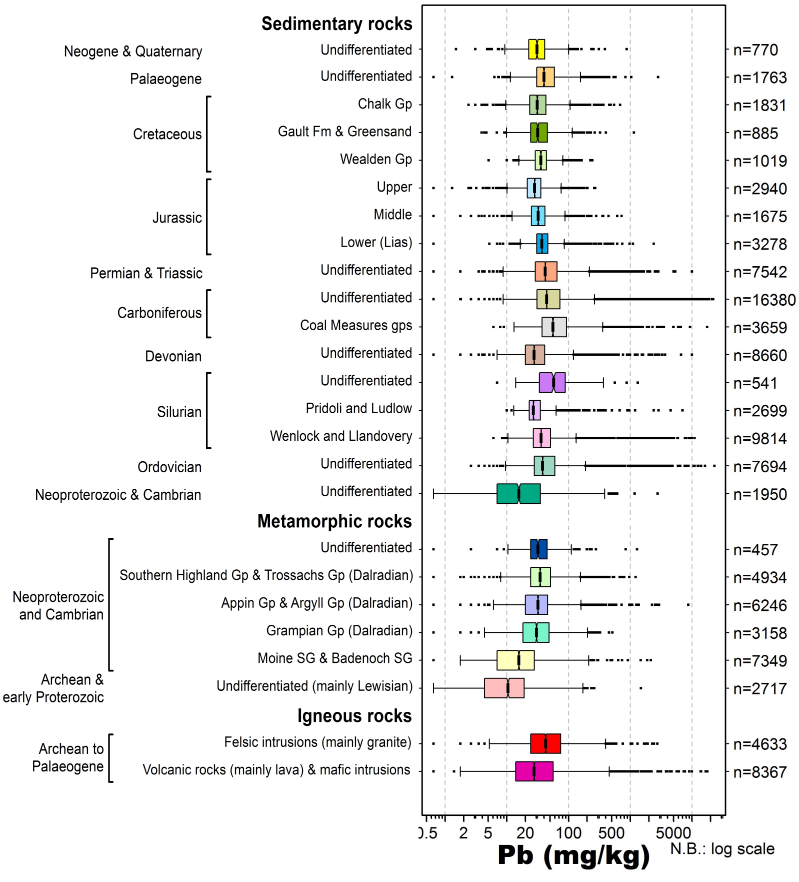
Moderate to high (33.8 – 583.6 mg/kg) sediment Pb concentrations are associated with felsic igneous intrusive rocks including the granites of north-east Scotland, south-west Scotland, Arran, south-west England and the Mourne mountains in northern Ireland. Felsic igneous rocks are typically enriched in Pb due to the relatively high proportion of K-feldspar they contain (De Vos and Tarvainen 2006). Rocks of the Carboniferous Coal Measures in Scotland, England and Wales typically yield high sediment Pb (52.8 – 146 mg/kg), possibly reflecting the organic matter and sulphide content of the coal-bearing strata within this sequence (Pb has an strong affinity for organic matter (see Alloway 2013)).

The UK has extensive Pb ore deposits that have been mined since pre-Roman times. Consequently, very high sediment Pb concentrations (> 146 mg/kg) occur in areas with metalliferous mining and mineralisation. The single highest value (22,982 mg/kg) occurs in the Lake District, downstream of historic mine workings near Dufton, and is associated with high levels of Zn and Ba; several other very high Pb concentrations were measured in this area. Extensive areas of high Pb in sediments are related to Pb-Zn-Ba mineralisation in the North and South Pennine Orefields in central England, the Central Wales Orefield to the east of Aberystwyth, and in Northern Ireland over the South Armagh – Monaghan Mining District. Other ore-mining related high Pb anomalies occur at Halkyn Mountain and Snowdonia in Wales; the Shelve mining district near the Welsh-English border; the Mendip orefield south of Bristol, the mineralised province of south-west England, the Lake District in north-west England, and at Leadhills in southern Scotland.

Very high sediment Pb concentrations (> 146 mg/kg) are also associated with urban areas, where the former use of Pb in petrol and paint, heavy industry, and fossil fuel burning have contributed to a significant anthropogenic impact. This is particularly evident around cities such as London, Birmingham and Glasgow.

Full page maps

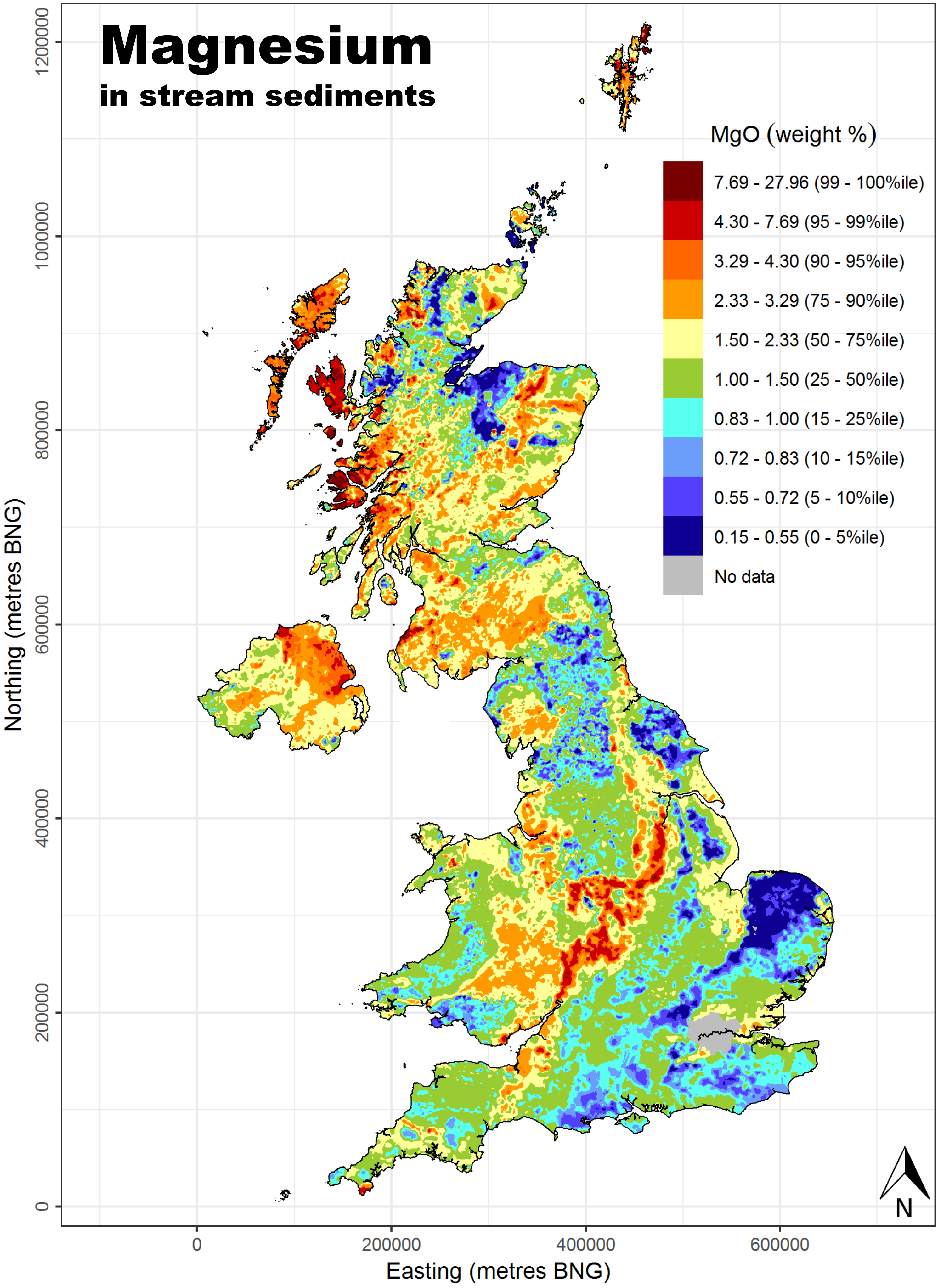
Legend and Boxplot



Show geology map **More (...)**

Magnesium

in stream sediments



Toggle map symbology: Percentile classified | Continuous scale

Distribution

Sediment Mg concentrations are expressed as magnesium oxide (MgO), and range from 0.15 to 27.96 wt%, with a median concentration of 1.5 wt%. MgO concentrations are primarily controlled by the composition of the underlying bedrock; little evidence of anthropogenic influences is discernible in the national scale maps.

Many of the lowest (<0.83 wt%) concentrations are observed across the Chalk Group in east and south-east England, where the bedrock is predominantly comprised of calcium carbonate minerals. Some other areas of similarly low MgO in Scotland (such as around Inverness) are associated with felsic igneous intrusions, relatively quartzo-feldspathic sandstone and metasedimentary bedrock. At the North York Moors and in parts of eastern England, the Middle Jurassic sequence is well defined by low Mg concentrations, due to its predominantly siliciclastic composition (BGS 1996).

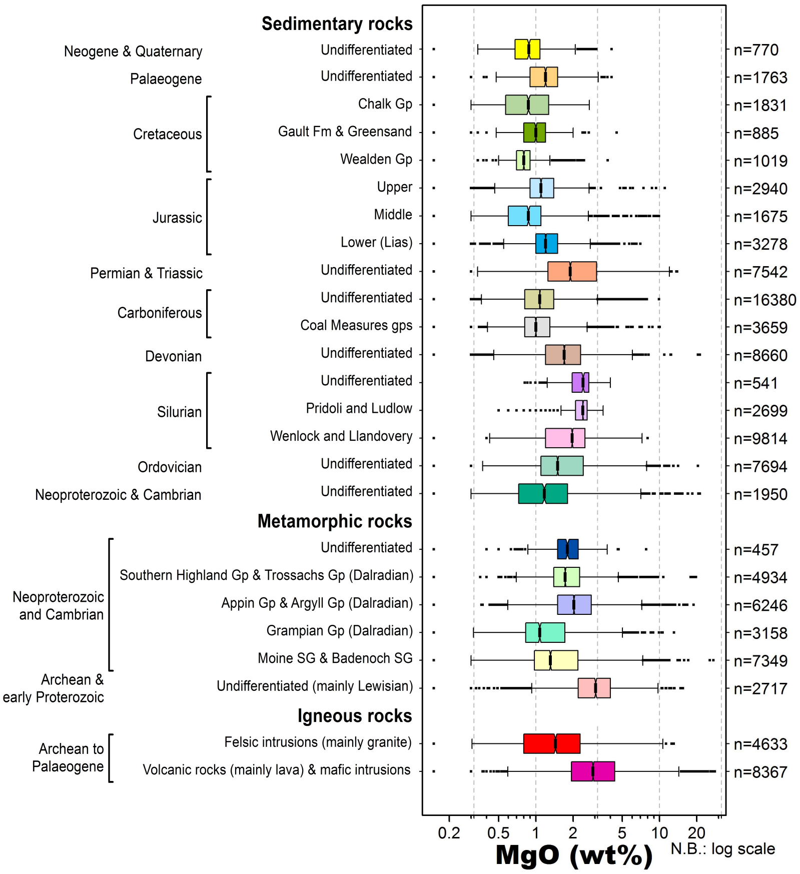
Sediment MgO concentrations are generally moderately low (<1.5 wt %) across most of the Carboniferous sedimentary rocks of the UK. Moderately high MgO (1.5 – 3.29 wt%) concentrations characterise sediments over the Devonian and the Silurian Pridoli and Ludlow successions of the Welsh borders and east Wales, as well as the Ordovician and Silurian (Wenlock and Llandovery) bedrock of southern Scotland. MgO raised to moderately high concentrations in sediments collected over bedrock assigned to the Argyll and Appin Groups has been variously produced by the presence of dolomitised carbonate metasediments, Mg-rich calc-schists and metabasic rocks within these predominantly metasedimentary, but lithologically diverse, bedrock units (BGS 1992a).

High MgO concentrations (>3.29 wt%) are measured in sediments collected over volcanic rocks and mafic igneous intrusions. This is particularly evident across the Palaeogene (mainly basaltic) lavas that crop out widely across the Inner Hebrides and Northern Ireland. Mafic and ultramafic intrusives, such as those in north-east Scotland and ophiolite complexes at Ballantrae (south-west Scotland), Portsoy (north-east Scotland) and the Lizard in south-west England are also well defined by high MgO concentration in stream sediments. Sediment MgO concentrations are also high across the outcrop of Permian rocks in central England between Bristol and Middlesbrough, reflecting Mg enrichment in the dolomitic limestone in this succession. Over the Permian Mercia Mudstone unit, elevated Mg values are spatially coincident with high K_2O content in stream sediments. The presence of evaporate deposits and relatively high proportions of clay minerals within these underlying strata are interpreted to be the source of elevated MgO (and K_2O) (BGS, 1996; Haslam and Sandon, 1990).

Locally enhanced (1.5 – 2.33 wt%) MgO sediment concentrations are observed over the alluvial deposits of the Fens, the Lincolnshire marshes and the Essex marshes, where marine inundation has led to increased Mg. It is possible that a similar influence is present across the Somerset levels in south-west England, where higher levels of sediment MgO are also measured, but these may also reflect the underlying Permian Mercia Mudstone Group strata.

Full page maps

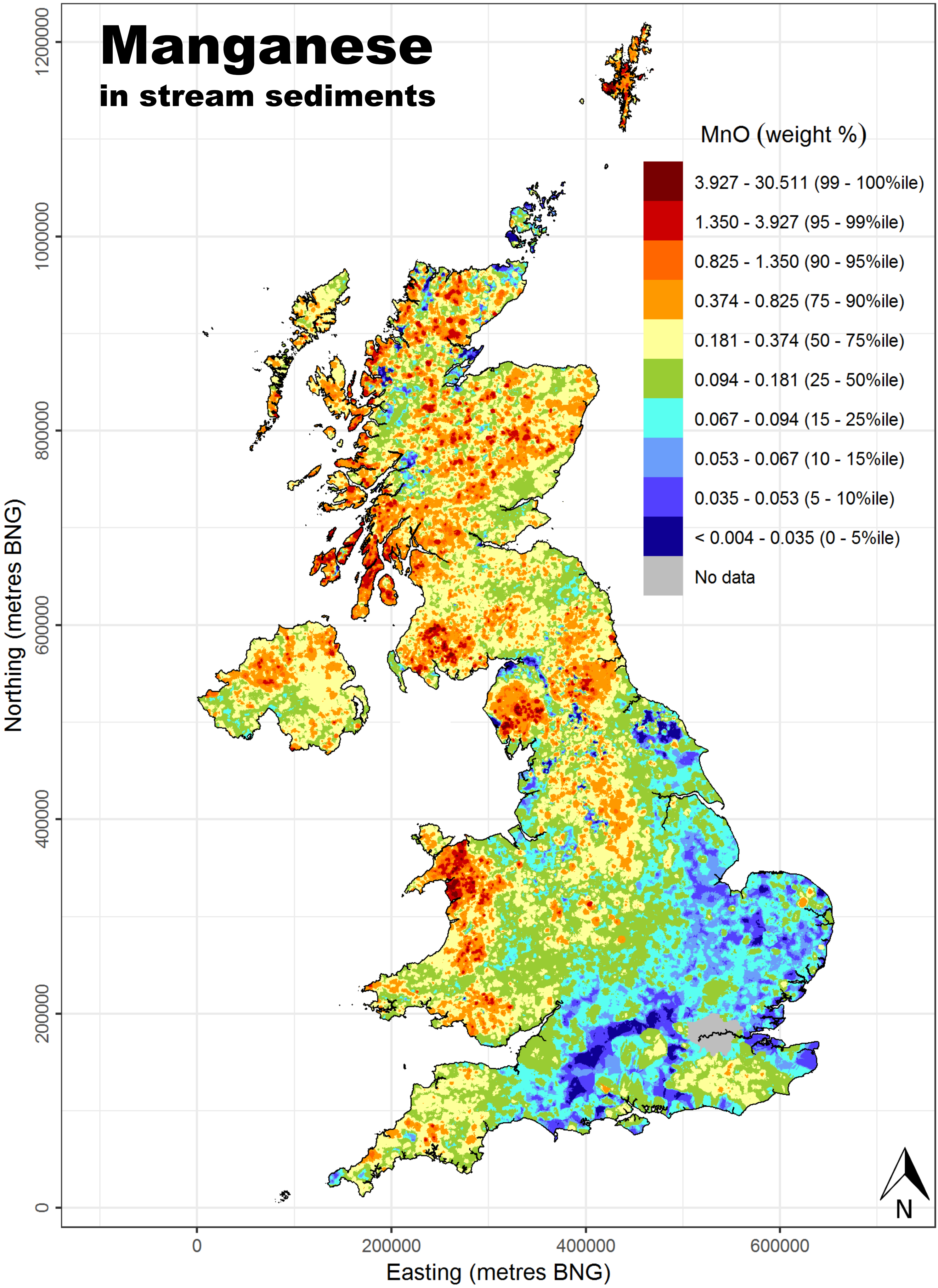
Legend and Boxplot



Show geology map **More (...)**

Manganese

in stream sediments



Toggle map symbology: Percentile classified | Continuous scale

Distribution

Sediment Mn concentrations are expressed as manganese oxide (MnO), and range from <0.004 – 30.511 wt%, with a median of 0.181 wt%. MnO distribution shows some primary lithological control, but strong secondary surface environment influences. MnO, Fe_2O_3 and Co concentrations are spatially associated, particularly where Mn has accumulated as secondary hydrous oxides during co-precipitation processes, a common factor in acidic surface environments such as upland areas with peaty soil cover.

The lowest (<0.067 wt%) MnO sediment concentrations observed across the UK occur in eastern and southern England, over areas underlain by sedimentary rocks of mid Jurassic age and younger, in particular the Cretaceous Greensands and Chalk.

Typically, MnO distribution over Silurian, Devonian and Triassic rocks show clear similarities to that of Fe_2O_3, with concentrations of MnO within the mid-range (0.094 wt% - 0.374 wt%) of the distribution. Little clear differentiation between lithological units can be discerned, likely due to the influence of secondary processes; for example, Wenlock and Landovery rocks in west Wales exhibit elevated MnO (0.181 – 3.927 wt%) which, in association with coincident low stream water pH and elevated Fe_2O_3, suggests this enrichment is due to the formation of secondary hydrous Mn (and Fe) oxides (BGS, 2000), rather than a primary lithological influence. Similar influences may also be responsible for the more limited enrichment (up to 0.825 wt%) displayed in sediments collected over the Cretaceous rocks of the Wealden Group.

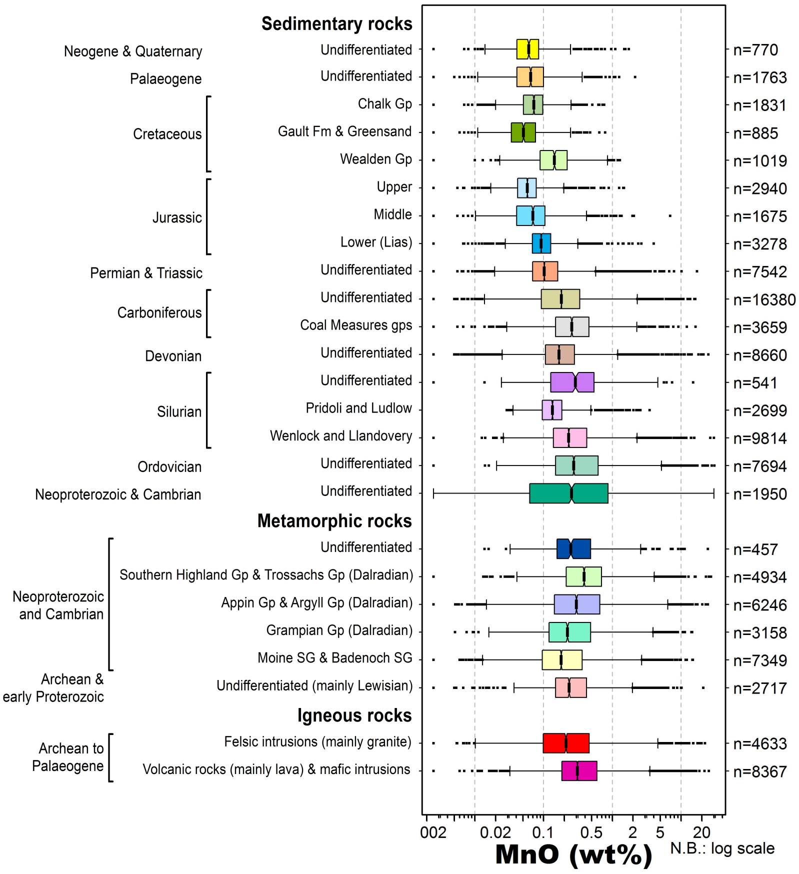
MnO levels over Carboniferous rocks are generally moderate (0.094 wt% - 0.374 wt%), but higher (>0.374 wt%) levels over the Coal Measures in Wales and central England are seen. Since these rocks crop out over upland areas with peaty soil cover, it is likely that enhanced Mn hydrous oxide precipitation is related to the upland areas; acid mine drainage from coal mines can cause further enrichment.

A broad range of MnO concentrations are displayed by sediments across the Moine and Dalradian Supergroups in northern Scotland, and lithostratigraphic boundaries are mostly indistinguishable. Sediment MnO levels here are, however, considerably higher than over the adjacent Devonian strata to the south of the Highland Boundary Fault, reflecting greater secondary precipitation of Mn oxides in the upland, organic-rich peaty soil and acidic stream water conditions north of the fault (BGS, 1992a). A clear pattern of Mn enrichment in upland areas (see also the Lake District) of the UK as a whole is observed for these reasons.

Prominent, very high MnO concentrations (in excess of 3.927 wt% in places) in north Wales relate to the Cambrian sedimentary rocks of the Harlech Dome which are rich in Mn (BGS 2000), as well as the presence of Mn mineralisation. Other parts of the UK where very high MnO is observed include the Shetland Islands, the Western Isles of Islay and Jura, the Kintyre Peninsula, and south-west Scotland, where the highest MnO concentration reported in UK stream sediments (30.5 wt%) occurs in association with elevated Co (159 mg/kg), Zn (971 mg/kg) and Fe_2O_3 (9.36 wt%), in coniferous forest with peaty soil, and again is most likely to be attributable to secondary oxide co-precipitation processes (BGS 1993).

Full page maps

Legend and Boxplot



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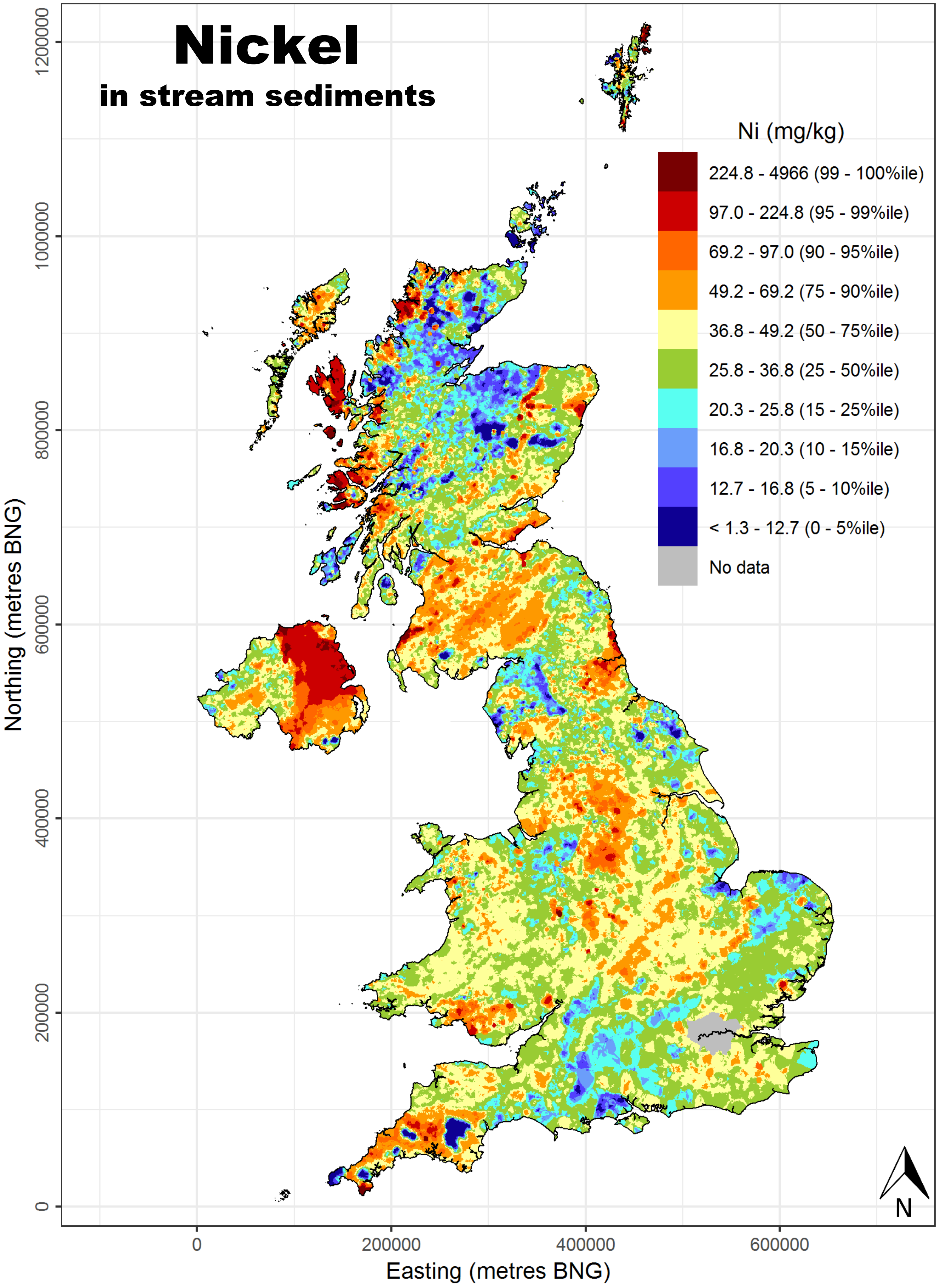


Toggle map symbology: Percentile classified | Continuous scale

Distribution

Sediment Ni concentrations range from < 1.3 to 4966 mg/kg, with a median value of 36.8 mg/kg. The lowest and highest concentrations are generally associated with felsic and mafic igneous rocks, respectively.

Similarly to Cr, the lowest Ni concentrations (<1.3 mg/kg) are reported in sediments collected over evolved felsic igneous intrusions, such as those between Aberdeen and the Cairngorm Mountains in Scotland, in south-west England, and the Mourne Mountains in Northern Ireland. The extents of these granite bodies are clearly delineated by anomalously low Ni sediment concentrations.

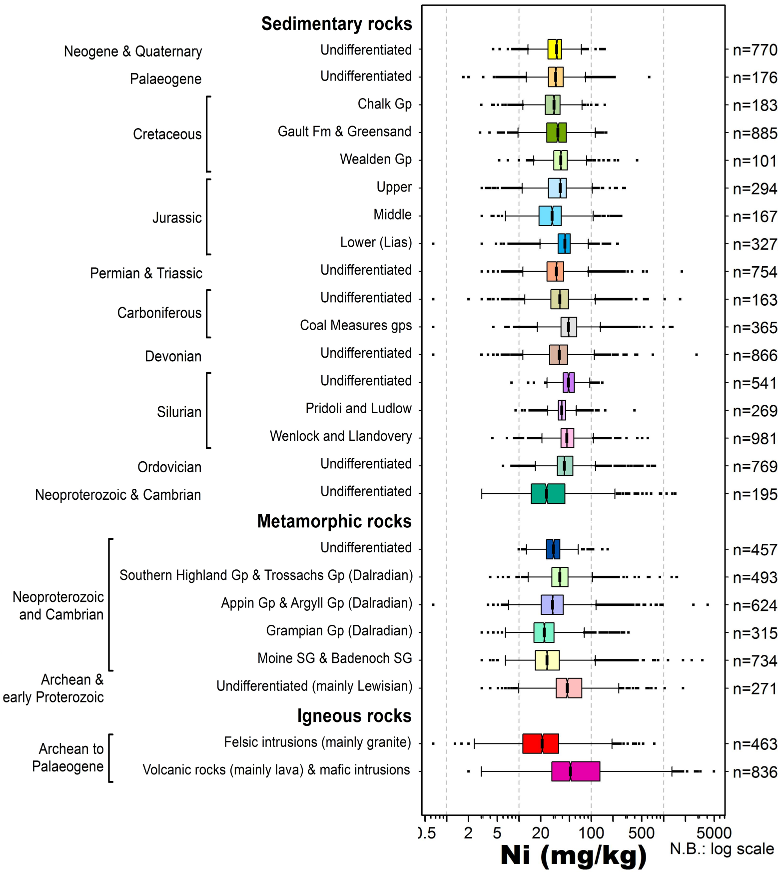
The metamorphic terrains of northern Scotland generally exhibit low stream sediment (<25.8 mg/kg) Ni concentrations, particularly over parts of the Moine Supergroup and the Grampian, Argyll and Appin groups of the Dalradian. Locally, higher Ni concentrations occur in some samples collected close by small-scale mafic intrusions and metamafic rocks hosted by these units. Similarly low Ni concentrations are evident over Permian and Triassic rocks of the Lake District, clay-rich sedimentary rocks of Jurassic age in the North York Moors, and parts of the Cretaceous Great Oolite Group and Jurassic White Chalk Group in central-southern England. Low concentrations of Ni to the west of Glasgow relate to trachytic volcanic rocks within the Clyde Plateau Volcanic Formation; parts of this compositionally diverse volcanic formation are comparatively mafic and produce higher sediment Ni concentrations.

The sedimentary rocks of the UK, from Ordovician in west Wales to the Cretaceous in south-east England, generally exhibit Ni stream sediment concentrations in the moderate to elevated range of 25.8 – 69.2 mg/kg, with localised high concentrations of up to 97 mg/kg. Concentrations over the Lower and Middle Jurassic rocks in central England are at the higher end of the range and correspond to elevated sediment Cr and Fe_2O_3 values, reflecting the presence of ironstones in the bedrock. Sediments over the Greensand units also display higher Ni values coincident with higher Fe and Cr; this pattern relates to the presence of ironstones and glauconite within this bedrock unit (Ellison et al. 2002). Marked lithological control is evident over Silurian rocks of southern Scotland, where differentiation between individual bedrock units can be discerned, reflecting different source provenance in the underlying metasedimentary sequence (Stone et al. 1991). The Carboniferous Coal measures of south Wales, central England, north-east England and central Scotland yield sediment Ni in higher abundance, typically ranging from 36.8 – 224.8 mg/kg, reflecting higher Ni content in these underlying organic-rich strata.

The highest concentrations of sediment Ni (>97 mg/kg) are associated with mafic and ultramafic rocks, as exhibited by the Palaeogene lavas in Northern Ireland and the islands of the Inner Hebrides in Scotland, and the ultramafic complexes of The Lizard in south-west England and Unst in the Shetland Islands, where the single highest (up to 4966 mg/kg) Ni concentration reported in the UK stream sediment dataset occurs. Widespread, relatively high Ni concentrations in south-west England are also related to the presence of small-scale mafic volcanic horizons dispersed throughout Devonian bedrock.

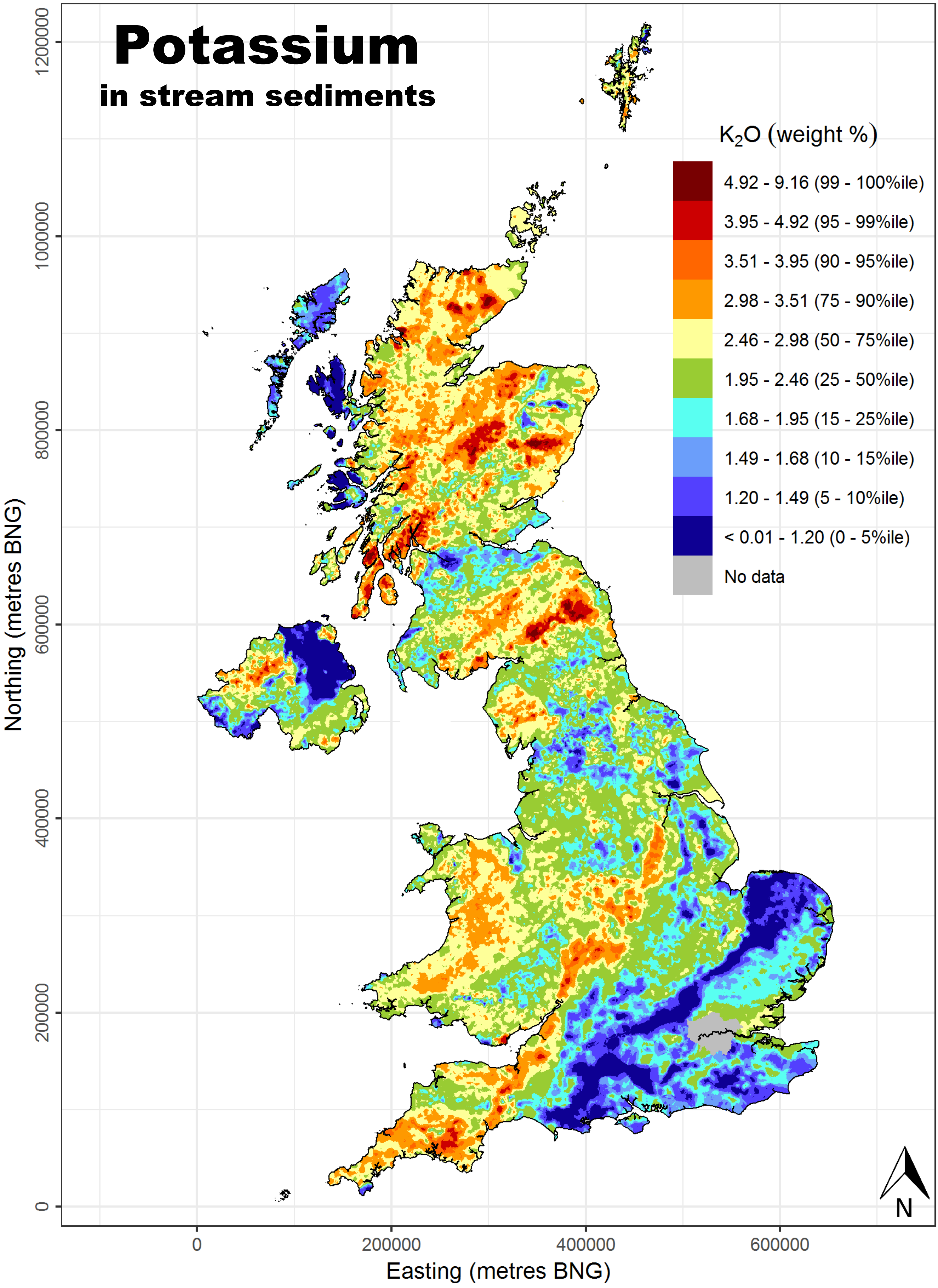
Full page maps

Legend and Boxplot



Show geology map

More (...)



Toggle map symbology: **Percentile classified** **Continuous scale**

Distribution

Sediment K concentrations are expressed as potassium oxide (K_2O), and range from < 0.01 to 9.16 wt%, with a median concentration of 2.46 wt%. Potassium concentrations in UK stream sediments are primarily controlled by the composition of the underlying bedrock, with little influence from anthropogenic activity or secondary processes being discernible in the national scale maps. This single type of control and the presence of K as a common major element in a wide range of rock types is reflected by the near-normal distribution of the measured K_2O data. The most notable features of the K_2O distribution map can be attributed to variations in the proportions of K-feldspars, micas, and clay minerals in the underlying bedrock.

The Cretaceous Chalk Group is characterised by very low (<1.49 wt%) stream sediment K_2O concentrations, which are related to its largely calcareous composition. While still below the median, locally higher sediment K_2O concentrations delineate the underlying Gault and Lower Greensand Formation and part of the Wealden Group due to comparatively more argillaceous, clay-rich strata in these units, with glauconite in the Greensand Formation (Ellison et al. 2002) also potentially contributing to increased K_2O.

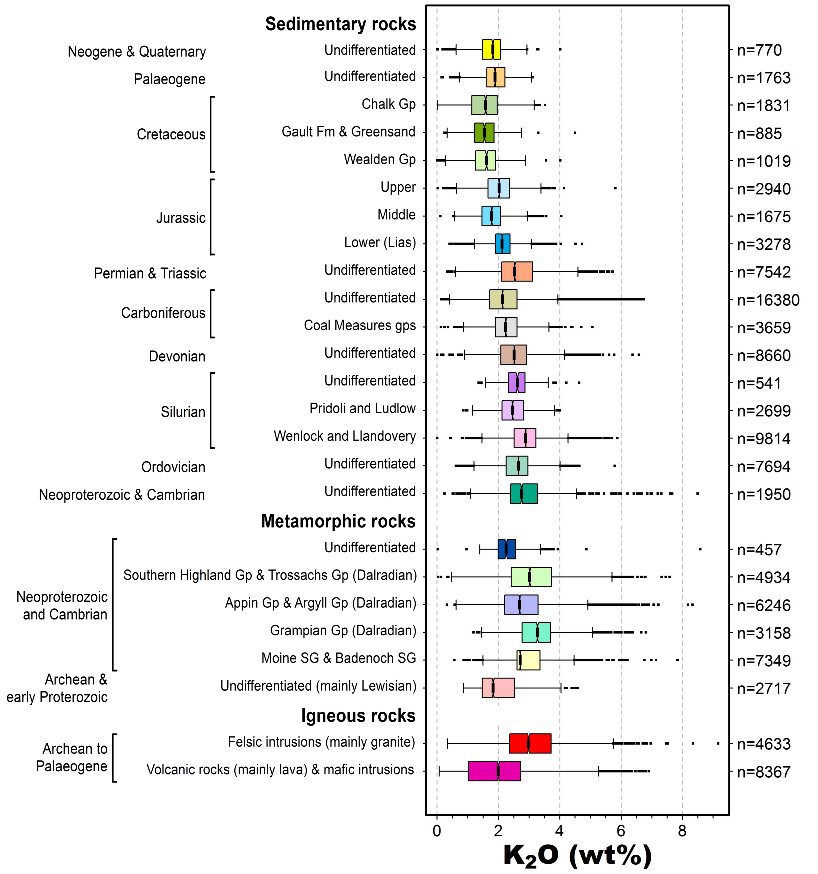
Concentrations of K_2O in stream sediments are generally low (<1.49 wt%) over mafic igneous and volcanic rocks, but are high (>2.98 wt%) across felsic igneous intrusions. This reflects magmatic differentiation processes whereby K is concentrated in more evolved (i.e. felsic) magmas, which accordingly form igneous rocks with greater proportions of K-bearing minerals such as alkali feldspars. As well as K, several other elements including Rb, caesium (Cs), strontium (Sr) and Ba (known as Large-Ion-Lithophile Elements (LILE)) also behave in this manner (White 2013). Stream sediments over the Archean and early Proterozoic (Lewisian) metamorphic rocks of north-west Scotland typically low K_2O values (<1.95 wt%), because LILE were expelled from these rock units due to deep-seated metamorphism (BGS 1990).

Sediment K_2O concentrations are generally below the median (2.46 wt%) across most of the UK's Carboniferous sedimentary sequence, which, although lithologically varied, consists predominantly of arenaceous sandstones. Moderately elevated (above the median, 2.46 wt%) sediment K_2O concentrations across the Ordovician, Wenlock and Llandovery successions of Wales are co-incident with elevated La concentrations, suggesting that the K (and La) is probably hosted by alkali feldspar and derived from a felsic/feldspar rich sediment source. Similar concentrations are observed over the relatively argillaceous Devonian strata in south-west England.

Close correspondence between high K_2O (>2.98 wt%) and high Mg values are notable in sediments over the argillaceous rocks of the Mercia Mudstone Group (within the Permian and Triassic succession), which is interpreted to reflect the high abundance of clay minerals and evaporite deposits in this rock unit. Similarly high values prevail over the felsic igneous intrusions of the UK.

Full page maps

Legend and Boxplot



Show geology map

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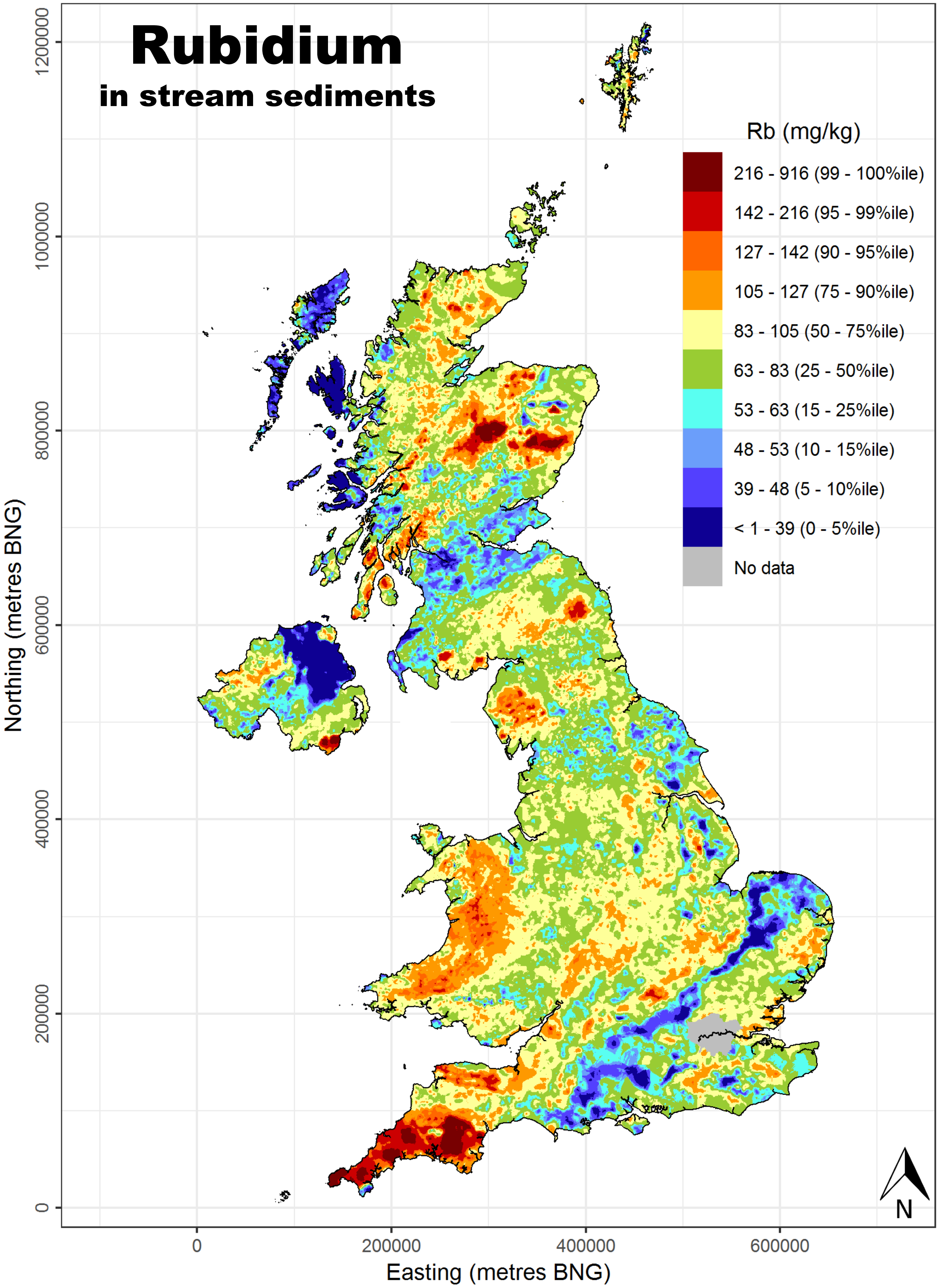


Rubidium

in stream sediments

Toggle map symbology: Percentile classified | Continuous scale

Distribution

Sediment Rb concentrations range from <1 – 916 mg/kg, with a median value of 83 mg/kg. The distribution of Rb throughout the UK shows strong lithological control and is closely associated with the regional distribution of K_2O, as Rb in detrital sediment normally occurs in K-feldspars, micas and clay minerals (De Vos and Tarvainen 2006). In general, the lowest concentrations occur over calcareous chalk and mafic igneous rocks. The highest concentrations are reported over felsic igneous rocks, reflecting their higher degree of magmatic evolution.

The Palaeogene lavas of Northern Ireland and the Scottish Inner Hebrides Islands display uniformly very low (<39 mg/kg) concentrations of Rb, indicative of the low K-feldspar content of these mafic igneous rocks. Over the Precambrian Lewisian Complex rocks of the Outer Hebrides, Rb values are typically at the low to very low end of the concentration range.

Low to very low (up to 63 mg/kg) Rb concentrations are also evident over the Cretaceous Grey Chalk subgroup of south-east England where this highly calcareous unit exhibits good lithological control on stream sediment chemistry. Parts of the adjacent White Chalk subgroup yield sediment Rb in similar concentrations. A noteworthy area of low sediment Rb concentrations is observed in the Midland Valley of Scotland, reflecting the occurrence of several extrusive mafic lavas in the region. Concentrations in the surrounding stream sediments are also low, a reflection of the low K-feldspar content of the underlying Carboniferous sedimentary rocks of this area.

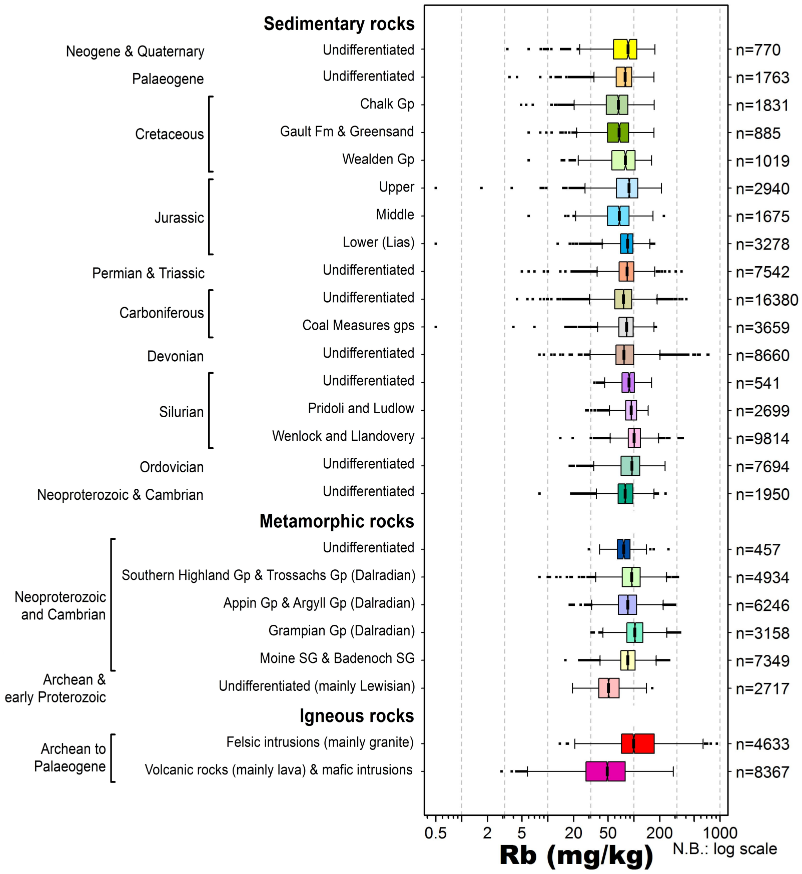
Over large tracts of the sedimentary rock sequences of the UK, stream sediments display Rb concentrations in the range 63 – 105 mg/kg. Some regional enhancement (up to 142 mg/kg) is seen over undifferentiated Triassic rocks in south-central England and, in particular, over the mid-Jurassic Kellaways and Oxford Clay Formations, where lithological control is evident. Sediment Rb concentrations across the metasedimentary rocks of the Moine and Dalradian Supergroups of northern Scotland fall into the same range.

Consistently moderately high (105 – 142 mg/kg) concentrations of Rb are displayed over Silurian rocks of west Wales, with little variation between units. By contrast, concentrations over the Devonian and Carboniferous basins of south-west England typically range from 63 – 216 mg/kg with evidence of strong lithological control. However, some of these higher Rb concentrations within samples collected close by the prominent granite intrusions of the area may be related to detritus derived from the granite being incorporated within stream sediments. This influence is probably further enhanced by the extensive china clay mining activity around the St Austell granite (Kirkwood et al. 2016).

The highest Rb concentrations (>216 mg/kg) occur over felsic igneous rocks in north-east and southern Scotland, the Mourne Mountains of Northern Ireland, the Lake District and south-west England, where the highest recorded Rb concentrations in the UK occur over the St. Austell granite. The extents of the felsic igneous bodies are clearly delineated by the surface expressions of their Rb content.

Full page maps

Legend and Boxplot



Show geology map

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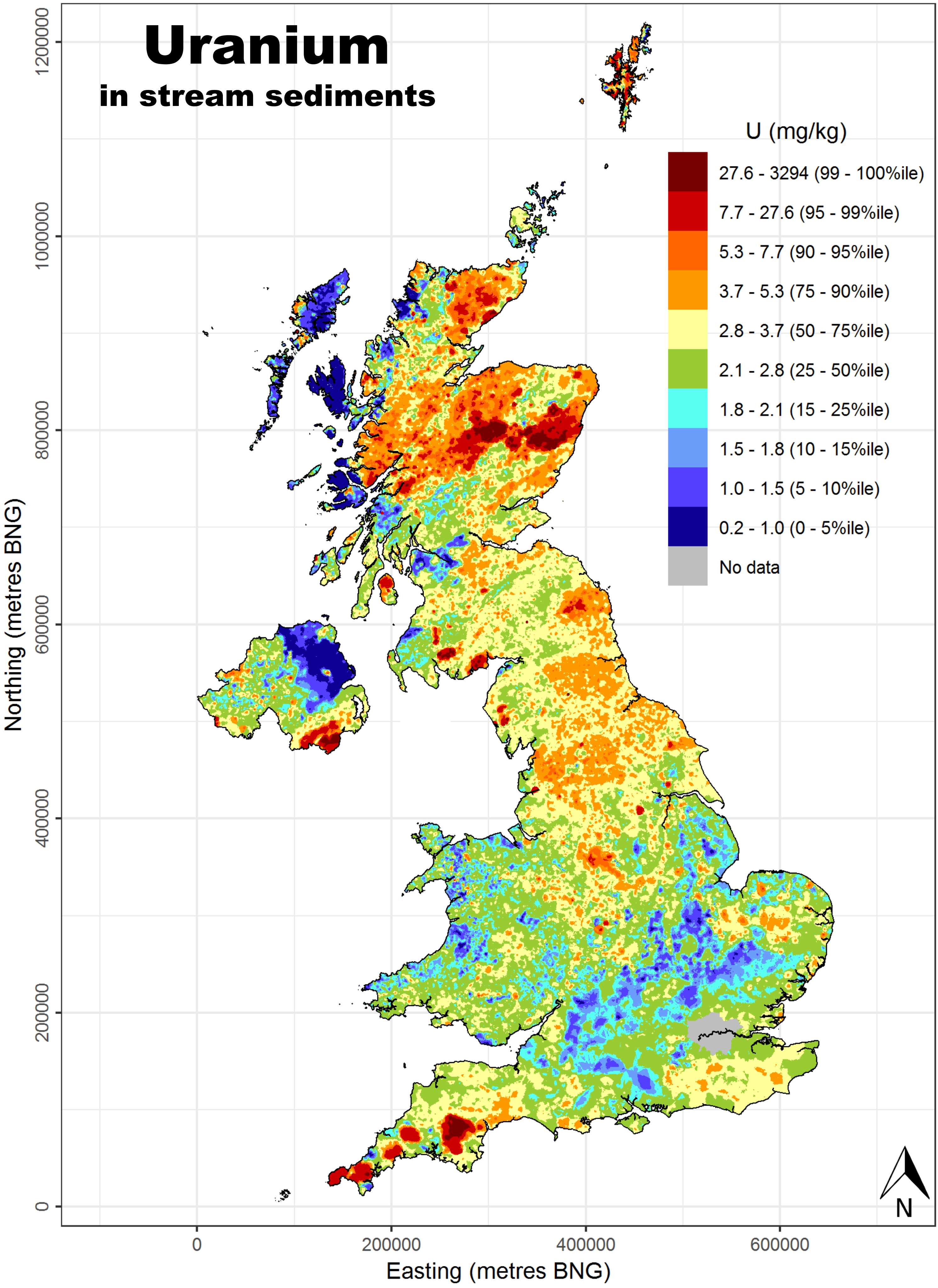

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Distribution

Sediment U concentrations range from 0.2 mg/kg to 3294 mg/kg, with a median concentration of 2.8 mg/kg. The distribution of U is principally controlled by the occurrence of igneous rocks, with low to very low concentrations being associated with mafic rocks, and the highest concentrations with felsic rocks. Sedimentary processes also affect U distribution: U can be enriched in organic-rich sediment, and it also displays a strong correlation with Zr, reflecting its tendency to be concentrated in resistate minerals such as zircon, monazite and allanite (De Vos and Tarvainen 2006).

Very low (< 1 mg/kg) sediment U concentrations occur over Lewisian Complex rocks of the Outer Hebrides and north-west Scotland, which are clearly differentiated from the adjacent Neoproterozoic (Torridonian) sedimentary rocks that display higher U levels in stream sediments. Mafic, Palaeogene lavas of Northern Ireland and the Inner Hebrides also display uniformly very low sediment U concentrations. In southern and south-east England, U concentrations in the lower quartile (<2.1 mg/kg) are evident over Mid Jurassic to Cretaceous limestone and chalk strata. Small areas of enhanced stream sediment U in these areas probably result from the accumulation of resistate minerals and/or organic matter in superficial deposits.

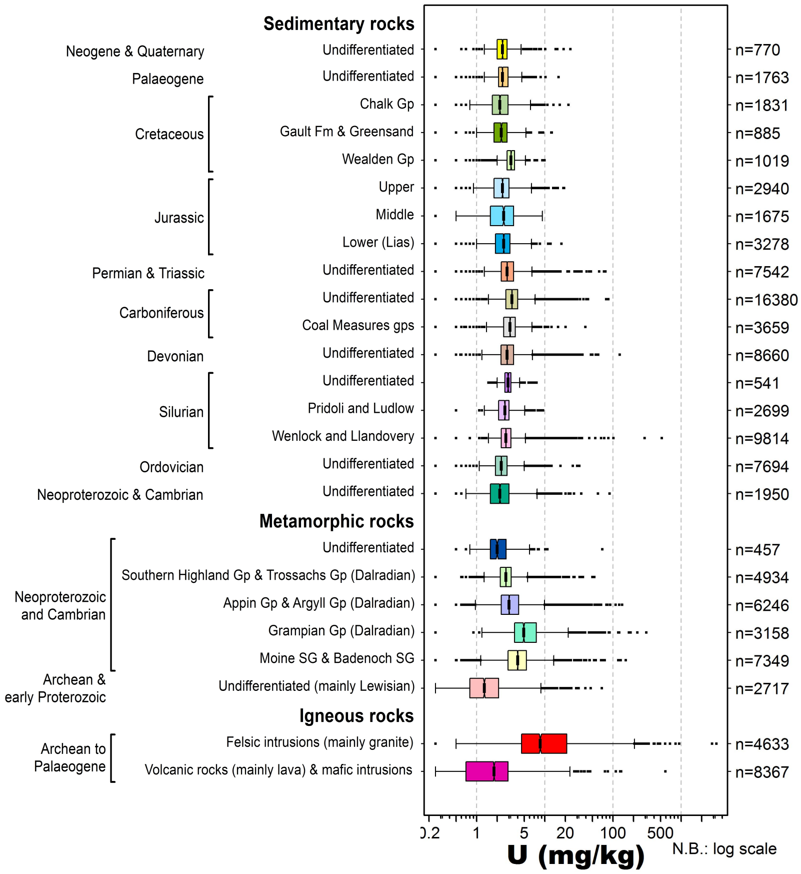
Over the Devonian and Carboniferous sedimentary rocks of south-west England, sediment U is uniformly within the range of 2.12 – 3.7 mg/kg, similar to the levels over Devonian sedimentary rocks of the Stratheden Group that crop out in the south of Scotland and immediately north of Glenrothes. Over the more extensive outcrops of Devonian strata in central and northern Scotland U concentrations are elevated (up to 7.7 mg/kg) by comparison. These are associated with enhanced Zr and therefore likely to reflect the presence of a larger proportion of resistate minerals in the bedrock. With the exception of the coal measures in south Wales and central England (where concentrations rarely exceed 3.7 mg/kg), moderate to high (2.8 – 7.7 mg/kg) U concentrations over Carboniferous sedimentary rocks are observed. These may relate to organic-rich horizons in these rocks, though correspondence with higher Zr concentrations in places suggests that resistate minerals are another influence on U distribution over the Carboniferous strata.

Over the Moine Supergroup in northern Scotland, psammite bedrock of the Morar group yields U in much lower abundance (1.5 – 5.3 mg/kg) than the adjacent migmatitic rocks to the east, where high to very high (3.7 – 27.6 mg/kg) concentrations dominate. A change in the composition of the protolith concentration of U during partial melting, or an influx of U-rich granitic material during migmatism could explain this pattern (IGS 1982). The southernmost units of the Moine Supergroup and Grampian Group are associated with high to very high U concentrations in sediments, in contrast to the Southern Highland Group, which is associated with U concentrations that range locally up to 5.3 mg/kg.

The highest sediment U concentrations occur over felsic rocks, particularly granites, many of which are extremely well delineated by anomalously high stream sediment U concentrations, e.g. those in north-east and south-west Scotland, Northern Ireland and south-west England.

Full page maps

Legend and Boxplot



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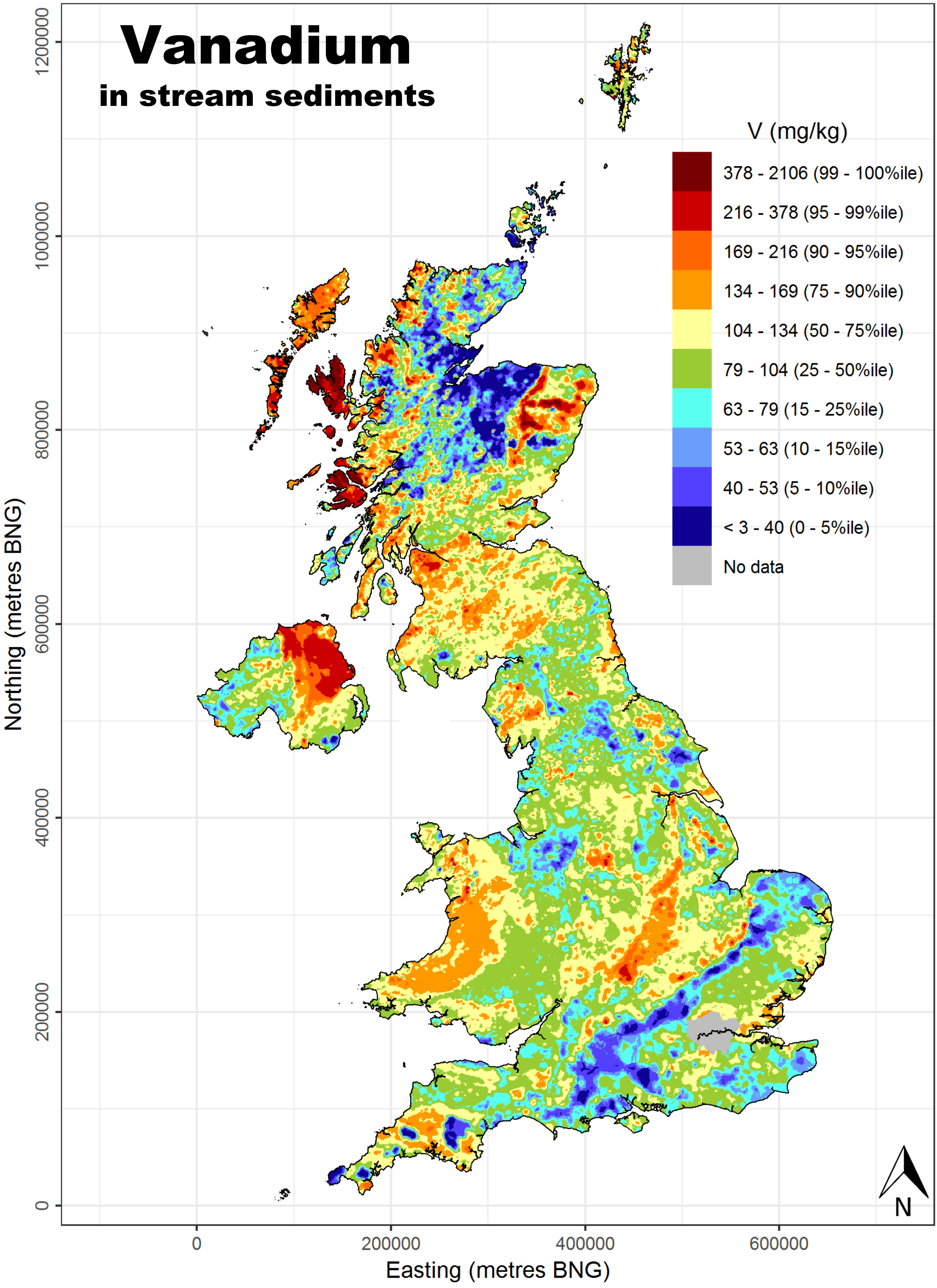

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Distribution

Sediment V concentrations range from <3 mg/kg to 2106 mg/kg, with a median concentration of 104 mg/kg. Vanadium is an element of mafic affinity (De Vos and Tarvainen 2006) and, as such, its spatial distribution is closely related to those of Cr and Ni. Therefore, the lowest and highest V sediment concentrations are associated with felsic and mafic igneous rocks, respectively. Over sedimentary rocks, the distribution of V is principally controlled by the proportion of detrital Fe-oxides and clay minerals. Strong geological control is displayed with clear differentiation evident between lithostratigraphic units in some areas.

The lowest sediment V concentrations in the UK occur over evolved felsic igneous rocks, most notably the granites of north-east and south-west Scotland, Northern Ireland (the Mourne Mountains) and south-west England, where V levels are uniformly very low (<40 mg/kg) over the centres of the mapped extents of the granitic bodies. This signature is echoed in the distributions of both sediment Ni and Cr. Very low concentrations of V (and Cr and Ni) are also seen over the north-east extent of the Dalradian Grampian Group psammites, consistent with previous findings (Plant et al. 1984). Strong geological control is evident in sediments over the Cretaceous Grey Chalk in south-east England, where concentrations of V are similarly low, with values below 79 mg/kg.

Other areas of conspicuously low V concentration include the Cheshire Basin, an area of ground to the north of Norwich, and the central Pennines, where Quaternary deposits of till and glaciofluvial sand and gravel are most likely responsible for V values generally <79 mg/kg in stream sediment samples.

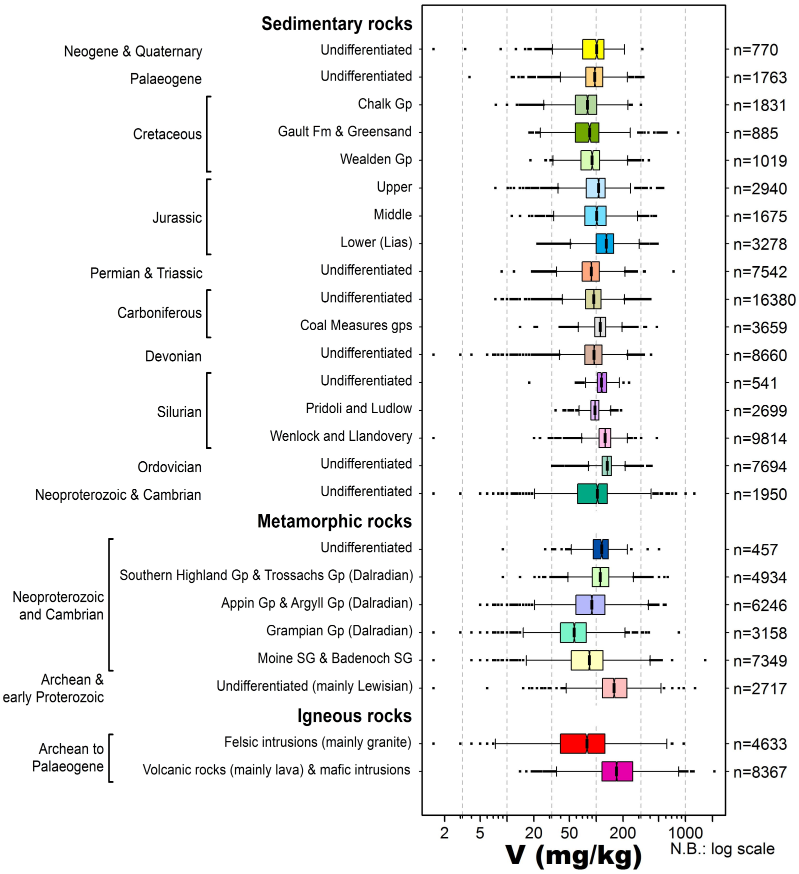
Sediment V concentrations over the Pridoli and Ludlow Silurian sequence in Wales, and Devonian, Carboniferous and early to mid-Triassic rocks throughout the UK typically fall within the mid-range of the dataset (between 63 and 134 mg/kg), with the exception of some limestone-bearing units within the Carboniferous (e.g. the Yoredale Group), which yield notably lower values in overlying stream sediments.

Older Silurian (Wenlock and Llandovery) rocks in west Wales exhibit significantly higher V concentrations in overlying stream sediments, with values up to 169 mg/kg, possibly reflecting an increased input of material derived from volcanic source rocks in this region (BGS 2000). Similar concentrations are seen over Silurian rocks of the southern Scotland and, to a slightly lesser extent, Northern Ireland. Lower and Middle Jurassic rocks in central England display good geological control, with elevated V values in the range 104 – 378 mg/kg in overlying stream sediments. This again reflects the presence of ironstones in this bedrock unit and relates to correspondingly elevated concentrations of Fe_2O_3, Cr, and Ni.

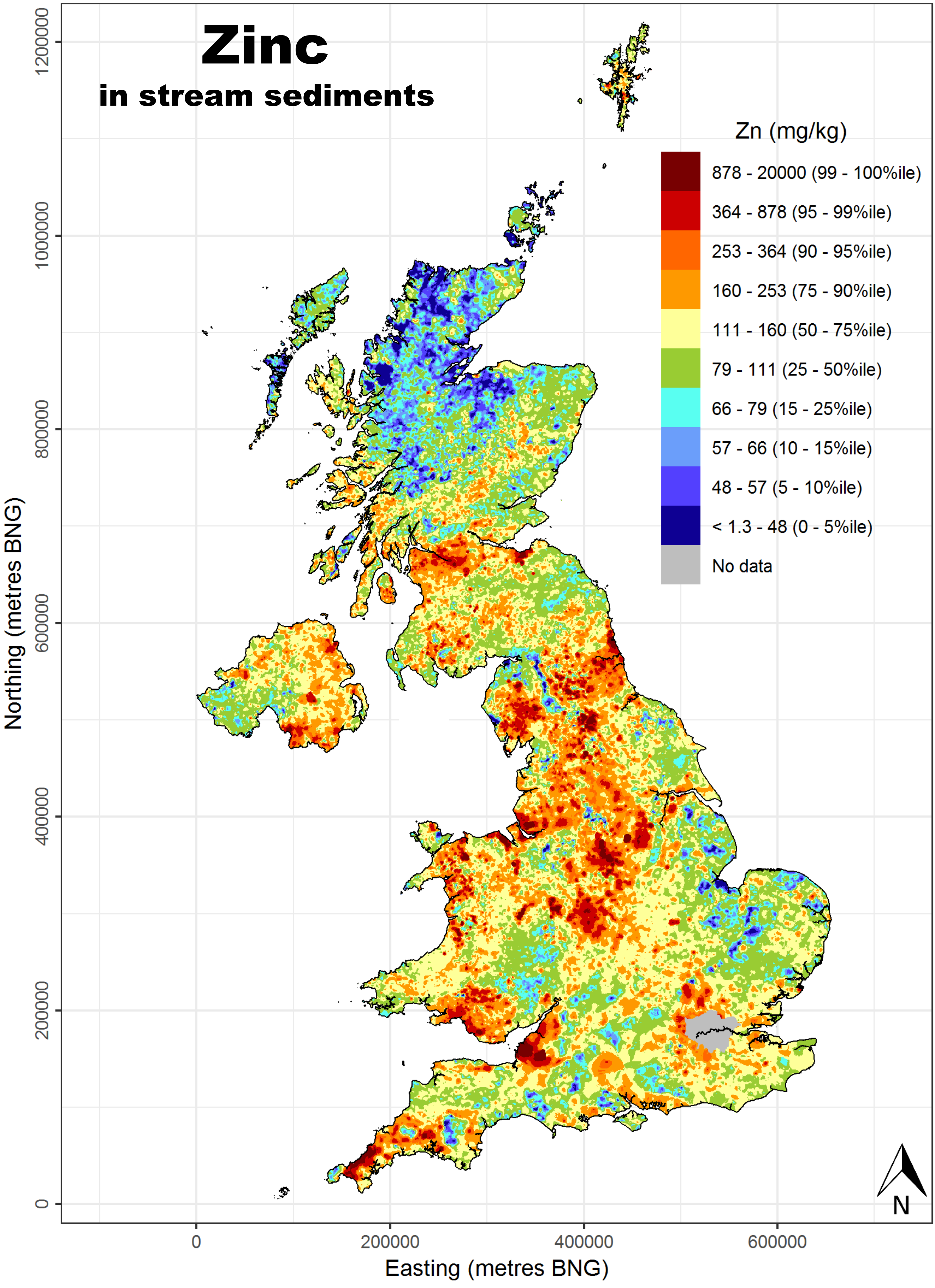
High to very high (104 – 378 mg/kg) sediment V values occur over the Lewisian Complex of the Outer Hebrides and north-west Scottish mainland reflecting the presence of amphibolites within this rock unit, while the highest V concentrations observed in the UK occur over mafic igneous rocks, in particular the basaltic lavas of Skye, Mull and Northern Ireland and mafic igneous intrusives in north-east Scotland, where the single highest value of 2106 mg/kg is located over the Tarland mafic body.

Full page maps

Legend and Boxplot



Show geology map **More (...)**



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Distribution

Sediment Zn concentrations range from < 1.3 mg/kg to 20000 mg/kg, with a median concentration of 111 mg/kg. The distribution of Zn is strongly influenced by the occurrence of metalliferous mineralisation and affected by anthropogenic activity. Where Zn is correlated with high MnO and Fe2O3, the co-precipitation of Zn with secondary Mn and Fe-oxides influences the distribution, particularly over organic-rich, peaty terrain.

The lowest (<48 mg/kg) Zn concentrations are seen over sandstones/mudstones of the Neoproterozoic Torridon Group and parts of the Moine Morar Group psammites in northern Scotland, indicating a scarcity of Zn-bearing minerals within these bedrock units. Psammites of the Dalradian Grampian Group also exhibit very low concentrations in some areas of northern Scotland. Very low values also characterise parts of the Triassic in the Lake District. Zn concentrations over the felsic igneous intrusions (granites) of south-west England are discernibly lower than those in the surrounding mineralised Devonian country rock. A number of low Zn features can be attributed to areas overlain by Quaternary deposits, principally alluvium and till, which are likely to be depleted in Zn bearing resistate minerals; the Fens in eastern England being a clear example.

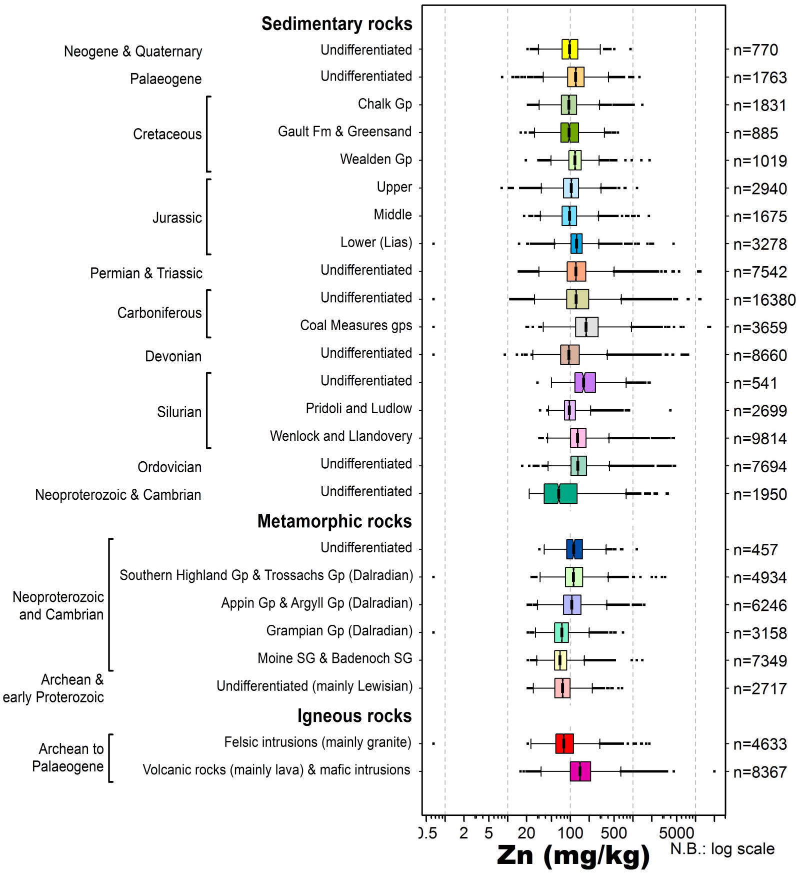
Over the sedimentary rock sequences of the UK, the distribution of Zn shows strong similarities to that of Pb, with Zn concentrations typically falling in the range between the 25th and 90th percentiles (79 – 253 mg/kg in the case of Zn). Rocks of the Carboniferous Coal Measures display above median to very high (111 – 878 mg/kg) Zn concentrations in overlying stream sediments; higher values possibly reflect the organic matter (Zn has an affinity for organic matter (Alloway 2013)) and sulphide content of the coal-bearing strata within this sequence.

Very high sediment Zn concentrations (>364 mg/kg) occur over areas associated with known mineralisation and historic metalliferous mining. In mining areas, in addition to the dispersal of mine waste, acid mine drainage may enhance the mobility of Zn and promote co-precipitation with Fe oxides, further increasing the levels of Zn measured in stream sediments. In particular, the orefields and former mining districts of the North and South Pennines, Lake District, south-west England, the Mendips, Harlech Dome and Halkyn are typically associated with very high Zn sediment concentrations and are almost always associated with very high Pb. The highest (20,000 mg/kg) Zn concentration recorded throughout the UK occurs in the Snowdonia orefield of north Wales; this anomalously high Zn value occurs in association with high As, Ba, Cu, Mo and Pb in sediment, as a consequence of sulphide mineralisation in the area.

Elevated levels around urban centres also reflect the legacy of heavy industrial activity and the associated burning of fossil fuel, which has resulted in a significant anthropogenic component of the geochemical baseline. This is particularly noticeable around larger cities including Edinburgh, Glasgow, London, Birmingham, Bristol and Leeds.

Full page maps

Legend and Boxplot



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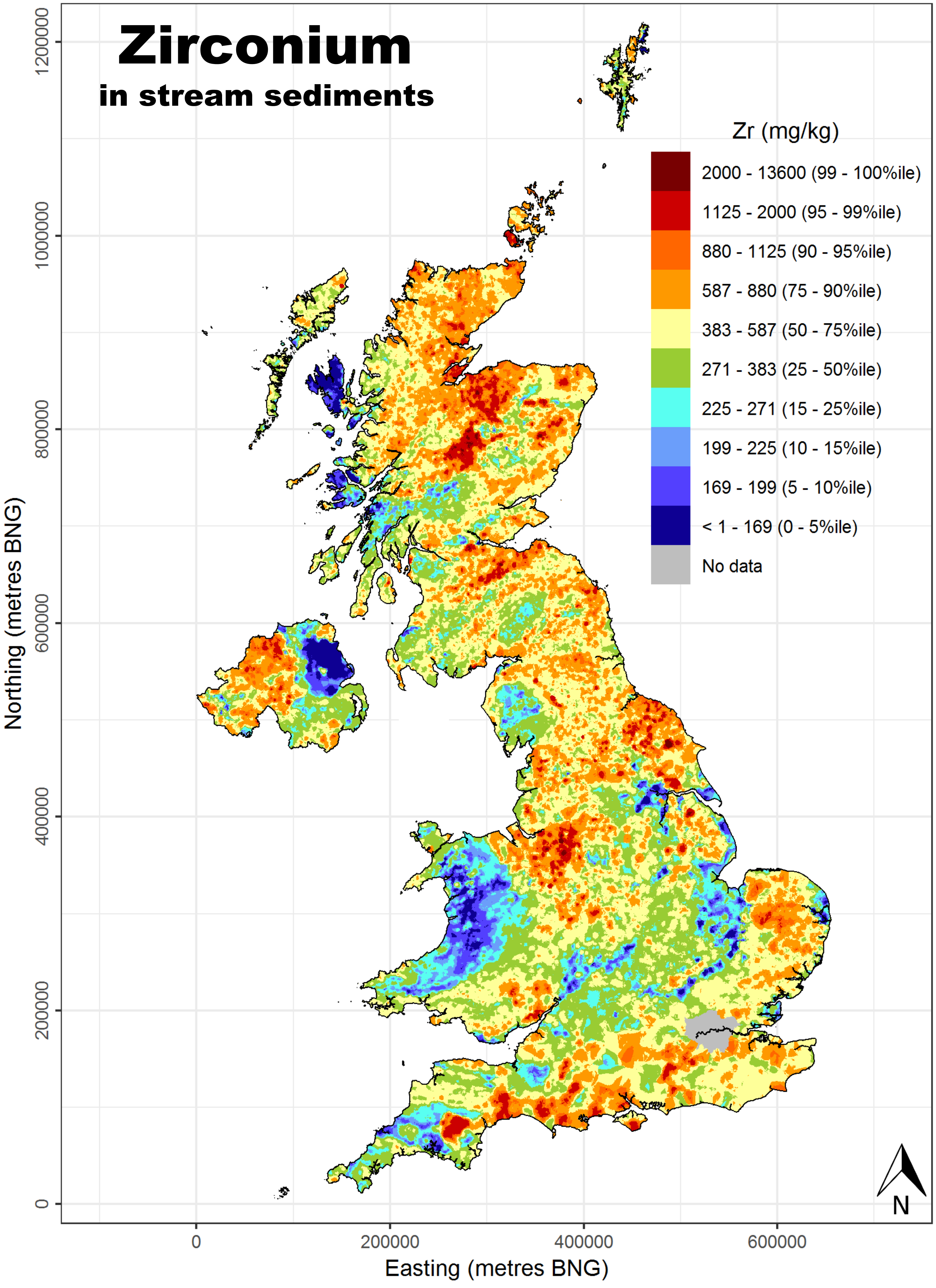

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Distribution

Sediment Zr concentrations range from <1 to 13,600 mg/kg, with a median value of 383 mg/kg. The distribution of Zr in detrital sediment is predominantly controlled by the abundance of Zr in resistate minerals such as zircon and sphene (De Vos and Tarvainen 2006). Throughout the metamorphic and sedimentary terrains of the UK, mechanical sorting of resistate grains during present day and palaeo-sedimentological weathering processes represents a major control on Zr distribution in stream sediments. Felsic igneous rocks are generally enriched in Zr relative to mafic igneous rocks (De Vos and Tarvainen, 2006) and as a result, the latter are associated with some of the UK's lowest stream sediment Zr concentrations.

The lowest Zr concentrations within the UK, with values <85 mg/kg, occur over Quaternary deposits of eastern England, east of Norwich, that predominantly consist of glacial lacustrine alluvium wherein the abundance of finer-grained sediment is likely to have diluted the relative proportion of heavier Zr minerals. Similarly low Zr concentrations are observed over alluvial deposits in other parts of the UK, such as north of Bristol (River Severn basin), Scunthorpe (River Humber basin) and Cambridge (River Ouse basin).

Very low Zr concentrations (<169 mg/kg) are widespread across mafic and ultramafic rocks of the northernmost Shetland Islands of Unst and Fetlar, Palaeogene lavas of Northern Ireland and the western Scottish islands of Skye and Mull, reflecting bedrock composition. Very low to low (<271 mg/kg) Zr concentrations dominate over rocks of Silurian age in west Wales. A notable discrete variation of sediment Zr concentration over individual parts of the Devonian-Carboniferous units of south-west England may reflect the relative abundance of resistate minerals deposited within several different sedimentary palaeo-basins preserved in the underlying bedrock. The Late Cretaceous Grey Chalk in south east England displays strong lithological control, yielding Zr concentrations in the lowest quartile of the distribution range.

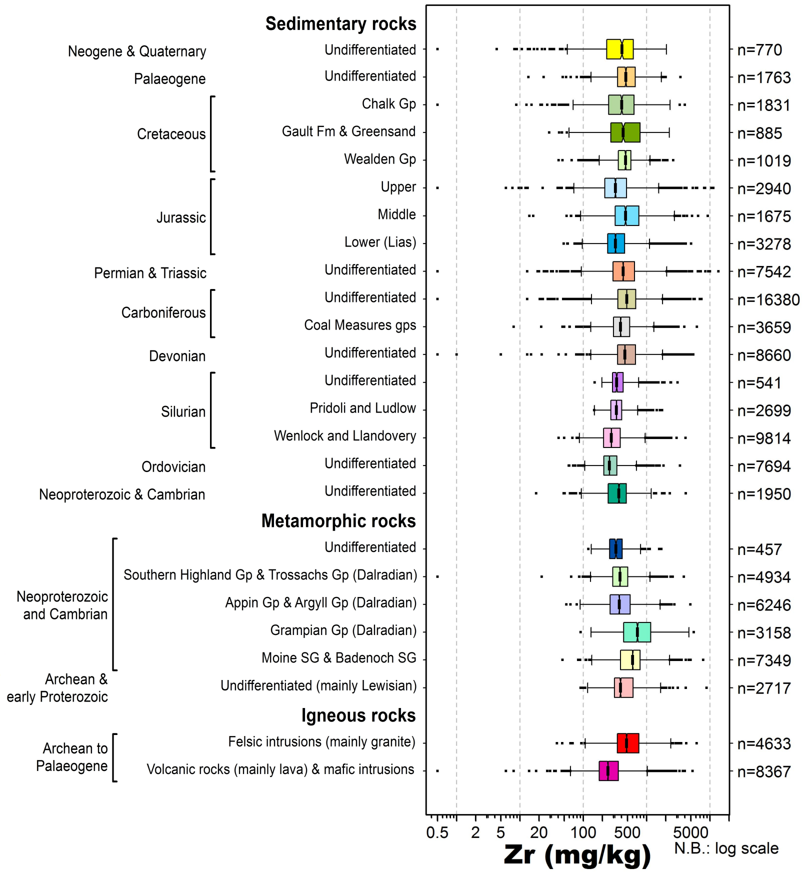
Concentrations of stream sediment Zr across the sedimentary rock sequence of the UK are variable and predominantly dependent upon the proportions of Zr-bearing resistate minerals in the underlying bedrock, with fluvio-deltaic arenaceous facies (e.g. Millstone Grit of Carboniferous age) typically enhanced in comparison to deep-water basinal deposits of fine-grained argillaceous facies (e.g. Carboniferous Limestone, and Lias rocks of Lower Jurassic age).

In northern Scotland, high Zr concentrations (>1125 mg/kg) in sediments are associated with metamorphic rocks of the Grampian Group, and Moine Supergroup, and are generally coincident with elevated U values. A similar pattern seen over metamorphic rocks of Northern Ireland can also be interpreted to reflect the presence of resistate minerals in the underlying bedrock.

Notable areas of very high Zr include sediments over the Dartmoor Granite in south-west England, the Cheshire Basin (where thick drift cover including glaciofluvial sands and gravels is considered to be the source of Zr (BGS 2000)) and Jurassic rocks of the North York Moors where the high Zr concentrations probably reflect physical concentration of resistant zircon grains in siliciclastic facies (BGS 1996a).

Full page maps

Legend and Boxplot



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Appendix: Geochemical behaviour of the elements

Arsenic

Arsenic (As) is a strongly chalcophile element and is partitioned into sulphides and sulpharsenides, forming several minerals including arsenopyrite (FeSAs), realgar (AsS) and orpiment (As_2S_3), but is more widely present as an accessory element in other sulphide minerals such as pyrite, galena and sphalerite. It is incorporated into primary rock-forming minerals, to a limited extent, by substitution of As^{3+} for Fe^{3+} or Al^{3+} in silicates. It can also be enriched in phosphates such as apatite by substitution of As^{5+} for P^{5+} (Tremearne and Jacob 1941) due to the similarity of the PO_4^{3-} and $As0_4^{3-}$ anionic groups.

Arsenic has an average crustal abundance of 1.5 mg/kg and concentrations range from 1.0 to 10 mg/kg in igneous and metamorphic rocks. In sedimentary rocks, highest concentrations (20 – 200 mg/kg) are generally found in phosphates, coal, shale and ironstone deposits (Plant et al. 2014).

Arsenic is not preferentially concentrated in felsic or mafic igneous lithologies, but can be highly enriched as a result of hydrothermal activity. Intense As anomalies are a common characteristic of epithermal ore deposits (often with enhanced Bi, Sb and Se), and the element is a valuable pathfinder for Au, Ag and platinum-group elements (e.g. Boyle 1979; Dunn 1989; Plant et al. 1989).

In sedimentary rocks, As is concentrated in clays and other fine-grained sediments, especially those rich in sulphides, organic matter or secondary Fe oxides. The average As concentration in shales is an order of magnitude greater than that of sandstones and carbonates (Wedepohl 1978). The element is strongly sorbed by hydrous oxides of Fe and Mn, with high concentrations in ferromanganese nodules and related manganiferous deposits. The highest concentrations in sedimentary rocks (20 – 200 mg/kg) are typically in phosphatic rocks (Tremearne and Jacob 1941), sedimentary ironstones, and organic-rich shales and coals.

Arsenic normally has relatively low element mobility in the environment. Due to weathering and reduction, it is released from arsenopyrite and sulphides, but in acidic conditions, it is then immobilised into compound form (Grosser et al. 1994). Arsenic is strongly adsorbed onto the surface of hydrous Fe oxides in a low pH environment (Odor et al. 1998). Manganese oxides may also have a role in adsorbing As, although Fe oxides dominate the process (Widerlund and Ingri 1995). The mobility of As is strongly governed by the oxidation state. It is released from arsenopyrite and other sulphides, due to oxidation, which may be microbially mediated (Plant et al. 2014).

Anthropogenic sources of As include coal combustion, sulphidic ore roasting and smelting, and pig and poultry sewage (Reimann and de Caritat 1998). Arsenic is generally toxic to most organisms. The toxicity depends on its speciation (As^{5+} compounds are less toxic than As^{3+}). Chronic exposure increases the risk of cancer and skin pigmentation; however, excess exposure from soil is rare in most natural settings (WHO 1996).

Barium

Barium (Ba) is a relatively common lithophile element forming several minerals including barite ($BaSO_4$) and witherite ($BaCO_3$), but is widely distributed as an accessory element in such minerals as apatite, K-feldspars, micas and calcite. The principal Ba mineral, barite, is commonly associated with occurrences of metalliferous mineralisation.

Barium has an average continental crustal abundance of 584 mg/kg (Wedepohl 1995). Its concentrations in igneous rocks ranges from 0.4 (ultramafic types) to 1600 mg/kg (syenite types); whereas in sedimentary rocks, highest Ba concentrations are associated with shale (580 mg/kg), with contents of approximately 10 mg/kg typical of carbonate and sandstone lithologies (Mielke 1979). Detrital feldspars, micas and, to a lesser extent, barite are the principal carriers of Ba in stream sediments (Ure and Berrow 1982).

During igneous processes Ba occurs mostly in K-feldspars and micas through the substitution of K^+ by Ba^{2+}, both of which have ionic radii of c. 1.45 Å (Wedepohl 1978). Barium concentrations tend to be higher in K-feldspars than in phyllosilicates. The Ba^{2+} ion also substitutes for Ca^{2+} in plagioclase, pyroxenes and amphiboles, and in the non-silicate minerals apatite and calcite. The Ba content of igneous rocks generally increases with increasing Si content (Ure and Berrow 1982), but very low concentrations (<200 mg/kg) have been reported in highly evolved granites (Plant et al. 1980).

Barium is thought to be largely immobile during prograde metamorphism, but may be subject to concentration in shear zones during post-greenschist retrogression (Drury 1974).

In sedimentary rocks, the concentration of Ba largely reflects the abundance of K-feldspars, clay minerals and hydrous Fe and Mn oxides (onto which the element may he adsorbed; Wedepohl 1978).

Barium has low environmental mobility as once weathered from rocks, it is readily precipitated as insoluble carbonate and sulphate salts. Anthropogenic sources of Ba include lead mining, paper and paint manufacturing, drilling muds in the oil industry, and in sewage treatment (Reimann and de Caritat 1998).

Barium has no known biological role. Its soluble compounds are toxic to humans, animals and plants. However, barium sulphate is insoluble, giving it a low toxicity, and health problems associated with natural environmental exposure are rare (Mertz 1987).

Calcium

Calcium (Ca) is the fifth most abundant element, constituting 5.29 % of the Earth's continental crust (McLennan and Taylor 1999). It is a widespread lithophile element, and forms several common minerals including calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$) gypsum ($CaSO_4.2H_2O$), and anhydrite ($CaSO_4$). It is also widely distributed in other minerals such as feldspar, amphibole and pyroxene, and is often associated with clay minerals such as illite, chlorite and Ca - montmorillonite (Zupancic and Pirc 1999).

Calcium concentrations in igneous rocks vary widely from 0.7 wt% in low-Ca granites to 10.63 wt% in basalts (Mielke 1979). It forms a major component of primary rock-forming minerals, such as plagioclase feldspar and diopside, and it is thus enriched in mafic and ultramafic rocks.

Calcium is generally unaffected by medium to high-grade metamorphism, but it may be mobilised during low-temperature alteration, forming secondary Ca minerals such as dolomite, calcite and garnet (Wedepohl 1978). Calcite and fluorite are also common in hydrothermal mineral veins.

In sedimentary rocks, the Ca content reflects the abundance of carbonate minerals and of detrital minerals such as plagioclase. It is accordingly a major constituent of limestones and dolomites; these carbonate sediments form an important sink in the global geochemical cycle of Ca. Calcium may also be present as calcite, dolomite, gypsum or anhydrite in sandstones, especially those in evaporite sequences. As Ca is often associated with clay minerals, Ca can also be enriched in argillaceous sedimentary successions.

Ca is often partially replaced by strontium in the calcite crystal lattice, and by magnesium in the process of dolomitisation. Calcium can also be incorporated into organic matter, e.g. as calcium carbonate in shell or bone.

Anthropogenic sources of Ca include lime and cement factories, fertilisers and dust. Geogenic sources are usually more important than anthropogenic ones in the environment (Reimann and de Caritat 1998).

Calcium is an essential nutrient for plants and animals, for the development of bones, nervous systems and cells (Emsley 2011).

Chromium

Chromium (Cr) is a lithophile element, forming several minerals including chromite and the rare crocoite, and is an accessory element in others, e.g. spinels, amphiboles, micas, pyroxenes and garnets.

Chromium has an average continental crustal abundance of 126 mg/kg (Wedepohl 1995). It is more abundant in mafic igneous rocks (1000 – 3000 mg/kg) than in granitic rocks (10 mg/kg);in sedimentary rocks, concentrations are generally higher in shales/mudstones (90 mg/kg) than in sandstones or limestones (11 – 35 mg/kg) (Mielke 1979).

Chromium is enriched in mafic and ultramafic rocks since the trivalent ion Cr^{3+} is partitioned into spinels and pyroxenes during the earliest stages of crystal fractionation, along with elements such as Mg and Ni. While the principal Cr ore mineral, chromite ($FeCr^2O^4$), is generally mined from ultramafic rocks, it is also a major carrier of Cr in basaltic magmas, along with Cr-enriched magnetite and ilmenite (Wedepohl 1978). Olivines are generally poor in Cr, but pyroxenes, amphiboles and micas may be enriched (Ure and Berrow 1982). Chromium is immobile during granulite, amphibolite and greenschist facies metamorphism (Field and Elliot 1974).

In sedimentary rocks, Cr may be present in primary detrital phases such as chromite, magnetite and ilmenite. During weathering, the behaviour of Cr^{3+} resembles that of Fe^{3+} and Al^{3+}, leading to widespread accumulation in secondary oxides and clays. Chromium concentrations are generally higher in mudrocks than in limestones, with the Cr content of arenites being very variable, depending on the source and content of the detrital heavy mineral fraction.

Anthropogenic sources of Cr include copper smelting, metal electroplating, tanning, the chemical industry, engineering and waste incineration (Reimann and de Caritat 1998).

The Cr^{3+} form, which predominates in most natural environments, is considered relatively harmless at levels normally encountered. It is an essential element, needed by the human body in small amounts for insulin action and metabolism of proteins and carbohydrates. However, Cr^{6+} (the largely industrial form) is toxic (causing liver and kidney damage) and a carcinogen, but health problems outside of occupational exposure are rare (WHO 1996).

Cobalt

Cobalt (Co) is a chalcophile/siderophile element forming several rather rare minerals including smaltite ($(Co,Ni)As_{2-2.5}$), cobaltite ($(Co,Fe)AsS$) and linnaeite ($(Co,Ni)_3S_4$), though it is present as an accessory element in olivine, pyroxenes, amphiboles, micas, garnets and sphalerite, and in synsedimentary Fe and Mn oxide minerals in sedimentary rocks.

Cobalt is generally enriched in mafic and ultramafic (150 mg/kg) relative to felsic (1 – 7 mg/kg) igneous rocks, and concentrations in shales and mudstones (19 mg/kg) are typically higher than in sandstone and carbonate sedimentary rocks (< 0.3 mg/kg) (Mielke 1979; Wedepohl 1978). It is sometimes associated with Cu, especially in sulphide ore bodies (Erdman and Modreski 1984).

Cobalt is enriched in mafic and ultramafic rocks relative to acid igneous rocks, since, during early magmatic processes, Co^{2+} substitutes for Fe^{2+} and Mg^{2+}, which are similar in charge and ionic radius (Wedepohl 1978). Cobalt displays chalcophile properties and is partitioned into sulphide and sulpharsenide phases, of which linnaeite and cobaltite are the pure Co end-member minerals. It may also occur in association with Fe sulphides (notably pyrite and pyrrhotite) and in oxide accessory minerals such as magnetite (Ure and Berrow 1982). Cobalt is considered to be immobile during metamorphism (Nicollet and Andriambololona 1980).

In sedimentary rocks, much Co is associated with synsedimentary iron and manganese oxide minerals and with residual detrital mafic minerals (Ure and Berrow 1982). In sedimentary rocks, Co tends to vary with the Fe and Mn content and is concentrated in the fine-grained fractions. Minerals such as quartz, feldspar and pure calcium carbonate contain very little Co, so pure sandstones and limestones are very low in Co. Arkoses and greywackes are more enriched, the higher Co content reflecting the greater abundance of mafic minerals (Ure and Berrow 1982). Cobalt values of more than 50 mg/kg are common in very fine mudrocks, but typical levels in black shales are somewhat lower (Vine and Tourtelot 1970), suggesting that organo-metallic and sedimentary sulphide complexation are not important enrichment mechanisms for Co in natural sedimentary processes.

The primary minerals holding Co in stream sediments include ferromagnesian silicates, oxides and sulphides, several of which (notably Co sulphides and sulpharsenides) liberate Co^{2+} readily during weathering under acid conditions. Under oxidising near-neutral conditions, Co is strongly sorbed to Fe and Mn oxides, by chemisorption and co-precipitation. Manganese oxides have a particular affinity for Co. As the pH value decreases, the solubility of Co increases; hence, it is highly mobile in acidic reducing conditions where the formation of Fe and Mn oxides is inhibited (McBride 1994). Cobalt may also bind to humic and fulvic acids and inorganic colloids (Qian et al. 1998).

Anthropogenic sources of Co include coal combustion, special steels, fertilizers and lead, iron and silver mining and processing (Reimann and de Caritat 1998).

Cobalt is a biologically essential element, and is found in vitamin B12. Cobalt can be toxic to humans at high doses. However, problems related to deficiency are more likely than excess dose toxicity. Cobalt has metabolic links with Fe and Cu, which can be depressed at high levels of Co intake, leading to anaemia in animals (Mertz 1987).

Copper

Copper is a chalcophile element, and whilst native Cu occurs rarely in nature, it more typically forms minerals such as chalcopyrite ($CuFeS_2$), covellite (CuS), and malachite ($Cu_2CO_3(OH)_2$). However, it is more widely dispersed at trace levels in micas, pyroxenes and amphiboles, thus showing a greater affinity for mafic (40 – 60 mg/kg) than for felsic igneous rocks (12 mg/kg) (Wedepohl 1978). Black shales and coals (40 – 45 mg/kg) typically contain elevated concentrations of Cu relative to sandstone and carbonate sedimentary rock types (2 – 15 mg/kg) (Alloway 2013).

During magmatic processes, the univalent Cu^+ ion is primarily concentrated in early differentiates. It is not readily incorporated into silicates, but is partitioned into either sulphides or oxides, depending on the ambient fugacities of sulphur and oxygen (Curtis 1964; Helgeson 1969). Chalcopyrite is a common accessory and primary Cu carrier in mafic igneous rocks. In common with other strongly chalcophile elements, Cu is strongly concentrated into sulphide minerals during hydrothermal mineralisation; sulphide minerals, notably chalcopyrite, are the main detrital Cu phases, particularly near to mineralisation sites.

In un-mineralised sediments, Cu concentrations are principally determined by mafic detritus, secondary Fe and Mn oxides, clay minerals and organic matter (Stevenson and Ardakani 1972; Williams 1992). Copper is mobile under the oxidising, saline conditions of some red-bed successions, which thus provide a source of Cu for enrichment in associated reducing environments.

Anthropogenic sources of Cu include Cu mining and smelting, agriculture, sewage sludge and steel works (Reimann and de Caritat 1998).

Copper is an essential trace element for all organisms and is a constituent of a number of key enzymes in the human body; however, it can be toxic at extremely high levels that are not normally encountered in natural settings (WHO 1996).

Iron

Iron (Fe) is the fourth most abundant element, constituting 5% of the Earth's crust. With both lithophile and chalcophile properties, it forms several common minerals including pyrite (FeS_2), magnetite (Fe_3O_4), haematite (Fe_2O_3), and siderite ($FeCO_3$), but it is also present in many rock-forming minerals including micas, garnets, amphiboles, pyroxenes and olivine, and is abundant in many oxides and sulphides.

During magmatic processes it becomes concentrated in mid-stage fractionates and is generally enriched in mafic (9.6 wt%) relative to felsic (2.2 wt%) igneous rocks. In sedimentary rocks, clay, shale and greywacke typically contain higher concentrations (6.7 wt%) than sandstone (1.5 wt%) and carbonate rocks (0.5 wt%). Sedimentary ironstone may contain more than 30 wt% (Williamson 1999).

Iron has been shown to be immobile at medium to high metamorphic grades in basic rocks (Nicollet and Andriambololona 1980), but Sheraton et al. (1973) and Beach and Tarney (1978) suggest that Fe may be lost during retrogressive metamorphism. During metasomatic alteration, Fe may also be concentrated by mineralising fluids into oxides such as hematite and sulphides such as pyrite.

The abundance of Fe in sedimentary rocks is determined by various factors including provenance, granulometry, sedimentary redox conditions and diagenetic history. In many rocks, secondary oxide coatings and cements are the predominant Fe phases, with primary oxides (e.g. magnetite), ferromagnesian silicates (amphiboles, pyroxenes etc.) and sulphides (e.g. pyrrhotite) of lesser importance. Authigenic pyrite (FeS_2) and siderite ($FeCO_3$) may also occur in fine-grained facies (e.g. Berner 1970, 1981). On account of the tendency for hydrous Fe phases to form surface oxide coatings on pre-existing minerals, there is often a direct relationship between total Fe content and the specific surface areas of sedimentary particles (Ure and Berrow 1982).

Whilst Fe has relatively low mobility under most environmental conditions, the Fe^{2+} ion is highly soluble in slightly acid waters. Precipitation is rapid with increasing pH or Eh and is responsible for the almost ubiquitous presence of hydrous oxide coatings (goethite, limonite, lepidocrocite, hematite) on stream clasts in aerated environments. Secondary Fe coatings exert a major control on the surface environment geochemistry of Ba, Mo, As and the first row transition metals, all of which are subject to adsorption to (and coprecipitation with) hydrous Fe oxides (e.g. Williams 1991, 1992).

Anthropogenic sources of Fe include the iron and steel industry, sewage and iron-mining dust (Reimann and de Caritat 1998). Iron is an essential nutrient for plants and animals and is involved in the production of haemoglobin in red blood cells (WHO 1996).

Lanthanum

Lanthanum (La) is a lithophile element, forming several minerals including the relatively common monazite ((Ce, La, Nd, Th)(PO_4SiO_4)) and rarer cerite ($(Ce, La)_9(Mg, Fe)Si_7(O, OH, F)_{28}$), though it is widely dispersed at trace levels in several rock-forming minerals, such as biotite, apatite, pyroxenes and feldspars. It has an average crustal abundance of 37 mg/kg (Mielke 1979).

Lanthanum has an affinity for felsic (45 - 55 mg/kg) rather than mafic igneous rocks (< 10 mg/kg) (Mielke 1979). In granites, the ratio of light to heavy REEs (normalised to chondritic abundance) increases with evolution to a critical threshold, beyond which the fractionation of plagioclase and accessory phases induces the loss of La and Ce (Wedepohl 1978).

In sedimentary rocks, a large proportion of the total La content is held in resistate mineral phases such as monazite, but can also be present in feldspars and clays. As such, shale and greywacke tend to contain more of the element (50 mg/kg) than sandstone and limestone (1 - 30 mg/kg) (Mielke 1979). La-bearing feldspars may provide an important supply of the element for incorporation into secondary clay minerals during weathering (e.g. Ronov et al. 1974). Quartzitic sandstones typically have very low concentrations of La compared with shales or greywackes. In limestones, La is mostly associated with fine clastic impurities, although direct precipitation of La in carbonates has also been recorded (Wedepohl 1978). Diagenetic enrichment of La and other light REEs is widely reported in laterites, bauxites and oolitic ironstones (e.g. Ure and Berrow 1982).

Lanthanum has very low mobility under most environmental conditions, mainly due to the very low solubility of the phosphate ($LaPO_4$). In stream sediments, the release of La from resistate phases such as monazite is generally very slow. A small fraction of the total La burden may be held in apatite and biotite, both of which are weathered rapidly at low pH. As a light rare earth element (REE), it is preferentially adsorbed onto organic matter (Leleyter et al. 1999) compared with heavier REEs.

Anthropogenic sources of La include mining and processing of alkaline rock, but natural sources are considered more important than anthropogenic ones. Lanthanum is considered biologically inactive and non-essential, and has a low toxicity (Reimann and de Caritat 1998).

Lead

Lead (Pb) has an average crustal abundance of 13 mg/kg. It is a strongly chalcophile metallic element forming several important minerals including galena (PbS), anglesite ($PbSO_4$), cerussite ($PbCO_3$) and minium (Pb_3O_4), but is also widely dispersed at trace levels in common minerals, which include K-feldspar, plagioclase, micas, zircon and magnetite.

Lead is mobile in late-stage magmatic processes (MacDonald et al. 1973). The Pb^{2+} ion is intermediate in size between K^+ and Ca^{2+}. It may thus replace these cations in K-feldspars, micas and, to a lesser extent, plagioclase and apatite, and as such, it is more abundant in felsic (15 – 19 mg/kg) rather than mafic (1 – 6 mg/kg) igneous rocks (Mielke 1979).

The distribution of Pb in sedimentary rocks is controlled by primary detrital minerals (such as feldspars, micas and sulphides), clay minerals (Heinrichs 1974) and organic matter. Pure limestones and sandstones are typically depleted relative to shales. Lead has a strong affinity for organic matter in the environment; hence, concentrations in black shale (up to 100 mg/kg) are significantly higher than in sandstone and limestone (5 – 10 mg/kg) sedimentary rocks (Alloway 2013).

The principal Pb-bearing phases in stream sediments are typically K-feldspars, micas and, to a lesser extent, plagioclase feldspars and ferromagnesian silicates. Close to hydrothermal mineralisation, Pb sulphides such as galena may also be present. At high pH, these phases may persist and accumulate to significant concentrations where there is a supply of dissolved SO_4^{2-} and CO_3^{2-} for the formation of protective low-solubility coatings. However, under acid conditions PbS is dissolved and dispersed at a rate determined largely by the availability of hydrous Fe and Mn oxides for sorption. Coprecipitation and adsorption of Pb in association with these oxides may give rise to anomalous levels of Pb in stream sediment, as indicated by its association with elements such as Fe, Mn, Co, Ba and As (BGS. 2000).

Anthropogenic sources of Pb include aerosols from car exhausts, (this had decreased in recent years with the introduction of Pb-free petrol), old Pb-based paints, pottery glazes, steel works, sewage sludge and smelting (Reimann and de Caritat 1998). Lead is biologically non-essential and is well known for its toxic properties. It can cause mental impairment in young children, and neuropathy and hypertension in adults (WHO 1996).

Magnesium

Magnesium (Mg) is the seventh most abundant element in the Earth's crust, with an average abundance of 2.76% (Fyfe 1999). It is a lithophile metallic element, which is a major constituent in several types of minerals, including silicates, carbonates, sulphates, phosphates and borates.

During magmatic processes Mg is concentrated into early fractionates and forms a major constituent of rock-forming minerals such as olivines and pyroxenes. It is also partitioned into amphiboles and micas under conditions of high H_2O and O_2 fugacity. Accordingly, mafic and ultramafic rocks are markedly richer in MgO than felsic igneous rocks.

The distribution of Mg is generally unaffected by medium- to high-grade metamorphism, but the element may become mobilised during greenschist-facies alteration and contact metamorphism of calcareous rocks, with the formation of dolomite, magnesian calcite, magnesite, periclase and talc (Wedepohl 1978).

In sedimentary rocks, Mg occurs in minerals such as dolomite, chlorite and glauconite. It is a common constituent of arenaceous sediments, but its concentration is typically greater in argillaceous rocks (Usdowski 1970), especially those with a high chlorite or mica content. Many limestones contain some Mg, the highest levels being in dolomite rocks.

A large proportion of the detrital Mg in stream sediments is held in ferromagnesian silicates (olivines, pyroxenes and amphiboles), most of which break down relatively rapidly during weathering (Wedepohl 1978). As many Mg compounds are very soluble, Mg displays high mobility after its release by weathering, under all environmental conditions.

Anthropogenic sources of Mg include fertilizers and liming (Reimann and de Caritat 1998).

Magnesium is essential for all organisms, and is non-toxic under normal circumstances. Deficiencies of magnesium are much more common than toxicity problems (Mertz 1987).

Manganese

Manganese (Mn) has an average continental crustal abundance of 0.1 wt% (Wedepohl 1995). It is a common lithophile element, forming several minerals including pyrolusite (MnO_2), rhodocrosite ($MnCO_3$), and manganite ($MnO(OH)$), and several oxides in sedimentary rocks. It is widely distributed as an accessory element in garnets, olivine, pyroxenes, amphiboles and calcite.

During magmatic processes (at low O_2 fugacity) Mn occurs in a divalent state that readily substitutes for Fe^{2+} and Mg^{2+} (Ure and Berrow 1982). It is thus partitioned into ferromagnesian silicates and Fe-Ti oxides, becoming strongly enriched in mafic (0.2 wt%) and ultramafic relative to felsic (0.05 - 0.07 wt%) igneous rocks. There is a close correlation between Mn and Fe^{2+} in most igneous rocks, with Mn:Fe ratios generally lying between 0.015 and 0.02.

Manganese is immobile during prograde regional and contact metamorphism (Wedepohl 1978), but may be redistributed extensively during granulite-amphibolite facies retrogression (Beach and Tamey 1978). Remobilisation of Mn may also occur as a result of hydrothermal activity or regional metasomatism (Senior and Leake 1978).

In sedimentary rocks, Mn concentrations are generally higher in shale, greywacke and limestone (0.07 – 0.09 wt%) than in sandstone (0.02 wt%) (Wedepohl 1978). The Mn content of sedimentary rocks is controlled by the geochemistry of the source rock and the redox conditions of the depositional environment (Wedepohl 1978). Manganese occurs in detrital phases such as ferromagnesian silicates, magnetite and ilmenite, but the largest fraction is generally held in secondary oxides. Further enrichment of certain fine-grained sediments may occur through the diagenetic formation of ferromanganese nodules (e.g. Jenkyns 1977; Williams and Owen 1990, 1992). Carbonate rocks (particularly dolomites) also hold Mn at high concentrations due to replacement of Ca^{2+} by Mn^{2+} producing manganoan calcite and dolomite.

Manganese enters stream sediments in a variety of solid phases, including ferromagnesian silicates, Fe-Ti oxides and adsorbed coatings on clay minerals. Although the $Mn^{2+}(aq)$ ion is readily soluble, manganese has generally low mobility in the environment, especially under oxidising conditions, as the Mn^{3+} and especially Mn^{4+} ions form insoluble oxyhydroxides. Mn-oxide formation is instrumental in scavenging trace elements such as As, Ba, Pb, Co, Cu and Zn from solution (e.g. Breward 1988; Williams 1992).

Anthropogenic sources of Mn include mining and smelting, engineering, traffic and agriculture. However, geogenic sources are more important than anthropogenic ones (Yang and Sanudo-Wilhelmy 1998).

Manganese is biologically active and is an essential trace element for all organisms. Manganese deficiency is more common in humans than toxicity, causing impaired reproduction and growth (Mertz 1987).

Nickel

Nickel (Ni) is a chalcophile or siderophile metallic element which forms several minerals including pentlandite ($(Fe, Ni)_9S_8$), nickeline (NiAs) and ullmannite (NiSbS), but it is more widely present at trace levels in olivine, pyroxenes, amphiboles and micas.

The Ni^{2+} ion is intermediate in size between Mg^{2+} and Fe^{2+}, for which it substitutes during magmatic processes. It is partitioned into ferromagnesian phases such as olivine (c. 3000 mg/kg Ni), orthopyroxene and spinels during the early stages of fractionation, and is, therefore, strongly enriched in ultramafic and mafic rocks relative to felsic igneous rocks, with abundances typically correlating with those of Mg, Cr and Co. Nickel also shows marked chalcophile properties, and a strong association between Ni and Cu is common in some types of sulphide deposits (Wedepohl 1978).

Nickel shows very limited mobility during low-temperature hydrothermal activity, low or high-grade metamorphism (Eade and Fahrig 1973), or retrogressive metamorphism (Beach and Tarney 1978).

In sedimentary rocks, Ni is mostly held in detrital ferromagnesian silicates, crystalline Fe phases, hydrous Fe and Mn oxides and clay minerals. It is strongly concentrated in shales (especially black shales) relative to greywackes, quartzitic sandstones and limestones. In tropical environments, Ni becomes strongly enriched in laterites due to its resistance to differential weathering (Ure and Berrow 1982), and ferromanganese nodules may also contain appreciable amounts of Ni.

A large proportion of the Ni in stream sediments is held in detrital silicates and oxides.

Nickel has a high environmental mobility under acidic, oxidising conditions. Under reducing conditions, nickel is incorporated into sulphides, lowering its mobility (Brookins 1988; McBride 1994). Nickel favours binding to organic matter, and may co-precipitate with Mn and Fe oxides.

Nickel is biologically active, and is essential for some organisms. Most Ni compounds are relatively non-toxic, but others can be toxic causing dermal and gastric irritation (WHO 1996).

Potassium

Potassium (K) is the eighth most abundant element in the Earth’s crust (1.84 %) (Fyfe, 1999). It is a lithophile/biophile metallic element forming several minerals including sylvite (KCl) and carnallite ($KMgCl_3.6H_2O$), which occur in evaporite deposits, but it is more widespread in several important rock-forming minerals including feldspars and micas.

Potassium is a major constituent of many rock-forming minerals, principally K-feldspars and micas. In magmas it is progressively concentrated during differentiation and is thus enriched in felsic relative to mafic igneous rocks; typical K concentrations in granites are in the range 2 – 5 wt% while they are <1 wt% in mafic igneous rock types such as basalt (<1 wt%) (Wedepohl 1978). It is especially enriched in late-stage hydrothermal solutions (particularly those associated with acid igneous bodies), giving rise to K-feldspar metasomatism.

Low and medium-grade metamorphic rocks generally have K_2O concentrations similar to those of their precursor lithologies, but levels are generally low, with correspondingly low K:Rb values, in granulite-facies gneisses (Tarney et al. 1972). Mobilisation and loss of K_2O during granulite-amphibolite facies retrogression has also been reported (Rollinson and Windley 1980).

Concentrations of K are higher in clay-rich sedimentary rock types and impure carbonates than in pure carbonates (< 2 wt%) and siliceous sandstone (< 1 wt%) (Wedepohl 1978). Clay minerals are the principal hosts of K in argillaceous sediments, with illite the most important mineral. In arenaceous rocks, it is typically contained in K-feldspars, micas and glauconite, and consequently is higher in arkoses and greywacke-arenites than in pure sandstones. Potassium concentrations are low in pure limestones, where the element may provide a useful indicator of the proportion of non-calcareous detritus.

Potassium has relatively low mobility under most environmental conditions, despite the high solubility of the K^+ ion, due mainly to strong sorption by clay minerals and incorporation into the biosphere via plants.

Anthropogenic sources of K include fertilizers, but natural sources are more important than anthropogenic ones (Reimann and de Caritat, 1998).

Potassium is an essential element for all organisms and natural toxic effects are rare. It is important for nervous system and muscle functioning in humans and is crucial for plant growth in agriculture (Armstrong 1998).

Rubidium

Rubidium (Rb) is a lithophile metallic element forming no 'pure' minerals of its own, but it is present in several common minerals replacing K, for example in K-feldspar, muscovite and biotite, as well as in rarer minerals, such as lepidolite, carnallite and pollucite (replacing Cs).

During magmatic processes, Rb^+ is partitioned into micas and K-feldspars through substitution for K. On account of its large ionic radius (1.52 Å), Rb^+ behaves incompatibly, becoming concentrated in late-stage differentiates. Pronounced enhancement of Rb and other large-ion lithophile (LIL) elements relative to incompatible high-field-strength (HFS) elements is common in alkaline and calc-alkaline rocks, and may relate to metasomatic enrichment of the magma source (Saunders et al. 1980). The K:Rb ratio provides an important petrogenetic index, generally decreasing with magmatic evolution (Shaw 1968).

Pervasive redistribution of Rb has been reported during deuteric and hydrothermal alteration of granite plutons (Bailey and MacDonald 1975; O'Brien et al. 1985). A general decrease in Rb levels occurs at high metamorphic grades (Tarney and Windley 1977). Retrogression from granulite to amphibolite may be accompanied by an increase in Rb levels (Drury 1974).

In sedimentary rocks, Rb is primarily held in K-feldspars, micas and clay minerals. The average Rb content of arkoses and feldspathic sandstones is thus higher than that of quartzites and most calcareous sediments. During weathering, ion exchange and adsorption mechanisms tend to concentrate Rb relative to K (Heier and Billings 1970). High Rb levels are common in mudstones rich in illite and related clay minerals.

In stream sediments, Rb normally occurs in detrital K-feldspars, micas and clay minerals. Rubidium displays low environmental mobility, despite the stability and solubility of Rb^+ and most of its compounds, mainly due to its very strong sorption by clay minerals such as illite.

Anthropogenic sources of Rb include glass dust, but geogenic sources are more important than anthropogenic ones (Reimann and de Caritat 1998). Rubidium is considered non-essential and non-toxic. It behaves very similarly to potassium in the human body, and may replace it if K levels are low (Mertz 1987).

Uranium

Uranium (U) is a low-abundance lithophile metallic element, with an average crustal content of 2.3 mg/kg (Mielke 1979). It occurs in several minerals including uraninite (UO_2), brannerite ($(U, Ca, Ce)(Ti, Fe)_2O_6$) and carnotite ($K_2(UO_2)_2(VO_4)_2.3H_2O$). It is also present as an accessory element in more common minerals, such as zircon, apatite, allanite and monazite, and in complexes with organic matter and phosphatic ironstones.

In magmas, the moderately large (0.89 Å) highly charged U^{4+} ion behaves incompatibly, becoming concentrated in late-stage differentiates, often in accessory minerals such as zircon and allanite. Concentrations are therefore higher in more evolved granitic rock types (3.0 mg/kg) than in mafic igneous rocks (0.001 – 1 mg/kg) (Mielke, 1979). Secondary concentration of U may occur as a result of deuteric and hydrothermal activity associated with the emplacement of felsic volcanics and intrusives.

Uranium concentrations in sedimentary rocks are closely controlled by the redox conditions of the depositional environment. Under anoxic conditions, it forms insoluble complexes with organic matter and phosphates. Hence, concentrations in organic-rich facies (deposited in anoxic regimes), such as black shales and coals (3 – 1244 mg/kg) and phosphatic deposits (50 – 300 mg/kg) are higher than coarse-grained inorganic rocks, such as sandstones, shales and carbonates (0.45 – 3.7 mg/kg) (Mielke 1979; Wedepohl 1978). Average U levels are generally lower in sandstones than in clay-rich sediments, and U tends to be enriched in lacustrine relative to fluviatile and marine sediments.

Anomalous levels are commonly observed at palaeo-redox fronts, where the soluble uranyl ion (UO_2^{2+}) is precipitated as insoluble U^{4+}.

Some U in stream sediments may be present in resistate minerals such as zircon, monazite and allanite derived from primary or secondary rock sources. However, the distribution of U in stream sediments is controlled principally by Eh and pH conditions, the main redox process being the oxidation of low-solubility U^{4+} to the highly soluble uranyl cation, which is re-precipitated by reduction at redox boundaries (BGS 2000).

Anthropogenic sources of U include U mining and milling, phosphate fertilizers and coal combustion (Reimann and de Caritat 1998).

Uranium is a non-essential element, it is chemotoxic and radiotoxic, but environmental exposure to the element is low in most settings. The radioactive decay of U releases radon gas, which is carcinogenic, but is dispersed to low concentrations in the atmosphere in most unconfined environments (ATSDR 2013).

Vanadium

Vanadium (V) is a lithophile metallic element forming several minerals including vanadian magnetite ((Fe,V)304), vanadinite ($Pb_5(VO_4)_3Cl$), and carnotite ($K_2(UO_2)_2(VO_4)_2.3H_2O$). It is also present as an accessory element in dark micas, apatite, pyroxenes and amphiboles.

The V^{3+} ion has an ionic radius (0.61 Å) almost identical to that of Fe^{3+} (0.65 Å) in octahedral coordination sites. Accordingly, V is frequently found as a substitute for Fe in magnetite and in the ferromagnesian silicates formed during primary magmatic processes (Curtis 1964). Mafic rocks are typically enriched in V relative to most intermediate and felsic rocks. Primitive magma types, including calc-alkaline, alkaline and tholeiitic types, have broadly similar V concentrations (Taylor et al. 1969). In ultramafic rocks, the V content generally reflects the abundance of minerals such as Fe-Ti-Cr oxides and pyroxenes.

The V content of sedimentary rocks primarily reflects the abundance of detrital Fe oxides, clay minerals, hydrous oxides of Fe and Mn, and organic matter. The redox regime is critical, V remaining mobile under oxidising conditions, but being subject to precipitation just above the sulphate/sulphide threshold within a pH range of 5.0-8.0 (Krauskopf 1956; Brookins 1988). The average V content of quartzitic sandstones and pure carbonate sediments is low, with higher values in greywackes, shales and clays. Coals may also contain appreciable amounts of V. The most V-rich sedimentary rocks are black shales, reflecting the affinity of the element to organic matter and its immobility under reducing conditions.

The principal hosts for V in stream sediments are resistate minerals (detrital Fe oxides and ferromagnesian silicates), organic complexes, hydrous oxides and clay minerals (BGS 2000).

Following its release by weathering, the behaviour of V is largely determined by its oxidation state. V^{4+} is reduced to V^{3+} under a variety of conditions, one of which may involve hydrogen sulphide (H_2S), especially in pyritic ore deposits (Wanty and Goldhaber 1992). V^{5+} is reduced to V^{4+} in reducing conditions associated with organic matter. The reduced forms of V are more likely to be sorbed by clay minerals and organic matter, thus being removed from solution.

Anthropogenic sources of V include oil and coal combustion, steel alloy tool production and traffic (Reimann and de Caritat 1998).

Although there is some evidence to suggest that V is an essential nutrient, a functional role for V in humans has not been established; increases in abortion rates and decreased milk production have been observed in V-deprived goats. Vanadium mimics insulin and stimulates cell proliferation and differentiation. In animal models, particularly streptozotoxin-induced diabetes in rats, V has been shown to normalize blood glucose and lipid levels, improve insulin sensitivity, and prevent or reverse secondary complications such as cardiomyopathy, cataract development, and impaired antioxidant status (ATSDR 2012). Vanadium toxicity is rare and greatly depends on speciation and oxidation state, usually occurring by intake of airborne anthropogenic V in occupational settings (WHO 1996).

Zinc

Zinc (Zn) is a chalcophile metallic element forming several minerals including sphalerite (ZnS), smithsonite ($ZnCO_3$), and zincite (ZnO). It is also widely dispersed as a trace element in pyroxenes, amphiboles, micas, garnets and magnetite.

During magmatic processes, Zn (like most other first-row transition metals) shows compatibility during early fractionation and becomes enriched in mafic relative to felsic igneous rocks. It is readily partitioned into oxides and silicates by substitution for Fe^{2+} and Mg^{2+}, both of which have similar ionic radii to Zn^{2+} (0.83 Å). In basic rocks, the principal Zn carrier is magnetite, while biotite is generally the most important in granites (Ure and Berrow 1982). Where the two minerals coexist, biotite typically holds more Zn. Enrichment in chrome spinels has been suggested as an explanation for the abundance of Zn in layered ultramafic bodies (Carter 1970). Sphalerite is a constituent of many igneous rocks and hydrothermal ore deposits, reflecting the chalcophile nature of Zn.

The distribution of Zn in sedimentary rocks is primarily controlled by the abundance of detrital ferromagnesian silicates, magnetite and clay minerals (Wedepohl 1978). It is also readily adsorbed onto ferric oxides, and co-variation with total Fe is common. Carbonate rocks and quartzo-feldspathic sandstones are generally poor in Zn compared with greywackes and shales. Zinc has an affinity for organic matter, and high values are often recorded in oil shales (Wedepohl 1978). High values of Zn (c. 1%) have been recorded in oolitic ironstones and ferromanganese nodules (Jenkyns, 1977).

In stream sediments, Zn primarily resides in detrital oxides and ferromagnesian silicates which weather slowly in most environments. Zinc is rapidly sorbed to secondary oxides (e.g. Jenne 1968; Robinson 1981), clay minerals and organic matter (e.g. Ure and Berrow 1982) in all but the most acid conditions (pH <4.5).

Anthropogenic sources of Zn include Zn smelters, combustion, sewage and waste-water (Reimann and de Caritat 1998).

Zinc is biologically active and is essential for all organisms. Toxicity in humans is low, and deficiency is more likely, causing growth retardation, dermatitis, and a defective immune system (WHO 1996).

Zirconium

Zirconium (Zr) is a lithophile metallic element forming several minerals including the common zircon ($ZrSiO_4$) and rarer baddeleyite (ZrO_2), and is also present at trace levels in pyroxenes, amphiboles, micas, garnets and ilmenite.

During magmatic processes, the large (0.80 Å) highly charged Zr^{4+} ion is incompatible with the lattice sites of most common rock-forming silicates. Accordingly, it is partitioned into accessory phases such as zircon, baddeleyite and sphene. Felsic igneous rocks are generally enriched in Zr relative to mafic types, though Zr levels may decrease markedly in the felsic members of calc-alkaline suites. Many alkaline rocks are enriched in Zr as a result of the formation of stable Na complexes (Watson 1979).

Limited remobilisation of Zr may occur during intense metasomatism and granite-related hydrothermal alteration (Simpson et al. 1979; Hynes 1980). Under most other circumstances, it appears to be immobile, with comparable levels prevailing in metamorphic rocks of all grades (Tarney and Saunders 1979).

The abundance of Zr in sedimentary rocks depends almost entirely on the presence of heavy minerals such as zircon and sphene. Trace quantities of authigenic zircon may also occur as adsorbed coatings on diagenetic clays (Nicholls and Loring 1962). The concentration of Zr in greywackes is typically higher than that in sandstones, shales or other mudstones. The abundance of Zr in limestones is generally very low.

Resistate phases (e.g. zircon and sphene) are the dominant carriers of Zr in stream sediments, and are generally highly resistant to weathering. Most of the Zr that is mobilised is derived from the weathering of mafic minerals and is typically rapidly adsorbed onto clays as $Zr(OH)_4$. Colloidal zirconium is also readily adsorbed by organic matter, macroplankton and siliceous material (Smith and Carson 1978).

Anthropogenic sources of Zr include nuclear fallout and ceramic dust, however, geogenic sources are more important than anthropogenic ones (Reimann and de Caritat 1998).

Zirconium is a non-essential element, having no known biological role. Little is known about its toxicity, however, it is regarded as being a low risk (Mertz 1987).

References

ALLOWAY, B E. 2013. Sources of heavy metals and metalloids in soils. In: ALLOWAY, B E. (editor). *Heavy metals in soils*. Environmental Pollution Series, Vol. 22, 11–50. (Netherlands: Springer).

ARMSTRONG, D L. (editor). 1998. Potassium for agriculture. *Better crops with plant food*, 82 (3). (Norcross: Potash and Phosphate Institute)

ARTHURS J W, AND EARLS G. 2004. Minerals. Chapter 21, 255-272 in: MITCHELL, W I (editor). *The Geology of Northern Ireland- our natural foundation*. *Second edition.* (Belfast: Geological Survey of Northern Ireland).

ATSDR. 2013. *Toxicological profile for uranium*. (Atlanta: Agency for Toxic Substances and Disease Registry)

ATSDR. 2012. *Toxicology profile for vanadium.* (Atlanta: Agency for Toxic Substances and Disease Registry)

BAILEY, D K, AND MACDONALD, D R. 1975. Fluorine and chlorine in peralkaline liquids and the need for magma generation in an open system. *Mineralogical Magazine*, Vol. 40, 405-414.

BEACH, A, AND TARNEY, J. 1978. Major and trace element patterns established during retrogressive metamorphism of granulite-facies gneisses, NW Scotland. *Precambrian Research,* Vol. 7, 325-348.

BERNER, R A. 1970. Sedimentary pyrite formation. *American Journal of Science,* Vol. 267, 19-42.

BERNER, R A. 1981. A new geochemical classification of sedimentary environments. *Journal of Sedimentary Petrology,* Vol. 51, 359-365.

BGS. 1987. *Regional geochemical atlas: Great Glen* (Keyworth: British Geological Survey).

BGS. 1990. *Regional geochemical atlas: Argyll* (Keyworth: British Geological Survey).

BGS. 1992a. *Regional geochemistry of the East Grampian area* (Keyworth: British Geological Survey).

BGS. 1992b. *Regional geochemistry of the Lake District and adjacent areas* (Keyworth: British Geological Survey).

BGS. 1993. *Regional geochemistry of Southern Scotland and part of Northern England* (Keyworth: British Geological Survey).

BGS. 1996a. *Regional geochemistry of north-east England* (Keyworth: British Geological Survey).

BGS. 1996b. Metallogenic map of Britain and Ireland. COLMAN T. B, SCRIVENER R. C., MORRIS J. H., LONG C. B., O'CONNOR, P. J., STANLEY, G., and LEGG, I. C. (compilers), 1: 1 500 000 (Keyworth: British Geological Survey).

BGS. 1997. *Regional geochemistry of parts of north-west England and North Wales* (Keyworth: British Geological Survey).

BGS. 1999. *Regional geochemistry stream water Wales* (Keyworth: British Geological Survey)

BGS. 2000. *Regional geochemistry of Wales and part of west-central England: Stream sediment and soil* (Keyworth: British Geological Survey).

BGS. 2011. London Earth soil geochemistry. (Keyworth: British Geological Survey) www.bgs.ac.uk/gbase/londonearth.html. Access date Dec 2017.

BGS. 2018a. BGS Lexicon of named rock units. (Keyworth: British Geological Survey) www.bgs.ac.uk/lexicon/home.html. Access date Jan 2018.

BGS. 2018b. BGS Geology – DiGMapGB: onshore geology map of Great Britain. (Keyworth: British Geological Survey) www.bgs.ac.uk/products/digitalmaps/dataInfo.html. Access Date Jan 2018.

BIVAND, R S, PEBESMA, E J, AND GOMEZ-RUBIO, V. 2013. *Applied spatial data analysis with R, Second edition.* (New York: Springer). http://www.asdar-book.org/

BOYLE, R W. 1979. Geochemistry of gold and its deposits. *Geological Survey of Canada Bulletin,* No. 20.

BREWARD, N. 1988. Effect of mineralised faults on stream-sediment geochemistry of an upland catchment at Plynlimon, mid-Wales. *Transactions of the Institution of Mining and Metallurgy (Section B: Applied earth science), Vol*. 97, 181-192.

BROOKINS, D G. 1988. *Eh-pH diagrams for Geochemistry.* (Berlin-Heidelberg: Springer-Verlag.)

CARTER, J L. 1970. Mineralogy and chemistry of the earth's upper mantle based on the partial fusion - partial crystallisation model. *Bulletin of the Geological Society of America*, Vol. 81, 2021

CEC 2000. *Establishing a framework for community action in the field of water policy*. EU Directive 2000/60/EC. (Brussels: Commission of the European Community)

COLMAN, T B, AND COOPER, D C. 2000. *Exploration for metalliferous and related minerals in Britain: a guide (2nd Edition)* DTI Minerals Programme Publication No. 1. (Keyworth: British Geological Survey).

COOPER, D C, NUTT, M J C, SMITH, I F, AND EASTERBROOK, G D. 1989. Base metal and gold mineralisation in north-west Anglesey, North Wales. *Mineral Resources Series Technical Report WF/89/2* (Keyworth: British Geological Survey).

CURTIS, C D. 1964. Applications of the crystal-field theory to the inclusion of trace transition elements in minerals during magmatic differentiation. *Geochimica et Cosmochimica Acta*, Vol. 28, 389-403.

DARNLEY, A G, BYÖRKLUND, A, BØLVIKEN, B, GUSTAVSSON, N, KOVAL, P V, PLANT, J A, STEENFELT, A, TAUCHID, M, XUEJING, X, GARRET, R G, and HALL, G E M. 1995. A global geochemical database for environmental and resource management: Final report of IGCP Project 259, *Earth Sciences, 19, (Paris: UNESCO Publishing).*

DE VOS, W, and TARVAINEN T. (editors). 2006. *FOREGS Geochemical Atlas of Europe. Part 2.* Forum of European Geological Surveys. (Espoo: Geological Survey of Finland)

DRURY, S A. 1974. Chemical changes during retrogressive metamorphism of Lewisian granulite facies rocks from Coll and Tiree. *Scottish Journal of Geology,* Vol. 10, 237-256.

DUNN, C E. 1989. Reconnaissance level biogeochemical surveys for gold in Canada. *Transactions of the Institution of Mining and Metallurgy (Section B: Applied earth science),* Vol. 98, 153-160.

EADE, K E, AND FAHRIG, W F. 1973. Regional lithological and temporal variation in the abundances of some of the trace elements. *Geological Survey of Canada, Paper,* No. 1, 72-46.

EDWARDS, W.N.; MITCHELL, G.H.; WHITEHEAD, T.H. 1950. Geology of the district north and east of Leeds. Explanation of sheet 70. *Memoirs of the Geological Survey of Great Britain.* (Keyworth: British Geological Survey). http://pubs.bgs.ac.uk/publications.html?pubID=B01538

ELLISON, R A, WILLIAMSON, I T, AND HUMPAGE, A J. 2002. Geology of the Guildford district – a brief explanation of the geological map. *Sheet Explanation of the British Geological Survey*. 1:50000 Sheet 285 Guildford (England and Wales).

EMSLEY, J. 2011. *Nature's building blocks: An A-Z guide to the elements*. (New York: Oxford University Press)

ERDMAN, J A, AND MODRESKI, P J. 1984. Copper and cobalt in aquatic mosses and stream sediments from the Idaho Cobalt Belt, *Journal of Geochemical Exploration,* Vol. 20 (1), 75-84.

FERREIRA, A M P J, JOHNSON, C C, APPLETON, J D, FLIGHT, D M A, LISTER, T R, KNIGHTS, K V, ANDER, E L, SCHEIB, C, SCHEIB, A, CAVE, M, WRAGG, J, FORDYCE, F M, AND LAWLEY, R S. 2017. *London Region Atlas of Topsoil Geochemistry.* (Keyworth: British Geological Survey) http://earthwise.bgs.ac.uk/index.php/Category:London_Region_Atlas_of_Topsoil_Geochemistry

FIELD, D, AND ELLIOT, R B. 1974. The chemistry of gabbro-amphibolite transitions in S. Norway 2: Trace elements. *Contributions to Mineralogy and Petrology,* Vol. 47, 63-76.

FILZMOSER, P. 2015. StatDA: Statistical Analysis for Environmental Data. *R package version 1.6.9.* https://CRAN.R-project.org/package=StatDA

FYFE, W S. 1999. Geochemistry. In: MARSHALL, C P, and FAIRBRIDGE, R W (editors). *Encyclopedia of geochemistry.* 572–575. (Dordrecht: Kluwer Academic Publishers).

GRÄLER, B, PEBESMA, E J, AND HEUVELINK, G. 2016. *Spatio-Temporal Interpolation using gstat.* The R Journal, Vol. 8(1), 204–218

GROSSER, J.R. HAGELGANS, V. HENTSCHEL, T. AND PRIESTER, M. 1994. Heavy-metals in stream sediments - a gold-mining area near Los Andes, southern Colombia S.A., *Ambio* Vol. 23 146-149.

HASLAM, H W AND SANDON, P T S. 1991. The geochemistry of some red-bed formations in the United Kingdom. *Technical Report WP/90/2* (Keyworth: British Geological Survey).

HEIER, K S, AND BILLINGS, G K. 1970. Rubidium. In *Handbook of Geochemistry*. WEDEPOHL, K H (editor). Section 37, A-N. (Berlin-Heidelberg: Springer-Verlag.)

HEINRICHS, H. 1974. Die untersuchung von gesteinen and gewassern auf Cd, Sb, Hg, Pb, Bi mit der flammenlosen atomabsorption. Dr. rer. nat. Thesis, Gottingen.

HELGESON, H C. 1969. Thermodynamics and hydrothermal systems at elevated temperatures and pressures. *American Journal of Science,* Vol. 267, 729-804.

HEM, J. 1992. *Study and interpretation of the chemical characteristics of natural water*. (Reston: US Geological Survey).

HYNES, A. 1980. Carbonisation and mobility of Ti, V and Zr in Ascot Formation metabasalts, SE Quebec. *Contributions to Mineralogy and Petrology*, Vol. 75, 79-87.

IGS. 1978a. *Regional geochemical atlas: Orkney* (London: Institute of Geological Sciences).

IGS. 1978b. *Regional geochemical atlas: Shetland* (London: Institute of Geological Sciences).

IGS. 1979. *Regional geochemical atlas: south Orkney and Caithness* (London: Institute of Geological Sciences).

IGS. 1982. *Regional geochemical atlas: Sutherland* (London: Institute of Geological Sciences).

IGS. 1983. *Regional geochemical atlas: The Hebrides* (London: Institute of Geological Sciences).

JACKSON, A A. 2008. *Bedrock Geology UK South.* (Keyworth: British Geological Survey)

JENKYNS, H C. 1977. Fossil manganese nodules. 87-109 in *marine manganese deposits.* GLASBY, G P (editor). (Amsterdam: Elsevier Oceanography Series.)

JENNE, E A. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in water. 337-387 in 11th American Chemical Society Symposium, Washington

JOHNSON, C C. 2005. G-BASE field procedures manual. *Internal Report IR/05/097* (Keyworth: British Geological Survey). http://nora.nerc.ac.uk/5190/

JOHNSON, C C, BREWARD, N, ANDER, E L AND AULT, L. 2005. G-BASE: baseline geochemical mapping of Great Britain and Northern Ireland. *Geochemistry: Exploration, Environment, Analysis*, Vol. 5. 347–357.

JOHNSON, C C, FLIGHT, D M A, ANDER, E L, LISTER, T R, BREWARD, N, FORDYCE, F M AND NICE, S E. 2008. The collection of drainage samples for environmental analyses from active stream channels. In: DE VIVO, B., BELKIN, H.E. AND LIMA, A. (editors) *Environmental Geochemistry: site characterization, data analysis and case histories.* (London: Elsevier), 59-92.

KIRKWOOD, C, EVERETT, P, FERREIRA, A M P J, LISTER, T R. 2016. Stream sediment geochemistry as a tool for enhancing geological understanding: An overview of new data from south west England. *Journal of Geochemical Exploration, Vol. 163, 28-40.*

KRAUSKOPF, K. 1956. Factors controlling the concentration of thirteen rare metals in seawater. *Geochimica et Cosmochimica Acta*, Vol. 9, 1-32.

LELEYTER, L, PROBST, J L, DEPETRIS, P, HAIDA, S, MORTATTI, J, ROUAULT, R, AND SAMUEL, J. 1999. REE distribution pattern in river sediments: partitioning into residual and labile fractions labile fractions. *Comptes Rendus de l'Academie des Sciences Series IIA Earth and Planetary Science,* Vol. 329 (1), 45–52(8).

LISTER, T R, AND JOHNSON, C C. 2005. G-BASE Data conditioning procedures for stream sediment and soil chemical analyses. *Internal Report IR/05/150*. (Keyworth: British Geological Survey).

MACDONALD, R, UPTON, B G T, AND THOMAS, J E. 1973. Potassium and fluorine-rich hydrous phase co-existing with peralkaline granite in south Greenland. *Earth and Planetary Science Letters,* Vol. 18, 217-222.

MCBRIDE, M B. 1994. *Environmental chemistry of soils.* (Oxford: Oxford University Press).

MCKNIGHT, D M, AND BENCALA, K E. 1990. The chemistry of iron, aluminium, and dissolved organic material in three acidic, metal-enriched, mountain streams, as controlled by watershed and in-stream processes. *Water Resources Research*, Vol. 26 (12), 3087-3100.

MCLENNAN, S M, AND TAYLOR, S R. 1999. Earth's continental crust. In: MARSHALL, C P., and FAIRBRIDGE, R W (editors). *Encyclopedia of geochemistry.* 145–150. (Dordrecht: Kluwer Academic Publishers).

MCMILLAN, A A, HAMBLIN, R J O, AND MERRITT, J W. 2005. An overview of the lithostratigraphical framework for the Quaternary and Neogene deposits of Great Britain (Onshore). *Research Report* RR/04/04 (Keyworth: British Geological Survey).

MERTZ, W. (editor). 1987*. Trace elements in human and animal nutrition.* (New York: Academic Press).

MIELKE, J E. 1979. Composition of the earth's crust and distribution of the elements. In: SIEGEL, F R (editor). *Review of research on modern problems in geochemistry*. Earth Science Series 16. 13–37. (Paris: UNESCO).

NICOLLETT, C, AND ANDRIAMBOLOLONA, D R. 1980. Distribution of transition metals in crustal metabasic igneous rocks. *Chemical Geology,* Vol. 28, 78-90.

NICOLLS, G D, AND LORING, D H. 1962. The geochemistry of some British Carboniferous sediments. *Geochimica et Cosmochimica Acta*, Vol. 26, 181- 223.

O'BRIEN C, PLANT J A, SIMPSON, P R, AND TARNEY, J. 1985. Geochemistry, metasomatism and petrogenesis of the granites of the English Lake District. *Journal of the Geological Society of London*, Vol. 142, 1139-1157.

ODOR, L. WANTY, R B, HORVATH, E, AND FUGEDI, U. 1998. Mobilization and attenuation of metals downstream from a base-metal mining site in the Matra Mountains, north-eastern Hungary. *Journal of Geochemical Exploration*. Vol. 65, 47-60

PEBESMA, E J. 2004. *Multivariable geostatistics in S: the gstat package.* Computers & Geosciences, Vol 30, 683–691.

Pebesma, E J, and Bivand, R S. 2005. Classes and methods for spatial data in R. *R News,* Vol. 5(2), 9–13. https://cran.r-project.org/doc/Rnews/.

Plant, J A. 1971. Orientation studies on stream sediment sampling for a regional geochemical survey in northern Scotland. *Transactions of the Institution of Mining and Metallurgy (Section B: Applied earth science)*, Vol. 80, 324-345.

Plant, J A. 1973. A random numbering system for geochemical samples. *Transactions of the Institution of Mining and Metallurgy (Section B: Applied earth science)*, Vol. 83, 64.

Plant, J A, and Moore, P J. 1979. Regional geochemical mapping and interpretation in Britain. *Philosophical Transactions of the Royal Society of London*, Vol. 288, 95-112.

Plant J A, Brown G C, Simpson P R, and Smith, R T. 1980. Signatures of metalliferous granites in the Scottish Caledonides. *Transactions of the Institution of Mining and Metallurgy (Section B: Applied earth science),* Vol. 89, 198-210.

Plant, J A. 1983. Regional geochemical maps of the United Kingdom: environmental and economic applications. *Mercian Geologist,* Vol. 9 (2), 75-87.

Plant, J A, Watson, J V, and Green, P M. 1984. Moine-Dalradian relationships and their palaeotectonic significance. *Philosophical Transactions of the Royal Society of London,* Vol. 395, 185-202.

Plant, J A, Breward, N, Forrest, M D, and Smith, R T. 1989. The gold pathfinder elements As, Sb, Bi - their distribution and significance in the south-west Highlands of Scotland. *Transactions of the Institution of Mining and Metallurgy (Section B: Applied earth science)*, Vol. 98, 91-101.

Plant, J A, Jones, D G, Haslam, H W, Warrington, G, Chadwick, R A, Milodowski, A E, Metcalfe, R, Ball, D F, Bulat, J, Evans, D J, Gale, I N, Hooker, P J, Hyslop, E K, Jones, N S, Kemp, S J, Kirby, G A, Leng, M J, Morton, A C, Nicholson, R A, Noy, D J, Rochelle, C A, Rowley, W J, Shepherd, T J, Smith, N J P, Spiro, B, Strong, G E, Walker, A S D, Young, S R. 2000. Cheshire Basin: basin evolution, fluid movement and mineral resources in a Permo-Triassic rift setting. *Subsurface geology memoirs*. (Keyworth: British Geological Survey). http://pubs.bgs.ac.uk/publications.html?pubID=B06159

Plant, J A, Bone, J, Voulvoulis, N, Kinniburgh, D G, Smedley, P L, Fordyce, F M, and Klinck, B. 2014. Chapter 11.2: Arsenic and selenium. In: Sherwood Lollar, B, Holland, H D, and Turekian, K K. (editors). *Treatise on geochemistry.* Second edition. Vol. 11. 13–57. (Oxford: Elsevier)

Qian, J. Xue, H B, Sigg, L, and Albrecht, A. 1998. Complexation of cobalt by natural ligands in freshwater. *Environmental Science & Technology.* Vol. 32, 2043-2050.

R Core team, 2014. R: A language and environment for statistical computing, R version 3.1.1 (2014-07-10) ed. (Vienna, Austria: R foundation for statistical computing).

Reimann, C, and de Caritat, P. 1998. *Chemical elements in the environment – factsheets for the geochemist and environmental scientist.* (Berlin: Springer-Verlag)

Robinson, G E. 1981. Adsorption of Cu, Zn and Pb near sulfide deposits by hydrous manganese-iron oxide coatings on stream alluvium. *Chemical Geology*, Vol. 33, 65-79.

Rollinson, H R, and Windley, B F. 1980. Selective depletion during metamorphism of Archean granulites, Scourie, north-west Scotland. *Contributions to Mineralogy and Petrology*, Vol. 72,257-263.

Ronov, A B, Balashov, A, Girin, Y P, and Bratishko, R K. 1974. Regularities of rare earth element distributions in the sedimentary shell and in the crust of the earth. *Sedimentology,* Vol. 21, 171-193.

Saunders, A D, Tarney, J, and Weaver, S D. 1980. Transverse geochemical variations across the Antarctic Peninsula: implications for the genesis of calc-alkaline magmas. *Earth and Planetary*

Science Letters, Vol. 46, 344-360.

SENIOR, A, AND LEAKE, B E. 1978. Regional metasomatism and the geochemistry of the Dalradian metasediments of Connemara, Western Ireland. *Journal of Petrology,* Vol. 19, 585-625.

SHAW, D M. 1968. A review of the K-Rb fractionation trends by co-variance analysis. *Geochimica et Cosmochimica Acta*, Vol. 32,573-601.

SHERATON, J W, SKINNER, A C, AND TARNEY, J. 1973. The geochemistry of the Scourian gneisses of the Assynt district. 13-30 in *The early Precambrian of Scotland and related rocks of Greenland.* PARK, R G, and TARNEY, J (editors). (Keele: University of Keele.)

SIMPSON, P R, BROWN, G C, PLANT, J, AND OSTLE, D. 1979. Uranium mineralisation and granite magmatism in the British Isles. Philosophical Transactions of the Royal Society of London, Vol. 291, 385-412.

SMITH, I C, AND CARSON, B L. 1978. *Trace metals in the environment. Volume 3 – Zirconium*. (Ann Arbor, Michigan: Ann Arbor Science Publishers Inc.), 405 pp.

SMITH, R T, COOPER, D C, AND BLAND, D J. 1994. The occurrence and economic potential of nodular monazite in south-central Wales. *Technical Report WF/94/1* (Keyworth: British Geological Survey).

STEVENSON, F J, AND ARDAKANI, M S. 1972. 47-71 in *Micronutrients in agriculture*. MORTVELDT, J J, GIORDIANO, P M, AND LINDSAY, W L (editors). (Madison, Wisconsin: Soil Science Society of America.)

STONE, P. 2008. *Bedrock Geology UK North*. (Keyworth: British Geological Survey)

STONE, P, GREEN P, LINTERN B C, PLANT J A, SIMPSON P R AND BREWARD N. 1991. Geochemistry characterises provenance in southern Scotland. *Geology Today*, Sept-Oct, 177 – 181.

TARNEY J, SKINNER A C, AND SHERATON, J W. 1972. A geochemical comparison of major Archaean gneiss units from north-west Scotland and east Greenland. 162-174 in *Proceedings of the 24th session of the International Geological Congress*, Montreal, 1972, Section 1.

TARNEY J, AND WINDLEY, B F. 1977. Chemistry, thermal gradients and evolution of the lower continental crust. *Journal of the Geological Society of London*, Vol. 134, 153-172.

TARNEY, J, AND SAUNDERS, A D. 1979. Trace element constraints on the origin of cordilleran batholiths. 90-105 in *Origin of granite batholiths: geochemical evidence.* ATHERTON, M P, AND TARNEY, J (editors). (Orpington, Kent: Shiva Publications.)

TAYLOR, S R, KAYE, M, WHITE, A J R, DUNCAN, A R, and EWART, A. 1969. Genetic significance of Co, Cr, Ni, Sc and V content of andesites. *Geochimica et Cosmochimica Acta*, Vol. 33, 275-286.

TREMEARNE, T H, AND JACOB, K D. 1941. Arsenic in natural phosphates and fertilizers. *US Department of Agriculture Technical Bulletin,* No. 781.

UN. 1992. *Agenda 21. Sustainable development*. UN conference on environment and development Rio de Janeiro, Brazil. (New York: United Nations)

URE, A M, AND BERROW, M L. 1982. The elemental constituents of soils. In: BOWEN, H J M. (editor). *Environmental chemistry*. Special Report Series 2. 94–204. (London: Royal Society of Chemistry)

USDOWSKI, H G. 1970. Magnesium. In *Handbook of geochemistry* (Section 12 G-2). WEDEPOHL, K H (editor). (Berlin-Heidelberg: Springer-Verlag.)

VINE, J D, AND TOURTELOT, E B. 1970. Geochemistry of black shale deposits: a summary report. *Economic Geology,* Vol. 65, 255-272.

WANTY, R, AND GOLDHABER, M. 1992. Thermodynamics and kinetics of reactions involving vanadium in natural systems - Accumulation of vanadium in sedimentary rocks. *Geochimica et Cosmochimica Acta*, Vol. 56, 1471-1483.

WATSON, E B. 1979. Zircon saturation in felsic liquids: experimental results and applications to trace element geochemistry. *Contributions to Mineralogy and Petrology*, Vol. 70, 407-420.

WEDEPOHL, K H. 1978. *Handbook of Geochemistry.* (Berlin: Springer-Verlag).

WEDEPOHL, K H. 1995. The composition of the continental crust. *Geochimica et Cosmochimica Acta*, Vol. 59 (7), 1217–1232.

WHITE, W.M., 2013. *Geochemistry.* (Chichester, UK: John Wiley & Sons, Ltd.).

WIDERLUND, A, AND INGRI, J. 1995. Early diagenesis of arsenic in sediments of the Kalix-river estuary, northern Sweden. *Chemical Geology.* Vol. 125, 185-196

WILLIAMS, T M, AND OWEN, R B. 1990. Authigenesis of ferric oolites in superficial sediments from lake Malawi, central Africa. *Chemical Geology,* Vol. 89, 179-188.

WILLIAMS, T M. 1991. A sedimentary record of the deposition of heavy metals and magnetic oxides in the Loch Dee basin, Galloway, Scotland. *The Holocene,* Vol. 1, 142-150.

WILLIAMS, T M. 1992. Diagenetic metal profiles in the recent sediments of a Scottish freshwater loch. *Environmental Geology and Water Sciences,* Vol. 20, 117-123.

WILLIAMS, T M, AND OWEN, R B. 1992. Geochemistry and origins of lacustrine ferromanganese nodules from the Malawi rift, central Africa. *Geochimica et Cosmochimica Acta,* Vol. 56, 2703-2712.

WILLIAMSON, M A. 1999. Iron. In: MARSHALL, C P, and FAIRBRIDGE, R W (editors). *Encyclopedia of Geochemistry,* 348–353. (Dordrecht: Kluwer Academic Publishers).

WHO, 1996. *Trace elements in human nutrition and health*. (Geneva*:* World Health Organisation).

YANG, M. AND SANUDO-WILHELMY, S. 1998. Cadmium and manganese distributions in the Hudson River estuary: interannual and seasonal variability. *Earth and Planetary Science Letters*, Vol. 160 (3-4), 403-418.

YOUNG, M E, AND DONALD, A W. (editors). 2013. *A guide to the Tellus data* (Belfast: Geological Survey of Northern Ireland).

YOUNG, M E, KNIGHTS, K V, SMYTH, D, GLENNON, M M, SCANLON, R P, AND GALLAGHER, V. 2016. ‘The Tellus geochemical surveys, results and applications’ in YOUNG, M E (editor), *Unearthed: impacts of the Tellus surveys of the north of Ireland*. (Dublin: Royal Irish Academy).

ZUPANČIČ, N, AND PIRC, S. 1999. Calcium distribution in soils and stream sediments in Istria (Croatia) and the Slovenian littoral. *Journal of Geochemical Exploration*, Vol. 65(3), 205–218.