British Geological Survey

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Environmental Change, Adaptation & Resilience Programme

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Reference Material Suite BGS110 to BGS119

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Foreword

In the pursuit of scientific excellence and operational efficiency, the importance of reliable quality control cannot be overstated. At the British Geological Survey (BGS), we recognise that access to high-quality reference materials is essential for ensuring the accuracy and consistency of analytical results across laboratories and research institutions.

This report presents ten new soil reference materials prepared by the BGS, and provides underpinning information to complement the previously published Data Sheets (Kalra et al., 2020). These materials are designed to offer robust quality control at a more accessible cost than traditional certified reference materials (CRM). These materials have been carefully produced to meet the practical needs of laboratories seeking dependable standards without compromising on quality.

By offering a cost-effective alternative, we aim to make quality control more inclusive and to support a broader range of users, from academic researchers to industry professionals, in maintaining high analytical standards. We hope this initiative will foster greater collaboration, innovation, and confidence in geochemical data across the sector.

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Summary

There is an ongoing need for well characterised soil reference materials to provide user confidence in analytical data. A suite of ten soils spanning a wide range of soil parent materials, organic carbon content and texture was developed. These materials were analysed by nine international laboratories, yielding total elemental mass fractions measured directly or following preparation by fusion or digestion procedures.

Data are presented for 64 major, minor, and trace elements, including bromine and iodine which are rarely included in such analyte suites. Due to the diverse concentrations of economically and environmentally significant elements, these materials can support a wide variety of users. Reference Values, mean and uncertainty, have been assigned for 29 to 33 elements, complemented by Information Values for 31 to 35 elements.

The distributions of elemental mass fractions are discussed in the context of expected natural ranges, exemplified for As, Br, Cd, Co, Cr, I, La, Li, Mo, Mn, Ni, S, Sb, Se, U and Zn. Additional supporting data, including pH, loss on ignition, and Hg mass fractions, further extend the utility of these materials. The materials are available in portions of 24 to 46 g from the BGS for use when analysing samples with similar soil matrices.

1 Introduction

Reference materials (RMs) are critical to demonstrate that analytical procedures can produce data that is representative of the elemental mass fractions in the analysed samples. Indeed, analysis of RMs alongside test materials is a strong recommendation of Standard ISO 17025 (ISO/IEC 17025, 2017). The need to demonstrate evidence of the quality of analytical measurement is recognised widely (e.g. IAEA, 2003), providing assurance that analysis meets the desired standard. Reference materials are essential for the validation and calibration of all measurements, including traditional analytical techniques that use bulk powders and beam measurements (Rostron and Ramsey, 2016) and have a role in estimating measurement uncertainty. Geoanalytical publications enhance the reliability of published data by inclusion of RMs that demonstrate the validity of analytical results (Jochum and Enzweiller, 2014).

Reference materials provide the basis for validation of new analytical procedures and for verification of existing analytical procedures (Eurachem, 2002), assessing their selectivity, specificity, ruggedness and robustness. Undertaking procedure validation remains important as the evolution of multi-element techniques with increasing sensitivity makes available data for an increasing range of elements that can be determined at lower mass fractions (Kane *et al.*, 2009), and the sample data is used in support of decision-making, such as monitoring or restoration of soil quality. Reference materials can also be used for Proficiency Testing schemes or other interlaboratory collaborative analysis exercises and are ideal materials to be used in training exercises, enabling new users of a procedure to demonstrate their competency and further enhancing data quality.

When available in sufficient quantities, RMs can be incorporated into Quality Assurance programmes to provide confidence in the reported data. Reference materials used for long term routine quality control analyses in commercial and research laboratories provide a rapid and consistent assessment of procedure performance. Inclusion of RMs in national scale geochemical survey programmes, where data may be acquired over many months or years, facilitates the implementation of analytical error control that would otherwise not be unequivocally discriminated from natural variation, particularly when those RMs are themselves matrix matched to real-life samples (Demetriades *et al.*, 2022).

Trace element determination in complex environmental samples is fundamental to the regulation of chemicals in the environment, providing regulatory control such as environmental impact assessments, public health assessments, and litigation decisions (Nagourney *et al.*, 2016). It is also important in international trade, and the management of the impact of soils on human health, identification of mineral deficiencies or elemental contamination (Joy *et al.*, 2015; Watts *et al*., 2019). The continual demand for elements such as Li, Be, Co, I and the rare earth elements (REE) from high-technology, low-carbon industries (Négrel *et al.*, 2019) require the ability to identify the distribution of such elements for both mineral prospecting and environmental protection purposes. The availability of well characterised, matrix matched soil RMs allows for the supply of reliable data to inform such decisions. As the study of climate change becomes increasingly important, so does the requirement to analyse a wider range of matrices (Kane *et al.*, 2009).

Jochum and Enzweiler (2014) recognised that soil and sediment RMs, produced from a large variety of parent materials, probably constitute the most used RMs in applied geochemistry and environmental analysis. Inherently, soils have a wide range of elemental compositions, which are representative of their underlying geology, i.e. parent material. It is recognised that statistical and spatial distributions at the continental scale are governed by geology (Reimann *et al.*, 2018). Soils of a desired matrix could be spiked with elements of interest to widen the applicability of an RM; however, such a mechanism can lead to procedure bias as aqueous spikes are likely to be solubilised differently to the natural mineral components, particularly in silicate matrices where digestion procedures do not achieve total dissolution (Nagourney *et al.*, 2016). Wilson *et al.* (2021) have used a selection of soil types to provide a range of elemental mass fractions while avoiding the need for spiking, thereby retaining their natural mineralogy that is essential for matching matrix and dissolution characteristics.

There is considerable interest worldwide in the use of matrix matched RMs characterised for a large suite of elements at mass fractions comparable to those in test materials, particularly as analysis techniques evolve to multi-element spectrometric methods. Initially targeted with specific elements of interest, some geological materials have been prepared as RMs with an expanding range of elemental mass fractions: e.g. Se and data for eight other elements (Tang *et al.*, 2020); Mo and data on up to 26 other elements (Liu *et al.*, 2018); and, Cl, Br and I in a variety of geological RMs, but not soils (Balcone-Boissard *et al.*, 2009; Sekimoto and Ebihara, 2017).

Existing sets of soil RMs have proven extremely popular, and supplies have become depleted, especially in those that had a comprehensive range of certified elemental mass fractions. Availability of soil RMs with matrices that resemble the test materials is a limiting factor in selection and use for geochemical analysis (Nakayama and Nakamura, 2014; Liu *et al.*, 2018; Tang *et al.*, 2020). Fiket *et al.* (2017) have expanded the range of analytical data for 46 major and trace elements for six soil and sediment RMs that previously had been characterised for limited suites of elements.

In recognising that no single soil can provide a “typical” matrix or have present “normal” elemental concentrations, the availability of a suite of soil RMs provides a range of matrices and elemental mass fractions to offer a wider choice to the end user. Suites of soil RMs have been produced by The Canadian Certified Reference Materials Project (CCRMP): SO-1 to SO-4 (Bowman *et al.*, 1979), The United States Geological Survey (USGS): GXR-1 to GXR-6 (Gladney, 1980), The Institute of Geophysical and Geochemical Exploration (IGGE), China: GSS-1 to GSS-8 (Xie *et al.*, 1989) and GSS10-to GSS16 (Gu *et al.*, 2003) and The National Institute of Standards and Technology (NIST), USA: SRM2709a to SRM2711a (Mackey *et al.*, 2010).

Existing commercially available stocks of soil RMs have largely been tailored to the mineral exploration sector rather than to the environmental protection/baseline sector, with the latter requiring materials reflecting a low natural abundance of elements of interest, as well as those at the upper end of the natural abundance mass fraction range. Furthermore, RMs with as wide a suite of elements as possible provide a source of quality control materials relevant to current and future needs, as new target elements, or contaminant sources, emerge (Demetriades *et al.*, 2022). Such RMs can be used to provide quality control for multielement geochemical analysis programmes (Smyth, 2007; Johnson *et al.*, 2008; de Caritat *et al.*, 2018; Szpak, 2020) and contaminated land analysis (Hamilton *et al.*, 2015). Equally, availability of RMs with specific elements of interest will appeal to smaller projects with specific focus. The additional cost of analysing an RM is often queried, which is perhaps the wrong perspective, and one should ask what the cost would be of not analysing an RM.

The selection of the suite of soils described in this report recognises the ongoing demand for RMs with substantial mass fraction ranges of elements of environmental significance (e.g. As, Cd, Pb), that have impact upon human and animal nutrition (e.g. Se, I, Co, Mo, Cu), or are of particular interest in geochemical exploration (e.g. Cr, Ni, Zn, Pb, Sb, U) from a range of parent material lithologies. The inclusion of an industrially contaminated soil extends the available mass fraction ranges of many of these important elements.

This document describes how this suite of 10 new soil RMs was prepared and characterised and provides a complete report of the elemental mass fraction values, with additional supporting data including pH, loss on ignition, and Hg mass fractions.

2 Materials and methods

2.1 SAMPLING

The materials for BGS110 to BGS118 were collected from nine different locations in Ireland, specifically selected to reflect the varied soil types and geochemistry across the country and represent a wide range of underlying geology (limestone, granite, Lower Palaeozoic metasediments and Old Red Sandstone bedrock terranes; Table 1) spanning areas studied by the Tellus Geochemical Survey of Ireland (Gallagher *et al.*, 2016). Bulk samples (50 to 100 kg) of each material were collected and transported to the BGS Keyworth laboratories, for subsequent preparation.

The material for BGS119 is a combination of soils from the UK sampled over a range of sites with varied industrial contamination. Homogenising such soils maximises the range of elements of interest, while mitigating the potentially anomalously high mass fractions that may be present at any one site.

Table 1. Soil texture, geological parent material, and sampling location of BGS110 to BGS119.

RM name	Description
BGS110	Silty sand soil overlying till, with Lower Palaeozoic and granitic clasts, from Valleymount, Co. Wicklow, Ireland.
BGS111	Silty clay soil overlying and immediately downslope of serpentinite body (chromite-bearing, with minor Ni sulfides), from Cummer, Co. Wexford, Ireland.
BGS112	Silty sand soil overlying granitic till, from Brittas, Co. Wicklow, Ireland.
BGS113	Silty clay soil overlying Silurian clastic metasediments, from an area of metalliferous mineralisation, (primarily Pb-Zn), from Castleblayney, Co. Monaghan, Ireland.
BGS114	Silty soil overlying Silurian clastic metasediments, from Carrickmacross, Co. Monaghan, Ireland.
BGS115	Organic-rich silty/peaty soil overlying Carboniferous Limestone, from Belturbet, Co. Cavan, Ireland.
BGS116	Silty soil overlying Carboniferous Limestone, from Carlingford, Co. Louth, Ireland.
BGS117	Silty soil overlying Devonian Old Red Sandstone, from Moorpark, Co. Cork, Ireland.
BGS118	Silty soil overlying Carboniferous shales with high metal (Mo, U) contents, from Glangevlin, Co. Cavan, Ireland.
BGS119	Soil with industrial contamination from various sites in the United Kingdom

2.2 PREPARATION

2.2.1 BGS110 to BGS118

The bulk materials were oven dried at 30˚C, before being disaggregated by hand to prevent the breakdown of clasts, and then sieved using 2 mm nylon mesh to remove stones and non-soil objects. The sieved materials were then milled in 500 mL agate vessels to avoid metallic contamination, using Retsch PM400 planetary ball mills. This produced powders with particle size substantially <32 µm. Portions of the milled samples were checked by wet sieving using Retsch test sieves to ensure they met the quality threshold: >99% at <53 µm and >95% at <32 µm. Although materials prepared in this way might not be entirely representative of soils prepared less finely (e.g. <63 µm), using a finely milled material as QC for less finely milled samples is preferable to using a coarsely milled QC to govern finely milled materials, which itself would introduce additional representivity issues.

Each milled bulk material was homogenised by rotation in bespoke in-house blenders with stainless steel or polypropylene vessels capable of homogenising a range of volumes from 30 L to 400 L of material at a time.

Representative sample division is critical to achieving reliable analytical results (Esbensen and Wagner, 2017). This was achieved by repeated use of a 12-channel unpainted stainless-steel riffle splitter (Endecotts Ltd) and a Retsch PT100 sample divider, fitted with an eight position dividing head and a DR100 vibratory feeder.

Immediately following homogenisation, bulk materials were each transferred to the laboratory where they were representatively divided into portions of approximately 4 kg using the riffle splitters. Working portions were temporarily stored in heavy duty plastic bags during the dividing process. These portions were further divided using the rotary divider into interim storage portions of approximately 500 g, which were uniquely identified and placed in labelled self-seal packets. The density of each material was calculated, and a weight of approximately 40 g was targeted for the final storage container (Nalgene wide-mouth LDPE and HDPE 60 ml bottles). Final portion size was achieved by re-combination of a number of interim portions as required of each material.

A total of 5,568 portions of these RMs were produced, with weights in the range of 38-46 g, apart from BGS115 (low-density peaty soil) which is 24-26 g, as shown in Table 2. Excess bulk materials remain in storage for future production of additional portions.

2.2.2 BGS119

BGS119 was prepared by amalgamation of soil samples taken from industrially contaminated sites across the UK. Each sample was prepared independently by drying, disaggregation and sieving to pass through a 250 µm sieve. The sieved portions were then combined, homogenised and divided following procedures used for BGS110 to BGS118, producing 320 final portions of 26 g (Table 2).

Table 2. Summary of Reference Material portions and portion weights produced.

RM name	Final portion weight (g)	Portions made (n)
BGS110	40-46	768
BGS111	38	512
BGS112	43	640
BGS113	38	640
BGS114	41	640
BGS115	24-26	448
BGS116	43	640
BGS117	41	768
BGS118	38	512
BGS119	26	320

2.3 HOMOGENEITY ASSESSMENT

Sample homogeneity testing was carried out at the interim portion stage of sample handling rather than at the final unit level as recommended in ISO 17034 (ISO/IEC 17034, 2016) and ISO Guide 35 (ISO/IEC Guide 35, 2017) in attempt to minimise production costs whilst maintaining fitness for purpose of the RMs for the anticipated end users. Depending upon the original mass of individual materials, 16, 20 or 24 bags were randomly selected for homogeneity assessment. From each selected bag, two or three subsamples were taken, using a horn spoon to minimise the risk of metal contamination, and prepared as pressed powder pellets for XRFS analysis. Pellets were created by milling 12 g of soil with 3 g of Clariant wax binder, and then using a Herzog HTP40 pellet press. For any one material, pellets were analysed in a single analytical run, in a fully randomised sequence, by WD-XRFS and ED(P)XRFS.

Statistical analysis was undertaken for each quantifiable analyte. Data were assessed for outliers at >3 standard deviations of the mean (Lister, 1982). This simplified approach (relative to that described in ISO Guide 35) was adopted in recognition of the range and size of the contributed dataset and as part of the remit of making the RMs more economically accessible. No data were excluded on the criterion of outliers. Homogeneity statistics were calculated for analytes where the mean was greater than the detection limit (DL). Where standard deviation was ≤DL, the homogeneity was deemed acceptable. Where standard deviation was >DL, and the RSD ≤5%, the homogeneity was deemed acceptable; for the small number of analytes which did not pass this test, analysis of variance (ANOVA) was used. Where the ANOVA F-statistic was below the critical value ($P \leq 0.05$), the variation between bags was not significantly greater than the variation within bags, thus the homogeneity was deemed acceptable. No tested data failed the homogeneity testing criteria.

Soil materials are regarded as being sufficiently stable over a period of tens of years. Although stability of these soil RMs has not explicitly been assessed, Jochum et al. (2015) reported that stability was not usually regarded as an issue for geological RMs because their property values did not change measurably during their shelf life of several tens of years. Soils can be included within this group of RMs following observations of no significant variation on elemental mass fractions before and after the materials underwent storage trials (Idris et al., 2019), and Llauradó et al. (2001) considered the soil materials they prepared to be homogeneous and stable.

2.4 COLLABORATIVE ANALYSIS

When collating data for the characterisation of an RM, elemental mass fractions should, where possible, be determined using more than one method to minimise the risk of method bias.

Analysis of candidate reference materials using their procedure of choice was requested of 15 laboratories who would be typical end users of the RMs, of which 12 returned data. Three of those laboratories reported data from only *aqua regia* procedures, which were assessed to be partial digestion, so reported data were excluded from this data compilation to avoid the potential for methodological bias. Nine laboratories with a range of analytical techniques used to determine total elemental mass fractions, provided data using different procedures and a range of instruments; five of the laboratories reported data from more than one procedure. Each laboratory used their standard analytical procedure, providing data from analysis of three replicate samples of each material. The range of procedures used to acquire data used in this compilation are shown in Table 3. The sample masses used during the characterisation covered a wide range: solution procedures typically used 0.25 g; and the XRF procedures between 2 g and 12 g. The reported uncertainty includes variability related to this range of masses, so it would be inappropriate to recommend a minimum sample size.

Table 3. Analytical procedures used to acquire characterisation data; some procedures were used only for specified materials.

Preparation	Measurement	Method code*	Materials analysed
HF, $HClO_4$, HCl digestion	AAS	a	BGS110, BGS112, BGS114, BGS116, BGS117, BGS118
Ashing pre-treatment; HF, $HClO_4$, HCl digestion	AAS	b	BGS111, BGS113, BGS115, BGS119
HNO_3, H_2O_2 digestion	ICP-MS	c	BGS110 - BGS119
HF, $HClO_4$, HCl digestion	ICP-MS	d	BGS110, BGS111, BGS112, BGS114, BGS116, BGS117, BGS118
Ashing pre-treatment; HF, $HClO_4$, HCl digestion	ICP-MS	e	BGS111, BGS113, BGS115, BGS119
HF, $HClO_4$, HNO_3 digestion	ICP-MS	f	BGS110 - BGS119
Sodium peroxide fusion	ICP-MS	g	BGS110 - BGS119
H_2O_2 pre-treatment; HCl, HNO_3, HF digestion	ICP-AES	h	BGS110 - BGS119
Lithium borate fusion	ICP-AES	i	BGS110 - BGS119
Lithium borate fusion bead	WD-XRFS	j	BGS110 - BGS119
Pressed powder pellet	WD-XRFS	k	BGS110 - BGS119
Pressed powder pellet	ED-XRFS	l	BGS110 - BGS119

* Data were assigned unique procedure codes to distinguish where laboratories reported data from more than one procedure. Procedure code used to identify preparation and measurement used for specific elements listed in Table 7.

2.5 DATA HANDLING, OUTLIER REMOVAL, AND CALCULATION OF RECOMMENDED VALUES

An archived version of all data from contributing laboratories was created and stored, before processing commenced on a duplicate working copy. Once the working copy was formatted to a common standard, data and metadata were imported into, and managed within, a relational database (MS Access) before being exported for data handling using MS Excel, and visualisations in R (R Core Team, 2017). Post-database, all data were managed independently for each RM, using a standardised workflow.

Data assessment followed a planned, staged approach involving (i) a technical review of the appropriateness of the analytical procedure employed, (ii) an objective statistical evaluation to provide a uniform approach, and (iii) a subjective screening to prevent incorporation of erroneous data, thereby improving the estimate of the true value by not simply using an average of the dataset.

i. Firstly, a technical review of the data provided resulted in excluding data reported by procedures assigned as ‘non-total’ (i.e. *aqua regia* extraction), to retain only data reported from ‘total’ procedures. Data reported from digestion or fusion procedures followed by ICP-MS, ICP-AES or AAS analysis or using XRFS techniques, being assessed as methods generating total mass fractions, were retained for subsequent data handling.
ii. Secondly, further data reduction was carried out objectively by single iteration outlier removal of data falling outside the range defined by mean ± 2 standard deviations of the dataset. Thereafter, it was noted that a small number of values for certain analytes from specific laboratories showed systematic bias.
iii. Thirdly, expert judgment was used subjectively to exclude such data as having been determined using an inappropriate method (i.e. analytes present at a mass fraction

beneath reasonable method detection limit, e.g. Te by XRFS); the data sets supplied for Al, Ba, Cd, Ga, La, Sn, Te, Tl, U, Yb and Zr had data removed from one provider, and for Cu from two providers, for all RMs.

In light of the different number of data points used to calculate tabulated mass fraction values and hence the reliability that can be placed on these values, tabulated mass fractions have been assigned a status of “Reference Value” or “Information Value”. Where at least 15 data points remained, the arithmetic mean is provided as the Reference Value together with the expanded uncertainty, which is twice the standard deviation of the mean. Where fewer than 15 data points remain, the mean of the data is provided as an Information Value. The number of data points used for calculation of Reference Values and Information Values are shown in Table 4.

Table 4. Number of data points used to calculate Reference and Information Values for BGS110 to BGS119.

Element	BGS110	BGS111	BGS112	BGS113	BGS114	BGS115	BGS116	BGS117	BGS118	BGS119
Ag	12	12	12	12	12	8	12	12	12	12
Al	18	18	18	18	18	16	18	15	18	18
As	22	26	25	23	21	21	21	24	24	24
B	3	3	3	3	3	3	3	3	3	3
Ba	24	24	23	24	24	21	23	23	22	24
Be	9	8	9	9	9	8	9	8	8	9
Bi	6	6	6	6	6	6	6	6	6	6
Br	8	9	9	9	6	9	9	9	9	6
Ca	25	24	26	24	24	24	24	24	23	24
Cd	12	9	6	21	10	12	12	10	12	12
Ce	14	14	14	15	14	15	15	15	15	15
Cl	5	6	6	6	6	6	6	6	6	5
Co	19	20	19	21	19	21	19	20	19	20
Cr	22	18	23	22	23	22	23	23	23	22
Cs	19	17	20	19	20	14	14	18	20	21
Cu	21	21	21	21	21	21	21	21	21	21
Dy	6	6	6	6	6	6	6	6	6	6
Er	6	6	6	6	6	6	6	6	6	6
Eu	6	6	6	6	6	6	6	6	6	6
Fe	26	25	26	26	25	27	26	24	24	27
Ga	18	18	18	18	18	18	18	18	18	18
Gd	6	6	6	6	6	6	6	6	6	6
Ge	6	9	8	9	9	6	8	8	9	9
Hf	11	12	12	12	12	11	12	12	12	12
Ho	6	6	6	6	6	6	6	6	6	6
I	6	6	6	6	6	6	9	6	6	6
In	3	3	3	3	3	3	3	3	3	6
K	24	24	23	24	24	22	24	23	23	21
La	15	15	15	14	15	15	15	15	15	15
Li	12	12	12	12	12	12	12	12	12	12
Lu	6	6	6	6	6	6	6	6	6	6

Element	BGS110	BGS111	BGS112	BGS113	BGS114	BGS115	BGS116	BGS117	BGS118	BGS119
Mg	23	21	24	21	21	23	21	22	24	21
Mn	27	26	25	27	27	26	27	26	25	26
Mo	22	22	22	21	22	16	22	21	23	22
Na	20	21	21	21	20	21	21	20	21	20
Nb	18	20	18	19	19	18	19	20	19	19
Nd	14	15	14	15	15	15	14	14	15	14
Ni	26	27	25	25	26	25	25	24	25	24
P	18	15	18	18	18	18	18	18	18	18
Pb	24	24	24	27	24	27	24	24	24	27
Pr	6	6	6	6	6	6	6	6	6	6
Rb	25	25	24	25	24	24	26	24	27	25
S	3	3	3	3	3	3	3	3	3	3
Sb	7	9	6	9	9	6	9	9	9	12
Sc	11	12	11	12	12	11	11	11	12	12
Se	13	14	13	18	12	17	11	13	18	14
Si	18	18	18	18	18	18	18	17	18	17
Sm	8	10	9	11	12	12	11	9	12	11
Sn	14	14	15	11	14	11	14	14	15	15
Sr	25	26	27	27	27	27	26	27	27	26
Ta	11	11	10	12	12	9	10	11	12	11
Tb	6	6	6	6	6	6	6	6	6	6
Te	3	3	3	3	3	3	3	3	3	3
Th	15	14	14	15	15	15	14	15	14	15
Ti	24	21	24	24	24	24	24	24	24	24
Tl	9	9	9	9	8	9	9	9	9	9
Tm	6	6	6	6	6	6	6	6	6	6
U	15	15	15	15	15	15	15	15	15	15
V	23	22	22	23	22	21	22	23	23	21
W	12	14	12	11	12	9	11	13	13	15
Y	17	15	18	18	18	18	18	15	18	18
Yb	6	6	6	8	6	6	6	6	6	6
Zn	23	24	26	24	26	24	24	25	25	24
Zr	18	18	18	18	18	18	18	18	18	18

3 Results

Reference Values and Information Values are compiled for 64 analytes in BGS110 to BGS119 (Table 5 and Table 6). The range of laboratory procedures used for each analyte are shown in Table 7, together with the number of procedures used for each analyte to indicate the relative robustness of the values. Individual data sheets for each RM are compiled in Kalra *et al.* (2020), also available from BGS (2022). The data that support the findings of this study are available upon reasonable request.

The staged method of data reduction ensured that appropriate data were incorporated into the final data set. This resulted in assignment of 29 to 33 Reference Values, and 31 to 35 Information Values for each of the RMs.

Soil pH, loss on ignition at 450˚C (LOI) and Hg mass fraction were additionally determined at characterisation but have not had reference values calculated; indicative values of these parameters are presented in Table 8.

Table 5. Reference Values and Information Values† for BGS110 to BGS114. Reference Values are mean and expanded uncertainty. All data in µg g^{-1}.

Element	BGS110	BGS111	BGS112	BGS113	BGS114
Ag	0.405 †	0.443 †	0.331 †	1.50 †	0.519 †
Al	39200 ± 6400	69900 ± 8800	79700 ± 13800	80600 ± 9600	78500 ± 16100
As	9.22 ± 0.94	44.0 ± 5.2	38.1 ± 12.2	40.9 ± 3.8	11.8 ± 3.3
B	26.9 †	66.8 †	15.2 †	30.3 †	55.4 †
Ba	194 ± 27	306 ± 36	402 ± 38	537 ± 61	427 ± 50
Be	2.79 †	2.01 †	3.43 †	1.96 †	2.30 †
Bi	0.192 †	0.318 †	0.403 †	0.312 †	0.191 †
Br	18.1 †	35.0 †	29.7 †	23.4 †	10.5 †
Ca	2310 ± 850	6080 ± 1110	3050 ± 820	4360 ± 690	2750 ± 620
Cd	0.430 †	0.334 †	0.218 †	64.2 ± 11.2	0.309 †
Ce	29.7 †	56.5 †	52.9 †	92.5 ± 15.0	72.6 †
Cl	97.4 †	87.8 †	111 †	60.8 †	54.9 †
Co	7.53 ± 1.52	33.4 ± 5.5	8.71 ± 1.20	46.0 ± 6.7	19.6 ± 3.0
Cr	39.5 ± 15.8	1490 ± 210	32.8 ± 13.3	130 ± 21	118 ± 29
Cs	4.76 ± 1.6	5.09 ± 2.15	9.36 ± 1.76	3.51 ± 2.56	5.68 ± 2.97
Cu	11.9 ± 1.9	27.9 ± 3.3	16.5 ± 2.3	91.6 ± 9.8	38.8 ± 4.2
Dy	1.67 †	3.29 †	2.62 †	8.65 †	5.57 †
Er	0.964 †	1.87 †	1.33 †	4.53 †	3.11 †
Eu	0.556 †	0.997 †	1.12 †	2.99 †	1.63 †
Fe	15300 ± 2100	53300 ± 6500	23000 ± 3900	46100 ± 6600	45200 ± 5500
Ga	8.45 ± 1.17	17.8 ± 2.4	18.2 ± 2.8	19.4 ± 3.1	16.6 ± 2.5
Gd	2.10 †	4.09 †	4.08 †	12.3 †	6.63 †
Ge	2.80 †	4.83 †	3.26 †	4.48 †	4.01 †
Hf	3.56 †	4.57 †	4.29 †	5.91 †	5.89 †
Ho	0.321 †	0.617 †	0.455 †	1.62 †	1.05 †
I	5.78 †	13.8 †	15.4 †	13.2 †	7.01 †
In	0.029 †	0.069 †	0.066 †	0.084 †	0.065 †
K	11800 ± 1200	16900 ± 1500	24100 ± 2400	17700 ± 1200	22100 ± 2600
La	15.2 ± 4.0	29.9 ± 3.1	30.1 ± 3.2	60.7 †	36.3 ± 4.1
Li	38.8 †	28.9 †	117 †	47.5 †	39.2 †
Lu	0.136 †	0.295 †	0.183 †	0.624 †	0.454 †
Mg	2580 ± 2150	19600 ± 8800	4960 ± 3680	9350 ± 4690	12500 ± 6600
Mn	823 ± 170	1850 ± 330	800 ± 147	1390 ± 260	1180 ± 220
Mo	1.21 ± 0.86	1.88 ± 1.25	0.999 ± 1.046	3.64 ± 0.88	1.14 ± 1.02

Element	BGS110	BGS111	BGS112	BGS113	BGS114
Na	8180 ± 1260	6130 ± 1760	12200 ± 1600	7730 ± 2320	7790 ± 1470
Nb	7.43 ± 1.53	13.7 ± 3.5	9.50 ± 1.41	11.8 ± 3.7	12.9 ± 2.8
Nd	12.0 †	22.6 ± 5.0	25.4 †	63.7 ± 5.1	33.5 ± 4.2
Ni	20.1 ± 6.7	227 ± 31	14.0 ± 4.5	147 ± 20	66.7 ± 12.9
P	860 ± 251	1780 ± 160	885 ± 221	1290 ± 140	657 ± 185
Pb	37.4 ± 4.8	24.7 ± 3.1	29.4 ± 3.7	481 ± 102	38.1 ± 4.3
Pr	3.33 †	6.38 †	7.24 †	15.1 †	8.99 †
Rb	72.3 ± 7.7	117 ± 21	140 ± 16	84.5 ± 16.1	100 ± 15
S	399 †	897 †	343 †	902 †	217 †
Sb	0.671 †	1.80 †	0.231 †	1.05 †	1.27 †
Sc	3.42 †	15.3 †	5.61 †	20.0 †	16.0 †
Se	0.644 †	1.01 †	0.734 †	3.07 ± 1.61	0.593 †
Si	367000 ± 48000	235000 ± 33000	313000 ± 25000	240000 ± 29000	301000 ± 29000
Sm	2.59 †	4.36 †	4.98 †	12.5 †	6.23 †
Sn	2.03 †	3.03 †	8.79 ± 3.48	1.87 †	1.60 †
Sr	70.3 ± 11.6	65 ± 11	102 ± 15	95 ± 15.1	71.9 ± 11.8
Ta	1.70 †	1.77 †	1.93 †	2.56 †	1.92 †
Tb	0.286 †	0.560 †	0.494 †	1.57 †	0.948 †
Te	0.098 †	0.138 †	0.131 †	0.245 †	0.183 †
Th	4.56 ± 2.49	7.30 †	9.31 †	11.9 ± 4.7	9.96 ± 3.08
Ti	2190 ± 720	5640 ± 1570	3170 ± 890	4160 ± 1330	4500 ± 1360
Tl	0.564 †	0.492 †	0.722 †	1.09 †	0.647 †
Tm	0.140 †	0.264 †	0.184 †	0.612 †	0.436 †
U	1.71 ± 0.69	2.77 ± 0.98	2.84 ± 0.81	4.85 ± 1.13	2.61 ± 0.82
V	45.8 ± 7.2	140 ± 23	58.4 ± 11.0	139 ± 31	118 ± 22
W	1.14 †	2.68 †	1.70 †	2.66 †	1.58 †
Y	10.6 ± 2.4	20.7 ± 2.7	14.5 ± 3.2	49.6 ± 7.9	31.1 ± 4.9
Yb	0.942 †	1.87 †	1.20 †	3.85 †	2.95 †
Zn	79.4 ± 14.1	82.6 ± 14.7	83.2 ± 11.8	2410 ± 290	106 ± 13
Zr	141 ± 18	185 ± 14	172 ± 31	180 ± 16	239 ± 20

Table 6. Reference Values and Information Values† for BGS115 to BGS119. Reference Values are mean and expanded uncertainty. All data in µg g^{-1}.

Element	BGS115	BGS116	BGS117	BGS118	BGS119
Ag	0.090 †	0.455 †	0.429 †	0.457 †	1.55 †
Al	21900 ± 3600	66700 ± 11900	34100 ± 9400	88100 ± 6900	75000 ± 17300
As	5.15 ± 1.88	14.5 ± 3.2	10.0 ± 2.1	17.1 ± 6.1	350 ± 34
B	12.2 †	33.5 †	35.1 †	51.9 †	58.5 †
Ba	168 ± 30	330 ± 24	158 ± 21	224 ± 21	500 ± 62
Be	0.864 †	1.69 †	0.712 †	2.01 †	3.10 †
Bi	0.093 †	0.176 †	0.131 †	0.264 †	0.818 †
Br	37.1 †	16.0 †	17.4 †	23.1 †	14.0 †

Element	BGS115	BGS116	BGS117	BGS118	BGS119
Ca	12200 ± 1800	8090 ± 1670	2250 ± 640	445 ± 362	17200 ± 2800
Cd	0.737 †	0.442 †	0.194 †	1.25 †	2.82 †
Ce	36.4 ± 8	54.7 ± 5.8	43.8 ± 5.9	86.4 ± 12.7	84.5 ± 22.4
Cl	244 †	75.1 †	90.4 †	117 †	259 †
Co	4.56 ± 2.82	13.1 ± 1.5	8.21 ± 1.39	10.4 ± 2.3	26.1 ± 5.6
Cr	30.0 ± 6.2	90.3 ± 26.2	53.7 ± 19.9	94.5 ± 17.9	127 ± 84
Cs	1.59 †	3.38 †	3.37 ± 2.60	4.88 ± 2.26	7.40 ± 3.81
Cu	22.8 ± 10.6	44.1 ± 4.6	16.5 ± 2.3	113 ± 13	77.1 ± 11.1
Dy	3.27 †	3.38 †	2.45 †	4.65 †	5.62 †
Er	1.74 †	1.94 †	1.49 †	2.48 †	3.09 †
Eu	0.983 †	1.01 †	0.658 †	1.42 †	1.59 †
Fe	18300 ± 3400	34000 ± 5400	21400 ± 3000	35500 ± 2800	76100 ± 13100
Ga	4.74 ± 0.74	13.2 ± 2.0	7.36 ± 1.10	20.4 ± 3.0	16.4 ± 2.2
Gd	3.99 †	4.06 †	2.93 †	6.00 †	6.73 †
Ge	2.54 †	3.83 †	2.88 †	3.59 †	7.26 †
Hf	2.33 †	5.34 †	6.92 †	3.81 †	5.94 †
Ho	0.617 †	0.648 †	0.477 †	0.872 †	1.04 †
I	5.97 †	85.6 †	6.71 †	7.69 †	7.83 †
In	0.027 †	0.050 †	0.034†	0.076 †	0.624 †
K	2370 ± 260	15700 ± 1900	8630 ± 1300	8760 ± 530	16200 ± 1600
La	22.9 ± 6.4	24.6 ± 2.7	21.4 ± 4.9	43.4 ± 7.4	40.1 ± 8.4
Li	20.7 †	26.9 †	20.7 †	76.4 †	81.9 †
Lu	0.222 †	0.277 †	0.234 †	0.334 †	0.446 †
Mg	1530 ± 940	11400 ± 5800	3140 ± 2560	4440 ± 3510	4630 ± 2750
Mn	95.0 ± 24.5	838 ± 173	704 ± 177	334 ± 119	1180 ± 230
Mo	0.984 ± 0.410	1.37 ± 1.07	0.92 ± 1.12	20.4 ± 3.1	5.94 ± 1.50
Na	1630 ± 530	13800 ± 2000	2190 ± 640	2010 ± 530	3210 ± 730
Nb	4.09 ± 1.45	10.7 ± 2.1	14.1 ± 3.5	17.5 ± 2.9	12.3 ± 2.9
Nd	21.1 ± 4.2	21.5 †	17.8 †	35.9 ± 5.0	36.0 †
Ni	23.4 ± 3.9	42.5 ± 8.6	18.0 ± 4.8	28.0 ± 4.2	67.0 ± 9.6
P	788 ± 64	1420 ± 310	1160 ± 330	1480 ± 200	1670 ± 340
Pb	29.9 ± 8.2	31.9 ± 3.4	23.1 ± 3.2	31.1 ± 4	870 ± 204
Pr	4.94 †	5.78 †	4.82 †	9.68 †	9.05 †
Rb	12.2 ± 3.1	84.2 ± 19.7	54.2 ± 6.1	68.2 ± 15.5	94.8 ± 17.6
S	6700 †	387 †	449 †	938 †	6260 †
Sb	0.403 †	0.684 †	0.988 †	2.04 †	22.5 †
Sc	5.46 †	9.99 †	4.65 †	13.5 †	14.5 †
Se	4.04 ± 2.33	0.560 †	0.623 †	4.35 ± 1.41	2.80 †
Si	103000 ± 21000	313000 ± 40000	372000 ± 51000	243000 ± 27000	231000 ± 46000
Sm	4.29 †	4.28 †	3.14 †	6.42 †	6.21 †
Sn	1.30 †	2.34 †	1.66 †	4.38 ± 2.82	12.5 ± 9.3
Sr	73.1 ± 12.2	129 ± 17	27.9 ± 5.1	77.2 ± 15.9	145 ± 25
Ta	0.777 †	1.51 †	1.58 †	2.42 †	2.01 †
Tb	0.567 †	0.576 †	0.403 †	0.811 †	0.950 †

Element	BGS115	BGS116	BGS117	BGS118	BGS119
Te	0.065 †	0.142 †	0.110 †	0.142 †	0.440 †
Th	3.23 ± 2.71	7.16 †	5.78 ± 2.98	9.45 †	13.7 ± 6.9
Ti	1310 ± 450	4020 ± 1270	3820 ± 1600	4590 ± 1000	3770 ± 1390
Tl	0.129 †	0.509 †	0.285 †	1.16 †	2.01 †
Tm	0.226 †	0.275 †	0.216 †	0.338 †	0.443 †
U	6.75 ± 1.68	3.17 ± 1.24	1.90 ± 0.64	9.54 ± 1.99	2.59 ± 0.97
V	36.1 ± 5.6	90.7 ± 18.0	49.5 ± 11.5	177 ± 35	177 ± 23
W	0.617 †	1.52 †	1.10 †	2.00 †	2.91 ± 2.88
Y	19.2 ± 2.3	19.2 ± 3.5	17.6 ± 1.4	24.7 ± 3.1	30.4 ± 8.5
Yb	1.48 †	1.87 †	1.49 †	2.23 †	2.94 †
Zn	24.6 ± 2.7	105 ± 12	63.8 ± 10.4	60.3 ± 8.3	338 ± 48
Zr	84.1 ± 17.7	212 ± 22	316 ± 45	130 ± 18	234 ± 29

Table 7. Analytical procedures used for determination of mass fractions of specific elements (procedure code defined in Table 3).

Element	No. of procedures	a	b	c	d	e	f	g	h	i	j	k	l
Ag	4				d	e	f						l
Al	5							g		i	j	k	l
As	6				d	e	f		h			k	l
B	1							g					
Ba	6				d	e	f	g				k	l
Be	4				d	e	f	g					
Bi	3				d	e	f						
Br	2											k	l
Ca	7	a	b				f			i	j	k	l
Cd	5				d	e	f					k	l
Ce	4				d	e		g				k	
Cl	2											k	l
Co	5				d	e	f			i		k	
Cr	7				d	e	f	g		i		k	l
Cs	6				d	e	f	g				k	l
Cu	5				d	e	f		h			k	
Dy	3				d	e		g					
Er	3				d	e		g					
Eu	3				d	e		g					
Fe	7	a	b				f			i	j	k	l
Ga	6				d	e	f	g				k	l
Gd	4				d	e	f	g					
Ge	3				d	e						k	
Hf	4				d	e		g				k	

Element	No. of procedures	a	b	c	d	e	f	g	h	i	j	k	l
Ho	3				d	e		g					
I	2											k	l
In	3				d	e							l
K	7	a	b				f	g		i	j		l
La	4				d	e		g				k	
Li	4				d	e	f		h				
Lu	3				d	e		g					
Mg	8	a	b				f	g		i	j	k	l
Mn	8	a	b				f	g		i	j	k	l
Mo	7				d	e	f	g	h			k	l
Na	7	a	b				f			i	j	k	l
Nb	5				d	e		g				k	l
Nd	4				d	e		g				k	
Ni	6				d	e	f			i		k	l
P	4						f				j	k	l
Pb	6				d	e	f		h			k	l
Pr	3				d	e		g					
Rb	7				d	e	f	g		i		k	l
S	1						f						
Sb	5				d	e	f					k	l
Sc	3				d	e						k	
Se	6				d	e	f	g				k	l
Si	5							g		i	j	k	l
Sm	4				d	e		g				k	
Sn	5				d	e		g				k	l
Sr	7				d	e	f	g		i		k	l
Ta	4				d	e		g				k	
Tb	3				d	e		g					
Te	2				d	e							
Th	4				d	e		g				k	
Ti	7				d	e		g		i	j	k	l
Tl	3				d	e	f						
Tm	3				d	e		g					
U	5				d	e	f	g				k	
V	6				d	e	f			i		k	l
W	5				d	e		g				k	l
Y	5				d	e		g				k	l
Yb	4				d	e		g				k	
Zn	6				d	e	f		h			k	l
Zr	4							g		i		k	l

Table 8. Indicative mass fractions of measurands additionally determined at characterisation

RM name	pH (0.01 mol l^{-1} $CaCl_2$)	pH (water)*	LOI (% m/m)	Hg (µg g^{-1})
BGS110	5.1	5.7	5.5	0.09
BGS111	6.2	6.8	13.7	0.09
BGS112	4.9	5.6	6.3	0.13
BGS113	5.3	5.9	13.8	0.37
BGS114	6.4	7.0	3.9	0.09
BGS115	4.2	5.0	61.9	0.24
BGS116	6.4	7.0	4.8	0.06
BGS117	5.7	6.3	6.2	0.08
BGS118	3.8	4.6	16	0.14
BGS119	6.7	7.3	9.2	3.25

* Estimated by correlation to Gawlik *et al.* 2003.

4 Discussion

Summary graphs of selected analytes shown in Figure 1 and Figure 2 visualise the range of elemental mass fractions in these RMs. These ranges cover those of relevance to typical background mass fractions in soil, with a range of soil texture, organic carbon and pH (Rawlins *et al.*, 2012; Reimann *et al.*, 2014; Gallagher *et al.*, 2016), as well as those more likely to be associated with metalliferous mineralisation or industrial contamination (Ander *et al.*, 2013), and 'high-tech' critical elements such as Be, Ce, Ga, Ge, In, La, Li and Tl (Reimann *et al.*, 2018). The assigned values also include elements for which values are rarely reported, e.g. Br and I.

Data were compiled following deliberate selection of analyte appropriate procedures closely approximating a total digest or a direct measurement of the solid (Table 3) and datasets further refined by exclusion of outliers more than two standard deviations from the mean. In this way partial extraction and inappropriate procedures were excluded at the outset. Where Reference Values are reported, these show a modest uncertainty in the datasets produced from this process and that there was no appreciable bias between procedures. The selection of procedures in this way is consistent with Byers *et al.* (2016) who reported the good agreement between XRFS and ICP-MS data for 49 elements determined in five soil CRMs, including 21 elements that had previously not been characterised. Wyse *et al.* (2004) recognised the need to incorporate data only from those procedures that achieved total digestion, i.e. by use of HF or fusion, or analysed solid samples without digestion, such as XRFS.

The mass fraction range for these and other distinguishing parameters are described in comparison with existing RM compilation data (Jochum *et al.*, 2005), using the median, 10^{th} and 90^{th} percentiles to describe the data distributions. Instances where the previously available mass fraction range is extended by this suite of RMs is described for Br, Cd, Cr, I, Mn and Zn. Additionally, the coverage at the upper mass fraction ranges of the currently available RMs is expanded in specified materials for Co, La, Li, Mo, Ni, S, Sb, Se and U.

4.1 RANGE OF SOIL PROPERTIES

The RMs represent a diverse compositional range of underlying geology which inherently influences the chemistry of the soil above. Parent materials are granite, serpentinite, limestone, sandstone, shale, clastic sediments (with and without associated metalliferous mineralisation), and a composite soil substantially altered by anthropogenic contamination. This suite is therefore flexible for analyses of a wide range of client soil matrices.

Six RMs had an LOI in the range 4 to 10%, three materials approximately 15%, and one peat-rich soil >60%. This is commensurate with the range of values reported for a study of 819 agricultural topsoils in Europe (GEMAS) (Reimann *et al.*, 2014); median 9.2%; 90th percentile 93% (converting between TOC and LOI by a factor of 2 (Bojko and Kabala, 2014)). This suite of soils covers a wider range of organic matrices than suites of RMs currently commercially available, e.g. 28 soil RMs NCS DC73023 to NCS DC73034, GBW07401 to GBW7408 and GBW 07423 to GBW07430 have equivalent-LOI in the range 0.2 to 4.2% (NACIS 2013; IGGE n.d.; IGGE n.d.) and CANMET RMs TILL-1 to TILL-4 have LOI in the range 3.6-6.8% (CCRMP 1995).

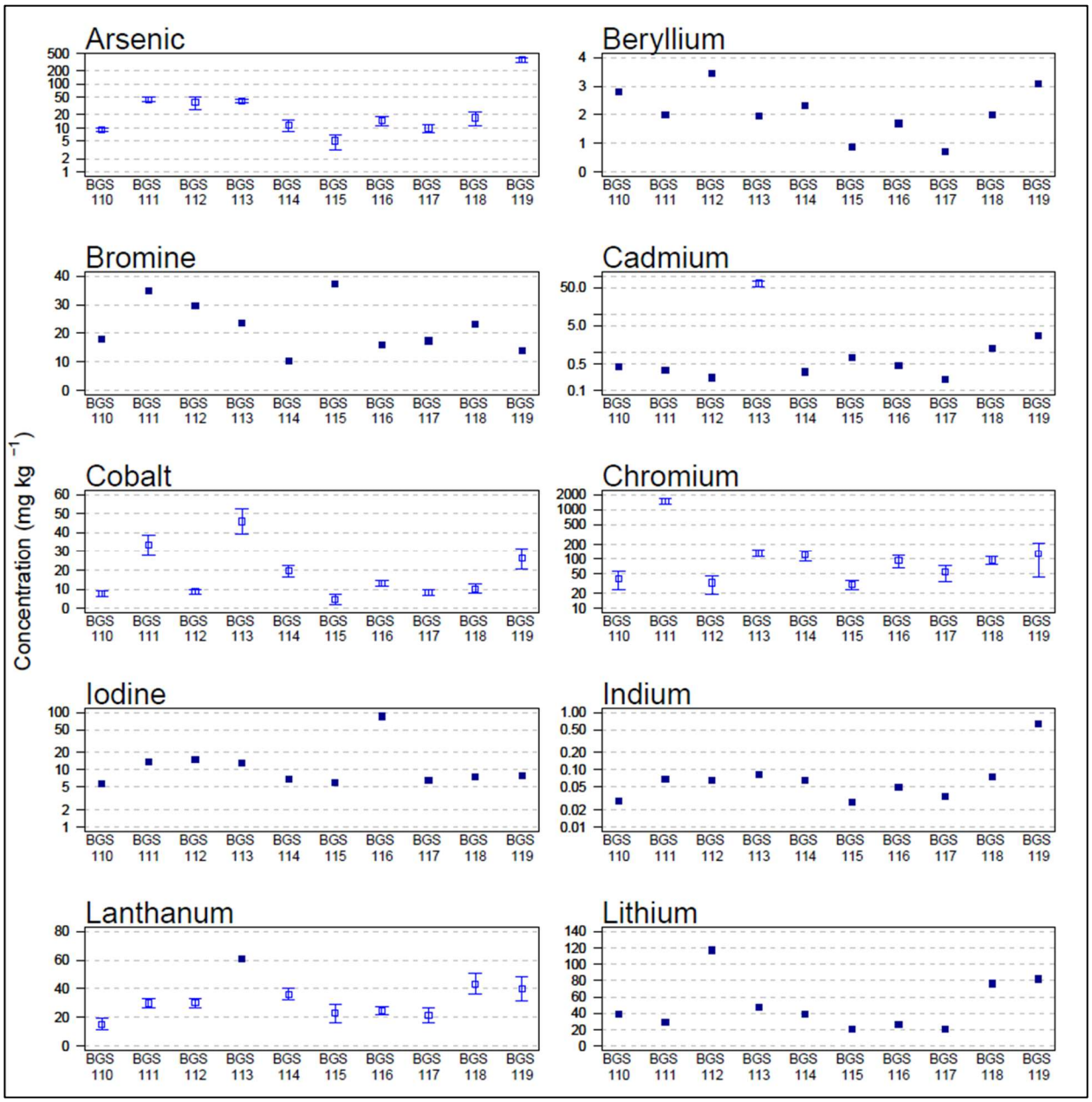

Figure 1. Distribution of mass fraction data reported for As, Be, Br, Cd, Co, Cr, I, In, La and Li. Reference values (light blue) are shown as open symbols together with uncertainty, and Information Values (dark blue) are shown as single points. Error bars show expanded uncertainty calculated as twice the standard deviation of the trimmed data set. The number of data points used for calculation of the values are shown in Table 4. Axis mass fraction values for As, Cd, Cr, I and In are plotted on $\log_{10}$ scale.

The soils had pH values in the range 3.8 to 6.7 as determined using a 0.01 mol l^{-1} $CaCl_2$ slurry procedure. This is commensurate with the range of values reported for a study of 4131 ploughed and grazing land agricultural soils in Europe (GEMAS) analysed using the $CaCl_2$ procedure (Fabian *et al.*, 2014): median pH 5.7; 10th percentile pH 4.4; 90th percentile of pH 7.4, and equivalent to approximately pH 4.6 to 7.3 if analysed using deioinsed water to create the slurry (correlation calculated by comparison with IRMM-443 Eurosoils (Gawlik *et al.*, 2003)). These soils represent soils with greater acidity than the few RMs for which pH values are available, for example although NCS DC 85105a is listed with pH 4.7, seven other RMs NCS DC 85101a to NCS DC 85116 have pH values listed in the range 6.1 to 8.6 (NACIS 2017).

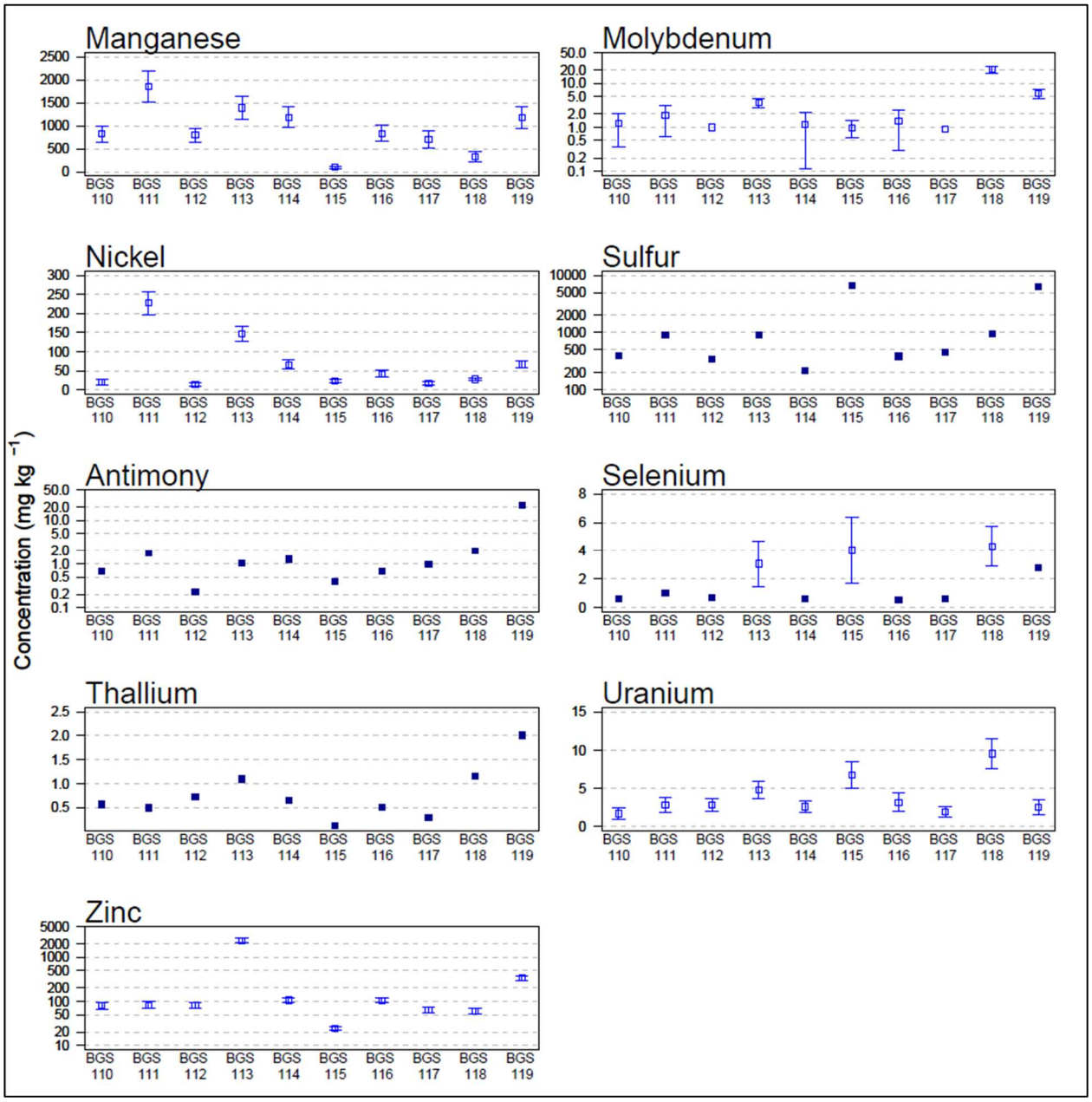

Figure 2. Distribution of mass fraction data reported for Mn, Mo, Ni, S, Sb, Se, Tl, U and Zn. Reference values (light blue) are shown as open symbols together with uncertainty, and Information Values (dark blue) are shown as single points. Error bars show expanded uncertainty calculated as twice the standard deviation of the trimmed data set. The number of data points used for calculation of the values are shown in Table 4. Axis mass fraction values for Mo, S, Sb and Zn are plotted on log_{10} scale.

4.2 ARSENIC

Nine materials had As mass fractions in the range 5 to 44 µg g^{-1} with one material at 350 µg g^{-1}. This is commensurate with 69 soil RMs (Jochum *et al.*, 2005): median 11.2 µg g^{-1}; 10^{th} percentile 3.6 µg g^{-1}; 90^{th} percentile 207 µg g^{-1}. The source of As in BGS110 to BGS118 is geogenic and in BGS119 is potentially enhanced by anthropogenic contamination.

4.3 BERYLLIUM

The materials had Be mass fractions in the range 0.7 to 3.5 µg g^{-1}. This is commensurate with 58 soil RMs (Jochum *et al.*, 2005): median 1.9 µg g^{-1}; 10^{th} percentile of 0.77 µg g^{-1}; 90^{th} percentile of 2.96 µg g^{-1}.

4.4 BROMINE

The ten materials had Br mass fractions that span the range 10 to 37 µg g^{-1} which is beyond the extent of all but one of the currently available 40 RMs (Jochum *et al.*, 2005): median 4.2 µg g^{-1}; 10^{th} percentile 1.4 µg g^{-1}; 90^{th} percentile 7.0 µg g^{-1}. This suite of RMs doubles the mass fraction range currently covered by commercially available RMs.

4.5 CADMIUM

Seven materials had Cd mass fractions in the range 0.2 to 0.7 µg g^{-1}, two materials at 1.25 µg g^{-1} and 2.82 µg $g^{-1}$and one at 64.2 µg g^{-1}. This is largely commensurate with the range of median values (0.08 to 0.35 µg g^{-1}) and maximum values (2 to 77 µg g^{-1}) listed for Cd in continental scale soil surveys (Birke *et al.*, 2016), covering the full mass fraction range for this element. The presence of Cd in soils can derive from mineralisation or association with underlying geology or subsequent industrial/anthropogenic activity. It can accumulate to high mass fractions in some plants, is toxic to others and to most animals and has adverse effects on soil biological activity (Birke *et al.*, 2016). The BGS RM range is generally commensurate with 70 soil RMs (Jochum *et al.*, 2005): median 0.27 µg g^{-1}; 10^{th} percentile 0.09 µg g^{-1}; 90^{th} percentile of 8.0 µg g^{-1}., Exceptionally, Cd is present at elevated mass fraction (64.2 µg g^{-1}) in BGS113.

4.6 COBALT

Six materials had Co mass fractions in the range 4.6 to 13.1 µg g^{-1}, and four materials at 19.6 to 46 µg g^{-1}. This is commensurate with 79 soil RMs (Jochum *et al.*, 2005): median 11.9 µg g^{-1}; 10^{th} percentile 5.5 µg g^{-1}; 90^{th} percentile 22.2 µg g^{-1}. Particularly BGS119, BGS111 and BGS113 span the upper 10% of the mass fraction distribution of currently available RMs.

4.7 CHROMIUM

Nine materials had Cr mass fractions in the range 30 to 130 µg g^{-1}, and one material at 1490 µg g^{-1}. This is commensurate with 77 soil RMs (Jochum *et al.*, 2005): median 64 µg g^{-1}; 10^{th} percentile 23.6 µg g^{-1}; 90^{th} percentile 174 µg g^{-1}. Exceptionally, the mass fraction of Cr in BGS111 (1490 µg g^{-1}), exceeds the previously highest mass fraction of currently available RMs (455 µg g^{-1}).

4.8 IODINE

Six materials had I mass fractions in the range 5.8 to 7.8 µg g^{-1}, three materials at 13-16 µg g^{-1} and one material at 85.6 µg g^{-1}. This is commensurate with the upper 20% of the mass fraction distribution of 33 soil RMs (Jochum *et al.*, 2005): median 2.2 µg g^{-1}; 10^{th} percentile 0.74 µg g^{-1}; 90^{th} percentile 14.4 µg g^{-1}. Exceptionally, the I mass fraction in BGS116 is at elevated mass fraction (85.6 µg g^{-1}), more than twice the value of the largest currently available RM.

4.9 INDIUM

Nine materials had In mass fractions in the range 0.027 to 0.084 µg g^{-1}, and one material at 0.624 µg g^{-1}. This is commensurate with 36 soil RMs (Jochum *et al.*, 2005): median

0.073 µg g^{-1}; 10th percentile 0.038 µg g^{-1}; 90th percentile 0.61 µg g^{-1}. The mass fraction of In in BGS119 (0.624 µg g^{-1}) exceeds the mass fractions of all but four of the currently available RMs.

4.10 LANTHANUM

Nine materials had La mass fractions in the range 15 to 44 µg g^{-1}, and one material at 60.7 µg g^{-1}. This is commensurate with 55 soil RMs (Jochum *et al.*, 2005): median 34 µg g^{-1}; 10th percentile 19.1 µg g^{-1}; 90th percentile 43.2 µg g^{-1}. The mass fraction of La in BGS113 (60.7 µg g^{-1}), exceeds the mass fractions of all but one of the currently available RMs. Lanthanum is one of the REE typically with higher mass fractions, and the relative abundance of La in BGS110 to BGS119 is presented as being representative of all the REE.

4.11 LITHIUM

Seven materials had Li mass fractions in the range 21 to 48 µg g^{-1}, and three materials at 76 to 117 µg g^{-1}. This is commensurate with 49 soil RMs (Jochum *et al.*, 2005): median 30.6 µg g^{-1}; 10th percentile 14.9 µg g^{-1}; 90th percentile 52.6 µg g^{-1}. The mass fractions of Li in BGS118 (76.4 µg g^{-1}), BGS119 (81.9 µg g^{-1}), and BGS112 (117 µg g^{-1}) exceeds the mass fractions of all but one of the currently available RMs.

4.12 MANGANESE

One material had Mn mass fraction at 95 µg g^{-1}, eight materials at 330 to 1400 µg g^{-1}, and one material at 1850 µg g^{-1}. This is commensurate with 80 soil RMs (Jochum *et al.*, 2005): median 645 µg g^{-1}; 10th percentile 270 µg g^{-1}; 90th percentile 1423 µg g^{-1}. Mn is present at elevated mass fraction (1850 µg g^{-1}) in BGS111 and exceptionally the mass fraction of Mn in BGS115 (95 µg g^{-1}), is lower than the previously lowest mass fraction of currently available RMs (173 µg g^{-1}).

4.13 MOLYBDENUM

Seven materials had Mo mass fractions in the range 0.92 to 1.88 µg g^{-1}, and three materials at 3.64 µg g^{-1}, 5.94 µg g^{-1} and 20.4 µg g^{-1}. This is commensurate with 53 soil RMs (Jochum *et al.*, 2005): median 1.16 µg g^{-1}; 10th percentile 0.61 µg g^{-1}; 90th percentile 16.7 µg g^{-1}. Particularly BGS113, BGS119 and BGS118 span the upper 15% of the mass fraction distribution of currently available RMs. The presence of high Mo mass fractions in soil can lead to molybdenosis in ruminants that graze over those soils, which can itself lead to copper deficiency (Frank, 1998).

4.14 NICKEL

Eight materials had Ni mass fractions in the range 14 to 67 µg g^{-1}, two materials at 147 µg g^{-1} and 227 µg g^{-1}. This is commensurate with 80 soil RMs (Jochum *et al.*, 2005): median 28.8 µg g^{-1}; 10th percentile 12.2 µg g^{-1}; 90th percentile 88.4 µg g^{-1}. Particularly BGS111 and BGS113 span the upper 10% of the mass fraction distribution of currently available RMs.

4.15 SULFUR

Eight materials had S mass fractions in the range 217 to 938 µg g^{-1}, and two materials at 6260 to 6700 µg g^{-1}. This is commensurate with 52 soil RMs (Jochum *et al.*, 2005): median 270 µg g^{-1}; 10th percentile 109 µg g^{-1}; 90th percentile 1930 µg g^{-1}. The mass fractions of S in BGS119 (6260 µg g^{-1}) and in BGS116 (6700 µg g^{-1}) exceed the mass fractions of all but three of the currently available RMs.

4.16 ANTIMONY

Nine materials had Sb mass fractions in the range 0.23 to 2.04 µg g^{-1}, and one material at 22.5 µg g^{-1}. This is commensurate with 61 soil RMs (Jochum *et al.*, 2005): median 1.5 µg g^{-1}; 10th percentile 0.42 µg g^{-1}; 90th percentile 19.4 µg g^{-1}. Notably the mass fraction of Sb in BGS119 exceeds the 90th percentile of the mass fraction distribution of currently available RMs.

4.17 SELENIUM

Six materials had Se mass fractions in the range 0.5 to 1.0 μg g^{-1} and four materials at 2.8 to 4.4 μg g^{-1}. This is commensurate with 54 soil RMs (Jochum *et al.*, 2005): median 0.26 μg g^{-1}; 10^{th} percentile 0.09 μg g^{-1}; 90^{th} percentile 1.55 μg g^{-1}. The mass fractions of Se in BGS119 (2.8 μg g^{-1}), BGS113 (3.07 μg g^{-1}), BGS115 (4.04 μg g^{-1}) and BGS118 (4.35 μg g^{-1}) exceed the 90^{th} percentile and fill the gap in mass fractions of the currently available RMs (2-8 μg g^{-1}).

4.18 THALLIUM

Nine materials had Tl mass fractions in the range 0.129 to 1.16 μg g^{-1}, and one material at 2 μg g^{-1}. This is commensurate with 40 soil RMs (Jochum *et al.*, 2005): median 0.61 μg g^{-1}; 10^{th} percentile 0.32 μg g^{-1}; 90^{th} percentile 2.22 μg g^{-1}.

4.19 URANIUM

Eight materials had U mass fractions in the range 1.7 to 4.9 μg g^{-1}, two materials at 6.75 μg g^{-1} and 9.54 μg g^{-1}. This is commensurate with 56 soil RMs (Jochum *et al.*, 2005): median 2.4 μg g^{-1}; 10^{th} percentile 1.5 μg g^{-1}; 90^{th} percentile 4.6 μg g^{-1}. Notably BGS115 (6.75 μg g^{-1}) and BGS118 (9.54 μg g^{-1}) span the upper 10% of the mass fraction distribution of currently available RMs.

4.20 ZINC

One material had Zn mass fraction at 24.6 μg g^{-1}, eight materials in the range 60 to 338 μg g^{-1}, and one material at 2410 μg g^{-1}. This is commensurate with 78 soil RMs (Jochum *et al.*, 2005): median 85.1 μg g^{-1}; 10^{th} percentile 45.5 μg g^{-1}; 90^{th} percentile 573 μg g^{-1}. The mass fraction of Zn in BGS113 (2410 μg g^{-1}) exceeds the mass fractions of all but two of the currently available RMs. Exceptionally, the mass fraction of Zn in BGS115 (24.6 μg g^{-1}), is lower than the previously lowest mass fraction of currently available RMs (29 μg g^{-1}).

4.21 MERCURY (INDICATIVE DATA ONLY)

Mercury analyses were conducted using a direct mercury analyser at the homogeneity testing stage. Five materials had Hg mass fractions in the range 0.05 to 0.10 μg g^{-1}, four materials in the range 0.1-0.4 μg $g^{-1}$and one, industrially contaminated soil at >3 μg g^{-1}. This is commensurate with the range of values reported for a study of 833 agricultural topsoils in Europe (GEMAS): median 0.037 μg g^{-1}; 90^{th} percentile 0.115 μg g^{-1}. Reimann *et al.* (2018) reported Hg mass fractions in 2108 agricultural ploughed soils: median 0.030 μg g^{-1}; 90^{th} percentile 0.076 μg g^{-1}; maximum 1.6 μg g^{-1}. Hg mass fractions in 28 soil RMs NCS DC73023 to NCS DC73034, GBW07401 to GBW7408 and GBW 07423 to GBW07430 are in the range 0.007 μg g^{-1} to 0.59 μg g^{-1} (NACIS 2013; IGGE n.d.; IGGE n.d.). BGS119 has Hg present at a level more usually associated with fluvial or marine sediments (e.g. HR-1, MESS-4). Other existing soil RMs at this mass fraction tend to have been influenced by influx of sediment rather than industrial processes.

5 Conclusion

This suite of ten soil RMs addresses a previously unmet need to have References Materials of appropriate matrices which allow the simultaneous quality control assessment of the multielement analysis now routinely reported by ICP-MS or XRFS. This allows for meaningful demonstration of data quality, and creates efficiencies in analytical programmes. Full methodological descriptions and elemental values are available in data sheets for each RM (Kalra *et al.*, 2020).

This set of materials includes soils encompassing diverse underlying geology, including areas of low normal background elemental mass fractions, enhanced mineralisation influences, and with high peat content. The elemental mass fraction distributions of determinands such as Br, Cd, Cr, I, Mn and Zn extend the range of currently available soil RMs and support the range of mass fractions previously covered by materials no longer commercially available. This means that data quality can be meaningfully assessed at the mass fractions expected in the analysis of unknown samples, providing greater flexibility for users to run RMs appropriate to the samples they have received for analysis.

The objective of making available a thoroughly characterised suite of ten soil reference materials with diverse matrices for total elemental mass fractions - offered as a cost-effective alternative to CRMs - has been successfully achieved. Future updates could include incorporation of partial extraction procedures (e.g. *aqua regia*, bioaccessibility) or isotope characterisation, as more data becomes available. Readers are encouraged to contact the authors if they would be interested in contributing.

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The British Geological Survey holds most of the references listed and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at https://ukrinerc.on.worldcat.org/discovery

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