Rialtas na hÉireann
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Geological Survey
Suirbhéireacht Gheolaíochta
Ireland | Éireann

Tellus Geochemical Survey: Deeper topsoil data from the midlands of Ireland

Geological Survey Ireland Report

April 2021

Geological Survey Ireland is a division of the Department of the Environment, Climate and Communications

Document information

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Change record

Version 1.1

Executive Summary

This report accompanies the publication of data and maps that present the inorganic geochemical data for deeper topsoil samples across part of the midlands of Ireland. Samples were collected between 2017 and 2019, as part of the Tellus geochemical survey project of Geological Survey Ireland.

Data are reported here for up to 4934 sites in the north midlands and western regions of Ireland. Sample sites are distributed at a typical density of one site per 4 km^2 and together they represent a variety of geological domains in Ireland, covering an area of over 17,000 km^2 (24.3% of the country).

Each sample was prepared and chemically measured by a number of techniques. Laboratory tests comprise: soil pH ($CaCl_2$); loss-on-ignition at 450°C and multi-element partial extract analyses of major, minor and trace elements by ICP following *aqua regia* digestion. ICP (*aqua regia*) analyses were conducted by ALS Minerals Ltd., Ireland. Further analysis by XRF will be conducted and results presented at a later date.

Acknowledgements

Geological Survey Ireland and the Tellus geochemistry team gratefully acknowledge all contributors and contractors for their efforts towards this report and accompanying data and publications. The Tellus survey would like to acknowledge the efforts of all project partners, contractors and especially field samplers, and the kind co-operation of all landowners and stakeholders.

This report is published with the approval of the Director, Geological Survey Ireland.

All data and publications are freely available at www.gsi.ie/tellus.

Disclaimer

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Introduction

Geological Survey Ireland is conducting a flagship project to sample and measure the geochemical characteristics of the surficial environment of Ireland. The Tellus project geochemistry workstream commenced in 2011. Its aim is to produce spatial data to determine the geochemical baseline of topsoil and deeper topsoil, stream sediment and stream water in predominantly rural Ireland. Work began in the border region to complement the Tellus project of Northern Ireland, completed in 2008, and surveying has systematically extended in a southerly direction since.

The report describes all aspects of data associated with deeper topsoil, denoted sample type 'S', collected from one survey site per 4 km^2. Details of the samples and laboratory analysis are provided and this report is the quality assurance delivered to accompany published datasets. Herein are descriptions of all quality control (QC) measures and data that are assessed to determine that the data are fit-for-purpose, which is to describe the regional geochemical baseline concentrations in the surficial environment. The authors do not define anomalies or recommend follow-up works or research.

This report details the analytical procedures and work undertaken to validate the geochemical analytical results. Validating the quality of an environmental dataset is critical given that any chemical analyses are confounded by uncertainty. Using reputable laboratories with accredited analytical and other procedures has been afforded the highest priority, yet it is still essential to assess the data in order to examine the reliability of the results and ensure that they are fit-for-purpose. To this end the geochemistry programme has employed a range of internal quality control (QC) procedures based on recommentations for comparable geochemical surveys (Plant et al., 1975). Broadly these comprise:

- Collection of field duplicate samples and preparation and analysis of field duplicate and analytical replicate samples
- Randomisation of sample IDs assigned to individual samples
- Blind insertion of international (preferably certified) or external reference materials
- Blind insertion of internal or secondary reference materials
- Use of analytical laboratory duplicates.

The trueness of the analytical results has been primarily assessed using certified reference materials, with a guidance of its accepted (statistically validated) element concentrations therein. These data are also used to gain an understanding of the systematic bias in the data.

The accuracy of the analytical results is typically assessed using repeated analyses of primary and secondary reference materials. Repeated determinations over the whole period of analytical works are useful and can identify analytical drift over time or abrupt changes, for example in the calibration set-up of the instrument. To this end, the laboratories were instructed to perform the analyses in sequential sample number order. Each sample analysis was reported with a date and time stamp to evaluate the time-series of the data.

The variance of the samples data is assessed using a series of randomly distributed duplicate and replicate samples to apportion the analytical variance to different sources.

Deeper topsoil samples

Sampling and sample summary

Survey design and sample locations

Maps displaying the survey extent and sample site locations of deeper topsoil samples are shown below (Map 1 and Map 2). The survey design is a systematic one based on a predefined fishnet of 2 km by 2 km grid cells, based on even-numbered easting and northing lines on the Irish National Grid (Geographic Coordinate System: GCS_TM65), as printed on the 1:50,000 published map series. Survey grid cells were planned in advance using GIS. The result is a total of 4278 sample sites in the survey area, at a typical density of one sample per four square kilometres (4 km^2).

The following criteria are required for sample site selection in the field:

- Samplers should make every effort to seek permission from relevant landowners prior to sampling.
- A soil sample site should be greater than 250 m from the edge of the 2 km by 2 km survey grid cell (except for coastal survey grid cells) and be located as close to the centre of the cell as possible, whilst representing the dominant land use in that cell.
- A soil sample site should be from undisturbed and unforested land *where possible*.
- Sample sites must be greater than 200 m from major infrastructure and water bodies/rivers and greater than 100 m from mapped and unmapped infrastructure and small water bodies/streams. Sites should be upslope and away from all observed contaminants at site where possible.

Each unique sampling location was designated a numerical six-digit site number, beginning with a numerical two-digit project code. In the field and for sample preparation and analyses, samples are organized into field batches of one hundred numbers.

Sample numbers were allocated to sampling teams so that samples were collected in predefined random sample order according to a series of random number checklists. Upon collection and checking, samples were then sorted into sequential numerical order for preparation and analyses.

Details of the field sampling logistics are reported by the contractor responsible for sample collection. Standard operating procedures are documented internally by the project.

Summary of regular and control samples by field hundred batch

Deeper topsoil samples collected by the Tellus survey are denoted sample type code ‘S’.

In each field batch of a hundred numbers, up to 90 were allocated to true soil sample site locations. The remaining 10 were set aside to be allocated to a variety of quality control samples (QCS). In summary:

- Two sets of field duplicates (DUP) were collected in each batch, denoted duplicate pairs A-B and C-D, with each pair collected from a single site. DUPA and DUPC are treated as true samples for the purpose of the survey.
- Each duplicate site number has a corresponding replicate or subsample (SS) number; the duplicate sample was subsampled in the laboratory to create the replicate sample, which was analysed blindly to the analytical laboratories. These replicate samples are denoted SSA, SSB, SSC and SSD. For example, a quartet of DUPA, DUPB, SSA and SSB together provide four results from a single sample location and data are used to evaluate data variability.

- Four sample numbers are reserved for a selection of standards (STD). These are analytical reference materials (RMs) and are used as quality control samples (QCS) for data quality assurance (QA) and quality control (QC) procedures.

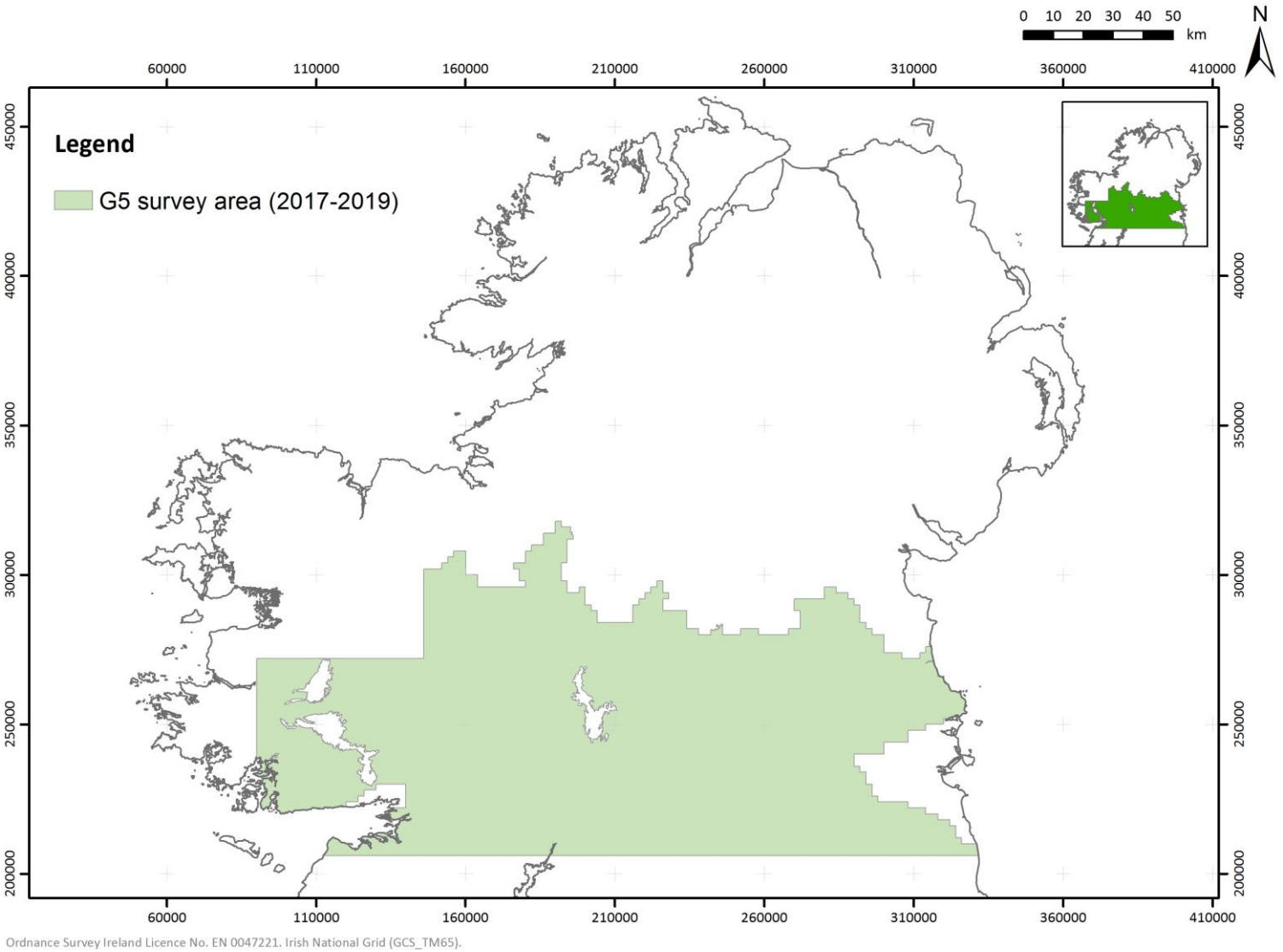
Typically, a field duplicate sample was collected at a rate of two sets (quartets) per field hundred batch of 100 samples. Sample and QCS numbers by field hundred batch are summarized in Table 1.

Table 1 Summary of QCS by field hundred batches.

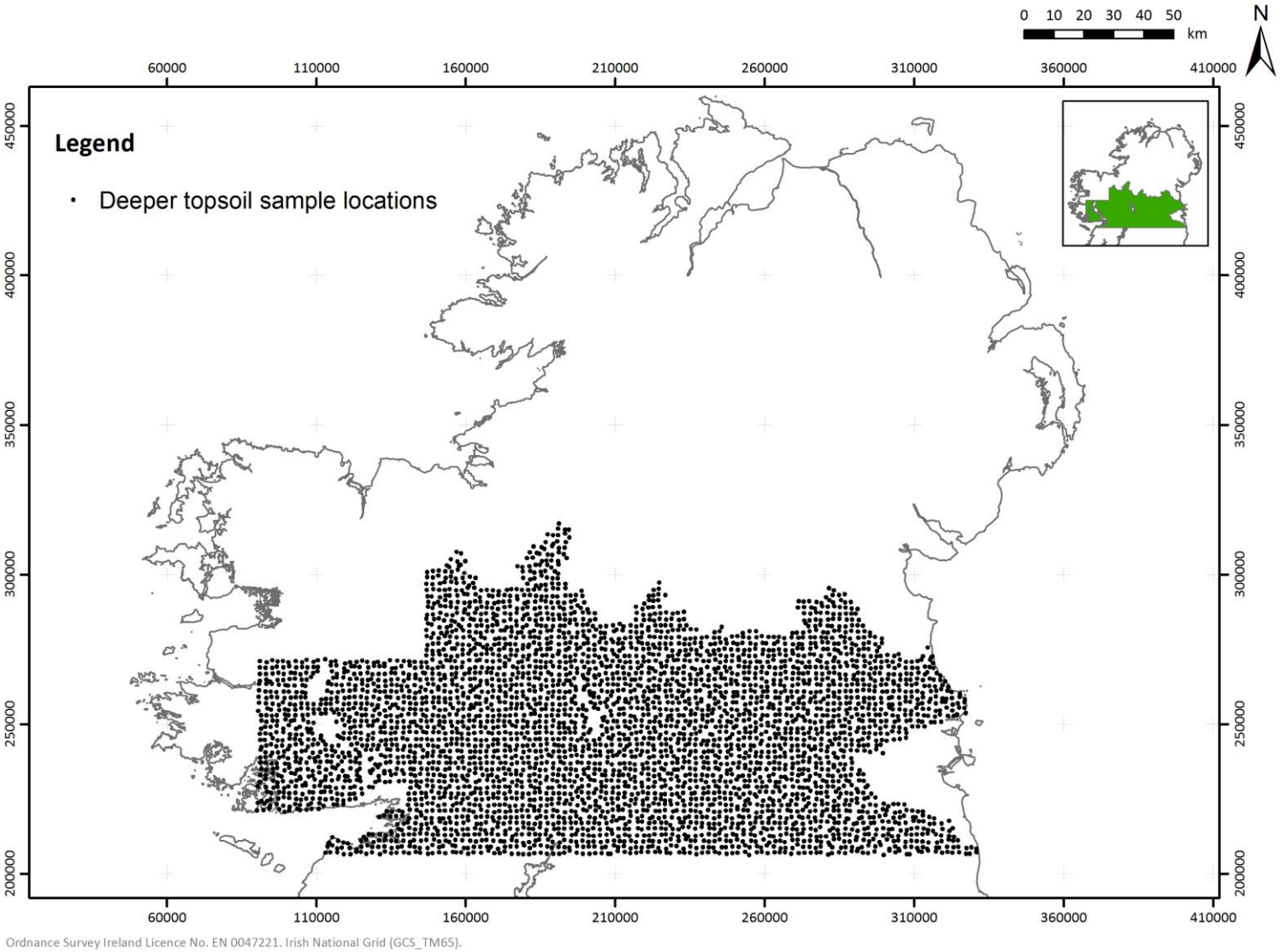
Random number checklist number	Field hundred batch	Sample ID range from	Sample ID range to	Sampling date from	Sampling date to	*n* samples in field hundred batch	*n* sample sites in field hundred batch	*n* blind CRMs	*n* blind SRMs	*n* DUP and SS QCS
6	6117xx	611701S	611800S	19/04/2016	06/05/2017	100	90	2	2	8
1	6118xx	611801S	611900S	04/05/2017	09/08/2017	100	90	2	2	8
2	6119xx	611901S	612000S	12/05/2017	20/05/2017	100	90	2	2	8
3	6120xx	612001S	612100S	18/05/2017	02/06/2017	100	90	2	2	8
4	6121xx	612101S	612200S	26/05/2017	08/06/2017	100	90	2	2	8
5	6122xx	612201S	612300S	01/06/2017	26/06/2017	100	90	2	2	8
6	6123xx	612301S	612400S	08/06/2017	23/06/2017	100	90	2	2	8
1	6124xx	612401S	612500S	14/06/2017	27/06/2017	100	90	2	2	8
2	6125xx	612501S	612600S	19/06/2017	26/06/2017	100	90	2	2	8
3	6126xx	612601S	612700S	23/06/2017	04/07/2017	100	90	2	2	8
4	6127xx	612701S	612800S	29/06/2017	17/07/2017	100	90	2	2	8
5	6128xx	612801S	612900S	12/07/2017	26/07/2017	100	90	2	2	8
6	6129xx	612901S	613000S	19/07/2017	27/07/2017	100	90	2	2	8
1	6130xx	613001S	613100S	25/07/2017	18/08/2017	100	90	2	2	8
2	6131xx	613101S	613200S	29/07/2017	09/08/2017	100	90	2	2	8
3	6132xx	613201S	613300S	04/08/2017	23/08/2017	100	90	2	2	8
4	6133xx	613301S	613400S	16/08/2017	25/08/2017	100	90	2	2	8
5	6134xx	613401S	613500S	22/08/2017	14/09/2017	100	90	2	2	8
6	6135xx	613501S	613600S	25/08/2017	11/09/2017	100	90	2	2	8
1	6136xx	613601S	613700S	28/08/2017	13/09/2017	100	90	2	2	8

Random number checklist number	Field hundred batch	Sample ID range from	Sample ID range to	Sampling date from	Sampling date to	*n* samples in field hundred batch	*n* sample sites in field hundred batch	*n* blind CRMs	*n* blind SRMs	*n* DUP and SS QCS
2	6137xx	613701S	613800S	29/08/2017	21/09/2017	100	90	2	2	8
3	6138xx	613801S	613900S	01/09/2017	08/09/2017	100	90	2	2	8
4	6139xx	613901S	614000S	04/09/2017	27/09/2017	100	90	2	2	8
5	6140xx	614001S	614100S	06/09/2017	09/09/2017	100	90	2	2	8
6	6141xx	614101S	614200S	07/09/2017	13/09/2017	100	90	2	2	8
1	6142xx	614201S	614300S	09/09/2017	22/09/2017	100	90	2	2	8
2	6143xx	614301S	614400S	12/09/2017	22/09/2017	100	90	2	2	8
3	6144xx	614401S	614500S	14/09/2017	22/09/2017	100	90	2	2	8
4	6145xx	614501S	614600S	15/09/2017	20/10/2017	100	90	2	2	8
5	6146xx	614601S	614700S	19/09/2017	11/10/2017	100	90	2	2	8
6	6147xx	614701S	614800S	20/09/2017	29/09/2017	100	90	2	2	8
1	61489xx	614801S	614900S	22/09/2017	06/10/2017	100	90	2	2	8
2	6149xx	614901S	615000S	27/09/2017	04/10/2017	100	90	2	2	8
3	6150xx	615001S	615100S	29/09/2017	26/10/2017	100	90	2	2	8
4	6151xx	615101S	615200S	03/10/2017	03/11/2017	100	90	2	2	8
5	6152xx	615201S	615300S	05/10/2017	09/10/2017	100	90	2	2	8
6	6153xx	615301S	615400S	07/10/2017	26/10/2017	100	90	2	2	8
1	6154xx	615401S	615500S	10/10/2017	26/10/2017	100	90	2	2	8
2	6155xx	615501S	615600S	11/10/2017	23/10/2017	100	90	2	2	8
3	6156xx	615601S	615700S	13/10/2017	26/11/2017	100	90	2	2	8
4	6157xx	615701S	615800S	23/10/2017	23/11/2017	100	90	2	2	8
5	6158xx	615801S	615900S	16/10/2017	07/11/2017	100	90	2	2	8
6	6159xx	615901S	616000S	25/10/2017	23/11/2017	100	90	2	2	8
1	6160xx	616001S	616100S	27/10/2017	24/11/2017	100	90	2	2	8
2	6161xx	616101S	616200S	02/11/2017	05/12/2017	100	90	2	2	8

Random number checklist number	Field hundred batch	Sample ID range from	Sample ID range to	Sampling date from	Sampling date to	*n* samples in field hundred batch	*n* sample sites in field hundred batch	*n* blind CRMs	*n* blind SRMs	*n* DUP and SS QCS
3	6162xx	616201S	616300S	06/11/2017	05/12/2017	100	90	2	2	8
4	6163xx	616301S	616399S	08/11/2017	08/12/2017	94	84	2	2	8
5	6164xx	616404S	616499S	10/11/2017	31/01/2018	44	34	2	2	8
6	6165xx	616504S	616597S	05/08/2019	05/08/2019	8	0	2	2	8
1	6166xx	616606S	616693S	12/08/2019	13/08/2019	8	0	2	2	8
2	6167xx	616706S	616792S	24/09/2019	24/09/2019	8	0	2	2	8
3	6168xx	616807S	616893S	23/08/2019	23/08/2019	8	0	2	2	8
4	6169xx	616905S	616995S	27/08/2019	10/09/2019	8	0	2	2	8
5	6170xx	617005S	617096S	02/09/2019	02/09/2019	8	0	2	2	8
6	6171xx	617104S	617197S	09/09/2019	09/09/2019	8	0	2	2	8
1	6172xx	617206S	617293S	16/09/2019	16/09/2019	8	0	2	2	8
2	6173xx	617306S	617392S	19/09/2009	19/09/2009	8	0	2	2	8
3	6174xx	617407S	617493S	26/09/2019	26/09/2019	8	0	2	2	8



Map 1 Survey campaign area G5. Field sampling was conducted using the national projection co-ordinate system Irish National Grid (Geographic Coordinate System: EN 0047221).



Map 2 Deeper topsoil sample locations for campaign area G5. Field sampling was conducted using the national projection co-ordinate system Irish National Grid (Geographic Coordinate System: EN 0047221).

Soil sample preparation

All soil samples were prepared in a trace-level facility without the use of metallic or otherwise contaminating apparatus.

In the field, soil samples collected in Kraft® paper bags were initially air dried. When practicable, samples were placed into warming cabinets at 30°C to evaporate additional moisture. Samples were packaged into Euro stacking crates in numerical order and transported to the contractor to undertake sample preparation. Sample preparation was conducted at the Inorganic Geochemistry Facility in the Centre for Environmental Geochemistry, British Geological Survey, Keyworth, UK.

Upon receipt, samples were routinely additionally dried. The dried sample was then disaggregated by hand using a ceramic mortar and pestle, taking care not to break up lithic clasts. Duplicate samples were riffle split to create replicate subsamples. The disaggregated material was cone-and-quartered to obtain a representative sub-sample of *c.*40 g (± 2 g) suitable for agate ball milling. Excess unmilled material was bagged, labelled and boxed. The *c.*40 g sub-sample was milled in a Retsch PM400 agate planetary ball mill with 20 mm Ø sized agate grinding balls at 300 rpm for between 30 and 45 minutes to produce a milled or pulped sample for chemical analyses so that nominally 99% of sample is <53 µm and 95% of sample is <32 µm. The mills are operated under conditions that cause minimal sample heating and that ensure a final product particle size of <32 µm. Cone-and-quartered milled sample splits for the different analytical methods (namely four different analyses: LOI at 450°C, pH by $CaCl_2$, and ICP_{ar}) were prepared at the same time. Sample splits of coarse <2 mm fraction proceed to pH analyses and all other tests are performed on splits of milled pulped powder material.

Condition of samples submitted from the field contractor

In 2019, 880 infill survey grid cells were spread throughout the 2017 midlands survey area and were re-sampled between July and September. Sampling took place in the core summer months and, overall, the weather did not cause any issues in terms of sampling or subsequent handling. Samples were encouraged to air-dry naturally by the field Contractor, with some re-bagging before dispatch to GSI. Samples were received in an appropriate state but after arrival to GSI we experienced mass Kraft bag failure and a high proportion of samples had to be re-bagged.

Sample split prepared for pH analyses

Sub-samples prepared for soil pH analyses were dried, disaggregated, and sieved to <2 mm but not milled. Typically, just over 10 g of sample mass were provided in a labelled securitainer, enough for the 5 g required plus more for repeat analysis if desired by the laboratory. Sample excesses are usually returned.

Sample split prepared for ICP_{ar} multi-element analyses

Sub-samples of prepared (disaggregated, sieved and milled) samples and reference materials were prepared for ICP_{ar} multi-element analyses. Typically, 10 g of sample mass were provided in a labelled securitainer, enough for the 1 g required plus more for repeats as desired by the laboratory. Sample excesses are usually returned.

Sample split prepared for loss-on-ignition (LOI) analyses

Sub-samples of prepared (disaggregated, sieved and milled) samples were prepared for LOI analyses. Typically, 2.5 g of sample mass were provided in a labelled securitainer, enough for the 1 g required plus more for repeats as desired by the laboratory. Sample excesses are usually returned.

Insertion of reference materials, blind to the analyst

The sample preparation contractor prepared a range of QCS, as per instructions, for blind submission within the randomized sequence of samples.

A range of reference materials (RMs) were portioned and potted in the exact same manner as regular samples and not identified in any way by their packaging or sample lists sent to the laboratory.

Soil chemical analyses

Soil samples were analysed by several methods:

- Soil loss-on-ignition at 450°C.
- Soil pH by $CaCl_2$ slurry.
- Multi-element analyses for a range of major, minor and trace elements by ICP following *aqua regia* digestion ("ICP_{ar}").

ALS Minerals Ltd. ('OMAC'), Loughrea, Ireland, provided analytical services for all tests. See Appendix C below for details of all soil analysis measurands, concentration units, methods, lower limits of detection (LLD), upper calibration limits (UCL), lower calibration limits (LCL) and method uncertainties.

Laboratory chemical analyses

Multi-element data are requested to be reported uncensored, *i.e.* without truncation or replacement of below- or above-detection or reporting limit values with a fixed value. A reported dataset commonly includes negative values. The advantages of this are manyfold for regional geochemical data. All interpolation spatial mapping makes use of uncensored data which provide a continuous variable dataset. All statistical measures and data transformations better cope with uncensored data and a proportion of data below a theoretical LLD can still be useful in the overall statistical assessment. Statistical tests such as ANOVA cannot be carried out on censored or false value data, or on zero concentration values. Uncensored data has an advantage of not having artefacts of rounding which can lead to step changes in the data distribution. This practice greatly facilitates the QC procedures and is particularly relevant where an analyte's natural abundance is low in relation to the detection limit. The reported uncensored concentration values are maintained throughout the QC process and uploaded in this format to the database.

Soil loss-on-ignition at 450°C

ALS Minerals Ltd. OA-GRA05f: Soil LOI analyses of 1 g prepared (milled) sub-sample

Method code OA-GRA05f is used for soil loss-on-ignition (LOI) analyses of prepared (milled/pulped) soil samples. A 1g weighed sample is combusted in a tared, pre-ignited crucible in a temperature-controlled Vecstar benchtop muffle furnace at 450°C for four hours. It is then cooled in a controlled (moisture-free) atmosphere and re-weighed. LOI is calculated as the proportionate mass difference before and after combustion.

Soil pH by $CaCl_2$ slurry

ALS Minerals Ltd. OA-ELE07: Soil pH analyses of 5 g prepared (not milled) sub-sample

Method code OA-ELE07 is used for soil pH analyses of prepared (<2 mm fraction) soil samples. A 5g weighed sample is mixed with 12.5mL of 0.01M $CaCl_2$ and placed on reciprocal shaker for *c.5* minutes to form a slurry. Soil suspension is allowed to settle for *c.*1 hour. A pH electrode and 794 Basic Titrando as well as TITRANDO 905 automated titrators are used to measure the solution pH potentiometrically. The pH meter is calibrated to a range of buffer calibration solutions.

Multi-element partial extract analyses of major, minor and trace elements by ICP following *aqua regia* digestion

ALS Minerals Ltd. MS41L: Multi-element ICP(-OES/-MS) analyses of 1 g prepared (milled) sub-sample after aqua regia extraction

Method code MS41L is used for multi-element sample analysis and combines a two-acid *aqua regia* digestion of homogenized soil sample followed by analysis by ICP-MS. Sample aliquot ca 0.5g is mixed with 75% *aqua regia,* 3:1 HNO_3:HCl, digested in a graphite heating block and made up to final volume of 12.5ml with dH_2O. This method is particularly well suited for samples with high calcium content. For reactive samples slow addition of acid mixture is required and/or reduction of the nominal sample weight.

Sample submission to the laboratories

All samples were packed in numerical order into archive boxes for transport from the preparation facility to the analytical laboratory. A total of 4934 samples were submitted to ALS Minerals Ltd. on 31/08/2020 for chemical analyses. Samples were analysed across 24 laboratory batches of ca 200 samples per batch. Data for 4934 sample IDs by LOI were reported to GSI by 16/11/2020. Data for 4934 sample IDs by pH were reported to GSI by 21/12/2020. Data for 4934 sample IDs by ICP_{ar} were reported to GSI on 27/11/2020.

Table 2 Deeper topsoil ICP_{ar} analytes, concentration units, methods, lower limits of detection and reporting (LLD/LRL), upper reporting limits (URL), accreditation statuses.

Element	Symbol	Unit	Lower reporting limit (LRL, also LLD)	URL	Instrument	Instrument method	Accredited
Gold	Au	mg kg^{-1}	0.000002	25	ICP-MS	MS41L-BLD	No
			0.0002	25	ICP-MS	ME-SM41L	Yes
Silver	Ag	mg kg^{-1}	0.00001	100	ICP-MS	MS41L-BLD	No
			0.001	100	ICP-MS	ME-SM41L	Yes
Aluminium	Al	weight %	0.0001	25	ICP-MS	MS41L-BLD	No
			0.01	25	ICP-MS	ME-SM41L	Yes
Arsenic	As	mg kg^{-1}	0.0001	10000	ICP-MS	MS41L-BLD	No
			0.01	10000	ICP-MS	ME-SM41L	Yes
Boron	B	mg kg^{-1}	0.1	10000	ICP-MS	MS41L-BLD	No
			10	10000	ICP-MS	ME-SM41L	Yes
Barium	Ba	mg kg^{-1}	0.005	10000	ICP-MS	MS41L-BLD	No
			0.5	10000	ICP-MS	ME-SM41L	Yes
Beryllium	Be	mg kg^{-1}	0.0001	1000	ICP-MS	MS41L-BLD	No
			0.01	1000	ICP-MS	ME-SM41L	Yes
Bismuth	Bi	mg kg^{-1}	0.000005	10000	ICP-MS	MS41L-BLD	No
			0.0005	10000	ICP-MS	ME-SM41L	Yes
Calcium	Ca	weight %	0.0001	25	ICP-MS	MS41L-BLD	No
			0.01	25	ICP-MS	ME-SM41L	Yes
Cadmium	Cd	mg kg^{-1}	0.00001	1000	ICP-MS	MS41L-BLD	No
			0.001	1000	ICP-MS	ME-SM41L	Yes
Cerium	Ce	mg kg^{-1}	0.00003	500	ICP-MS	MS41L-BLD	No
			0.003	500	ICP-MS	ME-SM41L	Yes
Cobalt	Co	mg kg^{-1}	0.00001	10000	ICP-MS	MS41L-BLD	No
			0.001	10000	ICP-MS	ME-SM41L	Yes
Chromium	Cr	mg kg^{-1}	0.0001	10000	ICP-MS	MS41L-BLD	No
			0.01	10000	ICP-MS	ME-SM41L	Yes

Element	Symbol	Unit	Lower reporting limit (LRL, also LLD)	URL	Instrument	Instrument method	Accredited
Caesium	Cs	mg kg^{-1}	0.00005	500	ICP-MS	MS41L-BLD	No
			0.005	500	ICP-MS	ME-SM41L	Yes
Copper	Cu	mg kg^{-1}	0.0001	10000	ICP-MS	MS41L-BLD	No
			0.01	10000	ICP-MS	ME-SM41L	Yes
Iron	Fe	weight %	0.00001	50	ICP-MS	MS41L-BLD	No
			0.001	50	ICP-MS	ME-SM41L	Yes
Gallium	Ga	mg kg^{-1}	0.00004	10000	ICP-MS	MS41L-BLD	No
			0.004	10000	ICP-MS	ME-SM41L	Yes
Germanium	Ge	mg kg^{-1}	0.00005	500	ICP-MS	MS41L-BLD	No
			0.005	500	ICP-MS	ME-SM41L	Yes
Hafnium	Hf	mg kg^{-1}	0.00002	500	ICP-MS	MS41L-BLD	No
			0.002	500	ICP-MS	ME-SM41L	Yes
Mercury	Hg	mg kg^{-1}	0.00004	10000	ICP-MS	MS41L-BLD	No
			0.004	10000	ICP-MS	ME-SM41L	Yes
Indium	In	mg kg^{-1}	0.00005	500	ICP-MS	MS41L-BLD	No
			0.005	500	ICP-MS	ME-SM41L	Yes
Potassium	K	weight %	0.0001	10	ICP-MS	MS41L-BLD	No
			0.01	10	ICP-MS	ME-SM41L	Yes
Lanthanum	La	mg kg^{-1}	0.00002	10000	ICP-MS	MS41L-BLD	No
			0.002	10000	ICP-MS	ME-SM41L	Yes
Lithium	Li	mg kg^{-1}	0.001	10000	ICP-MS	MS41L-BLD	No
			0.1	10000	ICP-MS	ME-SM41L	Yes
Magnesium	Mg	weight %	0.0001	25	ICP-MS	MS41L-BLD	No
			0.01	25	ICP-MS	ME-SM41L	Yes
Manganese	Mn	mg kg^{-1}	0.001	50000	ICP-MS	MS41L-BLD	No
			0.1	50000	ICP-MS	ME-SM41L	Yes
Molybdenum	Mo	mg kg^{-1}	0.0001	10000	ICP-MS	MS41L-BLD	No

Element	Symbol	Unit	Lower reporting limit (LRL, also LLD)	URL	Instrument	Instrument method	Accredited
			0.01	10000	ICP-MS	ME-SM41L	Yes
Sodium	Na	weight %	0.00001	10	ICP-MS	MS41L-BLD	No
			0.001	10	ICP-MS	ME-SM41L	Yes
Niobium	Nb	mg kg^{-1}	0.00002	500	ICP-MS	MS41L-BLD	No
			0.002	500	ICP-MS	ME-SM41L	Yes
Nickel	Ni	mg kg^{-1}	0.0004	10000	ICP-MS	MS41L-BLD	No
			0.04	10000	ICP-MS	ME-SM41L	Yes
Phosphorus	P	weight %	0.00001	1	ICP-MS	MS41L-BLD	No
			0.001	1	ICP-MS	ME-SM41L	Yes
Lead	Pb	mg kg^{-1}	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Palladium	Pd	mg kg^{-1}	0.00001	25	ICP-MS	MS41L-BLD	No
			0.001	25	ICP-MS	ME-SM41L	Yes
Platinum	Pt	mg kg^{-1}	0.00002	25	ICP-MS	MS41L-BLD	No
			0.002	25	ICP-MS	ME-SM41L	Yes
Rubidium	Rb	mg kg^{-1}	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Rhenium	Re	mg kg^{-1}	0.000002	50	ICP-MS	MS41L-BLD	No
			0.0002	50	ICP-MS	ME-SM41L	Yes
Sulphur	S	weight %	0.0001	10	ICP-MS	MS41L-BLD	No
			0.01	10	ICP-MS	ME-SM41L	Yes
Antimony	Sb	mg kg^{-1}	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Scandium	Sc	mg kg^{-1}	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Selenium	Se	mg kg^{-1}	0.00003	1000	ICP-MS	MS41L-BLD	No
			0.003	1000	ICP-MS	ME-SM41L	Yes

Element	Symbol	Unit	Lower reporting limit (LRL, also LLD)	URL	Instrument	Instrument method	Accredited
Tin	Sn	mg kg^{-1}	0.0001	500	ICP-MS	MS41L-BLD	No
			0.01	500	ICP-MS	ME-SM41L	Yes
Strontium	Sr	mg kg^{-1}	0.0001	10000	ICP-MS	MS41L-BLD	No
			0.01	10000	ICP-MS	ME-SM41L	Yes
Tantalum	Ta	mg kg^{-1}	0.00005	500	ICP-MS	MS41L-BLD	No
			0.005	500	ICP-MS	ME-SM41L	Yes
Tellurium	Te	mg kg^{-1}	0.00003	500	ICP-MS	MS41L-BLD	No
			0.003	500	ICP-MS	ME-SM41L	Yes
Thorium	Th	mg kg^{-1}	0.00002	10000	ICP-MS	MS41L-BLD	No
			0.002	10000	ICP-MS	ME-SM41L	Yes
Titanium	Ti	weight %	0.00001	10	ICP-MS	MS41L-BLD	No
			0.001	10	ICP-MS	ME-SM41L	Yes
Thallium	Tl	mg kg^{-1}	0.00001	10000	ICP-MS	MS41L-BLD	No
			0.001	10000	ICP-MS	ME-SM41L	Yes
Uranium	U	mg kg^{-1}	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Vanadium	V	mg kg^{-1}	0.001	10000	ICP-MS	MS41L-BLD	No
			0.1	10000	ICP-MS	ME-SM41L	Yes
Tungsten	W	mg kg^{-1}	0.00001	10000	ICP-MS	MS41L-BLD	No
			0.001	10000	ICP-MS	ME-SM41L	Yes
Yttrium	Y	mg kg^{-1}	0.00003	500	ICP-MS	MS41L-BLD	No
			0.003	500	ICP-MS	ME-SM41L	Yes
Zinc	Zn	mg kg^{-1}	0.001	10000	ICP-MS	MS41L-BLD	No
			0.1	10000	ICP-MS	ME-SM41L	Yes
Zirconium	Zr	mg kg^{-1}	0.0001	500	ICP-MS	MS41L-BLD	No
			0.01	500	ICP-MS	ME-SM41L	Yes

Table 3 Deeper topsoil pH ($CaCl_2$) and LOI (450°C) analytes, concentration units, methods, lower limits of detection and reporting (LLD/LRL), upper reporting limits (URL), accreditation statuses.

Analyte	Unit	Lower reporting limit (LRL, also LLD)	URL	Instrument	Accredited
Soil pH	pH unit	0.1		pH meter / $CaCl_2$ slurry	No
Soil LOI	%	0.01		Loss-on-ignition at 450°C	Yes

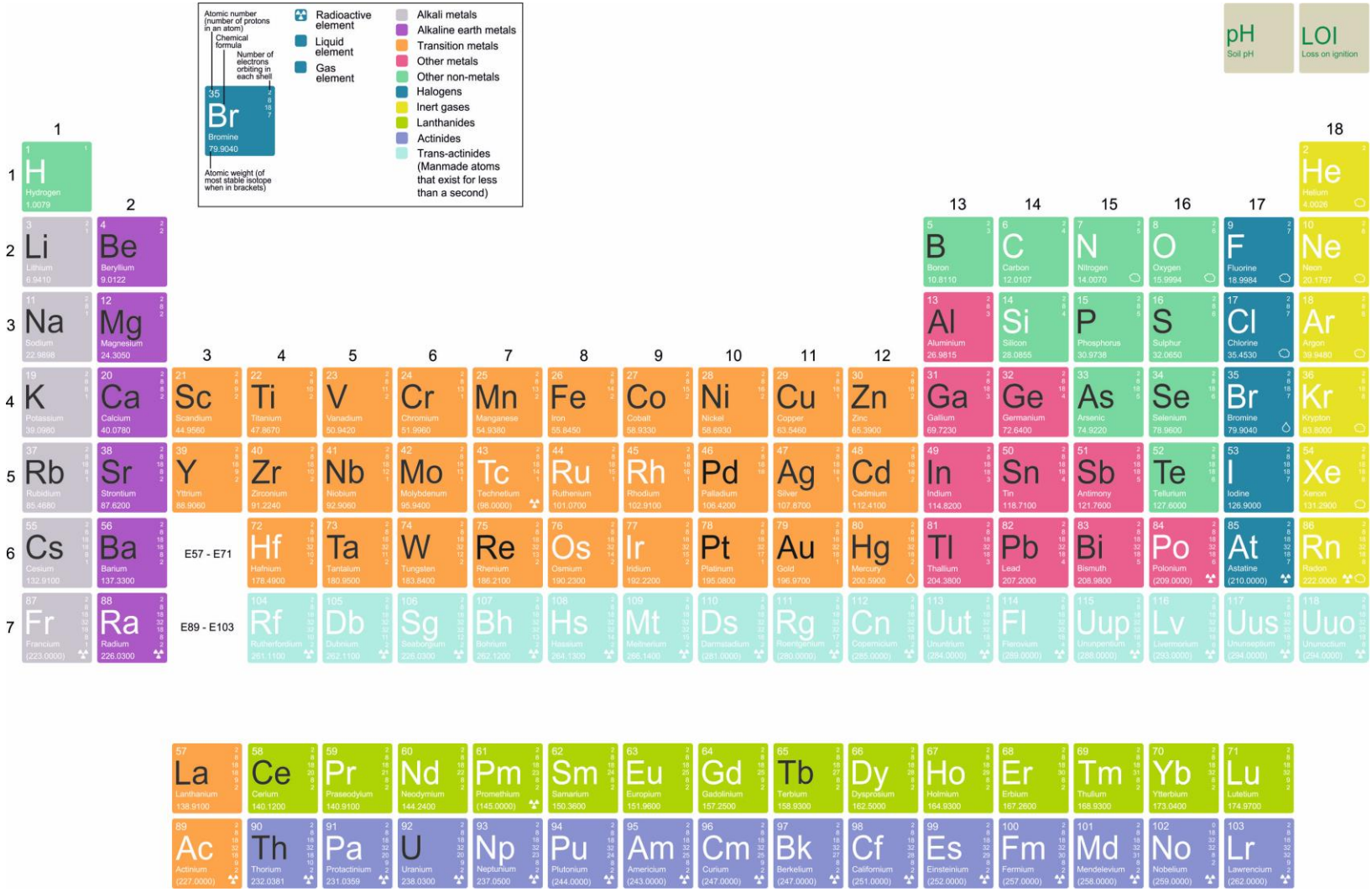


Figure 1 Graphic of the periodic table, with ICP_{ar} element analytes for deeper topsoil samples shown in black text, Soil pH ($CaCl_2$) and LOI (at 450°C) in green text. Adapted after http://www.sciencegeek.net/tables/PToE_

Quality control samples

The main types of quality control samples (QCS) employed for Tellus soil geochemistry are:

i. **Duplicate**: a sample collected from the same sample site location (typically 20 m away from original sampling location). It is used to assess the variability of the sampling process.
ii. **Replicate**: created in the laboratory by dividing a Duplicate sample into two identical parts, using a recognized subsampling method (e.g. cone and quarter). Replicates are used to assess analytical or laboratory errors.
iii. **Reference material**: a sample prepared and analysed previously by stated methods, with statistical validation provided through repeated testing, to achieve accepted results used as a reference. Reference materials are used to assess precision and accuracy of analysis. Ideally the reference material used should match the nature, sample type and matrix of the regular samples being analysed.
iv. **Blank**: a sample used to investigate risk of contamination from the handling, treatment and/or analysis of samples. Blanks are most applicable to solute or aqueous analysis.

Randomisation of sample identities

The field QC and analytical data quality checks are based upon pre-randomisation of sample identities (Plant, 1973). This serves several uses on a large-scale survey. In any measurement process, there *will* be a degree of both random error and systematic biases. Randomisation of the identities ensures that the errors are spread out evenly across all samples and ergo the survey area. Any errors that are dependent on a particular portion of time or processes within a laboratory are mitigated by spreading out the effects. In particular, very commonly there is slow analytical drift by analytical instruments. Where geographically contiguous (i.e. not randomized) samples are also analysed in the same sequence, any drift may be masked by natural geochemical variation and difficult to identify. If analytical drift occurs during analysis of samples that exhibit a natural increase or decrease in abundance of measurands it could result in artificial amplification or suppression of true measurands abundances. Therefore, non-randomized samples can lead to false geochemical spatial patterns.

Randomisation of sample identities allows the geochemist to check for quality concerns such as carry-over of high results (be they a memory effect or contamination) from one sample to another and to refine any data conditioning actions only to those samples with identifiable quality issues rather than across the board. Finding clues of sample misidentification is only possible if there is a number of placeholder QCS where an expected limited range of result(s) can be used to establish whether or not there is any evidence of samples being misidentified at the preparatory and/or laboratory analyses stages.

A chart for each analyte of lab-reported data is made to assure that the range of concentration values for the measurands are randomly distributed across the sample ID range. These data are also assessed with $\log_{10}$ transformation. Each analyte has been assessed alongside the control charts to identify inter-batch changes that might lead to boundary effects on the combined spatial dataset. Duplicate and replicate pairs are also examined against each other through x/y plots, stacked box residual plots and mean percent relative difference plots to identify any significant deviations.

Analysis of Variance (ANOVA) using duplicate and replicate QCS data

Collection and preparation of duplicates and replicates

In each field batch of one hundred sample numbers, two pairs of field duplicate samples (*i.e.* two samples collected from the same site) were collected: duplicate pair A-B and duplicate pair C-D. A field duplicate consists of a second complete composite sample, collected with a central point a small distance (*c*. 21 m) from the original sampling point (Figure 2). Thus, no two samples of a duplicate pair are strictly a duplicate of one another but are separated by a very short distance from what is considered the same site. There will necessarily be some variance between the duplicate samples, and this will depend on the setting and geochemical media.

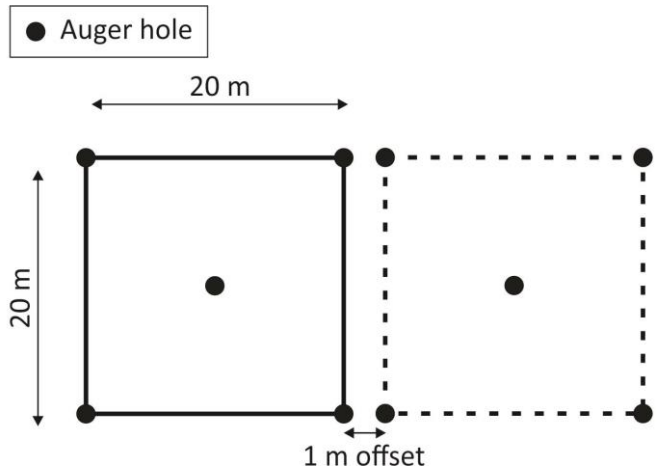


Figure 2 Diagrammatic plan for collection of a five auger hole composite soil sample and a field duplicate sample (indicated by dashed line pictogram).

For each of samples denoted DUPA, DUPB, DUPC and DUPD, each sample was especially prepared, and riffle split in half to produce a replicate sample, denoted SSA, SSB, SSC and SSD.

The relationship of duplicate and replicate samples is displayed diagrammatically in Figure 3. The quartet of samples from a field duplicate sample site is used to statistically evaluate the data variability, which is apportioned to between-site, between-sample and within-sample variability.

The locations of duplicate sample sites are quite randomly distributed across the survey area. Duplicate and replicate samples were each assigned a unique sample ID and were thus unknown as control samples by the laboratories.

Note that, for each duplicate pair in a field batch, by convention analytical data for DUPA and DUPC are reported as the "normal" sample data for the respective duplicate site.

Duplicate and replicate analyses

The geochemical (spatial) and technical (sampling plus analytical) variance in the chemical results can be examined using duplicate and replicate sampling. A duplicate sample is a sample that is collected from the same sampling site as an original sample. A replicate is an original sample subdivided prior to receipt by the laboratory. A duplicate sample will therefore indicate sampling variability within a single site whereas a replicate will indicate the variability of the laboratory preparation and analysis. In practice, replicate samples are the subsamples created from a duplicate sample. The laboratory may analyse *any* sample in replicate as

part of their own QA/QC, and may label these as “Duplicates”, and such samples should not be confused with Tellus duplicate and replicate samples.

The use of duplicates and replicates for quality control of data generated for large systematic geochemical surveys is a well-established approach (Johnson et al., 2008; Ramsey et al., 1992). This procedure allows for understanding of sample data repeatability and the types and sources of variability in the analytical chemical data. A fully nested analysis of variance of the duplicate and replicate samples data is used to quantify the systematic and random uncertainties caused by the sample collection, preparation/handling and sample analytical procedures.

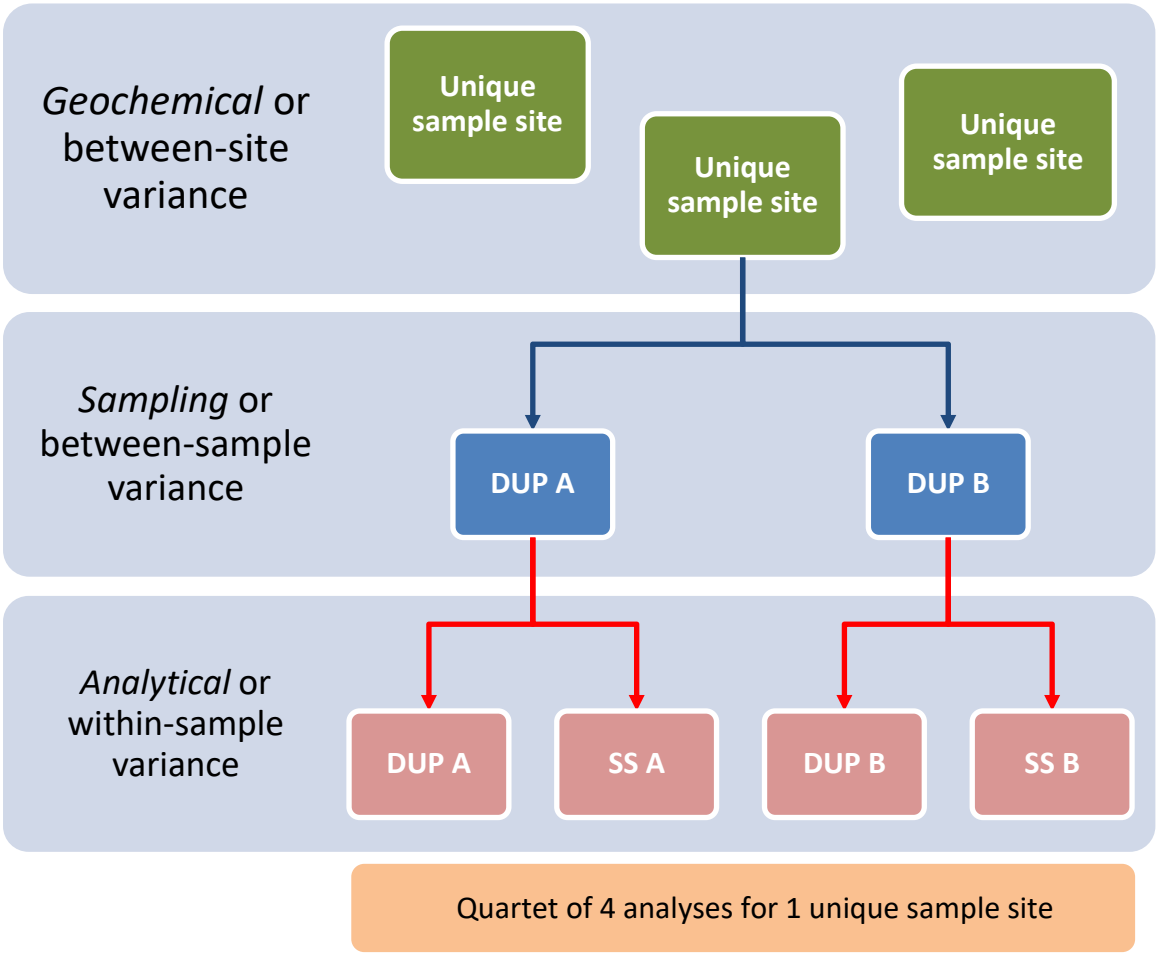


Figure 3 Diagram to show the relationship between field duplicates (“DUP”) and replicate (“SS”) samples, used to apportion data variance.

Evaluating the duplicate-replicate control samples data is undertaken in three ways:

- Compilation of the data into the quartets and inspecting conditionally formatted data to flag any large variations between duplicate and replicate pairs that may reflect erroneous results. For example, these might be due to sample misidentification.
- Data analysis using charts to visualize the data and to investigate anomalous data.
- Undertaking a hierarchical fully nested analysis of variance (after Sinclair, 1983) to quantify the proportions of data attributable to between-site, between-sample and within-sample variance.

For each analyte, the raw results (not modified or censored) are charted in a number of ways for two sets of paired values: (i) duplicate-duplicate (DUP-DUP) and (ii) duplicate-replicate (DUP-SS). Each is inspected to identify samples that do not exhibit a close equality and to follow up on samples where a sample misidentification is suspected.

A total of 464 samples of duplicates/ replicates from 60 and 58 unique sample sites (quartets of data), respectively, across the survey area are available to assess in this way. For elements where the between-sample (the same as within-site) variability is high, usually owing to local inhomogeneity, the duplicate-duplicate (DUP-DUP) relationships will show a greater scatter away from the 1:1 equality line. In replicates that are not homogeneous then a greater scatter of duplicate-replicate (DUP-SS) relationships will show this.

Analysis of variance (ANOVA)

Analysis of variance (ANOVA) is a statistical test applied to assess the representativity of geochemical results. Nested (hierarchical) ANOVA analysis is carried out on duplicate and replicate samples and quantifies the variability of within– and between–sample sites data. For applications to geochemical mapping, it is a requirement that the variance between sample sites is greater than the variance associated with the sampling and handling/analytical processes. The recommended variance portion limits are 80% for between site, 16% for between sample, and 4% for within sample (Johnson, 2002).

If there is any doubt about the sampling and subsampling methodologies being followed then ANOVA should not be applied. If any individual duplicate or replicate sample is suspected to be misidentified as part of a quartet, that quartet of results is best excluded. The ANOVA assessment is done without any concern for the site or geological characteristics. There is reliance on the random and even distribution of duplicate sample sites across the area and over the period of sampling and on the random assignment of sample collectors to duplicate sites.

ANOVA assumes a normal distribution that geochemical data rarely display. A transformation assists in this requirement but the effects of extreme outliers, poly-modal or non-($\log_{10}$) normal distributions will be apparent in the ANOVA test results. It is recommended that the sample data are examined by cumulative frequency and other charts for exploratory data analysis (EDA) in order to establish each variable's statistical behaviour and to assess the ANOVA results in the context of each variable's data distribution.

For each variable, the data are $\log_{10}$ transformed (since many geochemical datasets are log-normally distributed) and therefore it is a requirement that there are no zero or negative concentration values. Censored data distorts the ANOVA analysis and so any control quartet containing censored data (*i.e.* below detection data substituted by a constant value) was not used in the analysis. Any incomplete quartet cannot be used; for example if one of the four duplicate or replicate results is missing or not determined, the quartet is excluded. Deeper topsoil pH data are currently not included in the ANOVA analysis.

All variables had at least some data below LLD for every quartet of data available. Where fewer than 10 quartets are available for analysis, the ANOVA result is highlighted in light red. The data users are cautioned that the ANOVA results are limited for boron (B) and palladium (Pd). Where the within sample variance is >4%, the results are highlighted pale orange: tin (Sn), indium (In), platinum (Pt) and gold (Au).

ANOVA approach and results

The ANOVA test results based on all available duplicate site data for the survey area are presented in Table 4 and graphically in Chart 1.

Majority of analytes in the survey area dataset exhibit combined sampling variance of less than 5%, so the uncertainty associated with sampling and analyses is very small, and the data are excellently suited to regional geochemical mapping applications.

Table 4 ANOVA results for all duplicate site deeper topsoil data. Sorted by descending between site variance. Where fewer than 10 quartets are available for analysis, the ANOVA result is highlighted light red. Where the within sample variance is >4%, the results are highlighted pale orange.

		Variance component (100% sum)			
Variable	Method	Between site (%)	Between sample (%)	Within sample (%)	*n* quartets
V	ICP_{ar}	98.58	1.30	0.12	113
Fe	ICP_{ar}	98.51	1.44	0.06	116
Al	ICP_{ar}	98.46	1.46	0.08	116
Ce	ICP_{ar}	98.44	1.49	0.07	116
Cr	ICP_{ar}	98.26	1.54	0.20	110
Co	ICP_{ar}	98.19	1.74	0.06	115
La	ICP_{ar}	98.19	1.73	0.08	116
Ni	LOI at 450°C	98.15	1.78	0.06	114
Ga	ICP_{ar}	98.01	1.72	0.27	115
Zn	ICP_{ar}	97.90	1.98	0.11	116
Rb	ICP_{ar}	97.83	1.96	0.21	112
K	ICP_{ar}	97.77	1.93	0.30	111
S	ICP_{ar}	97.53	2.20	0.27	116
Mo	ICP_{ar}	97.52	2.28	0.19	116
LOI	ICP_{ar}	97.33	1.77	0.90	116
Sc	ICP_{ar}	97.33	2.33	0.34	112
Mn	ICP_{ar}	97.19	2.75	0.05	113
Y	ICP_{ar}	97.08	2.85	0.07	116
As	ICP_{ar}	96.91	2.86	0.22	115
Ti	ICP_{ar}	96.86	2.76	0.37	17
Mg	ICP_{ar}	96.72	3.12	0.16	116
Tl	ICP_{ar}	96.60	2.95	0.45	105
Cd	ICP_{ar}	96.43	3.47	0.10	116
U	ICP_{ar}	96.40	3.45	0.15	115
Se	ICP_{ar}	96.31	3.00	0.70	24
Sb	ICP_{ar}	96.23	2.79	0.97	113
Pb	ICP_{ar}	96.04	3.70	0.26	116
Ba	ICP_{ar}	95.73	4.14	0.13	113

Variable	Method	Variance component (100% sum)			*n* quartets
		Between site (%)	Between sample (%)	Within sample (%)	
Cu	ICP_{ar}	95.66	4.21	0.14	116
Li	ICP_{ar}	95.58	4.18	0.24	104
Nb	ICP_{ar}	94.67	4.07	1.26	110
Zr	ICP_{ar}	94.38	4.96	0.66	102
P	ICP_{ar}	94.29	5.47	0.24	116
Na	ICP_{ar}	93.33	3.68	2.99	115
Ag	ICP_{ar}	93.31	5.95	0.74	112
Th	ICP_{ar}	93.09	6.57	0.33	108
Be	ICP_{ar}	92.91	6.89	0.20	109
Re	ICP_{ar}	92.41	5.21	2.38	104
Pt	ICP_{ar}	92.08	2.11	5.81	28
Cs	ICP_{ar}	91.20	7.59	1.21	108
Bi	ICP_{ar}	90.90	7.36	1.74	114
Ca	ICP_{ar}	90.70	9.24	0.06	116
Sr	ICP_{ar}	89.86	9.97	0.17	116
Hf	ICP_{ar}	89.14	8.86	2.00	82
Hg	ICP_{ar}	78.19	17.28	4.53	96
Sn	ICP_{ar}	76.27	15.87	7.86	101
In	ICP_{ar}	71.97	14.87	13.16	40
B	ICP_{ar}	62.89	26.53	10.58	7
Pd	ICP_{ar}	55.87	24.71	19.42	6
Au	ICP_{ar}	54.99	13.21	31.80	84

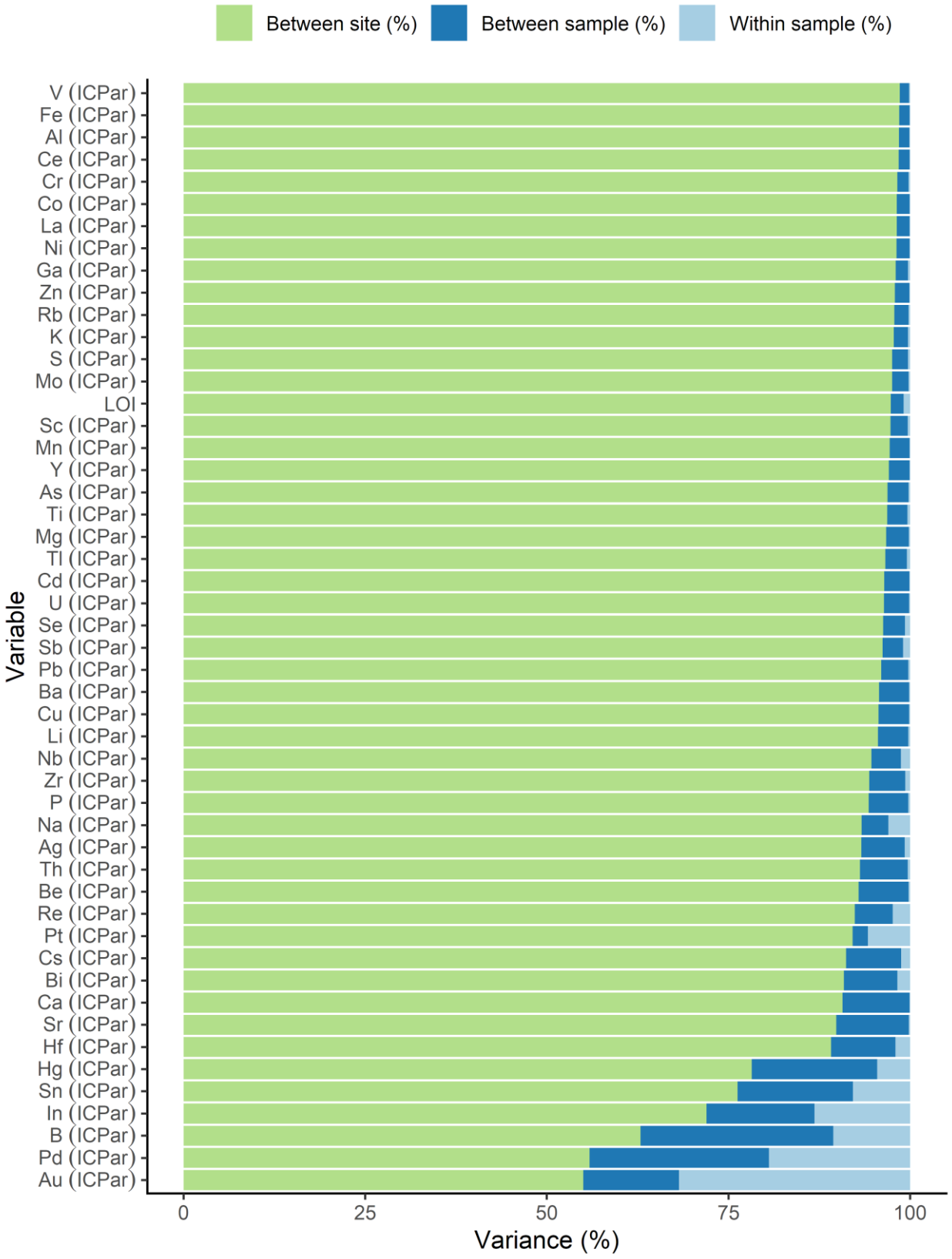


Chart 1 Stacked bar chart to display ANOVA results for all duplicate site deeper topsoil data.

Reference materials data

Reference materials (RMs) are a critical aspect of any chemical data quality assurance program. They are used to measure and monitor the accuracy and repeatability of analytical results within the same programme of works and the reproducibility of results compared to another programme. The selection of suitable RMs is based on (i) identifying the best match between the matrix of the sample media and the matrix of the reference material, (ii) the range of analytes in the RM, (iii) the concentration ranges expected to be encountered in the regular samples and (iv) the availability and cost of the materials.

RMs comprise primary or certified reference materials (CRMs), purchased from suppliers with an accompanying certificate of elemental analyses, and secondary reference materials (SRMs) produced and used by the geochemical mapping programme. All are submitted blindly to the laboratory in order to assess the results without bias. In addition to these control samples, the laboratory has used its own selection of blank sample solutions and CRMs in-house. Together they are a critical tool to evaluate data quality, which is necessary in particular to tie together multi-annual datasets that may span years or decades and multiple analytical facilities.

All RM concentration data are presented in Appendix A “RMs data QCS charts”.

Laboratory in-house RMs

The RMs used and reported by the laboratories for each analytical method are detailed below.

Table 5 In-house CRMs used for multi-element ICP_{ar} analyses

CRM name	CRM Manufacturer	Description
GBM908-10	Geostats Pty Ltd	Low Cu oxide.
MRGeo08	ORE Research & Exploration	Blend of copper, zinc, nickel, molybdenum and lead concentrate mixed with graniate, Australia.
OREAS 46	ORE Research & Exploration	Glacial, basal till collected in Quebec, Canada.
OREAS 920	ORE Research & Exploration	Blend of sixteen copper CRMs (OREAS 920 to OREAS 935) collected in New South Wales, Australia.

Table 6 In-house CRMs used for soil LOI analyses

CRM name	CRM Manufacturer	Description
GIOP 122	Geostats Pty Ltd	Pulp iron ore.
GIOP 123	Geostats Pty Ltd	Pulp iron ore.
GIOP 124	Geostats Pty Ltd	Pulp iron ore.

Randomized and blind-to-laboratory RMs

A range of reference materials (RMs) were used, comprising CRMs and SRMs submitted blind to the analyst (Table 7 and Table 8 respectively) in a randomized order amongst other QCS and regular site samples.

Certified reference materials (CRMs)

Table 7 Blind CRMs used for ICP_{ar} multi-element analyses.

CRM name	CRM Manufacturer	Description
STSD-1	CCRMP	Stream sediment from Lavant Creek, Ontario, Canada.
STSD-3	CCRMP	Stream sediment mixture from Hirok Stream, British Columbia, Canada and Lavant Creek, Ontario, Canada.
TILL - 1	CCRMP	Soil sample collected near Joe Lake 25 km northwest of Lanark, Ontario, Canada.
TILL - 2	CCRMP	Till sample collected near Scission's Brook, New Brunswick, Canada.
TILL - 3	CCRMP	Soil sample collected near O'Brien Mine, 8 km east of Cobalt, Ontario, Canada.

Secondary reference materials (SRMs)

A number of project SRMs have been collected from the island of Ireland with GSI having access to those used by the Tellus (GSNI) geochemical mapping project (Smyth, 2007) (Table 12) in Northern Ireland. The SEIRE material is a re-sieved, re-milled and homogenized bulk stream sediment material collected by GSI during its regional geochemical mapping programme in 1986. Bulk stream sediment samples MOC1 and SUC2 were collected as a joint BGS-GSI initiative at the start of the Tellus Border (Ireland) geochemical field programme in 2011. Materials DAL and LWRPALA were created for the Tellus (Northern Ireland) geochemical mapping programme.

Table 8 Blind SRMs used for ICP_{ar} multi-element analyses

SRM name	Location where collected by Tellus (Irish National Grid)	Material type	Primary land uses	Stream order	Description	Stream drainage type
CARLST	[322998 307155]	Topsoil	Potato crop field (BDC1)		Silty soil derived from Lr Palaeozoic sandstone and shale till, overlying Carboniferous limestone bedrock	
CNLST	[238834 317551]	Topsoil	Grass moor/rough grazing (AC00)		Silty soil derived from alluvial deposit, overlying Carboniferous shale and limestone	
DAL	[262562 406923]	Topsoil	Grass moor/rough grazing (AC00)		Mineral gley overlying Dalradian Southern Highland Group schist and psammite bedrock	
LDOWN	[289197 298786]	Topsoil	Arable land (BD00)		Silty soil derived from Lr Palaeozoic sandstone and shale till, overlying Silurian greywacke	

SRM name	Location where collected by Tellus (Irish National Grid)	Material type	Primary land uses	Stream order	Description	Stream drainage type
					bedrock	
LGRAN	[297200 195155]	Topsoil	Pasture (BAB0) and agricultural grassland (BA00)		Sandy soil derived from granite till, overlying quartz diorite bedrock	
LMGPSH	[203695 327205]	Topsoil	Pasture with goats (BAB0). Large open field surrounded by bog land.		Silty soil derived from Namurian sandstone and shale till, overlying Lower Carboniferous shale and sandstone bedrock	
LWRPALA	[299357 335362]	Topsoil	Agricultural grassland (BA00)		Mineral gley overlying Silurian greywacke bedrock	
MOC1	[321594 327107]	Stream sediment <150 µm	Agricultural grassland (BA00) and Pasture (BAB0)	Leitrim River. 2nd order	Sediment from stream overlying Silurian greywacke and draining the Mourne Mountains granite Complex	Small stream <3 m wide
MONPB	[287290 324485]	Topsoil	Long grassed fallow field with no livestock present or any evidence of (AC00)		Silty clay soil derived from Lr Palaeozoic sandstone and shale till, overlying Silurian black shale bedrock	
ORS	[182770 100880]	Topsoil	Agricultural grassland (BA00). Teagasc Moorpark agricultural research grassland, field 38C		Silty soil derived from Devonian sandstone (ORS) till, overlying Carboniferous Waulsortian limestone bedrock	
SEIRE	[311020 195470]	Stream sediment <180 µm	Coniferous woodland (AEB0)	Lugduff Brook. 2nd order.	Sediment from stream overlying Lower Palaeozoic slate and schist bedrock	Small stream <3 m wide
SUC2	[320580 327185]	Stream sediment <150 µm	Agricultural grassland (BA00)	Carcullion River, 2nd order.	Sediment from stream overlying Silurian greywacke	Small stream <3 m wide

SRM name	Location where collected by Tellus (Irish National Grid)	Material type	Primary land uses	Stream order	Description	Stream drainage type
					bedrock	
WWLPAL	[297025 208890]	Topsoil	Ploughed field. Arable land (BD00)		Till derived from Lr Palaeozoic sandstone and shale overlying granite bedrock	
WXSERP	[306332 166170]	Topsoil	Grass moor/rough grazing (AC00)		Silty clay topsoil overlying serpentinite and Ordovician slate and phyllite bedrock	
YELC1	[133789 309600]	Stream sediment <150 µm	Grass moor/rough grazing (AC00) to east with no livestock present. Coniferous woodland – established (AEBB) to the west of site and deciduous woodland – established (AEAB) along stream bank	Yellow River. 2nd order.	Stream sediment overlying equigranular granodiorite bedrock	Small stream <3 m wide

Assessment of RMs data

Data are monitored by statistically summarising and charting data batches.

All RMs data are charted by analyte concentration (y axis) against the sample ID (x axis). All sample IDs are expected to be analysed in numerical order. Data are compiled for each RM and statistically summarized to assess the proportions of data below the detection limits and the absolute values relative to the reference values. The certificate reference values are given priority but a series of information values in the literature are also used for elements where no certified or information reference values is supplied by the manufacturer. These RM data are considered in the context of the concentration range displayed by the sample data.

All data with the exception of LOI were reported with date and time stamps for each sample ID. Control charts were plotted for each analyte and the simplified Westgard rules for data quality (Westgard, 1981) are followed (only 1_{3s} and 2_{2s} violations are monitored). Control charts are used to assess, in particular, drift in the analytical instrument or mistaken IDs or inter-batch differences that might lead to the need to condition or level data when merging discrete batches of data.

A well-homogenized reference material would be expected to display a normal distribution of results around an accepted reference value, for each determinand. To verify this assumption, a histogram of all results is plotted for each RM to evaluate the spread of analytical data. The control charts display warning limits and, in a statistically normal dataset, approximately 5% of samples will fall outside of the warning limits. Therefore, results outside of these limits are expected and acceptable. If two *consecutive* points fall outside, the data are usually deemed to have failed this quality check. All SRMs are assumed to be somewhat less homogenous than CRMs. The magnitude of any failure is assessed here in the context of the overall analysis for a given analyte and the element response across all available RMs is used where possible when assessing whether there is a problematic tranche of results.

All data reported as a less-than "<" value below the LLD are plotted as "-LLD" and are essentially disregarded.

Control charts

Shewhart-style control charts (Shewhart, 1931) have been created for all blind RM data where date and time stamp data are available.

Using the ggQC package in R, the control charts are based on the data mean moving range (mR) value rather than just the mean and standard deviations of the whole data population. The mean moving range 'mean(mR)' is based on absolute differences between sequential pairwise measurements, *i.e.* one data point and its predecessor in the sequence. The upper and lower control limits are each three times the sequential deviation defined as mean(mR)/1.128, above and below the process mean, and that window accounts for 99.7% of data in a normally distributed data population. The sequential deviation is accounting for the sequential nature of the data points and control limits are less biased by systematic processes offsets. Therefore, these control charts give a clearer picture of (i) random error and (ii) allow for detection of systematic (assignable cause) variation which is sought to be identified.

The normal distribution of data is not required in the calculation of control limits, and these charts are robust for non-homogenous samples. Infrequent, one-off exceedances of the upper and lower control limits (process mean ± 3 sequential deviations, dark blue horizontal lines) are termed failures but are statistically acceptable. Exceedances of the warning limits (process mean ± 2 sequential deviations, medium blue horizontal lines) are more common and these charts are inspected to see if two or more consecutive data points lie outside a limit, where they then constitute a failure, one exceedance constitutes a warning. The lightest blue horizontal lines on the control charts (process mean ± 1 sequential deviation) are useful reference lines against which drift and shift can be observed but do not constitute a formal limit used for monitoring of the analytical process quality. These control charts are inspected for trends in the sequence and/or multiple analytes exhibiting patterns of behaviour. The main quality checks are for multiple analytes of the same sample presenting warning or failures and the periods of time for the analyses where multiple sample warnings or failures are seen. If the method LLD is ≥ upper control limit then any description of control failures is meaningless. These are not described in this report. However, it is still useful to assess the reproducibility of data results below the LLD in an uncensored dataset. A summary of flagged quality issues for ICPar analyses is presented in Table 9 below.

Most observed violations are classed as single analyte failures and/or warnings and are interpreted as random errors and deemed inconsequential for the quality of the data. Multiple analyte failures were further investigated in detail to rule out a true analysis failure. Fourteen such events were recorded where at least two analytes had fallen outside of lower/upper control limits. In majority of these cases the resultant failures were observed in analytes displaying very tight trends and narrow control limits, in CRMs where certified concentration of analytes was generally low, in many cases close to method LLD, and where greater variability was therefore to be expected. Most of the events are type 1_{3S} violations and only three 2_{2S} violations were recorded. Five observed events raise caution about potential implications for data quality within certain data ranges. These events do not invalidate reported data but

caution users that confidence is slightly lower than for the rest of the data. This increased uncertainty is not quantified. Users are cautioned to treat affected data accordingly.

- Between 21/09/2020 and 24/09/2020 three consecutive, multiple element failures and warnings occurred. Sodium (Na) and platinum (Pt) failed in more than one instance. Affected batches: LR20191320, LR20194497 and LR20198392. Possible cause: poor analytical performance.
- Between 06/10/2019 and 08/10/2019 seven consecutive, multiple element failures and warning occurred. Gold (Au), palladium (Pd), sodium (Na) and boron (B) failed in more than one instance. Four out of seven events took place on the 08/10/2020. Affected batches: LR20209443, LR20212299, LR20214452, LR20212313, LR20212385 and LR20203070. Possible cause: poor analytical performance.
- On 15/10/2020 more than expected analytes exhibited multiple failures and warnings: five (Al; Ba; Ge; Sn; Tl) and eight (Ag; Be; Cr; K; Pb; Rb; Sb; Ta) respectively. Affected batch: LR20215384. Possible cause: poor analytical performance.
- On 24/10/2020 more than expected analytes exhibited multiple failures: twelve (Ag; Al; Ba; Be; Cd; Fe; Li; Ni; Rb; Tl; Y; Zn). Affected batch: LR20215418. Possible cause: poor analytical performance.
- On 21/11/2020 more than expected analytes exhibited multiple failures and warnings: four (Ba; K; Li; Mn) and ten (Be; Ca; Cd; Fe; P; Pb; Re; Se; Y; Zn) respectively. Affected batch: LR20217825. Possible cause: poor analytical performance.

Table 9. Summary of CRM data quality issues observed by control charts for IPC_{ar} analyses.

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
TILL-2	612591S	LR20197551-091	ICP-MS	18/09/2020 02:45	Single analyte failure and multiple analyte warning: Re (Ce; Cs; La; Sb; Se).	Outwith upper/lower warning and control limits
STSD-3	611736S	LR20191320-036	ICP-MS	18/09/2020 05:48	Multiple analyte warning: Au; Cu; Y.	Outwith upper/lower warning limits
TILL-1	611803S	LR20191320-103	ICP-MS	21/09/2020 22:19	Multiple analyte warning: In; Se.	Outwith upper/lower warning limits
STSD-1	611824S	LR20191320-124	ICP-MS	21/09/2020 22:56	Multiple analyte failure and single analyte warning: Na; Pt (Se).	Outwith upper/lower warning and control limits
STSD-3	611952S	LR20192326-052	ICP-MS	22/09/2020 06:28	Multiple analyte warning: Co; S.	Outwith upper/lower warning limits
TILL-2	611991S	LR20192326-091	ICP-MS	22/09/2020 08:12	Single analyte warning: S.	Outwith upper/lower warning limits
STSD-1	612059S	LR20192326-159	ICP-MS	22/09/2020 09:46	Single analyte failure: Na.	Consecutively outwith upper/lower warning limits
TILL-3	612076S	LR20192326-176	ICP-MS	22/09/2020 12:04	Single analyte failure and multiple analyte warning: Te (Sn; Th; U).	Outwith upper/lower warning and control limits
STSD-3	612122S	LR20194497-022	ICP-MS	22/09/2020 14:03	Single analyte failure and warning: Cr (Ca).	Outwith upper/lower warning and control limits
STSD-1	612249S	LR20194497-149	ICP-MS	23/09/2020 01:48	Multiple analyte failure and multiple analyte warning: Na; Pt; V (Co; Se; Sr; Te).	Consecutively outwith upper/lower control and warning limits
STSD-1	612659S	LR20197551-159	ICP-MS	23/09/2020 18:22	Single analyte failure and multiple analyte warning: Na (Ga; Pt).	Consecutively outwith upper/lower warning limits
TILL-3	612676S	LR20197551-176	ICP-MS	23/09/2020 18:48	Single analyte warning: Cu.	Outwith upper/lower warning limits
STSD-3	612336S	LR20196694-036	ICP-MS	23/09/2020 21:40	Single analyte warning: Mo.	Outwith upper/lower warning

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
						limits
STSD-3	612722S	LR20198392-022	ICP-MS	24/09/2020 11:13	Single analyte warning: Cu.	Outwith upper/lower warning limits
STSD-1	612849S	LR20198392-149	ICP-MS	24/09/2020 16:06	Multiple analyte failure and multiple analyte warning: Bi; Re (As; In; Sr; Y).	Outwith upper/lower warning and control limits
STSD-3	612936S	LR20199771-036	ICP-MS	25/09/2020 01:57	Single analyte failure: Mo.	Outwith upper/lower control limits
STSD-3	613152S	LR20203070-052	ICP-MS	26/09/2020 00:12	Multiple analyte warning: Ba; Zr.	Outwith upper/lower warning limits
TILL-3	613276S	LR20203070-176	ICP-MS	28/09/2020 21:13	Single analyte warning: Cd.	Outwith upper/lower warning limits
TILL-3	613876S	LR20209441-176	ICP-MS	06/10/2020 04:09	Single analyte warning: P.	Outwith upper/lower warning limits
STSD-3	613536S	LR20209443-036	ICP-MS	06/10/2020 05:27	Multiple analyte failure and single analyte warning: Au; Pt (Nb).	Outwith upper/lower warning and control limits
STSD-3	613752S	LR20209441-052	ICP-MS	06/10/2020 08:47	Single analyte failure and multiple analyte warning: Na (Sc; Y).	Consecutively outwith upper/lower warning limits
TILL-2	613791S	LR20209441-091	ICP-MS	06/10/2020 12:47	Multiple analyte warning: As; Co.	Outwith upper/lower warning limits
STSD-1	613859S	LR20209441-159	ICP-MS	06/10/2020 14:19	Single analyte failure and multiple analyte warning: Na (Ge; Y).	Outwith upper/lower warning and control limits
TILL-1	613603S	LR20209443-103	ICP-MS	07/10/2020 01:01	Multiple analyte failure and multiple analyte warning: Au; Pd; Pt (Ta; Th; W).	Outwith upper/lower warning and control limits
STSD-1	613624S	LR20209443-124	ICP-MS	07/10/2020 01:37	Single analyte failure and multiple analyte warning: Ta (Ag; Pd; Pt; Sb; W).	Outwith upper/lower warning and control limits
STSD-1	614049S	LR20209459-149	ICP-MS	07/10/2020 08:40	Single analyte failure and single analyte warning: Na (U).	Outwith upper/lower warning and control limits
STSD-3	613922S	LR20209459-022	ICP-MS	07/10/2020 10:19	Single analyte failure and multiple analyte	Consecutively outwith upper/lower

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
					warning: Na (Ag; Al).	warning limits
STSD-1	614224S	LR20212299-124	ICP-MS	07/10/2020 17:56	Multiple analyte failure and multiple analyte warning: B; Pd; Sr (Na; Sr; Th; Zr).	Outwith upper/lower warning and control limits
TILL-1	614203S	LR20212299-103	ICP-MS	08/10/2020 02:12	Single analyte warning: K.	Outwith upper/lower warning limits
STSD-3	614136S	LR20212299-036	ICP-MS	08/10/2020 05:23	Multiple analyte failure: B; Bi; Na; Pd.	Consecutively outwith upper/lower warning limits
STSD-1	614824S	LR20214452-124	ICP-MS	08/10/2020 08:30	Multiple analyte failure and multiple analyte warning: B; Hf; Th; Zr (Pb; Pd; Sr).	Outwith upper/lower warning and control limits
STSD-3	614352S	LR20212313-052	ICP-MS	08/10/2020 10:07	Single analyte failure and single analyte warning: Th (Na).	Consecutively outwith upper/lower warning limits
STSD-1	614459S	LR20212313-159	ICP-MS	08/10/2020 16:52	Multiple analyte failure and single analyte warning: Mn; Na (Al).	Outwith upper/lower warning and control limits
STSD-3	614522S	LR20212385-022	ICP-MS	08/10/2020 19:12	Multiple analyte failure and multiple analyte warning: Na; Pd (Co; In).	Consecutively outwith upper/lower control and warning limits
TILL-2	614391S	LR20212313-091	ICP-MS	10/10/2020 00:39	Single analyte failure and single analyte warning: Ta (Pt).	Consecutively outwith upper/lower warning limits
TILL-1	613003S	LR20199771-103	ICP-MS	12/10/2020 13:29	Multiple analyte warning: Nb; Ti.	Outwith upper/lower warning limits
STSD-1	613024S	LR20199771-124	ICP-MS	13/10/2020 04:47	Single analyte failure and single analyte warning: Th (Zr).	Outwith upper/lower warning and control limits
STSD-1	613259S	LR20203070-159	ICP-MS	13/10/2020 06:35	Multiple analyte failure and multiple analyte warning: Ag; Au (Ca; Th; Zr).	Outwith upper/lower warning and control limits
STSD-1	615249S	LR20215384-149	ICP-MS	13/10/2020 07:18	Multiple analyte warning: Be; Fe; K; Li; Mg; Mn; Nb; P; Zn.	Outwith upper/lower warning limits
STSD-1	614649S	LR20212385-149	ICP-MS	13/10/2020 12:18	Multiple analyte warning: Al; Mg.	Outwith upper/lower warning limits

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
STSD-1	615059S	LR20214651-159	ICP-MS	15/10/2020 19:01	Single analyte failure: Sn.	Outwith upper/lower control limits
TILL-3	615076S	LR20214651-176	ICP-MS	15/10/2020 19:30	Multiple analyte warning: Hf; W.	Outwith upper/lower warning limits
STSD-3	615122S	LR20215384-022	ICP-MS	15/10/2020 23:25	Multiple analyte failure and multiple analyte warning: Al; Ba; Ge; Sn; Tl (Ag; Be; Cr; K; Pb; Rb; Sb; Ta).	Outwith upper/lower warning and control limits
STSD-1	615424S	LR20215399-124	ICP-MS	23/10/2020 04:24	Single analyte failure and multiple analyte warning: Hf (Ag; As).	Outwith upper/lower warning and control limits
TILL-1	615403S	LR20215399-103	ICP-MS	24/10/2020 00:34	Single analyte failure and multiple analyte warning: Ba (Cd; Mn; Mo).	Outwith upper/lower warning and control limits
STSD-3	615552S	LR20215418-052	ICP-MS	24/10/2020 02:17	Multiple analyte failure and multiple analyte warning: La; Mn (Ag; Al; Ba; Be; Cd; Fe; Li; Ni; Rb; Tl; Y; Zn)	Outwith upper/lower warning and control limits
STSD-3	615936S	LR20216638-036	ICP-MS	24/10/2020 05:50	Multiple analyte warning: La; Zr.	Outwith upper/lower warning limits
STSD-3	615936S	LR20216638-036	ICP-MS	24/10/2020 05:50	Single analyte warning: Zr.	Outwith upper/lower warning limits
STSD-1	615659S	LR20215418-159	ICP-MS	24/10/2020 14:11	Single analyte failure and single analyte warning: Hg (Pd).	Outwith upper/lower warning and control limits
TILL-3	615676S	LR20215418-176	ICP-MS	24/10/2020 15:14	Single analyte failure: Bi.	Outwith upper/lower control limits
STSD-3	615722S	LR20216617-022	ICP-MS	24/10/2020 16:32	Single analyte warning: Ni.	Outwith upper/lower warning limits
STSD-1	615849S	LR20216617-149	ICP-MS	03/11/2020 11:24	Multiple analyte warning: Ga; Ti; Tl; U.	Outwith upper/lower warning limits
STSD-1	616024S	LR20216638-124	ICP-MS	15/11/2020 12:51	Multiple analyte warning: Cu; Mo; Na; Ta.	Outwith upper/lower warning limits
TILL-2	616191S	LR20217805-091	ICP-MS	15/11/2020 14:14	Multiple analyte warning: Au; In.	Outwith upper/lower warning

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
						limits
STSD-3	616152S	LR20217805-052	ICP-MS	15/11/2020 20:50	Multiple analyte warning: Ca; K; La; W.	Outwith upper/lower warning limits
STSD-1	616259S	LR20217805-159	ICP-MS	16/11/2020 16:48	Single analyte warning: Na.	Outwith upper/lower warning limits
TILL-3	616276S	LR20217805-176	ICP-MS	16/11/2020 17:17	Multiple analyte warning: Au; Se; U; Zr.	Outwith upper/lower warning limits
STSD-3	616322S	LR20217825-022	ICP-MS	16/11/2020 19:07	Single analyte warning: Co.	Outwith upper/lower warning limits
STSD-1	616449S	LR20217825-117	ICP-MS	21/11/2020 05:33	Multiple analyte failure and multiple analyte warning: Ba; K; Li; Mn (Be; Ca; Cd; Fe; P; Pb; Re; Se; Y; Zn).	Outwith upper/lower warning and control limits

Linear regression plots and data conditioning

For all CRM data, a regression analysis of the certified reference concentration against the mean measured concentration was evaluated to assess analytical performance and precision. Where available certified values are reported for *aqua regia* digestions which are used in this survey and are referred to as 'partial' digestions. Where certified values obtained through 'partial' digestions are not available 'total' digestion values are used instead. The user is cautioned that in these cases the CRM values being compared were obtained through different extraction methods and the degree of correlation between the measured and certified values depends on unquantified factors other than analytical performance and precision. Users are thus advised to interpret the regression plots accordingly. For the ICP_{ar} analytes there are five CRMs available: STSD 1, STSD 3, TILL 1, TILL 2 and TILL 3. Each regression line and its equation are based on up to five data points. For the LOI analyses there are no CRMs but a series of project SRMs were used: APT, AST, SPT and SST.

A summary of the linear regression relationships is presented in Table 10 for the ICP_{ar} analytes. All analytes have a generally excellent fit except for Au, Hf, P, Sc, Sr, Ta, Ti, V, Y and Zr as detailed below. Regression plots were not constructed for Sn and W due to insufficient data points. In general, analytes characterized by slope values deviating significantly from unity show poor correlation of recovery between used and certified methods and data users are cautioned about the performance of measured against certified concentration values for these analytes. However, for the 10 analytes listed, the certified CRM values used for these analytes were all for "total" extractions, with the exception of P. Consequently the poor fit observed cannot be assumed to reflect poor analytical performance. No data are recommended to be conditioned.

Table 10 Linear regression relationships for ICP_{ar} analytes.

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R squared
Ag (mg kg^{-1})	TILL, STSD	partial	0.0578	0.925	1
Al (%)	TILL	partial	0.34	0.727	0.999
As (mg kg^{-1})	TILL, STSD	partial	4.91	0.975	0.999
Au (mg kg^{-1})	TILL, STSD	total	-0.00326	2.62	0.187
B (mg kg^{-1})	STSD	total	-21.7	0.338	1
Ba (mg kg^{-1})	TILL	partial	-7.45	1.07	1
Be (mg kg^{-1})	TILL	partial	-0.423	9	0.99
Bi (mg kg^{-1})	TILL, STSD	partial	5.01		0
Ca (%)	TILL	partial	-0.009	0.804	0.997
Cd (mg kg^{-1})	TILL, STSD	partial	0.00708	1.14	0.999
Ce (mg kg^{-1})	TILL, STSD	total	-4.54	0.765	0.942
Co (mg kg^{-1})	TILL, STSD	partial	0.229	1.02	0.926
Cr (mg kg^{-1})	TILL, STSD	partial	4.93	0.798	0.999
Cs (mg kg^{-1})	TILL, STSD	total	-0.0617	0.567	0.994
Cu (mg kg^{-1})	TILL, STSD	partial	0.37	0.983	0.999
Fe (%)	TILL, STSD	partial	0.225	0.921	0.935
Ga (mg kg^{-1})					

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R squared
Ge (mg kg^{-1})					
Hf (mg kg^{-1})	TILL, STSD	total	0.0106	0.00274	0.169
Hg (mg kg^{-1})	TILL, STSD	partial	-0.0157	1.15	0.978
In (mg kg^{-1})					
K (%)	TILL	partial	-0.0297	0.792	0.994
La (mg kg^{-1})	TILL, STSD	total	3.03	0.573	0.841
Li (mg kg^{-1})	TILL, STSD	total	1.11	0.743	0.97
Mg (%)	TILL	partial	-0.0806	1.01	1
Mn (mg kg^{-1})	TILL, STSD	partial	85.4	0.912	0.997
Mo (mg kg^{-1})	TILL, STSD	partial	-1.72	1.23	0.979
Na (%)	TILL	partial	0.00536	0.0564	1
Nb (mg kg^{-1})	TILL, STSD	total	-0.313	0.177	0.837
Ni (mg kg^{-1})	TILL, STSD	partial	2.73	0.992	0.943
P (%)	TILL	partial	0.0123	0.681	0.606
Pb (mg kg^{-1})	TILL, STSD	partial	2.29	0.971	0.993
Pd (mg kg^{-1})					
Pt (mg kg^{-1})					
Rb (mg kg^{-1})	TILL, STSD	total	-3.15	0.286	0.939
Re (mg kg^{-1})					
S (%)	STSD	total	-0.0205	1.33	1
Sb (mg kg^{-1})	STSD	partial	-0.539	1.4	1
Sc (mg kg^{-1})	TILL, STSD	total	5	-0.0902	0.0241
Se (mg kg^{-1})					
Sn (mg kg^{-1})	STSD	total	1.65		0
Sr (mg kg^{-1})	TILL, STSD	total	34.2	0.014	1.05E-03
Ta (mg kg^{-1})	TILL, STSD	total	0.00226	-2.95E-04	0.108
Te (mg kg^{-1})					
Th (mg kg^{-1})	TILL, STSD	total	-1.62	0.523	0.73
Ti (%)	TILL, STSD	total	0.0418	0.014	0.616
Tl (mg kg^{-1})					
U (mg kg^{-1})	TILL, STSD	total	-1.07	0.935	0.972
V (mg kg^{-1})	TILL, STSD	partial	21.6	0.547	0.662
W (mg kg^{-1})	TILL		1.96		0
Y (mg kg^{-1})	TILL, STSD	total	-3.83	0.613	0.557
Zn (mg kg^{-1})	TILL, STSD	partial	-3.17	1.01	1
Zr (mg kg^{-1})	TILL, STSD	total	0.425	0.00282	0.103

Table 11 Linear regression relationships for LOI at 450°C.

	Linear regression relationships		
Analyte	Intercept	Slope	R squared
LOI at 450°C (%)	-0.0924	1	1

Table 12 Linear regression relationship for in-house 'top-and-tail' ICP_{ar} analytes.

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R squared
Ag (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	0.00253	0.992	1
Al (%)	OREAS46, OREAS920, MRGeo08	partial	-0.00283	0.992	1
As (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	0.0175	1.02	1
Au (mg kg^{-1})	MRGeo08, GBM908-10	partial/total	-2.54E-04	0.99	1
B (mg kg^{-1})	OREAS46, OREAS920, MRGeo08, GBM908-10	n/a			
Ba (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-3.16	0.998	1
Be (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.00491	0.978	0.999
Bi (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-1.04E-03	0.976	1
Ca (%)	OREAS46, OREAS920, MRGeo08	partial	0.0191	0.977	0.999
Cd (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.0034	1.03	1
Ce (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.387	1	1
Co (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.673	1.08	1
Cr (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.773	1.02	1
Cs (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.0544	1.02	1
Cu (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	0.388	0.998	1
Fe (%)	OREAS46, OREAS920, MRGeo08	partial	-0.0757	1.03	1
Ga (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.598	1.09	0.997
Ge (mg kg^{-1})	OREAS46, MRGeo08	partial	0.0123	0.872	1
Hf (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.00454	0.98	0.981
Hg (mg kg^{-1})	OREAS46, MRGeo08	partial	0.00184	0.972	1
In (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.00189	1.01	1
K (%)	OREAS46, OREAS920, MRGeo08	partial	-0.0141	1.03	0.999
La (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.799	1.03	0.993
Li (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.123	1.01	1
Mg (%)	OREAS46, OREAS920, MRGeo08	partial	-0.0299	1.02	0.999
Mn (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	315	0.244	0.232
Mo (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.0103	1.02	1
Na (%)	OREAS46, MRGeo08	partial	-0.0013	1.05	1

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R squared
Nb (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.215	1.26	0.995
Ni (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	0.162	1.02	1
P (%)	OREAS46, OREAS920, MRGeo08	partial	0.00275	0.977	0.999
Pb (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.143	1.01	1
Pd (mg kg^{-1})	MRGeo08	partial	0.00405		0
Pt (mg kg^{-1})	MRGeo08	partial	0.00044		0
Rb (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.455	1.02	1
Re (mg kg^{-1})	MRGeo08	partial	0.00791		0
S (%)	OREAS920, MRGeo08	partial	1.23E-03	0.981	1
Sb (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	0.0277	0.969	0.999
Sc (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.325	1.08	1
Se (mg kg^{-1})	OREAS920, MRGeo08	partial	-0.728	1.11	1
Sn (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.0588	1.02	0.999
Sr (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-1.8	1.04	1
Ta (mg kg^{-1})	MRGeo08, GBM908-10	partial/total	0.0116	-0.00991	1
Te (mg kg^{-1})	OREAS46, MRGeo08	partial	-0.00789	1.41	1
Th (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.0559	0.995	1
Ti (%)	OREAS46, OREAS920, MRGeo08	partial	3.72E-03	0.981	1
Tl (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.0025	1.01	1
U (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.0392	1.03	1
V (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-1.28	1.04	1
W (mg kg^{-1})	OREAS46, MRGeo08	partial	0.00602	0.955	1
Y (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.00169	1	0.996
Zn (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	0.25	0.998	1
Zr (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.534	1.03	0.991

Gold (Au) by ICP_{ar} (MS41L-BLD)

Gold data from the MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Certified values are for "total" extraction. No data conditioning is recommended.

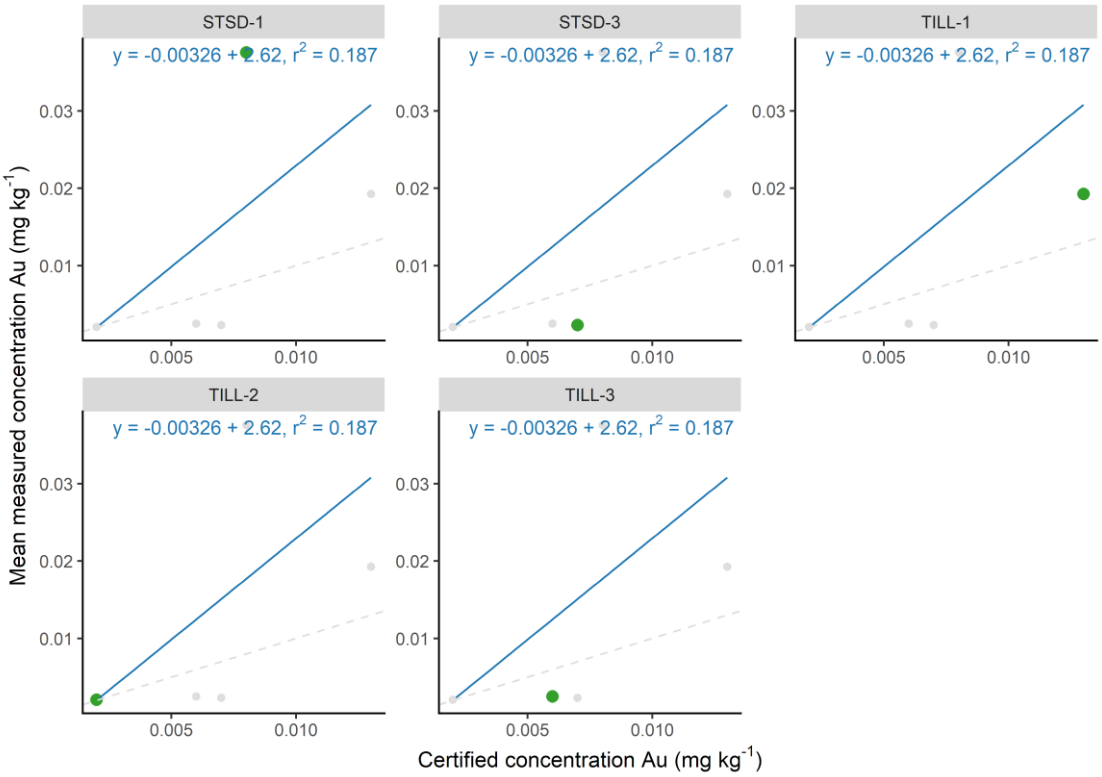


Chart 2 Gold (Au) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Hafnium (Hf) by ICP_{ar} (MS41L-BLD)

Regression curve for Hafnium data by MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Certified values are for "total" extraction. No data conditioning is recommended.

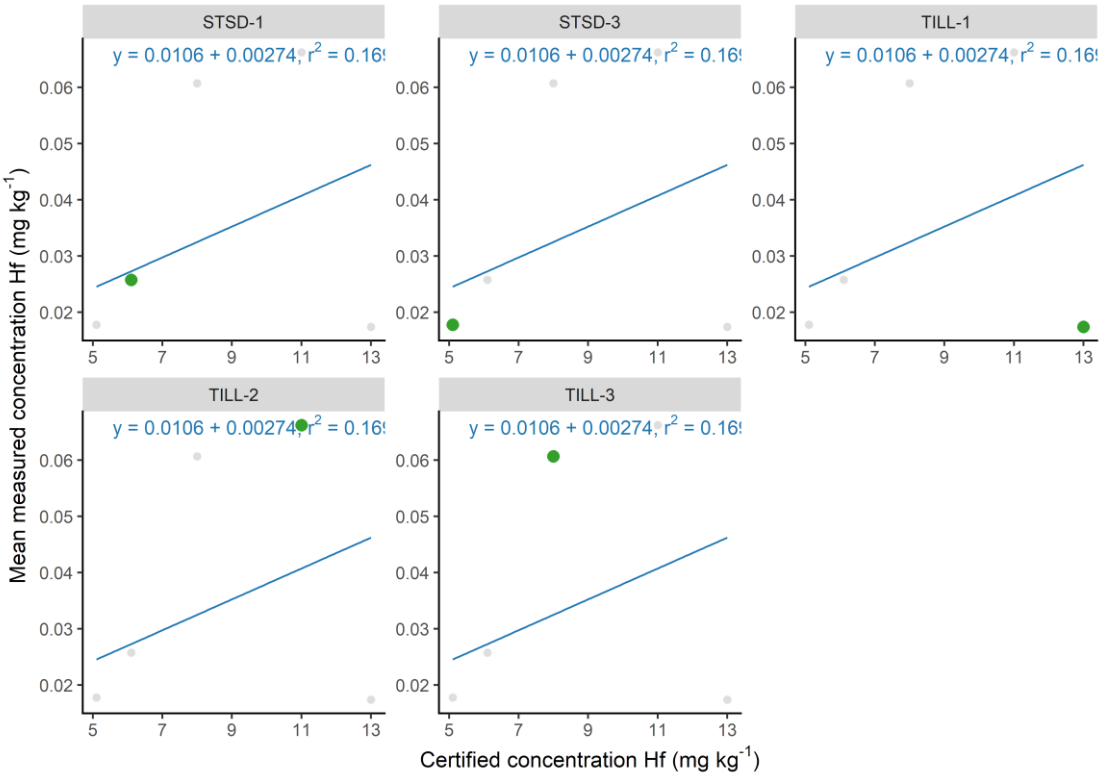


Chart 3 Hafnium (Hf) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Phosphorus (P) by ICP_{ar} (MS41L-BLD)

Regression curve for Phosphorus data by MS41L-BLD method are satisfactory but not excellent. No data conditioning is recommended.

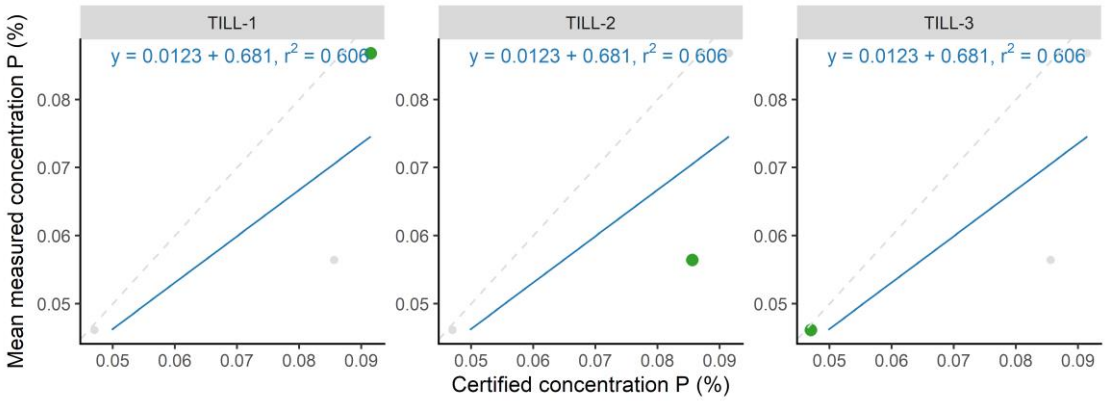


Chart 4 Phosphorus (P) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Scandium (Sc) by ICP_{ar} (MS41L-BLD)

Regression curve for Scandium data by MS41L-BLD method are generally poor in terms of fitting the certified values, with the TILL-1 and TILL-2 determination being particularly poor. Certified values are for "total" extraction. No data conditioning is recommended.

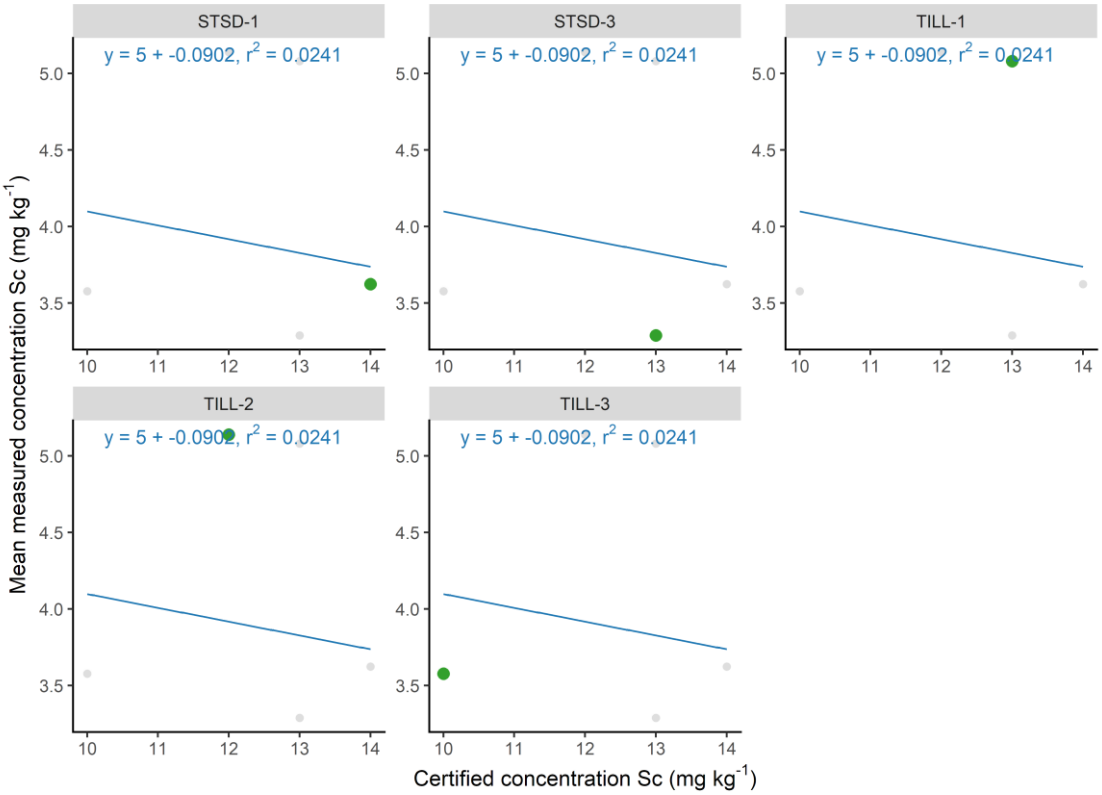


Chart 5 Scandium (Sc) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Strontium (Sr) by ICP_{ar} (MS41L-BLD)

Regression curve for Strontium data by MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Certified values are for "total" extraction. No data conditioning is recommended.

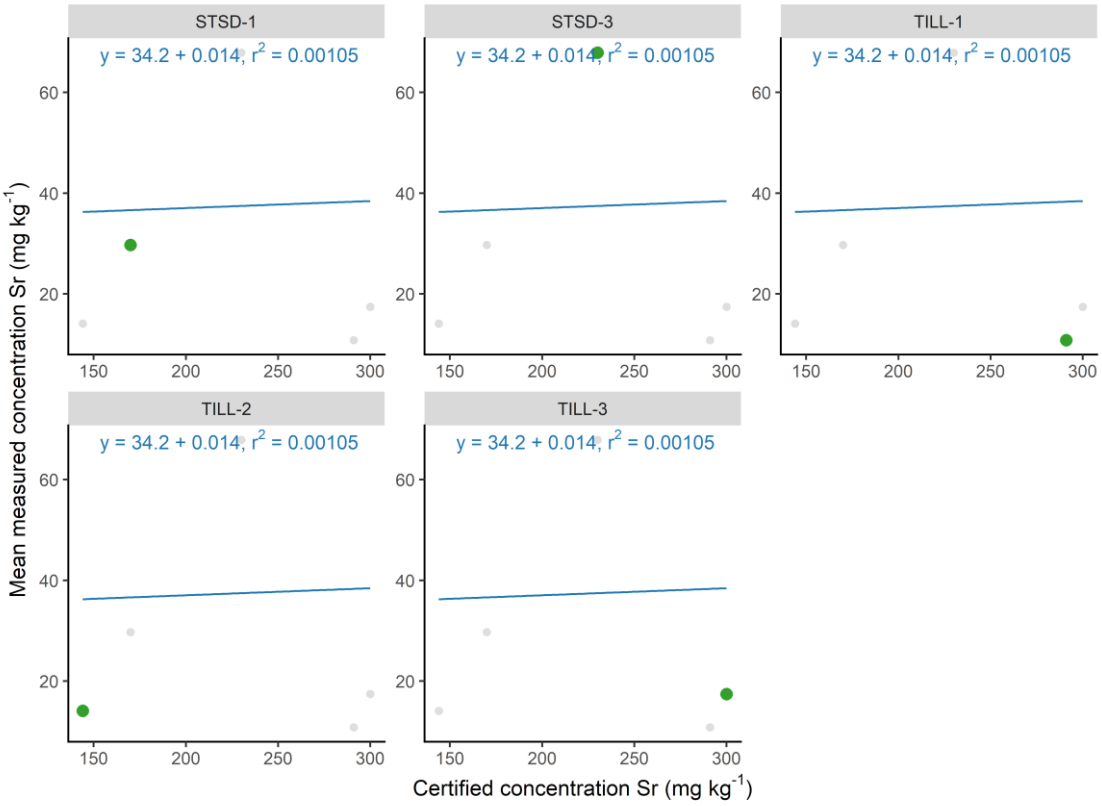


Chart 6 Strontium (Sr) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Tantalum (Ta) by ICP_{ar} (MS41L-BLD)

Regression curve for Tantalum data by MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Certified values are for "total" extraction. No data conditioning is recommended.

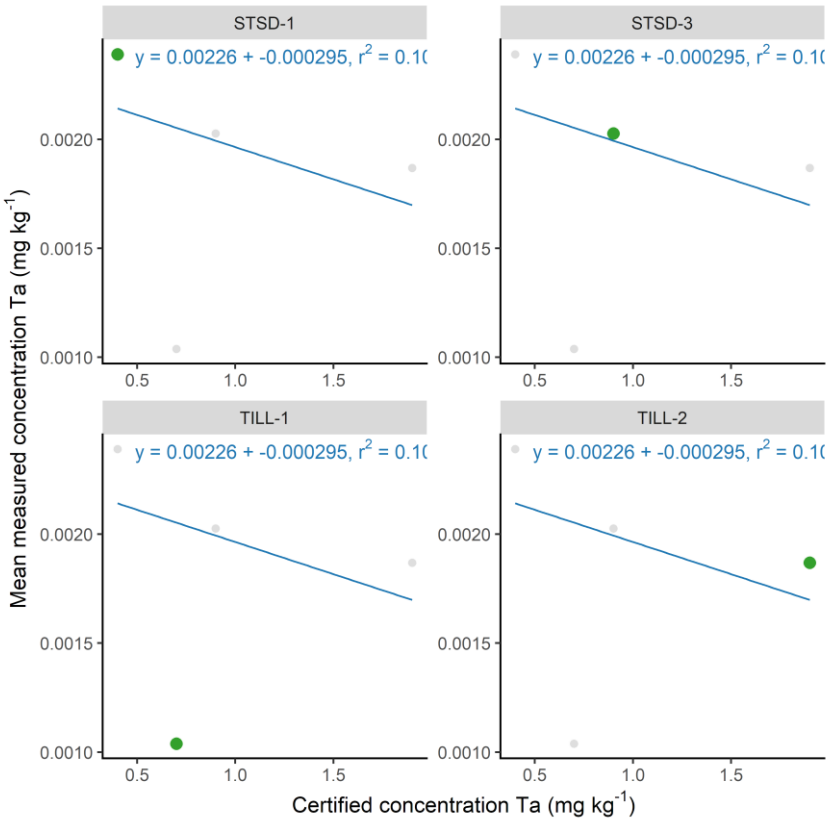


Chart 7 Tantalum (Ta) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Titanium (Ti) by ICP_{ar} (MS41L-BLD)

Regression curve for Titanium data by MS41L-BLD method are satisfactory but not excellent. Certified values are for "total" extraction. No data conditioning is recommended.

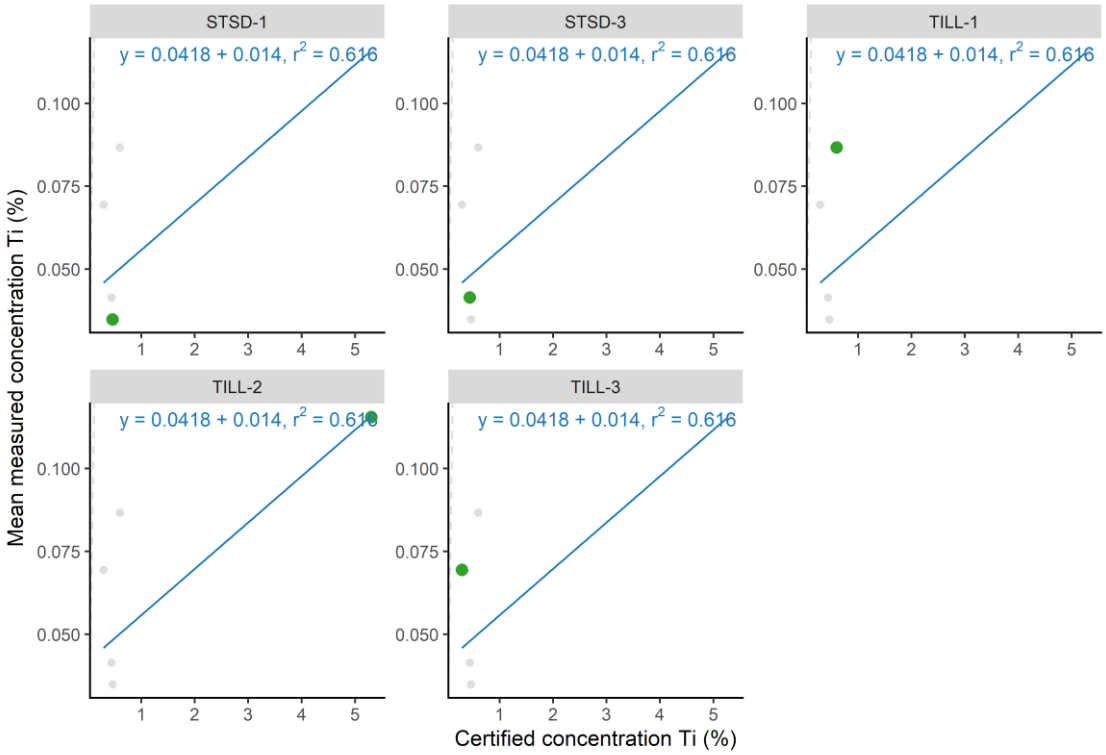


Chart 8 Titanium (Ti) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Vanadium (V) by ICP_{ar} (MS41L-BLD)

Regression curve for Vanadium data by MS41L-BLD method are satisfactory but not excellent. Certified values are for "total" extraction. No data conditioning is recommended.

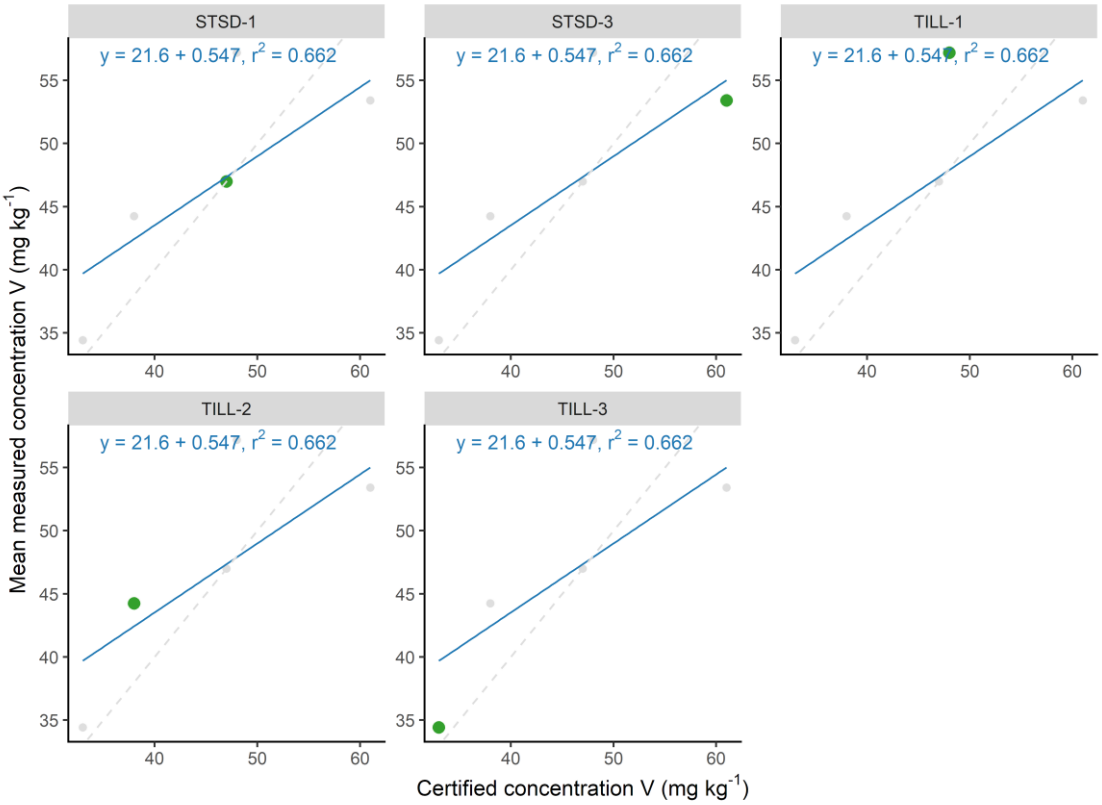


Chart 9 Vanadium (V) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Yttrium (Y) by ICP_{ar} (MS41L-BLD)

Regression curve for Yttrium data by MS41L-BLD method are satisfactory but not excellent. Certified values are for "total" extraction. No data conditioning is recommended.

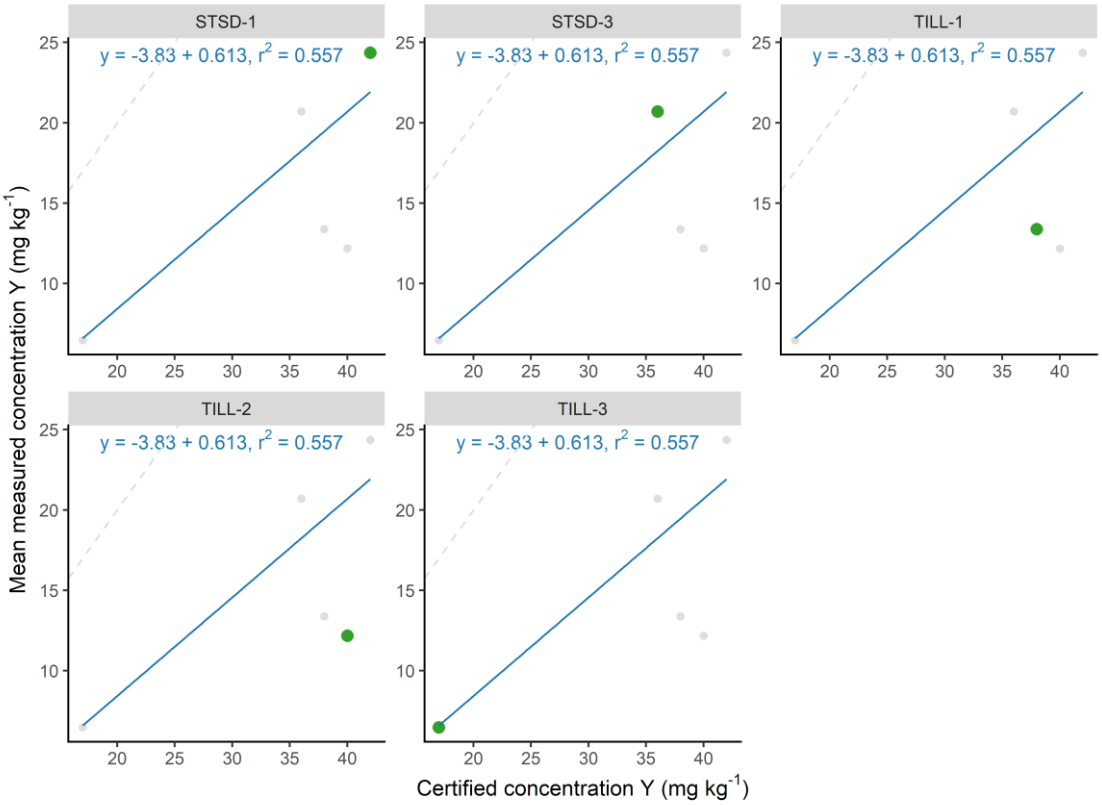


Chart 10 Yttrium (Y) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Zirconium (Zr) by ICP_{ar} (MS41L-BLD)

Regression curve for Zirconium data by MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Certified values are for "total" extraction. No data conditioning is recommended.

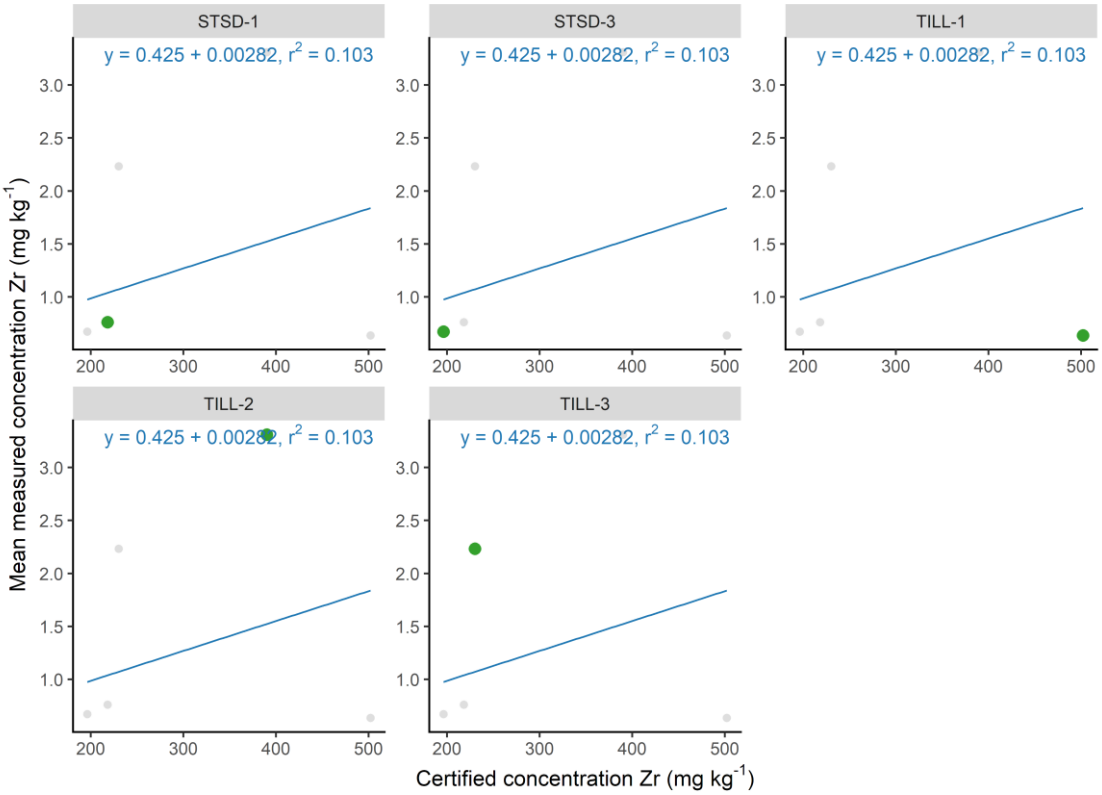


Chart 11 Zirconium (Zr) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Manganese (Mn) by ICP_{ar} (MS41L-BLD)

Regression curve for Manganese data by MS41L-BLD method are generally poor in terms of fitting the certified values, with the OREAS46 and OREAS920 determination being particularly poor. Certified values are for “total” extraction. No data conditioning is recommended.

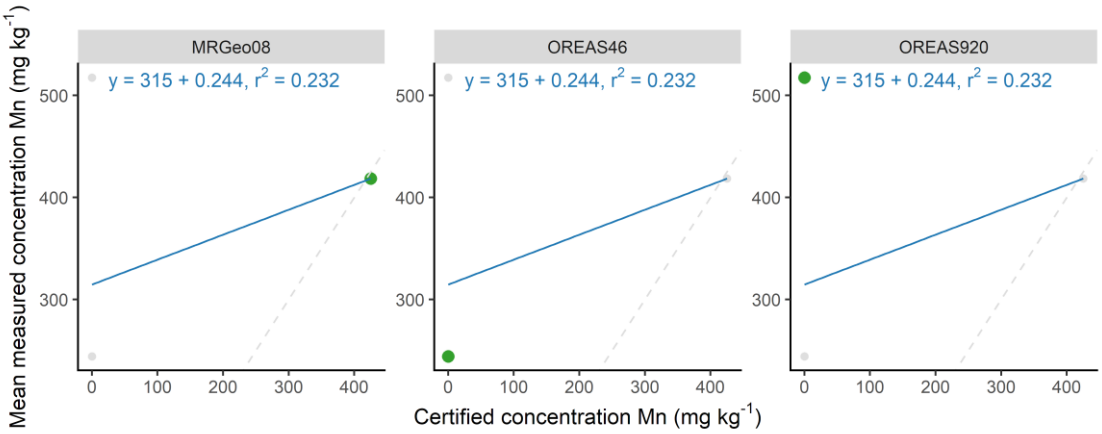


Chart 12 Manganese (Mn) (MS41L-BLD) determined by ICP-MS in blind in-house SRMs, faceted by SRM name. The 1:1 equality line is shown as a feint dashed grey line.

Calculating relative bias

$$\text{Relative bias } \% = \left\{\frac{(\text{Mean measured concentration} - \text{reference concentration})}{\text{reference concentration}}\right\} \times 100$$

Equation 1 Relative bias %.

The relative bias of each analyte available measured by CRMs: STSD-1; STSD-3; TILL-1; TILL-2 and TILL-3, are calculated and presented in Table 13, Table 14, Table 15, Table 16 and Table 17 included.

Table 13 Summary of relative bias calculated for CRM data by STSD-1 by ICP_{ar} (n=24). N/A where no reference concentration value is available.

	Au (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ag (mgkg^{-1}) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg^{-1}) ICP-MS (MS41L-BLD)	B (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ba (mgkg^{-1}) ICP-MS (MS41L-BLD)	Be (mgkg^{-1}) ICP-MS (MS41L-BLD)	Bi (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ca (%) ICP-MS (MS41L-BLD)	Cd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ce (mgkg^{-1}) ICP-MS (MS41L-BLD)	Co (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	171.51%	0.16%	1.06%	6.03%	1.19%	0.59%	1.49%	11.27%	1.34%	1.49%	2.76%	6.76%
% < method LLD	95.8%	0.0%	0.0%	0.0%	4.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cs (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cu (mgkg^{-1}) ICP-MS (MS41L-BLD)	Fe (%) ICP-MS (MS41L-BLD)	Ga (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ge (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hf (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hg (mgkg^{-1}) ICP-MS (MS41L-BLD)	In (mgkg^{-1}) ICP-MS (MS41L-BLD)	K (%) ICP-MS (MS41L-BLD)	La (mgkg^{-1}) ICP-MS (MS41L-BLD)	Li (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	7.99%	-1.92%	3.15%	-0.31%	-0.24%	-11.96%	-22.07%	5.77%	-0.26%	-0.22%	2.34%	6.51%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Mg (%) ICP-MS (MS41L-BLD)	Mn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Mo (mgkg^{-1}) ICP-MS (MS41L-BLD)	Na (%) ICP-MS (MS41L-BLD)	Nb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ni (mgkg^{-1}) ICP-MS (MS41L-BLD)	P (%) ICP-MS (MS41L-BLD)	Pb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pt (mgkg^{-1}) ICP-MS (MS41L-BLD)	Rb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Re (mgkg^{-1}) ICP-MS (MS41L-BLD)

Relative bias %	1.77%	1.15%	2.15%	65.74%	0.17%	7.27%	-1.51%	2.23%	-92.78%	456.26%	0.69%	-3.08%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	79.2%	0.0%	100.0%
	S (%) ICP-MS (MS41L-BLD)	Sb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sc (mgkg^{-1}) ICP-MS (MS41L-BLD)	Se (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ta (mgkg^{-1}) ICP-MS (MS41L-BLD)	Te (mgkg^{-1}) ICP-MS (MS41L-BLD)	Th (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg^{-1}) ICP-MS (MS41L-BLD)	U (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	2.07%	-2.83%	-3.72%	-20.62%	-3.48%	0.71%	-44.59%	-16.16%	-17.60%	-4.87%	0.42%	4.06%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	V (mgkg^{-1}) ICP-MS (MS41L-BLD)	W (mgkg^{-1}) ICP-MS (MS41L-BLD)	Y (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zr (mgkg^{-1}) ICP-MS (MS41L-BLD)							
Relative bias %	7.67%	-13.66%	2.83%	1.88%	-18.43%							
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%							

Table 14 Summary of relative bias calculated for CRM data by STSD-3 by by ICP_{ar} (n=24). N/A where no reference concentration value is available.

	Au (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ag (mgkg^{-1}) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg^{-1}) ICP-MS (MS41L-BLD)	B (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ba (mgkg^{-1}) ICP-MS (MS41L-BLD)	Be (mgkg^{-1}) ICP-MS (MS41L-BLD)	Bi (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ca (%) ICP-MS (MS41L-BLD)	Cd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ce (mgkg^{-1}) ICP-MS (MS41L-BLD)	Co (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	-24.74%	0.02%	2.10%	6.19%	-8.27%	1.61%	-2.23%	0.21%	2.47%	2.84%	1.40%	4.20%

% < method LLD	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cs (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cu (mgkg^{-1}) ICP-MS (MS41L-BLD)	Fe (%) ICP-MS (MS41L-BLD)	Ga (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ge (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hf (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hg (mgkg^{-1}) ICP-MS (MS41L-BLD)	In (mgkg^{-1}) ICP-MS (MS41L-BLD)	K (%) ICP-MS (MS41L-BLD)	La (mgkg^{-1}) ICP-MS (MS41L-BLD)	Li (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	4.91%	1.12%	3.44%	1.38%	3.03%	-11.47%	-8.10%	-1.50%	7.57%	1.17%	2.71%	1.94%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Mg (%) ICP-MS (MS41L-BLD)	Mn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Mo (mgkg^{-1}) ICP-MS (MS41L-BLD)	Na (%) ICP-MS (MS41L-BLD)	Nb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ni (mgkg^{-1}) ICP-MS (MS41L-BLD)	P (%) ICP-MS (MS41L-BLD)	Pb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pt (mgkg^{-1}) ICP-MS (MS41L-BLD)	Rb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Re (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	1.07%	1.88%	0.60%	101.53%	-0.03%	5.58%	-1.02%	0.83%	-88.95%	-5.78%	0.54%	-10.12%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	100.0%	0.0%	100.0%
	S (%) ICP-MS (MS41L-BLD)	Sb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sc (mgkg^{-1}) ICP-MS (MS41L-BLD)	Se (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ta (mgkg^{-1}) ICP-MS (MS41L-BLD)	Te (mgkg^{-1}) ICP-MS (MS41L-BLD)	Th (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg^{-1}) ICP-MS (MS41L-BLD)	U (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	2.29%	-1.69%	2.15%	-30.18%	0.79%	0.57%	-42.27%	-15.25%	0.80%	-3.13%	1.90%	3.10%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%

	V (mgkg^{-1}) ICP-MS (MS41L-BLD)	W (mgkg^{-1}) ICP-MS (MS41L-BLD)	Y (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zr (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	4.01%	-9.82%	2.67%	1.15%	-4.04%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%

Table 15 Summary of relative bias calculated for CRM data by TILL-1 by by ICP_{ar} (n=8). N/A where no reference concentration value is available.

	Au (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ag (mgkg^{-1}) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg^{-1}) ICP-MS (MS41L-BLD)	B (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ba (mgkg^{-1}) ICP-MS (MS41L-BLD)	Be (mgkg^{-1}) ICP-MS (MS41L-BLD)	Bi (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ca (%) ICP-MS (MS41L-BLD)	Cd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ce (mgkg^{-1}) ICP-MS (MS41L-BLD)	Co (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	81.41%	-42.69%	-16.55%	-28.39%	0.63%	12.10%	5.03%	45.19%	5.87%	33.23%	19.75%	-9.29%
% < method LLD	50.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cs (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cu (mgkg^{-1}) ICP-MS (MS41L-BLD)	Fe (%) ICP-MS (MS41L-BLD)	Ga (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ge (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hf (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hg (mgkg^{-1}) ICP-MS (MS41L-BLD)	In (mgkg^{-1}) ICP-MS (MS41L-BLD)	K (%) ICP-MS (MS41L-BLD)	La (mgkg^{-1}) ICP-MS (MS41L-BLD)	Li (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	-72.52%	-30.23%	-48.35%	-30.16%	-3.95%	-13.50%	-81.93%	12.49%	2.25%	-15.33%	17.61%	-9.11%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

	Mg (%) ICP-MS (MS41L-BLD)	Mn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Mo (mgkg^{-1}) ICP-MS (MS41L-BLD)	Na (%) ICP-MS (MS41L-BLD)	Nb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ni (mgkg^{-1}) ICP-MS (MS41L-BLD)	P (%) ICP-MS (MS41L-BLD)	Pb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pt (mgkg^{-1}) ICP-MS (MS41L-BLD)	Rb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Re (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	18.21%	27.11%	-16.38%	22.30%	23.44%	-60.99%	19.82%	-0.03%	-99.37%	-50.20%	-28.32%	-31.45%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	87.5%	0.0%	100.0%
	S (%) ICP-MS (MS41L-BLD)	Sb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sc (mgkg^{-1}) ICP-MS (MS41L-BLD)	Se (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ta (mgkg^{-1}) ICP-MS (MS41L-BLD)	Te (mgkg^{-1}) ICP-MS (MS41L-BLD)	Th (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg^{-1}) ICP-MS (MS41L-BLD)	U (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	-7.43%	42.33%	-51.43%	-35.31%	-13.72%	-7.41%	-46.00%	-31.60%	-35.72%	9.13%	6.97%	-13.25%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	V (mgkg^{-1}) ICP-MS (MS41L-BLD)	W (mgkg^{-1}) ICP-MS (MS41L-BLD)	Y (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zr (mgkg^{-1}) ICP-MS (MS41L-BLD)							
Relative bias %	-22.21%	14.12%	26.68%	22.12%	-84.76%							
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%							

Table 16 Summary of relative bias calculated for CRM data by TILL-2 by by ICP_{ar} (n=8). N/A where no reference concentration value is available.

	Au (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ag (mgkg^{-1}) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg^{-1}) ICP-MS (MS41L-BLD)	B (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ba (mgkg^{-1}) ICP-MS (MS41L-BLD)	Be (mgkg^{-1}) ICP-MS (MS41L-BLD)	Bi (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ca (%) ICP-MS (MS41L-BLD)	Cd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ce (mgkg^{-1}) ICP-MS (MS41L-BLD)	Co (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	-77.37%	8.61%	2.93%	-23.85%	-18.09%	-4.45%	28.25%	-46.73%	17.48%	29.62%	23.43%	-24.01%
% < method LLD	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cs (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cu (mgkg^{-1}) ICP-MS (MS41L-BLD)	Fe (%) ICP-MS (MS41L-BLD)	Ga (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ge (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hf (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hg (mgkg^{-1}) ICP-MS (MS41L-BLD)	In (mgkg^{-1}) ICP-MS (MS41L-BLD)	K (%) ICP-MS (MS41L-BLD)	La (mgkg^{-1}) ICP-MS (MS41L-BLD)	Li (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	-76.50%	21.47%	-39.92%	-47.99%	4.79%	-23.66%	-62.24%	25.33%	-37.70%	20.00%	20.11%	31.54%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Mg (%) ICP-MS (MS41L-BLD)	Mn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Mo (mgkg^{-1}) ICP-MS (MS41L-BLD)	Na (%) ICP-MS (MS41L-BLD)	Nb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ni (mgkg^{-1}) ICP-MS (MS41L-BLD)	P (%) ICP-MS (MS41L-BLD)	Pb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pt (mgkg^{-1}) ICP-MS (MS41L-BLD)	Rb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Re (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	21.67%	14.98%	19.03%	25.53%	24.29%	-60.72%	2.09%	-1.86%	-100.09%	-99.28%	23.26%	-49.03%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	100.0%	0.0%	100.0%
	S (%) ICP-MS (MS41L-BLD)	Sb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sc (mgkg^{-1}) ICP-MS (MS41L-BLD)	Se (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ta (mgkg^{-1}) ICP-MS (MS41L-BLD)	Te (mgkg^{-1}) ICP-MS (MS41L-BLD)	Th (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg^{-1}) ICP-MS (MS41L-BLD)	U (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	-9.48%	-4.42%	-69.81%	-37.29%	-8.96%	16.62%	-21.69%	-61.23%	-0.86%	5.87%	15.95%	16.57%

% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	V (mgkg^{-1}) ICP-MS (MS41L-BLD)	W (mgkg^{-1}) ICP-MS (MS41L-BLD)	Y (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zr (mgkg^{-1}) ICP-MS (MS41L-BLD)							
Relative bias %	-44.64%	-91.71%	15.23%	26.17%	-53.05%							
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%							

Table 17 Summary of relative bias calculated for CRM data by TILL-3 by by ICP_{ar} (n=8). N/A where no reference concentration value is available.

	Au (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ag (mgkg^{-1}) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg^{-1}) ICP-MS (MS41L-BLD)	B (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ba (mgkg^{-1}) ICP-MS (MS41L-BLD)	Be (mgkg^{-1}) ICP-MS (MS41L-BLD)	Bi (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ca (%) ICP-MS (MS41L-BLD)	Cd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ce (mgkg^{-1}) ICP-MS (MS41L-BLD)	Co (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	16.76%	44.22%	-14.65%	45.61%	-12.40%	-25.83%	-33.79%	11.71%	31.99%	-57.39%	-5.93%	-2.17%
% < method LLD	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cs (mgkg^{-1}) ICP-MS (MS41L-BLD)	Cu (mgkg^{-1}) ICP-MS (MS41L-BLD)	Fe (%) ICP-MS (MS41L-BLD)	Ga (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ge (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hf (mgkg^{-1}) ICP-MS (MS41L-BLD)	Hg (mgkg^{-1}) ICP-MS (MS41L-BLD)	In (mgkg^{-1}) ICP-MS (MS41L-BLD)	K (%) ICP-MS (MS41L-BLD)	La (mgkg^{-1}) ICP-MS (MS41L-BLD)	Li (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	24.71%	-10.75%	-3.45%	-8.45%	-3.16%	-6.40%	7.98%	3.82%	-29.01%	-43.03%	-5.02%	-9.23%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

	Mg (%) ICP-MS (MS41L-BLD)	Mn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Mo (mgkg^{-1}) ICP-MS (MS41L-BLD)	Na (%) ICP-MS (MS41L-BLD)	Nb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ni (mgkg^{-1}) ICP-MS (MS41L-BLD)	P (%) ICP-MS (MS41L-BLD)	Pb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pd (mgkg^{-1}) ICP-MS (MS41L-BLD)	Pt (mgkg^{-1}) ICP-MS (MS41L-BLD)	Rb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Re (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	5.51%	-38.51%	-12.76%	0.99%	42.10%	0.17%	-6.51%	-21.72%	-77.00%	-88.64%	-22.15%	-73.12%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	100.0%	0.0%	100.0%
	S (%) ICP-MS (MS41L-BLD)	Sb (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sc (mgkg^{-1}) ICP-MS (MS41L-BLD)	Se (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Sr (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ta (mgkg^{-1}) ICP-MS (MS41L-BLD)	Te (mgkg^{-1}) ICP-MS (MS41L-BLD)	Th (mgkg^{-1}) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg^{-1}) ICP-MS (MS41L-BLD)	U (mgkg^{-1}) ICP-MS (MS41L-BLD)
Relative bias %	-22.43%	5.19%	2.08%	-44.99%	12.24%	12.95%	-53.28%	-39.94%	11.59%	44.45%	-38.84%	11.91%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	V (mgkg^{-1}) ICP-MS (MS41L-BLD)	W (mgkg^{-1}) ICP-MS (MS41L-BLD)	Y (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zn (mgkg^{-1}) ICP-MS (MS41L-BLD)	Zr (mgkg^{-1}) ICP-MS (MS41L-BLD)							
Relative bias %	6.93%	32.08%	-18.43%	-24.99%	3.07%							
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%							

Blank sample data

Blank sample data are used as a quality check to see if any component of the analytical data can be measured and quantified as a contaminant introduced to a sample, where such contamination is introduced during the analytical processes.

The LLD is a theoretical concentration level calculated as three standard deviations (99.7% confidence interval) above the mean background count of run blanks. Notably, the mass of the samples has a direct relationship with the LLDs quoted so non-standard samples masses will be accompanied by a worsening of the LLD.

The raw data are examined and presented here. All data close to the lower limits of detection (LLD), nominally 10*LLD, are generally considered to be normal analytical noise and such low absolute quantities, even in the event of a contaminant component to the samples, are generally acceptable.

Analytes of concern and carry-over contamination investigated

Not every blank sample with detectable measurands is investigated in great detail. However, any blank sample with numerous analytes flagged as above the LLD is investigated especially in relation to the predecessor sample ID/LIMS code. Carry-over contamination and, rarely, sample mix-ups, can be a source of this and further quality checks and sometimes sample re-analyses are undertaken to rule these both out.

It is very important to assess the blank sample concentrations in the context of the real sample site data. If the blank samples are reported to contain a measurable analyte, above its LLD and some way above it, but that concentration is quantifiably low compared to the true sample sites dataset, then there is really no need to reject the data in the application for regional geochemical mapping. If, however the measured amounts in the blank samples are close to or similar to the concentrations reported for sample data, then caution in the data use is required. The naturally low baseline concentrations of precious metal analytes combined with advanced analytical chemistry, which is reaching very low limits of detection, together mean that an overlap is somewhat likely, at least for such metals.

Blank data reported for ICP_{ar}

ALS Minerals Limited employed procedural QC blanks of high purity pure silica sand approximately every 40 submitted samples (including laboratory standards) for ICP-MS analyses (ME-MS41L/MS41L-BLD method). These data are compiled and summarily reported at the end of each analytical batch as ‘Blanks’. Blank data for method ME-MS41L/MS41L-BLD are summarized in Table 18 and Table 19. In a standard, left-censored dataset baseline observations for a number of elements typically occurring close to LLD can be lost. To understand better the behaviour of these elements at the low end of the distribution, the lower limit of detection in the MS41L-BLD data set was lowered by a factor of 100 as opposed to censored values reported by the laboratory in the ME-MS41L dataset. It is therefore expected that frequent blank data exceedances will be observed in this dataset and the user is cautioned to interpret these data in this context. Most exceedances are <2*LLD and not systematic and indicate random deviations. For Re notable (>5%) exceedance is observed and user caution is advised when interpreting data at lower end of the concentration spectrum for these elements.

Table 18 Summary of above method LLD detectable ICP_{ar} ME-MS41L data in blank samples. Analytes with >5% of data above the LLD are orange highlighted.

	Au mg kg^{-1}	Ag mg kg^{-1}	Al %	As mg kg^{-1}	B mg kg^{-1}	Ba mg kg^{-1}	Be mg kg^{-1}	Bi mg kg^{-1}	Ca %	Cd mg kg^{-1}
Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	0	0	0	0	0	0	0	6	0	0
% > method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	2.7%	0.0%	0.0%

	Ce mg kg^{-1}	Co mg kg^{-1}	Cr mg kg^{-1}	Cs mg kg^{-1}	Cu mg kg^{-1}	Fe %	Ga mg kg^{-1}	Ge mg kg^{-1}	Hf mg kg-1	Hg mg kg-1
Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	0	0	2	0	3	0	0	0	0	1
% > method LLD	0.0%	0.0%	0.9%	0.0%	1.4%	0.0%	0.0%	0.0%	0.0%	0.5%

	In mg kg^{-1}	K %	La mg kg^{-1}	Li mg kg^{-1}	Mg mg kg^{-1}	Mn mg kg^{-1}	Mo mg kg^{-1}	Na mg kg^{-1}	Nb mg kg^{-1}	Ni mg kg^{-1}
Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	0	0	0	0	0	0	0	4	0	0
% > method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	1.8%	0.0%	0.0%

	P %	Pb mg kg^{-1}	Pd µg L-1	Pt mg kg-1	Rb mg kg^{-1}	Re mg kg^{-1}	S %	Sb mg kg^{-1}	Sc mg kg^{-1}	Se mg kg^{-1}
Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	0	0	0	14	1	0	3	0	0	0
% > method LLD	0.0%	0.0%	0.0%	6.3%	0.5%	0.0%	1.4%	0.0%	0.0%	0.0%

	Sn mg kg^{-1}	Sr mg kg^{-1}	Ta mg kg^{-1}	Te mg kg^{-1}	Th mg kg^{-1}	Ti %	Tl mg kg^{-1}	U mg kg^{-1}	V mg kg^{-1}	W mg kg^{-1}

Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	0	0	0	0	0	0	0	0	0	0
% > method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

	Y mg kg^{-1}	Zn mg kg^{-1}	Zn mg kg^{-1}
Count	222	222	222
Count > method LLD	0	1	0
% > method LLD	0.0%	0.5%	0.0%

Table 19 Summary of above method LLD detectable ICP_{ar} MS41L-BLD data in blank samples. Analytes with >5% of data above the LLD are orange highlighted.

	Au mg kg^{-1}	Ag mg kg^{-1}	Al %	As mg kg^{-1}	B mg kg^{-1}	Ba mg kg^{-1}	Be mg kg^{-1}	Bi mg kg^{-1}	Ca %	Cd mg kg^{-1}
Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	28	76	19	62	46	21	64	78	55	69
% > method LLD	12.6%	34.2%	8.6%	27.9%	20.7%	9.5%	28.8%	35.1%	24.8%	31.1%

	Ce mg kg^{-1}	Co mg kg^{-1}	Cr mg kg^{-1}	Cs mg kg^{-1}	Cu mg kg^{-1}	Fe %	Ga mg kg^{-1}	Ge mg kg^{-1}	Hf mg kg-1	Hg mg kg-1
Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	42	59	80	61	64	53	78	112	72	149
% > method LLD	18.9%	26.6%	36.0%	27.5%	28.8%	23.9%	35.1%	50.5%	32.4%	67.1%

	In mg kg^{-1}	K %	La mg kg^{-1}	Li mg kg^{-1}	Mg mg kg^{-1}	Mn mg kg^{-1}	Mo mg kg^{-1}	Na mg kg^{-1}	Nb mg kg^{-1}	Ni mg kg^{-1}
Count	222	222	222	222	222	222	222	222	222	222

Count > method LLD	65	23	30	49	3	65	77	60	68	56
% > method LLD	29.3%	10.4%	13.5%	22.1%	1.4%	29.3%	34.7%	27.0%	30.6%	25.2%

	P %	Pb mg kg^{-1}	Pd µg L^{-1}	Pt mg kg^{-1}	Rb mg kg^{-1}	Re mg kg^{-1}	S %	Sb mg kg^{-1}	Sc mg kg^{-1}	Se mg kg^{-1}
Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	89	61	85	51	48	38	57	87	61	78
% > method LLD	40.1%	27.5%	38.3%	23.0%	21.6%	17.1%	25.7%	39.2%	27.5%	35.1%

	Sn mg kg^{-1}	Sr mg kg^{-1}	Ta mg kg^{-}	Te mg kg^{-1}	Th mg kg^{-1}	Ti %	Tl mg kg^{-1}	U mg kg-1	V mg kg^{-1}	W mg kg^{-1}
Count	222	222	222	222	222	222	222	222	222	222
Count > method LLD	85	70	113	53	80	0	60	26	59	87
% > method LLD	38.3%	31.5%	50.9%	23.9%	36.0%	0.0%	27.0%	11.7%	26.6%	39.2%

	Y mg kg^{-1}	Zn mg kg^{-1}	Zn mg kg^{-1}
Count	222	222	222
Count > method LLD	51	72	73
% > method LLD	23.0%	32.4%	32.9%

Analytical interferences

In analytical chemistry there is always potential for interferences between analytes. This can be due to the chemical properties of a measurand, spectral interferences (where a signal overlaps or masks another) or physical matrix effects whereby the chemical behaviour in a given matrix needs to be specifically accounted for by calibration. Typically, these are addressed by the laboratory through adaptation of the method and/or instrument (*e.g.* sample dilution), or, by an approach to better process the data and correct for them. Analytical data reports are accompanied by notes from the analyst/laboratory that may flag the potential for analytical interferences.

Further, where there is a measurement of the same element or its species by more than one aliquot and/or method, it is good practice to check the relationship between them as a means to assess their performance independently.

Check on ICP_{ar} interferences

The analytical laboratory is primarily responsible for checking and where possible correcting for analytical interferences. As a quality check, all analytes are plotted against one another to look for systematic relationships. No interferences were suspected.

Univariate statistical summaries

The univariate statistics of published data are presented here. All data are freely available to download and to view from www.gsi.ie/tellus.

When published by GSI, all geochemical data are censored, so that results below the lower reporting (detection) limit are reported as one half the stated lower limit of detection. Dealing statistically with non-detects and data truncated to both a lower and upper reporting limit is challenging, as numerically there needs to be a systematic and robust way of including these data. Representing censored data on a map can be managed by statistically classifying the data, based on percentile breaks in the data. Below is a statistical summary of the data (Table 20, Table 21 and Table 22) including both ICP-MS methods. These statistical summaries are calculated using the R program (R Core Team, 2013) using the NADA (Non-detects and data analysis for environmental data) package (Lee, 2009). The percentile values calculated are default GSI recommended bins for constructing interpolated geochemical maps with Tellus data. For several analytes (B, Ta, Pd and Pt) most of the observations were below certified LLD (ME-MS41L method) and thus the accredited data set does not allow production of useful maps for these analytes. However, data below certified LLD (MS41L-BLD) may be used to generate useful maps. Users are cautioned that MS41L-BLD data provided for these four analytes were acquired using a non accredited method and all interpretation and conclusions arising from analysis of this data must take the above into consideration. Furthermore, since data used for these calculations are only right-censored (URL) and not-left censored (LLD) percentile values represent points calculated for the entire data population including values below LLD. Because of this the 0^{th} percentile does not always correspond to the minimum value of the data population. Should the user wish to plot interpolated maps from the MS41L-BLD data set recommended percentile values for classification purposes are given in Table 21 and Table 24. Data for MS41L method are provided in Table 22 and Table 25..

Three methods for robust estimators of descriptive statistics (median, mean and standard deviation) are employed and colour coded accordingly (Table 23, Table 24 and Table 25). For those elements with ≤50% of censored data, the Kaplan-Meier estimator method was used to estimate the median, mean and standard deviation of the data (Kaplan and Meier, 1958). For those elements where >50% and ≤80% of the data are censored, the maximum likelihood estimation (MLE) method was used to estimate the median, mean and standard deviation. Where >80% of the data were censored the median, mean and standard deviation are estimated using a regression on order statistics (ROS) method (Helsel, 2005). This follows some recommendations of the NADA package and of Antweiler and Taylor (2008) on estimators of environmental datasets.

Table 20 Univariate summary statistics for deeper topsoil pH ($CaCl_2$) and LOI (450°C) sample data.

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
pH	0.01	pH unit	4277	0	0	2.7	3.2	3.4	3.8	4.5	5.4	6	6.1	6.2	6.5	6.6	6.7	6.9	7.6
LOI (450°C)	0.01	%	4278	0	0	0.85	2.86	3.17	3.42	3.96	5.63	11.3	16.6	36.2	94.4	96.9	97.4	97.8	100

Table 21 Univariate summary statistics for deeper topsoil ICP_{ar} sample data calculated for MS41L-BLD method.

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
Ag	0.00001	mg kg^{-1}	4278	0	0.00	0.00156	0.0128	0.0199	0.0322	0.0573	0.0859	0.105	0.113	0.122	0.146	0.17	0.193	0.226	34
Al	0.0001	%	4278	0	0.00	0.0096	0.047	0.0684	0.24	0.643	1.22	1.59	1.7	1.81	2.12	2.41	2.65	2.95	7.67
As	0.0001	mg kg^{-1}	4278	0	0.00	0.0169	0.907	1.38	2.27	4.62	7.83	10.3	11.2	12.2	15.4	19.6	24.9	32.9	138
B	0.1	mg kg^{-1}	4278	108	2.52	0.2	1.2	1.8	2.5	3.5	5.6	7.2	7.7	8.2	9.7	11.2	13.1	15	33.3
Ba	0.005	mg kg^{-1}	4278	0	0.00	1.93	7.18	12.8	20.6	31.9	60	89.8	100	112	154	216	292	425	4850
Be	0.0001	mg kg^{-1}	4278	2	0.05	0.0018	0.0236	0.0461	0.135	0.326	0.677	0.91	0.97	1.04	1.24	1.38	1.53	1.73	16.3
Bi	0.000005	mg kg^{-1}	4278	0	0.00	0.000505	0.0273	0.0399	0.0514	0.067	0.0969	0.122	0.129	0.138	0.163	0.198	0.27	0.404	9.91
Ca	0.0001	%	4278	0	0.00	0.0097	0.0988	0.133	0.16	0.202	0.362	1.13	1.66	2.37	4.68	8.54	12.4	19.3	25
Cd	0.00001	mg kg^{-1}	4278	0	0.00	0.00714	0.0899	0.125	0.164	0.289	0.75	1.16	1.29	1.44	1.91	2.5	3.1	4.06	16
Ce	0.00003	mg kg^{-1}	4278	0	0.00	0.101	0.763	1.33	6.52	17.9	30.2	37.1	39.3	41.6	48	55	60.6	70.8	266
Co	0.00001	mg kg^{-1}	4278	0	0.00	0.0325	0.203	0.352	0.907	3.41	7.68	10.5	11.3	12.1	14.1	16.2	18.4	20.7	40
Cr	0.0001	mg kg^{-1}	4278	0	0.00	0.156	0.701	1.13	3.55	11.3	21.6	27.9	29.8	32	37.4	43.2	49.1	59.9	193
Cs	0.00005	mg kg^{-1}	4278	0	0.00	0.00237	0.0208	0.0397	0.166	0.395	0.69	0.907	0.974	1.06	1.31	1.61	2.01	3.16	28.7

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
Cu	0.0001	mg kg^{-1}	4278	0	0.00	0.609	1.89	2.57	4.11	8.4	15.2	20.3	21.8	23.9	29.7	35.8	42.5	52.4	154
Fe	0.00001	%	4278	0	0.00	0.0105	0.0654	0.171	0.387	0.906	1.63	2.17	2.33	2.49	2.95	3.33	3.73	4.28	17.4
Ga	0.00004	mg kg^{-1}	4278	0	0.00	0.0191	0.174	0.268	0.701	1.87	3.38	4.5	4.83	5.23	6.35	7.36	8.59	9.75	15.6
Ge	0.00005	mg kg^{-1}	4278	25	0.58	0.00047	0.00856	0.015	0.0215	0.0319	0.0503	0.0625	0.0657	0.0697	0.0805	0.0899	0.0988	0.112	0.219
Hf	0.00002	mg kg^{-1}	4278	11	0.26	0.00007	0.00193	0.00371	0.00879	0.0304	0.0694	0.0925	0.0991	0.106	0.124	0.141	0.156	0.185	0.403
Hg	0.00004	mg kg^{-1}	4278	0	0.00	0.008	0.0404	0.0496	0.055	0.0639	0.0818	0.0991	0.105	0.112	0.133	0.158	0.187	0.244	6.45
In	0.00005	mg kg^{-1}	4278	53	1.24	0.00015	0.00262	0.00477	0.00704	0.0113	0.0187	0.0242	0.0258	0.0275	0.0319	0.0357	0.0396	0.0458	0.0862
K	0.0001	%	4278	0	0.00	0.0015	0.0122	0.0187	0.0326	0.0787	0.158	0.222	0.239	0.256	0.299	0.338	0.372	0.418	0.566
La	0.00002	mg kg^{-1}	4278	0	0.00	0.058	0.376	0.709	3.55	8.85	15.3	19	20.1	21.3	24.9	28.3	32.1	37.2	101
Li	0.001	mg kg^{-1}	4278	121	2.83	0.003	0.0891	0.191	0.709	5.04	11	14.9	16.2	17.6	22	26.6	31.9	42.6	121
Mg	0.0001	%	4278	0	0.00	0.0136	0.0525	0.0699	0.084	0.11	0.172	0.254	0.284	0.326	0.472	0.625	0.775	1	7.07
Mn	0.001	mg kg^{-1}	4278	2	0.05	1.28	8.72	16.7	44.4	152	564	938	1030	1110	1370	1640	2070	2930	28900
Mo	0.0001	mg kg^{-1}	4278	0	0.00	0.0341	0.181	0.262	0.344	0.522	0.957	1.36	1.51	1.69	2.43	3.54	4.85	6.83	91.5
Na	0.00001	%	4278	0	0.00	0.00443	0.0153	0.0173	0.0187	0.0212	0.0272	0.0341	0.0361	0.0387	0.046	0.0531	0.0601	0.0702	0.552
Nb	0.00002	mg kg^{-1}	4278	0	0.00	0.00791	0.0296	0.0489	0.0995	0.195	0.284	0.38	0.425	0.482	0.667	0.892	1.2	1.76	7.76
Ni	0.0004	mg kg^{-1}	4278	0	0.00	0.162	0.9	1.44	3	12.8	28.5	39.5	42.3	45.7	54.6	62.7	70.7	82.9	206
P	0.00001	mg kg^{-1}	4278	0	0.00	27.9	177	214	251	325	461	595	636	681	844	1010	1210	1580	3320
Pb	0.00005	mg kg^{-1}	4278	0	0.00	0.086	6.58	9.26	11	13.5	19	23.9	25.5	27.2	33.2	40.8	51	77.3	283
Rb	0.00005	mg kg^{-1}	4278	0	0.00	0.0561	0.253	0.414	1.47	5.78	13.2	18	19.3	20.4	24	26.9	29.6	32.8	55.3
Re	0.000002	mg kg^{-1}	4278	102	2.38	0.000005	0.000739	0.000153	0.000209	0.000284	0.000466	0.000724	0.000846	0.00105	0.00247	0.00637	0.0115	0.0187	0.105
S	0.0001	%	4278	0	0.00	0.0037	0.0193	0.0216	0.0235	0.0267	0.0389	0.0784	0.115	0.204	0.347	0.434	0.523	0.641	1.35

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
Sb	0.00005	mg kg^{-1}	4278	0	0.00	0.00254	0.0961	0.131	0.162	0.222	0.37	0.52	0.578	0.65	0.888	1.12	1.37	1.73	8.18
Sc	0.00005	mg kg^{-1}	4278	0	0.00	0.0311	0.087	0.21	0.523	1.28	2.95	4.02	4.31	4.68	5.59	6.3	6.99	8.04	12.2
Se	0.00003	mg kg^{-1}	4278	0	0.00	0.053	0.344	0.401	0.449	0.526	0.729	1.02	1.14	1.33	2.15	3.31	4.85	8.29	63.3
Sn	0.0001	mg kg^{-1}	4278	0	0.00	0.0002	0.167	0.228	0.288	0.388	0.565	0.688	0.732	0.78	0.949	1.17	1.61	2.6	16.9
Sr	0.0001	mg kg^{-1}	4278	0	0.00	2.02	9.35	11.5	13.2	16.4	24.2	37.9	44.8	55.7	96.7	154	221	330	948
Ta	0.00005	mg kg^{-1}	4278	1560	36.47	n/a	0.0000155	0.0000279	0.0000415	0.00007	0.00024	0.00058	0.00074	0.00097	0.00168	0.00279	0.00482	0.00802	0.0819
Te	0.00003	mg kg^{-1}	4278	2	0.05	0.00024	0.00312	0.0043	0.00572	0.00892	0.0156	0.0214	0.0232	0.025	0.0308	0.0375	0.0435	0.0536	0.147
Th	0.00002	mg kg^{-1}	4278	7	0.16	0.0001	0.00628	0.0226	0.191	0.718	1.41	1.9	2.05	2.21	2.68	3.12	3.55	4.29	31
Ti	0.00001	%	4278	2	0.05	0.00024	0.00125	0.00182	0.00255	0.00351	0.00519	0.00715	0.00819	0.0095	0.0132	0.018	0.0251	0.0405	0.165
Tl	0.00001	mg kg^{-1}	4278	0	0.00	0.00022	0.00932	0.0151	0.0395	0.108	0.205	0.271	0.29	0.31	0.366	0.423	0.484	0.583	4.43
U	0.00005	mg kg^{-1}	4278	0	0.00	0.0154	0.081	0.269	0.545	0.761	1.03	1.3	1.4	1.55	2.36	3.99	7.09	13.3	196
V	0.001	mg kg^{-1}	4278	0	0.00	0.182	1.28	2.12	5.97	17	29.8	38.1	40.6	44.1	51.6	58.7	64.8	73.1	242
W	0.00001	mg kg^{-1}	4278	3	0.07	0.00034	0.0124	0.0182	0.0256	0.0349	0.0493	0.0624	0.067	0.0724	0.0918	0.113	0.146	0.261	23.7
Y	0.00003	mg kg^{-1}	4278	0	0.00	0.0562	0.297	0.558	1.93	5.21	13.6	19.9	21.7	23.6	29.1	34.9	40.8	49.5	123
Zn	0.001	mg kg^{-1}	4278	0	0.00	1.58	9.75	15.4	20.1	32.9	64.1	87.5	94.9	104	124	141	155	180	2960
Zr	0.0001	mg kg^{-1}	4278	3	0.07	0.0178	0.0661	0.127	0.327	1.08	2.5	3.3	3.47	3.69	4.27	4.82	5.37	6.47	12.1
Au	0.000002	mg kg^{-1}	4278	756	17.67	0.000003	0.0000362	0.0000549	0.0000739	0.000125	0.0004	0.000649	0.000738	0.000847	0.00124	0.00168	0.00221	0.00456	2.31
Pd	0.00001	mg kg^{-1}	4278	2708	63.30	n/a	0.00000322	0.00000626	0.00000981	0.000019	0.00006	0.00016	0.00029	0.00044	0.00088	0.00135	0.00193	0.00251	0.00597
Pt	0.00002	mg kg^{-1}	4278	2058	48.11	n/a	n/a	n/a	n/a	0.0000122	0.0000971	0.00074	0.00116	0.0022	0.0158	0.0377	0.0711	0.182	2.04

Table 22 Univariate summary statistics for deeper topsoil ICP_{ar} sample data calculated for ME-MS41L method.

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
Ag	0.001	mg kg^{-1}	4278	0	0.00	0.00156	0.0128	0.0199	0.0322	0.0573	0.0859	0.105	0.113	0.122	0.146	0.17	0.193	0.226	34
Al	0.01	%	4278	2	0.05	0.0111	0.047	0.0684	0.24	0.643	1.22	1.59	1.7	1.81	2.12	2.41	2.65	2.95	7.67
As	0.01	mg kg^{-1}	4278	0	0.00	0.0169	0.907	1.38	2.27	4.62	7.83	10.3	11.2	12.2	15.4	19.6	24.9	32.9	138
B	10	mg kg^{-1}	4278	3922	91.68	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	11.2	13.1	15	33.3
Ba	0.5	mg kg^{-1}	4278	0	0.00	1.93	7.18	12.8	20.6	31.9	60	89.8	100	112	154	216	292	425	4850
Be	0.01	mg kg^{-1}	4278	32	0.75	0.0102	0.0244	0.0461	0.135	0.326	0.677	0.91	0.97	1.04	1.24	1.38	1.53	1.73	16.3
Bi	0.0005	mg kg^{-1}	4278	0	0.00	0.000505	0.0273	0.0399	0.0514	0.067	0.0969	0.122	0.129	0.138	0.163	0.198	0.27	0.404	9.91
Ca	0.01	%	4278	1	0.02	n/a	n/a	0.133	0.16	0.202	0.362	1.13	1.66	2.37	4.68	8.54	12.4	19.3	25
Cd	0.001	mg kg^{-1}	4278	0	0.00	0.00714	0.0899	0.125	0.164	0.289	0.75	1.16	1.29	1.44	1.91	2.5	3.1	4.06	16
Ce	0.003	mg kg^{-1}	4278	0	0.00	0.101	0.763	1.33	6.52	17.9	30.2	37.1	39.3	41.6	48	55	60.6	70.8	266
Co	0.001	mg kg^{-1}	4278	0	0.00	0.0325	0.203	0.352	0.907	3.41	7.68	10.5	11.3	12.1	14.1	16.2	18.4	20.7	40
Cr	0.01	mg kg^{-1}	4278	0	0.00	0.156	0.701	1.13	3.55	11.3	21.6	27.9	29.8	32	37.4	43.2	49.1	59.9	193
Cs	0.005	mg kg^{-1}	4278	6	0.14	0.00504	0.0208	0.0397	0.166	0.395	0.69	0.907	0.974	1.06	1.31	1.61	2.01	3.16	28.7
Cu	0.01	mg kg^{-1}	4278	0	0.00	0.609	1.89	2.57	4.11	8.4	15.2	20.3	21.8	23.9	29.7	35.8	42.5	52.4	154
Fe	0.001	%	4278	0	0.00	0.0105	0.0654	0.171	0.387	0.906	1.63	2.17	2.33	2.49	2.95	3.33	3.73	4.28	17.4
Ga	0.004	mg kg^{-1}	4278	0	0.00	0.0191	0.174	0.268	0.701	1.87	3.38	4.5	4.83	5.23	6.35	7.36	8.59	9.75	15.6
Ge	0.005	mg kg^{-1}	4278	94	2.20	0.00502	0.0102	0.015	0.0215	0.0319	0.0503	0.0625	0.0657	0.0697	0.0805	0.0899	0.0988	0.112	0.219
Hf	0.002	mg kg^{-1}	4278	227	5.31	0.00201	0.00392	0.00613	0.00879	0.0304	0.0694	0.0925	0.0991	0.106	0.124	0.141	0.156	0.185	0.403
Hg	0.004	mg kg^{-1}	4278	0	0.00	0.008	0.0404	0.0496	0.055	0.0639	0.0818	0.0991	0.105	0.112	0.133	0.158	0.187	0.244	6.45

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
In	0.005	mg kg^{-1}	4278	456	10.66	n/a	0.00609	0.00678	0.00744	0.0113	0.0187	0.0242	0.0258	0.0275	0.0319	0.0357	0.0396	0.0458	0.0862
K	0.01	%	4278	130	3.04	0.0101	0.0145	0.0192	0.0326	0.0787	0.158	0.222	0.239	0.256	0.299	0.338	0.372	0.418	0.566
La	0.002	mg kg^{-1}	4278	0	0.00	0.058	0.376	0.709	3.55	8.85	15.3	19	20.1	21.3	24.9	28.3	32.1	37.2	101
Li	0.1	mg kg^{-1}	4278	343	8.02	0.101	0.287	0.73	1.09	5.04	11	14.9	16.2	17.6	22	26.6	31.9	42.6	121
Mg	0.01	%	4278	0	0.00	0.0136	0.0525	0.0699	0.084	0.11	0.172	0.254	0.284	0.326	0.472	0.625	0.775	1	7.07
Mn	0.1	mg kg^{-1}	4278	2	0.05	1.28	8.72	16.7	44.4	152	564	938	1030	1110	1370	1640	2070	2930	28900
Mo	0.01	mg kg^{-1}	4278	0	0.00	0.0341	0.181	0.262	0.344	0.522	0.957	1.36	1.51	1.69	2.43	3.54	4.85	6.83	91.5
Na	0.001	%	4278	0	0.00	0.00443	0.0153	0.0173	0.0187	0.0212	0.0272	0.0341	0.0361	0.0387	0.046	0.0531	0.0601	0.0702	0.552
Nb	0.002	mg kg^{-1}	4278	0	0.00	0.00791	0.0296	0.0489	0.0995	0.195	0.284	0.38	0.425	0.482	0.667	0.892	1.2	1.76	7.76
Ni	0.04	mg kg^{-1}	4278	0	0.00	0.162	0.9	1.44	3	12.8	28.5	39.5	42.3	45.7	54.6	62.7	70.7	82.9	206
P	0.001	mg kg^{-1}	4278	0	0.00	27.9	177	214	251	325	461	595	636	681	844	1010	1210	1580	3320
Pb	0.005	mg kg^{-1}	4278	0	0.00	0.086	6.58	9.26	11	13.5	19	23.9	25.5	27.2	33.2	40.8	51	77.3	283
Rb	0.005	mg kg^{-1}	4278	0	0.00	0.0561	0.253	0.414	1.47	5.78	13.2	18	19.3	20.4	24	26.9	29.6	32.8	55.3
Re	0.0002	mg kg^{-1}	4278	611	14.28	n/a	n/a	n/a	0.000209	0.000284	0.000466	0.000724	0.000846	0.00105	0.00247	0.00637	0.0115	0.0187	0.105
S	0.01	%	4278	2	0.05	n/a	0.0193	0.0216	0.0235	0.0267	0.0389	0.0784	0.115	0.204	0.347	0.434	0.523	0.641	1.35
Sb	0.005	mg kg^{-1}	4278	3	0.07	0.00624	0.0961	0.131	0.162	0.222	0.37	0.52	0.578	0.65	0.888	1.12	1.37	1.73	8.18
Sc	0.005	mg kg^{-1}	4278	0	0.00	0.0311	0.087	0.21	0.523	1.28	2.95	4.02	4.31	4.68	5.59	6.3	6.99	8.04	12.2
Se	0.003	mg kg^{-1}	4278	0	0.00	0.053	0.344	0.401	0.449	0.526	0.729	1.02	1.14	1.33	2.15	3.31	4.85	8.29	63.3
Sn	0.01	mg kg^{-1}	4278	6	0.14	0.012	0.167	0.228	0.288	0.388	0.565	0.688	0.732	0.78	0.949	1.17	1.61	2.6	16.9
Sr	0.01	mg kg^{-1}	4278	0	0.00	2.02	9.35	11.5	13.2	16.4	24.2	37.9	44.8	55.7	96.7	154	221	330	948
Ta	0.005	mg kg^{-1}	4278	4177	97.64	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.00802	0.0819

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
Te	0.003	mg kg^{-1}	4278	193	4.51	n/a	0.00338	0.0043	0.00572	0.00892	0.0156	0.0214	0.0232	0.025	0.0308	0.0375	0.0435	0.0536	0.147
Th	0.002	mg kg^{-1}	4278	64	1.50	0.00208	0.00873	0.0243	0.191	0.718	1.41	1.9	2.05	2.21	2.68	3.12	3.55	4.29	31
Ti	0.001	%	4278	97	2.27	n/a	0.00125	0.00182	0.00255	0.00351	0.00519	0.00715	0.00819	0.0095	0.0132	0.018	0.0251	0.0405	0.165
Tl	0.001	mg kg^{-1}	4278	2	0.05	0.00114	0.00932	0.0151	0.0395	0.108	0.205	0.271	0.29	0.31	0.366	0.423	0.484	0.583	4.43
U	0.005	mg kg^{-1}	4278	0	0.00	0.0154	0.081	0.269	0.545	0.761	1.03	1.3	1.4	1.55	2.36	3.99	7.09	13.3	196
V	0.1	mg kg^{-1}	4278	0	0.00	0.182	1.28	2.12	5.97	17	29.8	38.1	40.6	44.1	51.6	58.7	64.8	73.1	242
W	0.001	mg kg^{-1}	4278	9	0.21	0.00105	0.0124	0.0182	0.0256	0.0349	0.0493	0.0624	0.067	0.0724	0.0918	0.113	0.146	0.261	23.7
Y	0.003	mg kg^{-1}	4278	0	0.00	0.0562	0.297	0.558	1.93	5.21	13.6	19.9	21.7	23.6	29.1	34.9	40.8	49.5	123
Zn	0.1	mg kg^{-1}	4278	0	0.00	1.58	9.75	15.4	20.1	32.9	64.1	87.5	94.9	104	124	141	155	180	2960
Zr	0.01	mg kg^{-1}	4278	3	0.07	0.0178	0.0661	0.127	0.327	1.08	2.5	3.3	3.47	3.69	4.27	4.82	5.37	6.47	12.1
Au	0.0002	mg kg^{-1}	4278	1352	31.60	n/a	0.0000803	0.000106	0.000136	0.000182	0.0004	0.000649	0.000738	0.000847	0.00124	0.00168	0.00221	0.00456	2.31
Pd	0.001	mg kg^{-1}	4278	3918	91.58	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.00135	0.00193	0.00251	0.00597
Pt	0.002	mg kg^{-1}	4278	3392	79.29	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.00268	0.0158	0.0377	0.0711	0.182	2.04

Table 23 Univariate summary statistics including best fits based on proportions of pH (CaC2) and LOI (450°C) data below the LLD. All to 3 significant figures.

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
pH	0.01		4277	0	0.00	5.09	1.19	2.1	6.9	5.4	5.4	5.09	5.22	5.22	5.23	1.08	1.08	1.21	5.22

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
LOI	0.01	%	4278	0	0.00	9.46	3.4	-15	22.9	5.63	5.63	9.46	22.2	22.2	19.4	32.3	32.3	34.7	22.2

Table 24 Univariate summary statistics including best fits based on proportions of ICPar data below the MS41L-BLD LLD. All to 3 significant figures.

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
Ag	0.00001	mg kg^{-1}	4278	0	0.00	0.0957	0.0703	0.0416	-0.0268	0.141	0.0859	0.0859	0.0703	0.0957	0.0957	0.0955	4278	0	0.00
Al	0.0001	%	4278	0	0.00	1.19	0.787	0.776	-0.941	2.23	1.22	1.22	0.787	1.19	1.19	1.61	4278	0	0.00
As	0.0001	mg kg^{-1}	4278	0	0.00	8.73	6.26	4.83	-5.23	14.5	7.82	7.83	6.26	8.73	8.73	9.77	4278	0	0.00
B	0.1	mg kg^{-1}	4278	108	2.52	5.93	5.01	2.97	-2.45	9.85	5.6	5.6	4.52	5.79	5.81	6.84	4278	108	2.52
Ba	0.005	mg kg^{-1}	4278	0	0.00	83.1	53.1	47.3	-70.1	134	60	60	53.1	83.1	83.1	85.8	4278	0	0.00
Be	0.0001	mg kg^{-1}	4278	2	0.05	0.681	0.439	0.479	-0.64	1.29	0.677	0.677	0.437	0.68	0.68	0.944	4278	2	0.05
Bi	0.000005	mg kg^{-1}	4278	0	0.00	0.11	0.0874	0.0459	-0.026	0.16	0.0969	0.0969	0.0874	0.11	0.11	0.112	4278	0	0.00
Ca	0.0001	%	4278	0	0.00	1.77	0.566	0.335	-1.99	2.39	0.362	0.362	0.566	1.77	1.77	1.59	4278	0	0.00
Cd	0.00001	mg kg^{-1}	4278	0	0.00	0.936	0.592	0.724	-1.21	1.79	0.75	0.75	0.592	0.936	0.936	1.04	4278	0	0.00
Ce	0.00003	mg kg^{-1}	4278	0	0.00	28.7	18.6	15.4	-14.2	50	30.2	30.2	18.6	28.7	28.7	42.4	4278	0	0.00
Co	0.00001	mg kg^{-1}	4278	0	0.00	7.66	4.6	5.72	-8.39	15.2	7.68	7.68	4.6	7.66	7.66	11.3	4278	0	0.00
Cr	0.0001	mg kg^{-1}	4278	0	0.00	21.3	13.7	13.4	-16.3	39	21.6	21.6	13.7	21.3	21.3	29.6	4278	0	0.00
Cs	0.00005	mg kg^{-1}	4278	0	0.00	0.756	0.462	0.428	-0.473	1.26	0.69	0.69	0.462	0.756	0.756	1.06	4278	0	0.00
Cu	0.0001	mg kg^{-1}	4278	0	0.00	16.4	12.1	9.97	-11.7	28.5	15.2	15.2	12.1	16.4	16.4	17.9	4278	0	0.00
Fe	0.00001	%	4278	0	0.00	1.66	1.13	1.05	-1.22	3.04	1.63	1.63	1.13	1.66	1.66	2.15	4278	0	0.00
Ga	0.00004	mg kg^{-1}	4278	0	0.00	3.47	2.34	2.18	-2.57	6.31	3.37	3.38	2.34	3.47	3.47	4.44	4278	0	0.00
Ge	0.00005	mg kg^{-1}	4278	25	0.58	0.05	0.0415	0.0246	-0.018	0.0826	0.0503	0.0503	0.0399	0.0497	0.0497	0.059	4278	25	0.58

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
Hf	0.00002	mg kg^{-1}	4278	11	0.26	0.0681	0.0417	0.049	-0.0711	0.133	0.0694	0.0694	0.0409	0.0679	0.0679	0.106	4278	11	0.26
Hg	0.00004	mg kg^{-1}	4278	0	0.00	0.0908	0.0814	0.0297	0.00215	0.126	0.0818	0.0818	0.0814	0.0908	0.0908	0.0895	4278	0	0.00
In	0.00005	mg kg^{-1}	4278	53	1.24	0.0191	0.0153	0.0105	-0.00961	0.0329	0.0187	0.0187	0.0143	0.0188	0.0189	0.024	4278	53	1.24
K	0.0001	%	4278	0	0.00	0.162	0.114	0.119	-0.162	0.32	0.157	0.158	0.114	0.162	0.162	0.193	4278	0	0.00
La	0.00002	mg kg^{-1}	4278	0	0.00	14.7	9.52	8.09	-8.05	25.8	15.3	15.3	9.52	14.7	14.7	21.7	4278	0	0.00
Li	0.001	mg kg^{-1}	4278	121	2.83	11.9	6.17	7.87	-10.6	21.9	11	11	4.74	11.6	11.6	64.9	4278	121	2.83
Mg	0.0001	%	4278	0	0.00	0.237	0.177	0.114	-0.15	0.371	0.172	0.172	0.177	0.237	0.237	0.233	4278	0	0.00
Mn	0.001	mg kg^{-1}	4278	2	0.05	694	316	643	-1160	1460	564	564	315	694	694	1230	4278	2	0.05
Mo	0.0001	mg kg^{-1}	4278	0	0.00	1.31	0.881	0.708	-0.963	2.01	0.957	0.957	0.881	1.31	1.31	1.3	4278	0	0.00
Na	0.00001	%	4278	0	0.00	0.0304	0.0278	0.0105	-0.00112	0.0436	0.0272	0.0272	0.0278	0.0304	0.0304	0.0301	4278	0	0.00
Nb	0.00002	mg kg^{-1}	4278	0	0.00	0.358	0.247	0.162	-0.15	0.54	0.284	0.284	0.247	0.358	0.358	0.391	4278	0	0.00
Ni	0.0004	mg kg^{-1}	4278	0	0.00	28.9	17.5	21.8	-31.3	57	28.5	28.5	17.5	28.9	28.9	41.2	4278	0	0.00
P	0.00001	mg kg^{-1}	4278	0	0.00	512	445	228	-142	792	461	461	445	512	512	516	4278	0	0.00
Pb	0.00005	mg kg^{-1}	4278	0	0.00	21.2	17.7	8.8	-4.51	31.5	19	19	17.7	21.2	21.2	22.3	4278	0	0.00
Rb	0.00005	mg kg^{-1}	4278	0	0.00	12.9	7.51	9.81	-14.4	26	13.2	13.2	7.51	12.9	12.9	21	4278	0	0.00
Re	0.000002	mg kg^{-1}	4278	102	2.38	0.00148	0.000561	0.000341	-0.00056	0.00115	0.000466	0.000466	0.000486	0.00145	0.00145	0.00146	4278	102	2.38
S	0.0001	%	4278	0	0.00	0.113	0.059	0.0244	-0.105	0.159	0.0389	0.0389	0.059	0.113	0.113	0.102	4278	0	0.00
Sb	0.00005	mg kg^{-1}	4278	0	0.00	0.458	0.349	0.247	-0.313	0.756	0.37	0.37	0.349	0.458	0.458	0.47	4278	0	0.00
Sc	0.00005	mg kg^{-1}	4278	0	0.00	2.95	1.86	2.26	-3.26	5.83	2.94	2.95	1.86	2.95	2.95	4.09	4278	0	0.00
Se	0.00003	mg kg^{-1}	4278	0	0.00	1.18	0.833	0.377	-0.402	1.45	0.729	0.729	0.833	1.18	1.18	1.07	4278	0	0.00
Sn	0.0001	mg kg^{-1}	4278	0	0.00	0.625	0.509	0.256	-0.128	0.904	0.565	0.565	0.509	0.625	0.625	0.644	4278	0	0.00
Sr	0.0001	mg kg^{-1}	4278	0	0.00	45.2	28.6	15.3	-26.3	59	24.2	24.2	28.6	45.2	45.2	41.4	4278	0	0.00
Ta	0.00005	mg kg^{-1}	4278	1560	36.47	0.00117	0.000585	0.000519	-0.0011	0.00165	0.00024	0.00024	0.000144	0.000766	0.000765	0.00147	4278	1560	36.47
Te	0.00003	mg kg^{-1}	4278	2	0.05	0.0173	0.0135	0.0106	-0.0125	0.0303	0.0156	0.0156	0.0135	0.0173	0.0173	0.0183	4278	2	0.05

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
Th	0.00002	mg kg^{-1}	4278	7	0.16	1.45	0.719	0.983	-1.27	2.71	1.41	1.41	0.706	1.44	1.44	4.33	4278	7	0.16
Ti	0.00001	%	4278	2	0.05	0.00719	0.0052	0.00307	-0.0035	0.0105	0.00519	0.00519	0.00518	0.00718	0.00718	0.00709	4278	2	0.05
Tl	0.00001	mg kg^{-1}	4278	0	0.00	0.208	0.137	0.133	-0.164	0.38	0.205	0.205	0.137	0.208	0.208	0.273	4278	0	0.00
U	0.00005	mg kg^{-1}	4278	0	0.00	1.56	0.928	0.456	-0.199	1.72	1.02	1.03	0.928	1.56	1.56	1.55	4278	0	0.00
V	0.001	mg kg^{-1}	4278	0	0.00	29.3	19.8	17.3	-18.5	52.4	29.8	29.8	19.8	29.3	29.3	38.4	4278	0	0.00
W	0.00001	mg kg^{-1}	4278	3	0.07	0.0655	0.0456	0.0233	-0.0131	0.083	0.0493	0.0493	0.0453	0.0654	0.0654	0.0604	4278	3	0.07
Y	0.00003	mg kg^{-1}	4278	0	0.00	14.7	8.23	12.2	-19.5	29.9	13.6	13.6	8.23	14.7	14.7	22.4	4278	0	0.00
Zn	0.001	mg kg^{-1}	4278	0	0.00	69	52	46.1	-60.1	126	64.1	64.1	52	69	69	73.8	4278	0	0.00
Zr	0.0001	mg kg^{-1}	4278	3	0.07	2.39	1.48	1.67	-2.49	4.66	2.5	2.5	1.47	2.39	2.39	3.56	4278	3	0.07
Au	0.000002	mg kg^{-1}	4278	756	17.67	0.00161	0.000461	0.000384	-0.000569	0.00112	0.000399	0.0004	0.000144	0.00133	0.00134	0.00563	4278	756	17.67
Pd	0.00001	mg kg^{-1}	4278	2708	63.30	0.000704	0.000431	0.000489	-0.000854	0.0013	NA	0.00006	0.00000319	0.000271	0.000282	0.0591	4278	2708	63.30
Pt	0.00002	mg kg^{-1}	4278	2058	48.11	0.0194	0.00173	0.00132	-0.0113	0.012	0.00007	0.0000971	0.000038	0.0101	0.0101	1.79	4278	2058	48.11

Table 25 Univariate summary statistics including best fits based on proportions of ICPar data below the ME-MS41L LLD. All to 3 significant figures.

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
Ag	0.001	mg kg^{-1}	4278	0	0.00	0.0957	0.0703	0.0416	-0.0268	0.141	0.0859	0.0859	0.0703	0.0957	0.0957	0.0955	0.52	0.52	0.0878
Al	0.01	%	4278	2	0.05	1.19	0.789	0.775	-0.935	2.23	1.22	1.22	0.787	1.19	1.19	1.61	0.743	0.743	2.86
As	0.01	mg kg^{-1}	4278	0	0.00	8.73	6.26	4.83	-5.23	14.5	7.82	7.83	6.26	8.73	8.73	9.77	7.29	7.29	11.7
B	10	mg kg^{-1}	4278	3922	91.68	12.6	12.3	1.78	6.71	14.9	NA	5.26	0.163	10.3	5.85	2.63	1.05	2.81	42.2
Ba	0.5	mg kg^{-1}	4278	0	0.00	83.1	53.1	47.3	-70.1	134	60	60	53.1	83.1	83.1	85.8	136	136	109

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
Be	0.01	mg kg^{-1}	4278	32	0.75	0.685	0.452	0.473	-0.62	1.29	0.677	0.677	0.437	0.68	0.68	0.941	0.512	0.512	1.79
Bi	0.0005	mg kg^{-1}	4278	0	0.00	0.11	0.0874	0.0459	-0.026	0.16	0.0969	0.0969	0.0874	0.11	0.11	0.112	0.174	0.174	0.0907
Ca	0.01	%	4278	1	0.02	1.77	0.567	0.335	-1.99	2.4	0.362	0.362	0.566	1.77	1.77	1.59	3.5	3.5	4.17
Cd	0.001	mg kg^{-1}	4278	0	0.00	0.936	0.592	0.724	-1.21	1.79	0.75	0.75	0.592	0.936	0.936	1.04	0.903	0.903	1.52
Ce	0.003	mg kg^{-1}	4278	0	0.00	28.7	18.6	15.4	-14.2	50	30.2	30.2	18.6	28.7	28.7	42.4	17.7	17.7	86.5
Co	0.001	mg kg^{-1}	4278	0	0.00	7.66	4.6	5.72	-8.39	15.2	7.68	7.68	4.6	7.66	7.66	11.3	5.26	5.26	25.4
Cr	0.01	mg kg^{-1}	4278	0	0.00	21.3	13.7	13.4	-16.3	39	21.6	21.6	13.7	21.3	21.3	29.6	14.3	14.3	56.7
Cs	0.005	mg kg^{-1}	4278	6	0.14	0.757	0.466	0.428	-0.468	1.26	0.69	0.69	0.462	0.756	0.756	1.06	0.786	0.786	2.21
Cu	0.01	mg kg^{-1}	4278	0	0.00	16.4	12.1	9.97	-11.7	28.5	15.2	15.2	12.1	16.4	16.4	17.9	11.9	11.9	19.5
Fe	0.001	%	4278	0	0.00	1.66	1.13	1.05	-1.22	3.04	1.63	1.63	1.13	1.66	1.66	2.15	1.08	1.08	3.48
Ga	0.004	mg kg^{-1}	4278	0	0.00	3.47	2.34	2.18	-2.57	6.31	3.37	3.38	2.34	3.47	3.47	4.44	2.26	2.26	7.18
Ge	0.005	mg kg^{-1}	4278	94	2.20	0.0507	0.0435	0.024	-0.0158	0.0827	0.0503	0.0503	0.0408	0.0497	0.0498	0.054	0.0252	0.025	0.0469
Hf	0.002	mg kg^{-1}	4278	227	5.31	0.0716	0.0505	0.0454	-0.0538	0.132	0.0694	0.0694	0.0404	0.068	0.0682	0.108	0.0456	0.0453	0.267
Hg	0.004	mg kg^{-1}	4278	0	0.00	0.0908	0.0814	0.0297	0.00215	0.126	0.0818	0.0818	0.0814	0.0908	0.0908	0.0895	0.108	0.108	0.0409
In	0.005	mg kg^{-1}	4278	456	10.66	0.0208	0.0187	0.00936	-0.00502	0.033	0.0187	0.0187	0.0146	0.0191	0.0193	0.0215	0.00997	0.00973	0.0233
K	0.01	%	4278	130	3.04	0.167	0.124	0.114	-0.145	0.319	0.157	0.158	0.113	0.163	0.163	0.197	0.104	0.104	0.282
La	0.002	mg kg^{-1}	4278	0	0.00	14.7	9.52	8.09	-8.05	25.8	15.3	15.3	9.52	14.7	14.7	21.7	8.88	8.88	44.5
Li	0.1	mg kg^{-1}	4278	343	8.02	12.6	8.18	7.19	-7.61	21.6	11	11	5.19	11.6	11.7	36.5	9.59	9.52	253
Mg	0.01	%	4278	0	0.00	0.237	0.177	0.114	-0.15	0.371	0.172	0.172	0.177	0.237	0.237	0.233	0.244	0.244	0.2
Mn	0.1	mg kg^{-1}	4278	2	0.05	694	316	643	-1160	1460	564	564	315	694	694	1230	957	957	4650
Mo	0.01	mg kg^{-1}	4278	0	0.00	1.31	0.881	0.708	-0.963	2.01	0.957	0.957	0.881	1.31	1.31	1.3	2.15	2.15	1.4
Na	0.001	%	4278	0	0.00	0.0304	0.0278	0.0105	-0.00112	0.0436	0.0272	0.0272	0.0278	0.0304	0.0304	0.0301	0.019	0.019	0.0126
Nb	0.002	mg kg^{-1}	4278	0	0.00	0.358	0.247	0.162	-0.15	0.54	0.284	0.284	0.247	0.358	0.358	0.391	0.355	0.355	0.479
Ni	0.04	mg kg^{-1}	4278	0	0.00	28.9	17.5	21.8	-31.3	57	28.5	28.5	17.5	28.9	28.9	41.2	20.3	20.3	88

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
P	0.001	mg kg^{-1}	4278	0	0.00	512	445	228	-142	792	461	461	445	512	512	516	286	286	304
Pb	0.005	mg kg^{-1}	4278	0	0.00	21.2	17.7	8.8	-4.51	31.5	19	19	17.7	21.2	21.2	22.3	14.8	14.8	17
Rb	0.005	mg kg^{-1}	4278	0	0.00	12.9	7.51	9.81	-14.4	26	13.2	13.2	7.51	12.9	12.9	21	8.66	8.66	55.1
Re	0.0002	mg kg^{-1}	4278	611	14.28	0.00167	0.000712	0.000328	-0.000547	0.00127	0.000466	0.000466	0.000496	0.00146	0.00144	0.00121	0.00414	0.00415	0.00268
S	0.01	%	4278	2	0.05	0.113	0.0591	0.0243	-0.106	0.159	0.0389	0.0389	0.059	0.113	0.113	0.102	0.153	0.153	0.145
Sb	0.005	mg kg^{-1}	4278	3	0.07	0.458	0.35	0.247	-0.313	0.756	0.37	0.37	0.349	0.458	0.458	0.47	0.383	0.383	0.424
Sc	0.005	mg kg^{-1}	4278	0	0.00	2.95	1.86	2.26	-3.26	5.83	2.94	2.95	1.86	2.95	2.95	4.09	2	2	8.04
Se	0.003	mg kg^{-1}	4278	0	0.00	1.18	0.833	0.377	-0.402	1.45	0.729	0.729	0.833	1.18	1.18	1.07	1.92	1.92	0.865
Sn	0.01	mg kg^{-1}	4278	6	0.14	0.626	0.513	0.255	-0.127	0.904	0.565	0.565	0.509	0.625	0.625	0.645	0.549	0.549	0.502
Sr	0.01	mg kg^{-1}	4278	0	0.00	45.2	28.6	15.3	-26.3	59	24.2	24.2	28.6	45.2	45.2	41.4	64.8	64.8	43.5
Ta	0.005	mg kg^{-1}	4278	4177	97.64	0.00998	0.00841	0.00258	-0.00107	0.0128	NA	0.000235	4.86E-09	0.00514	0.000692	0.654	0.00164	0.00214	88000000
Te	0.003	mg kg^{-1}	4278	193	4.51	0.018	0.0148	0.0101	-0.0105	0.0303	0.0156	0.0156	0.0133	0.0173	0.0173	0.0184	0.0117	0.0116	0.0175
Th	0.002	mg kg^{-1}	4278	64	1.50	1.47	0.785	0.964	-1.2	2.71	1.41	1.41	0.706	1.44	1.45	4.26	1.1	1.1	25.4
Ti	0.001	%	4278	97	2.27	0.00733	0.00543	0.00301	-0.00341	0.0107	0.00519	0.00519	0.00515	0.00719	0.00718	0.00714	0.00851	0.00851	0.00685
Tl	0.001	mg kg^{-1}	4278	2	0.05	0.208	0.137	0.133	-0.164	0.38	0.205	0.205	0.137	0.208	0.208	0.273	0.157	0.157	0.47
U	0.005	mg kg^{-1}	4278	0	0.00	1.56	0.928	0.456	-0.199	1.72	1.02	1.03	0.928	1.56	1.56	1.55	3.99	3.99	2.09
V	0.1	mg kg^{-1}	4278	0	0.00	29.3	19.8	17.3	-18.5	52.4	29.8	29.8	19.8	29.3	29.3	38.4	18.2	18.2	63.7
W	0.001	mg kg^{-1}	4278	9	0.21	0.0655	0.0459	0.0232	-0.013	0.083	0.0493	0.0493	0.0455	0.0654	0.0654	0.0594	0.378	0.378	0.0499
Y	0.003	mg kg^{-1}	4278	0	0.00	14.7	8.23	12.2	-19.5	29.9	13.6	13.6	8.23	14.7	14.7	22.4	11.7	11.7	56.7
Zn	0.1	mg kg^{-1}	4278	0	0.00	69	52	46.1	-60.1	126	64.1	64.1	52	69	69	73.8	66.3	66.3	74.4
Zr	0.01	mg kg^{-1}	4278	3	0.07	2.39	1.48	1.67	-2.49	4.66	2.5	2.5	1.47	2.39	2.39	3.49	1.58	1.58	7.48
Au	0.0002	mg kg^{-1}	4278	1352	31.60	0.00191	0.000632	0.000351	-0.000424	0.00119	0.000399	0.0004	0.000305	0.00137	0.00135	0.000719	0.036	0.036	0.00153
Pd	0.001	mg kg^{-1}	4278	3918	91.58	0.00172	0.00161	0.000489	-0.00002	0.00244	NA	0.000318	0.0000146	0.00108	0.000465	0.000465	0.000286	0.000487	0.0148
Pt	0.002	mg kg^{-1}	4278	3392	79.29	0.0478	0.0156	0.0165	-0.0426	0.0528	NA	0.000306	0.0000238	0.0115	0.0103	1.02	0.066	0.0661	43500

Regional-scale mapping and interpolation of sample data recommendations

All geochemical data have been assessed to see if the data are suitable to map, primarily as single-element interpolated or point geochemical maps. Tellus produces a series of geochemical maps available to download from www.gsi.ie/tellus and/or viewed on the GSI web map viewer. They will be added at a later date as GIS layers and layer packages to the data package. Below are GSI-recommended parameters used to create provisional interpolated maps.

Each single variable map is derived from a naïve interpolation method, Inverse Distance Weighting (IDW). The interpolation predicts new values as an inverse distance weighted average of surrounding observations, *i.e.* a predicted value will be more similar to nearby observations than to distant observations and will not extrapolate beyond the chosen search radius range of observed values. The interpolation makes no assumptions about the vector of relationships between data points. The interpolated mapping parameters are in Table 26. The IDW function determines the value of a raster surface (grid cell) using a linear weighted combination set of sample points (Childs, 2004). The weighting is based on the distance of an input (sample data) point from the output cell location, therefore the greater the distance the less influence the cell has on the output value.

Table 26 Geochemical map series interpolation mapping parameters.

Interpolation type	Search radius (m)	Fixed/variable	Power distance exponent	Output cell size (m)	Best viewed at maximum scale
Inverse distance weighted (IDW)	2000	Fixed	2	250	1:200,000

The inverse distance weighted (IDW) interpolation was performed on all geochemical data (at a regional scale). These parameters were selected to account for the typical inter-sample distances across the whole survey area. Interpolated mapped images have been generated for the dataset on a *regional scale*, therefore they are not suitable to evaluate the predicted distribution at a localized scale. It is acknowledged that alternative and geostatistical interpolation techniques might be equally or more useful depending on the application and scale of use of these data.

Use of data beyond reporting limits in interpolation mapping

The LLDs are theoretical values for the concentration equivalent to three standard deviations above the background count rate for the analyte in a 'pure' matrix. Individual results are not reliable below the quoted lower limits but reliable estimates of average or typical values over an area may be obtained at lower levels of concentration; meaningful patterns may thus be recognized for some elements at levels lower than the reported LLD/LRL. For geochemical mapping, the optimum is to use uncensored data that are not truncated to the LLD in the mapping process to present the data in such a way that the lower concentrations are not unduly emphasized numerically and to describe below-LLD values as such in the classification. Reliability also decreases above the URL but results do, nevertheless, give an indication of the concentration in the sample. Results outside the limits were therefore reported and entered into the database.

Elements for which data conditioning/levelling are required

All data can be interpolated to form a geochemical map series but not all data are suitable for presentation in this way. The following analytes are not suitable for regional interpolated mapping, either due to a very

high proportion of data below the certified ME-MS41L method LLD (rendering this presentation meaningless) and/or due to the apparent boundary affects between field or analytical phases. The following analytes can be represented as interpolated maps by using the MS41L-BLD method data but the user is cautioned that these data are obtained through a non accredited method.

Table 27 Deeper topsoil analytes where mapping is not recommended and/or conditioning is required in order to seamlessly merge discrete dataset.

Variable	Method	Issue	Recommendation
Ta	ICP-MS (ME-MS41L)	<LLD to 99th percentile.	Better presented as proportional colour/symbol point map.
Au	ICP-MS (MS41L-BLD)	<LLD to 97.5th percentile.	Perhaps better presented as proportional colour/symbol point map.
B	ICP-MS (ME-MS41L)	<LLD to 95th percentile.	Perhaps better presented as proportional colour/symbol point map.
Pd	ICP-MS (ME-MS41L)	<LLD to 95th percentile.	Perhaps better presented as proportional colour/symbol point map.
Pt	ICP-MS (ME-MS41L)	<LLD to 80th percentile.	Perhaps better presented as proportional colour/symbol point map.

Abbreviations and glossary

Abbreviation		Description
CRM	Certified reference material	Interchangeable with international reference standard and primary reference materials.
DUP	Duplicate (field duplicate)	Sample code in used in geochemistry field database.
GIS	Geographical Information System	Digital mapping software environment.
GSI	Geological Survey Ireland	Irish national geological agency. The contracting and project leading authority.
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer	Analytical instrument which utilizes inductively generated plasma flame which ionizes analytes which are then separated according to their mass and quantified by mass spectrometer
IDW	Inverse distance weighted	Spatial data interpolation approach.
IQR	Interquartile range	Statistical dispersion of distribution between the 25^{th} and 75^{th} percentile. Represents 50% of the data set.
K-M	Kaplan-Meier	Non-parametric method. Method of calculating summary statistics with a moderate proportion of data below the LLD.
LIMS	Laboratory Information Management System	An IT solution for supporting operations of modern analytical laboratory.
LLD	Lower limit of detection	Concentration at which the analyst's instrument gives a significantly different signal to that of a "background" or blank signal. Different analytical methods will define it in different ways and it can be quite arbitrary. A value that is above the lower limit of detection can be regarded as quantifiable and reproducible. It is important that a value is quotable for each laboratory batch of samples analysed.
LOI	Loss-on-ignition	Analytical method measuring content of volatile analytes
LRL	Lower reporting limit	Concentration at which analyte is exceeding lower calibration range of an analytical run or instrument.
MAD	Median absolute deviation	Parametric method. Method of calculating summary statistics with a moderate proportion of data below the LLD.
MLE	Maximum likelihood estimation	Parametric method. Method fits a distribution curve with non-detects included and represented proportionally in the observation population.
OES	Optical Emission Spectrometer	Analytical instrument/detector
OSI	Ordnance Survey of Ireland	Irish topographic mapping agency and map publisher (paper and digital).
QA	Quality assurance	Describes the overall set of procedures in assuring the quality of data. A system of protocols, checks, audits, and corrective actions to ensure that all analytical results prepared for the geochemistry database are of high and consistent quality.

Abbreviation		Description
QC	Quality control	Describes the overall set of procedures in controlling the quality of data. A collection of documented procedures applied to the raw data to continuously assess whether the laboratory is producing results of acceptable quality as assessed by the inclusion of control samples in all procedures from sampling through to analysis.
QCS	Quality control sample(s)	Samples that do not represent sites but are used in the assessment of analytical data to monitor error, precision and accuracy. Interchangeable with control sample.
REP	Replicate sample	Also known as analytical duplicate, also known as a subsample.
RM	Reference material	Used as an umbrella for either CRM and/or SRM.
RNL	Random number list or checklist	Used to assign sample site numbers in the field.
ROS	Regression on Order Statistics	Statistical transformation and modelling of data utilised with data sets containing non-detects, zero, negative and left censored data. Method of calculating summary statistics with a high proportion of data below the LLD.
SRM	Secondary reference material	A reference material that is not internationally certified (and therefore less expensive to use), it is submitted blind to the analyst and is more likely to have a matrix/mineralogical composition similar to the routine samples being analysed. In other contexts, SRM is an abbreviation of Standard Reference Material, a more generic term for reference samples.
SS	Subsample	Sample code in used in geochemistry field database. Code used to denote a replicate sample.
STD	Standard or control sample (generic)	Sample code in used in geochemistry field database. Used to describe compilation of RMs data extracted from the database.
URL	Upper reporting limit	Concentration at which analyte is exceeding upper calibration range of an analytical run or instrument.

Terminology	Description
Accepted value	It is never possible to determine the exact concentration (true value) of an element in a sample due to limitations of the analytical method. The result determined by one or more analyses is the measured value. After repeated analyses an accepted value can be computed and the sample can be certified as having that element concentration. Different analytical methodologies will have differing accepted values so the accepted value should always be quoted in the context of the analytical method used.
Accuracy	Accuracy measures how close to a true or accepted value a measurement lies. This can be seen graphically on a Shewhart plot.
ANOVA Analysis of variance	Statistical test. Analysis of Variance (ANOVA) is a statistical procedure dependent on the fact that the total variability in a data set can be attributed to various sources. With the use of duplicate and replicate samples random nested analysis of variance can be performed to attribute variability to within a site, "between" and "within" samples.
Bias	Bias is the tendency to favour one analytical value over another. Analytical errors fall into two major categories: bias (systematic error) and variability (random error). Bias causes consistently positive or negative deviation in the results from the accepted value. Repeated measurements of SRMs over time provide evidence of both inter- and intra-batch systematic bias and random variability in the laboratory analytical procedures.
Blind sample	Means of analysing a sample without a distinctive identity. A blind sample is a control sample that has been submitted for analysis presented in such a way that its identity is unknown to the analyst.
Censored	Censored data that are replaced or rounded. When results (usually reported as semi-quantitative values) are replaced by a substitute value, the data can be described as censored data.
Conditioning/conditioned date	Conditioning is the process of making data fit for the purpose for which it is to be used following the QA procedures documented in this report It can represent the accumulation of error checking, verification, quality control, quality assurance and levelling processes. It is important that conditioned data is accompanied by a statement as to what processes it has been subjected to.
Control chart	A control chart is a graphical representation (plot) showing how the value of a sample varies over a period of time in relation to an accepted value or range of values as defined by a control sample. A particular type of control chart showing how a value varies over time within an envelope of mean ± *n* standard deviations is referred to as a Shewhart chart or plot. Both these can also be more generally referred to as a time-series plot.
Drift	Drift is the continuous, incremental change of analytical instrument signal over a period of time relative to the baseline value.
Duplicate sample (or field duplicate sample)	A duplicate sample is collected from the same site as another sample. A control sample that can be used to show the variability in results that can be attributed to the process of sampling by collecting two samples from the same location. A duplicate sample collected in the field is sometimes also referred to as a "field duplicate".
Error	Deviation from what is believed to be correct, right, or true is the error of a measurement, *i.e.* the measured result minus the true value.
Laboratory batch	When samples are submitted for analyses they are grouped together to form a laboratory batch. The number of samples in each batch will vary according to the sample type and analytical method. Each batch is assigned a unique laboratory batch number which must be associated with metadata such as date of analysis, analytical calibration, detection limits, *etc.*.
Levelling	Process to decide how disparate data sets are combined to form a single discrete data set. May require data conditioning/normalisation using RMs which are repeatedly analysed in each laboratory batch.
Levelling factor or conditioning factor	This is a mathematical function that is applied to results in order to combine data sets into a single discrete data set and is determined during the process of data conditioning by normalisation of the results from RMs repeatedly determined in each analytical batch over a period of time.

Terminology	Description
Lower limit of reporting	This is a quantitative value representing the lowest measurement that the analyst is prepared to report to the client.
Matrix matching	An approach in instrumental analysis where calibration and standardization procedures are performed on materials that share or match major chemical and/or physical properties of analysed samples in an attempt to reduce the impact of sample matrix on the determination of desired property.
Measured value	A quantitative result reported by the analyst following analysis of a sample.
Normalisation	The data conditioning process uses the term normalisation in a mathematical sense, *i.e.* "to adjust the representation of a quantity so that this representation lies within a prescribed range, or, any process of rescaling a quantity so that a given integral or other functional of the quantity takes on a pre-determined value" rather than in the statistical sense, where it denotes a transformation of a data set so that it has a mean of zero and a variance of one. Normalisation is a process to determine levelling factors carried out using control samples.
Precision	Precision is a measurement of how closely the analytical results can be reproduced. It should not be confused with the term accuracy. Results can have a good precision (*i.e.* consistently fall at or near a specified value), yet the mean of these results may be a long way off the accepted value.
Raw data	The results as received from the analyst.
Replicate sample (or analytical duplicate)	This is a control sample created in the laboratory by dividing a sample into two identical parts according to a well-defined protocol. It is used to help define laboratory error. Also termed a sub-sample when derived in the field.
Sensitivity	Analytical sensitivity is the lowest concentration that can be distinguished from background noise or more correctly called the assay's detection limit. When a technique is described as being sensitive the implication is it has a low limit of detection.
Shewhart chart or x-chart	A process control tool used to determine if a process is in a state of control *i.e.* showing performance deviations. A process is deemed to be in control over a period of time if measured data do not exceed specified control limits or if frequency of exceedances does not exceed specified limits. This a control chart or time series plot with defined quality limits named after the person who first documented their use (Shewhart, 1931).
Shift	Shift is a significant sudden change in a measured value compared with the previous measurement of the same measurand. This can be seen graphically on a time-series or Shewhart plot and is usually the consequence of an instrument recalibration. It differs from drift in that the change in measurement is large and sudden.
Time-series plot	When a measurement is repeatedly determined over a time period, a plot of quantity against time graphically shows how the result is varying over time. A Shewhart plot is an example of a time-series plot.
Variability	Variability is a random error that affects the ability to reproduce results (see bias and precision).
Validation	Process of establishing a documentary evidence demonstrating that process or activity is reproducible and compliant at all stages
Verification	Verification is the first data conditioning procedure that checks that the laboratory has analysed and reported all the samples submitted to the specifications of the analytical request form/as detailed in the contract.

Concentration units		Description
%	Percentage	
σ	Sigma	Standard deviation(s)
weight oxide %	Weight oxide percent equivalent	Normally of the element oxide, for major element determinands.
mg kg^{-1}	milligramme per kilogramme	Equivalent to part(s) per million (ppm).
µg kg^{-1}	microgramme per kilogramme	Equivalent to part(s) per billion (ppb).

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Appendices

The following appendices present the data analysis charts for quality control samples (QCS) and univariate exploratory data analysis for all sample data.

These are published as part of the quality assurance procedures of the Tellus geochemical survey in Ireland, providing transparency and context for all data and products accompanied by this report.

Please contact tellus@gsi.ie for further information regarding data quality.

A. RMs data QCS charts

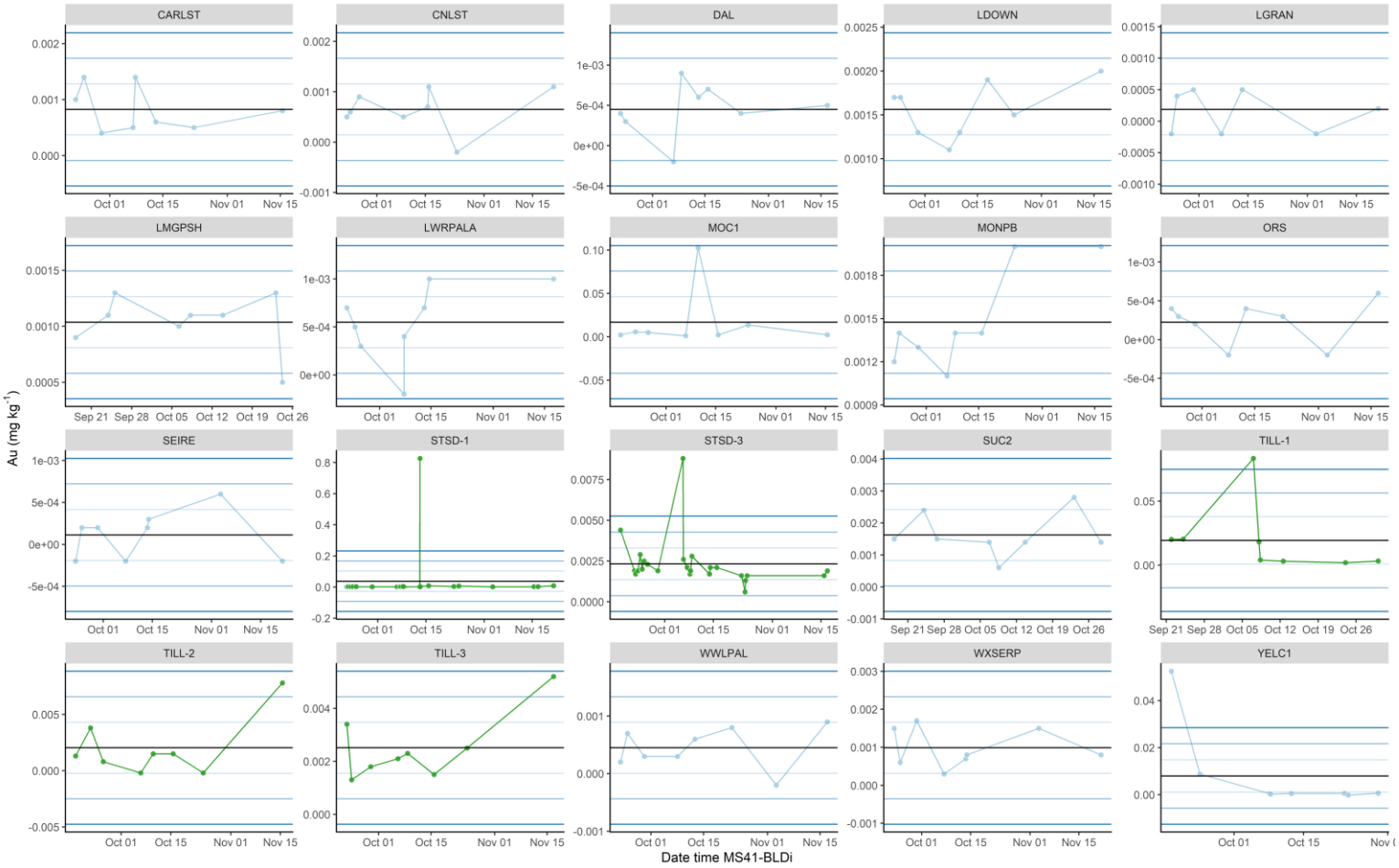
In this appendix all of the reference materials data are presented in two ways for each analyte (in the same order as data are reported by instrument and distributed):

- The first chart is of analyte concentration (y axis) against the sample ID (x axis), faceted by the reference material (name in the grey banner at the top). With the assumption that all samples are run in the numerical order as required and directed, each chart displays the repeatability of the reference material across the laboratory analytical batches. The dashed horizontal line denotes the reference value (certified, information or provisional).
- The second is a control chart of analyte concentration (y axis) against the measurement date and time (x axis) for each reference material. Each control chart displays the process mean of the data (central horizontal black line) and a series of control limits at 1, 2 and 3 times the process mean ± the sequential deviation (shown as light, medium and dark blue horizontal lines respectively. Each date point is connected by a line to show the sequence of analyses. The dashed horizontal line denotes the reference value (certified, information or provisional).

All "<LLD" values have been replaced with "-LLD" to make them stand out. These data are not modified or censored. Concentration units are shown in parentheses. For reference, the interquartile range (IQR) of the sample's sites data is displayed at the bottom-right of each plot (to 3 significant figures). Thus, it can be seen where the QCS data are validating the sample data in the appropriate concentration range for this media.

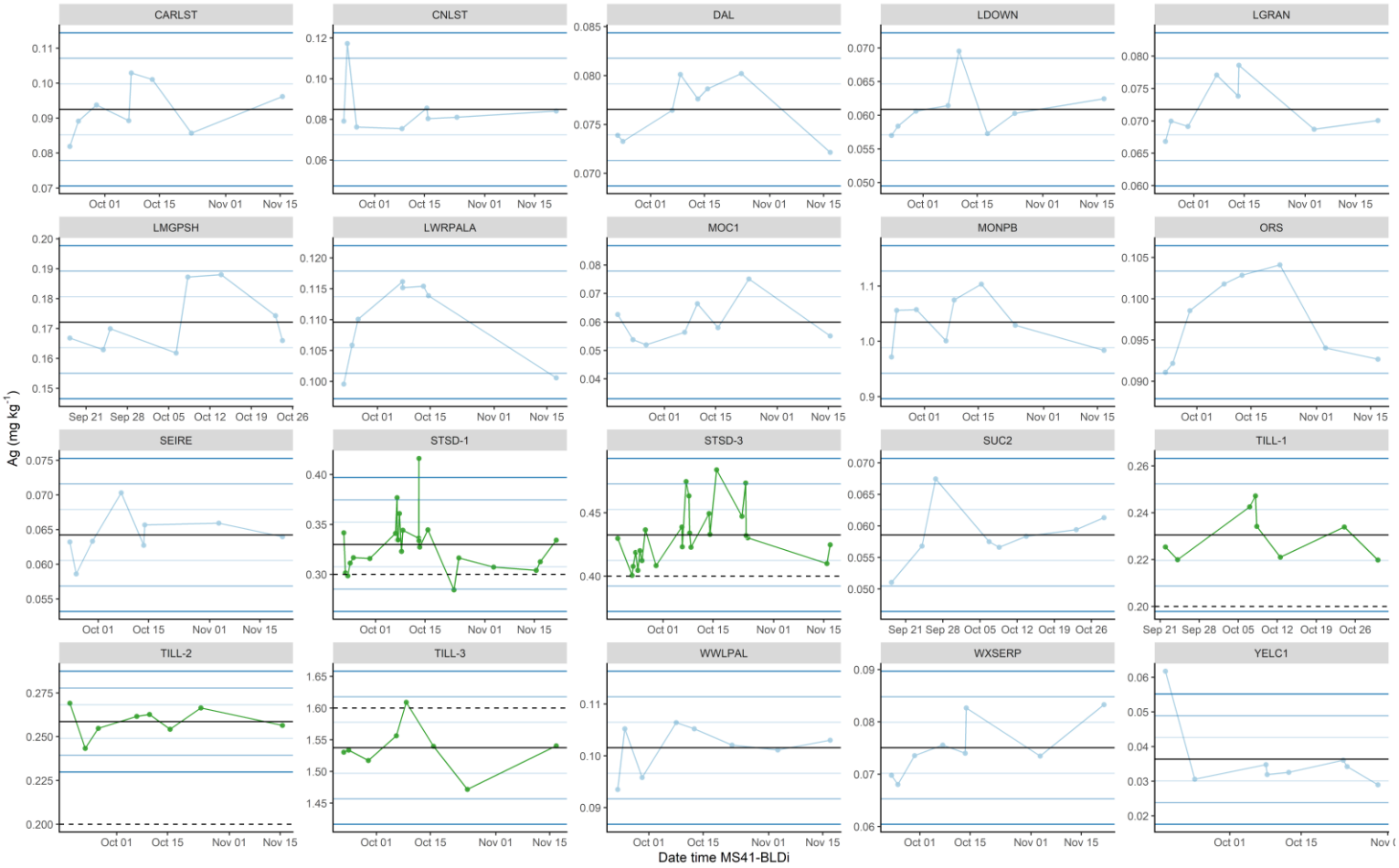
ICP_{ar} RMs data by ALS Minerals Ltd method code MS41L-BLD

Gold (Au) MS41L-BLD



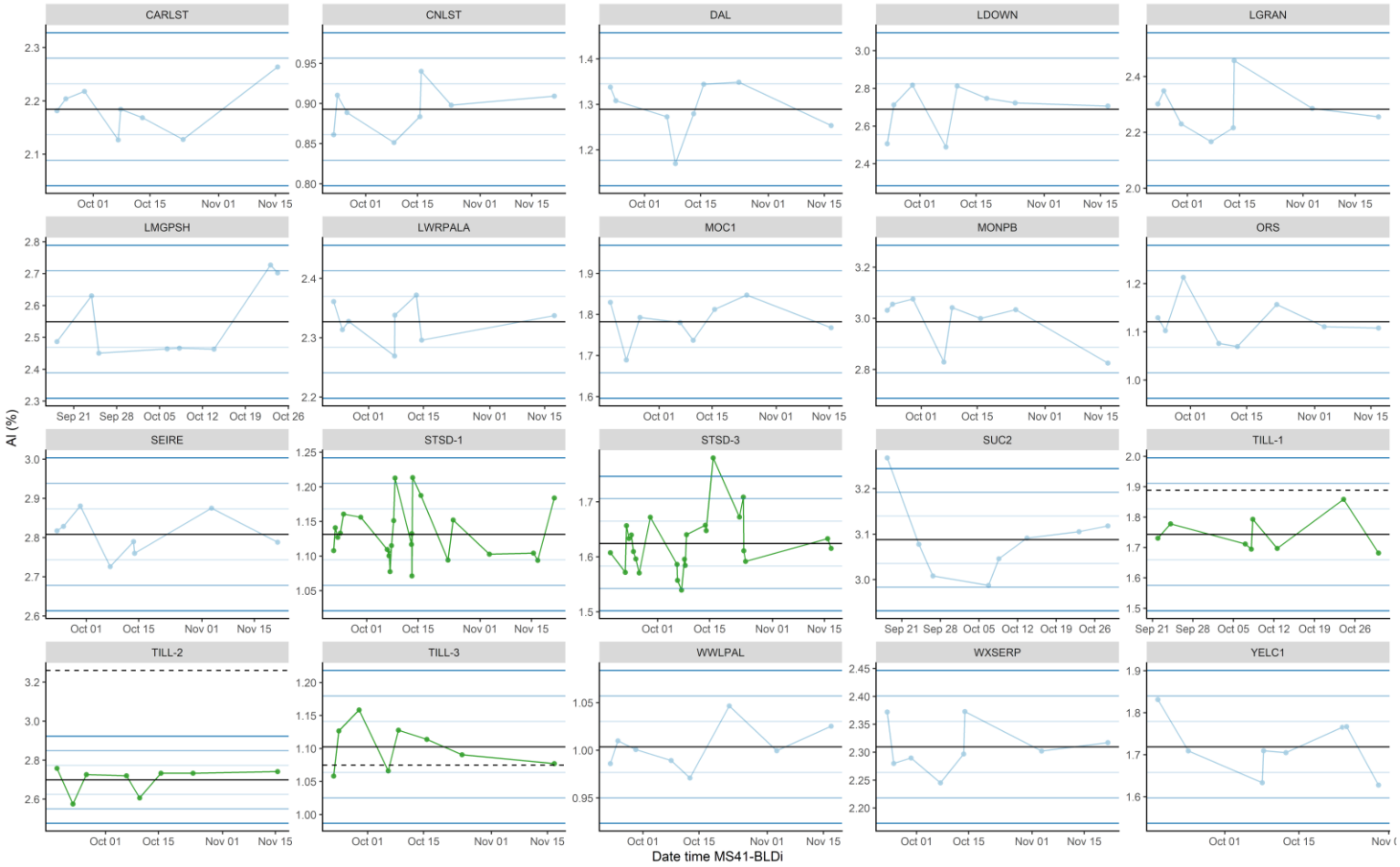
Gold (Au) sample data IQR: 0.000125–0.000738 mg kg^{-1}

Silver (Ag) MS41L-BLD



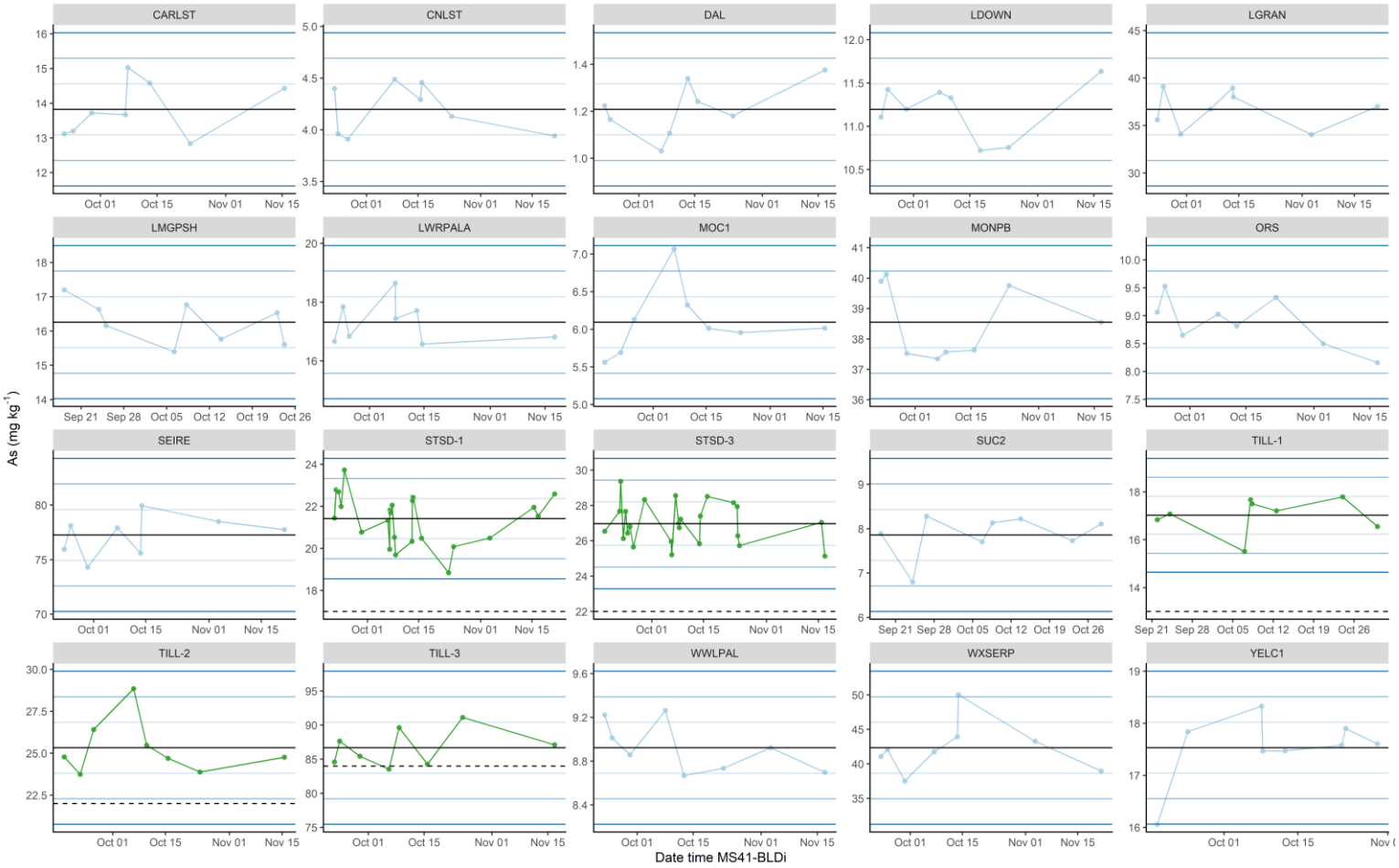
Silver (Ag) sample data IQR: 0.0573–0.1130 mg kg^{-1}

Aluminium (Al) MS41L-BLD



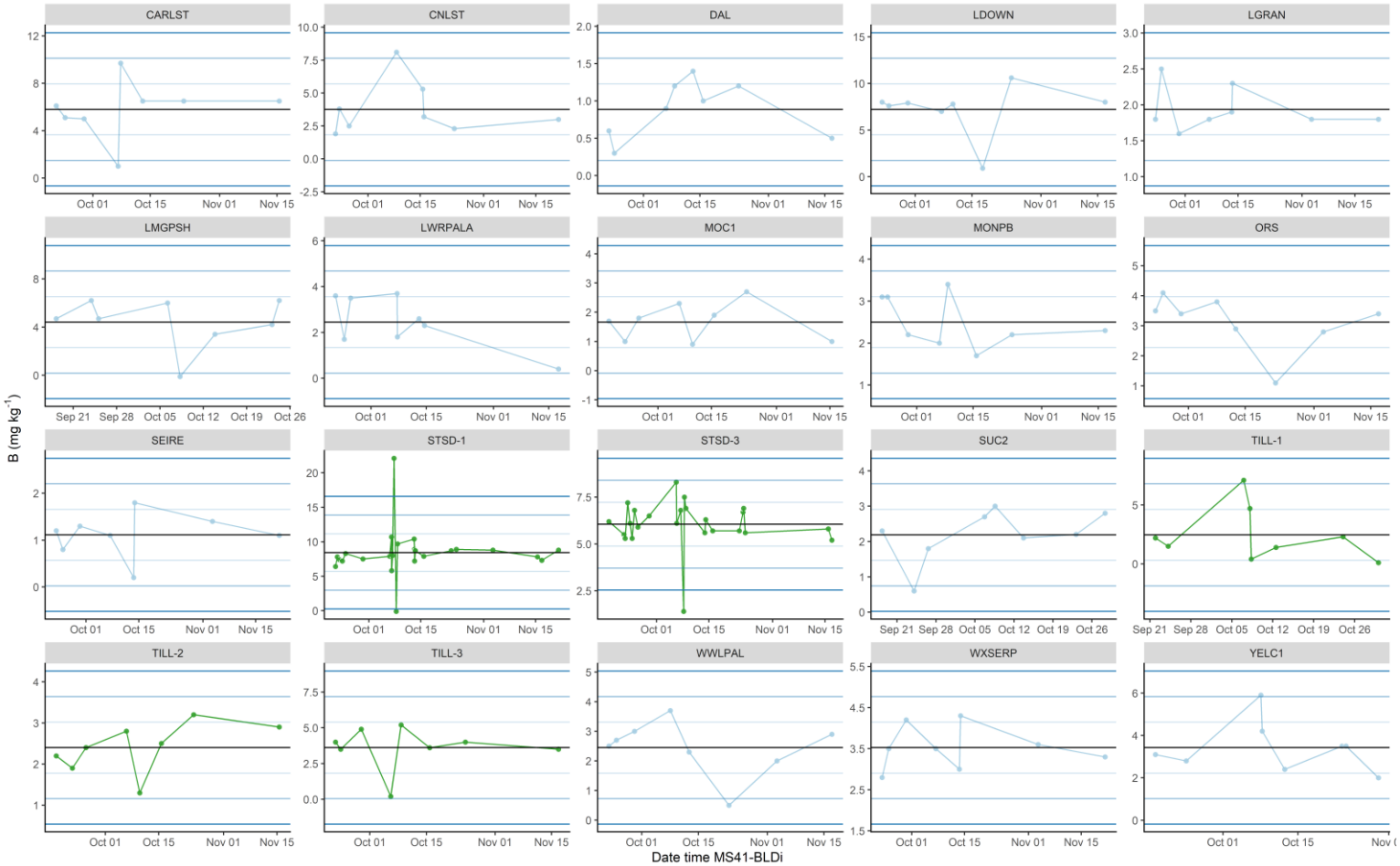
Aluminium (Al) sample data IQR: 0.643–1.700 %

Arsenic (As) MS41L-BLD



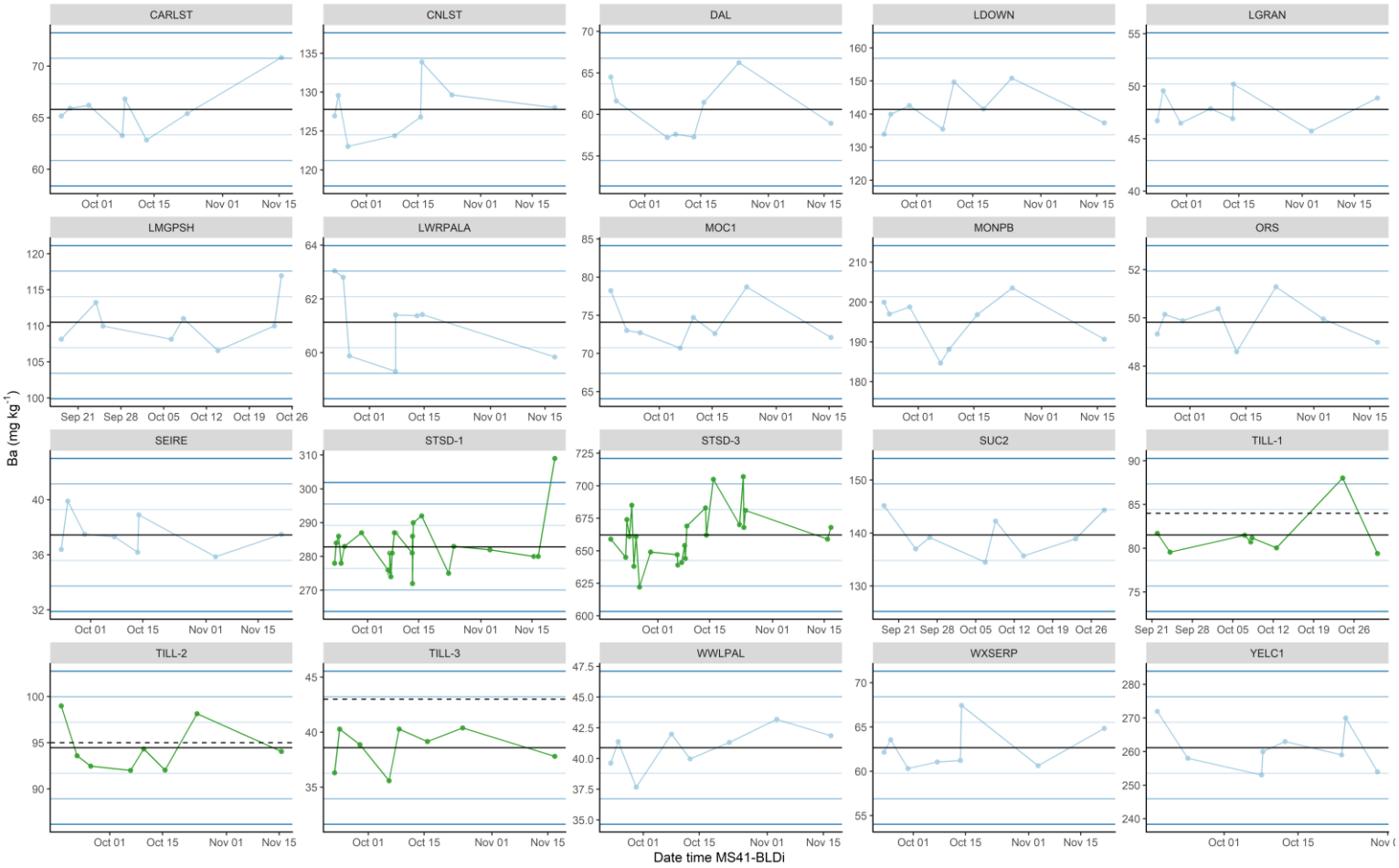
Arsenic (As) sample data IQR: 4.62–11.2 mg kg^{-1}

Boron (B) MS41L-BLD



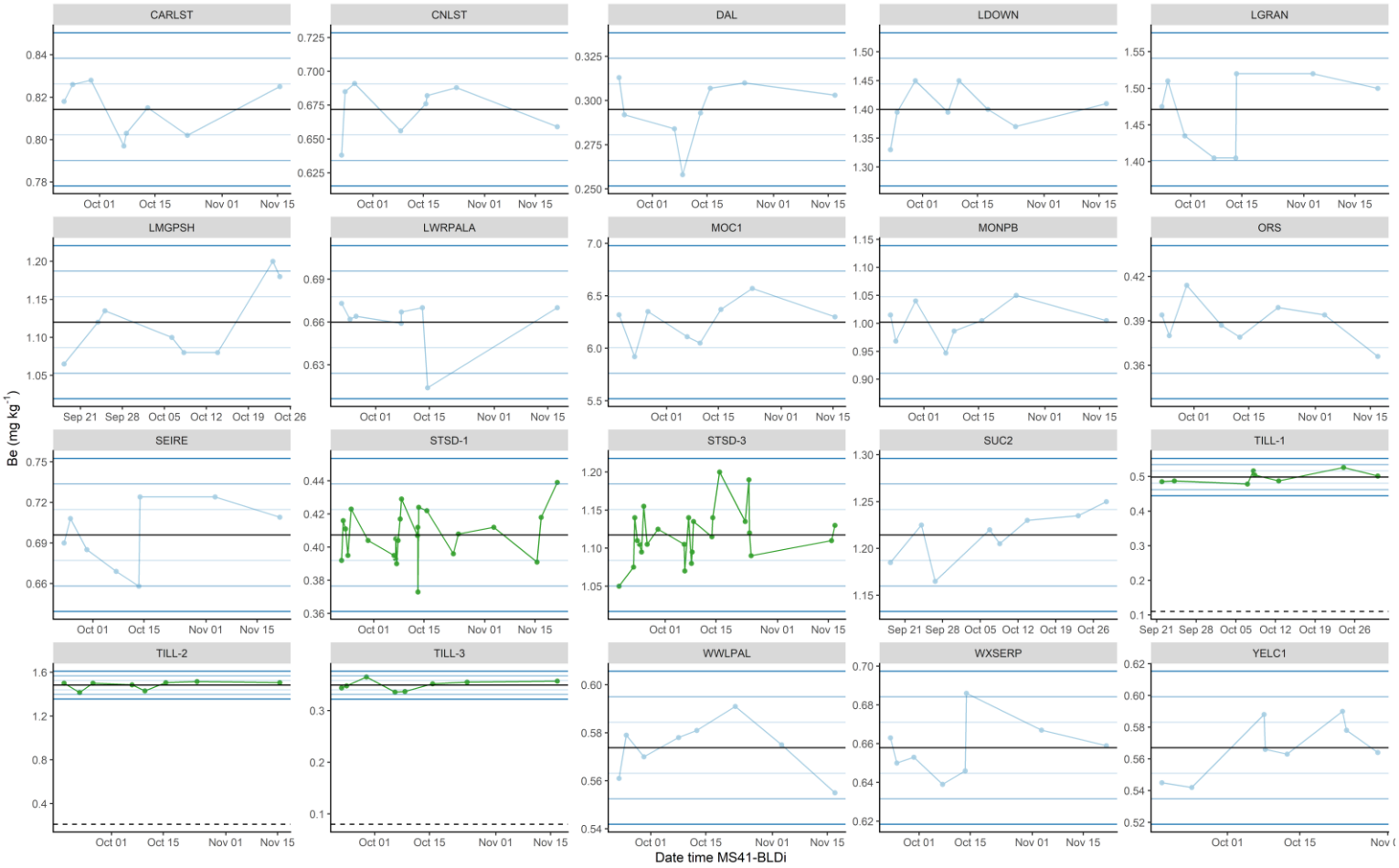
Boron (B) sample data IQR: 3.5-7.7 mg kg^{-1}

Barium (Ba) MS41L-BLD



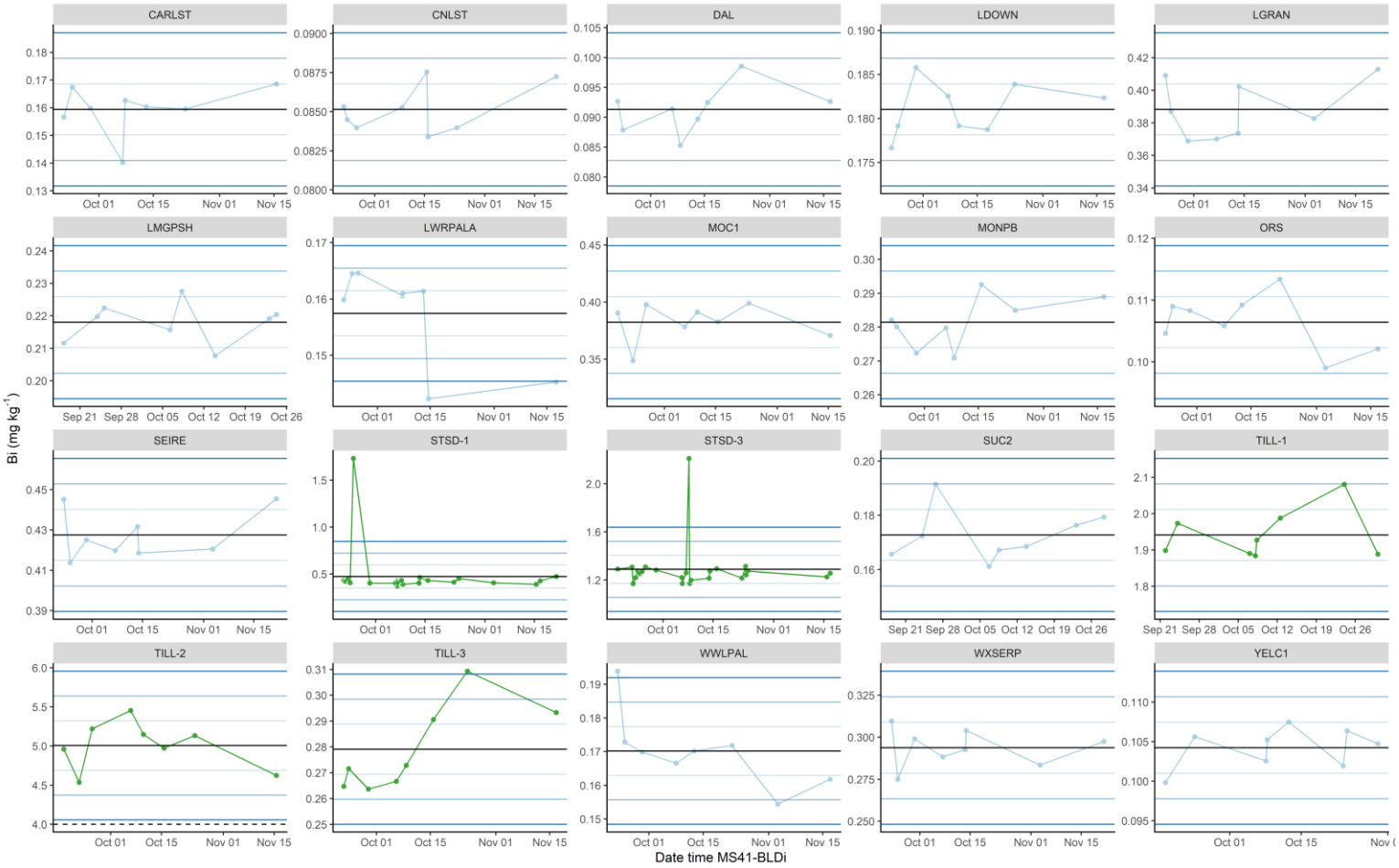
Barium (Ba) sample data IQR: 31.9–100.0 mg kg-1

Beryllium (Be) MS41L-BLD



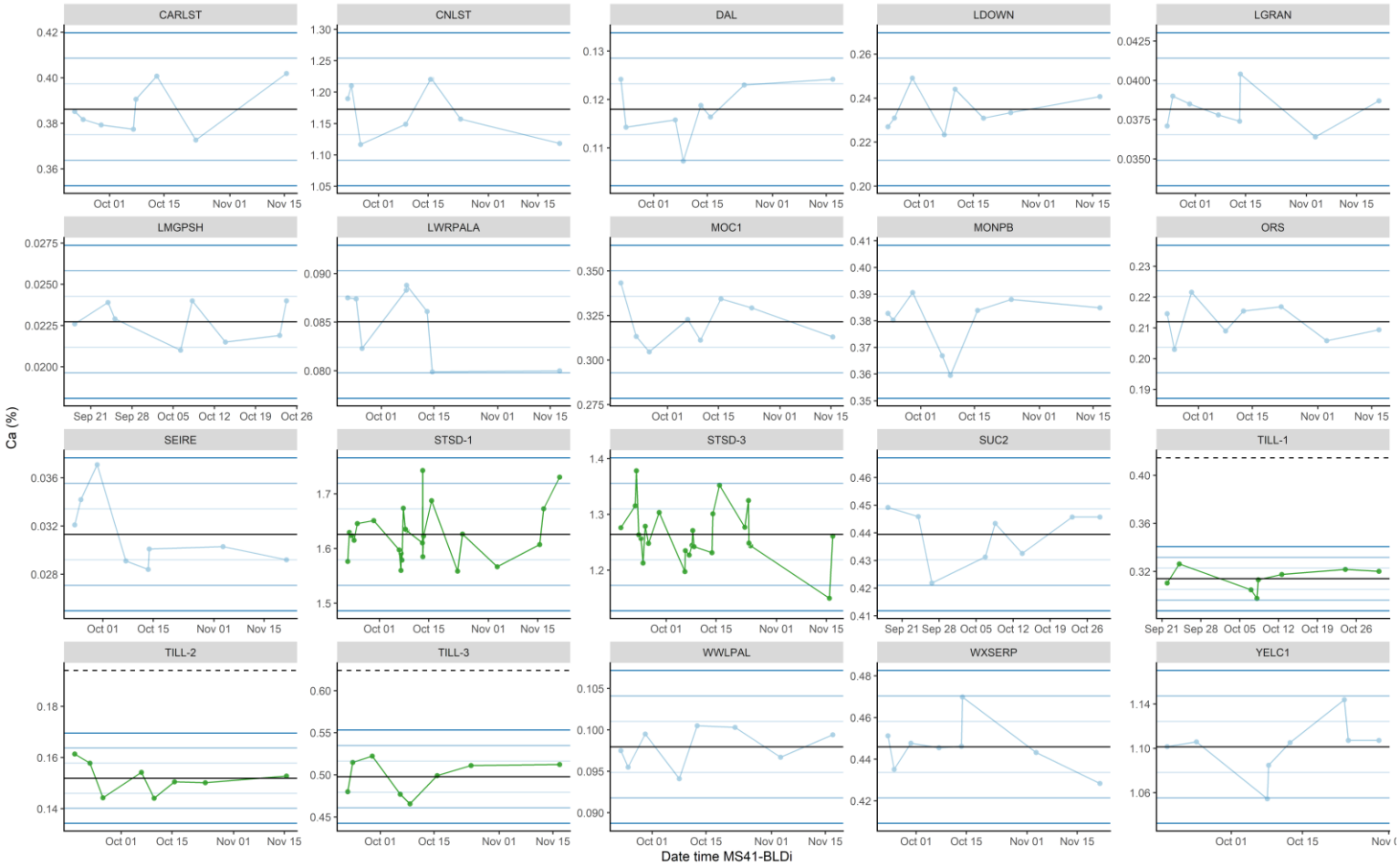
Beryllium (Be) sample data IQR: 0.326–0.970 mg kg^{-1}

Bismuth (Bi) MS41L-BLD



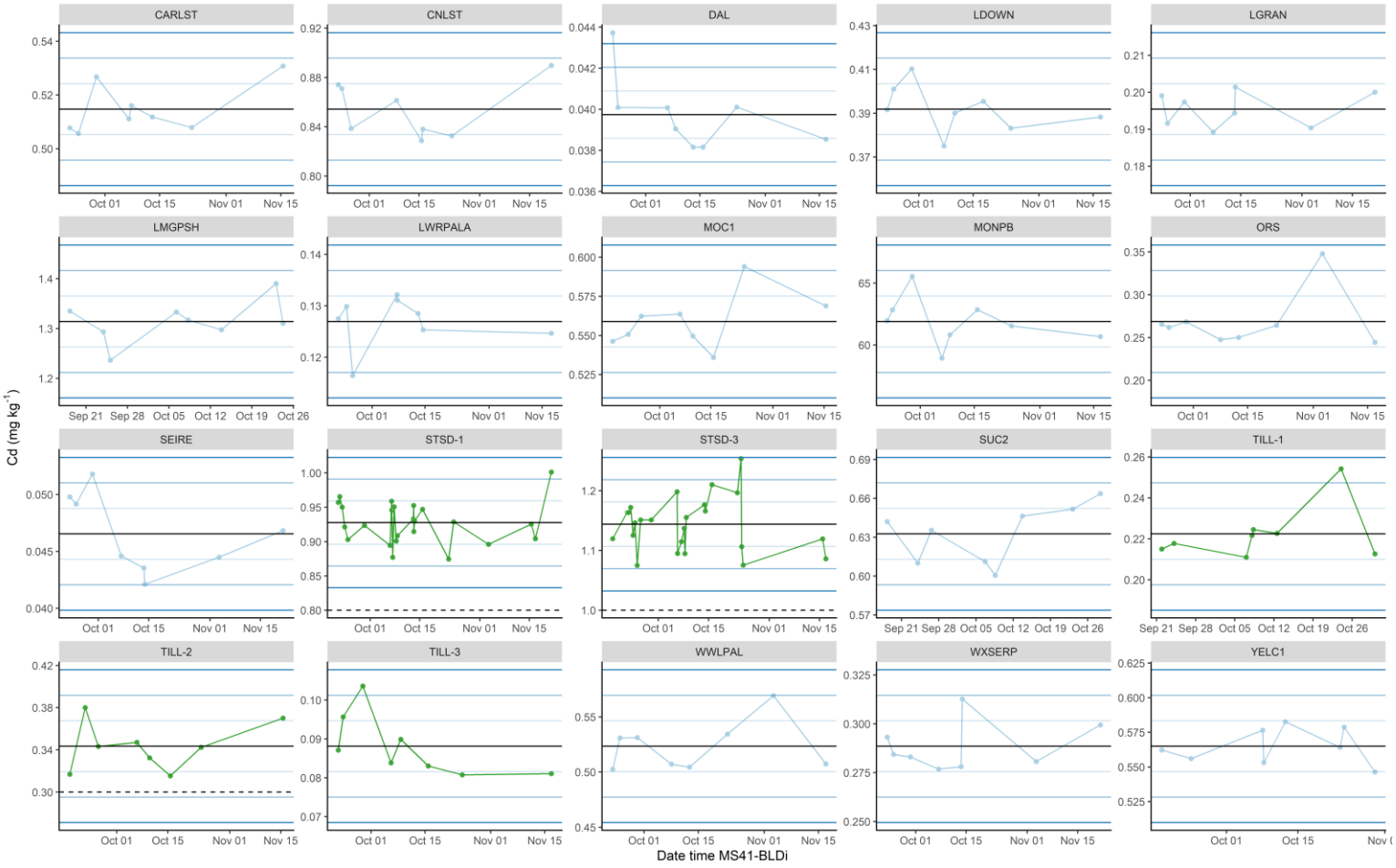
Bismuth (Bi) sample data IQR: 0.067–0.129 mg kg^{-1}

Calcium (Ca) MS41L-BLD



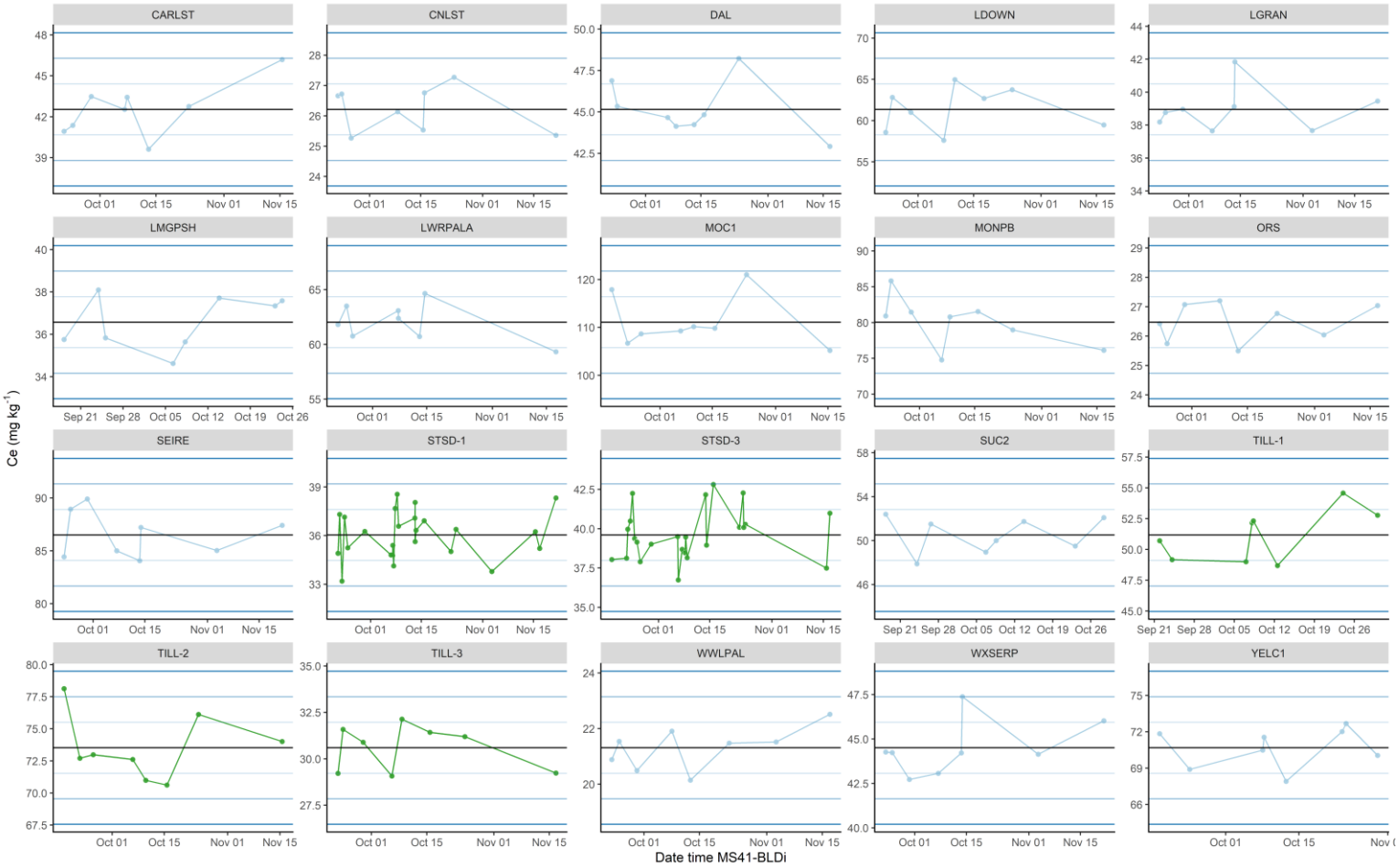
Calcium (Ca) sample data IQR: 0.202–1.660 %

Cadmium (Cd) MS41L-BLD



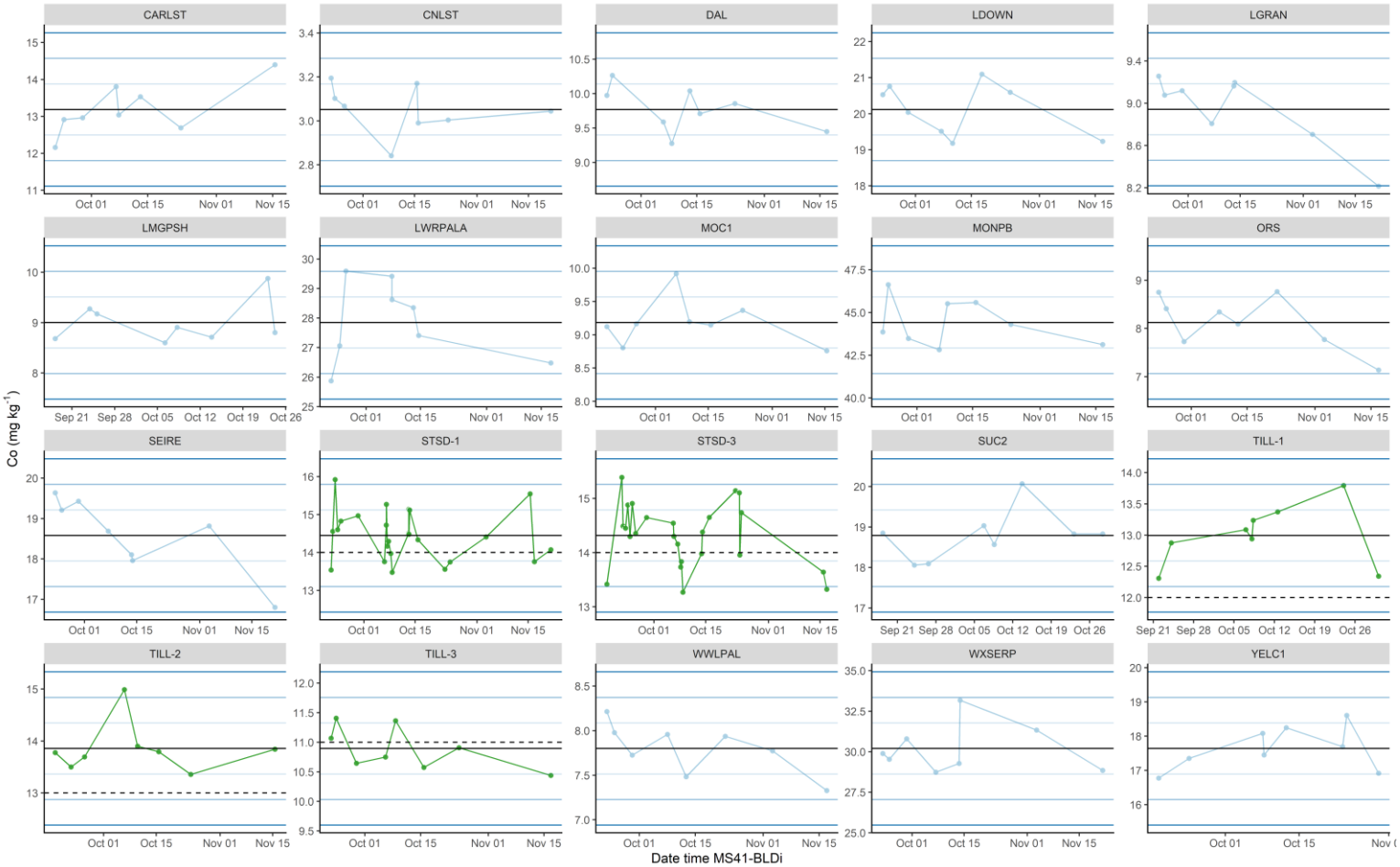
Cadmium (Cd) sample data IQR: 0.289–1.290 mg kg^{-1}

Cerium (Ce) MS41L-BLD



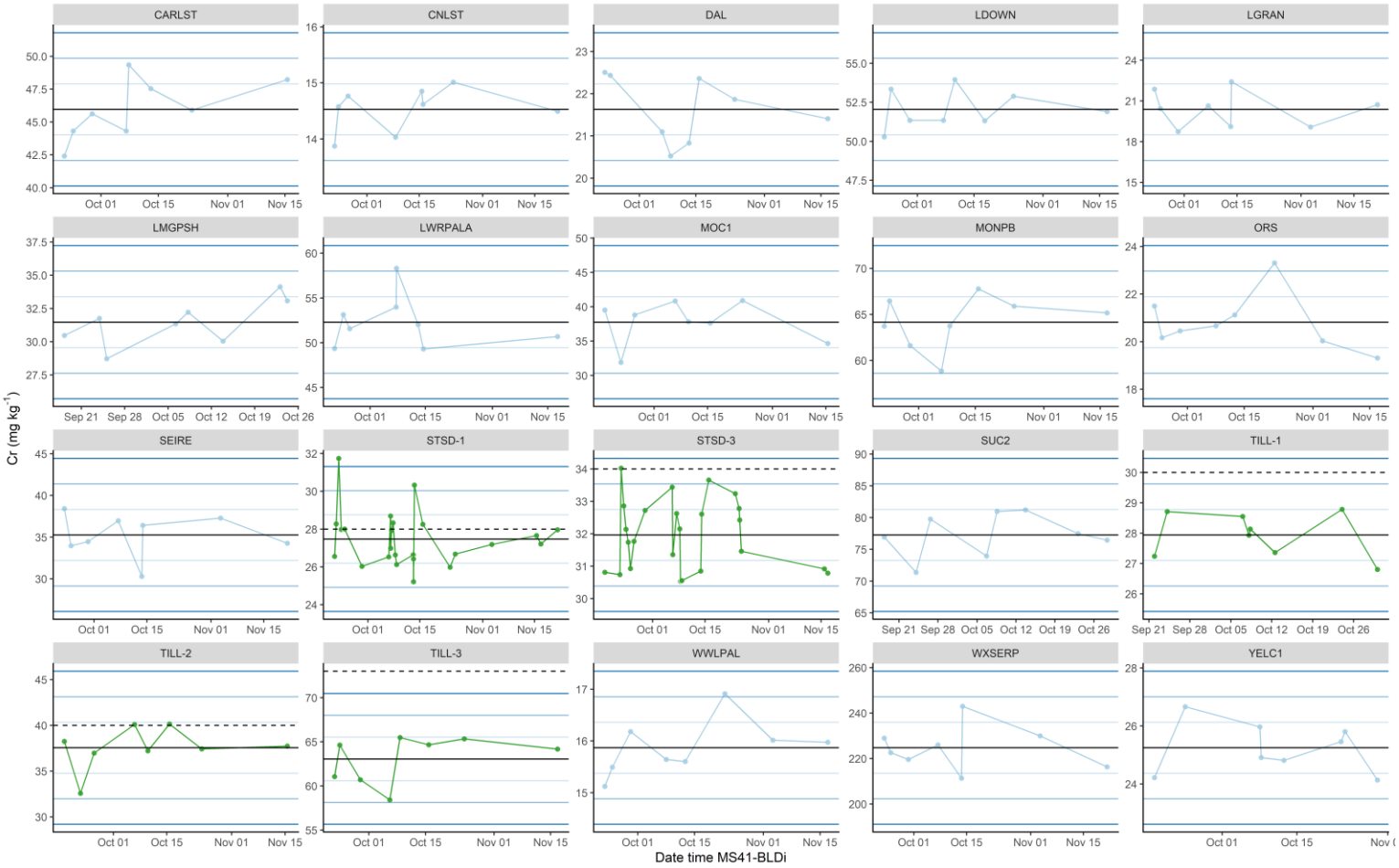
Cerium (Ce) sample data IQR: 17.9–39.3 mg kg^{-1}

Cobalt (Co) MS41L-BLD



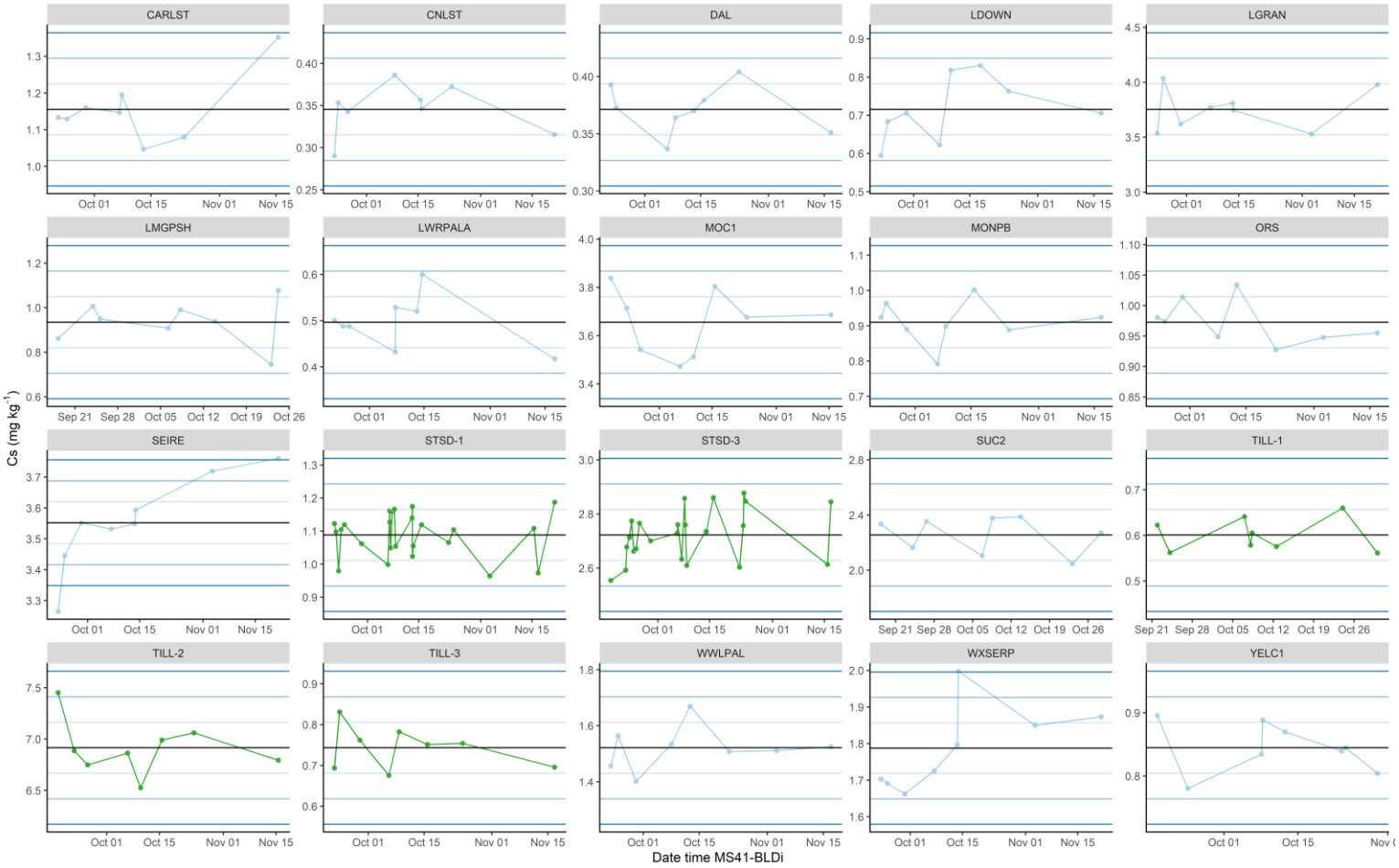
Cobalt (Co) sample data IQR: 3.41–11.3 mg kg^{-1}

Chromium (Cr) MS41L-BLD



Chromium (Cr) sample data IQR: 11.3–29.8 mg kg^{-1}

Caesium (Cs) MS41L-BLD

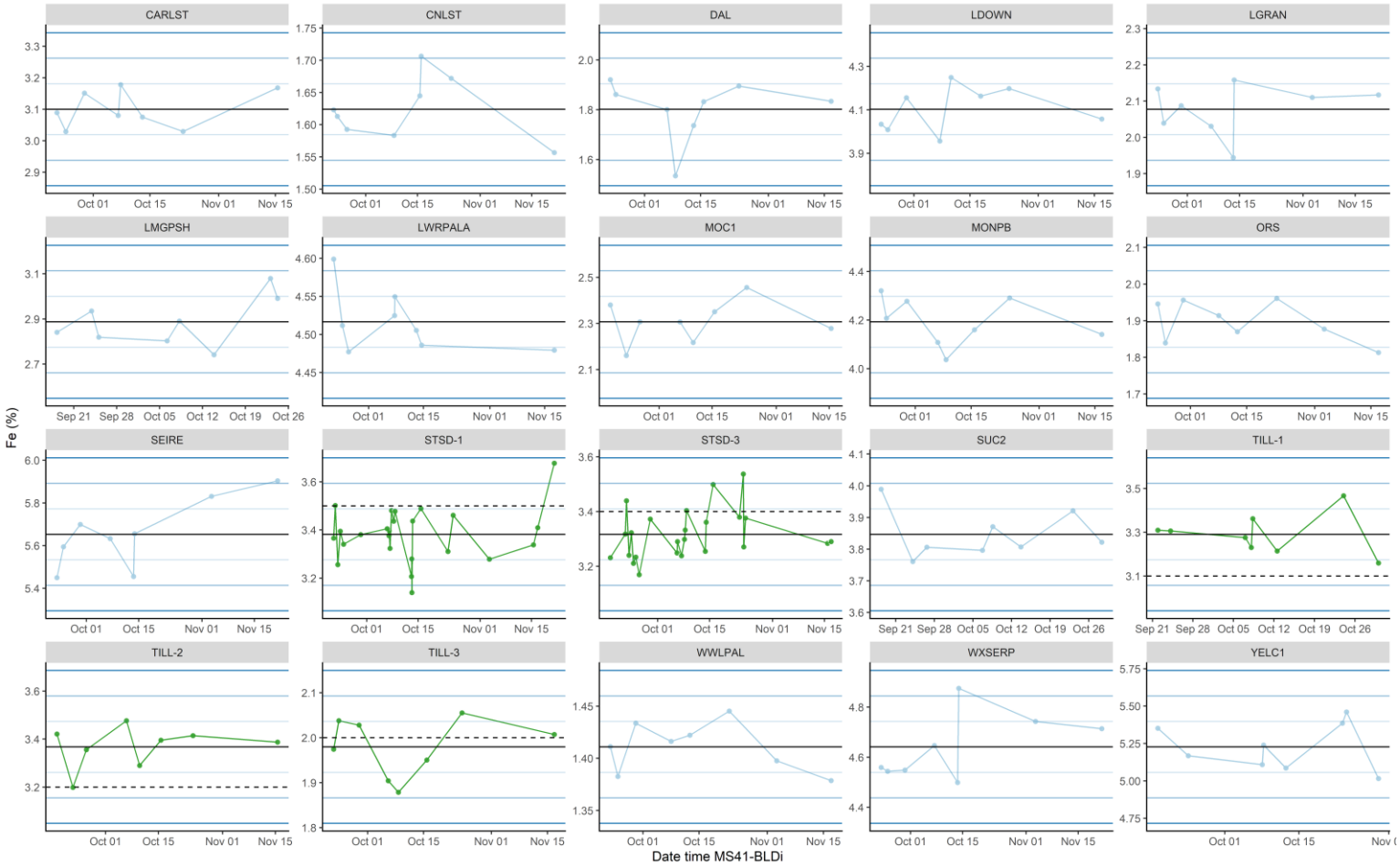


Caesium (Cs) sample data IQR: 0.395–0.974 mg kg^{-1}

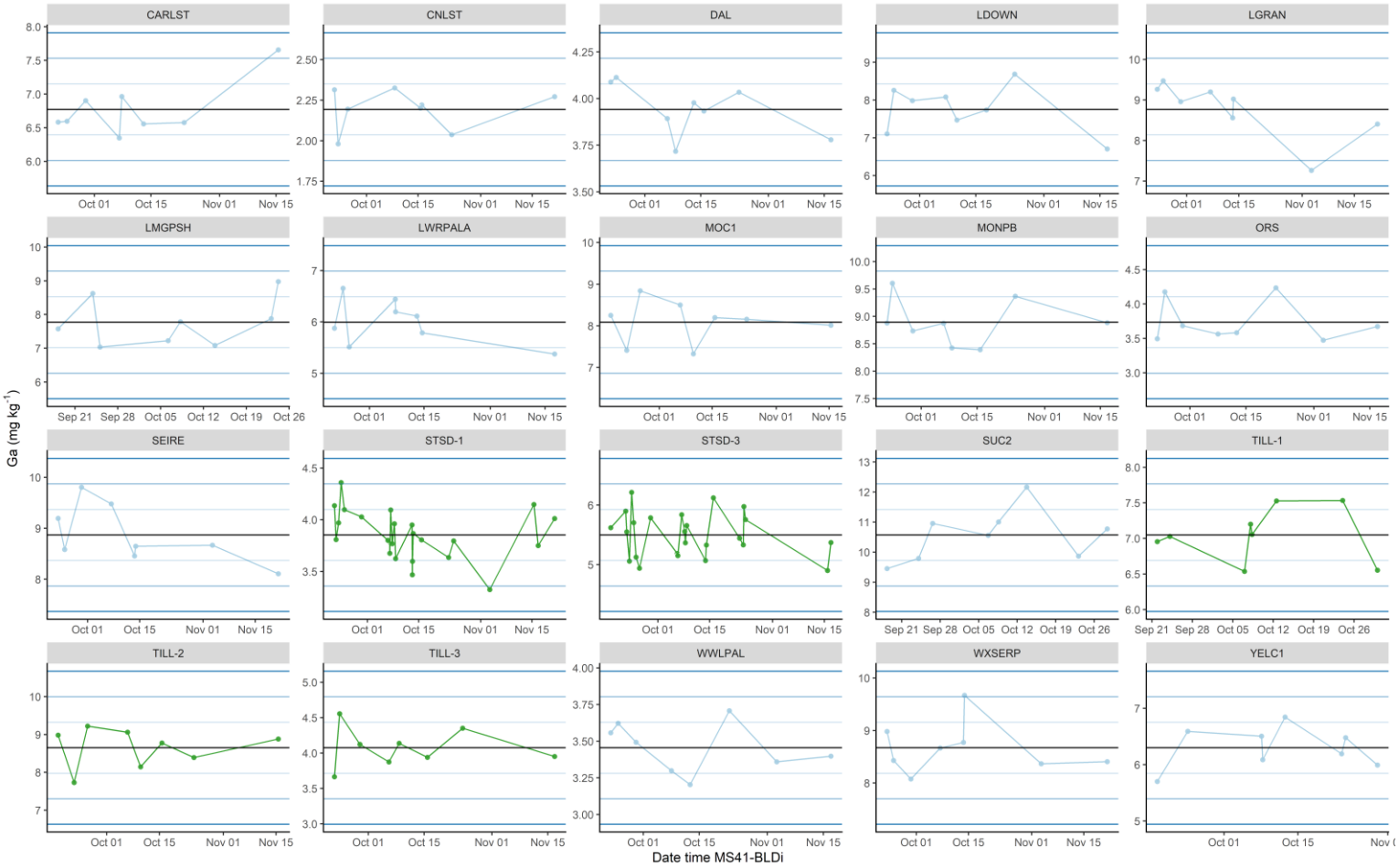
Copper (Cu) MS41L-BLD

Copper (Cu) sample data IQR: 8.4–21.8 mg kg^{-1}

Iron (Fe) MS41L-BLD

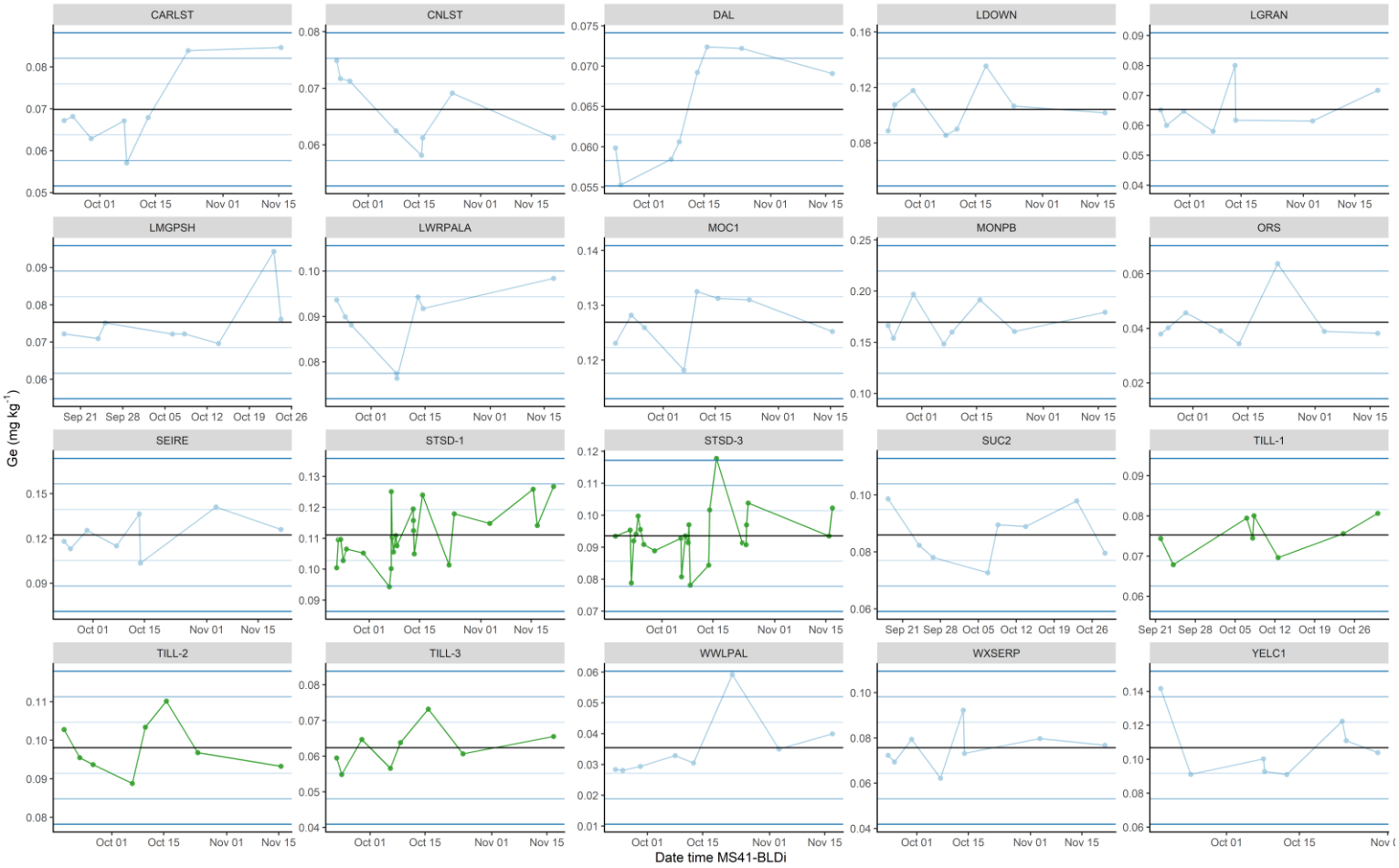


Iron (Fe) sample data IQR: 0.906–2.330 %



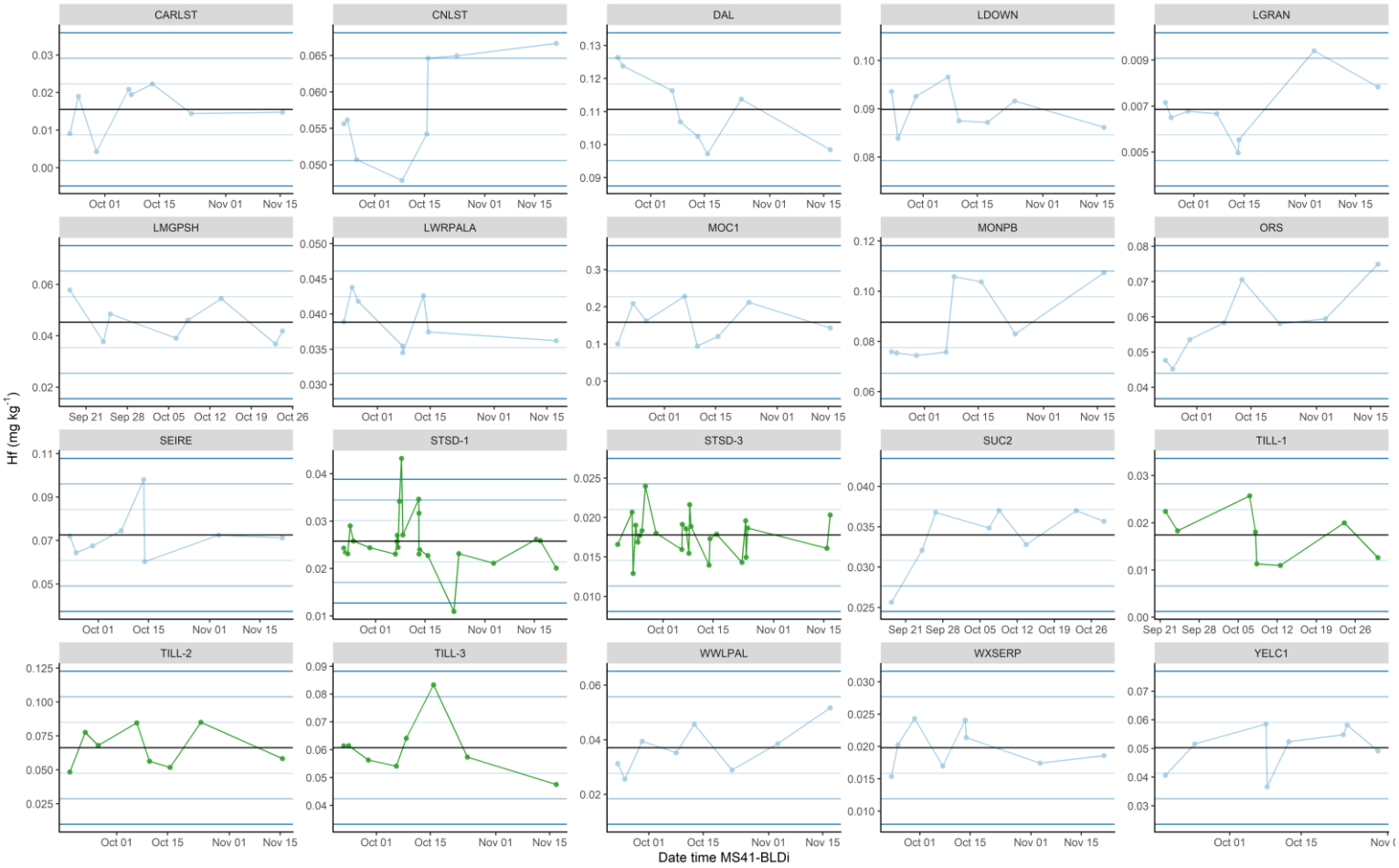
Gallium (Ga) sample data IQR: 1.87–4.83 mg kg^{-1}

Germanium (Ge) MS41L-BLD



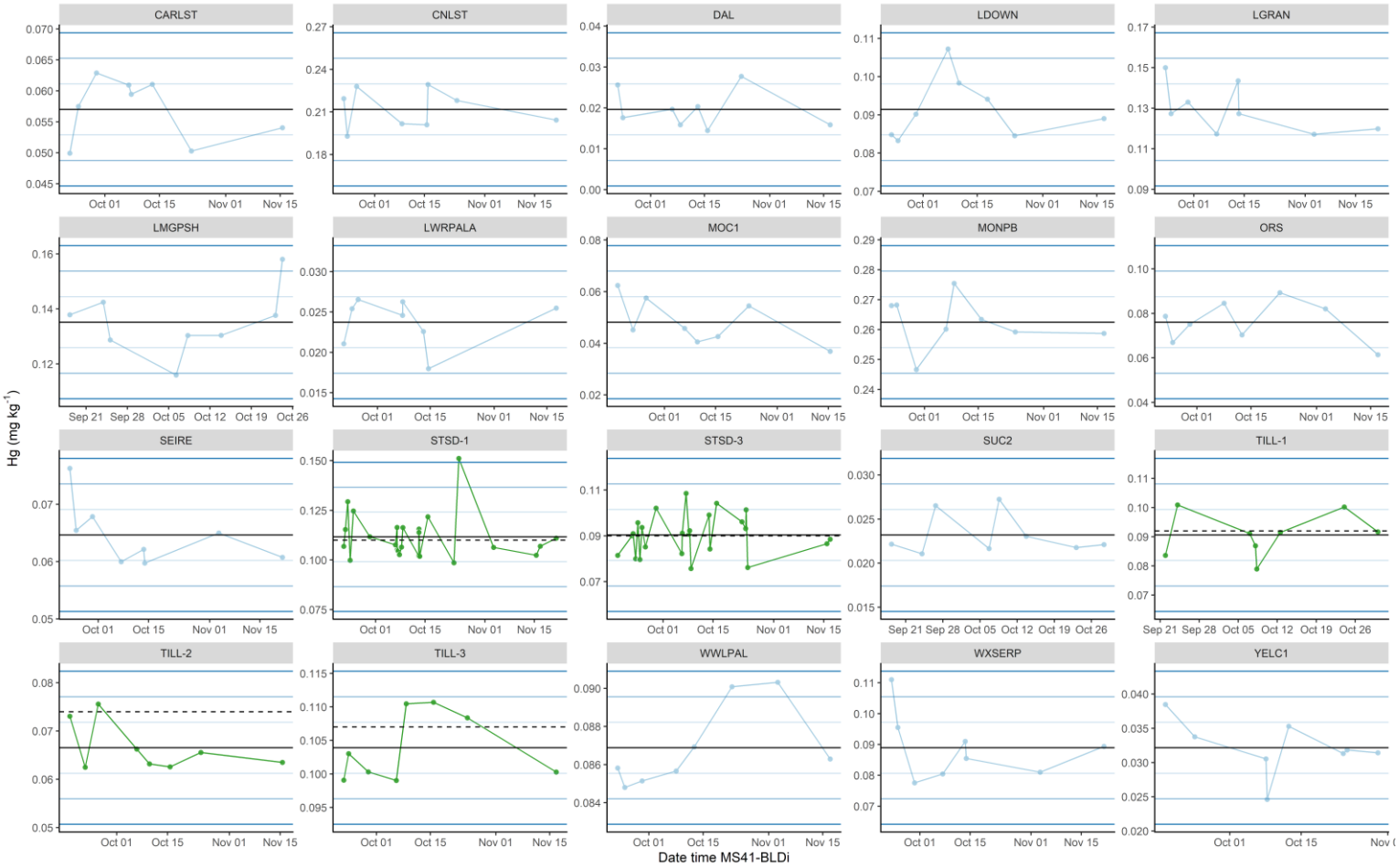
Germanium (Ge) sample data IQR: 0.0319-0.0657 mg kg^{-1}

Hafnium (Hf) MS41L-BLD



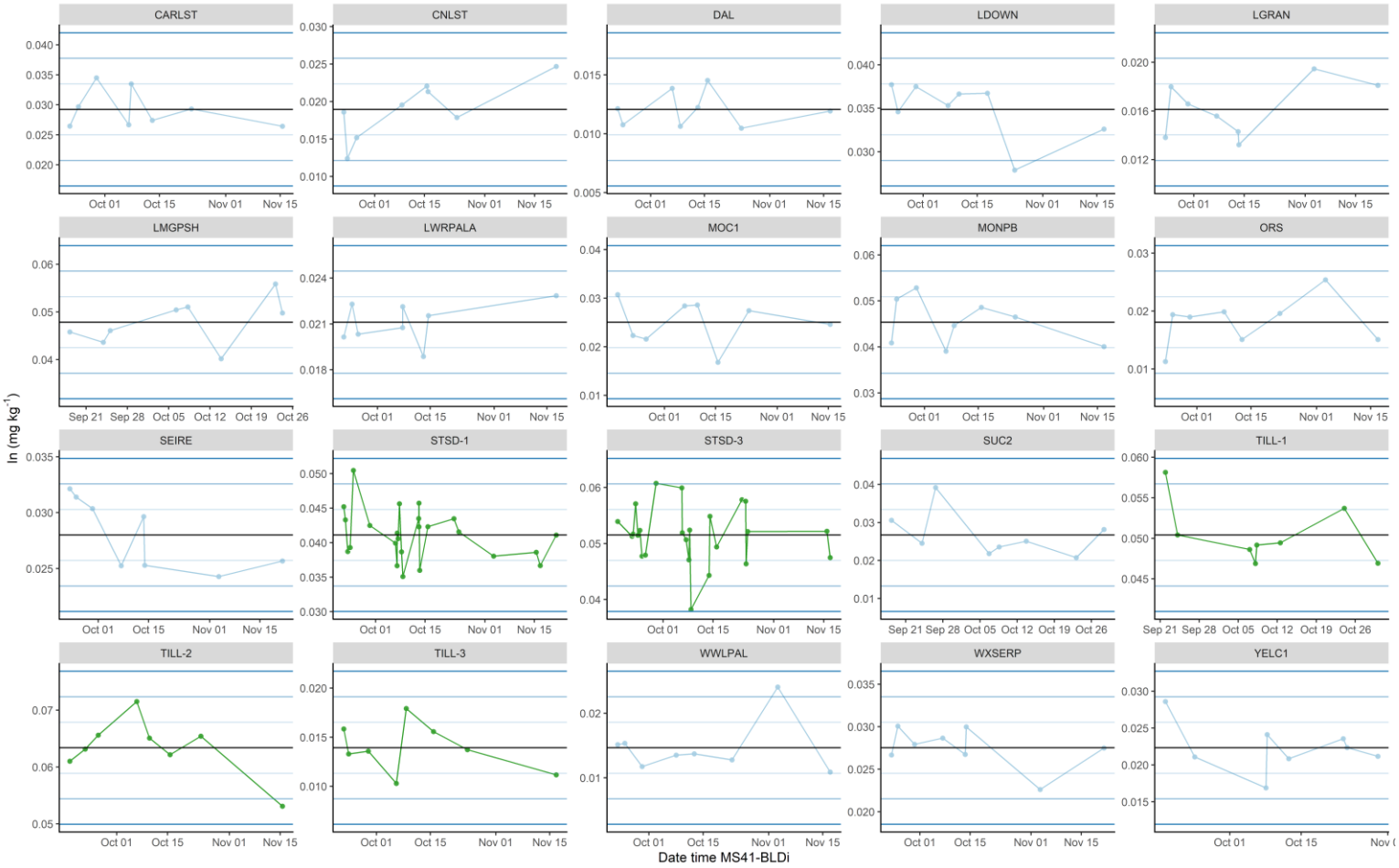
Hafnium (Hf) sample data IQR: 0.0304–0.0991mg kg^{-1}

Mercury (Hg) MS41L-BLD



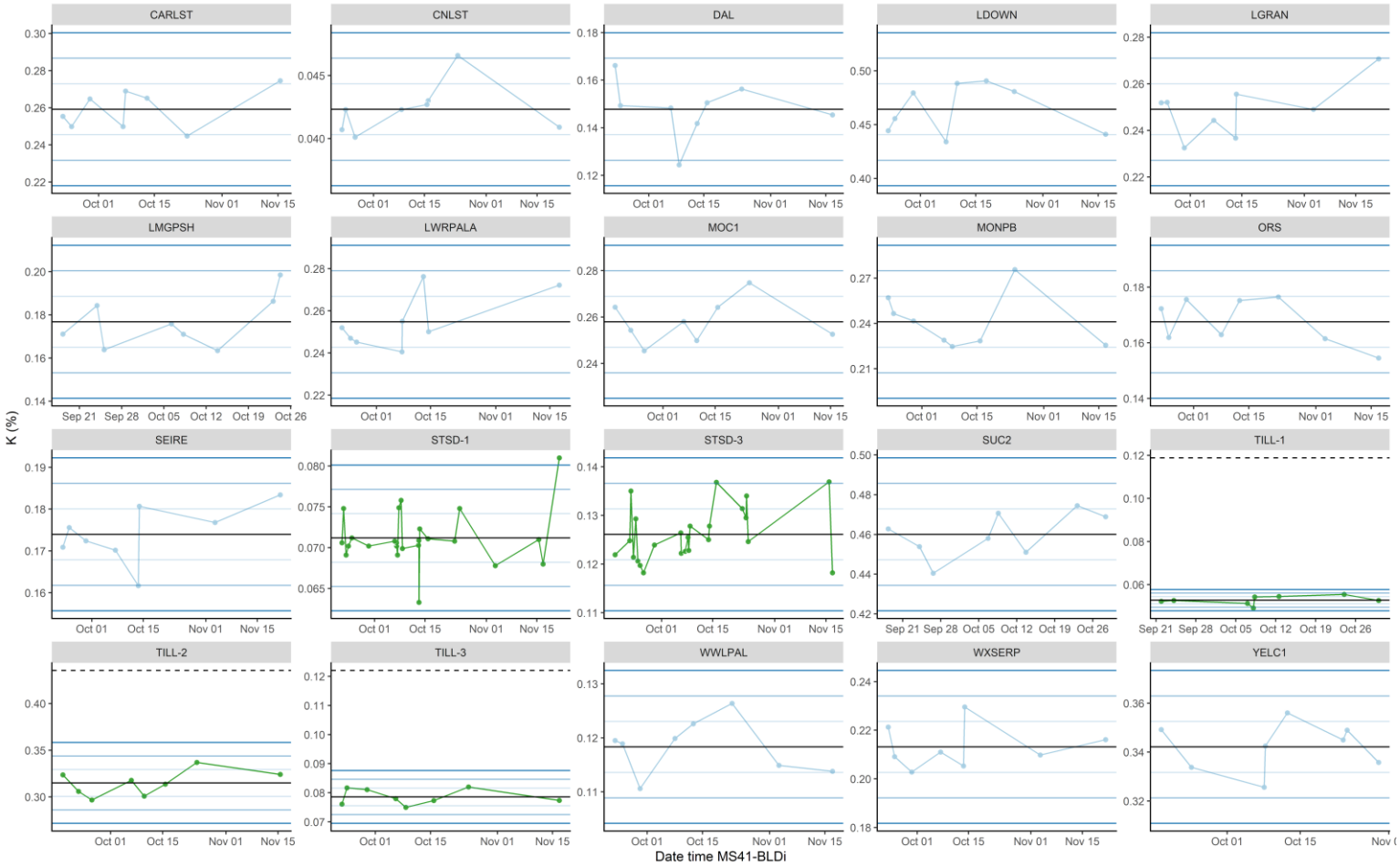
Mercury (Hg) sample data IQR: 0.0639–0.1050 mg kg^{-1}

Indium (In) MS41L-BLD



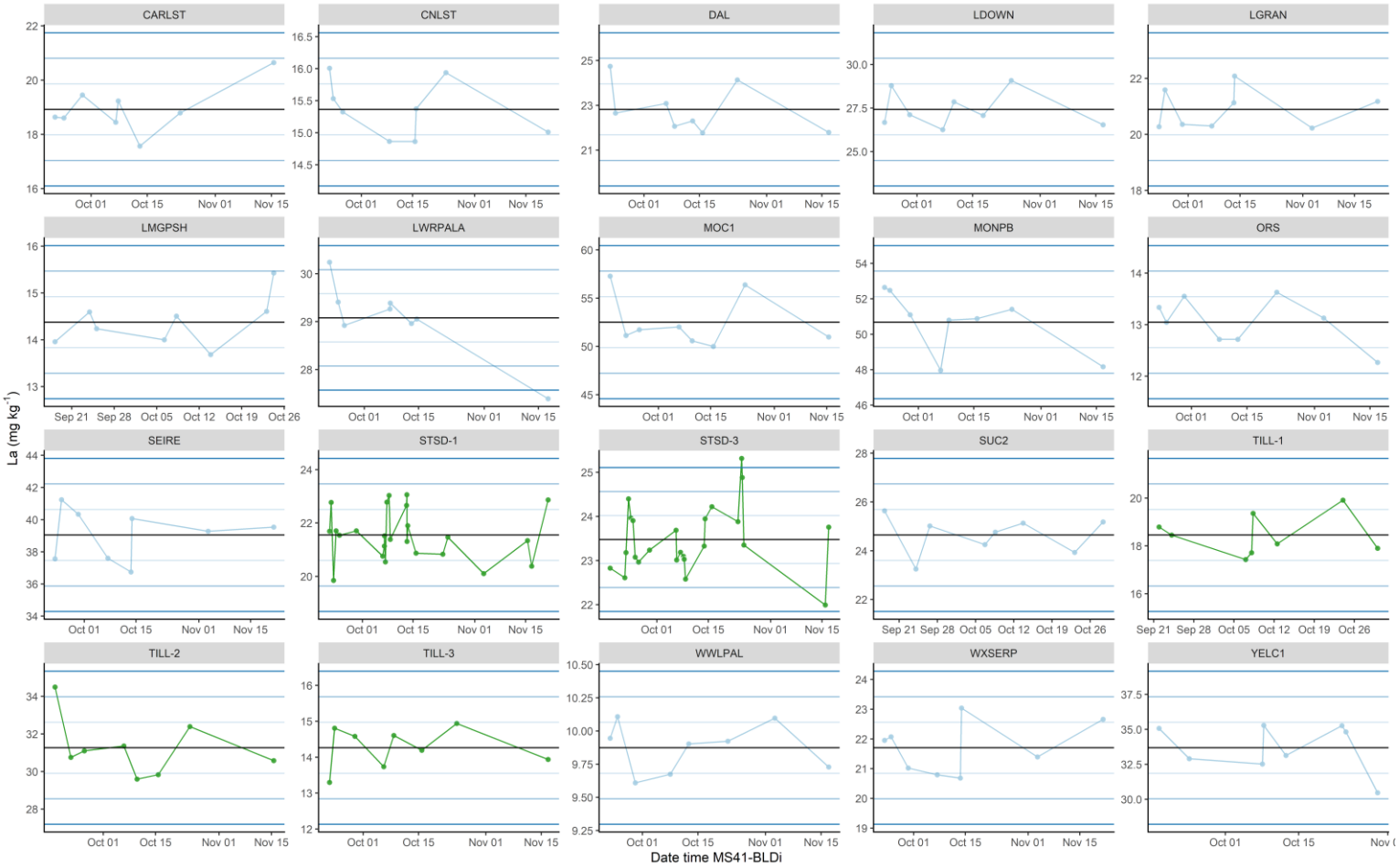
Indium (In) sample data IQR: 0.0113–0.0258 mg kg^{-1}

Potassium (K) MS41L-BLD



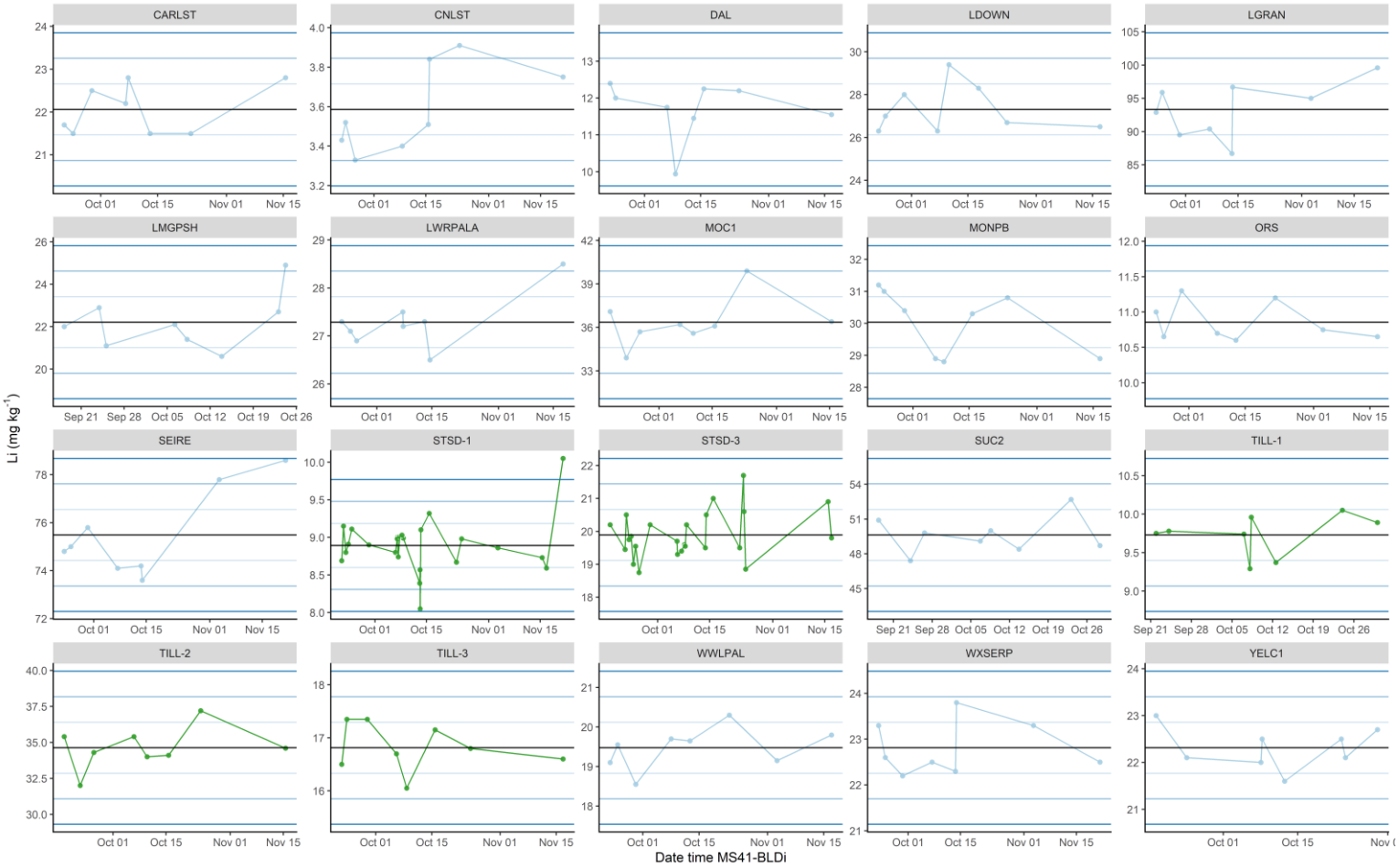
Potassium (K) sample data IQR: 0.0787–0.2390 %

Lanthanum (La) MS41L-BLD



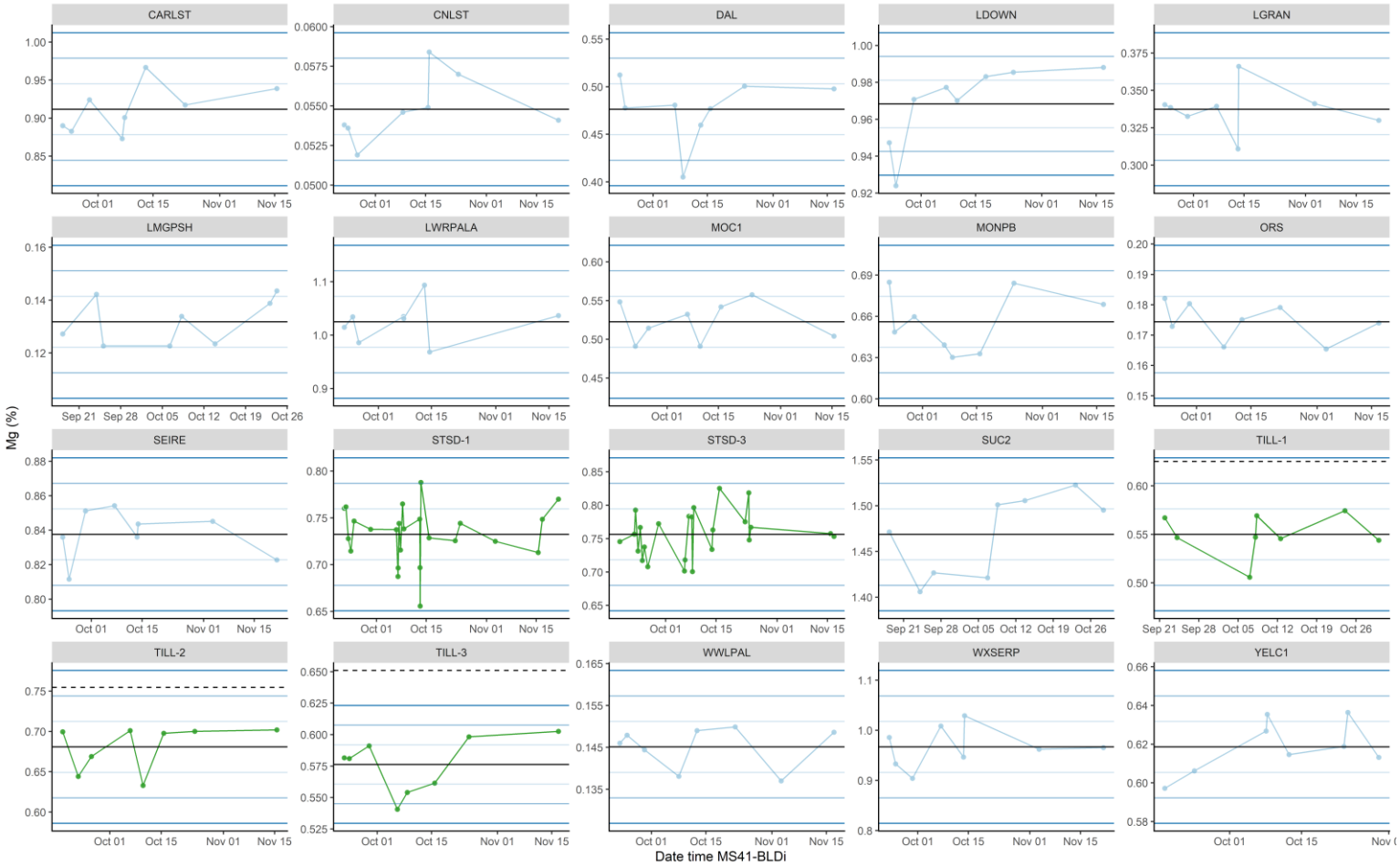
Lanthanum (La) sample data IQR: 8.85–20.10 mg kg^{-1}

Lithium (Li) MS41L-BLD



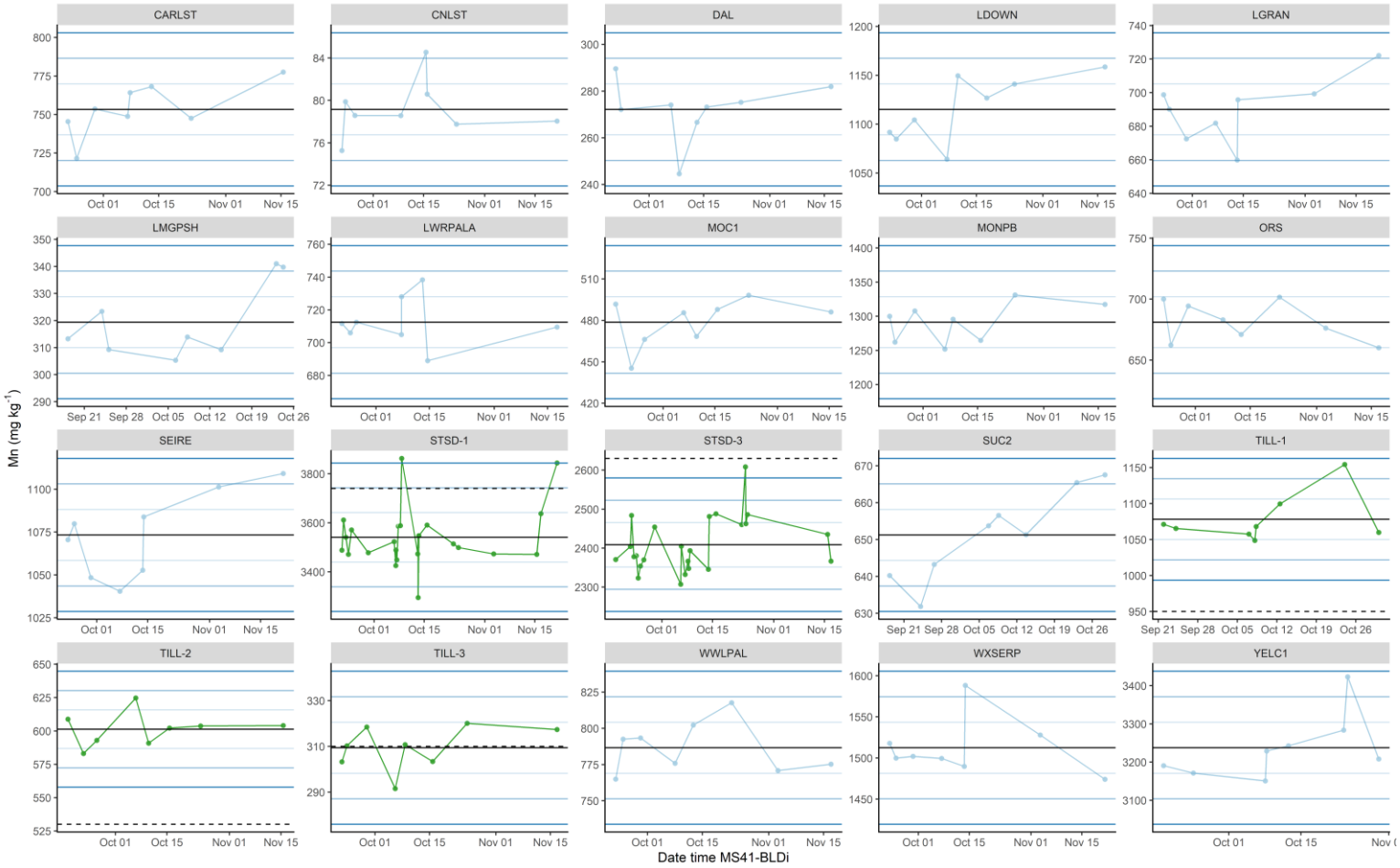
Lithium (Li) sample data IQR: 5.04–16.20 mg kg^{-1}

Magnesium (Mg) MS41L-BLD



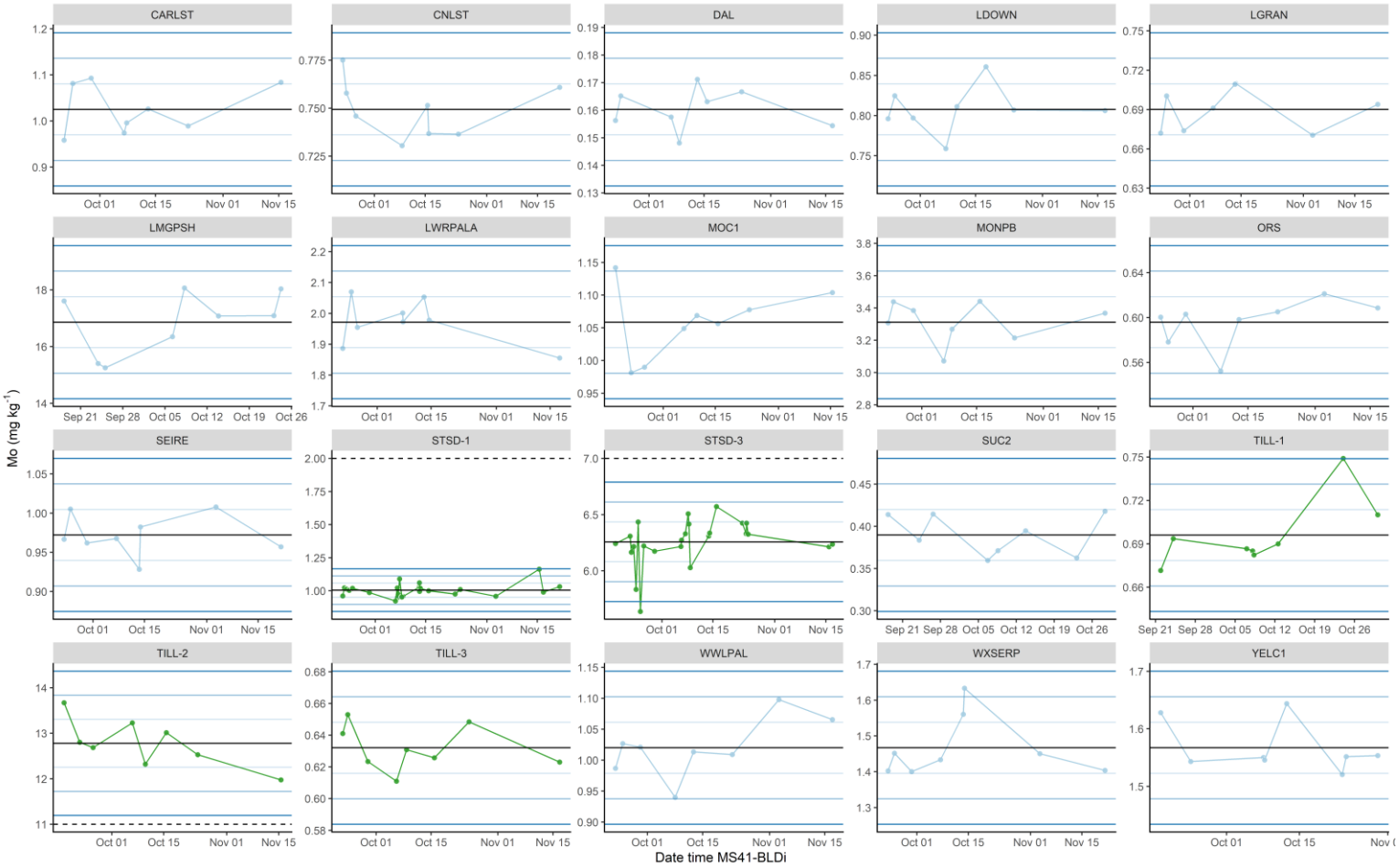
Magnesium (Mg) sample data IQR: 0.110–0.284 %

Manganese (Mn) MS41L-BLD



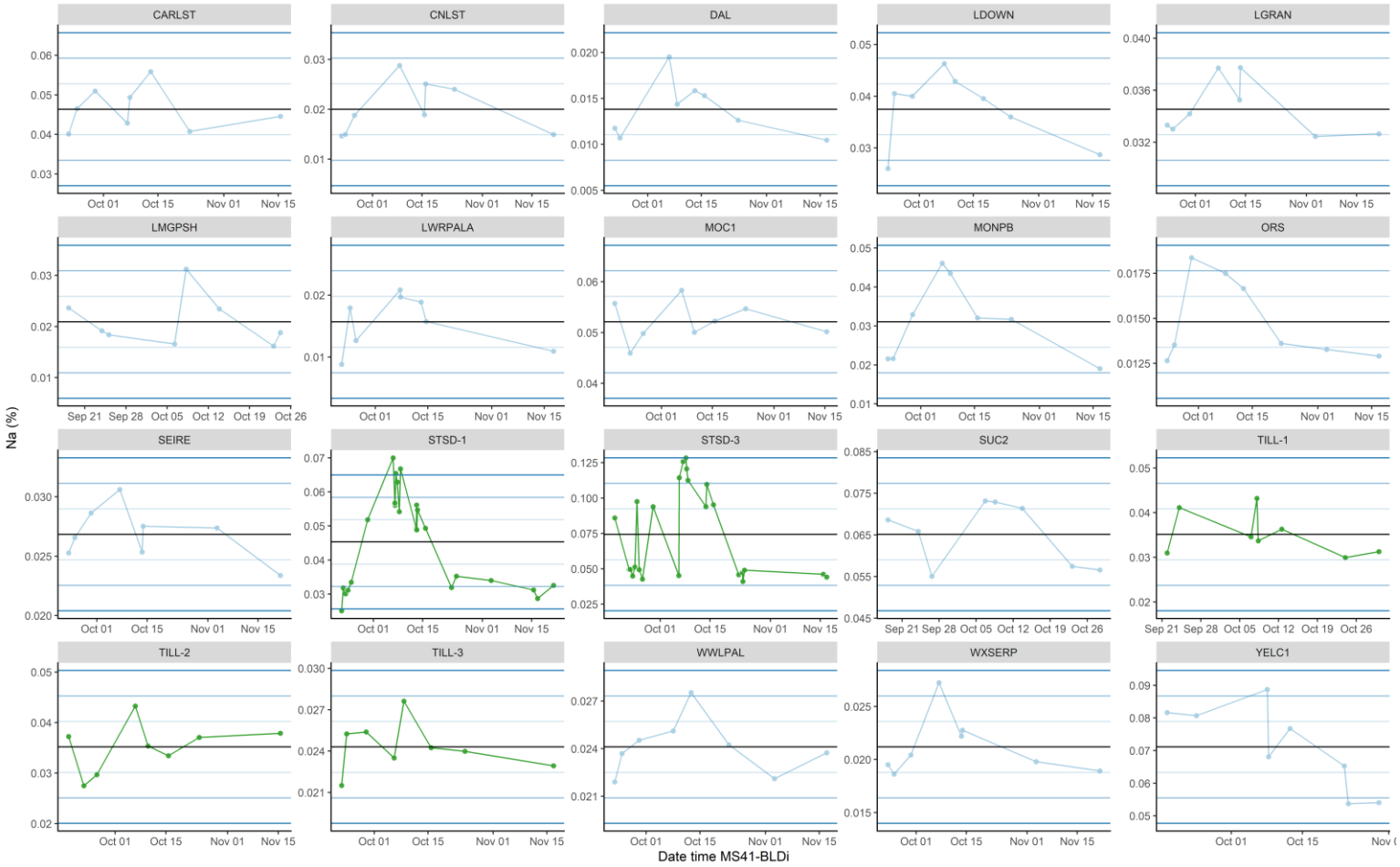
Manganese (Mn) sample data IQR: 152–1030 mg kg^{-1}

Molybdenum (Mo) MS41L-BLD



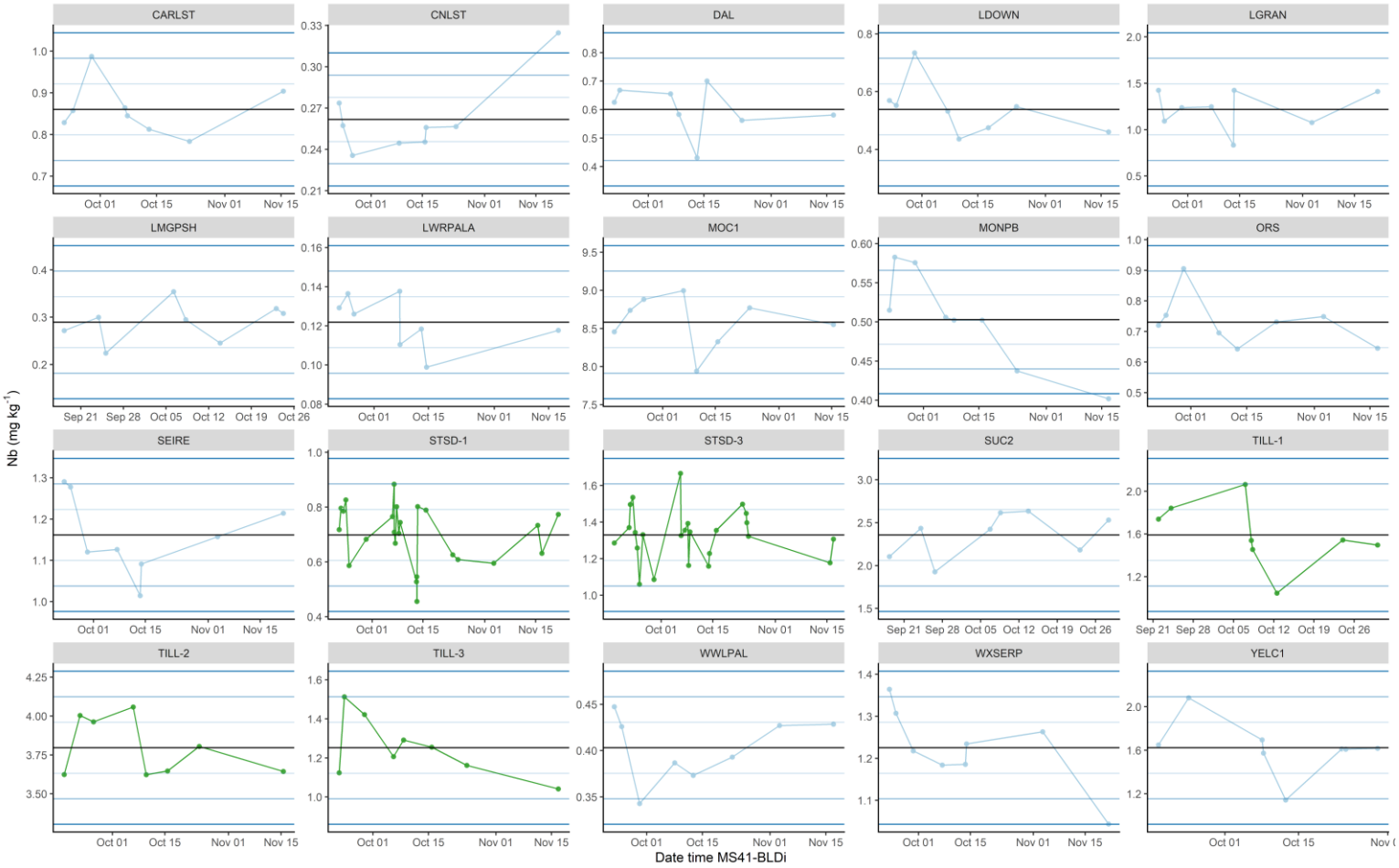
Molybdenum (Mo) sample data IQR: 0.522–1.510 mg kg^{-1}

Sodium (Na) MS41L-BLD



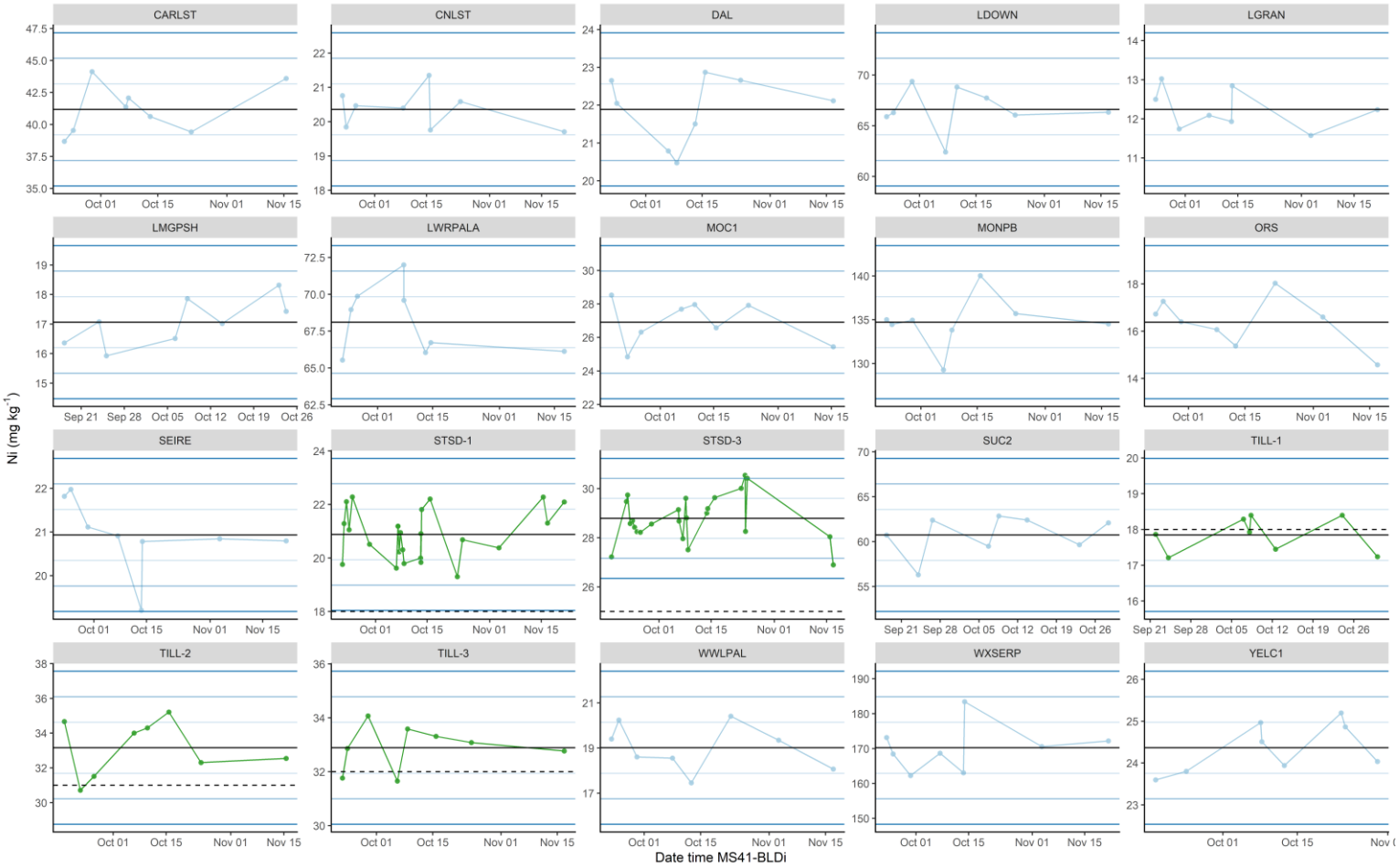
Sodium (Na) sample data IQR: 0.0212–0.0361 %

Niobium (Nb) MS41L-BLD



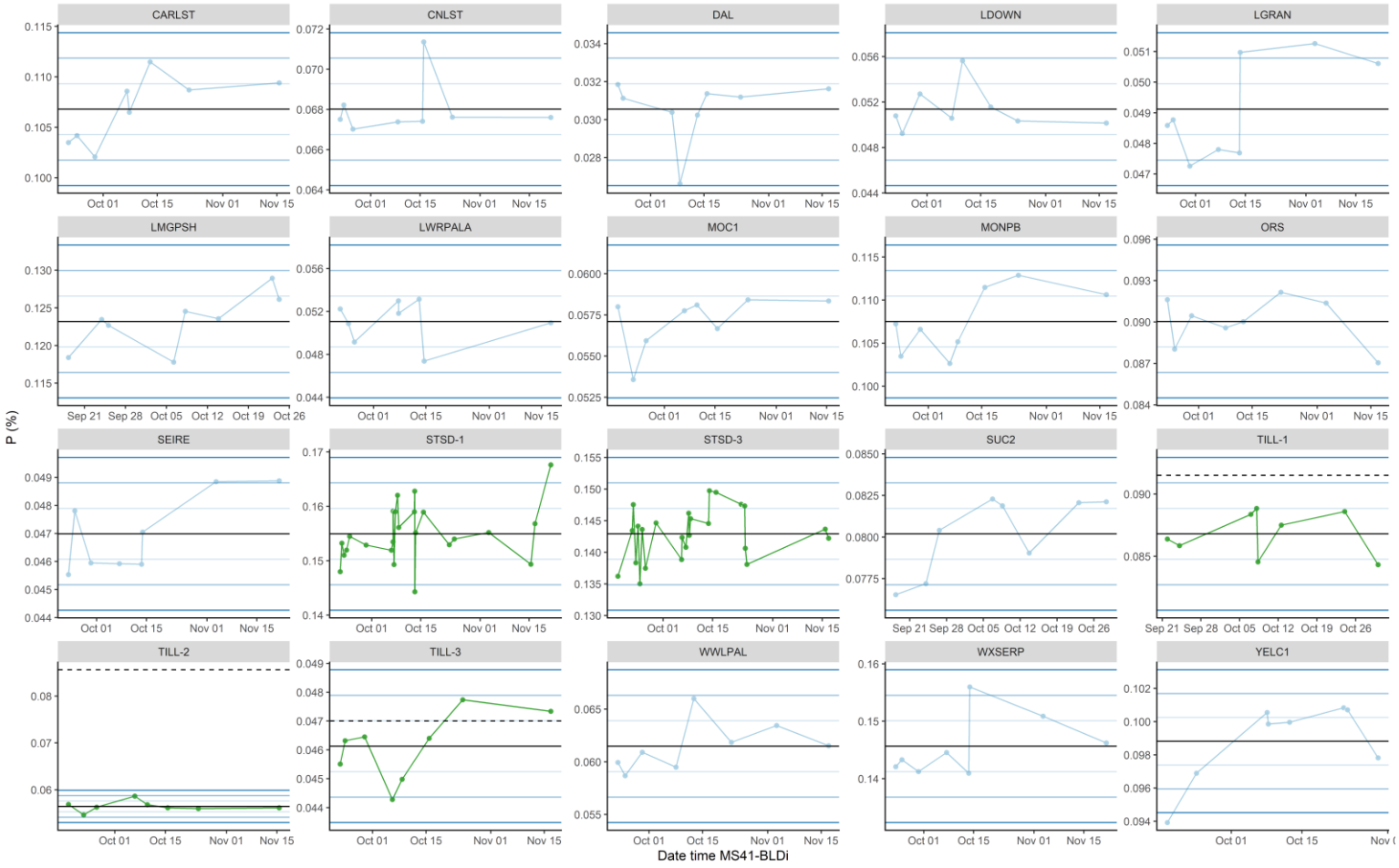
Niobium (Nb) sample data IQR: 0.195–0.425 mg kg^{-1}

Nickel (Ni) MS41L-BLD



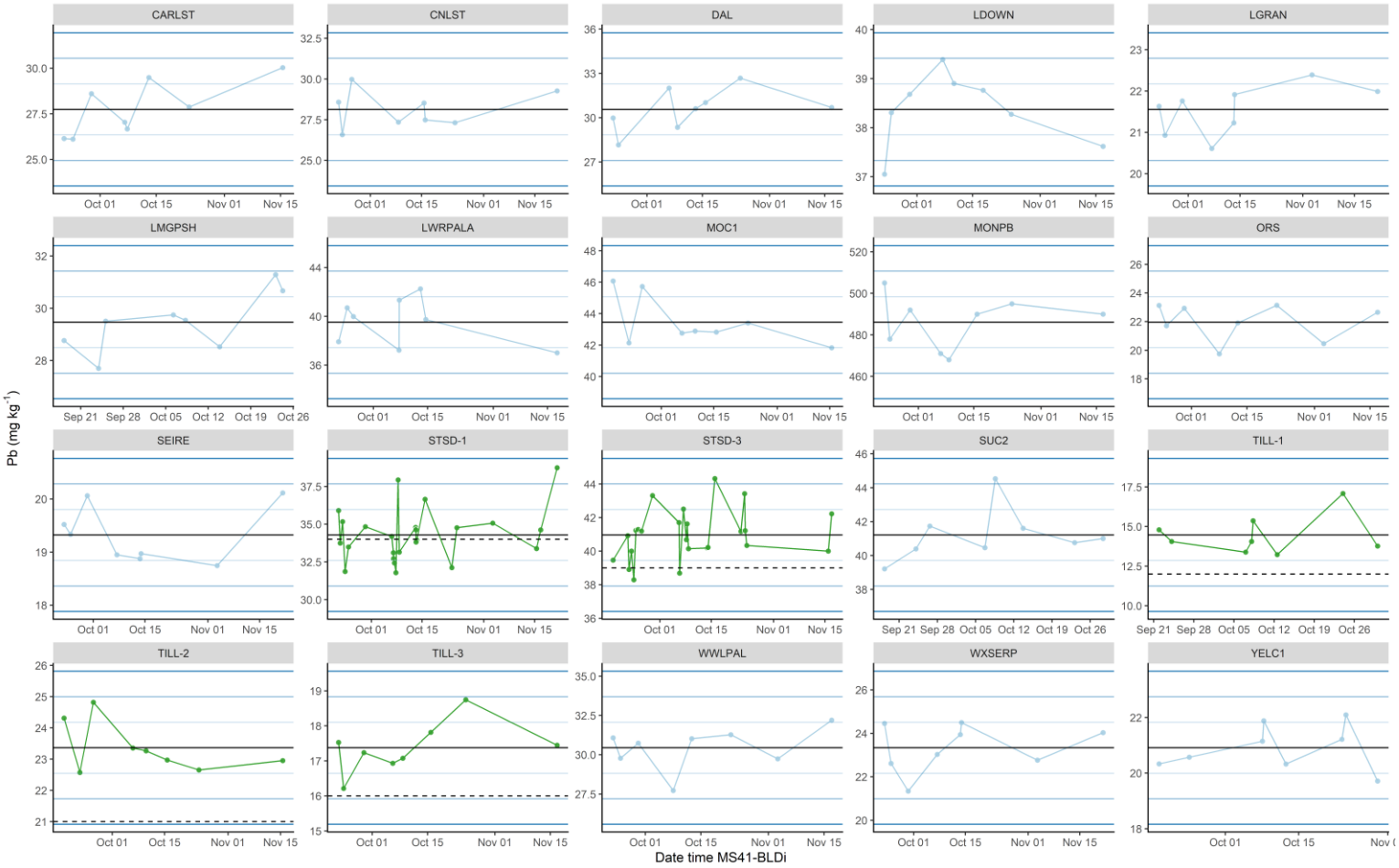
Nickel (Ni) sample data IQR: 12.8–42.3 mg kg^{-1}

Phosphorus (P) MS41L-BLD



Phosphorus (P) sample data IQR: 325–636 mg kg^{-1}

Lead (Pb) MS41L-BLD



Lead (Pb) sample data IQR: 13.5–25.5 mg kg^{-1}

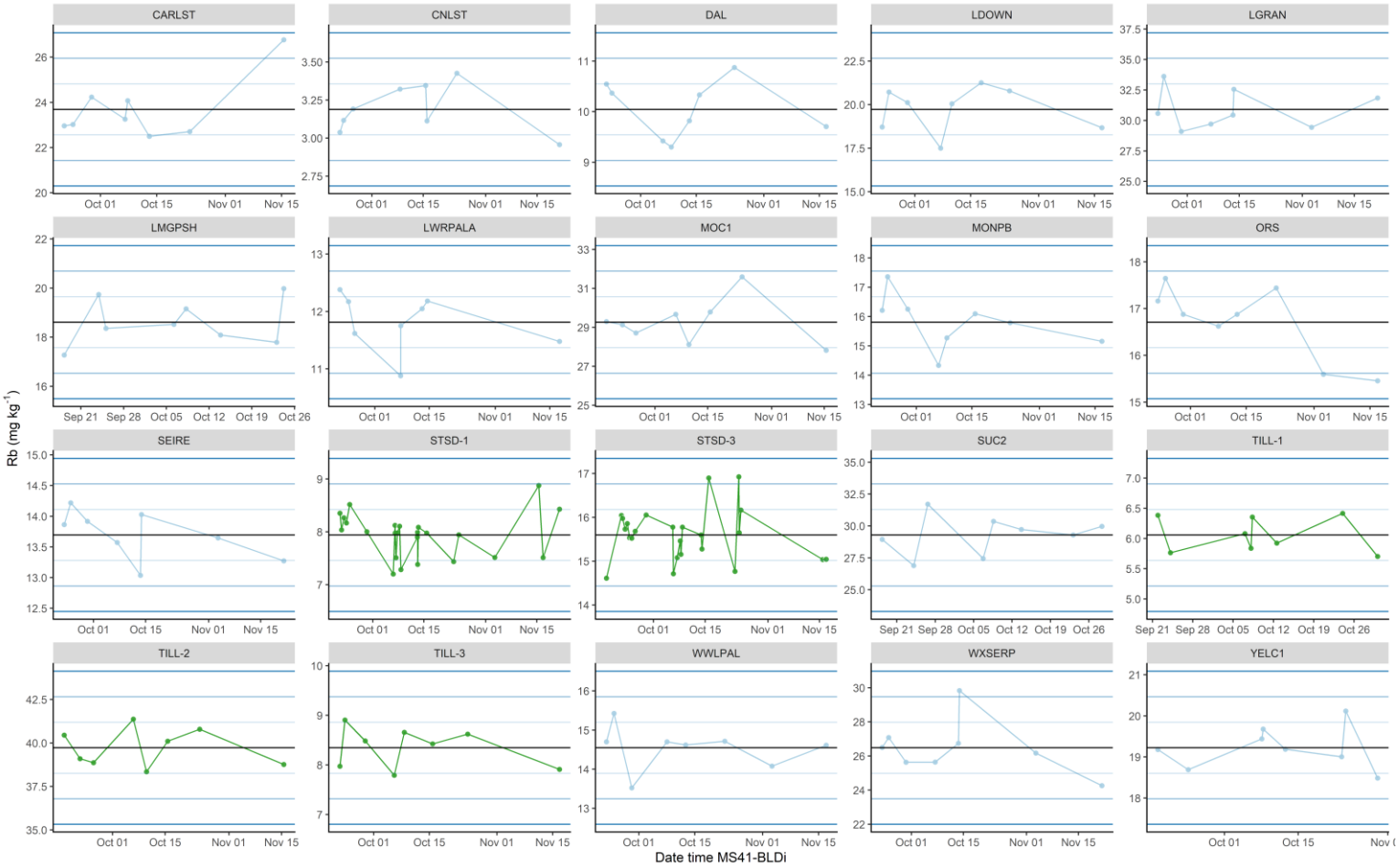
Palladium (Pd) MS41L-BLD

Palladium (Pd) sample data IQR: 0.000019–0.000290 mg kg^{-1}

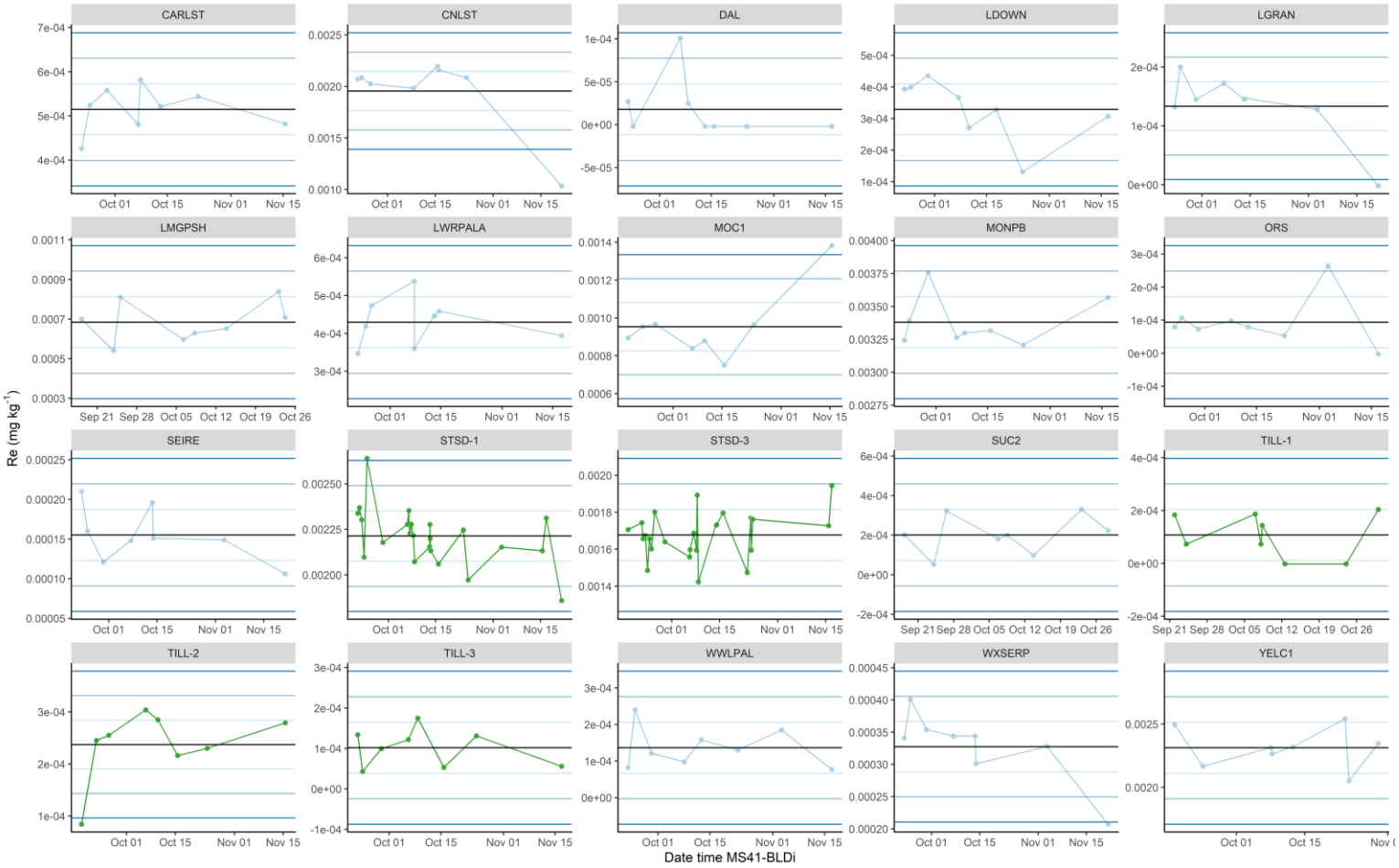
Platinum (Pt) MS41L-BLD

Platinum (Pt) sample data IQR: 0.0000122–0.0016000 mg kg^{-1}

Rubidium (Rb) MS41L-BLD

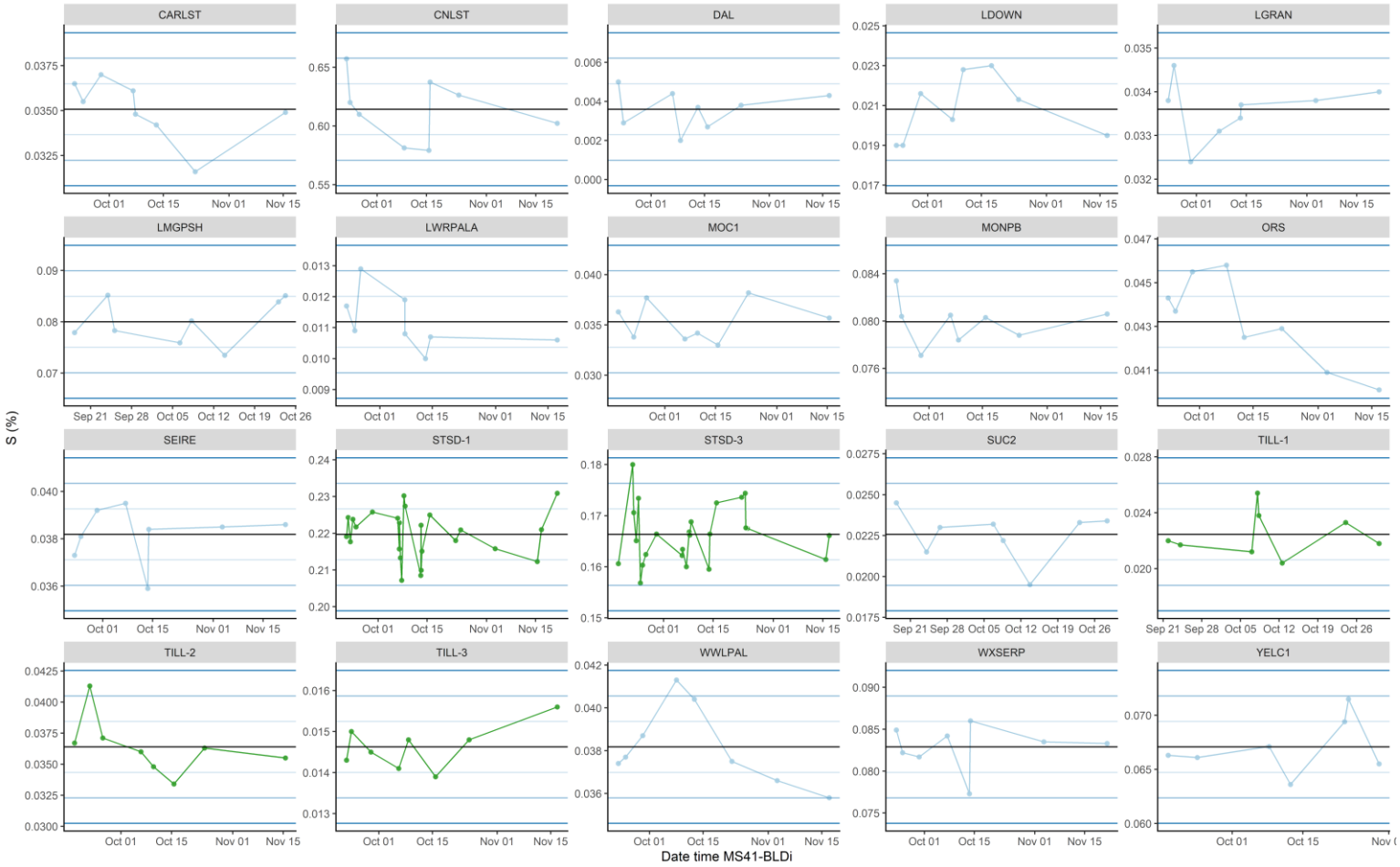


Rubidium (Rb) sample data IQR: 5.78–19.30 mg kg^{-1}



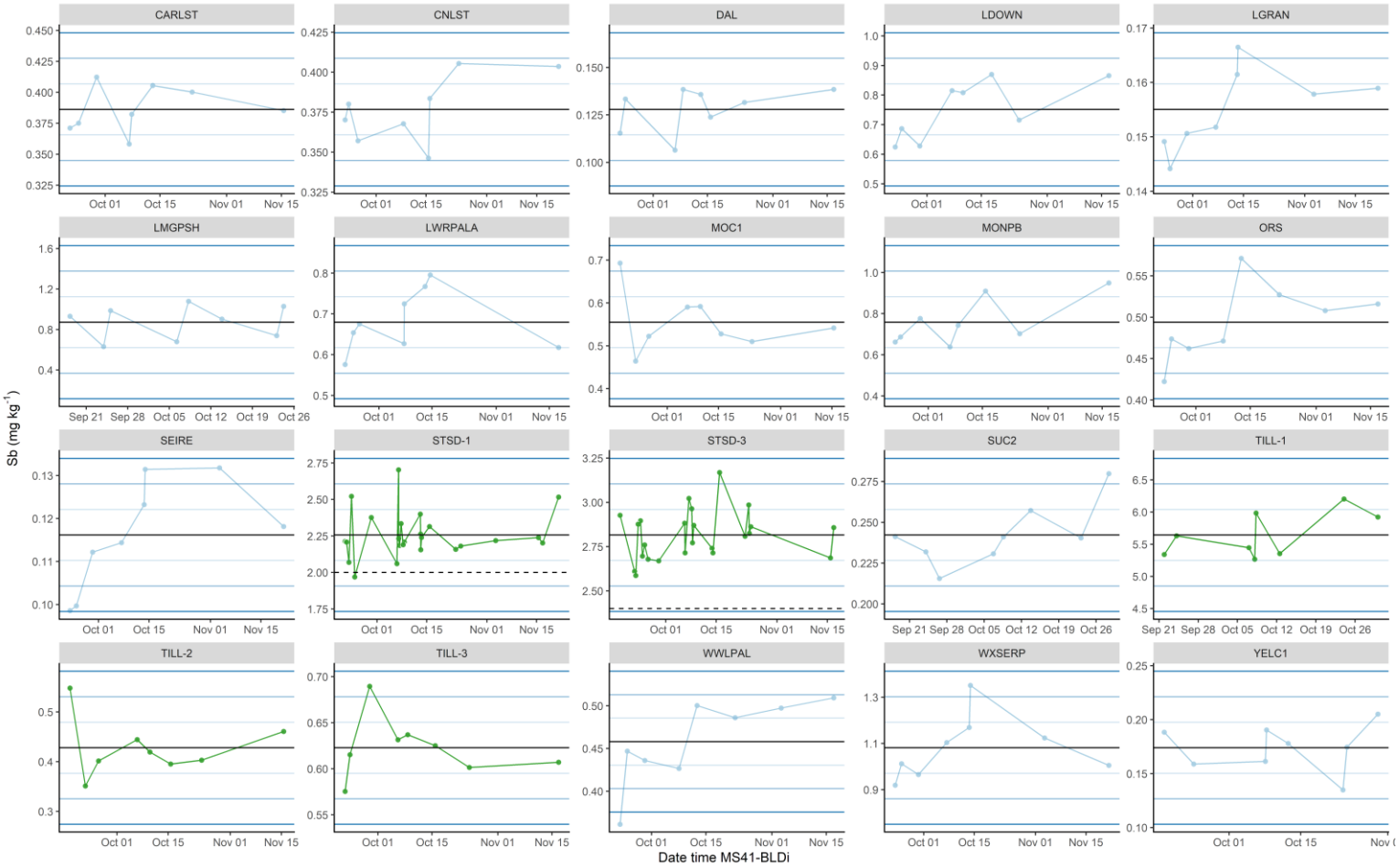
Rhenium (Re) sample data IQR: 0.000284–0.000846 mg kg^{-1}

Sulphur (S) MS41L-BLD

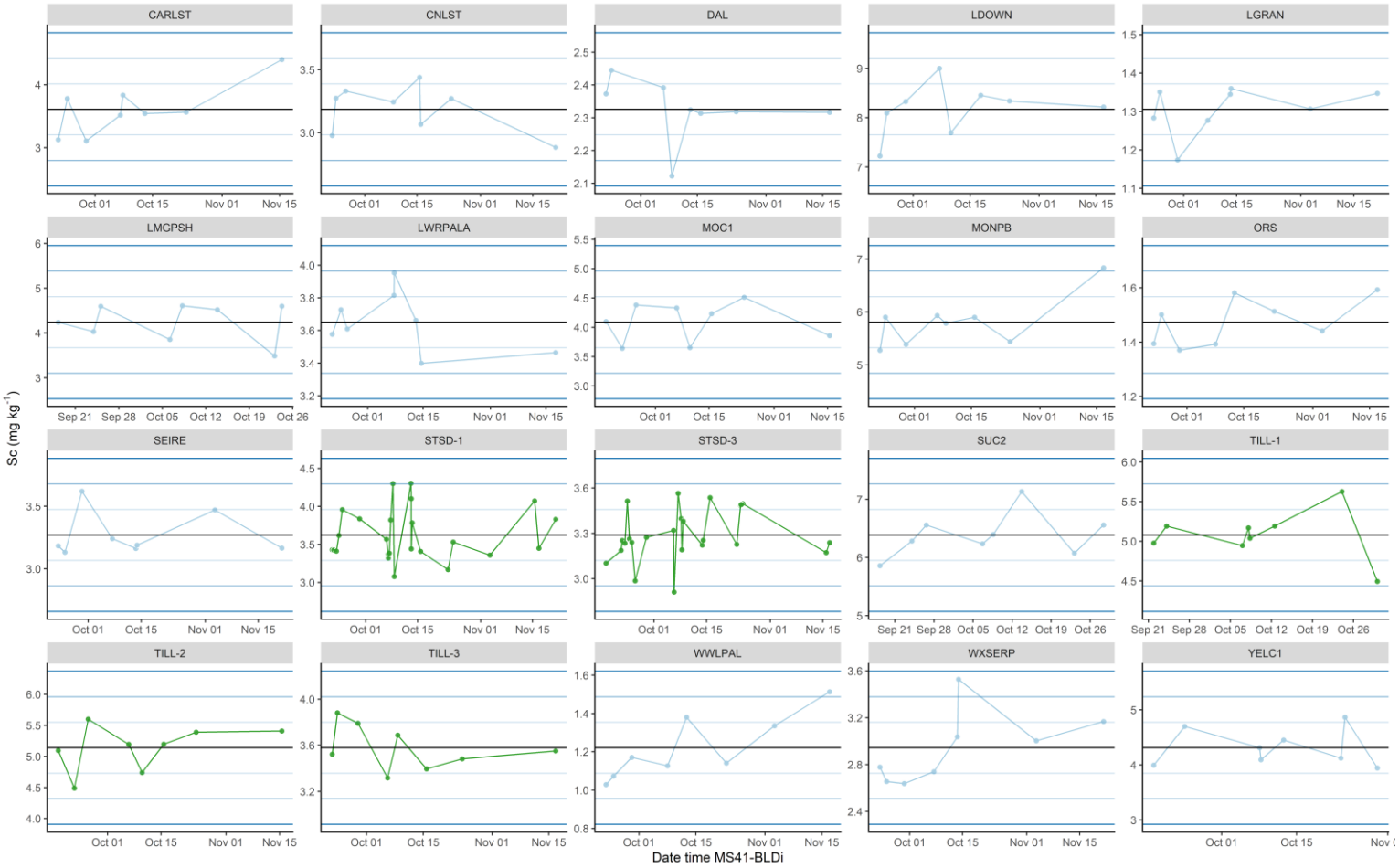


Sulphur (S) sample data IQR: 0.0267–0.1510 %

Antimony (Sb) MS41L-BLD

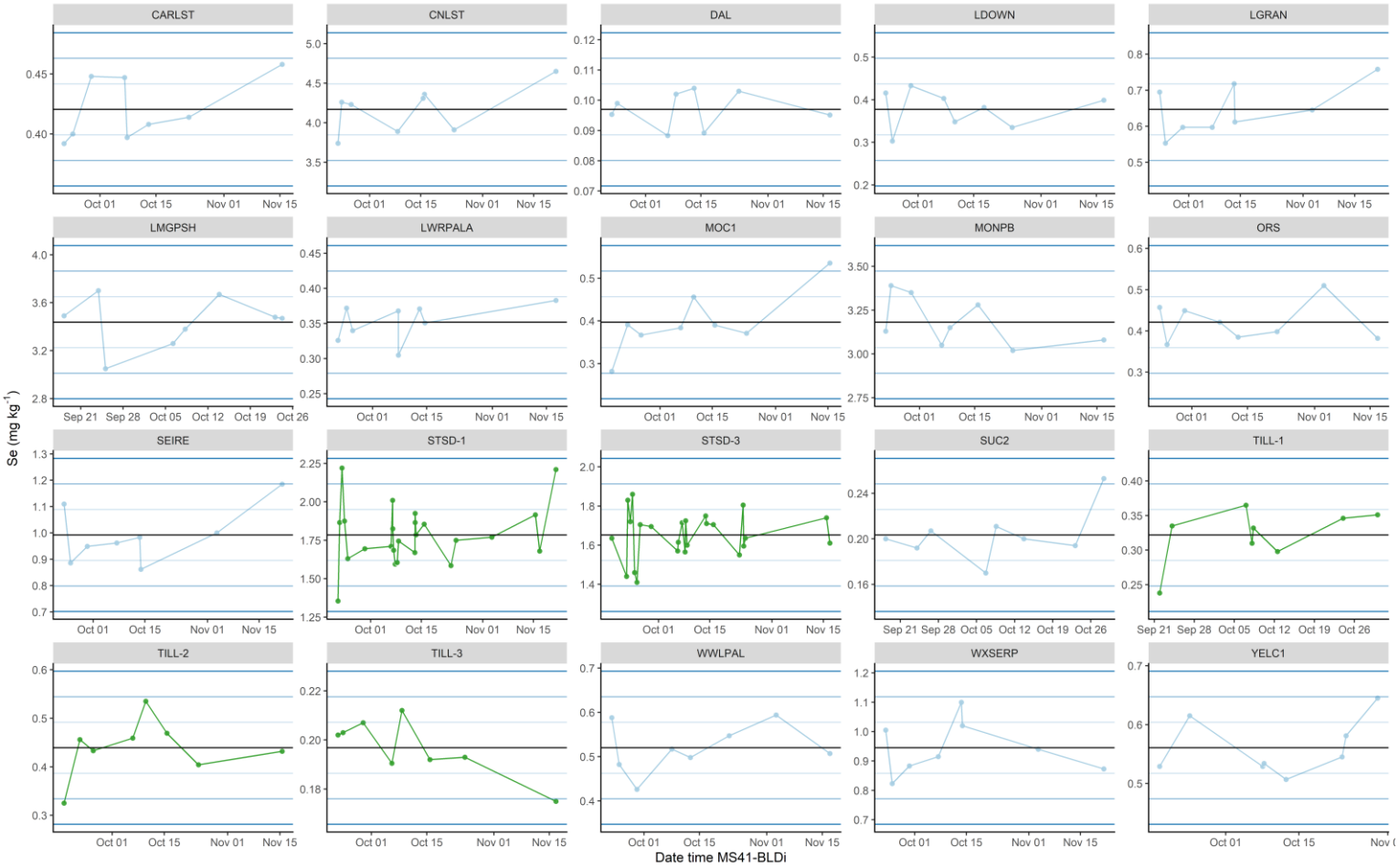


Antimony (Sb) sample data IQR: 0.222–0.578 mg kg^{-1}



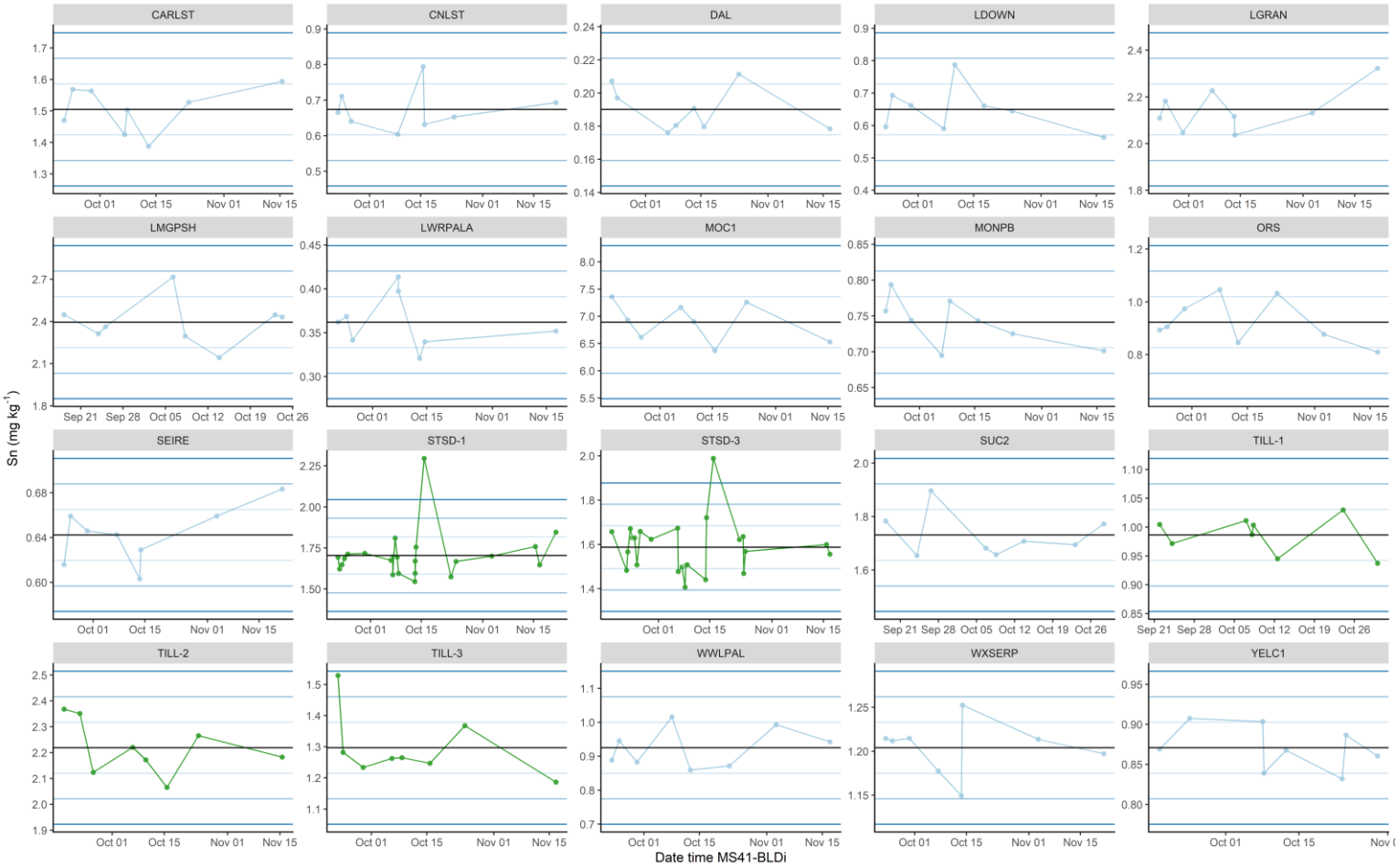
Scandium (Sc) sample data IQR: 1.28–4.31 mg kg^{-1}

Selenium (Se) MS41L-BLD



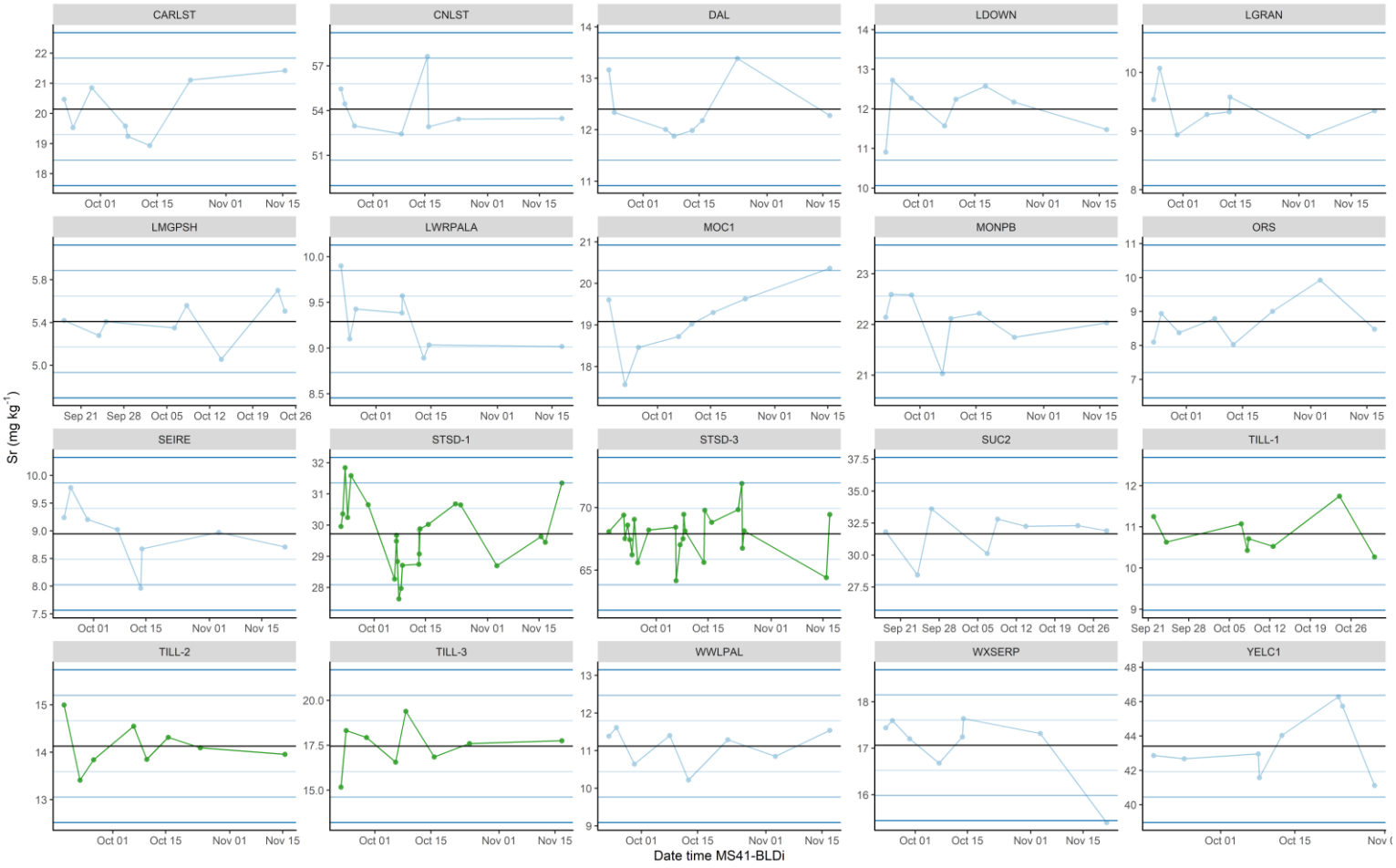
Selenium (Se) sample data IQR: 0.526–1.140 mg kg^{-1}

Tin (Sn) MS41L-BLD

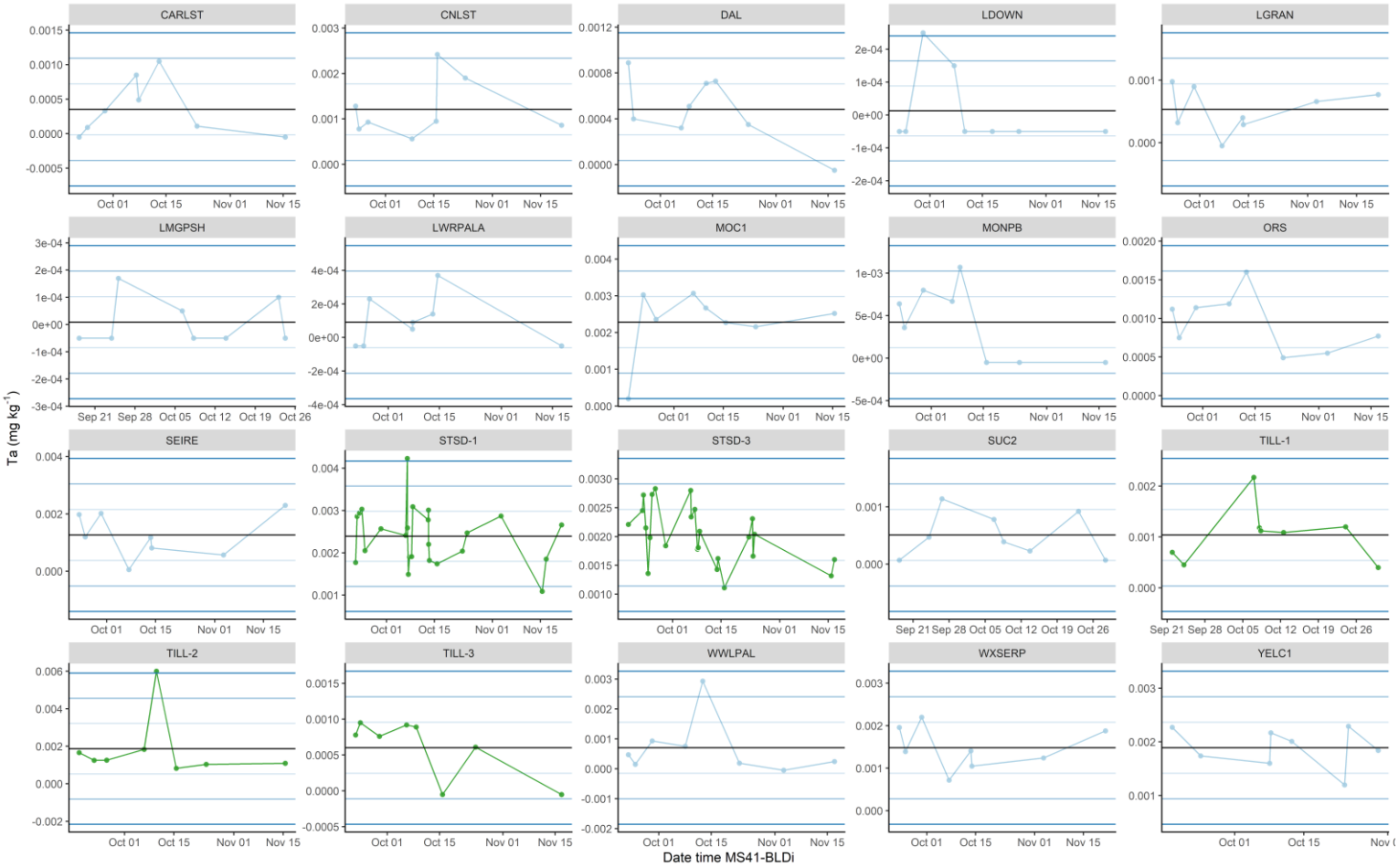


Tin (Sn) sample data IQR: 0.388–0.732 mg kg^{-1}

Strontium (Sr) MS41L-BLD

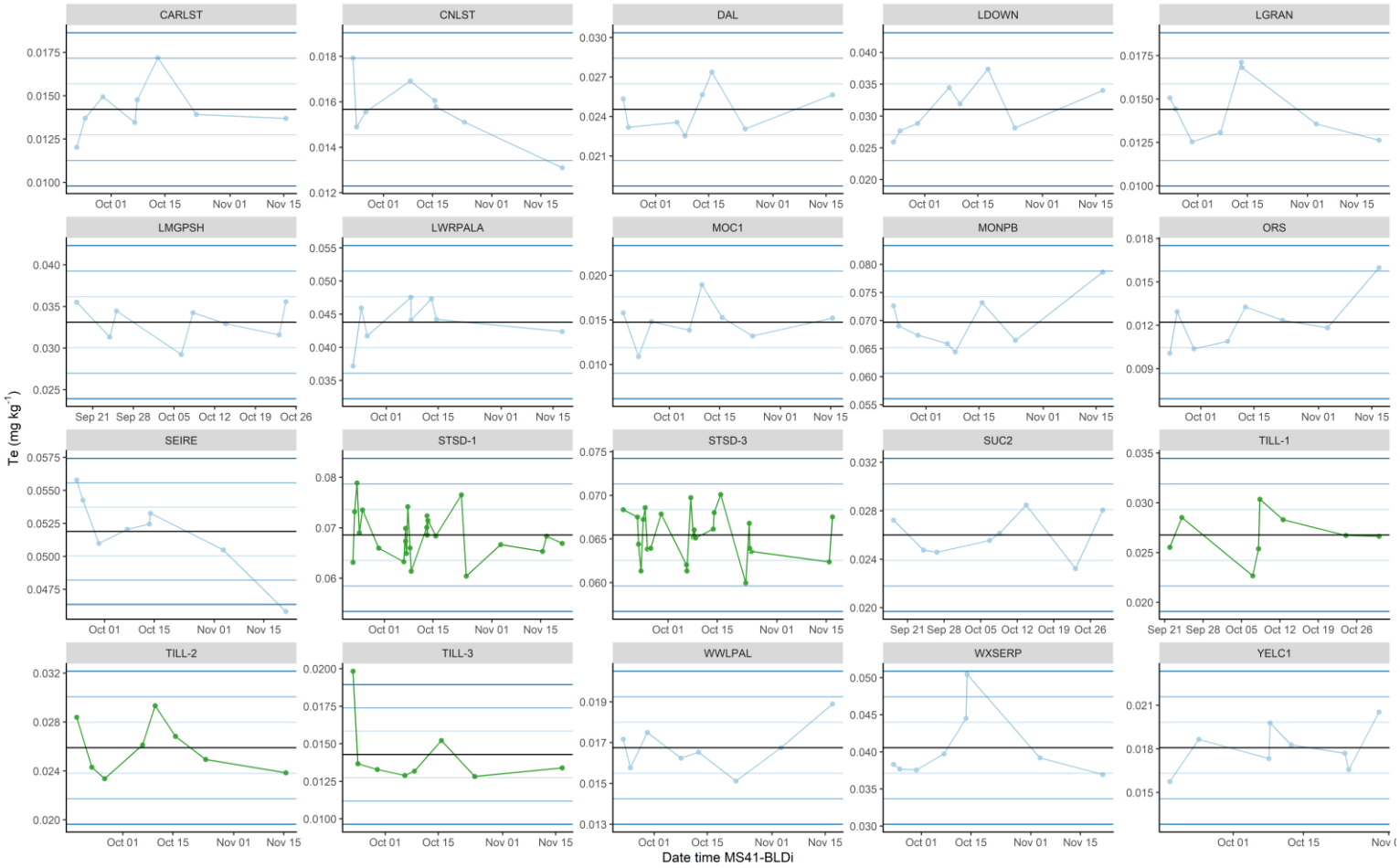


Strontium (Sr) sample data IQR: 16.4–44.8 mg kg^{-1}



Tantalum (Ta) sample data IQR: 0.00007-0.00074 mg kg^{-1}

Tellurium (Te) MS41L-BLD

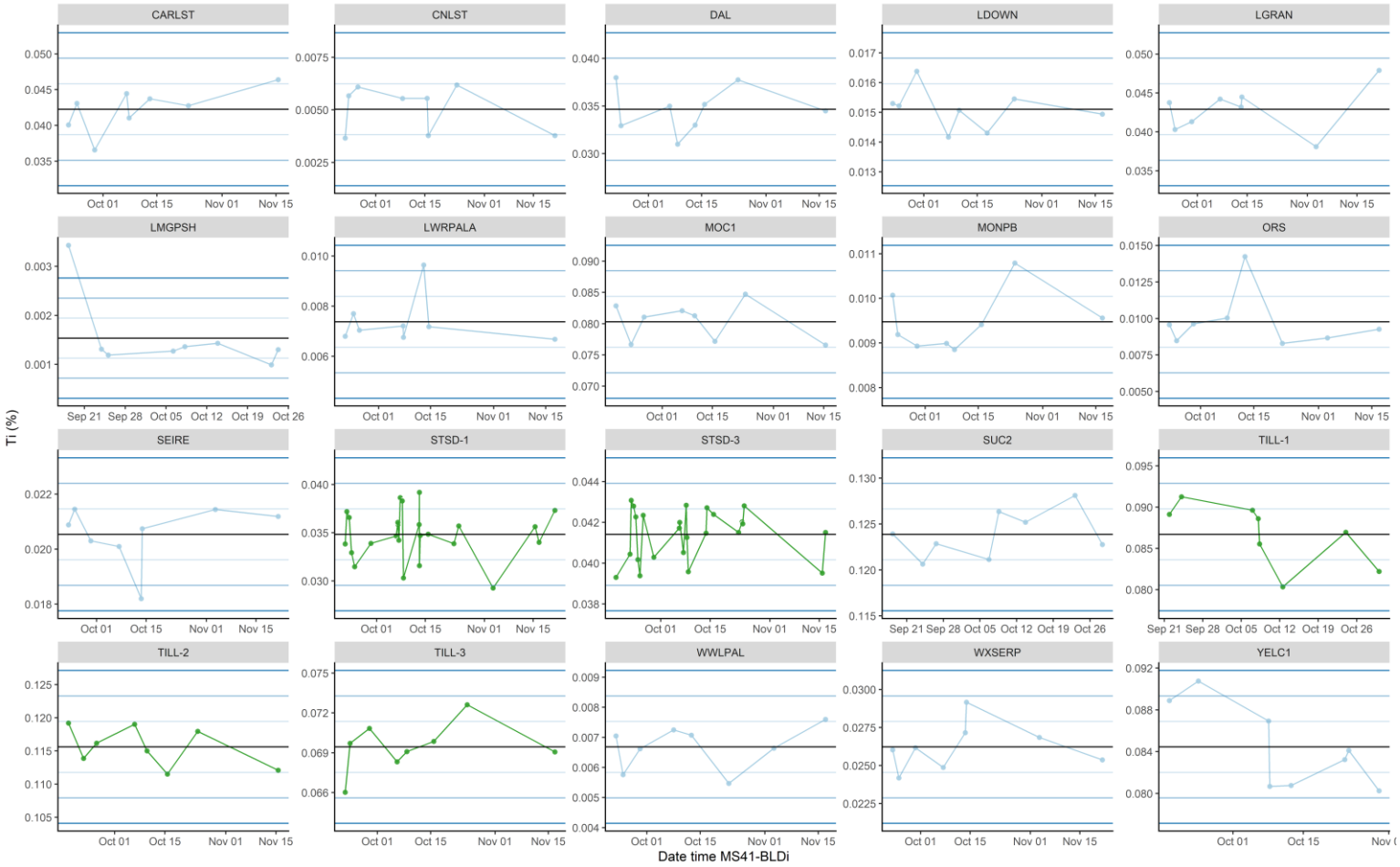


Tellurium (Te) sample data IQR: 0.00892-0.02320 mg kg^{-1}

Thorium (Th) MS41L-BLD

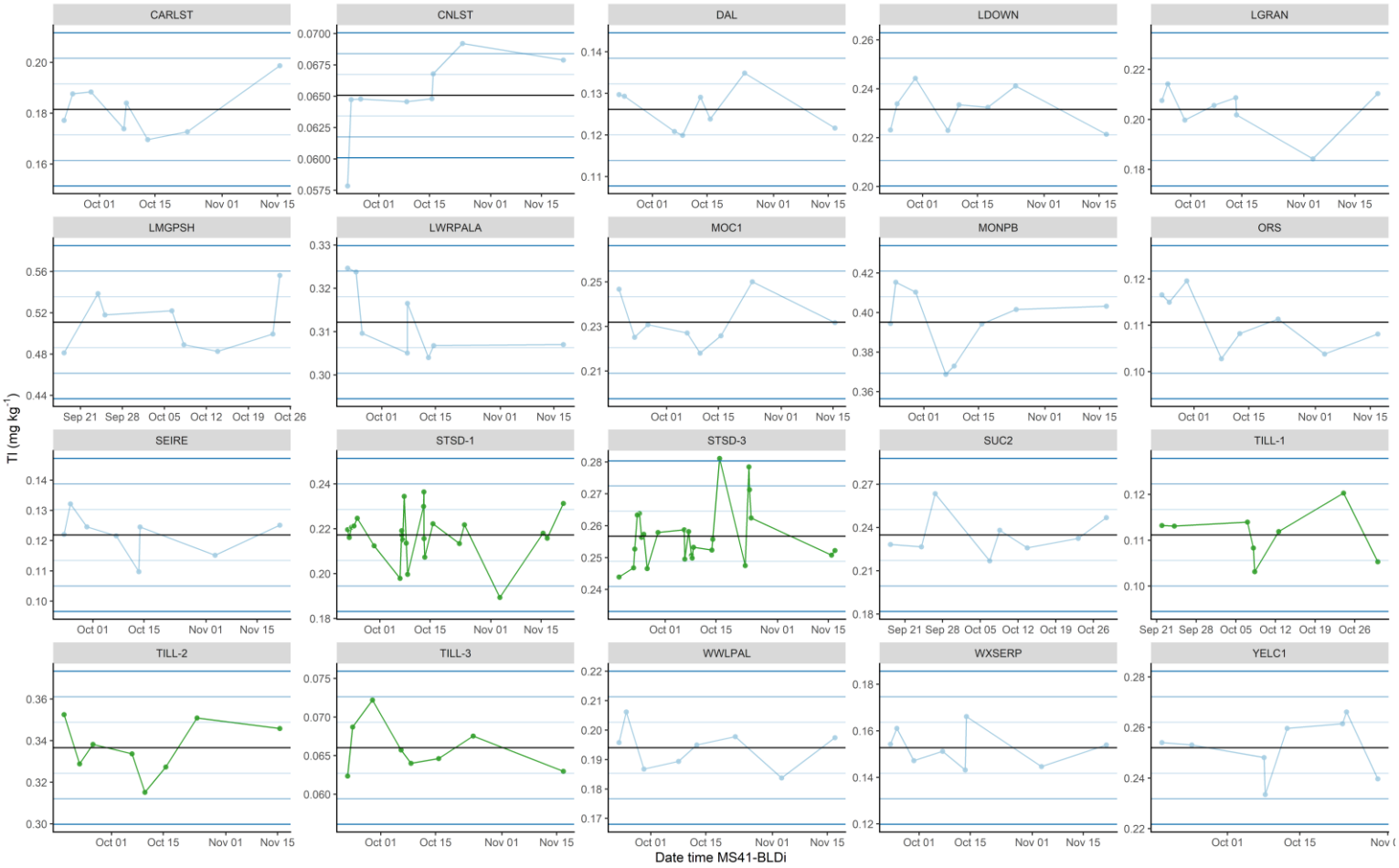
Thorium (Th) sample data IQR: 0.718–2.050 mg kg^{-1}

Titanium (Ti) MS41L-BLD



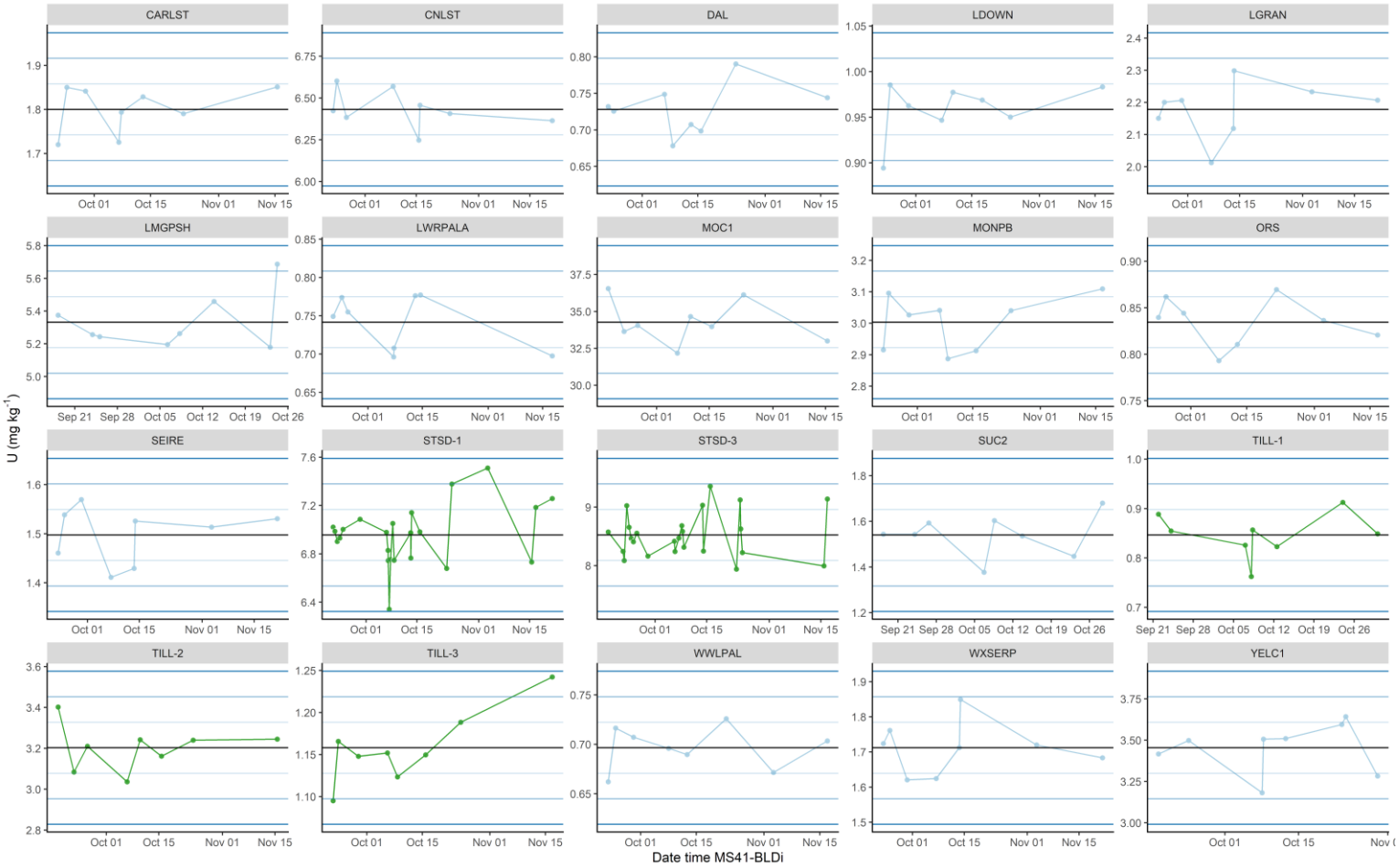
Titanium (Ti) sample data IQR: 0.00351-0.00819 %

Thallium (Tl) MS41L-BLD



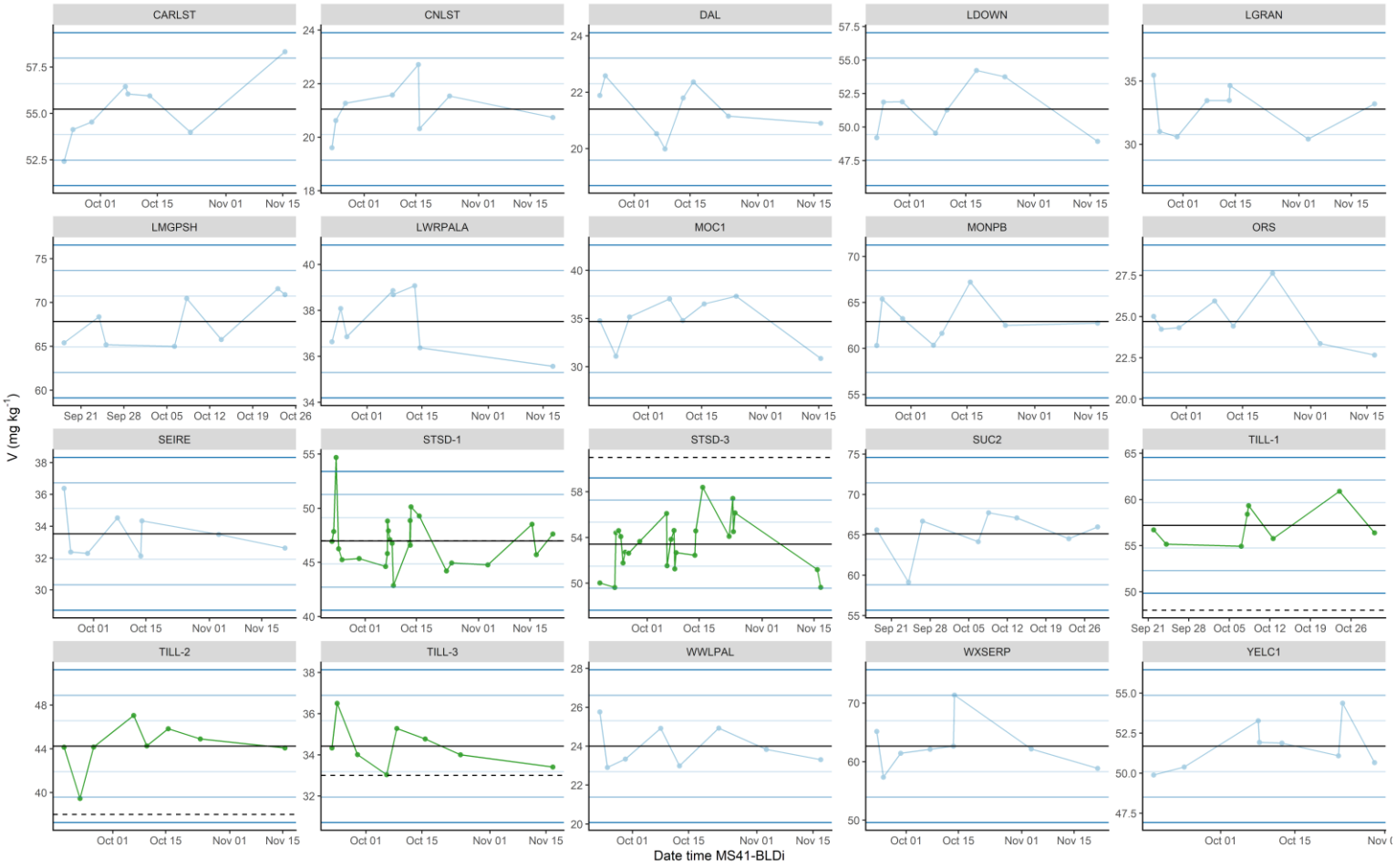
Thallium (Tl) sample data IQR: 0.108–0.290 mg kg^{-1}

Uranium (U) MS41L-BLD



Uranium (U) sample data IQR: 0.761–1.400 mg kg^{-1}

Vanadium (V) MS41L-BLD

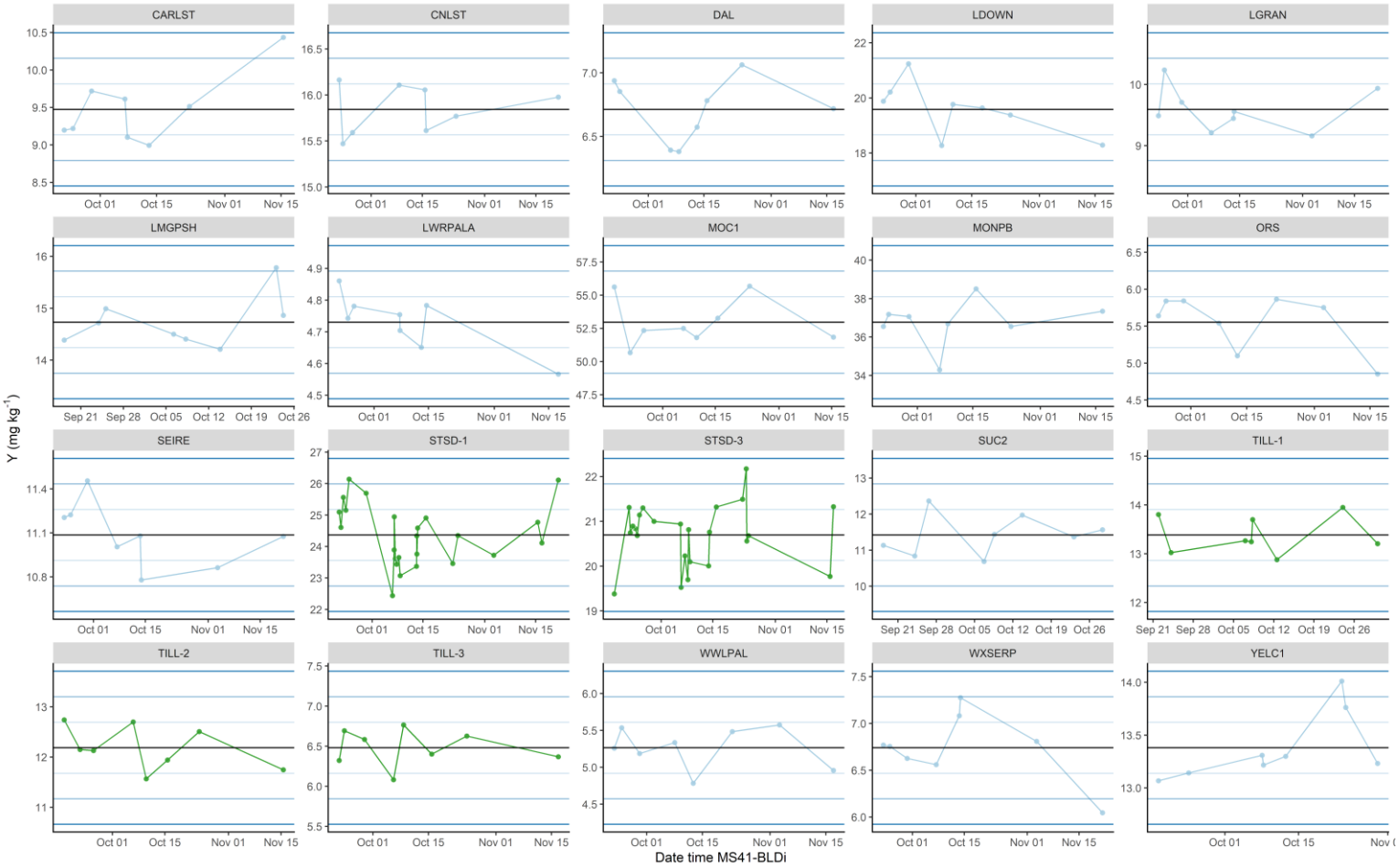


Vanadium (V) sample data IQR: 17.0–40.6 mg kg^{-1}

Tungsten (W) MS41L-BLD

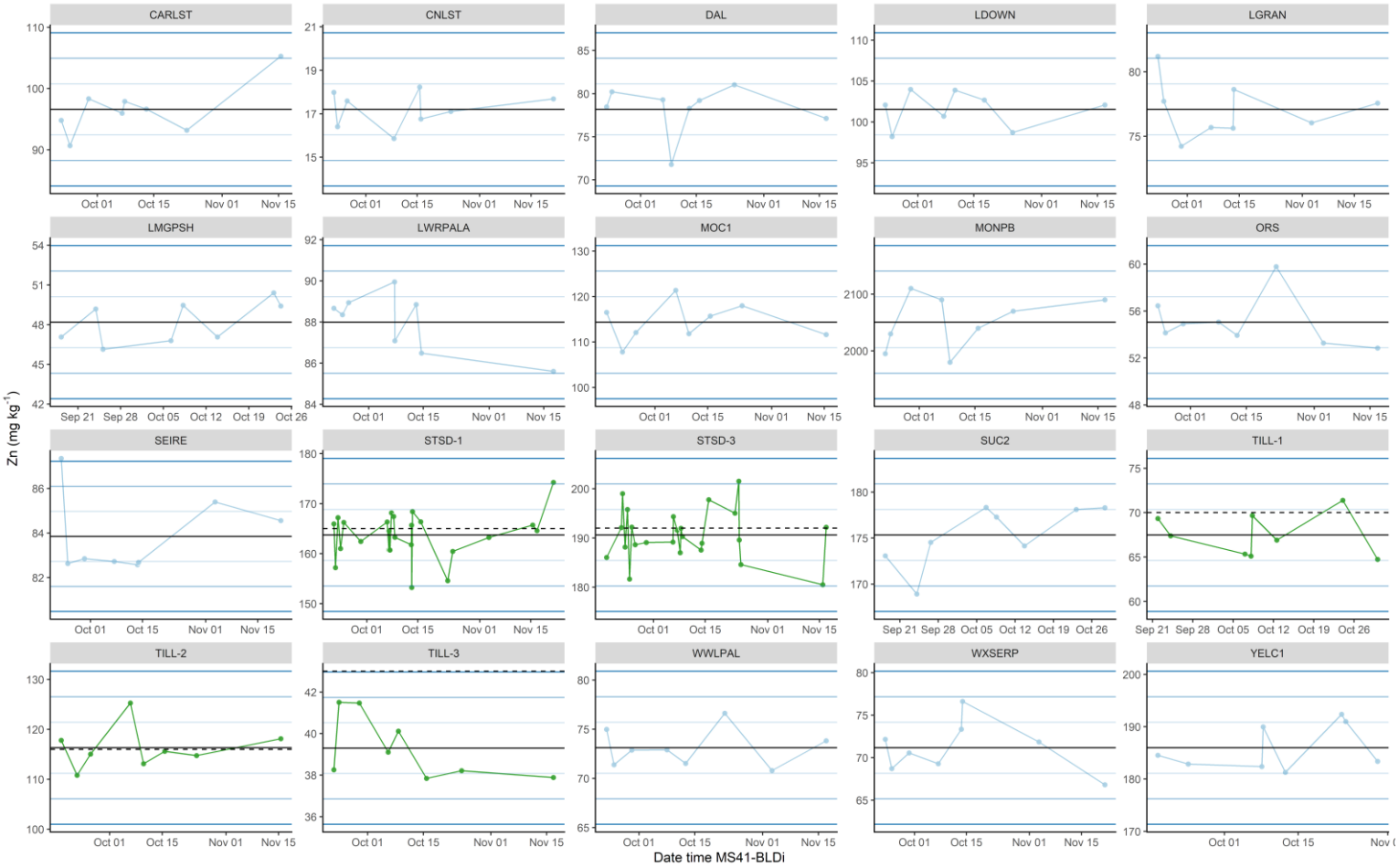
Tungsten (W) sample data IQR: 0.0349-0.0670 mg kg^{-1}

Yttrium (Y) MS41L-BLD



Yttrium (Y) sample data IQR: 5.21–21.70 mg kg^{-1}

Zinc (Zn) MS41L-BLD



Zinc (Zn) sample data IQR: 32.9–94.9 mg kg^{-1}

Zirconium (Zr) MS41L-BLD

Zirconium (Zr) sample data IQR: 1.08–3.47 mg kg^{-1}

B. Univariate exploratory data analysis: sample site data general release

In this appendix all regular samples (*i.e.* non-QCS) samples data are presented (in the same order as data are reported by instrument and distributed):

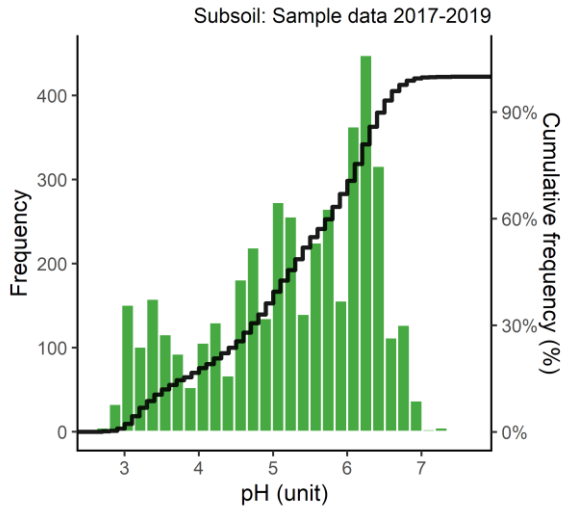
- The first chart (left) is the combined cumulative frequency and histogram. The histogram frequency (y axis left) and the cumulative frequency % (y axis right) are plotted against the analyte concentration (x axis).
- The second chart (right) is the same but data are $\log_{10}$ transformed (an exception is pH).

These data are censored. All "<LLD" values have been replaced with 0.5*"LLD" and for these deeper topsoil data where the LLDs vary by batch, a working LLD has been indicated for each analyte to cover all sample data. Concentration units are shown in parentheses.

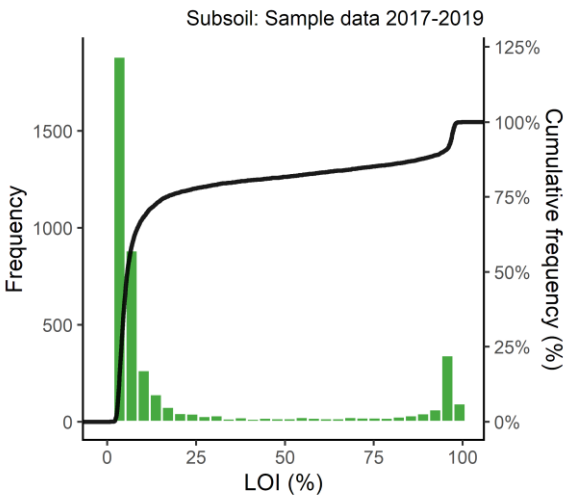
Typically a log transformation results in a less skewed distribution, and geochemical data are broadly log-normal. Censored data will sometimes display as an isolated histogram bar away from the normal data population above the LLD.

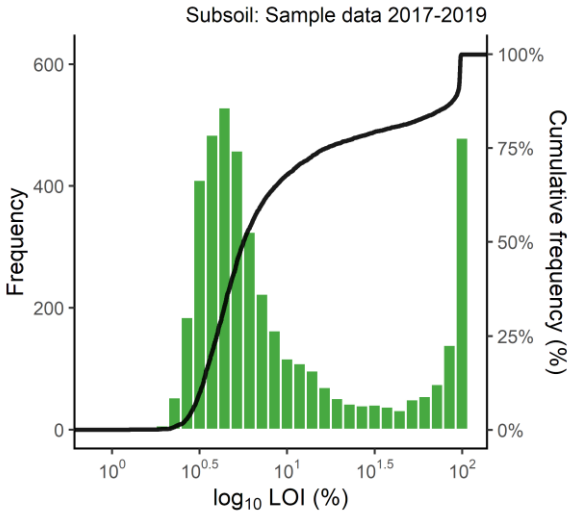
pH and LOI sample site data

Soil pH ($CaCl_2$)



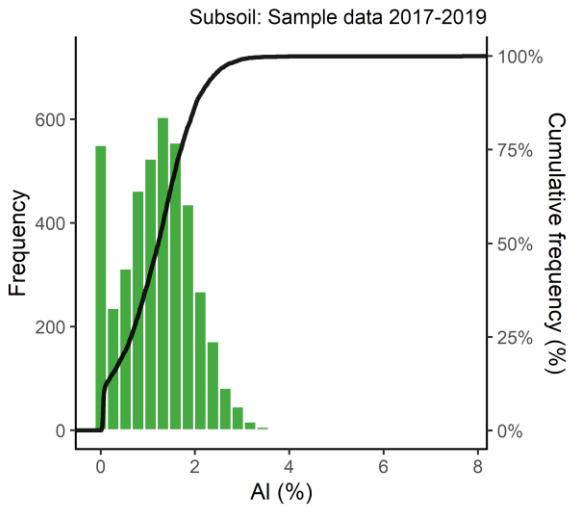
Soil loss-on-ignition (at 450C) %

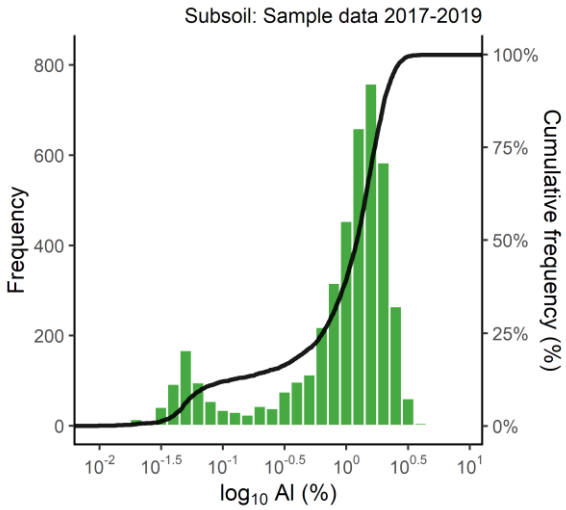




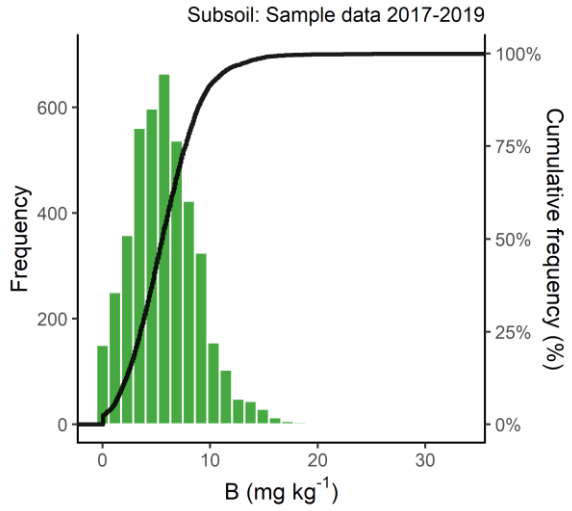
ICP_{ar} sample site data

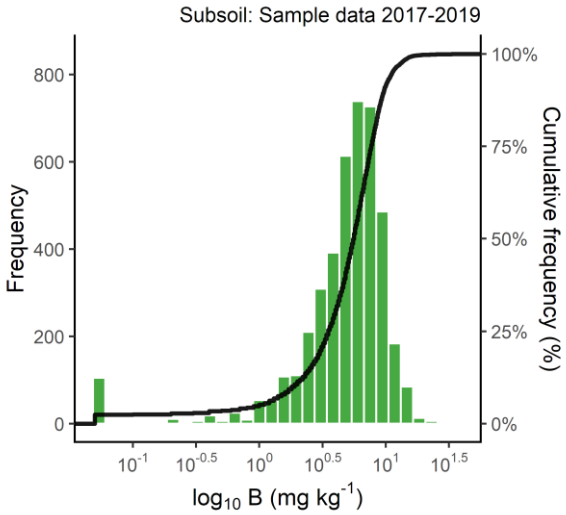
Aluminium (Al) ICP_{ar}



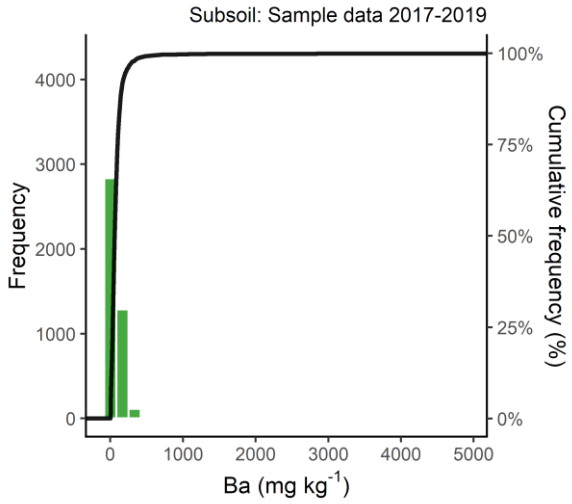


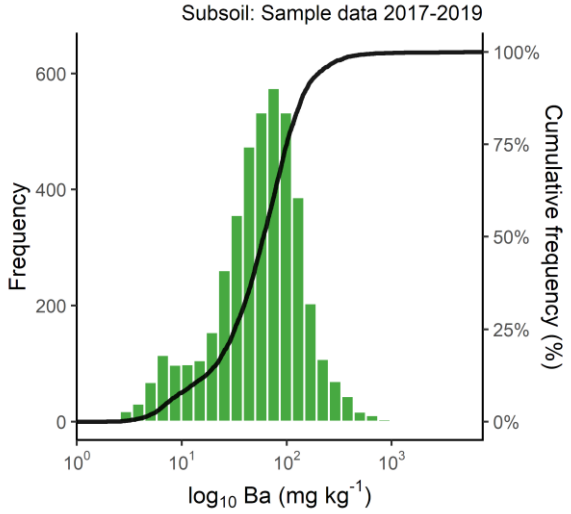
Boron (B) ICP_{ar}



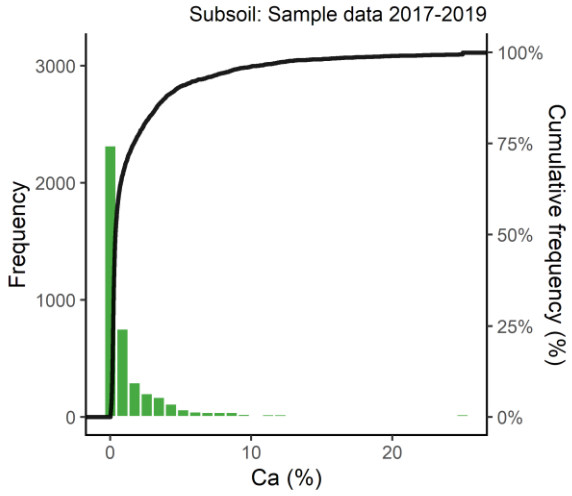


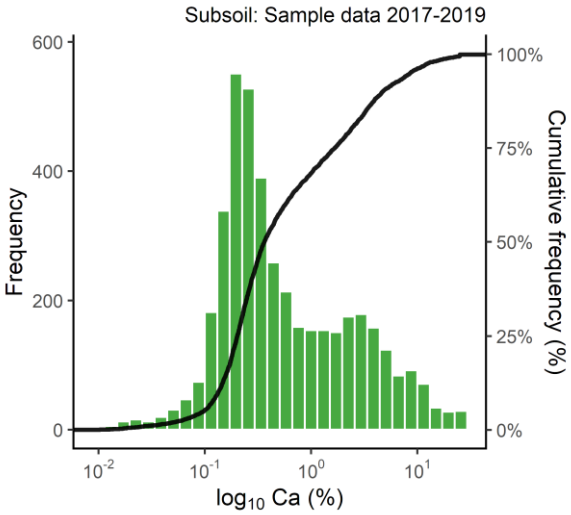
Barium (Ba) ICP_{ar}



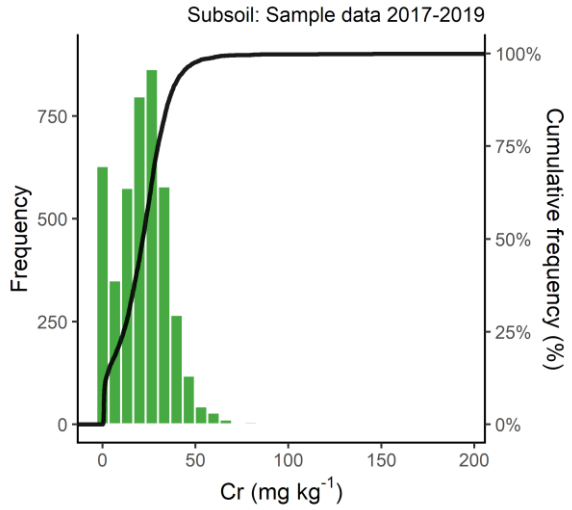


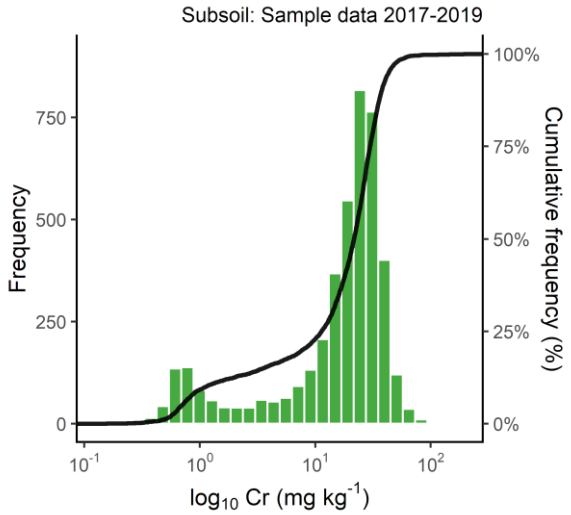
Calcium (Ca) ICP_{ar}



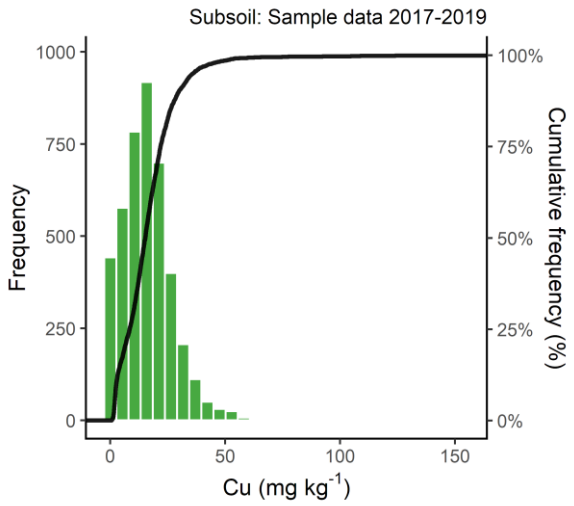


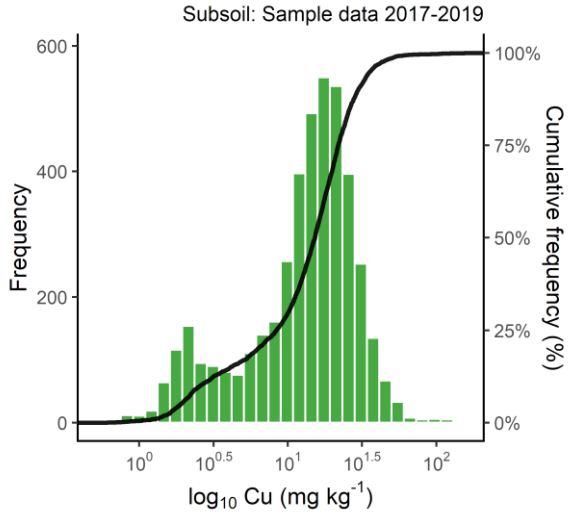
Chromium (Cr) ICP_{ar}



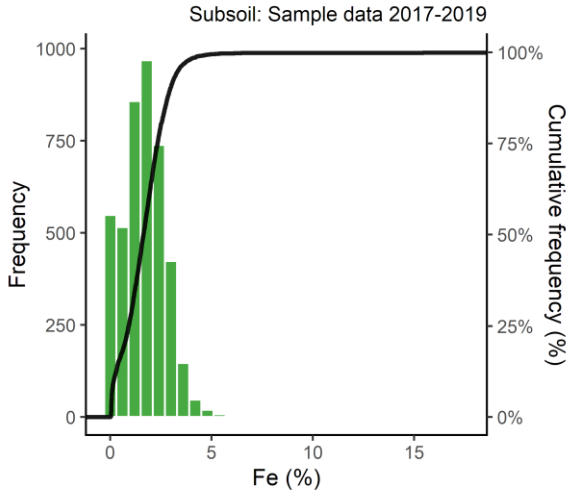


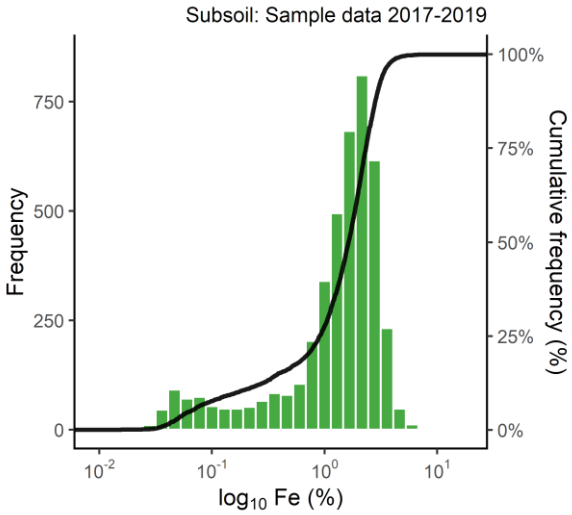
Copper (Cu) ICP_{ar}



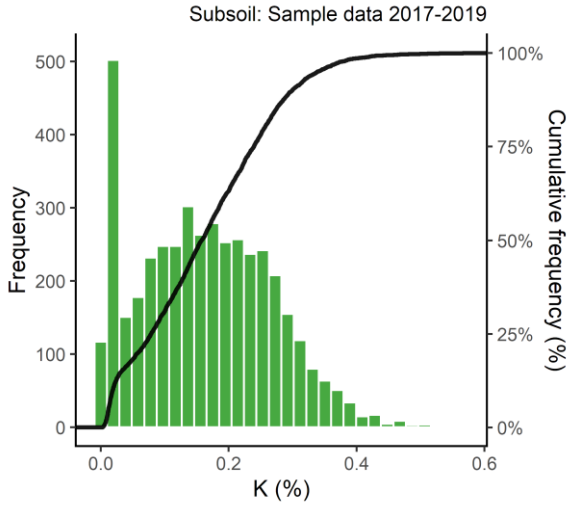


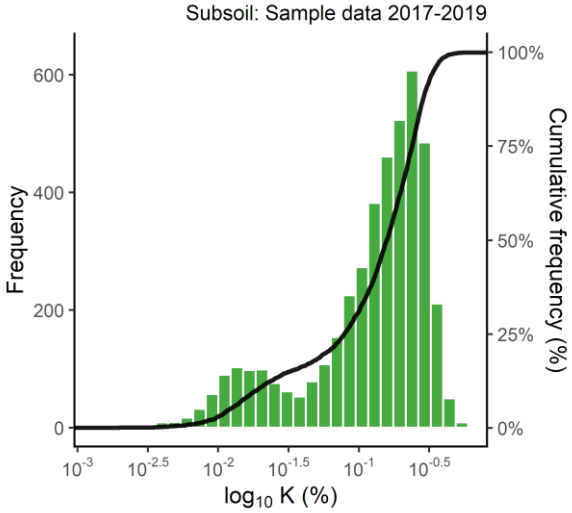
Iron (Fe) ICP_{ar}



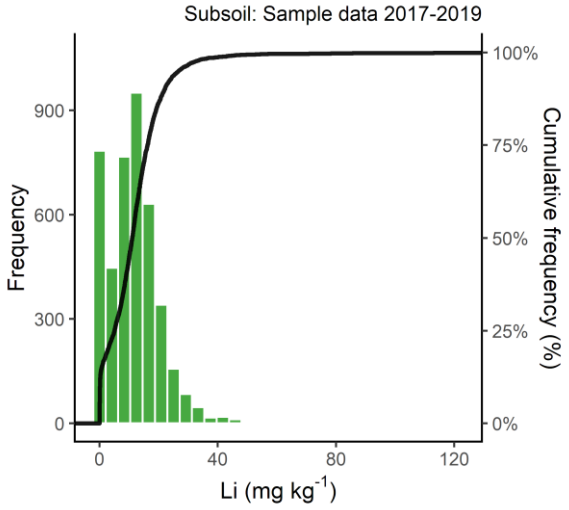


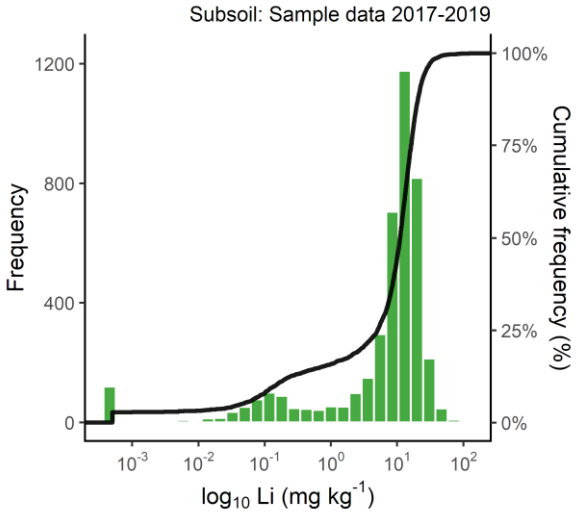
Potassium (K) ICP_{ar}



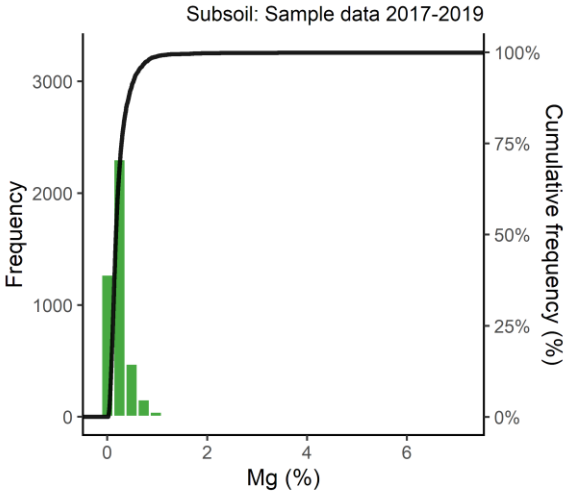


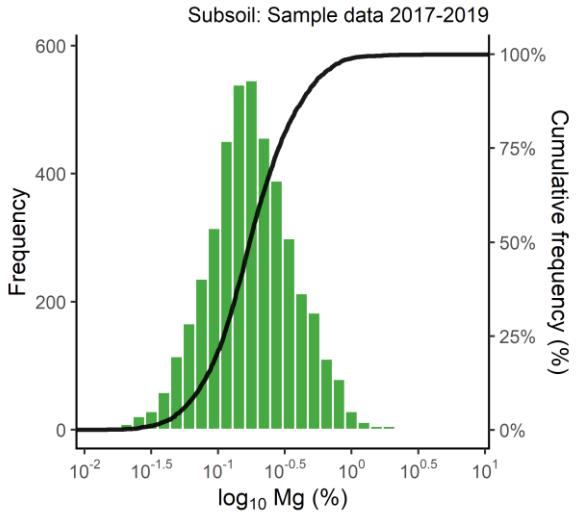
Lithium (Li) ICP_{ar}



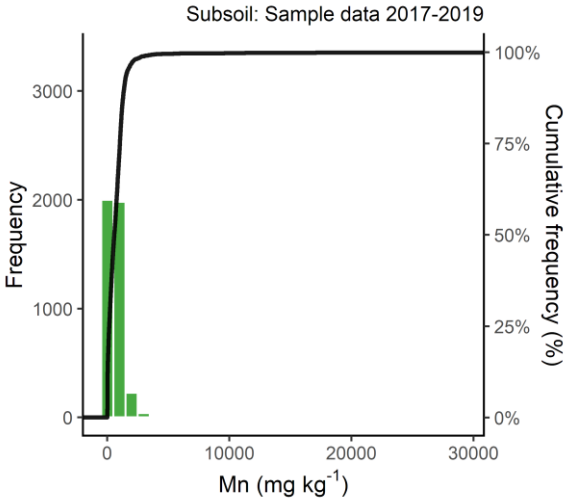


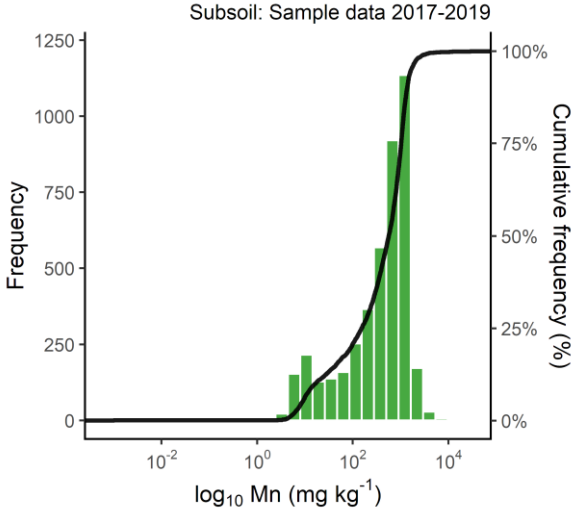
Magnesium (Mg) ICP_{ar}



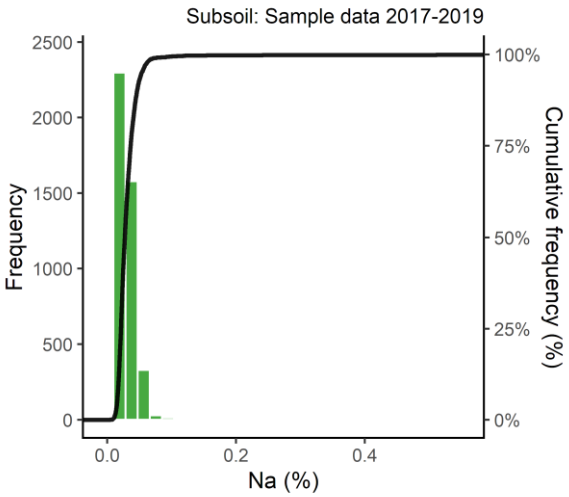


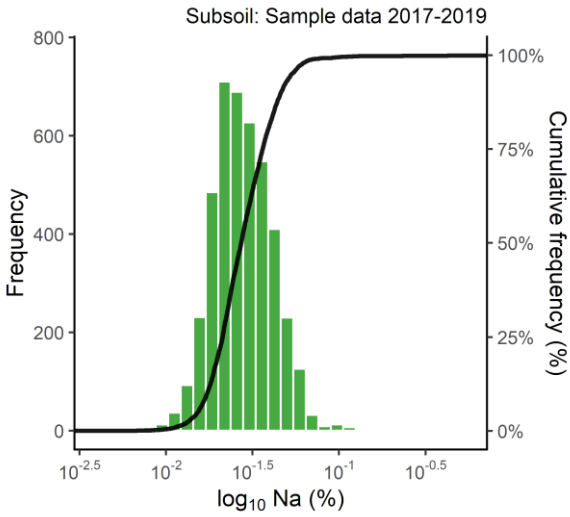
Manganese (Mn) ICP_{ar}



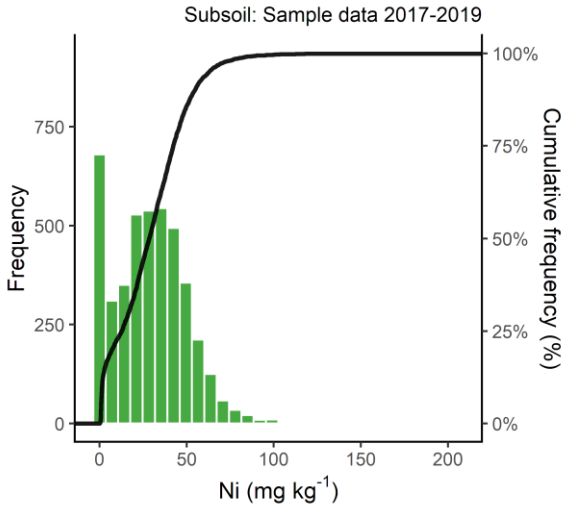


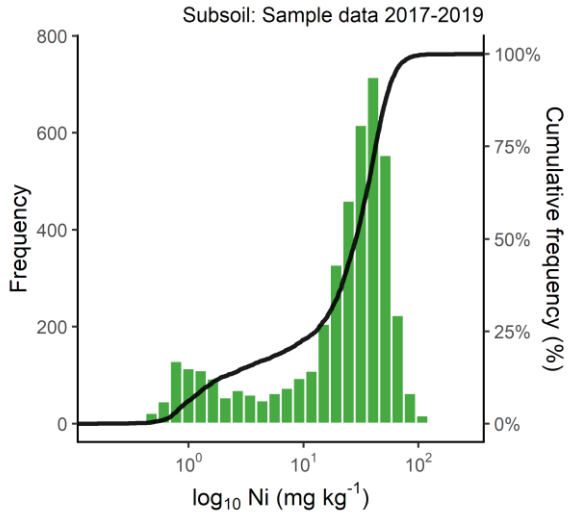
Sodium (Na) ICP_{ar}



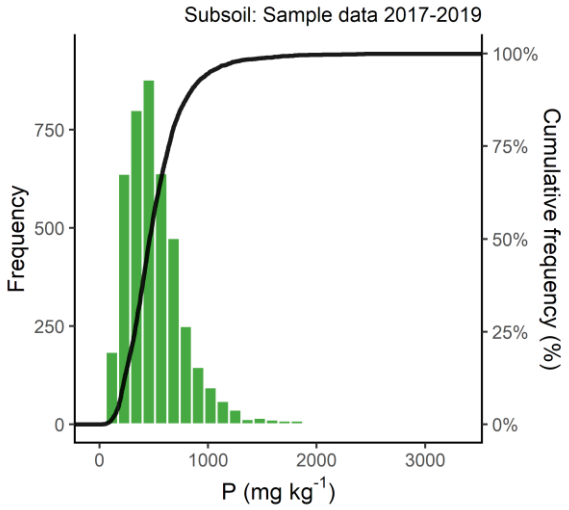


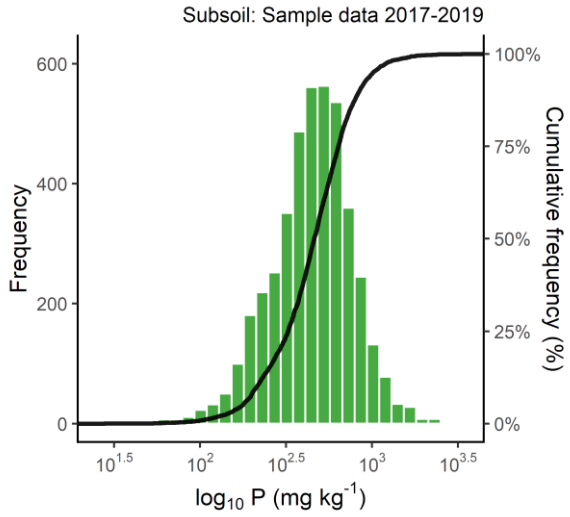
Nickel (Ni) ICP_{ar}



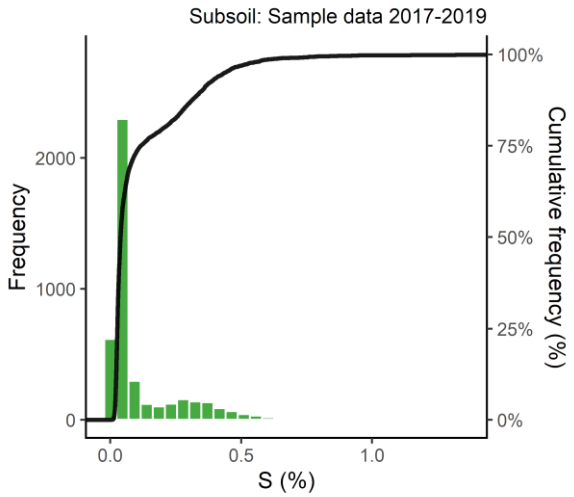


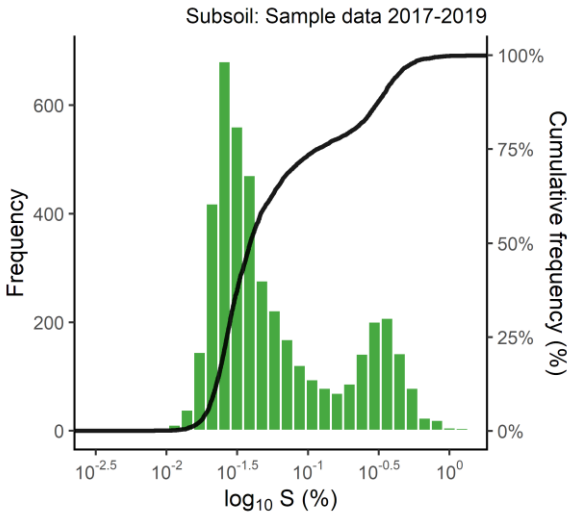
Phosphorus (P) ICP_{ar}



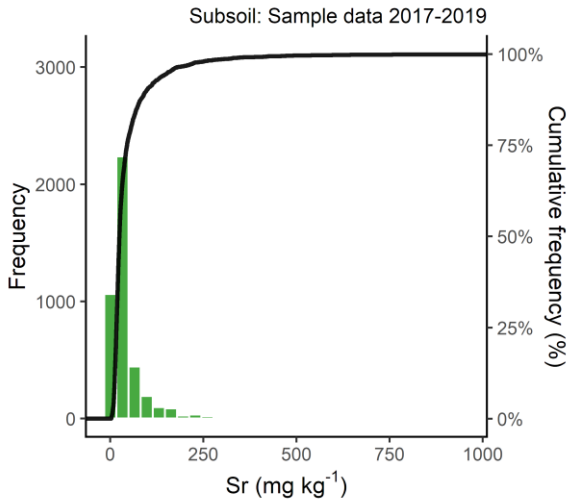


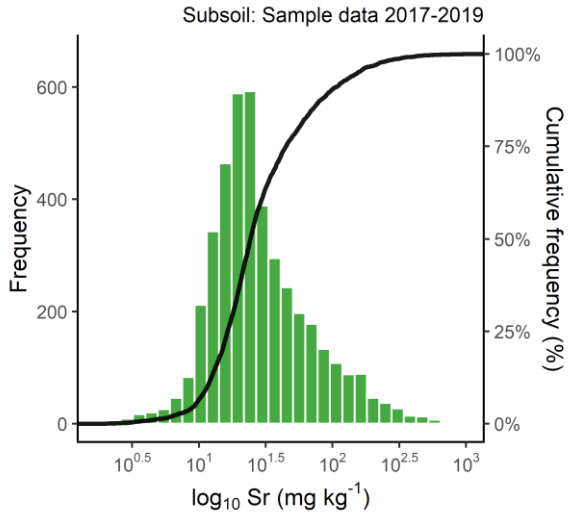
Sulphur (S) ICP_{ar}



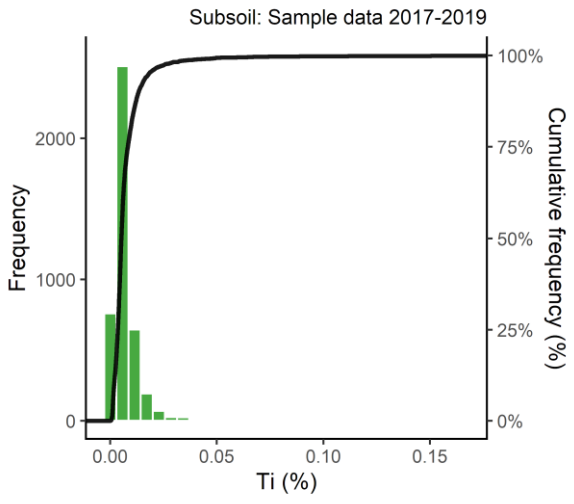


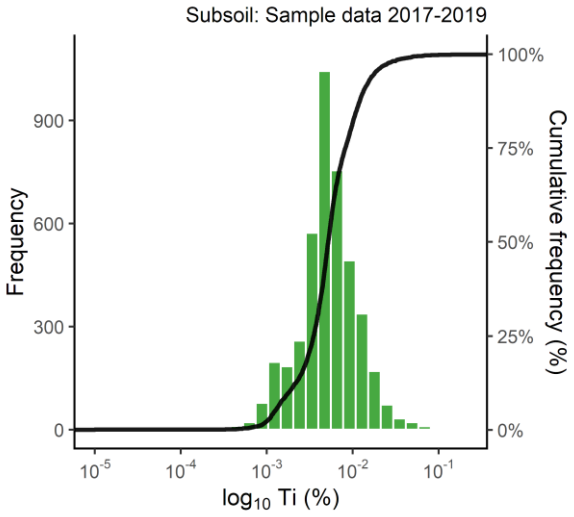
Strontium (Sr) ICP_{ar}



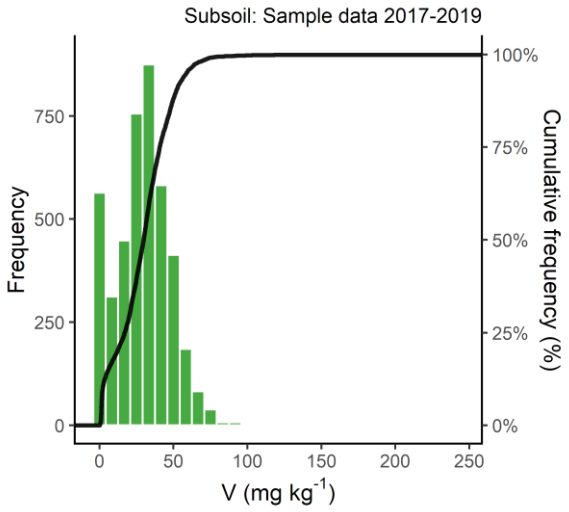


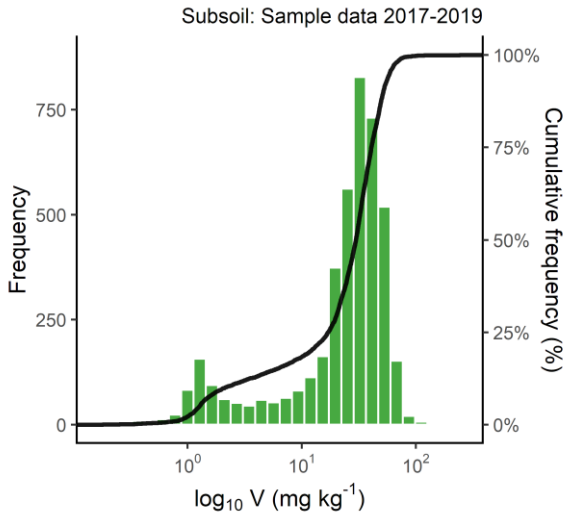
Titanium (Ti) ICP_{ar}



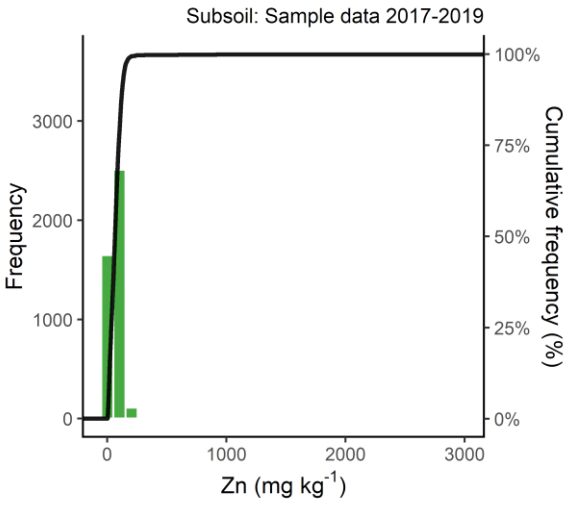


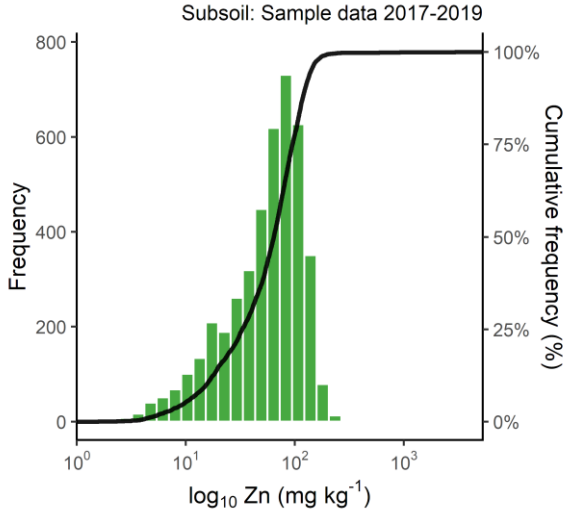
Vanadium (V) ICP_{ar}



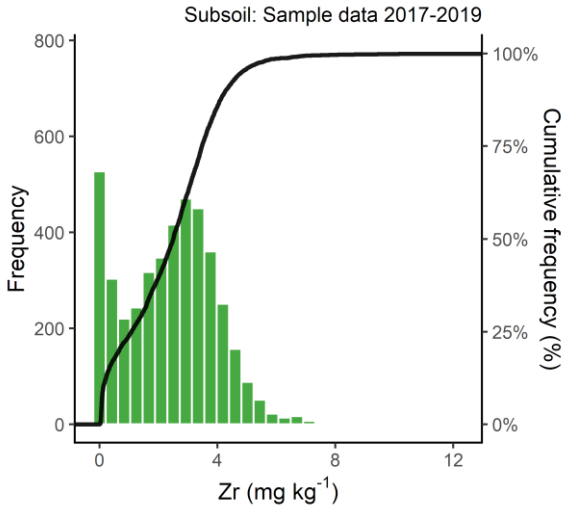


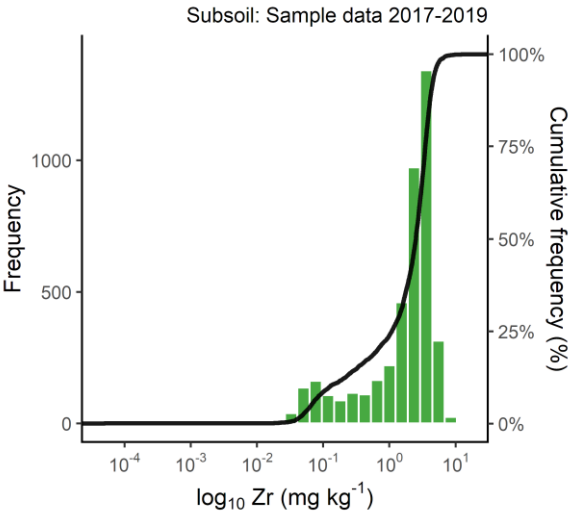
Zinc (Zn) ICP_{ar}



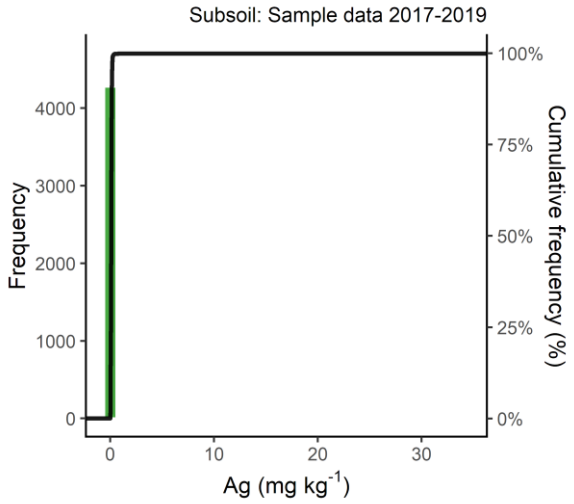


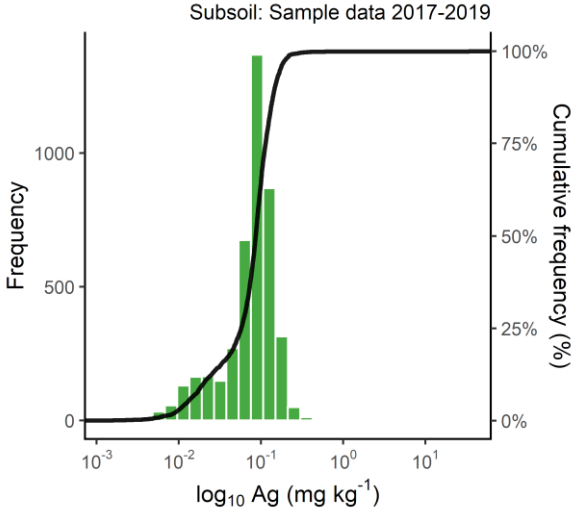
Zirconium (Zr) ICP_{ar}



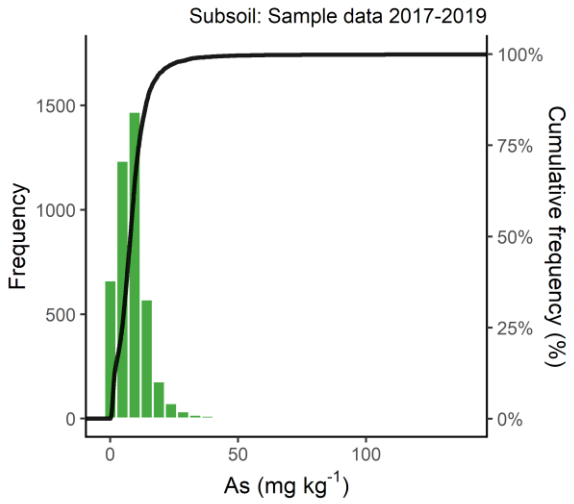


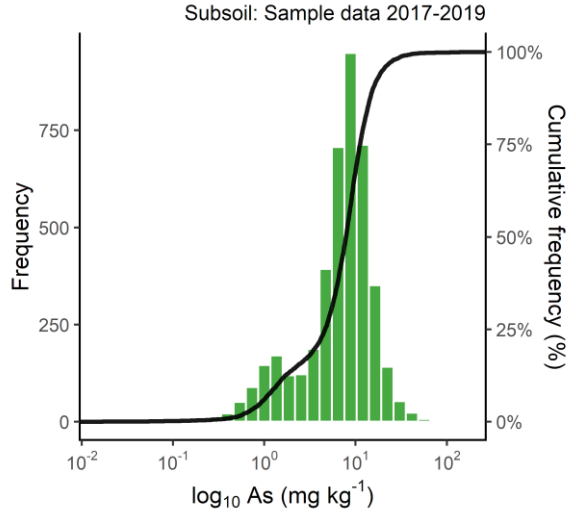
Silver (Ag) ICP_{ar}



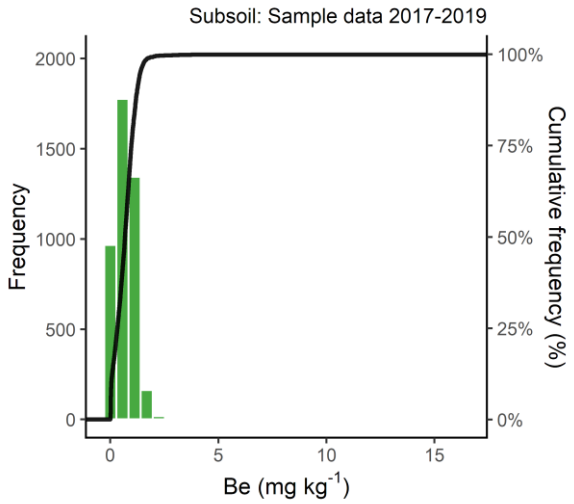


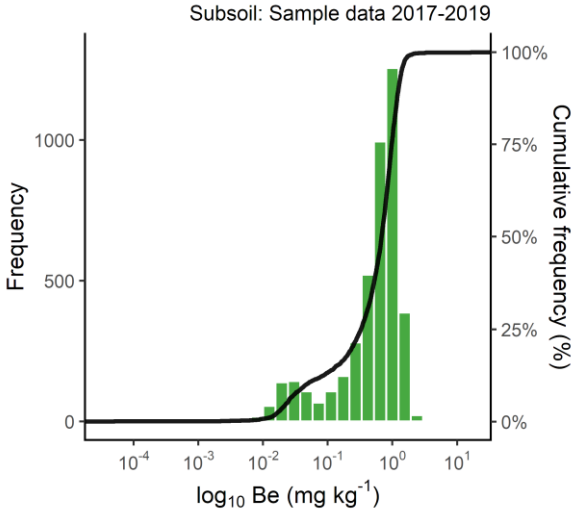
Arsenic (As) ICP_{ar}



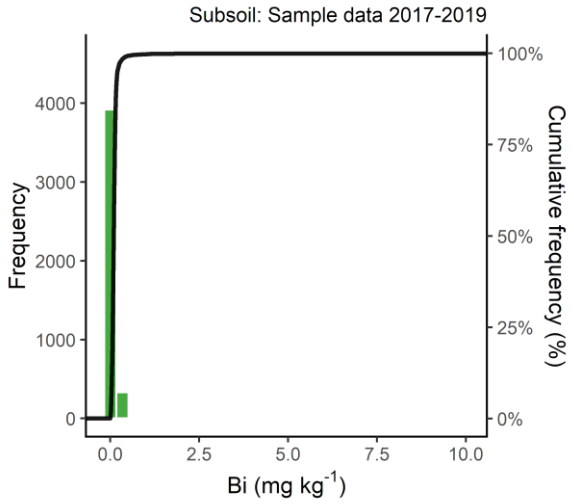


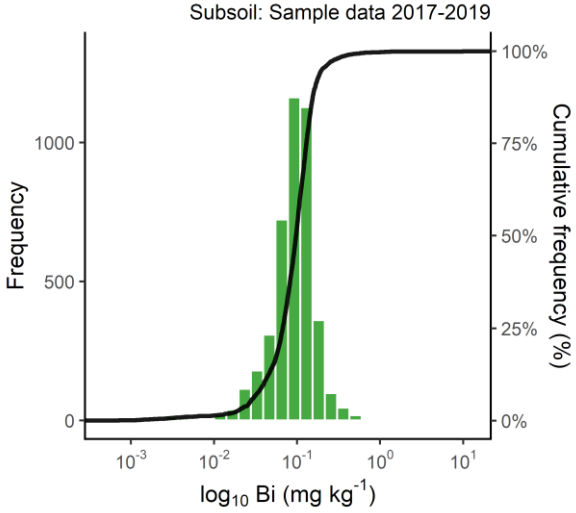
Beryllium (Be) ICP_{ar}



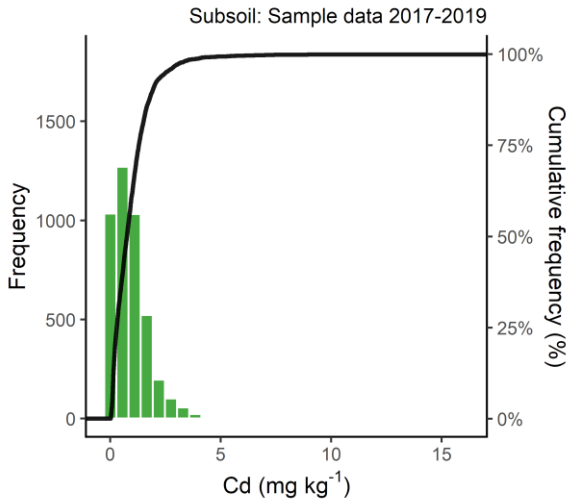


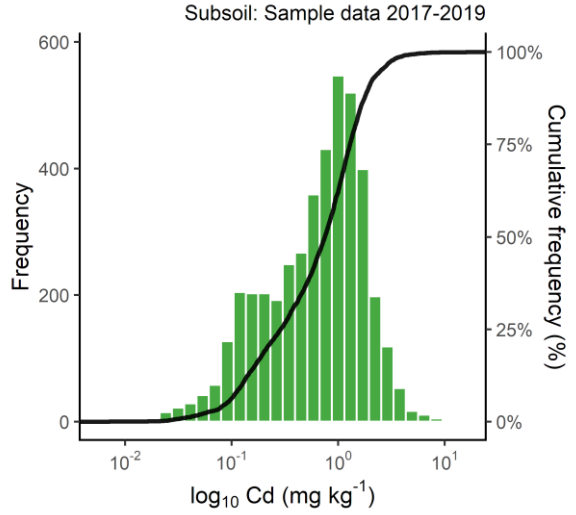
Bismuth (Bi) ICP_{ar}



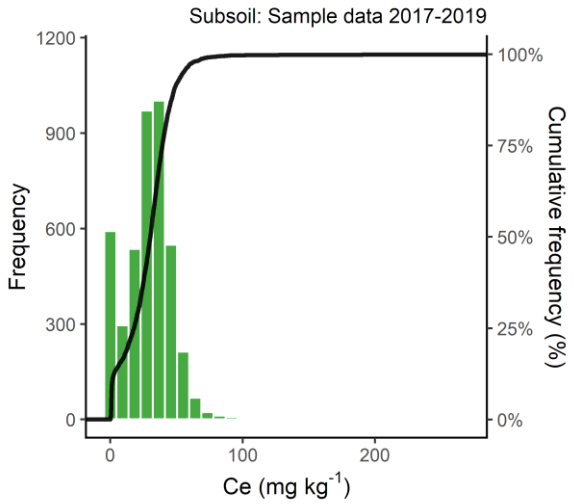


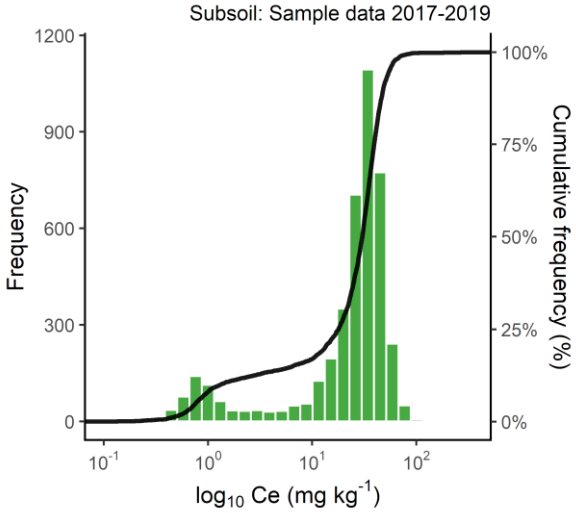
Cadmium (Cd) ICP_{ar}



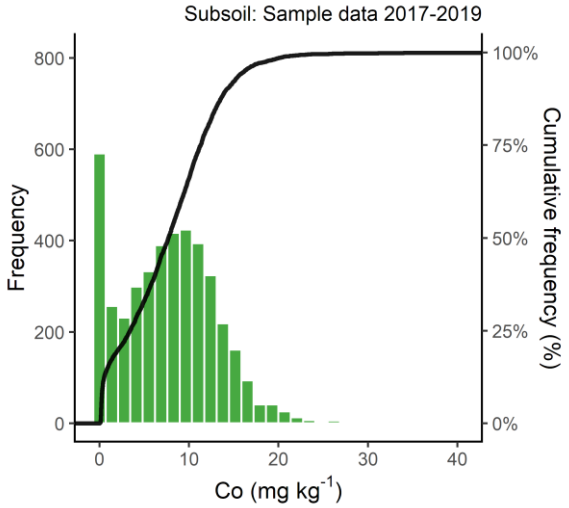


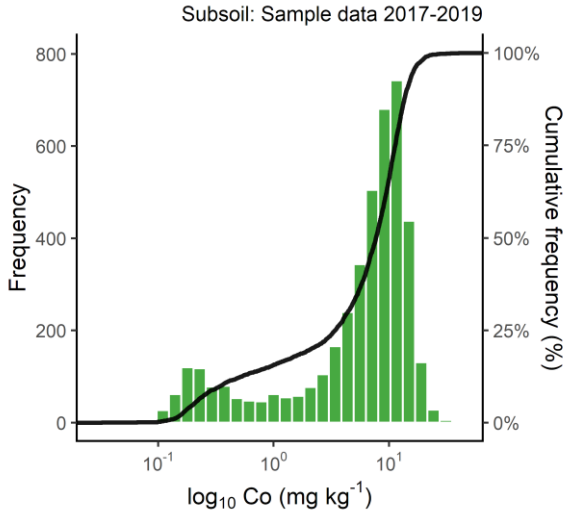
Cerium (Ce) ICP_{ar}



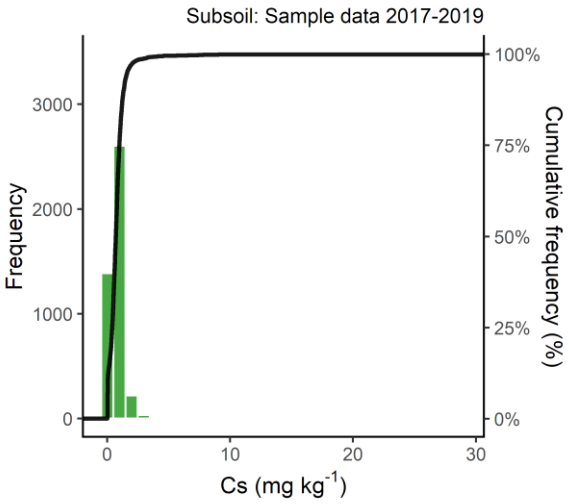


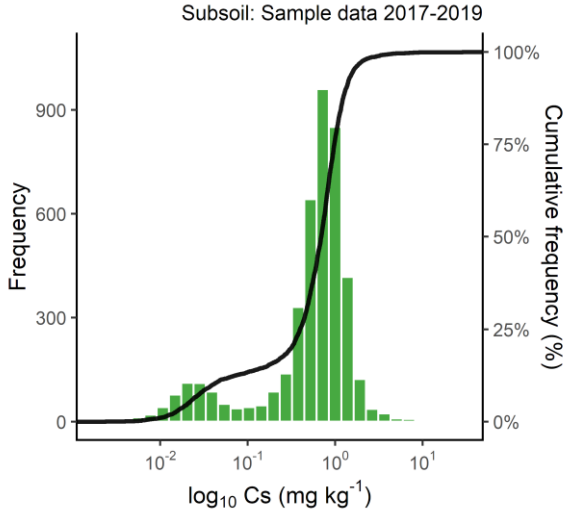
Cobalt (Co) ICP_{ar}



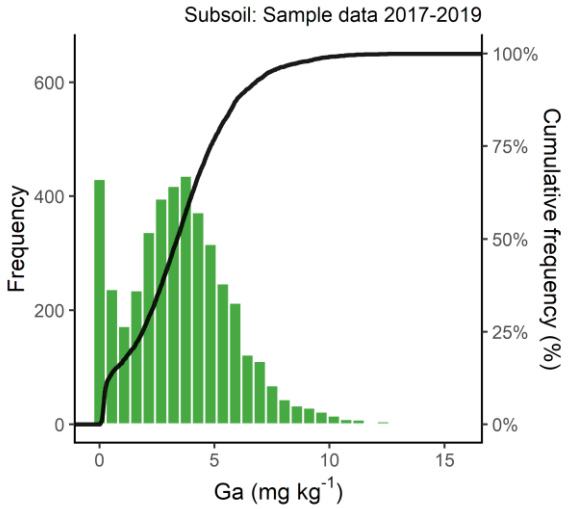


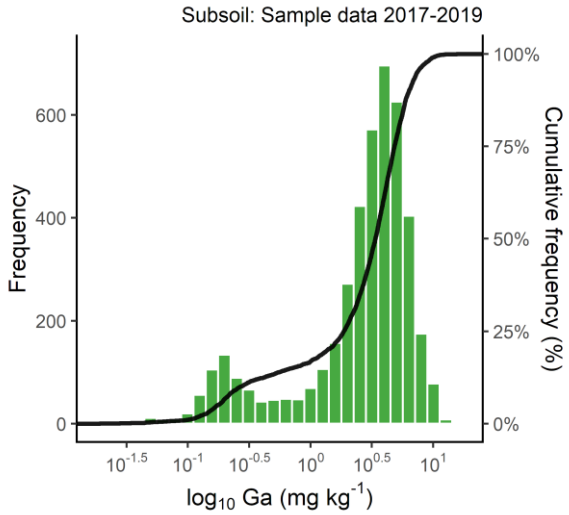
Caesium (Cs) ICP_{ar}



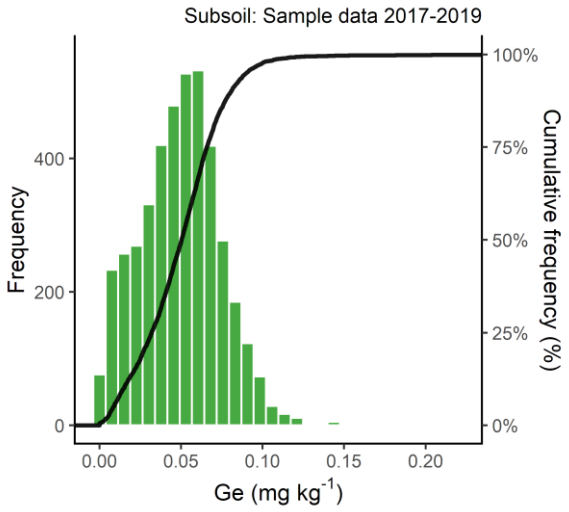


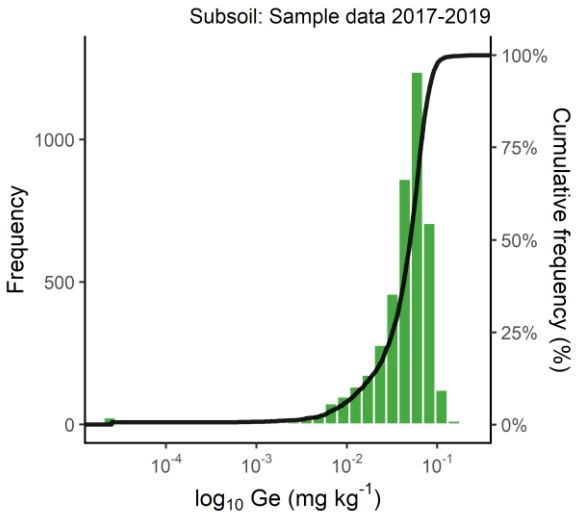
Gallium (Ga) ICP_{ar}



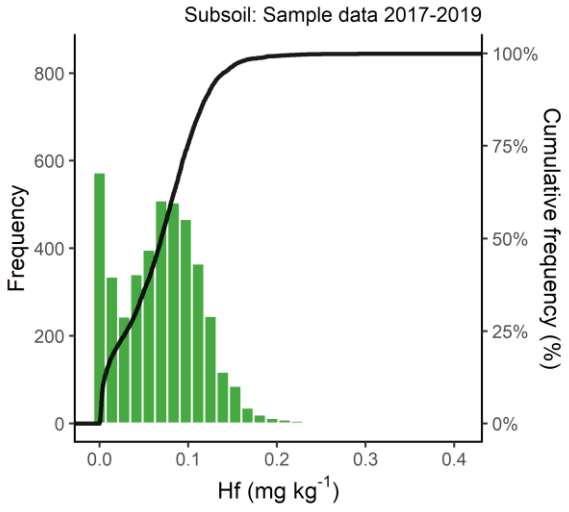


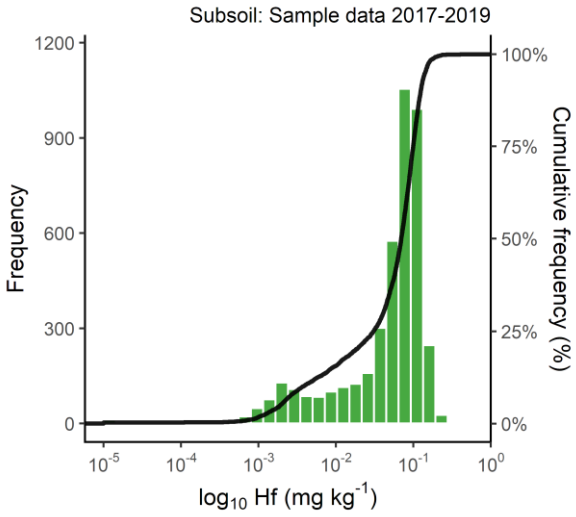
Germanium (Ge) ICP_{ar}



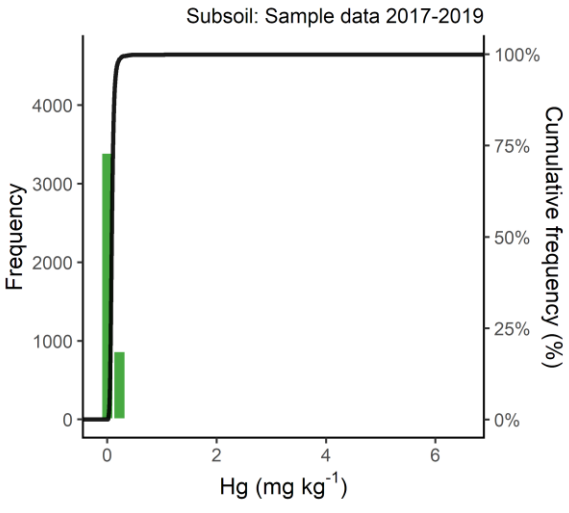


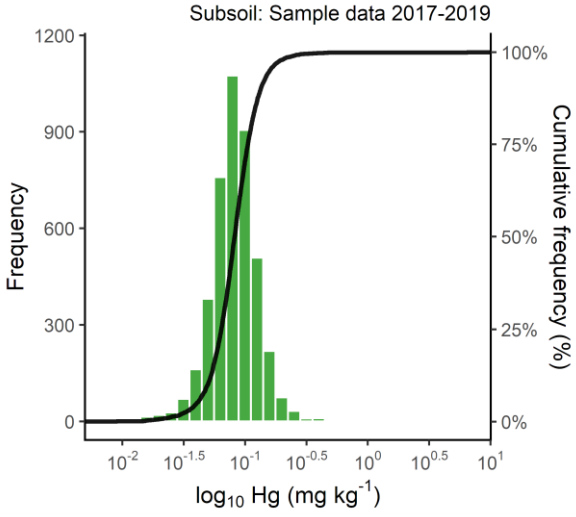
Hafnium (Hf) ICP_{ar}



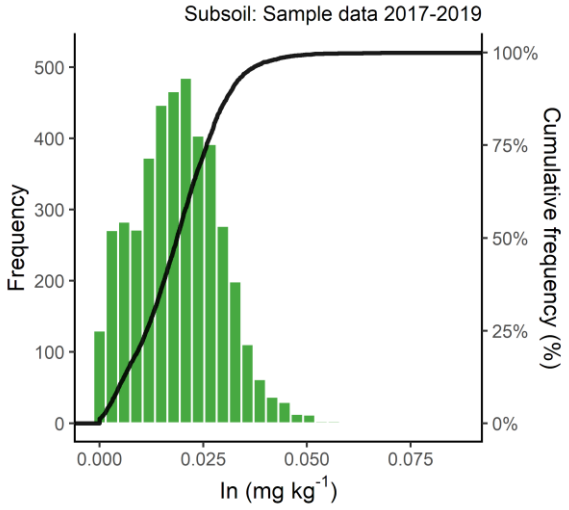


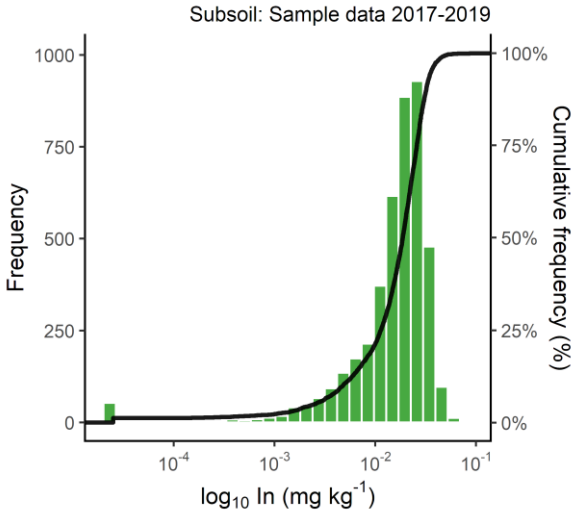
Mercury (Hg) ICP_{ar}



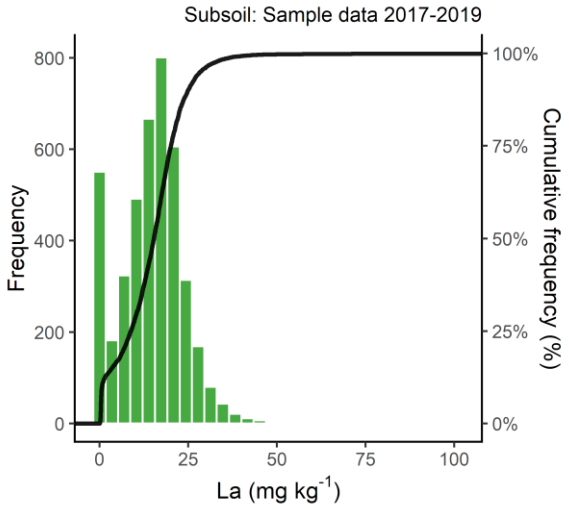


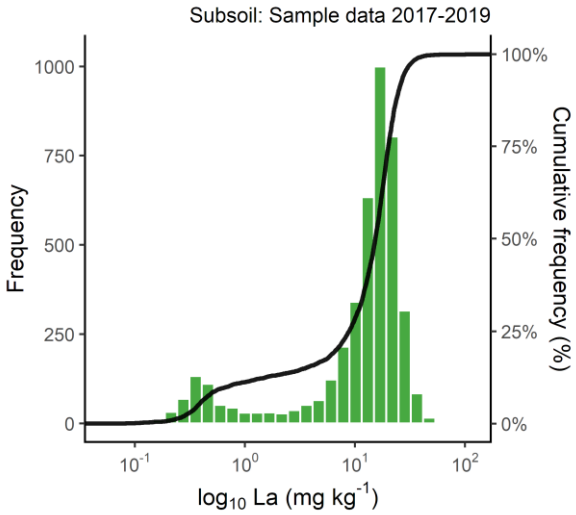
Indium (In) ICP_{ar}



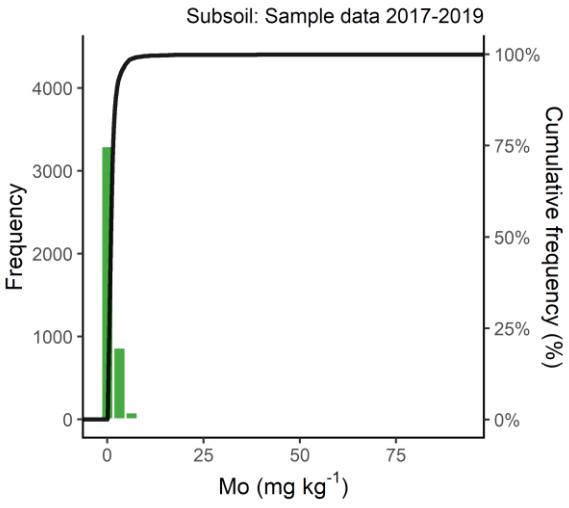


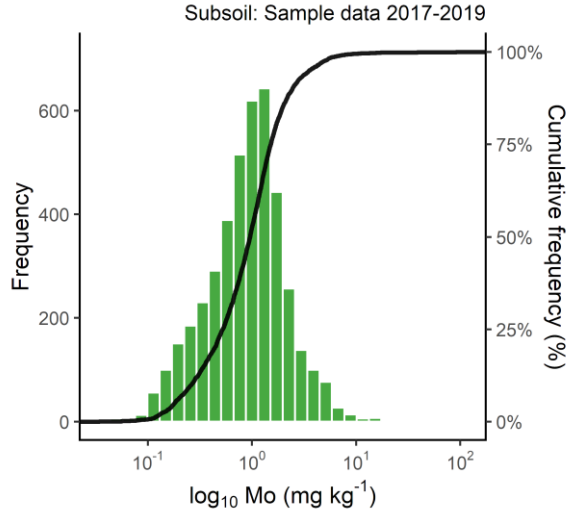
Lanthanum (La) ICP_{ar}



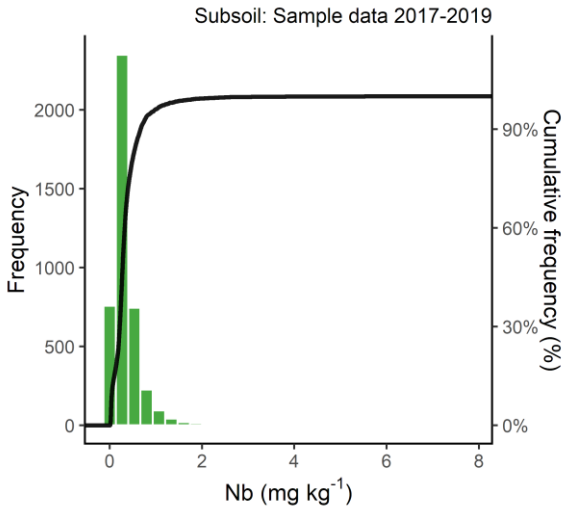


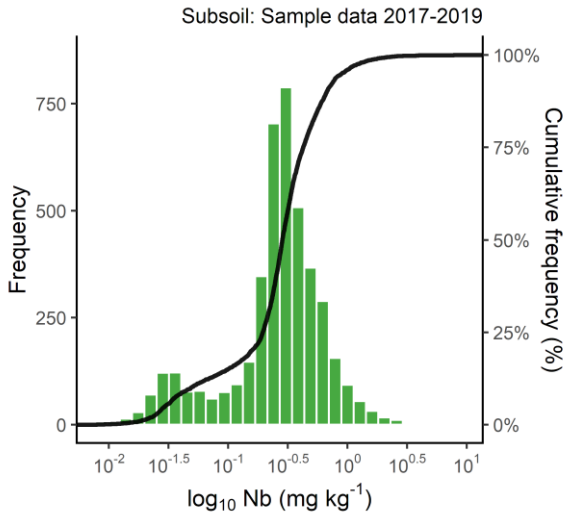
Molybdenum (Mo) ICP_{ar}



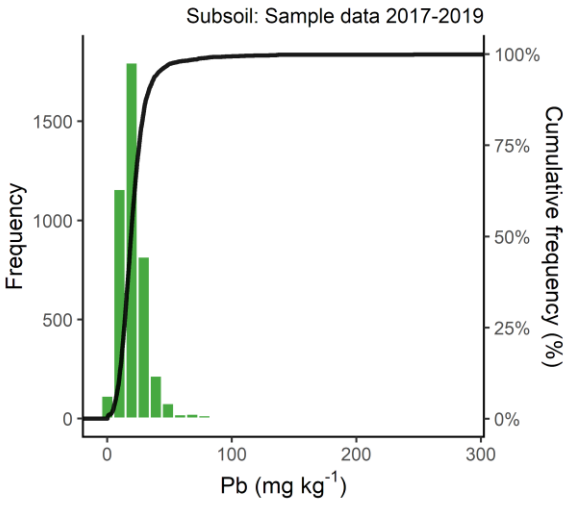


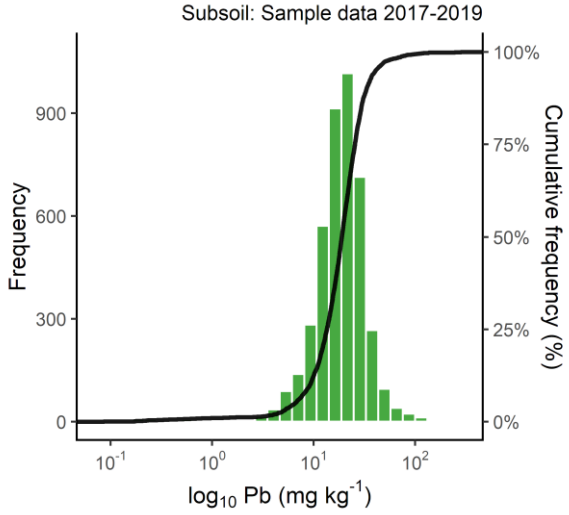
Niobium (Nb) ICP_{ar}



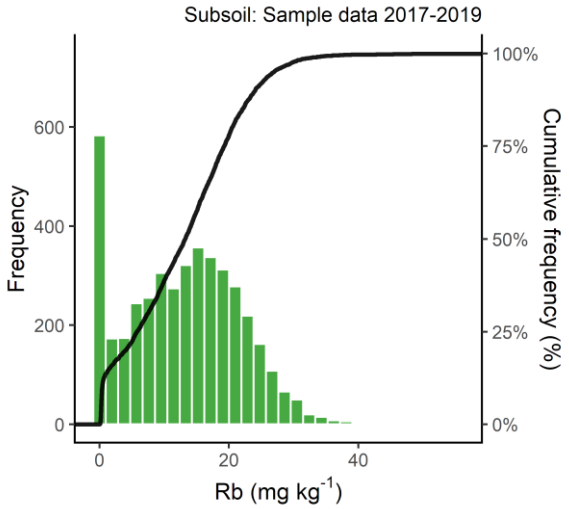


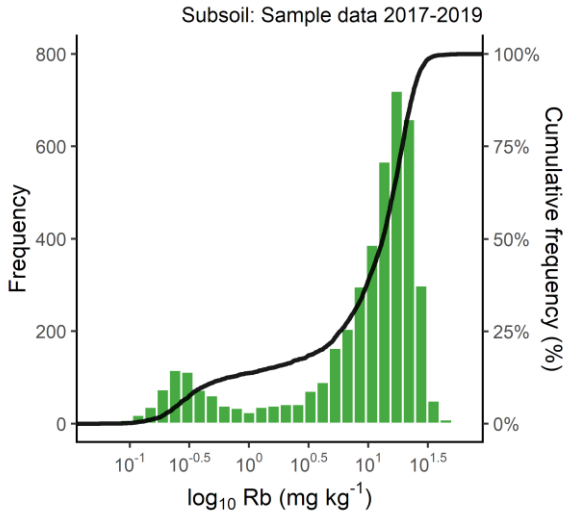
Lead (Pb) ICP_{ar}



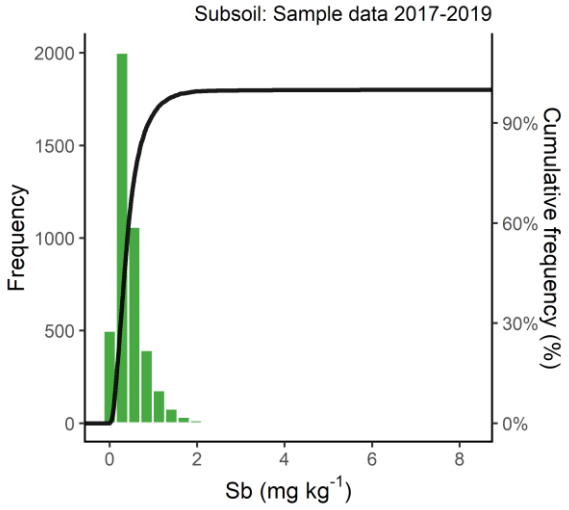


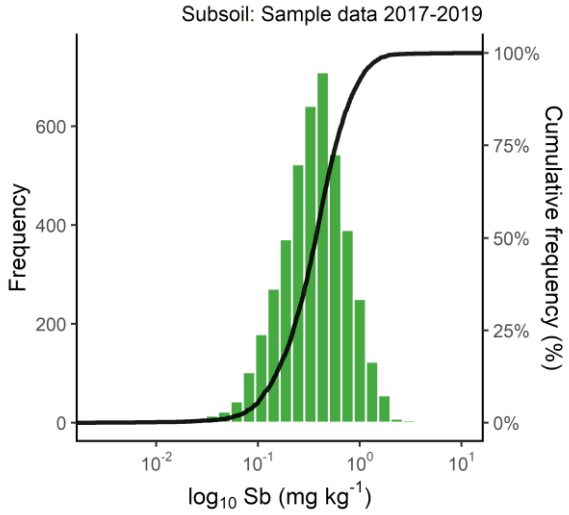
Rubidium (Rb) ICP_{ar}



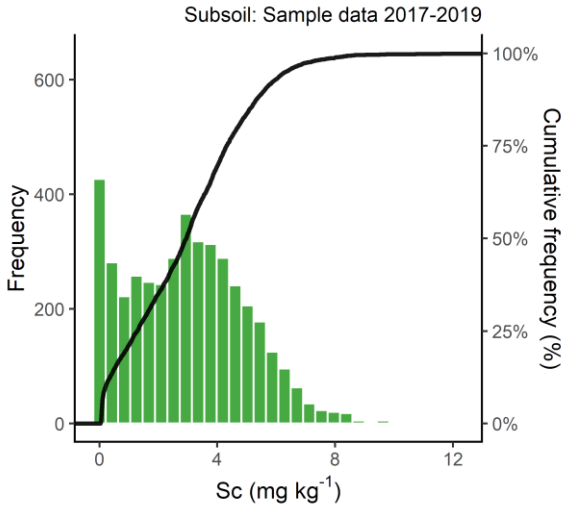


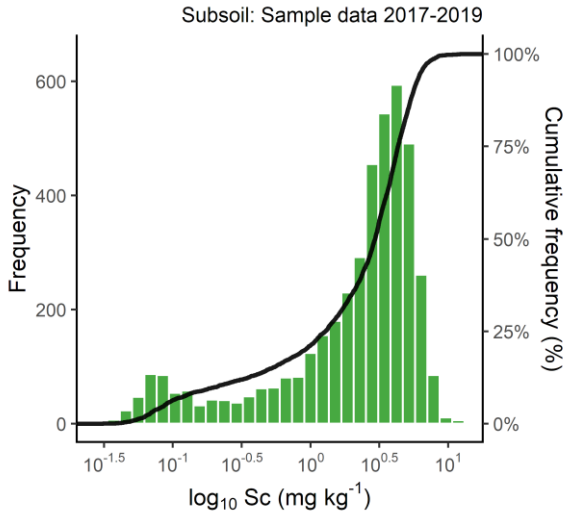
Antimony (Sb) ICP_{ar}



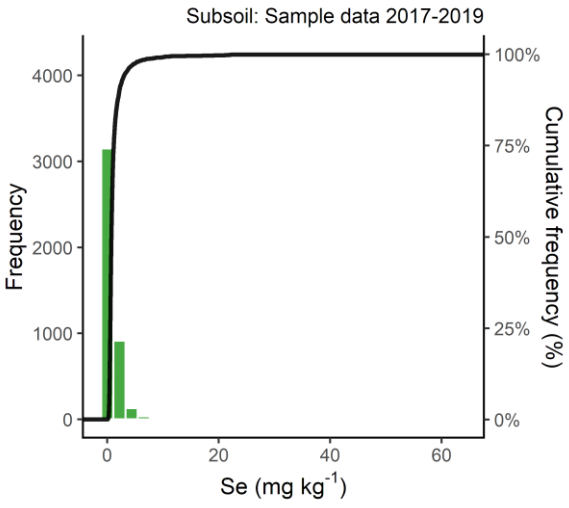


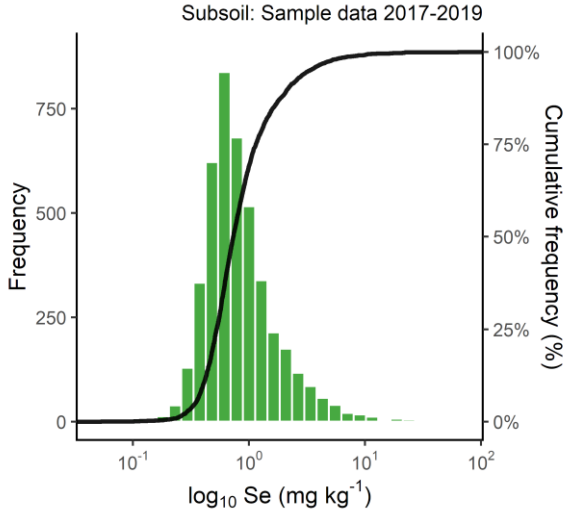
Scandium (Sc) ICP_{ar}



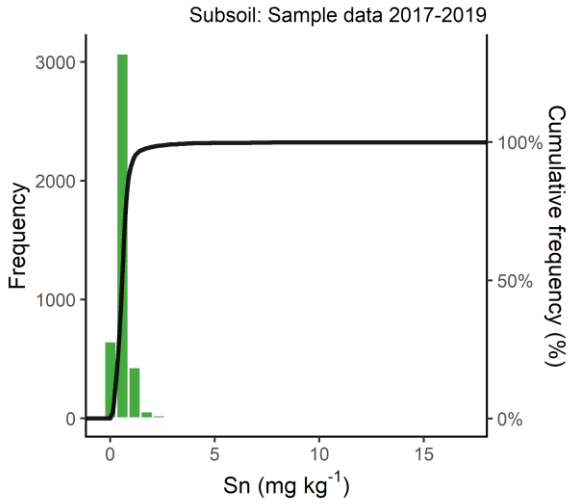


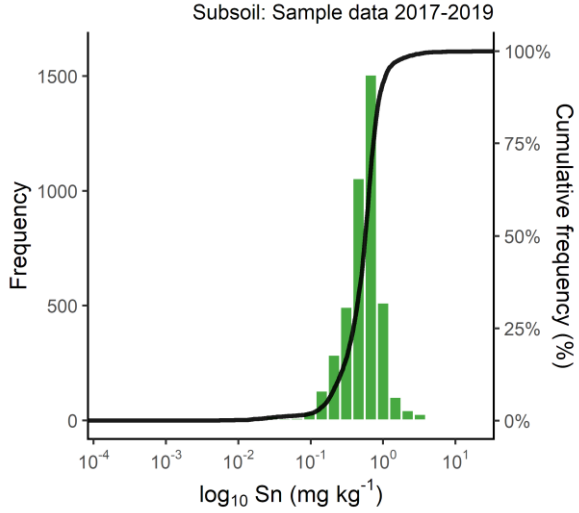
Selenium (Se) ICP_{ar}



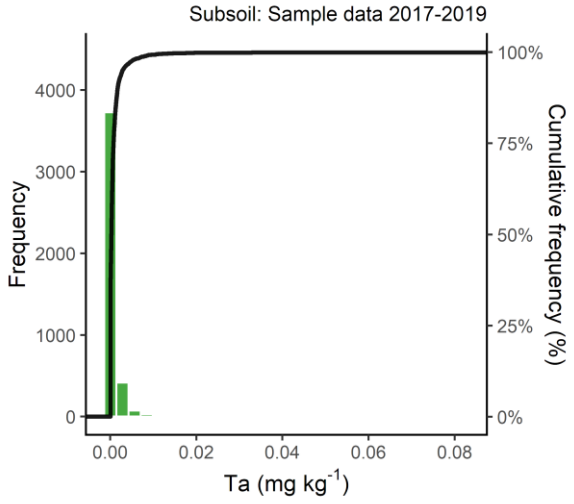


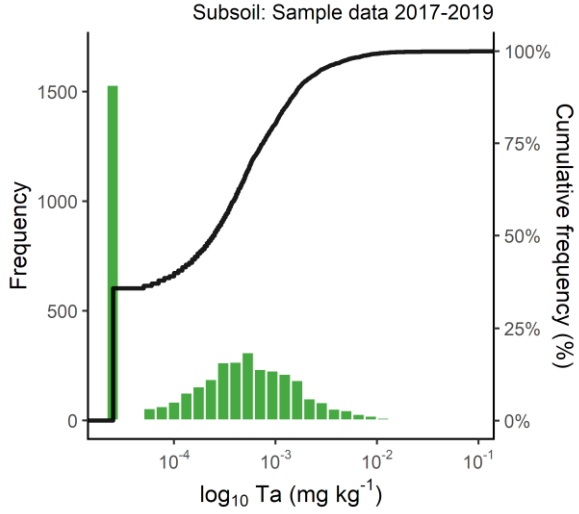
Tin (Sn) ICP_{ar}



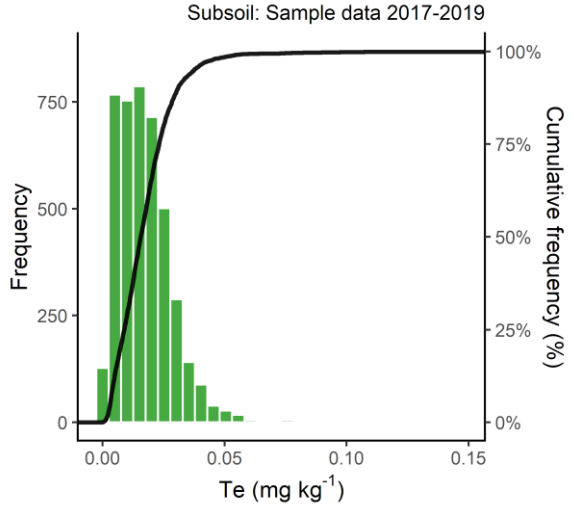


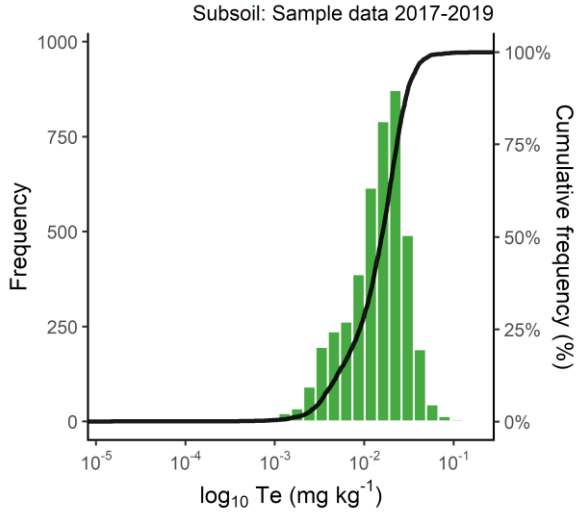
Tantalum (Ta) ICP_{ar}



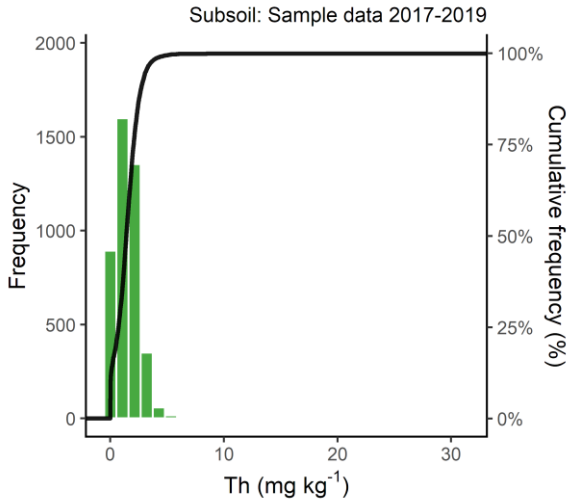


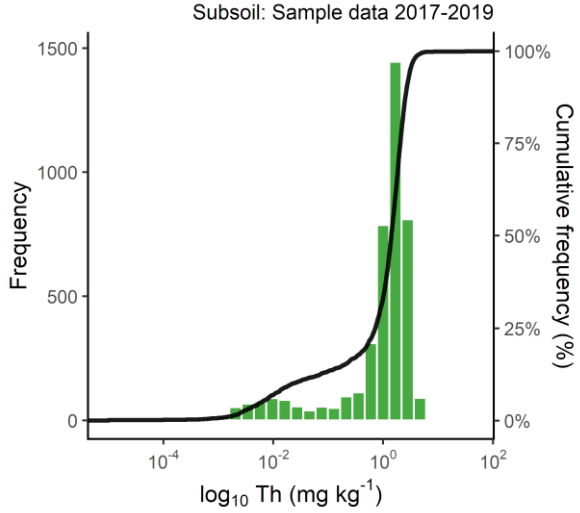
Tellurium (Te) ICP_{ar}



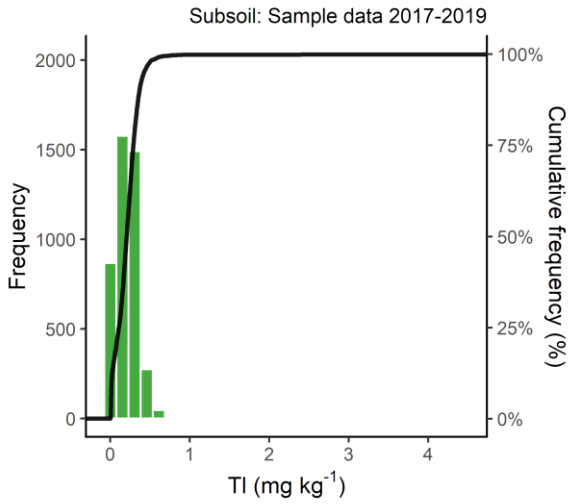


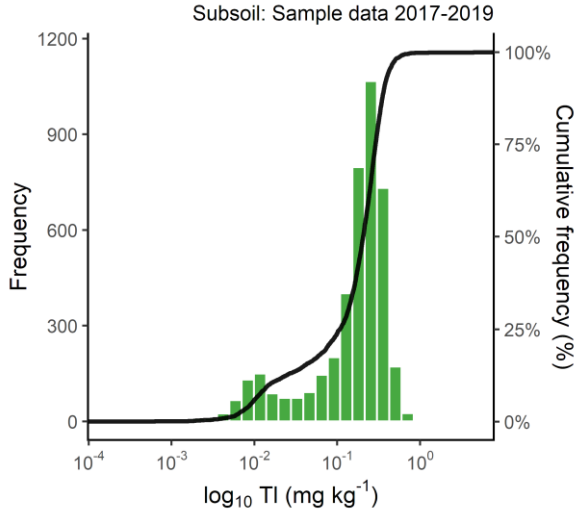
Thorium (Th) ICP_{ar}



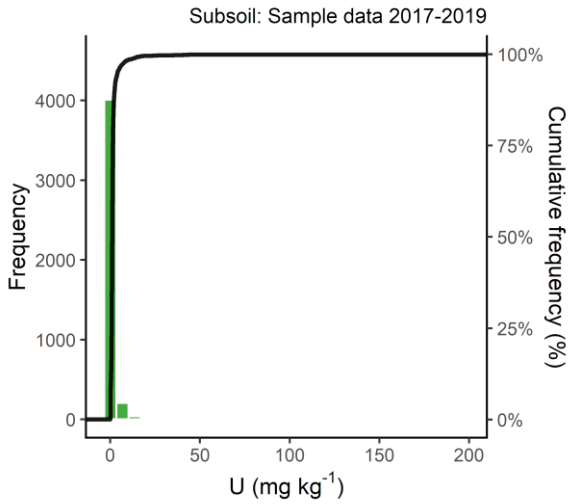


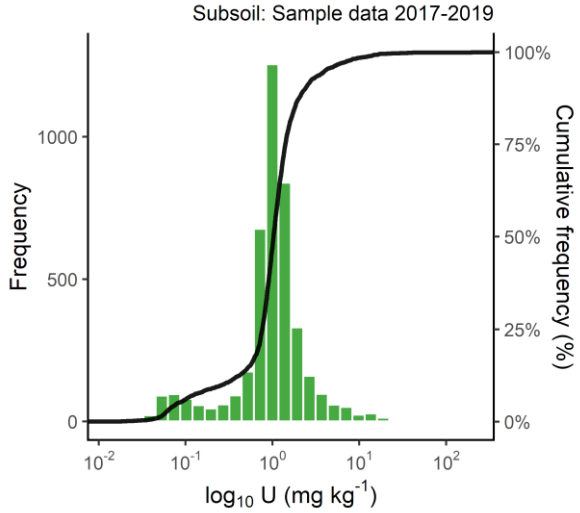
Thallium (Tl) ICP_{ar}



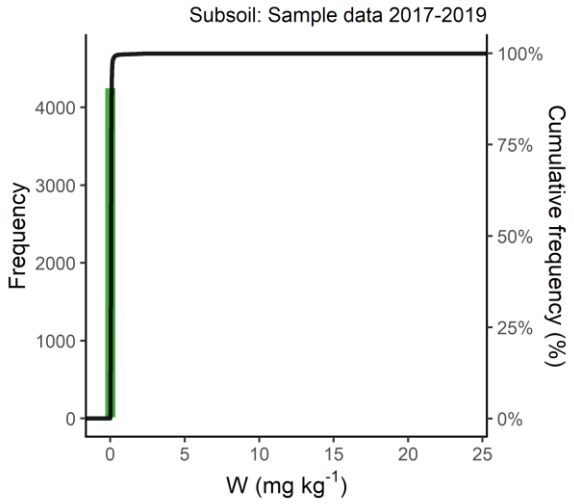


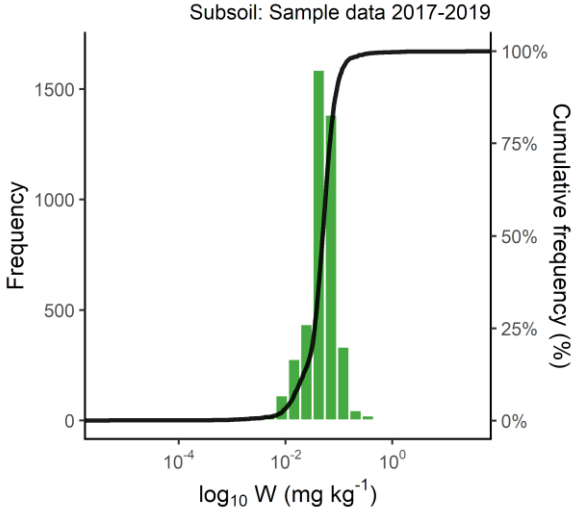
Uranium (U) ICP_{ar}



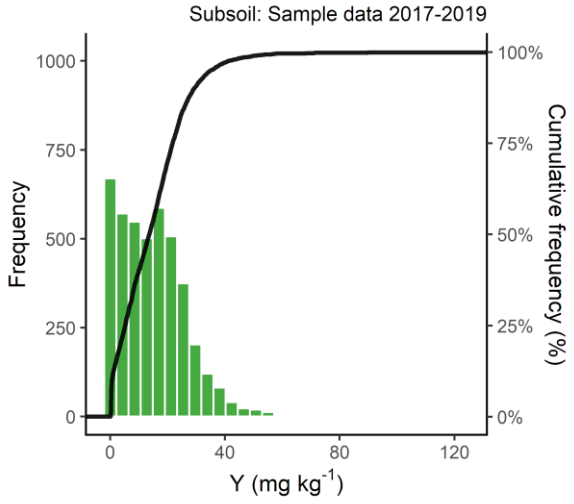


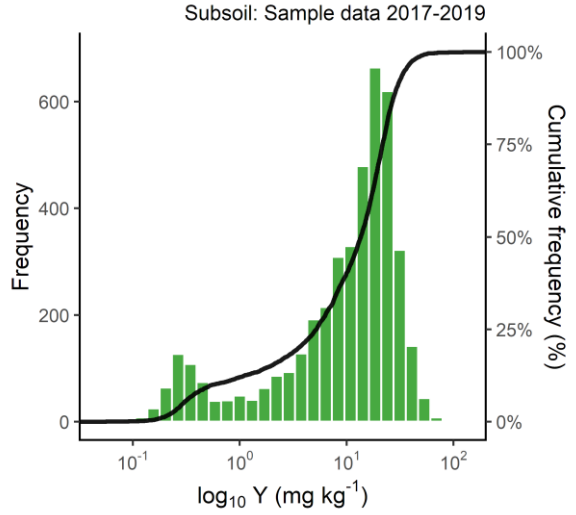
Tungsten (W) ICP_{ar}



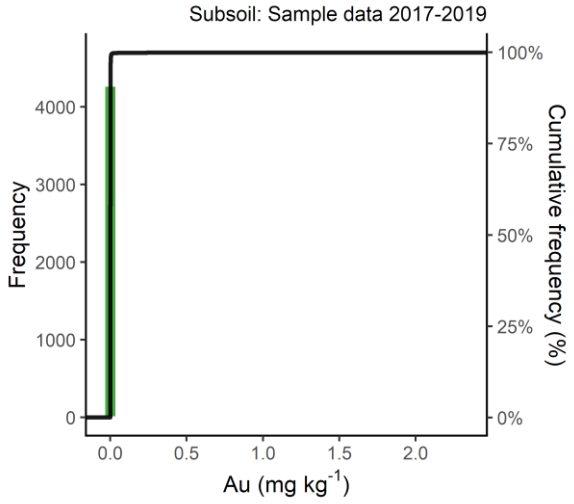


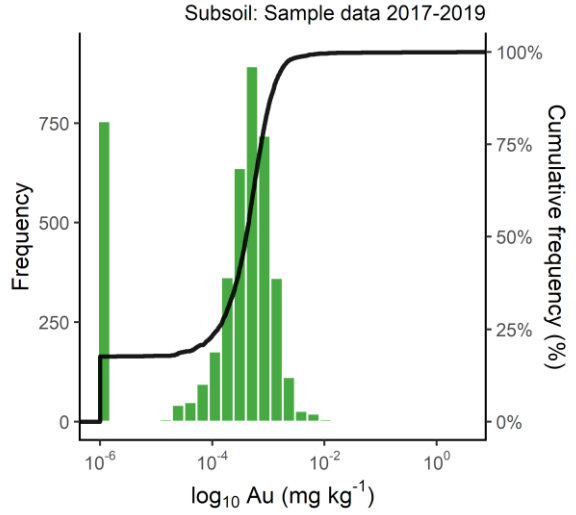
Yttrium (Y) ICP_{ar}



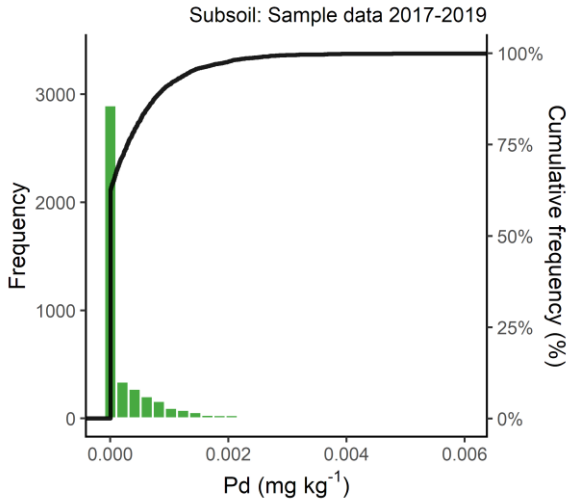


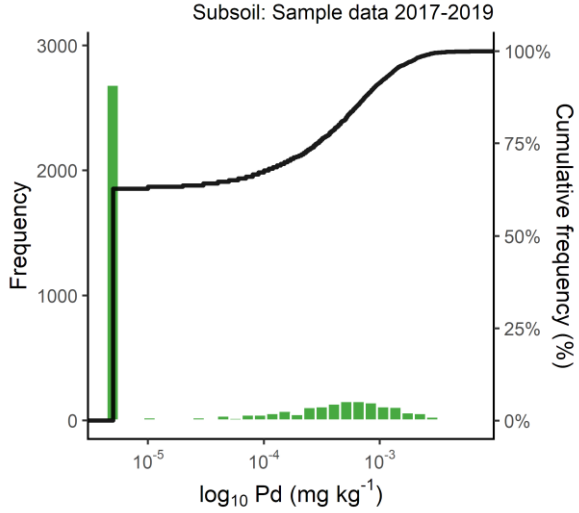
Gold (Au) ICP_{ar}



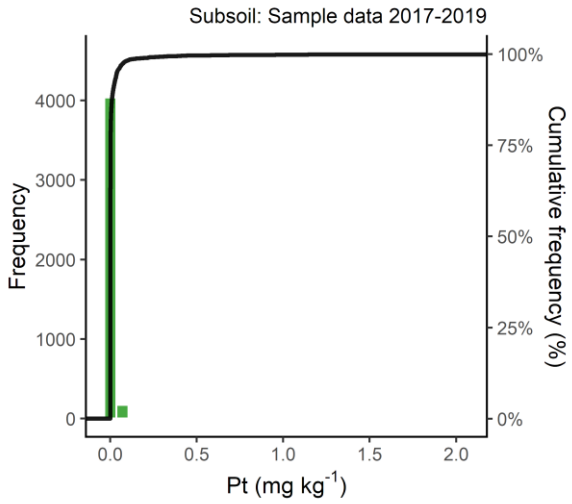


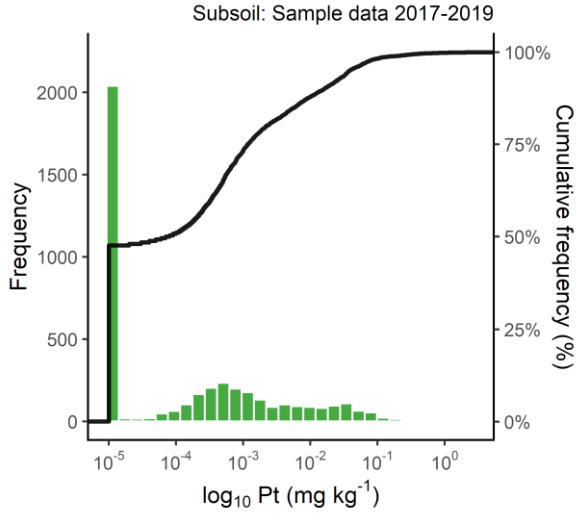
Palladium (Pd) ICP_{ar}



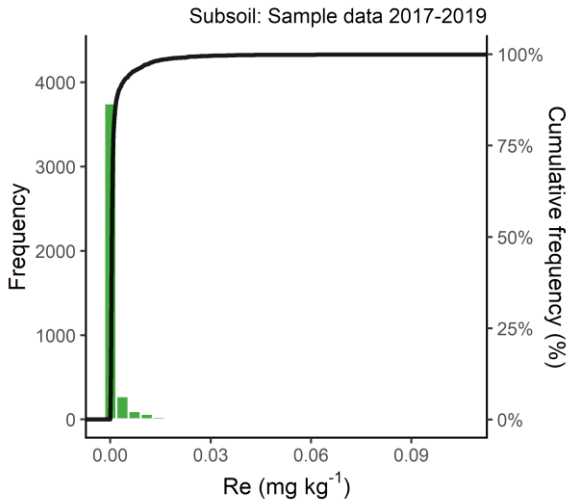


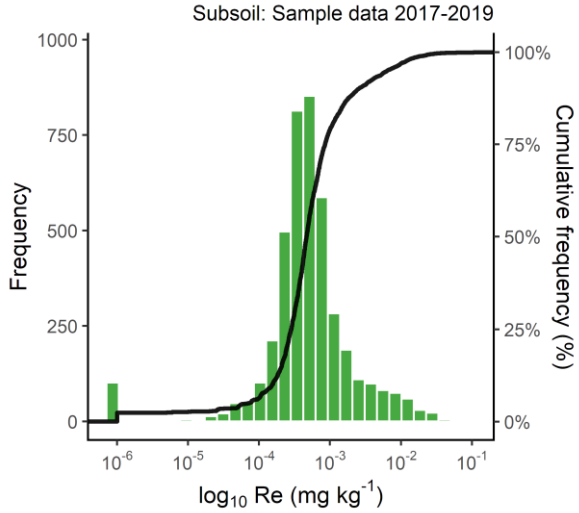
Platinum (Pt) ICP_{ar}





Rhenium (Re) ICP_{ar}





C. Method summaries

In this appendix are method summaries from the contracted laboratories.

- ALS Minerals Limited with trading name OMAC Laboratories Ltd., Loughrea, Ireland

Principles of Method – ME-MS41L

ME-MS41L – Lowest Detection Limit Super Trace Analysis for Soils and Sediments by Aqua Regia Digestion and ICP-MS/ICP-AES

Sample Decomposition:

Aqua Regia (GEO-AR01)

Analytical Method:

Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

These Super Trace methods combine an aqua regia digestion with ICP-MS instrumentation utilizing collision/reaction cell technologies to provide ultra-low detection limits. Instrumentation has been optimized for long-term ICP-MS signal stability, in particular for samples with high Ca content.

The extremely low detection limits are particularly useful for exploration in soils or sediments, and the methods can also be performed on the clay fraction of soils. (Clay size fraction separation is available using ALS method SCR-CLAY.) This method is not appropriate for mineralized samples.

ME-MS41L: For the ALS standard aqua regia digestion a prepared sample (nominal 0.5g ±10%) is digested with 75% aqua regia (3:1 ratio of HCl:HNO3) in a graphite heating block and made up to 12.5 ml of final volume using demineralized water.

NOTE 1: Reactive samples may require slow acid addition and/or reduction of the nominal sample weight by half.

NOTE 2: An aqua regia leach is an ideal medium for the dissolution of sulphide minerals and for the release of elements adsorbed on clay particles or trapped in manganese and iron oxides and oxyhydroxides. However, it represents only the leachable portion of the particular analyte and will not dissolve significant quantities of the silicate and alumino-silicate minerals. Major refractory minerals such as chromite, columbite, tantalite, cassiterite, rutile, scheelite, wolfram and zircon are only slightly soluble. The solubility of certain elements such as Ba and Sr will depend on the mineralisation in which they occur. The sulphates of these elements (barite and celestite) are basically insoluble, whereas the carbonates are readily soluble.

Coarse and malleable minerals such as native gold and silver, platinum and palladium are not representatively characterized by the small sample size.

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Phone: 091-841741 Email: www.alsglobal.com

Resulting solutions are analysed using ICP-OES spectrometer for major and minor elements and by ICP-MS spectrometer for minor and trace elements. Inter-element interference corrections are applied as required. Results from the two instruments merged in LIMS into a final report that is distributed to the customer.

List of Reportable Analytes for ME-MS41L:

Analyte	Symbol	Units	Lower Limit	Upper Limit
Gold	Au	ppm	0.0002	25
Silver	Ag	ppm	0.001	100
Aluminum	Al	%	0.01	25
Arsenic	As	ppm	0.01	10000
Boron	B	ppm	10	10000
Barium	Ba	ppm	0.5	10000
Beryllium	Be	ppm	0.01	1000
Bismuth	Bi	ppm	0.0005	10000
Calcium	Ca	%	0.01	25
Cadmium	Cd	ppm	0.001	1000
Cerium	Ce	ppm	0.003	500
Cobalt	Co	ppm	0.001	10000
Chromium	Cr	ppm	0.01	10000
Cesium	Cs	ppm	0.005	500
Copper	Cu	ppm	0.01	10000
Iron	Fe	%	0.001	50
Gallium	Ga	ppm	0.004	10000
Germanium	Ge	ppm	0.005	500
Hafnium	Hf	ppm	0.002	500
Mercury	Hg	ppm	0.004	10000
Indium	In	ppm	0.005	500
Potassium	K	%	0.01	10
Lanthanum	La	ppm	0.002	10000
Lithium	Li	ppm	0.1	10000
Magnesium	Mg	%	0.01	25
Manganese	Mn	ppm	0.1	50000
Molybdenum	Mo	ppm	0.01	10000
Sodium	Na	%	0.001	10
Niobium	Nb	ppm	0.002	500
Nickel	Ni	ppm	0.04	10000
Phosphorus	P	%	0.001	1
Lead	Pb	ppm	0.005	10000
Palladium	Pd	ppm	0.001	25
Platinum	Pt	ppm	0.002	25
Rubidium	Rb	ppm	0.005	10000
Rhenium	Re	ppm	0.0002	50
Sulphur	S	%	0.01	10
Antimony	Sb	ppm	0.005	10000
Scandium	Sc	ppm	0.005	10000
Selenium	Se	ppm	0.003	1000
Tin	Sn	ppm	0.01	500
Strontium	Sr	ppm	0.01	10000

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Analyte	Symbol	Units	Lower Limit	Upper Limit
Tantalum	Ta	ppm	0.005	500
Tellurium	Te	ppm	0.003	500
Thorium	Th	ppm	0.002	10000
Titanium	Ti	%	0.001	10
Thallium	Tl	ppm	0.001	10000
Uranium	U	ppm	0.005	10000
Vanadium	V	ppm	0.1	10000
Tungsten	W	ppm	0.001	10000
Yttrium	Y	ppm	0.003	500
Zinc	Zn	ppm	0.1	10000
Zirconium	Zr	ppm	0.01	500

***Please note that the detection limits for the highlighted analytes above have improved since analysis was carried out on GSI samples.**

See table below for previous low reporting limits for the highlighted elements:

Improved Detection Limits

	Analyte	Previous LDL ppm	New LDL ppm	Improvement factor
4-Acid	As	0.05	0.02	2.5
	Bi	0.005	0.002	2.5
	Re	0.002	0.0004	5
	Se	0.2	0.006	33.33
	Te	0.04	0.005	8
	Tl	0.004	0.001	4
Aqua Regia	Bi	0.001	0.0005	2
	Re	0.001	0.0002	5
	Se	0.1	0.003	33.33
	Te	0.01	0.003	3.33
	Tl	0.002	0.001	2

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Principles of Method – OA-GRA05f (Loss on Ignition)

Loss on Ignition (L.O.I.) is to measure the amount of water and volatile compounds lost when the sample is ignited under the conditions specified for various method codes. Weight measurements are taken before and after the samples are in the furnace.

For TELLUS project a pulverised sample is pre-weighed into a disposable glass vial and placed for drying to an oven set at 105 (0.5g) for a minimum of 1 hour. Dried samples are then placed into a desiccator and cooled to room temperature. 0.5g of pre-dried sample is weighed into a ceramic crucible using 4-decimal place balance. The crucible with sample is placed in a muffle furnace set at 450°C for four hours. After ignition samples are cooled and then weighed again. The percent loss on ignition is calculated from the difference in weight.

Formula used:

$$\%\,LOI = \frac{\text{Wt. of crucible and sample before furnacing - Wt. of crucible and sample after furnacing}}{\text{Wt. of crucible and sample before furnacing - Wt. of empty crucible}} \times 100\%$$

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Principles of Method – OA-ELE07

For TELLUS project 5g±10% of dried soil sample, sieved to <2mm, is mixed with 12.5 ml of 0.01M CaCl2 solution in a 50ml disposable plastic vial and homogenised on the shaker for 5 minutes. The suspension is then left to settle for 1 hour. After that samples are presented for measurement on Metrohm titration system equipped with measurement unit, pH electrode and sample changer. pH electrode is calibrated using a series of standard solutions of known pH.

Applicable Analyte Ranges

ALS Code	Symbol	Description	Detection Limit	Upper Limit	Units
OA-ELE07	pH	Paste pH	0.1	14	Unity

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