



# Geological Survey Ireland

## Tellus geochemical survey: shallow topsoil data from the midlands of Ireland

September 2020



Rialtas na hÉireann  
Government of Ireland



**Geological Survey**

Suirbhéireacht Gheolaíochta  
Ireland | Éireann

## Document information

Author: M.T. Szpak

Contributors: V Gallagher, J. Mather, K.V. Knights

## Change record

Version 1.1

## Executive Summary

This report accompanies the publication of data and maps that present the inorganic geochemical data for shallow topsoil samples across 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 4278 sites in the north midlands and western regions of Ireland. Sample sites are distributed at a typical density of one site per 4 km<sup>2</sup> and together they represent a variety of geological domains in Ireland, covering an area of over 17,000 km<sup>2</sup> (24.3% of the country).

Each sample was prepared and chemically measured by a number of techniques. Laboratory tests comprise: soil pH (CaCl<sub>2</sub>); 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](http://www.gsi.ie/tellus).

## Disclaimer

Although every effort has been made to ensure the accuracy of the material contained in this report, complete accuracy cannot be guaranteed. Neither Geological Survey Ireland nor the authors accept any responsibility whatsoever for loss or damage occasioned, or claimed to have been occasioned, in part or in full as a consequence of any person acting, or refraining from acting, as a result of a matter contained in this report.

## Copyright

Base maps are published subject to OSI copyrights. © Government of Ireland. Ordnance Survey Ireland Licence No. EN 0047220 © Ordnance Survey Ireland/Government of Ireland.

## Table of contents

Introduction.....	8
Shallow topsoil samples .....	9
Sampling and sample summary.....	9
Survey design and sample locations .....	9
Summary of regular and control samples by field hundred batch .....	9
Soil sample preparation.....	15
Condition of samples submitted from the field contractor .....	15
Sample split prepared for pH analyses.....	15
Sample split prepared for ICP <sub>ar</sub> multi-element analyses .....	15
Sample split prepared for loss-on-ignition (LOI) analyses.....	16
Insertion of reference materials, blind to the analyst .....	16
Soil chemical analyses .....	17
Laboratory chemical analyses.....	17
Soil loss-on-ignition at 450°C .....	17
ALS Minerals Ltd. OA-GRA05f: Soil LOI analyses of 1 g prepared (milled) sub-sample.....	17
Soil pH by CaCl <sub>2</sub> slurry .....	17
ALS Minerals Ltd. OA-ELE07: Soil pH analyses of 5 g prepared (not milled) sub-sample.....	17
Multi-element partial extract analyses of major, minor and trace elements by ICP following <i>aqua regia</i> digestion .....	18
ALS Minerals Ltd. MS41L: Multi-element ICP(-OES/-MS) analyses of 1 g prepared (milled) sub-sample after aqua regia extraction .....	18
Sample submission to the laboratories .....	18
Quality control samples.....	25
Randomisation of sample identities .....	25
Analysis of Variance (ANOVA) using duplicate and replicate QCS data .....	26
Collection and preparation of duplicates and replicates.....	26
Duplicate and replicate analyses .....	26
Analysis of variance (ANOVA) .....	29
ANOVA approach and results.....	30
Reference materials data .....	33
Laboratory in-house RMs.....	33
Randomised and blind to laboratory RMs.....	33
Certified reference materials (CRMs) .....	34
Secondary reference materials (SRMs).....	34

Assessment of RMs data.....	36
Control charts.....	37
Linear regression plots and data conditioning.....	43
Calculating relative bias .....	60
Blank sample data .....	68
Analytes of concern and carry-over contamination investigated .....	68
Blank data reported for ICP <sub>ar</sub> .....	68
Analytical interferences.....	72
Check on ICP <sub>ar</sub> interferences.....	72
Univariate statistical summaries .....	73
Regional-scale mapping and interpolation of sample data recommendations .....	85
Use of data beyond reporting limits in interpolation mapping.....	85
Elements for which data conditioning/levelling are required .....	85
Abbreviations and glossary .....	87
References.....	92
Appendices .....	93
A. RMs data QCS charts.....	94
ICP <sub>ar</sub> RMs data by ALS Minerals Ltd method code MS41L-BLD .....	95
B. Univariate exploratory data analysis: sample site data general release .....	149
pH and LOI sample site data .....	150
ICP <sub>ar</sub> sample site data.....	151
C. Method summaries.....	169

## List of Charts

Chart 1 Stacked bar chart to display ANOVA results for all duplicate site shallow topsoil data.....	32
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. ....	47
Chart 3 Bismuth (Bi) (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. ....	48
Chart 4 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. ....	49
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. ....	50
Chart 6 Tin (Sn) (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. ....	51
Chart 7 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. ....	52
Chart 8 Tungsten (W) (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. ....	53
Chart 9 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. ....	54
Chart 10 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. ....	55
Chart 11 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.....	56
Chart 12 Palladium (Pd) (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.....	57
Chart 13 Platinum (Pt) (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.....	58
Chart 14 Rhenium (Re) (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.....	59

## List of Equations

Equation 1 Relative bias %.....	60
---------------------------------	----

## List of Figures

Figure 1 Graphic of the periodic table, with ICP <sub>ar</sub> element analytes for shallow topsoil samples shown in black text, Soil pH (CaCl <sub>2</sub> ) and LOI (at 450°C) in green text. Adapted after <a href="http://www.sciencegeek.net/tables/PToE_24">http://www.sciencegeek.net/tables/PToE_24</a>	
Figure 2 Diagrammatic plan for collection of a five auger hole composite soil sample and a field duplicate sample (indicated by dashed line pictogram). ....	26

Figure 3 Diagram to show the relationship between field duplicates (“DUP”) and replicate (“SS”) samples, used to apportion data variance. ....	27
--	----

## List of Maps

Map 1 Survey campaign areas G5. Field sampling was conducted using the national projection co-ordinate system Irish National Grid (Geographic Coordinate System: GCS_TM65). ....	13
Map 2 Shallow topsoil sample locations for campaign areas G5. Field sampling was conducted using the national projection co-ordinate system Irish National Grid (Geographic Coordinate System: GCS_TM65). GCS_TM65). ....	14

## List of Tables

Table 1 Summary of QCS by field hundred batches.....	10
Table 2 Shallow topsoil ICP <sub>ar</sub> analytes, concentration units, methods, lower limits of detection and reporting (LLD/LRL), upper reporting limits (URL), accreditation statuses.....	19
Table 3 Shallow topsoil pH (CaCl <sub>2</sub> ) and LOI (450°C) analytes, concentration units, methods, lower limits of detection and reporting (LLD/LRL), upper reporting limits (URL), accreditation statuses. ....	23
Table 4 ANOVA results for all duplicate site shallow 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. ....	30
Table 5 In-house CRMs used for multi-element ICP <sub>ar</sub> analyses.....	33
Table 6 In-house CRMs used for soil LOI analyses.....	33
Table 7 Blind CRMs used for ICP <sub>ar</sub> multi-element analyses.....	34
Table 8 Blind SRMs used for XRFs and ICP <sub>ar</sub> multi-element analyses.....	34
Table 9. Summary of CRM data quality issues observed by control charts for IPC <sub>ar</sub> analyses. ....	38
Table 10 Linear regression relationships for ICP <sub>ar</sub> analytes. ....	43
Table 11 Linear regression relationships for LOI at 450°C. ....	44
Table 12 Linear regression relationship for in-house 'top-and-tail' ICP <sub>ar</sub> analytes. ....	45
Table 13 Summary of relative bias calculated for CRM data by STSD-1 by ICP <sub>ar</sub> (n=24). N/A where no reference concentration value is available. ....	60
Table 14 Summary of relative bias calculated for CRM data by STSD-3 by by ICP <sub>ar</sub> (n=24). N/A where no reference concentration value is available. ....	61
Table 15 Summary of relative bias calculated for CRM data by TILL-1 by by ICP <sub>ar</sub> (n=8). N/A where no reference concentration value is available. ....	63
Table 16 Summary of relative bias calculated for CRM data by TILL-2 by by ICP <sub>ar</sub> (n=8). N/A where no reference concentration value is available. ....	64
Table 17 Summary of relative bias calculated for CRM data by TILL-3 by by ICP <sub>ar</sub> (n=8). N/A where no reference concentration value is available. ....	66

Table 18 Summary of above method LLD detectable ICP <sub>ar</sub> ME-MS41L data in blank waters. Analytes with >5% of data above the LLD are orange highlighted. ....	69
Table 19 Summary of above method LLD detectable ICP <sub>ar</sub> MS41L-BLD data in blank waters. Analytes with >5% of data above the LLD are orange highlighted. ....	70
Table 20 Univariate summary statistics for shallow topsoil pH (CaCl <sub>2</sub> ) and LOI (450°C) sample data. ....	74
Table 21 Univariate summary statistics for shallow topsoil ICP <sub>ar</sub> sample data calculated for MS41L-BLD method. ....	74
Table 22 Univariate summary statistics for shallow topsoil ICP <sub>ar</sub> sample data calculated for ME-MS41L method. ....	77
Table 23 Univariate summary statistics including best fits based on proportions of pH (CaCl <sub>2</sub> ) and LOI (450°C) data below the LLD. All to 3 significant figures. ....	79
Table 24 Univariate summary statistics including best fits based on proportions of ICP <sub>ar</sub> data below the MS41L-BLD LLD. All to 3 significant figures. ....	79
Table 25 Univariate summary statistics including best fits based on proportions of ICP <sub>ar</sub> data below the ME-MS41L LLD. All to 3 significant figures. ....	82
Table 26 Geochemical map series interpolation mapping parameters. ....	85
Table 27 Shallow topsoil analytes where mapping is not recommended and/or conditioning is required in order to seamlessly merge discrete dataset. ....	86

# Introduction

---

Geological Survey Ireland is conducting a flagship project to sample and measure the geochemical characteristics of the shallow subsurface of Ireland. The Tellus project geochemistry workstream commenced in 2011. Its aim is to produce spatial data to determine the geochemical baseline of shallow 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 shallow topsoil, denoted sample type 'A', collected from one survey site per 4 km<sup>2</sup>. 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 recommendations 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.



# Shallow topsoil samples

---

## Sampling and sample summary

### Survey design and sample locations

Maps displaying survey extent and sample site locations of shallow 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<sup>2</sup>).

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/streams 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 organised 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

Shallow topsoil samples collected by the Tellus survey are denoted sample type code 'A'.

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 sample was prepared and analysed in replicate, blindly to the analytical laboratories. These 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 QCS used for data quality assurance (QA) and quality control (QC) procedures.

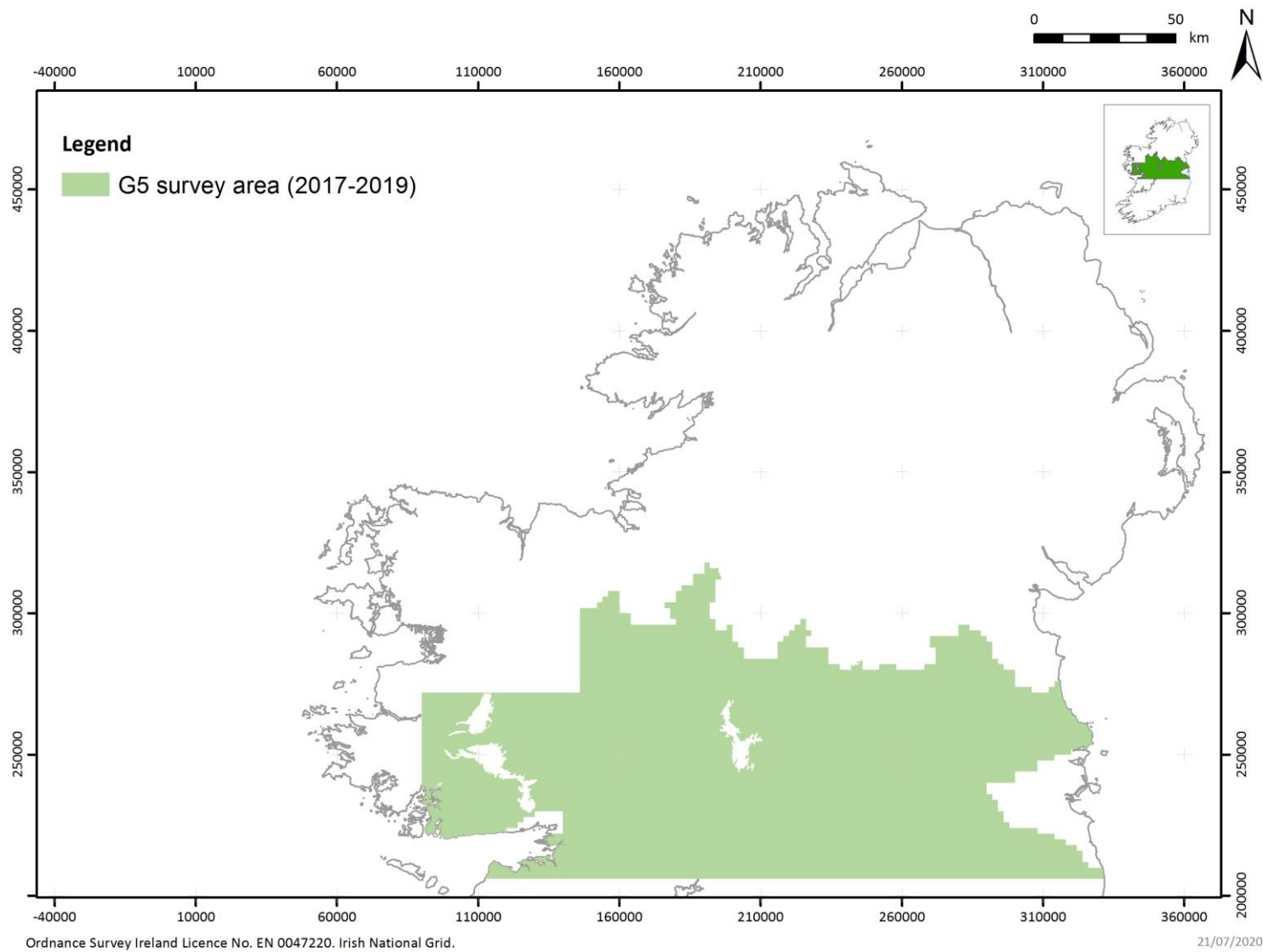
Typically, a field duplicate sample was collected at a rate of two sets (quartets) per field hundred batch of 100 samples. Sample and QCS numbers by field hundred batch are summarised in Table 1.

**Table 1 Summary of QCS by field hundred batches.**

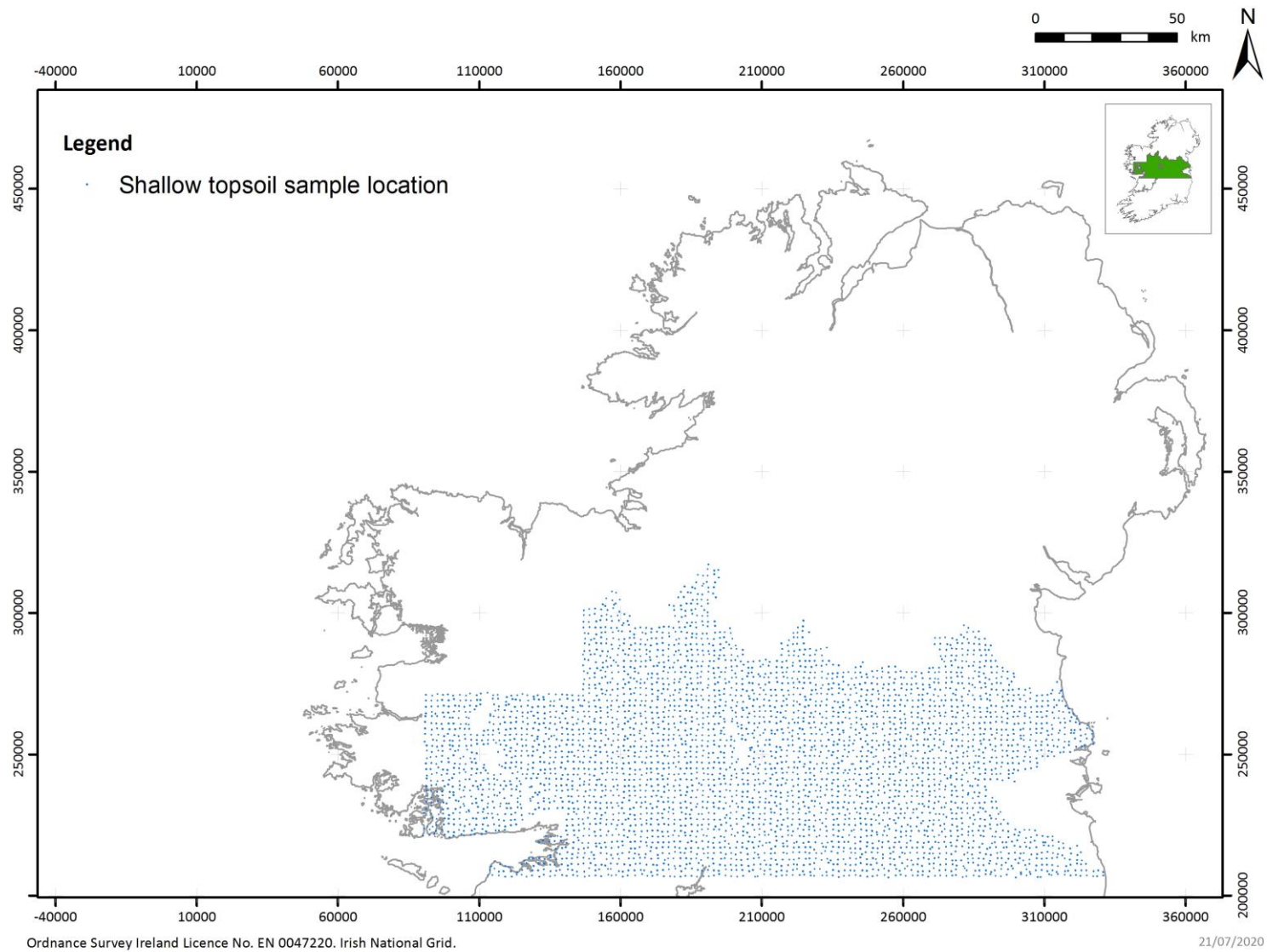
Random number checklist number	Field hundred batch	Sample ID range from	Sample ID range to	Sampling date from	Sampling date to	<i>n</i> samples in field hundred batch	<i>n</i> sample sites in field hundred batch	<i>n</i> blind CRMs	<i>n</i> blind SRMs	<i>n</i> DUP and SS QCS
6	6117xx	611701A	611800A	19-04-17	06-05-17	100	90	2	4	8
1	6118xx	611801A	611900A	04-05-17	09-08-17	100	90	2	4	8
2	6119xx	611901A	612000A	12-05-17	06-08-19	100	90	2	4	8
3	6120xx	612001A	612100A	18-05-17	06-08-19	100	90	2	4	8
4	6121xx	612101A	612200A	26-05-17	15-08-19	100	90	2	4	8
5	6122xx	612201A	612300A	01-06-17	16-08-19	100	90	2	4	8
6	6123xx	612301A	612400A	08-06-17	24-09-19	100	90	2	4	8
1	6124xx	612401A	612500A	14-06-17	02-09-19	100	90	2	4	8
2	6125xx	612501A	612600A	19-06-17	05-09-19	100	90	2	4	8
3	6126xx	612601A	612700A	23-06-17	26-08-19	100	90	2	4	8
4	6127xx	612701A	612800A	29-06-17	12-09-19	100	90	2	4	8
5	6128xx	612801A	612900A	12-07-17	12-09-19	100	90	2	4	8
6	6129xx	612901A	613000A	19-06-17	02-09-19	100	90	2	4	8
1	6130xx	613001A	613100A	25-06-17	23-09-19	100	90	2	4	8
2	6131xx	613101A	613200A	29-07-17	23-09-19	100	90	2	4	8
3	6132xx	613201A	613300A	04-08-17	07-10-19	100	90	2	4	8
4	6133xx	613301A	613400A	16-08-17	23-09-19	100	90	2	4	8
5	6134xx	613401A	613500A	22-08-17	27-08-19	100	90	2	4	8
6	6135xx	613501A	613600A	25-08-17	27-08-19	100	90	2	4	8
1	6136xx	613601A	613700A	28-08-17	23-09-19	100	90	2	4	8
2	6137xx	613701A	613800A	29-08-17	23-09-19	100	90	2	4	8
3	6138xx	613801A	613900A	01-09-17	04-09-19	100	90	2	4	8

Random number checklist number	Field hundred batch	Sample ID range from	Sample ID range to	Sampling date from	Sampling date to	<i>n</i> samples in field hundred batch	<i>n</i> sample sites in field hundred batch	<i>n</i> blind CRMs	<i>n</i> blind SRMs	<i>n</i> DUP and SS QCS
4	6139xx	613901A	614000A	00-01-00	05-09-19	100	90	2	4	8
5	6140xx	614001A	614100A	06-09-17	20-09-19	100	90	2	4	8
6	6141xx	614101A	614200A	07-09-17	05-09-19	100	90	2	4	8
1	6142xx	614201A	614300A	09-09-17	26-09-19	100	90	2	4	8
2	6143xx	614301A	614400A	12-09-17	10-09-19	100	90	2	4	8
3	6144xx	614401A	614500A	14-09-17	17-09-19	100	90	2	4	8
4	6145xx	614501A	614600A	15-09-17	12-09-19	100	90	2	4	8
5	6146xx	614601A	614700A	12-09-17	13-09-19	100	90	2	4	8
6	6147xx	614701A	614800A	20-09-17	17-09-19	100	90	2	4	8
1	61489xx	614801A	614900A	22-09-17	16-09-19	100	90	2	4	8
2	6149xx	614901A	615000A	27-09-17	17-09-19	100	90	2	4	8
3	6150xx	615001A	615100A	29-09-17	17-09-19	100	90	2	4	8
4	6151xx	615101A	615200A	03-10-17	20-09-19	100	90	2	4	8
5	6152xx	615201A	615300A	05-10-17	20-09-19	100	90	2	4	8
6	6153xx	615301A	615400A	07-10-17	20-09-19	100	90	2	4	8
1	6154xx	615401A	615500A	10-10-17	26-09-19	100	90	2	4	8
2	6155xx	615501A	615600A	11-10-17	23-09-19	100	90	2	4	8
3	6156xx	615601A	615700A	13-10-17	25-09-19	100	90	2	4	8
4	6157xx	615701A	615800A	23-10-17	25-09-19	100	90	2	4	8
5	6158xx	615801A	615900A	16-10-17	25-09-19	100	90	2	4	8
6	6159xx	615901A	616000A	25-10-17	09-10-19	100	90	2	4	8
1	6160xx	616001A	616100A	27-10-17	25-09-19	100	90	2	4	8
2	6161xx	616101A	616200A	02-11-17	07-10-19	100	90	2	4	8
3	6162xx	616201A	616300A	06-11-17	26-09-19	100	90	2	4	8
4	6163xx	616301A	616399A	08-11-17	26-09-19	94	84	2	4	8

Random number checklist number	Field hundred batch	Sample ID range from	Sample ID range to	Sampling date from	Sampling date to	<i>n</i> samples in field hundred batch	<i>n</i> sample sites in field hundred batch	<i>n</i> blind CRMs	<i>n</i> blind SRMs	<i>n</i> DUP and SS QCS
5	6164xx	616404A	616499A	10-11-17	25-09-19	44	34	2	4	8
6	6165xx	616504A	616597A	05-08-19	05-08-19	8	0	0	0	8
1	6166xx	616606A	616693A	12-08-19	13-08-19	8	0	0	0	8
2	6167xx	616706A	616792A	24-09-19	24-09-19	8	0	0	0	8
3	6168xx	616807A	616893A	23-08-19	23-08-19	8	0	0	0	8
4	6169xx	616905A	616995A	27-08-19	10-09-19	8	0	0	0	8
5	6170xx	617005A	617096A	02-09-19	02-09-19	8	0	0	0	8
6	6171xx	617104A	617197A	09-09-19	09-09-19	8	0	0	0	8
1	6172xx	617206A	617293A	16-09-19	16-09-19	8	0	0	0	8
2	6173xx	617306A	617392A	19-09-19	19-09-19	8	0	0	0	8
3	6174xx	617407A	617493A	26-09-19	26-09-19	8	0	0	0	8



Map 1 Survey campaign areas G5. Field sampling was conducted using the national projection co-ordinate system Irish National Grid (Geographic Coordinate System: GCS\_TM65).



Map 2 Shallow topsoil sample locations for campaign areas G5. Field sampling was conducted using the national projection co-ordinate system Irish National Grid (Geographic Coordinate System: GCS\_TM65). GCS\_TM65).

## 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 ( $\pm 2$  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  $\varnothing$  sized agate grinding balls at 300 rpm for between 30 and 45 minutes to produce a milled or pulped sample so that nominally 99% of sample is  $<53 \mu\text{m}$  and 95% of sample is  $<32 \mu\text{m}$  fraction for chemical analyses. The mills are operated under conditions that cause minimal sample heating, and to ensure a final product particle size of  $<32 \mu\text{m}$ . Cone-and-quartered milled sample splits for the different analytical methods (namely four different analyses: LOI at 450°C, pH by  $\text{CaCl}_2$ , and  $\text{ICP}_{\text{ar}}$ ) 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, to the extent where it was agreed with the preparation laboratory to stand all Kraft bag samples in an open self-seal plastic bag as a safety precaution during transportation. The final poor status of Kraft bags received by the preparation laboratory was through no fault of the field Contractor but did result in the preparation laboratory taking additional measures to handle and dry the samples with an additional incurred cost to the project.

#### *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 $\text{ICP}_{\text{ar}}$ multi-element analyses*

Sub-samples of prepared (disaggregated, sieved and milled) samples and reference materials were prepared for  $\text{ICP}_{\text{ar}}$  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 randomised 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 chemically analysed by several methods:

- Soil loss-on-ignition at 450°C.
- Soil pH by CaCl<sub>2</sub> slurry.
- Multi-element analyses for a range of major, minor and trace elements by ICP following *aqua regia* digestion (“ICP<sub>ar</sub>”).

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 manifold 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<sub>2</sub> 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<sub>2</sub> 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 homogenised soil sample followed by analysis by ICP-MS. Sample aliquot ca 0.5g is mixed with 75% *aqua regia*, 3:1 HNO<sub>3</sub>:HCl, digested in a graphite heating block and made up to final volume of 12.5ml with dH<sub>2</sub>O. 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 4818 samples were submitted to ALS Minerals Ltd. on 14/02/2020 for chemical analyses. Samples were analysed across 24 laboratory batches of ca 200 samples per batch. Data for 4818 sample IDs by LOI were reported back to GSI by 31/03/2020. Data for 4818 sample IDs by pH were reported back to GSI by 06/04/2020. Thirteen reports were reissued to correct minor formatting errors. Data for 4818 sample IDs by ICP<sub>ar</sub> were reported back to GSI on 24/04/2020. Five reports were reissued to correct for minor formatting errors.

**Table 2 Shallow topsoil ICP<sub>ar</sub> 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 <sup>-1</sup>	0.000002	25	ICP-MS	MS41L-BLD	No
			0.0002	25	ICP-MS	ME-SM41L	Yes
Silver	Ag	mg kg <sup>-1</sup>	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 <sup>-1</sup>	0.0001	10000	ICP-MS	MS41L-BLD	No
			0.01	10000	ICP-MS	ME-SM41L	Yes
Boron	B	mg kg <sup>-1</sup>	0.1	10000	ICP-MS	MS41L-BLD	No
			10	10000	ICP-MS	ME-SM41L	Yes
Barium	Ba	mg kg <sup>-1</sup>	0.005	10000	ICP-MS	MS41L-BLD	No
			0.5	10000	ICP-MS	ME-SM41L	Yes
Beryllium	Be	mg kg <sup>-1</sup>	0.0001	1000	ICP-MS	MS41L-BLD	No
			0.01	1000	ICP-MS	ME-SM41L	Yes
Bismuth	Bi	mg kg <sup>-1</sup>	0.00001	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 <sup>-1</sup>	0.00001	1000	ICP-MS	MS41L-BLD	No
			0.001	1000	ICP-MS	ME-SM41L	Yes
Cerium	Ce	mg kg <sup>-1</sup>	0.00003	500	ICP-MS	MS41L-BLD	No
			0.003	500	ICP-MS	ME-SM41L	Yes
Cobalt	Co	mg kg <sup>-1</sup>	0.00001	10000	ICP-MS	MS41L-BLD	No
			0.001	10000	ICP-MS	ME-SM41L	Yes
Chromium	Cr	mg kg <sup>-1</sup>	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 <sup>-1</sup>	0.00005	500	ICP-MS	MS41L-BLD	No
			0.005	500	ICP-MS	ME-SM41L	Yes
Copper	Cu	mg kg <sup>-1</sup>	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 <sup>-1</sup>	0.00004	10000	ICP-MS	MS41L-BLD	No
			0.004	10000	ICP-MS	ME-SM41L	Yes
Germanium	Ge	mg kg <sup>-1</sup>	0.00005	500	ICP-MS	MS41L-BLD	No
			0.005	500	ICP-MS	ME-SM41L	Yes
Hafnium	Hf	mg kg <sup>-1</sup>	0.00002	500	ICP-MS	MS41L-BLD	No
			0.002	500	ICP-MS	ME-SM41L	Yes
Mercury	Hg	mg kg <sup>-1</sup>	0.00004	10000	ICP-MS	MS41L-BLD	No
			0.004	10000	ICP-MS	ME-SM41L	Yes
Indium	In	mg kg <sup>-1</sup>	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 <sup>-1</sup>	0.00002	10000	ICP-MS	MS41L-BLD	No
			0.002	10000	ICP-MS	ME-SM41L	Yes
Lithium	Li	mg kg <sup>-1</sup>	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 <sup>-1</sup>	0.001	50000	ICP-MS	MS41L-BLD	No
			0.1	50000	ICP-MS	ME-SM41L	Yes
Molybdenum	Mo	mg kg <sup>-1</sup>	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 <sup>-1</sup>	0.00002	500	ICP-MS	MS41L-BLD	No
			0.002	500	ICP-MS	ME-SM41L	Yes
Nickel	Ni	mg kg <sup>-1</sup>	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 <sup>-1</sup>	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Palladium	Pd	mg kg <sup>-1</sup>	0.00001	25	ICP-MS	MS41L-BLD	No
			0.001	25	ICP-MS	ME-SM41L	Yes
Platinum	Pt	mg kg <sup>-1</sup>	0.00002	25	ICP-MS	MS41L-BLD	No
			0.002	25	ICP-MS	ME-SM41L	Yes
Rubidium	Rb	mg kg <sup>-1</sup>	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Rhenium	Re	mg kg <sup>-1</sup>	0.00001	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 <sup>-1</sup>	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Scandium	Sc	mg kg <sup>-1</sup>	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Selenium	Se	mg kg <sup>-1</sup>	0.001	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 <sup>-1</sup>	0.0001	500	ICP-MS	MS41L-BLD	No
			0.01	500	ICP-MS	ME-SM41L	Yes
Strontium	Sr	mg kg <sup>-1</sup>	0.0001	10000	ICP-MS	MS41L-BLD	No
			0.01	10000	ICP-MS	ME-SM41L	Yes
Tantalum	Ta	mg kg <sup>-1</sup>	0.00005	500	ICP-MS	MS41L-BLD	No
			0.005	500	ICP-MS	ME-SM41L	Yes
Tellurium	Te	mg kg <sup>-1</sup>	0.0001	500	ICP-MS	MS41L-BLD	No
			0.003	500	ICP-MS	ME-SM41L	Yes
Thorium	Th	mg kg <sup>-1</sup>	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 <sup>-1</sup>	0.00002	10000	ICP-MS	MS41L-BLD	No
			0.001	10000	ICP-MS	ME-SM41L	Yes
Uranium	U	mg kg <sup>-1</sup>	0.00005	10000	ICP-MS	MS41L-BLD	No
			0.005	10000	ICP-MS	ME-SM41L	Yes
Vanadium	V	mg kg <sup>-1</sup>	0.001	10000	ICP-MS	MS41L-BLD	No
			0.1	10000	ICP-MS	ME-SM41L	Yes
Tungsten	W	mg kg <sup>-1</sup>	0.00001	10000	ICP-MS	MS41L-BLD	No
			0.001	10000	ICP-MS	ME-SM41L	Yes
Yttrium	Y	mg kg <sup>-1</sup>	0.00003	500	ICP-MS	MS41L-BLD	No
			0.003	500	ICP-MS	ME-SM41L	Yes
Zinc	Zn	mg kg <sup>-1</sup>	0.001	10000	ICP-MS	MS41L-BLD	No
			0.1	10000	ICP-MS	ME-SM41L	Yes
Zirconium	Zr	mg kg <sup>-1</sup>	0.0001	500	ICP-MS	MS41L-BLD	No
			0.01	500	ICP-MS	ME-SM41L	Yes

**Table 3 Shallow topsoil pH (CaCl<sub>2</sub>) 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 <sub>2</sub> slurry	No
Soil LOI	%	0.01		Loss-on-ignition at 450°C	Yes

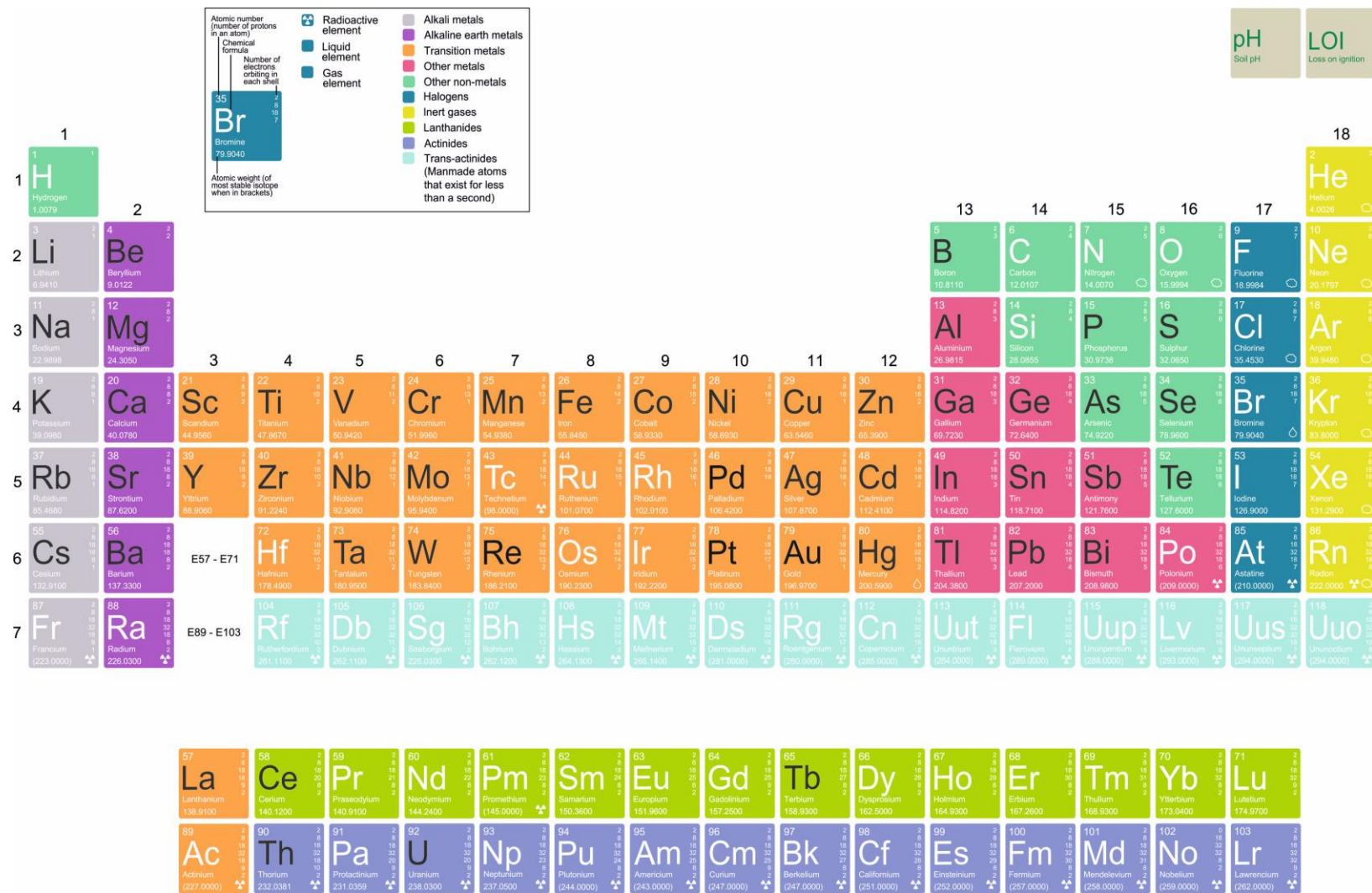


Figure 1 Graphic of the periodic table, with ICP<sub>ar</sub> element analytes for shallow topsoil samples shown in black text, Soil pH (CaCl<sub>2</sub>) and LOI (at 450°C) in green text. Adapted after <http://www.sciencegeek.net/tables/PTOE>



# 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 sample into two identical parts, using a recognised 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 the sequential (i.e. not randomised) sample identities are also analysed in the same sequence, any drift is masked and cannot be identified. There is a likelihood that analytical drift may occur during analysis of samples that exhibit natural increase or decrease in abundance of measurands and result in artificial amplification or suppression of true measurands abundances. Therefore, non-randomised 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 (within tens of metres) 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.

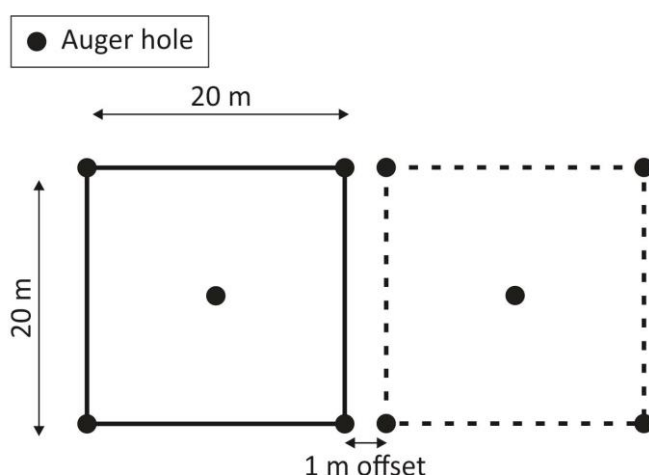


Figure 2 Diagrammatic plan for collection of a five auger hole composite soil sample and a field duplicate sample (indicated by dashed line pictogram).

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.

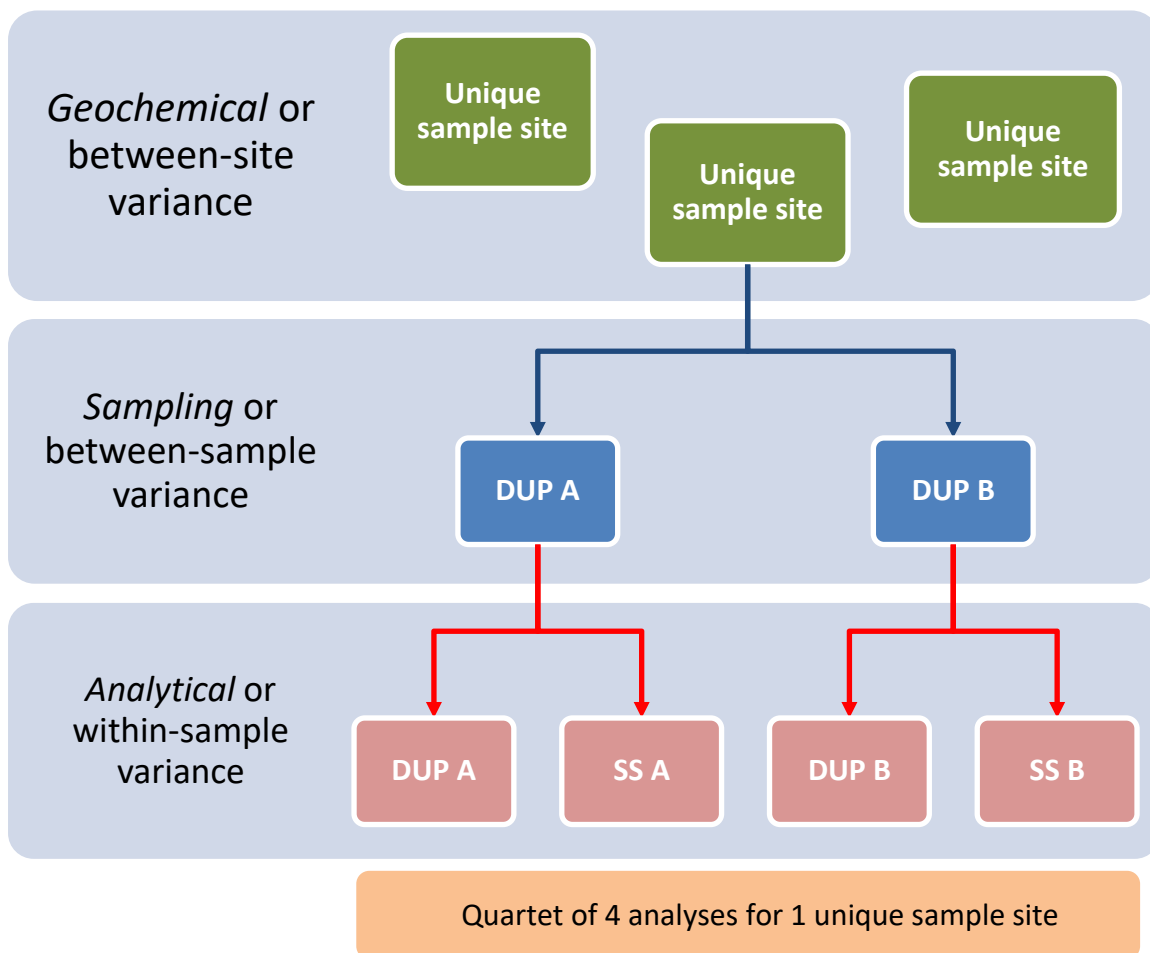


Figure 3 Diagram to show the relationship between field duplicates (“DUP”) and replicate (“SS”) samples, used to apportion data variance.

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 visualise 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 480 samples of duplicates/ replicates for pH and 464 for ICP<sub>ar</sub> and LOI 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 (as 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. Shallow topsoil pH data are automatically excluded.

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 these analytes: palladium (Pd). Where the within sample variance is >4%, the results are highlighted pale orange: tin (Sn), germanium (Ge), mercury (Hg), rhenium (Re), indium (In), tellurium (Te), boron (B), platinum (Pt), gold (Au), tantalum (Ta), tungsten (W).

## 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.

The 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 shallow 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.**

Variable	Method	Variance component (100% sum)			n quartets
		Between site (%)	Between sample (%)	Within sample (%)	
Fe	ICP <sub>ar</sub>	99.27	0.69	0.04	116
Cr	ICP <sub>ar</sub>	99.12	0.67	0.20	116
V	ICP <sub>ar</sub>	99.10	0.78	0.11	116
Al	ICP <sub>ar</sub>	99.01	0.89	0.10	116
Co	ICP <sub>ar</sub>	98.93	0.99	0.08	116
Rb	ICP <sub>ar</sub>	98.82	0.99	0.19	116
Tl	ICP <sub>ar</sub>	98.78	0.83	0.39	115
LOI	LOI at 450°C	98.78	1.15	0.07	116
Ce	ICP <sub>ar</sub>	98.76	1.15	0.09	116
Ni	ICP <sub>ar</sub>	98.74	1.13	0.13	116
Be	ICP <sub>ar</sub>	98.73	1.14	0.13	116
Zn	ICP <sub>ar</sub>	98.69	1.19	0.12	116
Ba	ICP <sub>ar</sub>	98.62	1.28	0.10	116
La	ICP <sub>ar</sub>	98.61	1.28	0.11	116
Ga	ICP <sub>ar</sub>	98.57	0.96	0.47	116
Mn	ICP <sub>ar</sub>	98.54	1.37	0.09	116
Y	ICP <sub>ar</sub>	98.50	1.42	0.08	116
Cd	ICP <sub>ar</sub>	98.48	1.36	0.16	116
Mg	ICP <sub>ar</sub>	98.42	1.37	0.21	116
As	ICP <sub>ar</sub>	98.34	1.24	0.42	116
K	ICP <sub>ar</sub>	98.27	1.47	0.26	116
Zr	ICP <sub>ar</sub>	98.27	1.14	0.59	116
Mo	ICP <sub>ar</sub>	98.18	1.62	0.20	116
U	ICP <sub>ar</sub>	98.14	1.72	0.14	116
S	ICP <sub>ar</sub>	97.82	2.05	0.13	116
Nb	ICP <sub>ar</sub>	97.80	1.08	1.12	116
Sc	ICP <sub>ar</sub>	97.68	1.60	0.72	116
Hf	ICP <sub>ar</sub>	97.48	1.33	1.19	112

Variance component (100% sum)

Variable	Method	Between site (%)	Between sample (%)	Within sample (%)	<i>n</i> quartets
Ti	ICP <sub>ar</sub>	97.47	1.70	0.83	116
Cs	ICP <sub>ar</sub>	97.46	2.13	0.41	116
Th	ICP <sub>ar</sub>	97.34	1.85	0.81	116
P	ICP <sub>ar</sub>	97.33	2.52	0.15	116
Ag	ICP <sub>ar</sub>	97.31	1.81	0.88	116
Cu	ICP <sub>ar</sub>	96.94	2.93	0.14	116
Sb	ICP <sub>ar</sub>	96.69	2.09	1.23	116
Sr	ICP <sub>ar</sub>	96.32	3.32	0.35	116
Ca	ICP <sub>ar</sub>	96.10	3.82	0.08	116
Bi	ICP <sub>ar</sub>	95.83	2.20	1.97	116
Li	ICP <sub>ar</sub>	95.81	2.54	1.65	110
Se	ICP <sub>ar</sub>	94.87	3.57	1.56	116
Na	ICP <sub>ar</sub>	94.57	2.65	2.78	116
Pb	ICP <sub>ar</sub>	94.47	3.72	1.80	116
Sn	ICP <sub>ar</sub>	88.21	5.60	6.18	116
Ge	ICP <sub>ar</sub>	86.55	4.38	9.07	116
Hg	ICP <sub>ar</sub>	85.69	6.29	8.03	116
Re	ICP <sub>ar</sub>	84.97	7.61	7.42	86
In	ICP <sub>ar</sub>	83.93	7.34	8.74	115
Te	ICP <sub>ar</sub>	83.21	4.91	11.88	116
B	ICP <sub>ar</sub>	80.22	6.28	13.50	112
Pt	ICP <sub>ar</sub>	70.28	6.61	23.11	48
Au	ICP <sub>ar</sub>	65.54	12.79	21.67	107
Ta	ICP <sub>ar</sub>	64.17	13.06	22.77	43
W	ICP <sub>ar</sub>	61.34	11.47	27.19	114
Pd	ICP <sub>ar</sub>	45.65	18.72	35.63	9

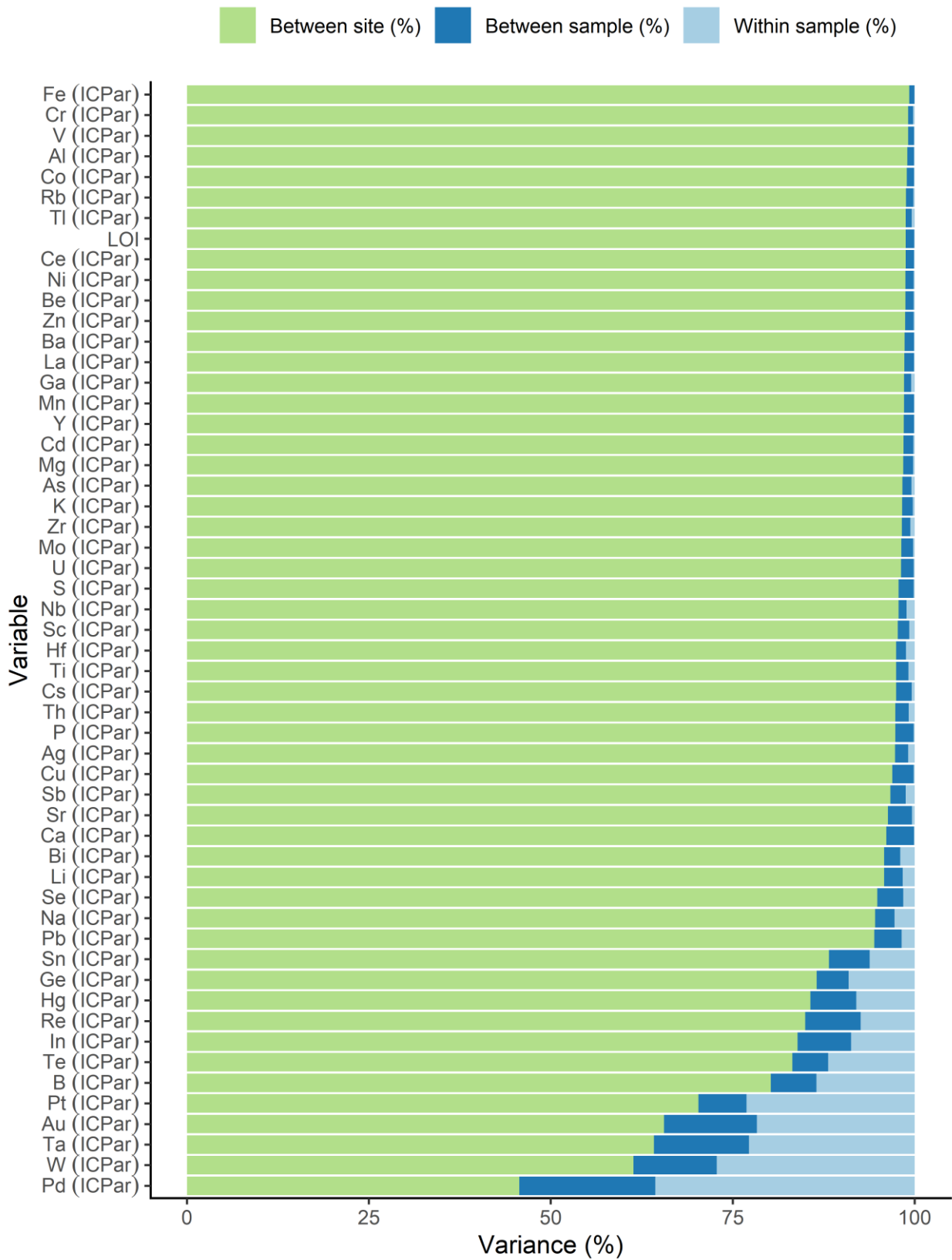


Chart 1 Stacked bar chart to display ANOVA results for all duplicate site shallow topsoil data.



# 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<sub>ar</sub> 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.

## Randomised and blind to laboratory RMs

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

## Certified reference materials (CRMs)

Table 7 Blind CRMs used for ICP<sub>ar</sub> 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 homogenised 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 XRFS and ICP<sub>ar</sub> 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]	Shallow topsoil	Potato crop field (BDC1)		Silty soil derived from Lr Palaeozoic sandstone and shale till, overlying Carboniferous limestone bedrock	
CNLST	[238834 317551]	Shallow topsoil	Grass moor/rough grazing (AC00)		Silty soil derived from alluvial deposit, overlying Carboniferous shale and limestone	
DAL	[262562 406923]	Shallow topsoil	Grass moor/rough grazing (AC00)		Mineral gley overlying Dalradian Southern Highland Group schist and psammite bedrock	
LDOWN	[289197 298786]	Shallow 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
LGRAN	[297200 195155]	Shallow topsoil	Pasture (BAB0) and agricultural grassland (BA00)		bedrock Sandy soil derived from granite till, overlying quartz diorite bedrock	
LMGPSH	[203695 327205]	Shallow 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]	Shallow 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. 2 <sup>nd</sup> order	Sediment from stream overlying Silurian greywacke and draining the Mourne Mountains granite Complex	Small stream <3 m wide
MONPB	[287290 324485]	Shallow 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]	Shallow 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. 2 <sup>nd</sup> 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, 2 <sup>nd</sup> 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
WWLPAL	[297025 208890]	Shallow topsoil	Ploughed field. Arable land (BD00)		bedrock Till derived from Lr Palaeozoic sandstone and shale overlying granite bedrock	
WXSERP	[306332 166170]	Shallow 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. 2 <sup>nd</sup> 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 summarised 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 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<sub>3s</sub> and 2<sub>2s</sub> 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-homogenised 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  $\text{mean(mR)}/1.128$ , 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  $\pm 3$  sequential deviations, dark blue horizontal lines) are termed failures but are statistically acceptable. Exceedances of the warning limits (process mean  $\pm 2$  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 are not r limits (process mean  $\pm 1$  sequential deviation) but are useful reference lines against which drift and shift can be observed. These control charts are inspected for trends in the sequence and/or multiple analytes exhibiting patterns of behaviour. The main quality check is for multiple analytes of the same sample presenting warning or failures and periods of time for the analyses where multiple sample warnings or failures are seen. If the method LLD is  $\geq$  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. Nine such events were recorded where at least two analytes had fallen outside of lower/upper control limits. In all 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<sub>3s</sub> violations and only three 2<sub>2s</sub> violations were recorded.

Table 9. Summary of CRM data quality issues observed by control charts for IPC<sub>ar</sub> analyses.

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
STSD-3	611736A	LR20036970-036	ICP-MS	19-02-2020 22:27	Single analyte warning: Ba	Outwith upper/lower warning limits
TILL-2	611991A	LR20036987-091	ICP-MS	21-02-2020 20:11	Single analyte failure and multiple analyte warning: Sb (Cd; Ce; Cu; Nb; Pb).	Outwith upper/lower warning and control limits
TILL-3	612076A	LR20036987-176	ICP-MS	21-02-2020 20:40	Single analyte failure and warning: Mn (As).	Outwith upper/lower warning and control limits
STSD-3	612122A	LR20037019-022	ICP-MS	21-02-2020 22:50	Single analyte failure and multiple analyte warning: Sc (As; Ca; Ti; Zn).	Consecutively outwith upper/lower warning and control limits
STSD-3	611952A	LR20036987-052	ICP-MS	26-02-2020 02:33	Single analyte failure and multiple analyte warning: Sc (Ga; Se; Zr).	Consecutively outwith upper/lower warning and control limits
STSD-1	612059A	LR20036987-159	ICP-MS	26-02-2020 10:07	Single analyte failure and warning: Au (Cd).	Outwith upper/lower warning and control limits
TILL-1	611803A	LR20036970-103	ICP-MS	26-02-2020 15:08	Multiple analyte warning: Cd; Cu; Ge; La; Mo; Sb; Th; V.	Outwith upper/lower warning limits
STSD-1	611824A	LR20036970-124	ICP-MS	26-02-2020 15:47	Multiple analyte failure and warning: Cd; Sc; Th; Zr (Bi; Cs; Re; Ti).	Outwith upper/lower warning and control limits
STSD-1	612249A	LR20037019-149	ICP-MS	26-02-2020 18:34	Single analyte failure and multiple analyte warning: W (Ba; Mn).	Outwith upper/lower warning and control limits
STSD-3	612336A	LR20037062-036	ICP-MS	26-02-2020 23:31	Multiple analyte failure and warning: Ba; Be; K; W (Al; Re; U).	Outwith upper/lower warning and control limits
STSD-3	612552A	LR20037156-052	ICP-MS	27-02-2020 01:23	Single analyte warning: K.	Outwith upper/lower warning limits
TILL-2	612591A	LR20037156-091	ICP-MS	27-02-2020 02:57	Single analyte warning: In.	Outwith upper/lower warning limits
STSD-1	612659A	LR20037156-159	ICP-MS	27-02-2020 12:09	Single analyte failure and warning: B (Bi).	Outwith upper/lower warning and

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
						control limits
TILL-1	612403A	LR20037062-103	ICP-MS	27-02-2020 23:55	Multiple analyte warning: Cu; W.	Outwith upper/lower warning limits
TILL-3	612676A	LR20037156-176	ICP-MS	28-02-2020 21:01	Single analyte warning: Se.	Outwith upper/lower warning limits
TILL-1	613003A	LR20037827-103	ICP-MS	03-03-2020 00:54	Single analyte warning: Mn.	Outwith upper/lower warning limits
TILL-2	613191A	LR20037833-091	ICP-MS	05-03-2020 05:04	Single analyte warning: Ag.	Outwith upper/lower warning limits
STSD-3	612936A	LR20037827-036	ICP-MS	05-03-2020 21:40	Single analyte warning: Ca.	Outwith upper/lower warning limits
STSD-3	613152A	LR20037833-052	ICP-MS	05-03-2020 23:42	Multiple analyte warning: Rb; Tl.	Outwith upper/lower warning limits
STSD-1	613259A	LR20037833-159	ICP-MS	06-03-2020 02:56	Single analyte failure: Ni.	Consecutively outwith upper/lower warning limits
STSD-3	614136A	LR20038953-036	ICP-MS	06-03-2020 20:52	Multiple analyte warning: Ca; S.	Outwith upper/lower warning limits
STSD-3	613536A	LR20037923-036	ICP-MS	07-03-2020 04:16	Multiple analyte warning: B; Cd; Ti.	Outwith upper/lower warning limits
STSD-3	613752A	LR20037968-052	ICP-MS	09-03-2020 19:54	Single analyte failure: Hf.	Outwith upper/lower warning and control limits
TILL-3	613276A	LR20037833-176	ICP-MS	09-03-2020 23:55	Single analyte warning: S.	Outwith upper/lower warning limits
STSD-1	613449A	LR20037866-149	ICP-MS	10-03-2020 14:59	Single analyte failure and warning: Mo (Ni).	Consecutively outwith upper/lower warning limits
TILL-1	613603A	LR20037923-103	ICP-MS	12-03-2020 11:12	Single analyte warning: Zr.	Outwith upper/lower warning limits

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
STSD-1	613624A	LR20037923-124	ICP-MS	12-03-2020 11:49	Multiple analyte failure and warning: Ni; Re (As; Ge).	Consecutively outwith upper/lower warning and control limits
TILL-2	613791A	LR20037968-091	ICP-MS	12-03-2020 14:13	Single analyte warning: Fe.	Outwith upper/lower warning limits
STSD-1	613859A	LR20037968-159	ICP-MS	12-03-2020 23:22	Multiple analyte failure and warning: Pb; Sn (Ga; Mo; Sr).	Outwith upper/lower warning and control limits
TILL-3	613876A	LR20037968-176	ICP-MS	13-03-2020 00:23	Multiple analyte warning: Co; Mo; Ni; Pb; Rb; Sn; V; Y.	Outwith upper/lower warning limits
STSD-3	613322A	LR20037866-022	ICP-MS	14-03-2020 01:05	Multiple analyte failure and warning: Cd; Mo; Sn; Y (Cs; Sb; Sr; Te; V).	Outwith upper/lower warning and control limits
STSD-3	613922A	LR20038939-022	ICP-MS	14-03-2020 04:02	Multiple analyte warning: Bi; Ti.	Outwith upper/lower warning limits
TILL-1	614203A	LR20038953-103	ICP-MS	19-03-2020 13:27	Multiple analyte warning: Hf; Nb; Re.	Outwith upper/lower warning limits
STSD-1	614224A	LR20038953-124	ICP-MS	19-03-2020 14:04	Single analyte warning: Sb.	Outwith upper/lower warning limits
STSD-1	614049A	LR20038939-149	ICP-MS	20-03-2020 23:48	Single analyte warning: Cs.	Outwith upper/lower warning limits
STSD-1	614459A	LR20039006-159	ICP-MS	20-03-2020 23:48	Single analyte failure and multiple analyte warning: Ag (Hg; Sb).	Outwith upper/lower warning and control limits
STSD-3	614352A	LR20039006-052	ICP-MS	21-03-2020 13:16	Multiple analyte warning: Al; Cs; Hf; Li; Mg; Ni.	Outwith upper/lower warning limits
TILL-3	614476A	LR20039006-176	ICP-MS	21-03-2020 21:14	Multiple analyte warning: As; Re.	Outwith upper/lower warning limits
STSD-3	614522A	LR20039103-022	ICP-MS	21-03-2020 23:02	Multiple analyte failure and warning: Ag; Au (Be; Cr; P).	Outwith upper/lower warning and control limits
STSD-1	614649A	LR20039103-149	ICP-MS	28-03-2020 00:10	Multiple analyte warning: Bi; Ca; Se; Tl.	Outwith upper/lower warning



CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
						limits
STSD-1	614824A	LR20039962-124	ICP-MS	28-03-2020 03:20	Multiple analyte failure: Hg; In.	Outwith upper/lower warning limits
STSD-3	614952A	LR20039973-052	ICP-MS	28-03-2020 08:57	Single analyte failure and multiple analyte warning: Fe (Bi; Hf; Te).	Outwith upper/lower warning and control limits
STSD-1	615059A	LR20039973-159	ICP-MS	28-03-2020 17:55	Multiple analyte failure and single analyte warning: La; Te (Ni).	Outwith upper/lower warning and control limits
TILL-3	615076A	LR20039973-176	ICP-MS	28-03-2020 18:29	Single analyte warning: Hg.	Outwith upper/lower warning limits
TILL-2	614991A	LR20039973-091	ICP-MS	29-03-2020 00:07	Single analyte failure and warning: Sb (Nb).	Outwith upper/lower warning and control limits
TILL-2	614991A	LR20039973-091	ICP-MS	29-03-2020 00:07	Single analyte failure: Sb.	Outwith upper/lower control limits
TILL-1	615403A	LR20040015-103	ICP-MS	02-04-2020 07:16	Multiple analyte warning: Ni; Rb; Y.	Outwith upper/lower warning limits
STSD-3	615122A	LR20039978-022	ICP-MS	03-04-2020 05:57	Single analyte failure and multiple analyte warning: Sb (Hg; Th).	Outwith upper/lower warning and control limits
STSD-3	615336A	LR20040015-036	ICP-MS	03-04-2020 10:49	Single analyte warning: Th.	Outwith upper/lower warning limits
STSD-1	615249A	LR20039978-149	ICP-MS	03-04-2020 12:47	Multiple analyte warning: La; Ni; Sb.	Outwith upper/lower warning limits
TILL-2	615591A	LR20040033-091	ICP-MS	08-04-2020 09:35	Single analyte failure: Sb.	Consecutively outwith upper/lower warning limits
STSD-3	615936A	LR20040981-036	ICP-MS	08-04-2020 21:02	Single analyte warning: Mn.	Outwith upper/lower warning limits
STSD-3	616152A	LR20040994-052	ICP-MS	08-04-2020 22:52	Single analyte failure: In.	Outwith upper/lower control limits
TILL-1	616003A	LR20040981-103	ICP-MS	09-04-2020 15:50	Single analyte failure and multiple analyte warning: Cu (Mo; Nb; Ni; Rb; Se; Ti; Y).	Outwith upper/lower warning and control limits

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
STSD-1	616024A	LR20040981-124	ICP-MS	09-04-2020 16:22	Multiple analyte warning: Rb; Sr.	Outwith upper/lower warning limits
STSD-1	616024A	LR20040981-124	ICP-MS	09-04-2020 16:22	Single analyte warning: Sr.	Outwith upper/lower warning limits
STSD-1	616259A	LR20040994-159	ICP-MS	09-04-2020 17:53	Single analyte warning: Tl.	Outwith upper/lower warning limits
TILL-3	616276A	LR20040994-176	ICP-MS	09-04-2020 23:33	Single analyte warning: B.	Outwith upper/lower warning limits
STSD-3	616322A	LR20040999-022	ICP-MS	10-04-2020 17:37	Multiple analyte warning: B; Ni.	Outwith upper/lower warning limits
STSD-3	616322A	LR20040999-022	ICP-MS	10-04-2020 17:37	Single analyte warning: Ni.	Outwith upper/lower warning limits
STSD-1	616449A	LR20040999-117	ICP-MS	10-04-2020 20:24	Single analyte failure and multiple analyte warning: B (Al; Mg).	Outwith upper/lower warning and control limits
TILL-2	616191A	LR20040994-091	ICP-MS	14-04-2020 03:51	Multiple analyte failure and warning: Ge; Sb (Al; Ce; Cu; Tl; Y).	Consecutively 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 regardless of differences between method used by the laboratory and method used to obtain certified values. For the ICP<sub>ar</sub> analytes there are five CRMs available: STSD 1, STSD 3, TILL 1, TILL 2 and TILL 3. Each regression line and its equation is based on up to five data points. For the LOI analyses there are no CRMs but a series of project SRMs were created: APT, AST, SPT and SST.

Each linear regression relationship was assessed to see would its application as a data conditioning factor improve or disimprove the results with respect to merging of discrete dataset. Further, the reference and mean measured values are considered alongside the typical sample data concentration range. It is not recommended to apply a data modification based on CRM data that are very dissimilar to the sample site dataset.

A summary of the linear regression relationships is presented in Table 10 for the ICP<sub>ar</sub> analytes. All analytes have a generally excellent fit except for Au, Bi, Hf, Sn, Sr, W and Zr as detailed below. Analytes characterized by slope values deviating significantly from unity show poor correlation of recovery between used and certified methods. Data users are cautioned about the performance of measured against certified concentration values for these analytes. No data are recommended to be conditioned.

**Table 10 Linear regression relationships for ICP<sub>ar</sub> analytes.**

Analyte	CRMs	Digestion	Linear regression relationships		
			Intercept	Slope	R squared
Ag (mg kg <sup>-1</sup> )	TILL, STSD	partial	0.0684	0.887	0.999
Al (%)	TILL	partial	0.33	0.736	0.996
As (mg kg <sup>-1</sup> )	TILL, STSD	partial	4.68	0.941	0.999
Au (mg kg <sup>-1</sup> )	TILL, STSD	total	0.00847	1.16	0.0597
B (mg kg <sup>-1</sup> )	STSD	total	-16.5	0.276	1
Ba (mg kg <sup>-1</sup> )	TILL	partial	-8.98	1.1	0.998
Be (mg kg <sup>-1</sup> )	TILL	partial	-0.419	8.99	0.992
Bi (mg kg <sup>-1</sup> )	TILL, STSD	partial	4.83		0
Ca (%)	TILL	partial	-0.00775	0.817	0.999
Cd (mg kg <sup>-1</sup> )	TILL, STSD	partial	0.0147	1.13	0.998
Ce (mg kg <sup>-1</sup> )	TILL, STSD	total	-5.39	0.782	0.946
Co (mg kg <sup>-1</sup> )	TILL, STSD	partial	-0.31	1.04	0.913
Cr (mg kg <sup>-1</sup> )	TILL, STSD	partial	4.62	0.778	0.998
Cs (mg kg <sup>-1</sup> )	TILL, STSD	total	-0.0748	0.57	0.994
Cu (mg kg <sup>-1</sup> )	TILL, STSD	partial	-0.34	0.992	1
Fe (%)	TILL, STSD	partial	0.246	0.914	0.92
Ga (mg kg <sup>-1</sup> )					
Ge (mg kg <sup>-1</sup> )					
Hf (mg kg <sup>-1</sup> )	TILL, STSD	total	0.00346	0.00311	0.259
Hg (mg kg <sup>-1</sup> )	TILL, STSD	partial	-0.0222	1.21	0.94

Analyte	CRMs	Digestion	Linear regression relationships		
			Intercept	Slope	R squared
In (mg kg <sup>-1</sup> )					
K (%)	TILL	partial	-0.0301	0.786	0.994
La (mg kg <sup>-1</sup> )	TILL, STSD	total	2.51	0.589	0.811
Li (mg kg <sup>-1</sup> )	TILL, STSD	total	0.73	0.755	0.977
Mg (%)	TILL	partial	-0.122	1.07	1
Mn (mg kg <sup>-1</sup> )	TILL, STSD	partial	87.6	0.909	0.995
Mo (mg kg <sup>-1</sup> )	TILL, STSD	partial	-1.61	1.21	0.985
Na (%)	TILL	partial	0.0112	0.0353	0.866
Nb (mg kg <sup>-1</sup> )	TILL, STSD	total	-0.312	0.17	0.855
Ni (mg kg <sup>-1</sup> )	TILL, STSD	partial	4.43	0.896	0.924
P (%)	TILL	partial	0.00983	0.716	0.651
Pb (mg kg <sup>-1</sup> )	TILL, STSD	partial	1.02	0.995	0.995
Pd (mg kg <sup>-1</sup> )					
Pt (mg kg <sup>-1</sup> )					
Rb (mg kg <sup>-1</sup> )	TILL, STSD	total	-3.39	0.286	0.936
Re (mg kg <sup>-1</sup> )					
S (%)	STSD	total	-0.0389	1.44	1
Sb (mg kg <sup>-1</sup> )	STSD	partial	-0.242	1.3	1
Sc (mg kg <sup>-1</sup> )	TILL, STSD	total	5.02	-0.109	0.0367
Se (mg kg <sup>-1</sup> )					
Sn (mg kg <sup>-1</sup> )	STSD	total	1.69		0
Sr (mg kg <sup>-1</sup> )	TILL, STSD	total	33.5	0.0106	0.000674
Ta (mg kg <sup>-1</sup> )	TILL, STSD	total	0.00207	-0.000783	0.837
Te (mg kg <sup>-1</sup> )					
Th (mg kg <sup>-1</sup> )	TILL, STSD	total	-1.78	0.538	0.744
Ti (%)	TILL, STSD	total	0.0414	0.014	0.607
Tl (mg kg <sup>-1</sup> )					
U (mg kg <sup>-1</sup> )	TILL, STSD	total	-0.994	0.913	0.97
V (mg kg <sup>-1</sup> )	TILL, STSD	partial	20	0.561	0.668
W (mg kg <sup>-1</sup> )	TILL		1.96		0
Y (mg kg <sup>-1</sup> )	TILL, STSD	total	-4.58	0.638	0.579
Zn (mg kg <sup>-1</sup> )	TILL, STSD	partial	-2.91	1	1
Zr (mg kg <sup>-1</sup> )	TILL, STSD	total	0.273	0.00315	0.134

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<sub>ar</sub> analytes.

Analyte	CRMs	Digestion	Linear regression relationships		
			Intercept	Slope	R squared
Ag (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	0.00254	0.974	1
Al (%)	OREAS46, OREAS920, MRGeo08	partial	-0.0263	1.02	0.994
As (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	0.145	1	1
Au (mg kg <sup>-1</sup> )	MRGeo08, GBM908-90	partial/total	-0.0000776	1.03	1
B (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08, GBM908-10	n/a			
Ba (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-3.48	1.02	1
Be (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.0125	1.01	0.99
Bi (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-6.13E-04	0.959	1
Ca (%)	OREAS46, OREAS920, MRGeo08	partial	-0.0305	1.09	1
Cd (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.00238	1.02	1
Ce (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.534	1.01	1
Co (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.647	1.06	0.999
Cr (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-1.16	1.04	1
Cs (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.0983	1.04	1
Cu (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	0.668	1	1
Fe (%)	OREAS46, OREAS920, MRGeo08	partial	-0.0378	1.02	0.999
Ga (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.572	1.06	0.992
Ge (mg kg <sup>-1</sup> )	OREAS46, MRGeo08	partial	0.00533	0.976	1
Hf (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.00704	0.968	0.949
Hg (mg kg <sup>-1</sup> )	OREAS46, MRGeo08	partial	0.00139	1.01	1
In (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.0011	1.02	1
K (%)	OREAS46, OREAS920, MRGeo08	partial	-0.0211	1.04	0.999
La (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.312	1.01	0.984
Li (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.0702	1.01	1
Mg (%)	OREAS46, OREAS920, MRGeo08	partial	-0.0267	1.02	1
Mn (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	382	0.0833	0.0218
Mo (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.0278	1.04	1
Na (%)	OREAS46, MRGeo08	partial	-0.00389	1.09	1
Nb (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.355	1.5	0.998
Ni (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	0.0851	1.01	1
P (%)	OREAS46, OREAS920, MRGeo08	partial	0.00501	0.943	0.998

Analyte	CRMs	Digestion	Linear regression relationships		
			Intercept	Slope	R squared
Pb (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.329	1.01	1
Pd (mg kg <sup>-1</sup> )	MRGeo08	partial	0.00398		0
Pt (mg kg <sup>-1</sup> )	MRGeo08	partial	0.00194		0
Rb (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-1.03	1.03	1
Re (mg kg <sup>-1</sup> )	MRGeo08	partial	0.00789		0
S (%)	OREAS920, MRGeo08	partial	6.14E-04	0.98	1
Sb (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	0.02	0.966	1
Sc (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.26	1.07	1
Se (mg kg <sup>-1</sup> )	OREAS920, MRGeo08	partial	-0.722	1.1	1
Sn (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.108	1.06	0.997
Sr (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-3.39	1.12	1
Ta (mg kg <sup>-1</sup> )	MRGeo08, GBM908-10	partial/total	0.0159	-0.0143	1
Te (mg kg <sup>-1</sup> )	OREAS46, MRGeo08	partial	-0.00795	1.42	1
Th (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.134	1.01	1
Ti (%)	OREAS46, OREAS920, MRGeo08	partial	7.18E-04	1	1
Tl (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.00394	0.984	1
U (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.0417	0.997	1
V (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-2.02	1.06	1
W (mg kg <sup>-1</sup> )	OREAS46, MRGeo08	partial	0.0217	0.933	1
Y (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	0.102	0.98	0.986
Zn (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	0.338	0.999	1
Zr (mg kg <sup>-1</sup> )	OREAS46, OREAS920, MRGeo08	partial	-0.187	0.987	0.978

### Gold (Au) by ICP<sub>ar</sub> (MS41L-BLD)

Gold data from the MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Use of this data is not recommended. No data conditioning is recommended.

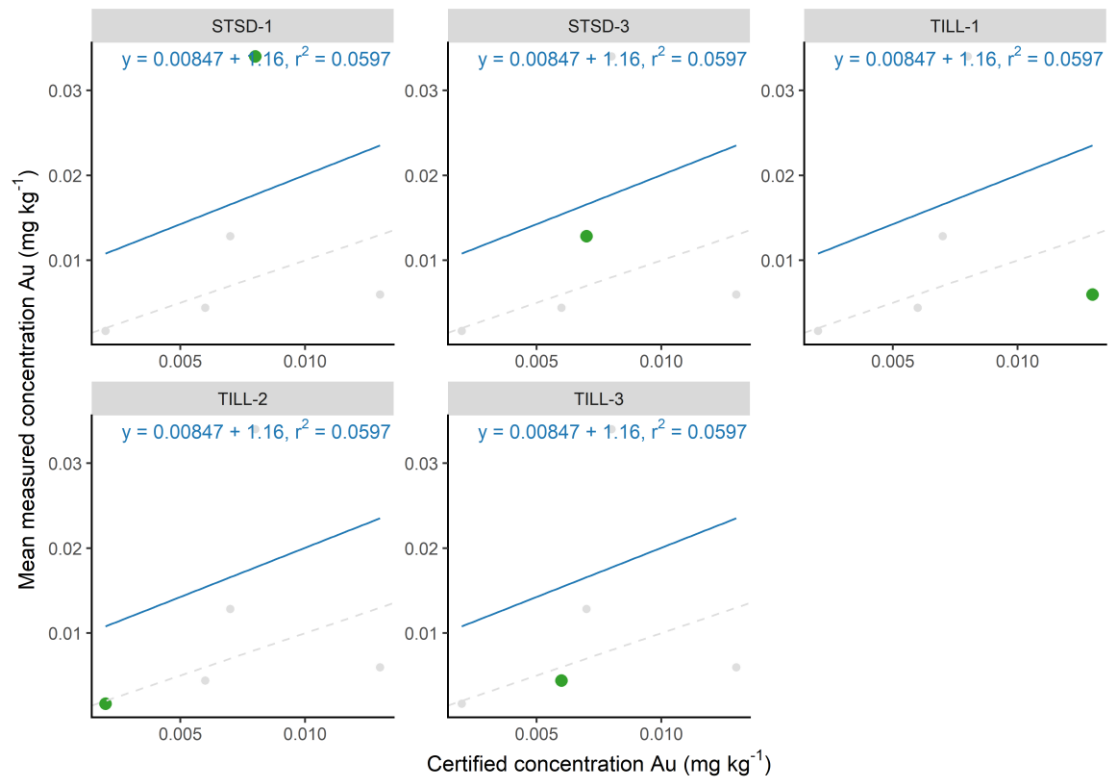


Chart 2 Gold (Au) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a faint dashed grey line.

*Bismuth (Bi) by ICP<sub>ar</sub> (MS41L-BLD)*

Regression curve for bismuth data by MS41L-BLD method was not constructed due to insufficient number of determinations. No data conditioning is recommended.

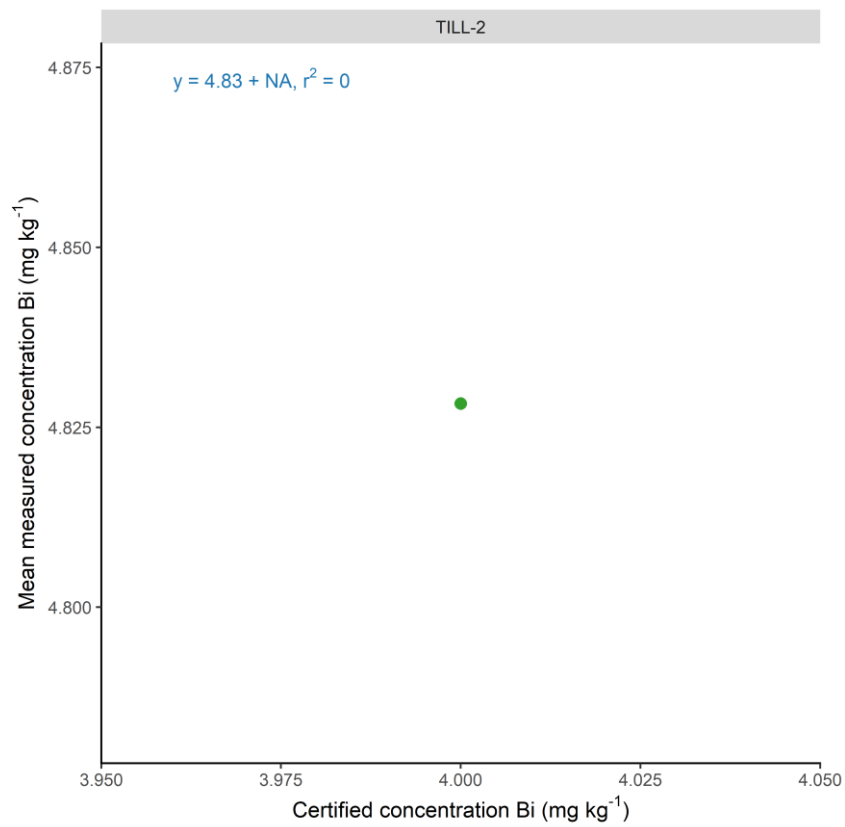


Chart 3 Bismuth (Bi) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a faint dashed grey line.



### Hafnium (Hf) by ICP<sub>ar</sub> (MS41L-BLD)

Regression curve for Hafnium data by MS41L-BLD method are generally poor in terms of fitting the certified values, with the TILL-1, TILL-2 and TILL-3 determination being particularly poor. No data condition is recommended.

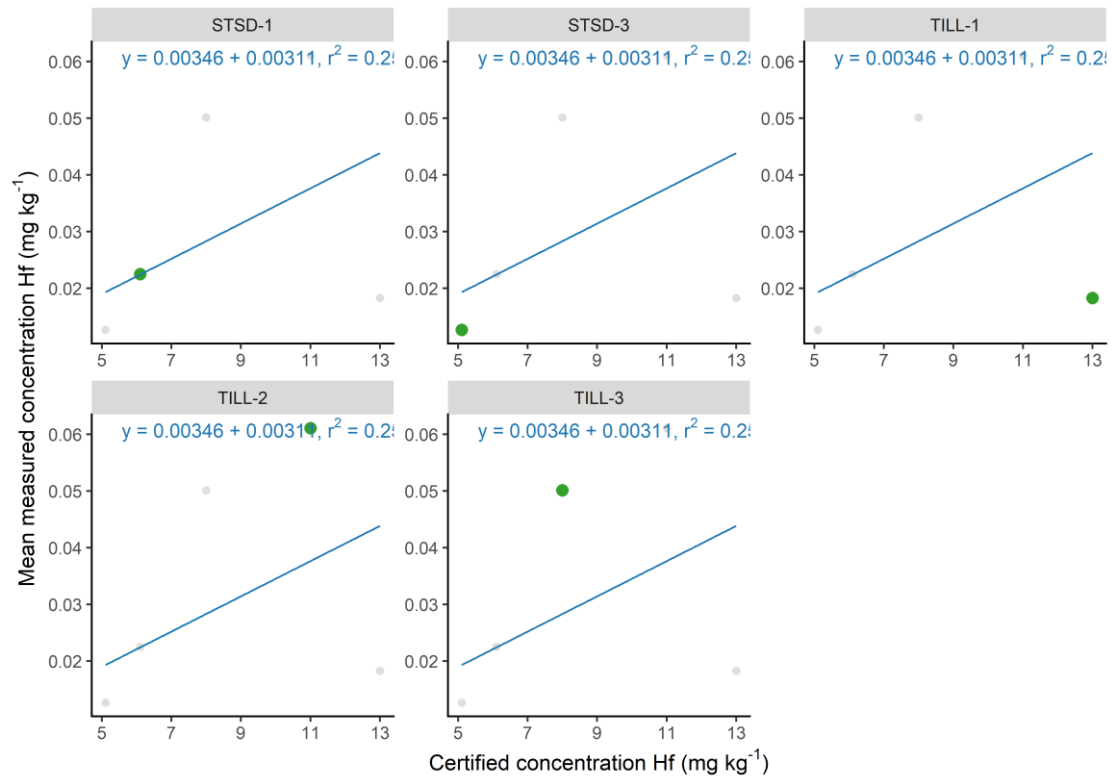


Chart 4 Hafnium (Hf) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a faint dashed grey line.

Scandium (Sc) by ICP<sub>or</sub> (MS41L-BLD)

Regression curve for Scandium data by MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Use of this data is not recommended. No data condition is recommended.

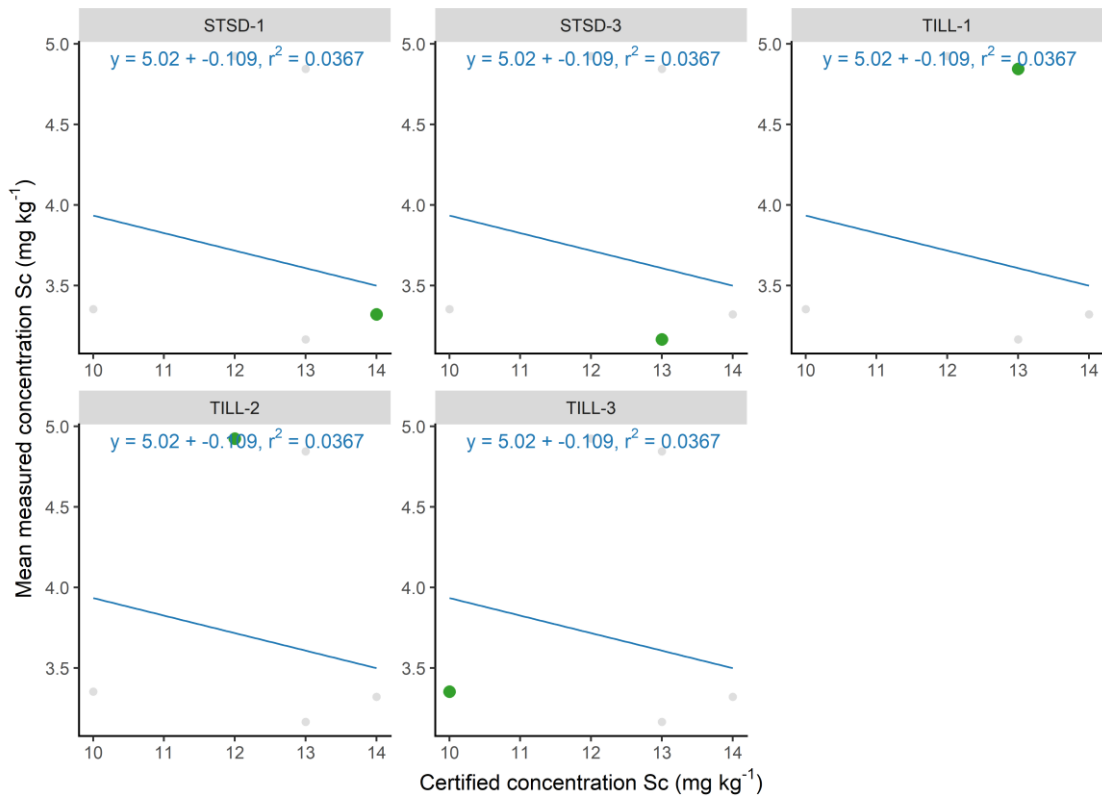


Chart 5 Scandium (Sc) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a faint dashed grey line.

Tin (Sn) by ICP<sub>ar</sub> (MS41L-BLD)

Regression curve for Hafnium data by MS41L-BLD method was not constructed due to insufficient number of determinations. No data condition is recommended.

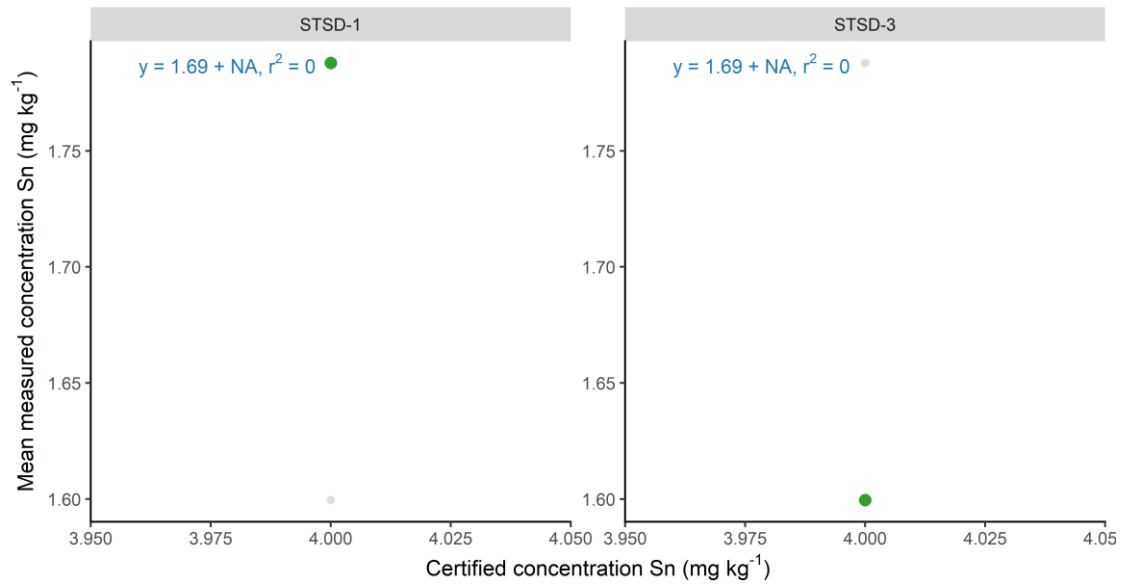


Chart 6 Tin (Sn) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a faint dashed grey line.

Strontium (Sr) by ICP<sub>ar</sub> (MS41L-BLD)

Regression curve for Strontium data by MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Use of this data is not recommended. No data condition is recommended.

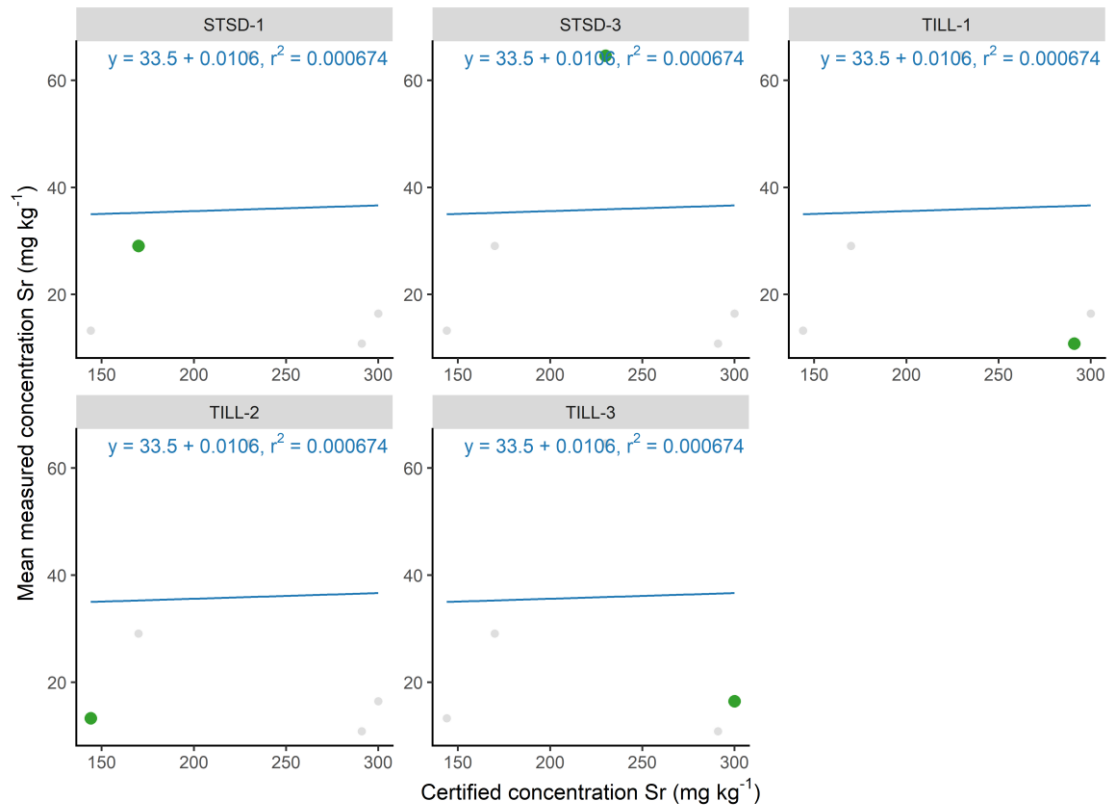


Chart 7 Strontium (Sr) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a faint dashed grey line.

*Tungsten (W) by ICP<sub>or</sub> (MS41L-BLD)*

Regression curve for Tungsten data by MS41L-BLD method was not constructed due to insufficient number of determinations. No data condition is recommended.

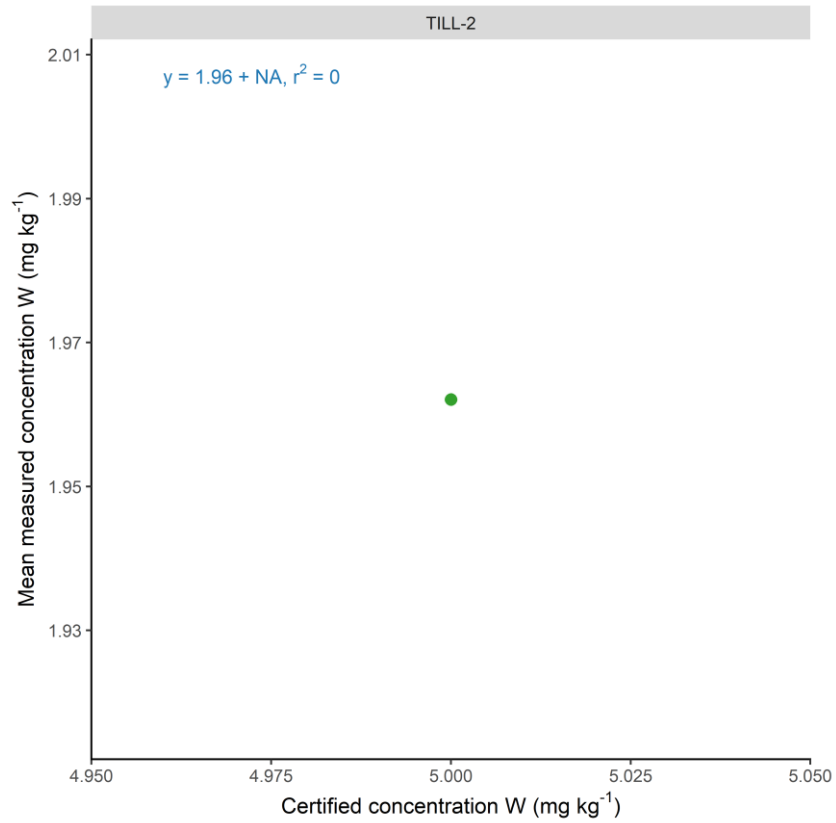


Chart 8 Tungsten (W) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Yttrium (Y) by ICP<sub>or</sub> (MS41L-BLD)

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

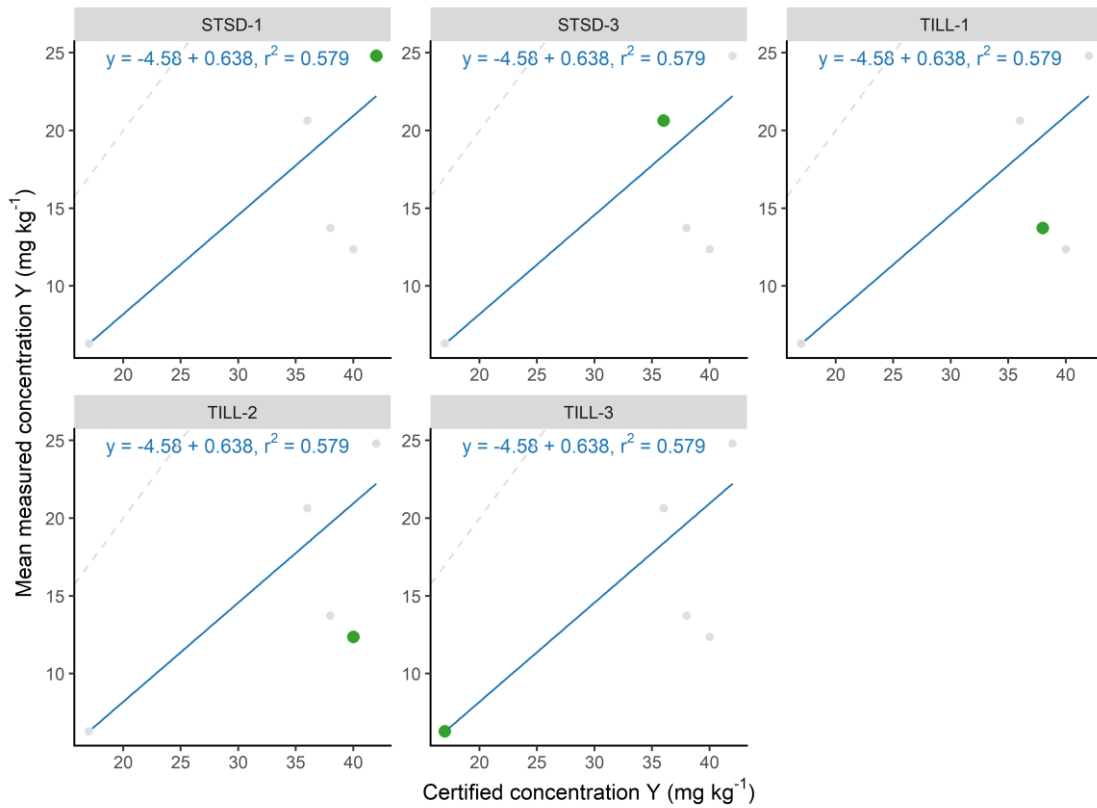


Chart 9 Yttrium (Y) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a faint dashed grey line.

Zirconium (Zr) by ICP<sub>or</sub> (MS41L-BLD)

Regression curve for Zirconium 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. No data condition is recommended.

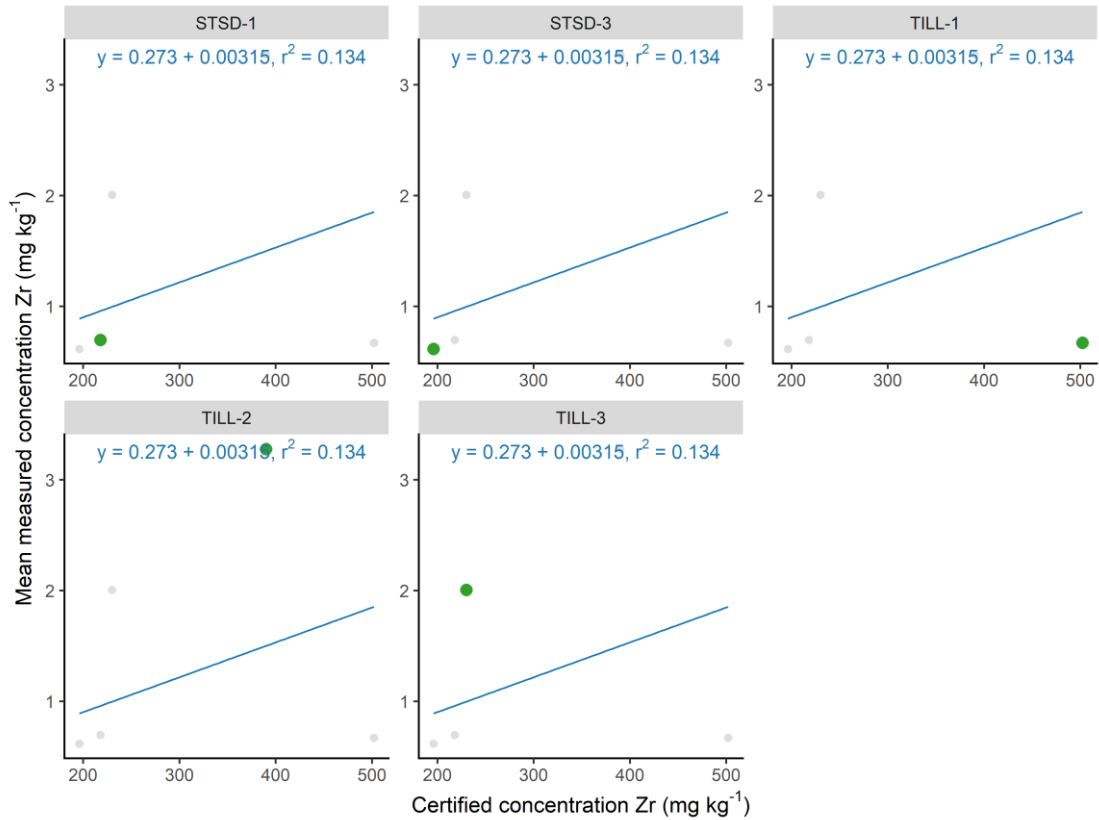


Chart 10 Zirconium (Zr) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a faint dashed grey line.

Manganese (Mn) by ICP<sub>ar</sub> (MS41L-BLD)

Regression curve for Manganese data by MS41L-BLD method do not fit well at all to certified concentrations in the CRMs. Use of this data is not recommended.. No data condition is recommended.

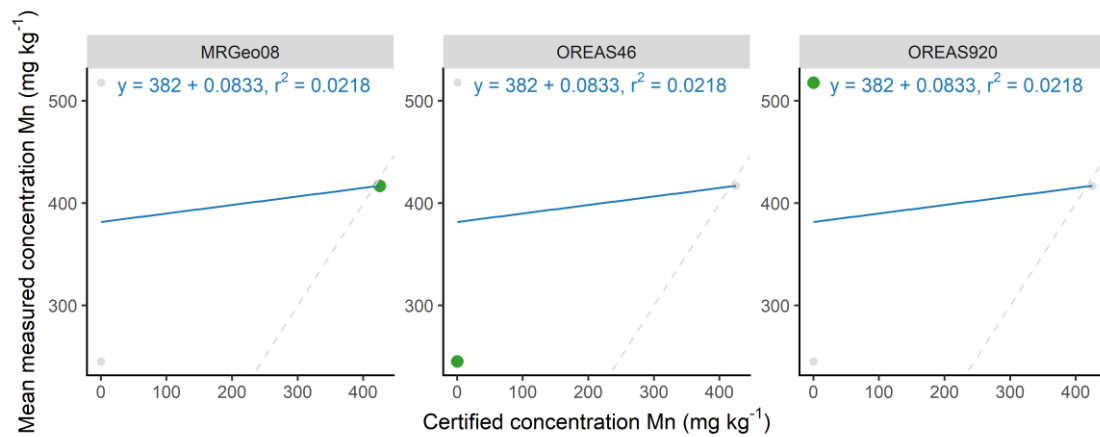


Chart 11 Manganese (Mn) (MS41L-BLD) determined by ICP-MS in blind in-house SRMs, faceted by SRM name. The 1:1 equality line is shown as a faint dashed grey line.



*Palladium (Pd) by ICP<sub>ar</sub> (MS41L-BLD)*

Regression curve for Palladium data by MS41L-BLD method was not constructed due to insufficient number of determinations. No data condition is recommended.

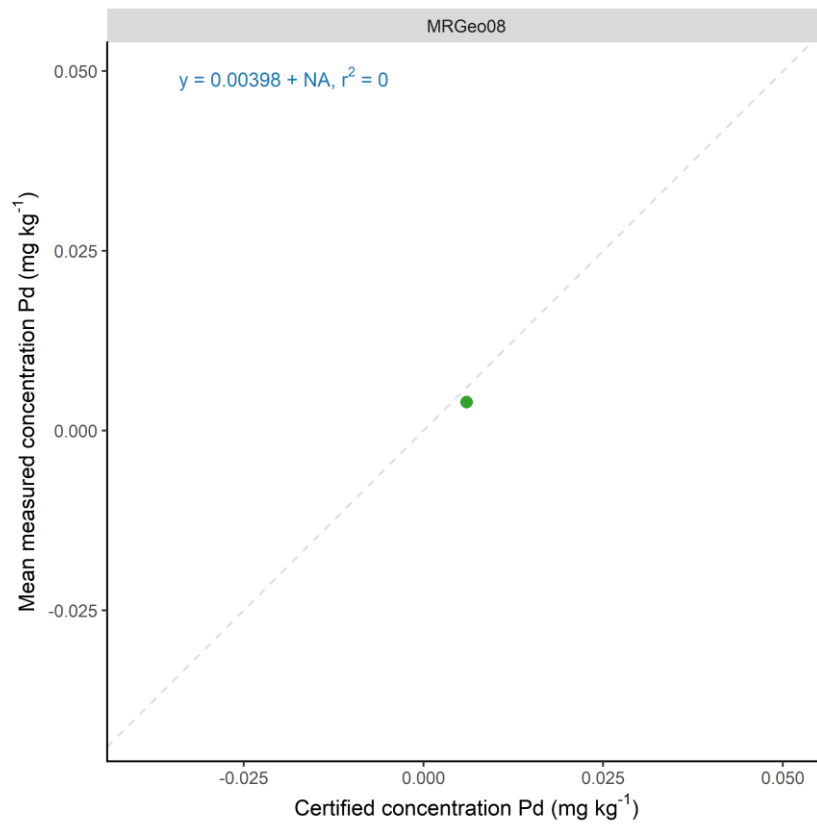


Chart 12 Palladium (Pd) (MS41L-BLD) determined by ICP-MS in blind in-house SRMs, faceted by SRM name. The 1:1 equality line is shown as a feint dashed grey line.

Platinum (Pt) by ICP<sub>ar</sub> (MS41L-BLD)

Regression curve for Platinum data by MS41L-BLD was not constructed due to insufficient number of determinations. No data condition is recommended.

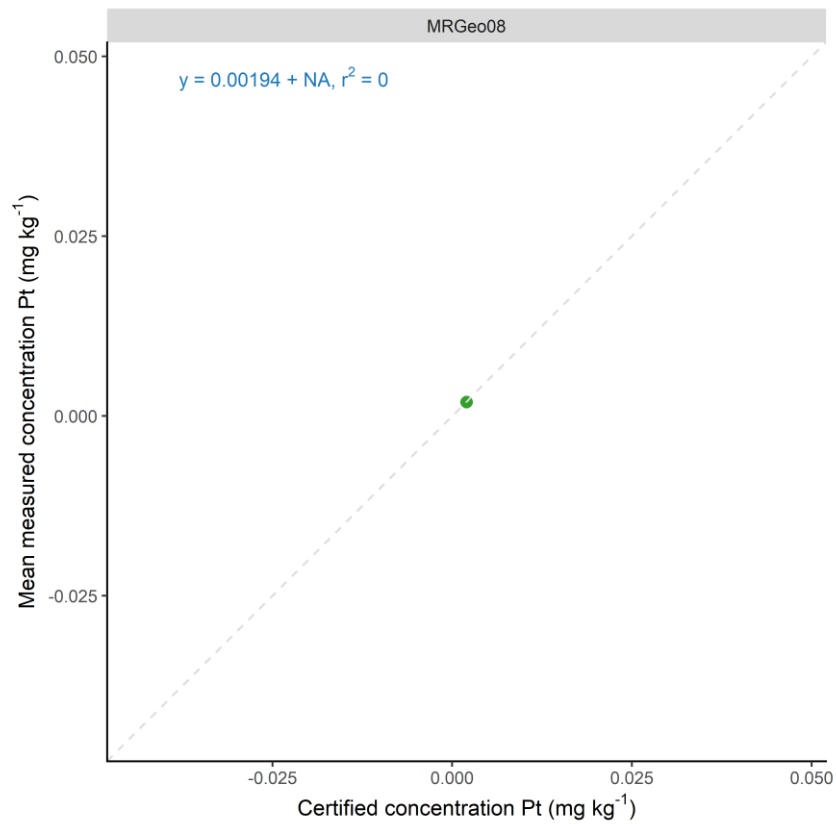


Chart 13 Platinum (Pt) (MS41L-BLD) determined by ICP-MS in blind in-house SRMs, faceted by SRM name. The 1:1 equality line is shown as a faint dashed grey line.

Rhenium (Re) by ICP<sub>or</sub> (MS41L-BLD)

Regression curve for Rhenium data by MS41L-BLD method was not constructed due to insufficient number of determinations. No data condition is recommended.

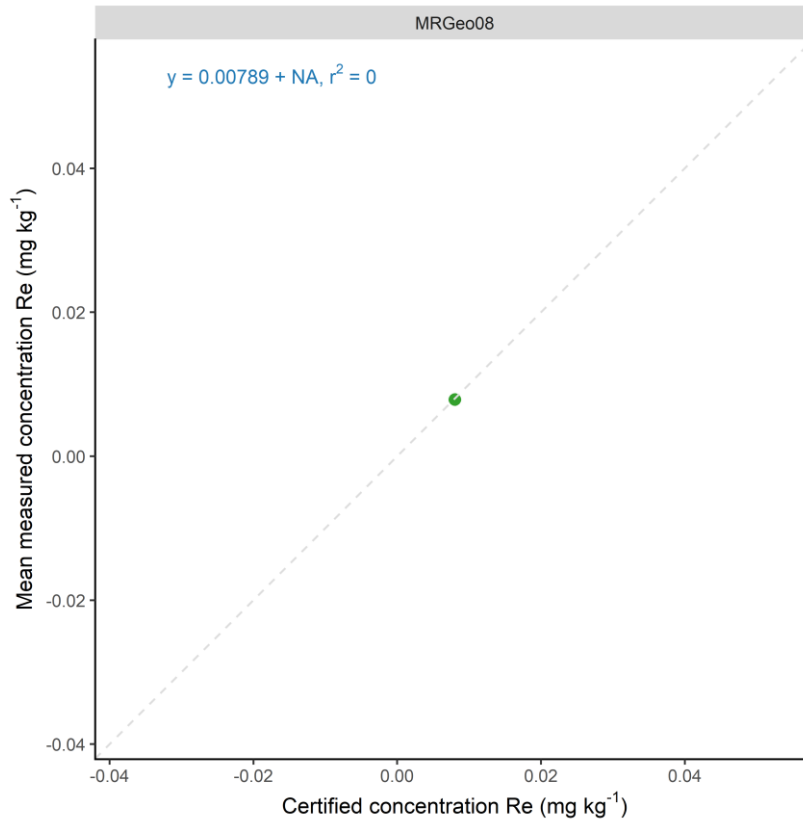


Chart 14 Rhenium (Re) (MS41L-BLD) determined by ICP-MS in blind in-house SRMs, faceted by SRM name. The 1:1 equality line is shown as a faint dashed grey line.

## 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<sub>ar</sub> (n=24). N/A where no reference concentration value is available.**

	Au (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ag (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	B (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ba (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Be (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Bi (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ca (%) ICP- MS (MS41L- BLD)	Cd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ce (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Co (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	145.76%	0.13%	0.46%	2.28%	-3.76%	0.81%	0.98%	-1.39%	2.49%	1.83%	3.81%	5.14%
% < method LLD	83.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cs (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cu (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Fe (%) ICP- MS (MS41L- BLD)	Ga (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ge (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hf (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hg (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	In (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	K (%) ICP- MS (MS41L- BLD)	La (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Li (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	5.01%	-2.84%	2.50%	0.19%	-1.46%	-9.47%	-31.99%	5.39%	4.81%	-0.58%	4.33%	5.29%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Mo (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Na (%) ICP- MS (MS41L- BLD)	Nb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ni (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	P (%) ICP- MS (MS41L- BLD)	Pb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pt (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Rb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Re (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	1.80%	1.19%	3.87%	19.07%	-3.75%	6.17%	-4.21%	1.42%	-63.18%	4.49%	-1.15%	-6.20%

% < method LLD	0.0%	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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sc (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Se (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ta (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Te (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Th (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	U (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	
Relative bias %	2.54%	1.77%	-11.79%	-25.36%	1.30%	-1.43%	-58.36%	-15.63%	-25.11%	-6.06%	-1.63%	3.29%	
% < 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%	0.0%
	V (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	W (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Y (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)								
Relative bias %	6.35%	123.69%	4.72%	1.53%	-25.30%								
% < 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 ICP<sub>ar</sub> (n=24). N/A where no reference concentration value is available.**

	Au (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ag (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	B (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ba (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Be (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Bi (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ca (%) ICP-MS (MS41L-BLD)	Cd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ce (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Co (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	
Relative bias %	315.70%	0.42%	-0.98%	2.17%	-7.89%	-0.78%	-4.68%	5.36%	2.77%	1.93%	2.16%	2.52%	
% < method LLD	91.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

	Cr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cs (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cu (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Fe (%) ICP- MS (MS41L- BLD)	Ga (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ge (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hf (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hg (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	In (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	K (%) ICP- MS (MS41L- BLD)	La (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Li (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	2.39%	1.34%	1.38%	0.26%	0.38%	-9.10%	-34.60%	-5.16%	6.07%	-1.51%	2.39%	0.02%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	25.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Mg (%) ICP- MS (MS41L- BLD)	Mn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Mo (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Na (%) ICP- MS (MS41L- BLD)	Nb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ni (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	P (%) ICP- MS (MS41L- BLD)	Pb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pt (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Rb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Re (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	-0.75%	0.70%	1.63%	44.45%	-2.28%	4.13%	-2.52%	-0.31%	-6.02%	56.22%	-1.70%	-19.41%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	95.8%	95.8%	0.0%	100.0%
	S (%) ICP- MS (MS41L- BLD)	Sb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sc (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Se (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ta (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Te (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Th (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ti (%) ICP- MS (MS41L- BLD)	Tl (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	U (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	0.25%	0.72%	-1.70%	-31.65%	1.58%	-4.28%	-58.11%	-12.42%	-2.92%	-4.41%	-2.38%	0.68%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	W (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Y (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)							
Relative bias %	2.09%	33.45%	2.40%	0.02%	-11.94%							

% < 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 ICP<sub>ar</sub> (n=8). N/A where no reference concentration value is available.

	Au (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ag (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	B (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ba (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Be (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Bi (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ca (%) ICP- MS (MS41L- BLD)	Cd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ce (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Co (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	-43.95%	-43.70%	-15.00%	-29.96%	-19.29%	13.07%	7.24%	48.73%	9.38%	33.13%	18.20%	-10.87%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cs (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cu (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Fe (%) ICP- MS (MS41L- BLD)	Ga (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ge (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hf (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hg (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	In (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	K (%) ICP- MS (MS41L- BLD)	La (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Li (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	-73.62%	-29.65%	-48.29%	-29.98%	-5.79%	-10.20%	-81.03%	21.69%	21.88%	-16.53%	15.04%	-10.57%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Mo (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Na (%) ICP- MS (MS41L- BLD)	Nb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ni (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	P (%) ICP- MS (MS41L- BLD)	Pb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pt (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Rb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Re (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	17.51%	28.74%	-14.45%	9.41%	21.15%	-60.65%	20.11%	-5.21%	-95.66%	-96.35%	-28.59%	-26.91%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sc (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Se (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ta (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Te (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Th (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	U (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	-7.79%	44.82%	-53.68%	-38.12%	-9.40%	-7.38%	-42.16%	-25.71%	-39.34%	10.90%	3.03%	-12.50%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	W (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Y (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)							
Relative bias %	-23.54%	19.54%	29.99%	21.87%	-83.95%							
% < 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 ICP<sub>ar</sub> (n=8). N/A where no reference concentration value is available.**

	Au (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ag (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	B (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ba (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Be (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Bi (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ca (%) ICP-MS (MS41L-BLD)	Cd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ce (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Co (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	-81.61%	4.74%	3.25%	-27.45%	-31.74%	-2.03%	28.31%	-48.62%	19.20%	28.99%	25.14%	-24.76%
% < method LLD	100.0%	0.0%	0.0%	0.0%	12.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cs (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cu (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Fe (%) ICP-MS (MS41L-BLD)	Ga (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ge (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hf (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hg (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	In (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	K (%) ICP-MS (MS41L-BLD)	La (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Li (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)



Relative bias %	-77.78%	21.74%	-39.69%	-47.40%	-2.57%	-19.56%	-65.16%	19.21%	-35.20%	18.93%	20.81%	33.11%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Mo (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Na (%) ICP-MS (MS41L-BLD)	Nb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ni (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	P (%) ICP-MS (MS41L-BLD)	Pb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pt (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Rb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Re (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	22.72%	18.30%	16.32%	0.75%	18.49%	-62.79%	4.28%	-5.91%	-94.49%	-98.13%	23.19%	-69.95%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sc (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Se (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ta (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Te (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Th (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	U (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	-10.32%	-6.06%	-71.07%	-40.25%	-6.98%	9.33%	-76.59%	-61.10%	0.54%	5.28%	12.93%	17.75%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	W (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Y (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)							
Relative bias %	-46.60%	-91.70%	16.93%	25.07%	-53.53%							
% < 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 ICP<sub>ar</sub> (n=8). N/A where no reference concentration value is available.

	Au (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ag (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Al (%) ICP-MS (MS41L-BLD)	As (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	B (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ba (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Be (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Bi (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ca (%) ICP- MS (MS41L- BLD)	Cd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ce (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Co (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	104.34%	39.16%	-15.95%	40.62%	-15.43%	-25.57%	-34.24%	11.07%	34.13%	-58.40%	-8.29%	-5.18%
% < method LLD	87.5%	0.0%	0.0%	0.0%	12.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cs (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Cu (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Fe (%) ICP- MS (MS41L- BLD)	Ga (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ge (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hf (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Hg (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	In (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	K (%) ICP- MS (MS41L- BLD)	La (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Li (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	21.56%	-14.20%	-4.65%	-8.24%	-5.94%	2.54%	-10.83%	2.02%	-27.77%	-44.00%	-9.45%	-9.63%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	12.5%	0.0%	0.0%	0.0%
	Mg (%) ICP- MS (MS41L- BLD)	Mn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Mo (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Na (%) ICP- MS (MS41L- BLD)	Nb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ni (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	P (%) ICP- MS (MS41L- BLD)	Pb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pd (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Pt (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Rb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Re (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	5.73%	-39.92%	-13.04%	-4.14%	24.86%	-3.92%	-8.27%	-26.87%	103.38%	50.70%	-25.79%	-44.31%
% < method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	87.5%	100.0%	0.0%	100.0%

	S (%) ICP-MS (MS41L-BLD)	Sb (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sc (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Se (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Sr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ta (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Te (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Th (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Ti (%) ICP-MS (MS41L-BLD)	Tl (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	U (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)
Relative bias %	-20.58%	0.26%	-4.33%	-48.57%	10.22%	6.55%	-65.81%	-31.85%	4.17%	40.94%	-42.48%	7.89%
% < 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 <sup>-1</sup> ) ICP-MS (MS41L-BLD)	W (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Y (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zn (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)	Zr (mgkg <sup>-1</sup> ) ICP-MS (MS41L-BLD)							
Relative bias %	2.46%	14.25%	-20.80%	-26.25%	-7.33%							
% < 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  $10 \times \text{LLD}$ , 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<sub>ar</sub>**

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 summarised 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  $< 2 \times \text{LLD}$  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<sub>ar</sub> ME-MS41L data in blank waters. Analytes with >5% of data above the LLD are orange highlighted.

	Au mg kg <sup>-1</sup>	Ag mg kg <sup>-1</sup>	Al %	As mg kg <sup>-1</sup>	B mg kg <sup>-1</sup>	Ba mg kg <sup>-1</sup>	Be mg kg <sup>-1</sup>	Bi mg kg <sup>-1</sup>	Ca %	Cd mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	2	0	0	2	0	0	0	5	0	3
% > method LLD	1.1%	0.0%	0.0%	1.1%	0.0%	0.0%	0.0%	2.7%	0.0%	1.6%
	Ce mg kg <sup>-1</sup>	Co mg kg <sup>-1</sup>	Cr mg kg <sup>-1</sup>	Cs mg kg <sup>-1</sup>	Cu mg kg <sup>-1</sup>	Fe %	Ga mg kg <sup>-1</sup>	Ge mg kg <sup>-1</sup>	Hf mg kg <sup>-1</sup>	Hg mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	0	5	1	0	0	0	0	0	3	0
% > method LLD	0.0%	2.7%	0.5%	0.0%	0.0%	0.0%	0.0%	0.0%	1.6%	0.0%
	In mg kg <sup>-1</sup>	K %	La mg kg <sup>-1</sup>	Li mg kg <sup>-1</sup>	Mg mg kg <sup>-1</sup>	Mn mg kg <sup>-1</sup>	Mo mg kg <sup>-1</sup>	Na mg kg <sup>-1</sup>	Nb mg kg <sup>-1</sup>	Ni mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	0	0	0	0	0	0	0	0	1	0
% > method LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.5%	0.0%
	P %	Pb mg kg <sup>-1</sup>	Pd µg L <sup>-1</sup>	Pt mg kg <sup>-1</sup>	Rb mg kg <sup>-1</sup>	Re mg kg <sup>-1</sup>	S %	Sb mg kg <sup>-1</sup>	Sc mg kg <sup>-1</sup>	Se mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	0	7	2	0	1	11	0	1	3	0
% > method LLD	0.0%	3.8%	1.1%	0.0%	0.5%	5.9%	0.0%	0.5%	1.6%	0.0%
	Sn mg kg <sup>-1</sup>	Sr mg kg <sup>-1</sup>	Ta mg kg <sup>-1</sup>	Te mg kg <sup>-1</sup>	Th mg kg <sup>-1</sup>	Ti %	Tl mg kg <sup>-1</sup>	U mg kg <sup>-1</sup>	V mg kg <sup>-1</sup>	W mg kg <sup>-1</sup>

Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	0	0	5	0	0	0	6	0	0	2
% > method LLD	0.0%	0.0%	2.7%	0.0%	0.0%	0.0%	3.2%	0.0%	0.0%	1.1%
	Y mg kg <sup>-1</sup>	Zn mg kg <sup>-1</sup>	Zn mg kg <sup>-1</sup>							
Count	186	186	186							
Count > method LLD	1	1	0							
% > method LLD	0.5%	0.5%	0.0%							

Table 19 Summary of above method LLD detectable ICP<sub>ar</sub> MS41L-BLD data in blank waters. Analytes with >5% of data above the LLD are orange highlighted.

	Au mg kg <sup>-1</sup>	Ag mg kg <sup>-1</sup>	Al %	As mg kg <sup>-1</sup>	B mg kg <sup>-1</sup>	Ba mg kg <sup>-1</sup>	Be mg kg <sup>-1</sup>	Bi mg kg <sup>-1</sup>	Ca %	Cd mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	28	61	13	53	22	38	41	65	28	54
% > method LLD	15.1%	32.8%	7.0%	28.5%	11.8%	20.4%	22.0%	34.9%	15.1%	29.0%
	Ce mg kg <sup>-1</sup>	Co mg kg <sup>-1</sup>	Cr mg kg <sup>-1</sup>	Cs mg kg <sup>-1</sup>	Cu mg kg <sup>-1</sup>	Fe %	Ga mg kg <sup>-1</sup>	Ge mg kg <sup>-1</sup>	Hf mg kg <sup>-1</sup>	Hg mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	47	58	61	37	69	27	69	64	53	71
% > method LLD	25.3%	31.2%	32.8%	19.9%	37.1%	14.5%	37.1%	34.4%	28.5%	38.2%
	In mg kg <sup>-1</sup>	K %	La mg kg <sup>-1</sup>	Li mg kg <sup>-1</sup>	Mg mg kg <sup>-1</sup>	Mn mg kg <sup>-1</sup>	Mo mg kg <sup>-1</sup>	Na mg kg <sup>-1</sup>	Nb mg kg <sup>-1</sup>	Ni mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186

Count > method LLD	43	5	57	22	10	35	55	25	55	52
% > method LLD	23.1%	2.7%	30.6%	11.8%	5.4%	18.8%	29.6%	13.4%	29.6%	28.0%
	P %	Pb mg kg <sup>-1</sup>	Pd µg L <sup>-1</sup>	Pt mg kg <sup>-1</sup>	Rb mg kg <sup>-1</sup>	Re mg kg <sup>-1</sup>	S %	Sb mg kg <sup>-1</sup>	Sc mg kg <sup>-1</sup>	Se mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	41	61	82	65	43	46	23	50	48	49
% > method LLD	22.0%	32.8%	44.1%	34.9%	23.1%	24.7%	12.4%	26.9%	25.8%	26.3%
	Sn mg kg <sup>-1</sup>	Sr mg kg <sup>-1</sup>	Ta mg kg <sup>-1</sup>	Te mg kg <sup>-1</sup>	Th mg kg <sup>-1</sup>	Ti %	Tl mg kg <sup>-1</sup>	U mg kg <sup>-1</sup>	V mg kg <sup>-1</sup>	W mg kg <sup>-1</sup>
Count	186	186	186	186	186	186	186	186	186	186
Count > method LLD	63	63	122	51	66	7	52	32	46	65
% > method LLD	33.9%	33.9%	65.6%	27.4%	35.5%	3.8%	28.0%	17.2%	24.7%	34.9%
	Y mg kg <sup>-1</sup>	Zn mg kg <sup>-1</sup>	Zn mg kg <sup>-1</sup>							
Count	186	186	186							
Count > method LLD	51	55	48							
% > method LLD	27.4%	29.6%	25.8%							

# 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<sub>ar</sub> 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, and they are not discussed further in this report.



# 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](http://www.gsi.ie/tellus).

When published by GSI, all geochemical data are censored, so that results below the lower reporting (detection) limit are censored to one half the stated lower limit of detection. Dealing 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 and spatially 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 (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. 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.

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  $\leq 50\%$  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  $\leq 80\%$  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 shallow topsoil pH (CaCl<sub>2</sub>) 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	4278	0	0	2.7	3.1	3.4	3.7	4.4	5	5.5	5.7	5.86	6.1	6.4	6.5	6.7	7.1
LOI (450°C)	0.01	%	4278	0	0	2.03	5.37	6.49	7.22	8.33	11.4	19.6	31.6	54.1	94.4	96.5	97	97.4	99.9

Table 21 Univariate summary statistics for shallow topsoil ICP<sub>ar</sub> 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 <sup>-1</sup>	4278	1	0.02	0.0012 2	0.0196	0.0333	0.0451	0.0642	0.0884	0.109	0.114	0.123	0.148	0.169	0.196	0.238	0.65
Al	0.0001	%	4278	0	0	0.0097	0.0502	0.0747	0.204	0.535	1.03	1.35	1.42	1.53	1.83	2.04	2.25	2.48	9.27
As	0.0001	mg kg <sup>-1</sup>	4278	0	0	0.0676	1.33	2.03	2.86	4.76	7.93	10.4	11.2	12.1	15.3	19.8	25.7	36	146
B	0.1	mg kg <sup>-1</sup>	4278	151	3.53	0.2	1.2	1.7	2.3	3.1	4.7	6	6.4	6.9	8.1	9.4	10.6	12.2	78.3
Ba	0.005	mg kg <sup>-1</sup>	4278	0	0	2.02	9.76	14.3	19.6	30.4	56.8	83.8	92.6	105	147	196	273	403	2120
Be	0.0001	mg kg <sup>-1</sup>	4278	0	0	0.0006	0.0292	0.0504	0.128	0.284	0.608	0.801	0.85	0.905	1.05	1.18	1.3	1.52	17.1
Bi	0.00001	mg kg <sup>-1</sup>	4278	8	0.19	0.0003	0.0382	0.0558	0.065	0.0788	0.106	0.13	0.137	0.145	0.173	0.219	0.318	0.54	15.6
Ca	0.0001	%	4278	0	0	0.0151	0.117	0.154	0.182	0.234	0.359	0.635	0.819	1.14	2.47	4.11	6.94	12	25
Cd	0.00001	mg kg <sup>-1</sup>	4278	0	0	0.0138	0.153	0.208	0.256	0.374	0.773	1.17	1.28	1.43	1.84	2.3	2.85	3.77	12.4
Ce	0.00003	mg kg <sup>-1</sup>	4278	0	0	0.128	0.946	1.53	5.46	14.7	26.8	33.3	35.2	37.4	43.2	49	54.1	62.6	282
Co	0.00001	mg kg <sup>-1</sup>	4278	0	0	0.0407	0.238	0.358	0.817	2.73	6.52	8.87	9.46	10.1	11.7	13.2	14.6	17.3	40.2
Cr	0.0001	mg kg <sup>-1</sup>	4278	0	0	0.168	0.83	1.27	3.19	9.93	19	24	25.4	27.3	32.9	38.2	42.7	49.9	148
Cs	0.00005	mg kg <sup>-1</sup>	4278	3	0.07	0.0002 1	0.0246	0.0462	0.128	0.35	0.646	0.859	0.927	0.997	1.25	1.5	1.85	2.86	27.2
Cu	0.0001	mg kg <sup>-1</sup>	4278	0	0	0.0838	2.67	3.55	5.31	9.54	16.4	21.8	23.6	25.5	31.4	37.5	45.7	61.9	315

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	
Fe	0.00001	%	4278	0	0	0.0096	0.0874	0.183	0.421	0.886	1.56	2.02	2.14	2.28	2.66	3.01	3.42	4.15	17	
Ga	0.00004	mg kg <sup>-1</sup>	4278	0	0	0.0198	0.228	0.343	0.666	1.58	2.91	3.83	4.09	4.44	5.45	6.29	7.39	8.76	17	
Ge	0.00005	mg kg <sup>-1</sup>	4278	8	0.19	0.0008 8	0.0163	0.0211	0.0251	0.0322	0.0465	0.0565	0.0594	0.0629	0.0727	0.0815	0.0954	0.129	0.341	
Hf	0.00002	mg kg <sup>-1</sup>	4278	175	4.09	0.0000 3	0.0022 3	0.0035	0.0060 9	0.0211	0.0576	0.0829	0.0898	0.0974	0.115	0.13	0.144	0.163	0.324	
Hg	0.00004	mg kg <sup>-1</sup>	4278	1	0.02	0.0119	0.054	0.0628	0.0688	0.0773	0.0982	0.124	0.134	0.145	0.186	0.228	0.274	0.369	9.26	
In	0.00005	mg kg <sup>-1</sup>	4278	57	1.33	0.0000 8	0.0035 9	0.0066 7	0.0086 8	0.0117	0.0181	0.023	0.0244	0.0258	0.0302	0.0346	0.0397	0.0511	0.334	
K	0.0001	%	4278	0	0	0.0021	0.0199	0.0299	0.0414	0.0648	0.119	0.164	0.177	0.191	0.227	0.255	0.284	0.311	0.431	
La	0.00002	mg kg <sup>-1</sup>	4278	0	0	0.0701	0.479	0.815	2.93	7.49	13.4	16.9	17.8	19.1	22.7	26.1	29.1	33.8	115	
Li	0.001	mg kg <sup>-1</sup>	4278	213	4.98	0.002	0.0875	0.221	0.467	3.97	9.07	12.6	13.6	15	18.6	21.8	25.8	32.1	78.8	
Mg	0.0001	%	4278	0	0	0.0153	0.0522	0.0659	0.0785	0.0987	0.145	0.198	0.223	0.252	0.36	0.476	0.583	0.731	3.68	
Mn	0.001	mg kg <sup>-1</sup>	4278	1	0.02	1.38	9.79	17.8	46.4	154	495	818	901	995	1240	1510	1870	2760	15300	
Mo	0.0001	mg kg <sup>-1</sup>	4278	0	0	0.0354	0.257	0.349	0.444	0.6	1.01	1.41	1.57	1.75	2.46	3.47	4.57	6.48	62.8	
Na	0.00001	%	4278	1	0.02	0.0029 8	0.0113	0.0128	0.0139	0.0157	0.0197	0.0253	0.0273	0.0301	0.0375	0.0435	0.0508	0.0571	0.916	
Nb	0.00002	mg kg <sup>-1</sup>	4278	0	0	0.0042 5	0.0343	0.0524	0.1	0.172	0.265	0.356	0.393	0.438	0.584	0.763	0.994	1.33	5.82	
Ni	0.0004	mg kg <sup>-1</sup>	4278	0	0	0.186	1.21	1.71	2.99	10.1	23.5	31.8	34	36.5	42.3	48.8	54.7	63.6	121	
P	0.00001	mg kg <sup>-1</sup>	4278	0	0	56.4	261	335	465	625	822	981	1030	1100	1290	1470	1650	1940	3630	
Pb	0.00005	mg kg <sup>-1</sup>	4278	0	0	0.0683	9.55	12.1	13.8	16.6	22.4	27.5	29.2	31.6	39.3	50.5	70.4	116	649	
Rb	0.00005	mg kg <sup>-1</sup>	4278	0	0	0.0255	0.345	0.576	1.23	4.44	10.9	15.1	16.3	17.5	21.1	24	26.6	29.4	54.3	
Re	0.00001	mg kg <sup>-1</sup>	4278	775	18.12	<LLD	0.0000 242	0.0000 398	0.0000 556	0.0001 2	0.0003 7	0.0006 5	0.0007 9	0.001	0.0023 7	0.0052 7	0.0094 8	0.0166	0.101	
S	0.0001	%	4278	0	0	0.0076	0.036	0.0422	0.0466	0.0535	0.0727	0.13	0.186	0.257	0.34	0.404	0.471	0.565	1.09	
Sb	0.00005	mg kg <sup>-1</sup>	4278	0	0	0.0048 5	0.139	0.177	0.213	0.266	0.395	0.543	0.596	0.657	0.881	1.14	1.39	1.83	11.6	

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	
Sc	0.00005	mg kg <sup>-1</sup>	4278	0	0	0.0215	0.123	0.217	0.456	0.945	2.15	2.96	3.15	3.38	4.05	4.57	5.09	5.73	10.9	
Se	0.001	mg kg <sup>-1</sup>	4278	0	0	0.013	0.377	0.438	0.487	0.562	0.821	1.21	1.38	1.6	2.61	4.03	6.03	9.4	39.6	
Sn	0.0001	mg kg <sup>-1</sup>	4278	1	0.02	0.0019	0.283	0.38	0.431	0.525	0.685	0.831	0.878	0.955	1.23	1.68	2.5	3.64	19	
Sr	0.0001	mg kg <sup>-1</sup>	4278	0	0	0.656	9.64	11.6	12.9	15.1	20.7	28	31.4	36.1	56.6	85.8	123	179	630	
Ta	0.00005	mg kg <sup>-1</sup>	4278	1956	45.72	<LLD	<LLD	<LLD	<LLD	0.0000725	0.000182	0.00069	0.00085	0.00109	0.00188	0.00299	0.00421	0.00654	0.1	
Te	0.0001	mg kg <sup>-1</sup>	4278	5	0.12	0.00019	0.0039	0.0054	0.0067	0.0093	0.0158	0.0213	0.023	0.0248	0.0302	0.036	0.0424	0.0551	1.83	
Th	0.00002	mg kg <sup>-1</sup>	4278	39	0.91	0.00007	0.00756	0.0234	0.125	0.403	0.948	1.31	1.42	1.54	1.87	2.19	2.45	2.81	20.4	
Ti	0.00001	%	4278	0	0	0.00025	0.00128	0.00172	0.00212	0.00286	0.00407	0.00553	0.00621	0.00714	0.0097	0.0129	0.017	0.0268	0.131	
Tl	0.00002	mg kg <sup>-1</sup>	4278	30	0.70	0.00036	0.00956	0.0176	0.0353	0.0966	0.183	0.237	0.252	0.269	0.315	0.365	0.428	0.523	3.42	
U	0.00005	mg kg <sup>-1</sup>	4278	0	0	0.0129	0.104	0.253	0.573	0.806	1.09	1.41	1.53	1.71	2.66	4.51	7.68	13	109	
V	0.001	mg kg <sup>-1</sup>	4278	0	0	0.196	1.74	2.77	5.68	15.4	27	35	37.5	40.3	47.4	53	60.2	68	216	
W	0.00001	mg kg <sup>-1</sup>	4278	29	0.68	0.00026	0.0175	0.0256	0.0317	0.0399	0.0588	0.0774	0.0852	0.0948	0.127	0.188	0.314	1.01	16.4	
Y	0.00003	mg kg <sup>-1</sup>	4278	0	0	0.0611	0.369	0.616	1.81	4.94	11.7	17.5	19	20.5	25.4	32.1	38.9	48	132	
Zn	0.001	mg kg <sup>-1</sup>	4278	0	0	1.23	10.8	16.5	22.8	34.3	65.2	88	95.1	102	120	134	150	171	9120	
Zr	0.0001	mg kg <sup>-1</sup>	4278	0	0	0.0282	0.0872	0.143	0.282	0.783	1.97	2.76	2.98	3.23	3.81	4.29	4.71	5.45	9.07	
Au	0.000002	mg kg <sup>-1</sup>	4278	153	3.58	0.00003	0.0000752	0.000144	0.000213	0.000324	0.000565	0.000823	0.000919	0.00103	0.00142	0.00187	0.00264	0.00585	1.29	
Pd	0.00001	mg kg <sup>-1</sup>	4278	2579	60.29	<LLD	<LLD	<LLD	<LLD	0.000018	0.00008	0.00039	0.0006	0.000936	0.00198	0.00331	0.00581	0.022	0.257	
Pt	0.00002	mg kg <sup>-1</sup>	4278	1134	26.51	<LLD	<LLD	<LLD	0.0000321	0.0000633	0.00043	0.001	0.00131	0.00185	0.00447	0.00984	0.0505	0.151	1.3	

Table 22 Univariate summary statistics for shallow topsoil ICP<sub>ar</sub> 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 <sup>-1</sup>	4278	3	0.07	0.002	0.02	0.033	0.045	0.064	0.088	0.109	0.114	0.124	0.148	0.169	0.196	0.238	0.65
Al	0.01	%	4278	16	0.37	0.0197	0.05	0.07	0.2	0.54	1.03	1.35	1.43	1.53	1.83	2.04	2.25	2.48	9.27
As	0.01	mg kg <sup>-1</sup>	4278	0	0	0.07	1.33	2.03	2.86	4.76	7.94	10.4	11.2	12.2	15.3	19.9	25.7	36	146
B	10	mg kg <sup>-1</sup>	4278	4262	99.62	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	10.4	80
Ba	0.5	mg kg <sup>-1</sup>	4278	0	0	2	9.79	14.3	19.6	30.4	56.8	83.8	92.6	106	148	197	273	403	2120
Be	0.01	mg kg <sup>-1</sup>	4278	43	1.00	0.0121	0.03	0.05	0.13	0.283	0.61	0.8	0.85	0.906	1.05	1.18	1.3	1.52	17.1
Bi	0.0005	mg kg <sup>-1</sup>	4278	12	0.28	0.0009	0.0382	0.0559	0.0651	0.0788	0.105	0.13	0.137	0.145	0.173	0.219	0.318	0.54	15.6
Ca	0.01	%	4278	0	0	0.02	0.12	0.15	0.18	0.23	0.36	0.63	0.82	1.14	2.46	4.11	6.94	12	25
Cd	0.001	mg kg <sup>-1</sup>	4278	0	0	0.014	0.153	0.208	0.256	0.374	0.774	1.18	1.28	1.43	1.83	2.3	2.85	3.77	12.4
Ce	0.003	mg kg <sup>-1</sup>	4278	0	0	0.128	0.946	1.53	5.46	14.7	26.8	33.3	35.2	37.4	43.2	49	54.1	62.7	282
Co	0.001	mg kg <sup>-1</sup>	4278	0	0	0.041	0.238	0.358	0.817	2.73	6.53	8.87	9.46	10.2	11.8	13.2	14.6	17.3	40.2
Cr	0.01	mg kg <sup>-1</sup>	4278	0	0	0.17	0.83	1.27	3.18	9.93	18.9	24	25.5	27.3	32.9	38.2	42.7	49.9	148
Cs	0.005	mg kg <sup>-1</sup>	4278	21	0.49	0.006	0.0249	0.046	0.128	0.35	0.646	0.859	0.927	0.997	1.25	1.5	1.85	2.85	27.2
Cu	0.01	mg kg <sup>-1</sup>	4278	0	0	0.08	2.68	3.55	5.32	9.54	16.4	21.8	23.6	25.6	31.4	37.5	45.6	61.8	315
Fe	0.001	%	4278	0	0	0.01	0.087	0.183	0.421	0.886	1.56	2.02	2.14	2.28	2.66	3.01	3.42	4.15	17.1
Ga	0.004	mg kg <sup>-1</sup>	4278	0	0	0.02	0.228	0.343	0.665	1.58	2.91	3.83	4.09	4.44	5.45	6.28	7.39	8.76	17
Ge	0.005	mg kg <sup>-1</sup>	4278	43	1.00	0.006	0.016	0.021	0.025	0.032	0.0465	0.056	0.059	0.063	0.073	0.081	0.095	0.129	0.341
Hf	0.002	mg kg <sup>-1</sup>	4278	365	8.53	<LLD	0.004	0.006	0.0080 7	0.021	0.058	0.083	0.09	0.097	0.115	0.13	0.144	0.163	0.324
Hg	0.004	mg kg <sup>-1</sup>	4278	1	0.02	0.012	0.054	0.063	0.069	0.077	0.098	0.124	0.134	0.145	0.186	0.228	0.274	0.368	9.26
In	0.005	mg kg <sup>-1</sup>	4278	335	7.83	<LLD	0.0062 1	0.0072 6	0.009	0.012	0.018	0.023	0.024	0.026	0.03	0.035	0.04	0.051	0.334
K	0.01	%	4278	129	3.01	<LLD	0.02	0.03	0.04	0.06	0.12	0.16	0.18	0.19	0.23	0.26	0.28	0.31	0.43
La	0.002	mg kg <sup>-1</sup>	4278	0	0	0.07	0.479	0.815	2.93	7.49	13.4	16.9	17.8	19.1	22.7	26.1	29.1	33.8	114

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	
Li	0.1	mg kg <sup>-1</sup>	4278	503	11.76	0.176	0.6	1.1	1.5	4	9.1	12.6	13.7	15	18.7	21.8	25.8	32.1	78.8	
Mg	0.01	%	4278	0	0	0.02	0.05	0.07	0.08	0.1	0.15	0.2	0.22	0.25	0.36	0.48	0.58	0.732	3.68	
Mn	0.1	mg kg <sup>-1</sup>	4278	1	0.02	1.38	9.8	17.8	46.4	154	494	818	901	995	1240	1510	1870	2770	15300	
Mo	0.01	mg kg <sup>-1</sup>	4278	0	0	0.04	0.26	0.35	0.44	0.6	1.01	1.41	1.57	1.75	2.46	3.47	4.57	6.48	62.8	
Na	0.001	%	4278	1	0.02	0.003	0.011	0.013	0.014	0.016	0.02	0.025	0.027	0.03	0.038	0.044	0.051	0.057	0.916	
Nb	0.002	mg kg <sup>-1</sup>	4278	0	0	0.004	0.034	0.052	0.1	0.172	0.265	0.356	0.393	0.438	0.584	0.763	0.994	1.33	5.82	
Ni	0.04	mg kg <sup>-1</sup>	4278	0	0	0.19	1.21	1.71	2.99	10.1	23.5	31.8	34	36.5	42.3	48.8	54.7	63.6	121	
P	0.001	mg kg <sup>-1</sup>	4278	0	0	60	260	337	470	620	820	980	1030	1100	1290	1470	1650	1940	3630	
Pb	0.005	mg kg <sup>-1</sup>	4278	0	0	0.068	9.55	12.1	13.8	16.6	22.4	27.5	29.2	31.6	39.3	50.5	70.4	116	649	
Rb	0.005	mg kg <sup>-1</sup>	4278	0	0	0.026	0.345	0.576	1.23	4.44	10.9	15.2	16.4	17.5	21.1	24	26.6	29.3	54.3	
Re	0.0002	mg kg <sup>-1</sup>	4278	1560	36.47	<LLD	0.0000 281	0.0000 489	0.0000 709	0.0001 23	0.0004	0.0007	0.0008	0.001	0.0024	0.0053	0.0095	0.0166	0.102	
S	0.01	%	4278	1	0.02	<LLD	0.04	0.04	0.05	0.05	0.07	0.13	0.19	0.26	0.34	0.4	0.47	0.562	1.09	
Sb	0.005	mg kg <sup>-1</sup>	4278	1	0.02	0.007	0.139	0.177	0.213	0.266	0.395	0.543	0.596	0.657	0.88	1.14	1.4	1.83	11.6	
Sc	0.005	mg kg <sup>-1</sup>	4278	0	0	0.022	0.123	0.217	0.456	0.945	2.15	2.96	3.15	3.38	4.05	4.57	5.09	5.73	10.9	
Se	0.003	mg kg <sup>-1</sup>	4278	0	0	0.013	0.377	0.438	0.487	0.562	0.821	1.21	1.38	1.6	2.61	4.03	6.03	9.4	39.6	
Sn	0.01	mg kg <sup>-1</sup>	4278	10	0.23	0.02	0.28	0.38	0.43	0.53	0.69	0.83	0.88	0.956	1.23	1.68	2.5	3.63	19	
Sr	0.01	mg kg <sup>-1</sup>	4278	0	0	0.66	9.64	11.6	12.9	15.2	20.8	28	31.4	36.1	56.6	85.7	123	179	630	
Ta	0.005	mg kg <sup>-1</sup>	4278	4217	98.57	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.1	
Te	0.003	mg kg <sup>-1</sup>	4278	160	3.74	<LLD	0.004	0.005	0.007	0.009	0.016	0.021	0.023	0.025	0.03	0.036	0.0421	0.0552	1.83	
Th	0.002	mg kg <sup>-1</sup>	4278	93	2.17	0.003	0.01	0.027	0.125	0.403	0.948	1.31	1.42	1.54	1.87	2.19	2.45	2.8	20.4	
Ti	0.001	%	4278	319	7.46	<LLD	0.0014 1	0.002	0.002	0.003	0.004	0.006	0.006	0.007	0.01	0.013	0.017	0.027	0.131	
Tl	0.001	mg kg <sup>-1</sup>	4278	39	0.91	0.002	0.01	0.018	0.035	0.097	0.183	0.237	0.252	0.269	0.315	0.365	0.428	0.523	3.42	
U	0.005	mg kg <sup>-1</sup>	4278	0	0	0.013	0.104	0.253	0.573	0.806	1.09	1.42	1.52	1.71	2.66	4.51	7.68	13	109	

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	
V	0.1	mg kg <sup>-1</sup>	4278	0	0	0.2	1.7	2.8	5.7	15.4	27.1	35	37.5	40.3	47.4	53	60.2	67.9	216	
W	0.001	mg kg <sup>-1</sup>	4278	43	1.00	0.002	0.017	0.026	0.032	0.04	0.059	0.077	0.085	0.095	0.126	0.188	0.314	1.01	16.4	
Y	0.003	mg kg <sup>-1</sup>	4278	0	0	0.061	0.369	0.616	1.81	4.94	11.7	17.4	19	20.5	25.4	32.1	38.9	48	132	
Zn	0.1	mg kg <sup>-1</sup>	4278	0	0	1.2	10.8	16.5	22.8	34.3	65.2	88	95.1	102	120	134	150	171	9120	
Zr	0.01	mg kg <sup>-1</sup>	4278	0	0	0.03	0.09	0.14	0.28	0.78	1.97	2.76	2.98	3.23	3.81	4.29	4.71	5.45	9.07	
Au	0.0002	mg kg <sup>-1</sup>	4278	780	18.23	<LLD	<LLD	<LLD	0.0002 34	0.0003	0.0006	0.0008	0.0009	0.001	0.0014	0.0019	0.0026 1	0.0058 2	1.28	
Pd	0.001	mg kg <sup>-1</sup>	4278	3704	86.58	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.002	0.003	0.006	0.022	0.257	
Pt	0.002	mg kg <sup>-1</sup>	4278	3599	84.12	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.004	0.01	0.0504	0.151	1.3	

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		4.95	4.85	0.89	2.45	6.35	5	5	4.85	4.95	4.95	4.95	0.959	0.959	1.05	4.95	4.85	0.89	
LOI	0.01	%	27.7	16.4	6.2	-26.7	43.3	11.4	11.4	16.4	27.7	27.7	26	31.4	31.4	32	27.7	16.4	6.2	

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	

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 <sup>-1</sup>	4278	1	0.02	0.0922	0.0777	0.0371	-0.0109	0.14	0.0884	0.0884	0.0775	0.0922	0.0922	0.0984	0.0494	0.0494
Al	0.0001	%	4278	0	0	1.01	0.685	0.656	-0.799	1.87	1.03	1.03	0.685	1.01	1.01	1.3	0.634	0.634	2.11
As	0.0001	mg kg <sup>-1</sup>	4278	0	0	9	6.74	4.76	-4.85	14.4	7.93	7.93	6.74	9	9	9.54	7.89	7.89	9.57
B	0.1	mg kg <sup>-1</sup>	4278	151	3.53	5.07	4.38	2.37	-1.5	8.1	4.7	4.7	3.8	4.9	4.93	5.91	2.9	2.85	7.03
Ba	0.005	mg kg <sup>-1</sup>	4278	0	0	76.6	51.7	44	-62.7	124	56.8	56.8	51.7	76.6	76.6	78.1	91.9	91.9	88.6
Be	0.0001	mg kg <sup>-1</sup>	4278	0	0	0.596	0.4	0.409	-0.564	1.13	0.608	0.608	0.4	0.596	0.596	0.762	0.464	0.464	1.24
Bi	0.00001	mg kg <sup>-1</sup>	4278	8	0.19	0.123	0.0996	0.0431	-0.00849	0.166	0.106	0.106	0.0979	0.122	0.122	0.132	0.252	0.252	0.12
Ca	0.0001	%	4278	0	0	1.07	0.473	0.256	-0.645	1.11	0.359	0.359	0.473	1.07	1.07	0.876	2.28	2.28	1.37
Cd	0.00001	mg kg <sup>-1</sup>	4278	0	0	0.953	0.683	0.649	-0.981	1.73	0.773	0.773	0.683	0.953	0.953	0.997	0.829	0.829	1.06
Ce	0.00003	mg kg <sup>-1</sup>	4278	0	0	25.5	17	14.3	-16.1	45.5	26.8	26.8	17	25.5	25.5	35.2	16.1	16.1	64.1
Co	0.00001	mg kg <sup>-1</sup>	4278	0	0	6.43	4.01	4.85	-7.38	12.8	6.52	6.52	4.01	6.43	6.43	8.86	4.37	4.37	17.4
Cr	0.0001	mg kg <sup>-1</sup>	4278	0	0	18.5	12.3	11.3	-13.3	33.2	18.9	19	12.3	18.5	18.5	24.1	12	12	40.8
Cs	0.00005	mg kg <sup>-1</sup>	4278	3	0.07	0.71	0.437	0.427	-0.515	1.22	0.646	0.646	0.434	0.709	0.709	0.987	0.763	0.763	2.01
Cu	0.0001	mg kg <sup>-1</sup>	4278	0	0	18	13.6	10.4	-11.6	30.6	16.4	16.4	13.6	18	18	19.1	14.2	14.2	18.8
Fe	0.00001	%	4278	0	0	1.56	1.1	0.925	-0.998	2.77	1.56	1.56	1.1	1.56	1.56	1.91	1.05	1.05	2.69
Ga	0.00004	mg kg <sup>-1</sup>	4278	0	0	2.98	2.11	1.86	-2.18	5.35	2.91	2.91	2.11	2.98	2.98	3.58	1.93	1.93	4.94
Ge	0.00005	mg kg <sup>-1</sup>	4278	8	0.19	0.0479	0.0421	0.0202	-0.00839	0.073	0.0465	0.0465	0.0415	0.0478	0.0478	0.0506	0.0248	0.0248	0.0352
Hf	0.00002	mg kg <sup>-1</sup>	4278	175	4.09	0.0614	0.0389	0.0484	-0.0713	0.124	0.0576	0.0576	0.0279	0.0589	0.059	0.212	0.0428	0.0426	1.6
Hg	0.00004	mg kg <sup>-1</sup>	4278	1	0.02	0.117	0.103	0.0378	-0.00705	0.162	0.0982	0.0982	0.103	0.117	0.117	0.115	0.155	0.155	0.0584
In	0.00005	mg kg <sup>-1</sup>	4278	57	1.33	0.0191	0.0159	0.00922	-0.00667	0.0307	0.0181	0.0181	0.0147	0.0188	0.0189	0.0234	0.0122	0.0121	0.0289
K	0.0001	%	4278	0	0	0.125	0.0976	0.0828	-0.103	0.233	0.119	0.119	0.0976	0.125	0.125	0.136	0.0744	0.0744	0.133
La	0.00002	mg kg <sup>-1</sup>	4278	0	0	13.1	8.69	7.57	-7.93	22.9	13.4	13.4	8.69	13.1	13.1	17.9	8.26	8.26	32.3
Li	0.001	mg kg <sup>-1</sup>	4278	213	4.98	10.1	5.49	6.63	-8.4	18.4	9.07	9.07	3.45	9.58	9.59	98.4	7.63	7.61	2800
Mg	0.0001	%	4278	0	0	0.189	0.15	0.0819	-0.0877	0.285	0.145	0.145	0.15	0.189	0.189	0.186	0.172	0.172	0.137



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
Mn	0.001	mg kg <sup>-1</sup>	4278	1	0.02	625	297	544	-968	1280	494	495	296	625	625	1000	821	821	3230
Mo	0.0001	mg kg <sup>-1</sup>	4278	0	0	1.34	0.975	0.678	-0.86	2.06	1.01	1.01	0.975	1.34	1.34	1.32	1.71	1.71	1.21
Na	0.00001	%	4278	1	0.02	0.0234	0.0209	0.00764	-0.0018	0.0332	0.0197	0.0197	0.0209	0.0234	0.0234	0.0231	0.0205	0.0205	0.0107
Nb	0.00002	mg kg <sup>-1</sup>	4278	0	0	0.319	0.229	0.158	-0.158	0.503	0.265	0.265	0.229	0.319	0.319	0.344	0.288	0.288	0.387
Ni	0.0004	mg kg <sup>-1</sup>	4278	0	0	23.2	15	17.2	-25.9	46	23.5	23.5	15	23.2	23.2	29.9	15.8	15.8	51.5
P	0.00001	mg kg <sup>-1</sup>	4278	0	0	840	749	303	11	1240	822	822	749	840	840	858	371	371	480
Pb	0.00005	mg kg <sup>-1</sup>	4278	0	0	26.1	21.5	9.2	-2.39	35.5	22.4	22.4	21.5	26.1	26.1	27	23.1	23.1	20.5
Rb	0.00005	mg kg <sup>-1</sup>	4278	0	0	10.9	6.57	8.68	-13.4	22.3	10.9	10.9	6.57	10.9	10.9	15.9	7.66	7.66	34.9
Re	0.00001	mg kg <sup>-1</sup>	4278	775	18.12	0.00148	0.000548	0.000383	-0.000812	0.00133	0.00037	0.00037	0.000219	0.00121	0.00122	0.00295	0.00367	0.00367	0.0396
S	0.0001	%	4278	0	0	0.137	0.096	0.0388	-0.145	0.252	0.0727	0.0727	0.096	0.137	0.137	0.132	0.133	0.133	0.125
Sb	0.00005	mg kg <sup>-1</sup>	4278	0	0	0.491	0.391	0.227	-0.229	0.761	0.395	0.395	0.391	0.491	0.491	0.493	0.444	0.444	0.377
Sc	0.00005	mg kg <sup>-1</sup>	4278	0	0	2.16	1.46	1.64	-2.36	4.25	2.15	2.15	1.46	2.16	2.16	2.67	1.44	1.44	4.07
Se	0.001	mg kg <sup>-1</sup>	4278	0	0	1.36	0.948	0.467	-0.665	1.79	0.821	0.821	0.948	1.36	1.36	1.25	1.84	1.84	1.07
Sn	0.0001	mg kg <sup>-1</sup>	4278	1	0.02	0.817	0.672	0.26	-0.0045	1.06	0.685	0.685	0.67	0.817	0.817	0.832	0.742	0.742	0.612
Sr	0.0001	mg kg <sup>-1</sup>	4278	0	0	30.6	23.1	10.3	-9.15	39.5	20.7	20.7	23.1	30.6	30.6	28.9	35.6	35.6	21.6
Ta	0.00005	mg kg <sup>-1</sup>	4278	1956	45.72	0.00137	0.000758	0.000697	-0.00129	0.00207	0.00016	0.000182	0.0000928	0.000774	0.000782	0.00282	0.00237	0.00236	0.0857
Te	0.0001	mg kg <sup>-1</sup>	4278	5	0.12	0.0183	0.0141	0.0101	-0.0111	0.0298	0.0158	0.0158	0.0141	0.0183	0.0183	0.0184	0.0349	0.0349	0.0154
Th	0.00002	mg kg <sup>-1</sup>	4278	39	0.91	0.982	0.517	0.745	-1.09	1.93	0.948	0.948	0.47	0.973	0.973	3.16	0.763	0.763	21
Ti	0.00001	%	4278	0	0	0.0054	0.00415	0.00221	-0.00216	0.00788	0.00407	0.00407	0.00415	0.0054	0.0054	0.0053	0.00562	0.00562	0.00419
Tl	0.00002	mg kg <sup>-1</sup>	4278	30	0.70	0.184	0.125	0.112	-0.133	0.33	0.183	0.183	0.118	0.182	0.182	0.289	0.136	0.136	0.651
U	0.00005	mg kg <sup>-1</sup>	4278	0	0	1.67	1.01	0.501	-0.274	1.89	1.09	1.09	1.01	1.67	1.67	1.68	3.43	3.43	2.24
V	0.001	mg kg <sup>-1</sup>	4278	0	0	26.9	19	16.3	-17.7	48.5	27	27	19	26.9	26.9	33.1	16.6	16.6	47.3
W	0.00001	mg kg <sup>-1</sup>	4278	29	0.68	0.107	0.059	0.0315	-0.0271	0.108	0.0588	0.0588	0.0556	0.106	0.106	0.102	0.486	0.486	0.157
Y	0.00003	mg kg <sup>-1</sup>	4278	0	0	13.1	7.61	10.4	-16.2	26.1	11.7	11.7	7.61	13.1	13.1	18.6	10.8	10.8	41.3

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
	Zn	0.001	mg kg <sup>-1</sup>	4278	0	0	70.2	53.3	45.1	-56.9	126	65.2	65.2	53.3	70.2	70.2	72.9	145	145
Zr	0.0001	mg kg <sup>-1</sup>	4278	0	0	1.99	1.26	1.63	-2.52	4.09	1.97	1.97	1.26	1.99	1.99	2.61	1.39	1.39	4.73
Au	0.000002	mg kg <sup>-1</sup>	4278	153	3.58	0.00144	0.000553	0.000408	-0.000521	0.00123	0.000564	0.000565	0.000447	0.00139	0.00139	0.00126	0.0235	0.0235	0.00333
Pd	0.00001	mg kg <sup>-1</sup>	4278	2579	60.29	0.00299	0.000891	0.000964	-0.00198	0.00279	NA	0.00008	0.0000042	0.0012	0.00121	1.82	0.00779	0.00779	789000
Pt	0.00002	mg kg <sup>-1</sup>	4278	1134	26.51	0.00786	0.00091	0.000771	-0.00224	0.00292	0.00043	0.00043	0.000217	0.00578	0.00579	0.0126	0.0373	0.0373	0.726

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 <sup>-1</sup>	4278	3	0.07	0.0923	0.0778	0.0371	-0.0118	0.14	0.088	0.088	0.0776	0.0922	0.0922	0.0978	0.0494	0.0494
Al	0.01	%	4278	16	0.37	1.01	0.696	0.652	-0.795	1.88	1.03	1.03	0.684	1.01	1.01	1.31	0.634	0.634	2.14
As	0.01	mg kg <sup>-1</sup>	4278	0	0	9	6.74	4.77	-4.83	14.3	7.93	7.94	6.74	9	9	9.54	7.89	7.89	9.57
B	10	mg kg <sup>-1</sup>	4278	4262	99.63	25	22.8	0	20	20	NA	0.605	0.0118	20	1.28	0.284	0.998	2.42	6.82
Ba	0.5	mg kg <sup>-1</sup>	4278	0	0	76.6	51.7	44	-62.9	124	56.8	56.8	51.7	76.6	76.6	78.1	92	92	88.6
Be	0.01	mg kg <sup>-1</sup>	4278	43	1.00	0.602	0.416	0.4	-0.525	1.12	0.61	0.61	0.399	0.596	0.597	0.765	0.464	0.464	1.25
Bi	0.0005	mg kg <sup>-1</sup>	4278	12	0.28	0.123	0.1	0.043	-0.00769	0.166	0.1055	0.105	0.0986	0.122	0.122	0.126	0.252	0.252	0.101
Ca	0.01	%	4278	0	0	1.07	0.473	0.252	-0.655	1.11	0.36	0.36	0.473	1.07	1.07	0.876	2.28	2.28	1.36
Cd	0.001	mg kg <sup>-1</sup>	4278	0	0	0.953	0.683	0.649	-0.984	1.73	0.773	0.774	0.683	0.953	0.953	0.997	0.829	0.829	1.06
Ce	0.003	mg kg <sup>-1</sup>	4278	0	0	25.5	17	14.3	-16.1	45.5	26.8	26.8	17	25.5	25.5	35.2	16.1	16.1	64.1
Co	0.001	mg kg <sup>-1</sup>	4278	0	0	6.43	4.01	4.86	-7.37	12.8	6.52	6.53	4.01	6.43	6.43	8.86	4.37	4.37	17.4
Cr	0.01	mg kg <sup>-1</sup>	4278	0	0	18.5	12.3	11.3	-13.4	33.2	18.95	18.9	12.3	18.5	18.5	24.1	12	12	40.8
Cs	0.005	mg kg <sup>-1</sup>	4278	21	0.49	0.712	0.446	0.423	-0.505	1.21	0.646	0.646	0.436	0.709	0.709	0.965	0.763	0.763	1.91

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
	Cu	0.01	mg kg <sup>-1</sup>	4278	0	0	18	13.6	10.4	-11.5	30.6	16.35	16.4	13.6	18	18	19.1	14.2	14.2
Fe	0.001	%	4278	0	0	1.56	1.1	0.927	-0.994	2.77	1.56	1.56	1.1	1.56	1.56	1.91	1.05	1.05	2.69
Ga	0.004	mg kg <sup>-1</sup>	4278	0	0	2.98	2.11	1.86	-2.17	5.34	2.91	2.91	2.11	2.98	2.98	3.58	1.93	1.93	4.94
Ge	0.005	mg kg <sup>-1</sup>	4278	43	1.01	0.0483	0.043	0.0208	-0.0075	0.0735	0.046	0.0465	0.042	0.0479	0.0479	0.0488	0.0247	0.0247	0.0288
Hf	0.002	mg kg <sup>-1</sup>	4278	365	8.53	0.0643	0.0461	0.046	-0.062	0.124	0.058	0.058	0.0337	0.0591	0.0593	0.0896	0.0425	0.0422	0.221
Hg	0.004	mg kg <sup>-1</sup>	4278	1	0.02	0.117	0.103	0.0371	-0.0085	0.163	0.098	0.098	0.103	0.117	0.117	0.115	0.154	0.154	0.0564
In	0.005	mg kg <sup>-1</sup>	4278	335	7.83	0.0202	0.0181	0.0089	-0.005	0.031	0.018	0.018	0.016	0.0191	0.0191	0.0193	0.0118	0.0118	0.013
K	0.01	%	4278	129	3.02	0.129	0.106	0.0741	-0.095	0.235	0.12	0.12	0.0976	0.126	0.126	0.136	0.0739	0.0739	0.132
La	0.002	mg kg <sup>-1</sup>	4278	0	0	13.1	8.69	7.56	-7.9	22.9	13.4	13.4	8.69	13.1	13.1	17.9	8.26	8.26	32.3
Li	0.1	mg kg <sup>-1</sup>	4278	503	11.76	10.9	7.9	5.93	-6.1	18.5	9.1	9.1	4.35	9.61	9.73	26.6	7.61	7.46	160
Mg	0.01	%	4278	0	0	0.189	0.15	0.089	-0.08	0.28	0.15	0.15	0.15	0.189	0.189	0.186	0.172	0.172	0.137
Mn	0.1	mg kg <sup>-1</sup>	4278	1	0.02	625	297	544	-968	1270	494	494	297	625	625	990	821	821	3150
Mo	0.01	mg kg <sup>-1</sup>	4278	0	0	1.34	0.975	0.682	-0.855	2.06	1.01	1.01	0.975	1.34	1.34	1.32	1.71	1.71	1.2
Na	0.001	%	4278	1	0.02	0.0234	0.0209	0.00741	-0.0005	0.0325	0.02	0.02	0.0209	0.0234	0.0234	0.023	0.0205	0.0205	0.0103
Nb	0.002	mg kg <sup>-1</sup>	4278	0	0	0.319	0.229	0.157	-0.159	0.503	0.265	0.265	0.229	0.319	0.319	0.344	0.288	0.288	0.387
Ni	0.04	mg kg <sup>-1</sup>	4278	0	0	23.2	15	17.2	-25.9	46	23.5	23.5	15	23.2	23.2	29.9	15.8	15.8	51.5
P	0.001	mg kg <sup>-1</sup>	4278	0	0	840	749	297	5	1240	820	820	749	840	840	858	371	371	481
Pb	0.005	mg kg <sup>-1</sup>	4278	0	0	26.1	21.5	9.19	-2.42	35.5	22.4	22.4	21.5	26.1	26.1	27	23.1	23.1	20.5
Rb	0.005	mg kg <sup>-1</sup>	4278	0	0	10.9	6.57	8.67	-13.4	22.3	10.9	10.9	6.57	10.9	10.9	15.9	7.66	7.66	34.8
Re	0.0002	mg kg <sup>-1</sup>	4278	1560	36.47	0.00187	0.000844	0.000445	-0.00095	0.00175	0.0004	0.0004	0.00034	0.0013	0.00122	0.00111	0.00365	0.00367	0.00346
S	0.01	%	4278	1	0.02	0.137	0.0962	0.0297	-0.16	0.26	0.07	0.07	0.0961	0.137	0.137	0.132	0.133	0.133	0.125
Sb	0.005	mg kg <sup>-1</sup>	4278	1	0.02	0.491	0.392	0.227	-0.229	0.761	0.395	0.395	0.392	0.491	0.491	0.493	0.444	0.444	0.377
Sc	0.005	mg kg <sup>-1</sup>	4278	0	0	2.16	1.46	1.63	-2.36	4.25	2.15	2.15	1.46	2.16	2.16	2.67	1.44	1.44	4.07
Se	0.003	mg kg <sup>-1</sup>	4278	0	0	1.36	0.948	0.467	-0.665	1.79	0.821	0.821	0.948	1.36	1.36	1.25	1.84	1.84	1.07

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
	Sn	0.01	mg kg <sup>-1</sup>	4278	10	0.23	0.819	0.678	0.252	0.005	1.05	0.69	0.69	0.671	0.817	0.817	0.826	0.742	0.742
Sr	0.01	mg kg <sup>-1</sup>	4278	0	0	30.6	23.1	10.3	-9.19	39.5	20.7	20.8	23.1	30.6	30.6	28.9	35.6	35.6	21.6
Ta	0.005	mg kg <sup>-1</sup>	4278	4217	98.57	0.0122	0.00947	0.00297	0	0.012	NA	0.0000796	0.0000952	0.00609	0.000466	0.000489	0.00188	0.0023	0.00246
Te	0.003	mg kg <sup>-1</sup>	4278	160	3.74	0.019	0.0152	0.0104	-0.0095	0.0295	0.016	0.016	0.0142	0.0184	0.0184	0.0181	0.0348	0.0348	0.0145
Th	0.002	mg kg <sup>-1</sup>	4278	93	2.17	0.995	0.56	0.734	-1.04	1.93	0.948	0.948	0.49	0.973	0.974	2.33	0.764	0.763	10.9
Ti	0.001	%	4278	319	7.46	0.00577	0.00467	0.00148	-0.003	0.009	0.004	0.004	0.00407	0.00549	0.00543	0.00537	0.00556	0.0056	0.00463
Tl	0.001	mg kg <sup>-1</sup>	4278	39	0.91	0.184	0.126	0.111	-0.132	0.33	0.183	0.183	0.121	0.182	0.182	0.246	0.136	0.136	0.438
U	0.005	mg kg <sup>-1</sup>	4278	0	0	1.67	1.01	0.503	-0.272	1.88	1.095	1.09	1.01	1.67	1.67	1.68	3.43	3.43	2.24
V	0.1	mg kg <sup>-1</sup>	4278	0	0	26.9	19	16.4	-17.8	48.6	27	27.1	19	26.9	26.9	33.1	16.6	16.6	47.4
W	0.001	mg kg <sup>-1</sup>	4278	43	1.00	0.107	0.0599	0.0311	-0.025	0.107	0.059	0.059	0.0574	0.106	0.106	0.086	0.486	0.486	0.0962
Y	0.003	mg kg <sup>-1</sup>	4278	0	0	13.1	7.61	10.4	-16.1	26	11.7	11.7	7.61	13.1	13.1	18.6	10.8	10.8	41.3
Zn	0.1	mg kg <sup>-1</sup>	4278	0	0	70.2	53.3	45.1	-56.9	125	65.2	65.2	53.3	70.2	70.2	72.9	145	145	68.2
Zr	0.01	mg kg <sup>-1</sup>	4278	0	0	1.99	1.26	1.63	-2.52	4.08	1.97	1.97	1.26	1.99	1.99	2.61	1.39	1.39	4.74
Au	0.0002	mg kg <sup>-1</sup>	4278	780	18.23	0.00167	0.000726	0.000445	-0.00025	0.00125	0.0006	0.0006	0.000526	0.00142	0.0014	0.000813	0.0235	0.0235	0.000961
Pd	0.001	mg kg <sup>-1</sup>	4278	3704	86.58	0.00771	0.00374	0.00148	-0.0025	0.0065	NA	0.000139	0.0000657	0.00277	0.00123	0.00142	0.00761	0.00779	0.0306
Pt	0.002	mg kg <sup>-1</sup>	4278	3599	84.13	0.0338	0.00948	0.00445	-0.011	0.019	NA	0.000107	0.000103	0.00789	0.00558	0.00839	0.0371	0.0374	0.683

# 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](http://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)	2500	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 localised 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 recognised 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 emphasised 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 Shallow 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 97.5 <sup>th</sup> percentile.	Better presented as proportional colour/symbol point map.
B	ICP-MS (ME-MS41L)	<LLD to 95 <sup>th</sup> percentile.	Perhaps better presented as proportional colour/symbol point map.
Pd	ICP-MS (ME-MS41L)	<LLD to 80 <sup>th</sup> percentile.	Perhaps better presented as proportional colour/symbol point map.
Pt	ICP-MS (ME-MS41L)	<LLD to 80 <sup>th</sup> percentile.	Perhaps better presented as proportional colour/symbol point map.
Pd	ICP-MS (MS41L-BLD)	<LLD to 15 <sup>th</sup> 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 utilises 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 <sup>th</sup> and 75 <sup>th</sup> 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 data	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 $\pm n$ 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>i.e.</i> 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, <i>etc.</i>
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>i.e.</i> "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>i.e.</i> 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>i.e.</i> 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 is 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	
$\sigma$	Sigma	Standard deviation(s)
weight oxide %	Weight oxide percent equivalent	Normally of the element oxide, for major element determinands.
$\text{mg kg}^{-1}$	milligramme per kilogramme	Equivalent to part(s) per million (ppm).
$\mu\text{g kg}^{-1}$	microgramme per kilogramme	Equivalent to part(s) per billion (ppb).

# References

---

- ANTWEILER, R. C. & TAYLOR, H. E. 2008. Evaluation of Statistical Treatments of Left-Censored Environmental Data using Coincident Uncensored Data Sets: I. Summary Statistics. *Environmental Science & Technology*, 42, 3732-3738.
- CHILDS, C. 2004. Interpolating surfaces in ArcGIS Spatial Analyst. *ArcUser*. Summer 2004 ed. California, USA: ESRI.
- EATHERINGTON, N. & JOSEPH, W. 2018. TELLUS QC Summary Report. *Malvern Panalytical*
- EATHERINGTON, N. 2019. TELLUS QC Summary Report. *Malvern Panalytical*.
- HELSEL, D. R. 2005. More Than Obvious: Better Methods for Interpreting Nondetect Data. *Environmental Science & Technology*, 39, 419A-423A.
- JOHNSON, C. C. 2002. Within site and between site nested analysis of variance (ANOVA) for Geochemical Surveys using MS EXCEL. Nottingham, UK: British Geological Survey.
- JOHNSON, C. C., ANDER, L. E., LISTER, R. T. & FLIGHT, D. M. A. 2008. Data Conditioning of Environmental Geochemical Data: Quality Control Procedures Used in the British Geological Survey's Regional Geochemical Mapping Project. 93-118.
- KAPLAN, E. L. & MEIER, P. 1958. Nonparametric Estimation from Incomplete Observations. *Journal of the American Statistical Association*, 53, 457-481.
- LEE, L. 2009. NADA: Non-detects And Data Analysis for environmental data. 1.5.2 ed.
- PLANT, J. A. 1973. A random numbering system for geochemical samples. *Transactions of the Institution of Mining & Metallurgy*, 82B, 64-65.
- PLANT, J. A., JEFFREY, K., GILL, E. & FAGE, C. 1975. The systematic determination of accuracy and precision in geochemical exploration data. *Journal of Geochemical Exploration*, 4, 467-486.
- RAMSEY, M. H., THOMPSON, M. & HALE, M. 1992. Objective evaluation of precision requirements for geochemical analysis using robust analysis of variance. *Journal of Geochemical Exploration*, 44, 23-36.
- SINCLAIR, A. J. 1993. Univariate Analysis: Handbook of Exploration Geochemistry. Vol 2, 59-81.
- SGS MINERALS SERVICES LTD. 2013. Tellus Border Project: Summary Report for Work Performed on Lot 2-A Geochemical Analysis of Soil Samples. *Report to the Geological Survey of Ireland*. Toronto, Canada.
- SHEWHART, W. A. 1931. *Economic control of quality of manufactured product*, New York, D. Van Nostrand Company, Inc.
- SMYTH, D. 2007. Methods used in the Tellus geochemical mapping of Northern Ireland. Keyworth, Nottingham, UK: British Geological Survey.
- TEAM, R. C. 2013. R: A language and environment for statistical computing.
- WESTGARD, J.O., BARRY, P.L., HUNT, M.R., GROTH, T. 1981. A mult-rule Shewhart chart for quality control in clinical chemistry. *Clinical Chemistry*, 27, 493-501.

# 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](mailto:tellus@gsi.ie) for further information regarding data quality.

## A. RMs data QCS charts

---

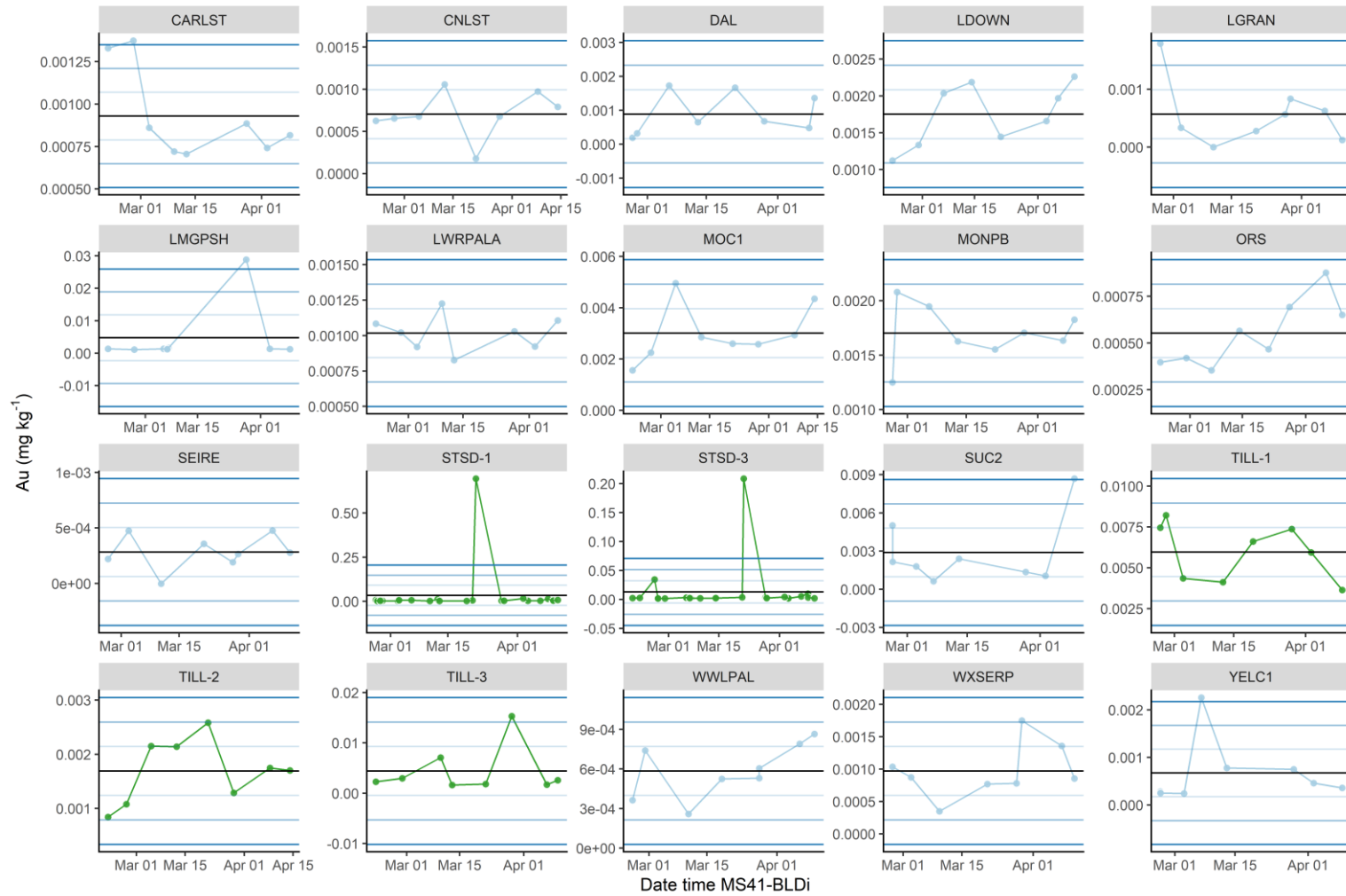
In this appendix all of the reference materials data are presented in two ways for each analyte (in the same order as data are reported by instrument and distributed):

- 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  $\pm$  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<sub>ar</sub> RMs data by ALS Minerals Ltd method code MS41L-BLD**

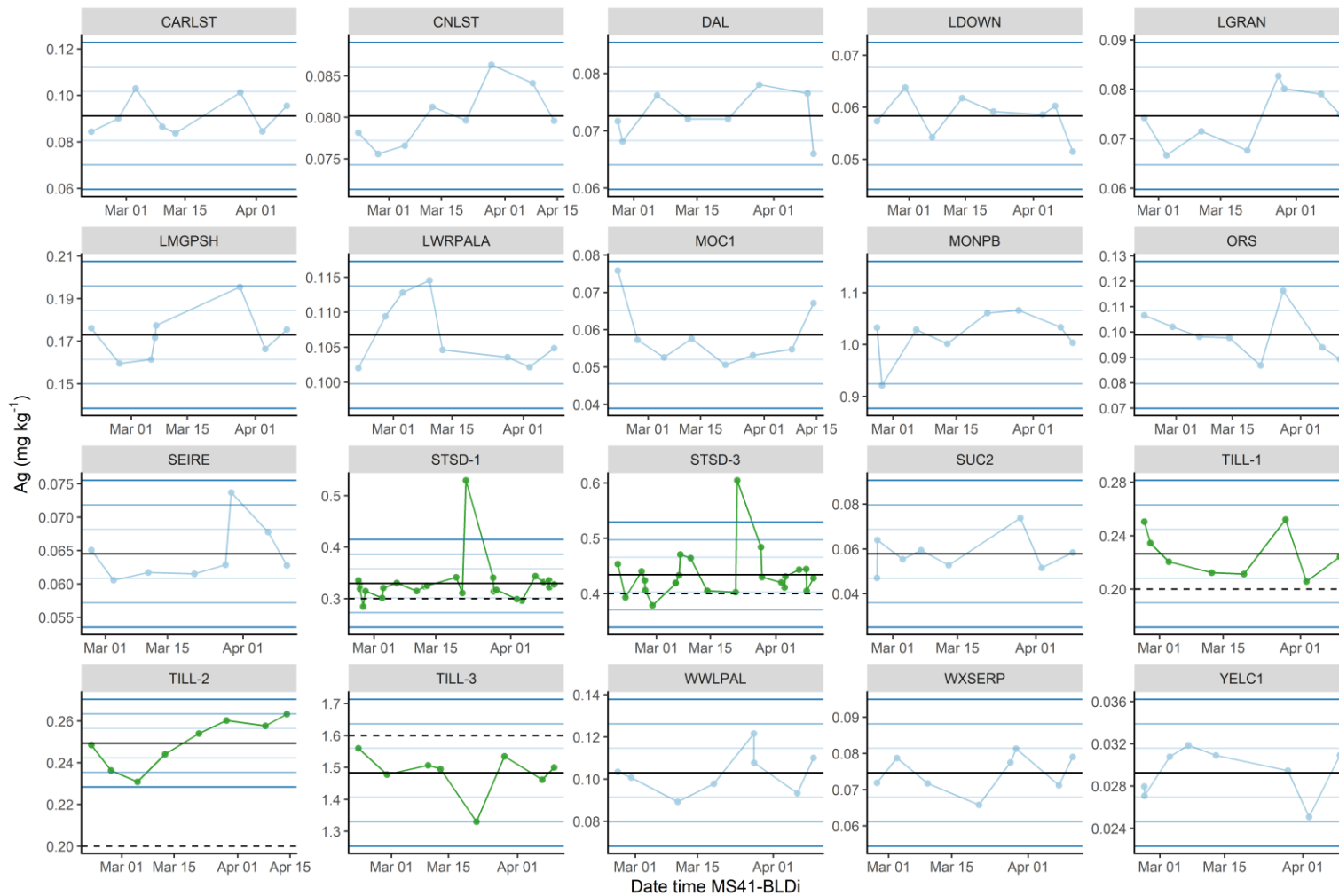
Gold (Au) MS41L-BLD



Gold (Au) sample data IQR: 0.000326–0.000913 mg kg<sup>-1</sup>

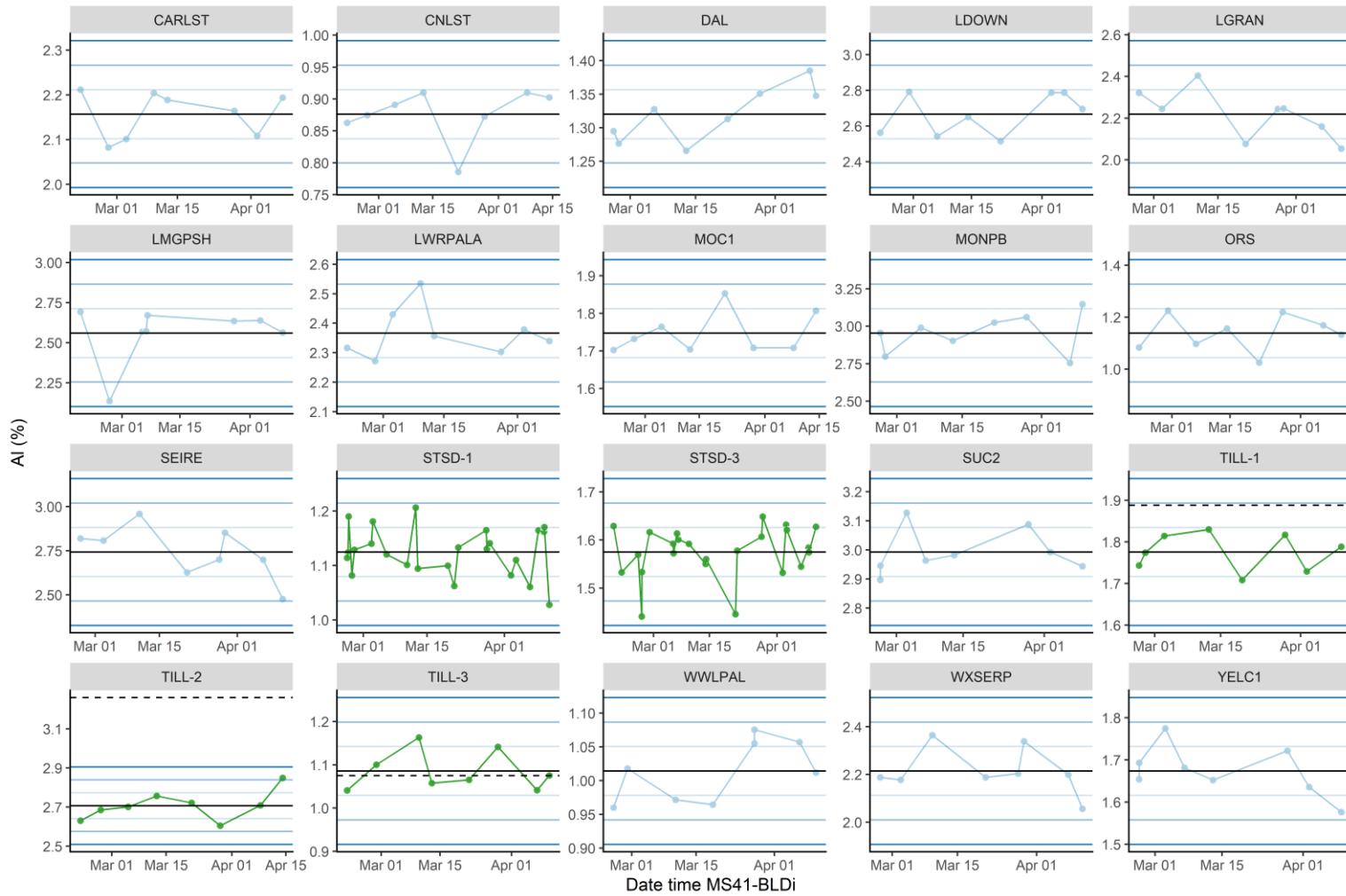


Silver (Ag) MS41L-BLD



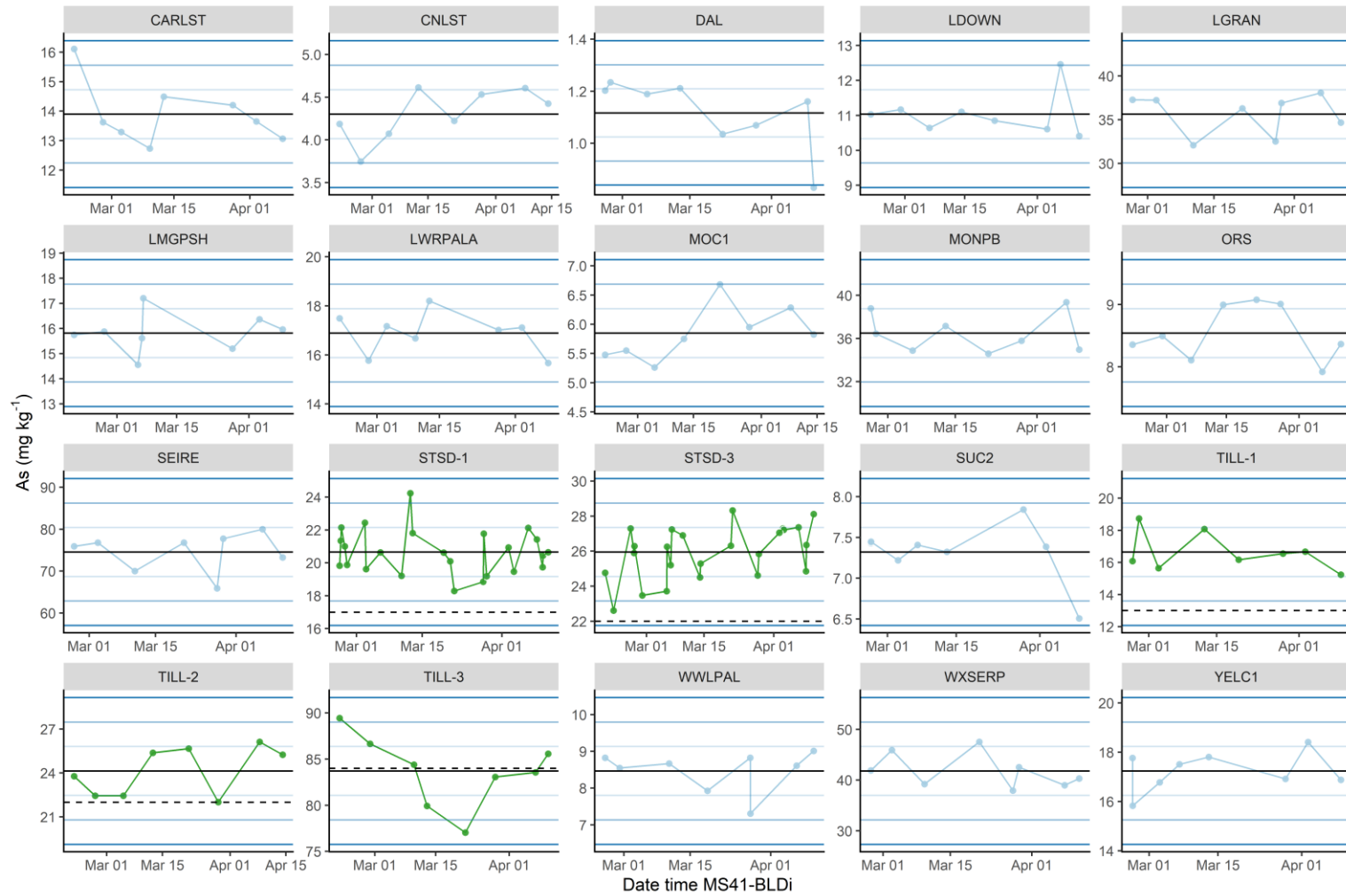
Silver (Ag) sample data IQR: 0.0645–0.113  $\text{mg kg}^{-1}$

Aluminium (Al) MS41L-BLD



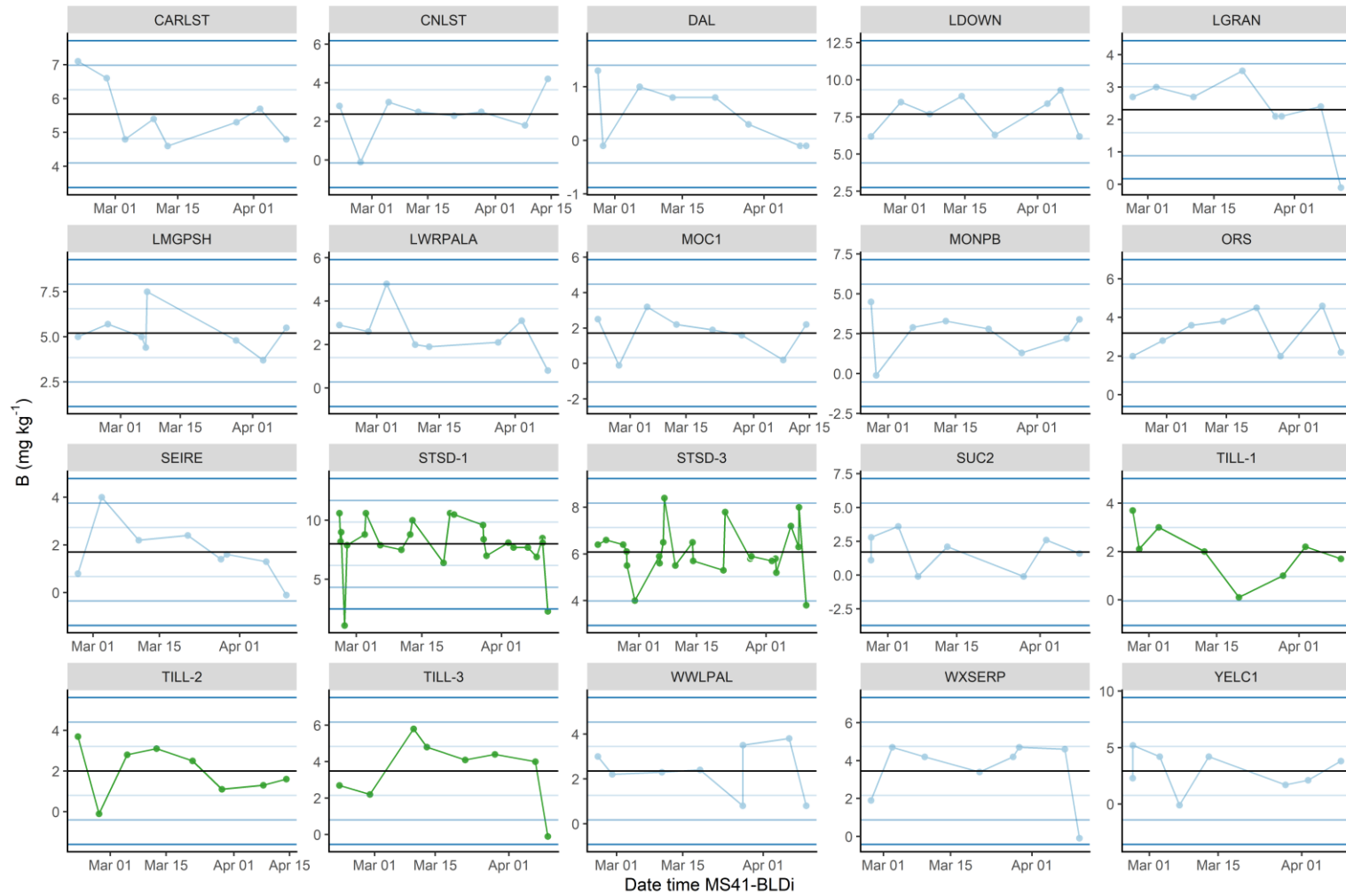
Aluminium (Al) sample data IQR: 0.547–1.43 %

Arsenic (As) MS41L-BLD



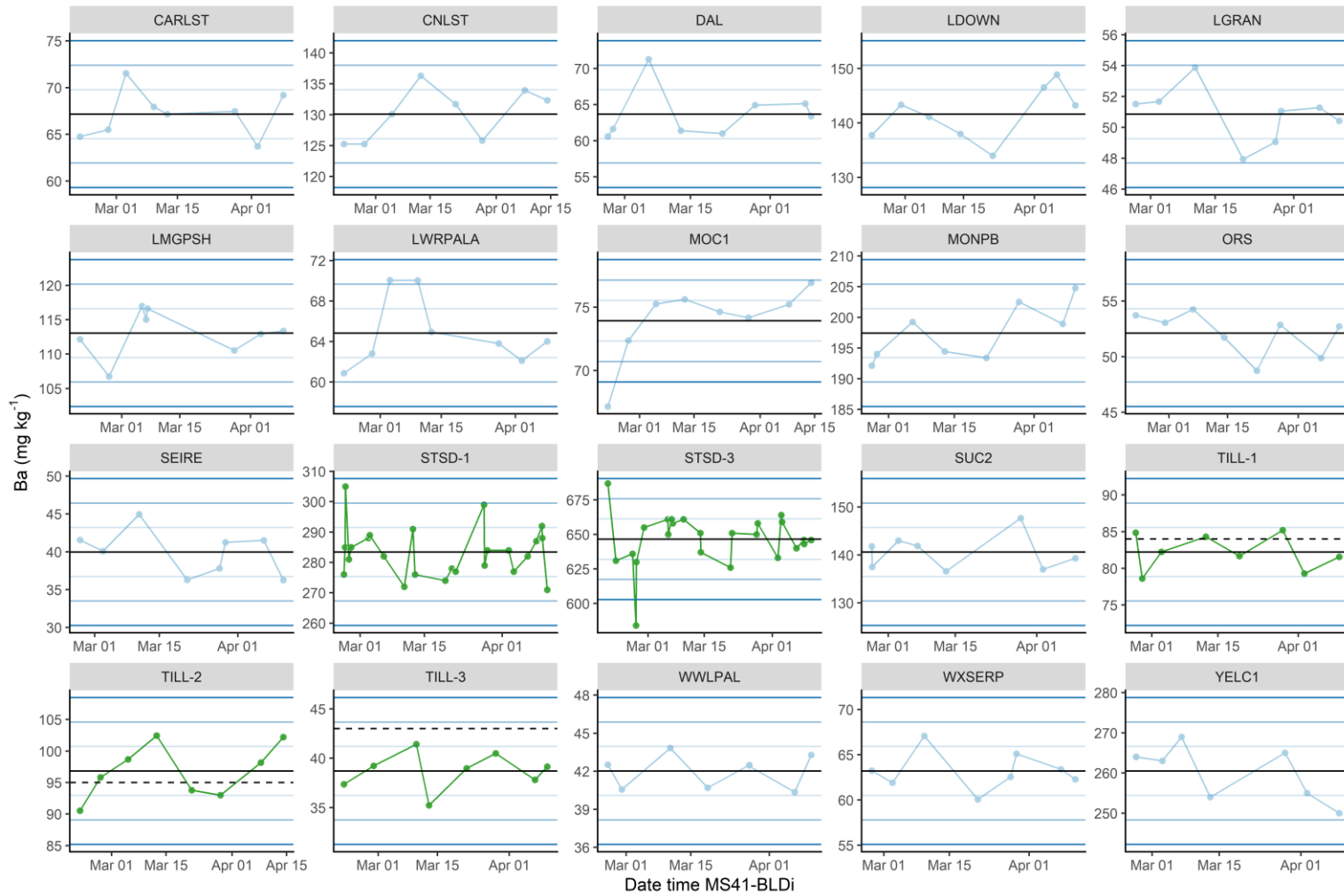
Arsenic (As) sample data IQR: 4.82–11.2  $\text{mg kg}^{-1}$

Boron (B) MS41L-BLD



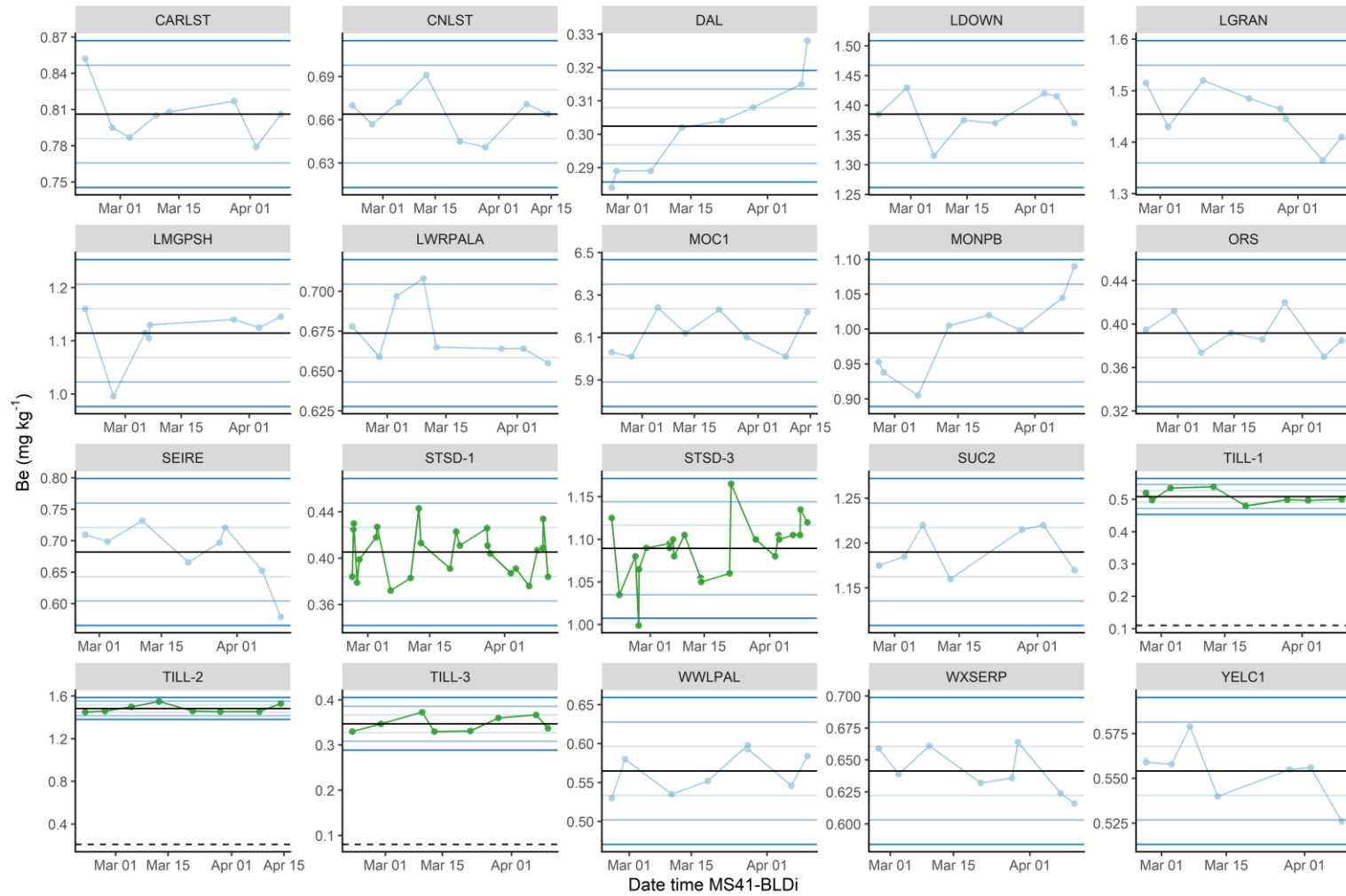
Boron (B) sample data IQR: 3.1-6.4 mg kg<sup>-1</sup>

Barium (Ba) MS41L-BLD



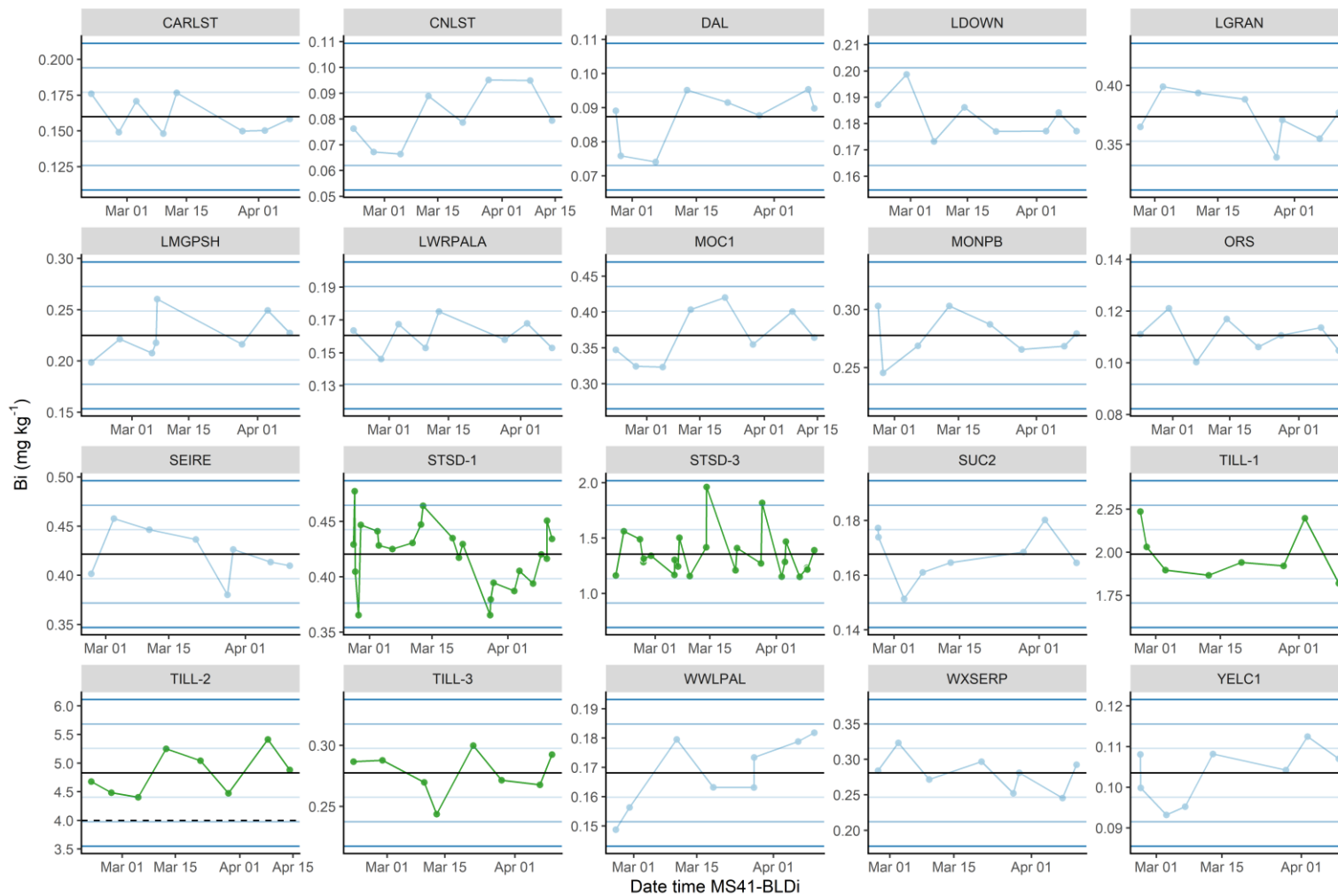
Barium (Ba) sample data IQR: 30.6–90.9 mg kg<sup>-1</sup>

Beryllium (Be) MS41L-BLD



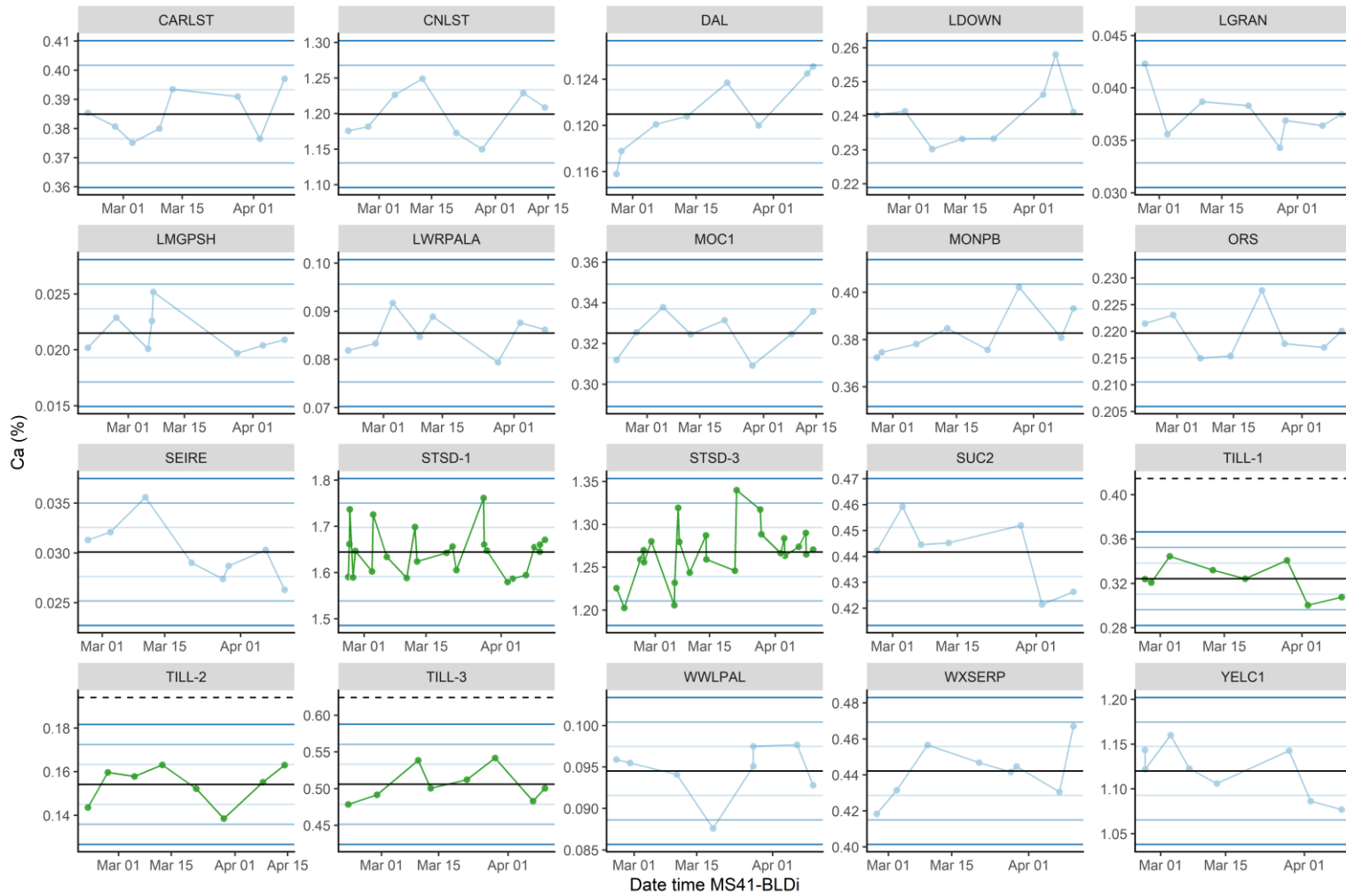
Beryllium (Be) sample data IQR: 0.291–0.85 mg kg<sup>-1</sup>

Bismuth (Bi) MS41L-BLD



Bismuth (Bi) sample data IQR: 0.0788–0.137 mg kg<sup>-1</sup>

Calcium (Ca) MS41L-BLD



Calcium (Ca) sample data IQR: 0.234–0.804 %

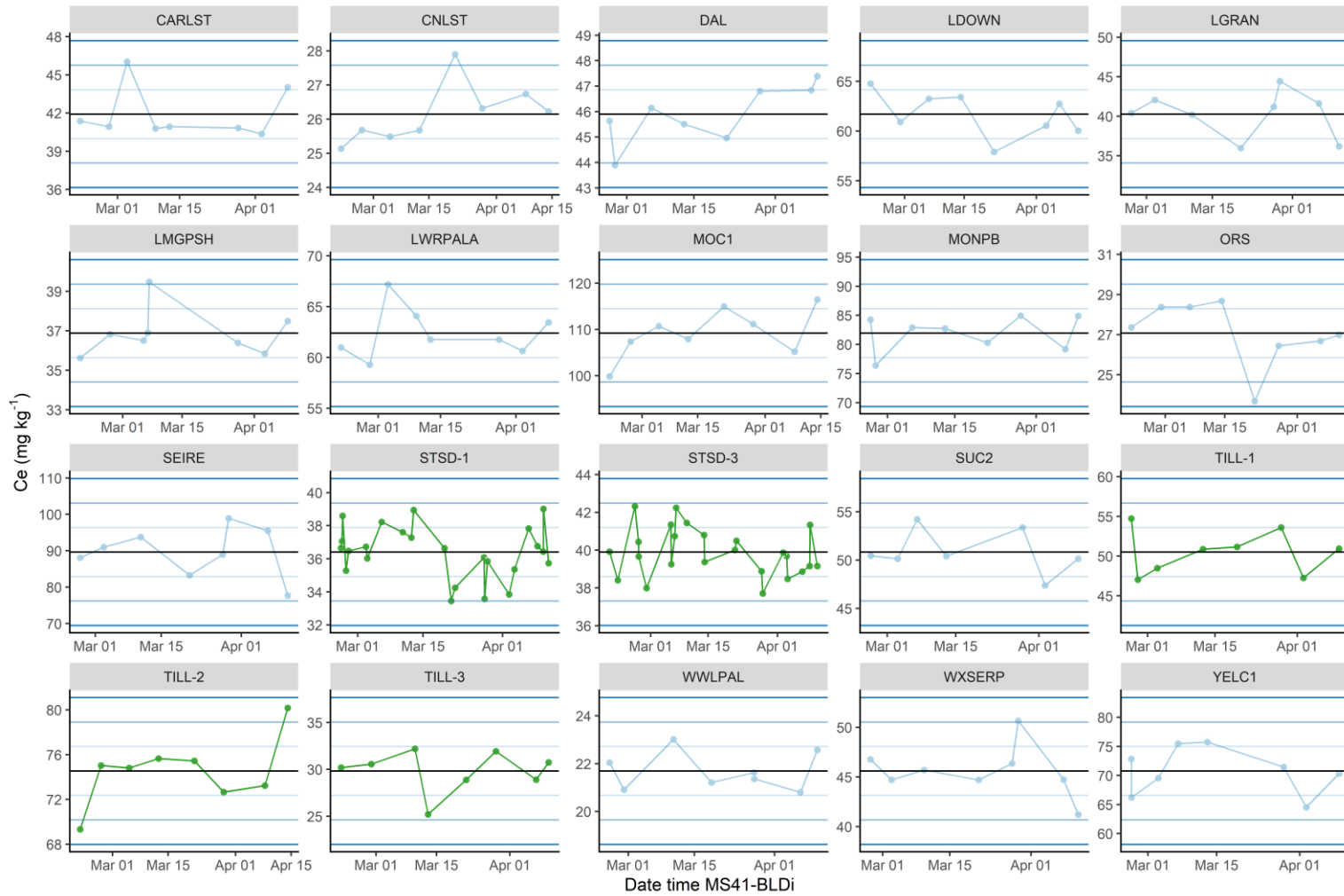


Cadmium (Cd) MS41L-BLD



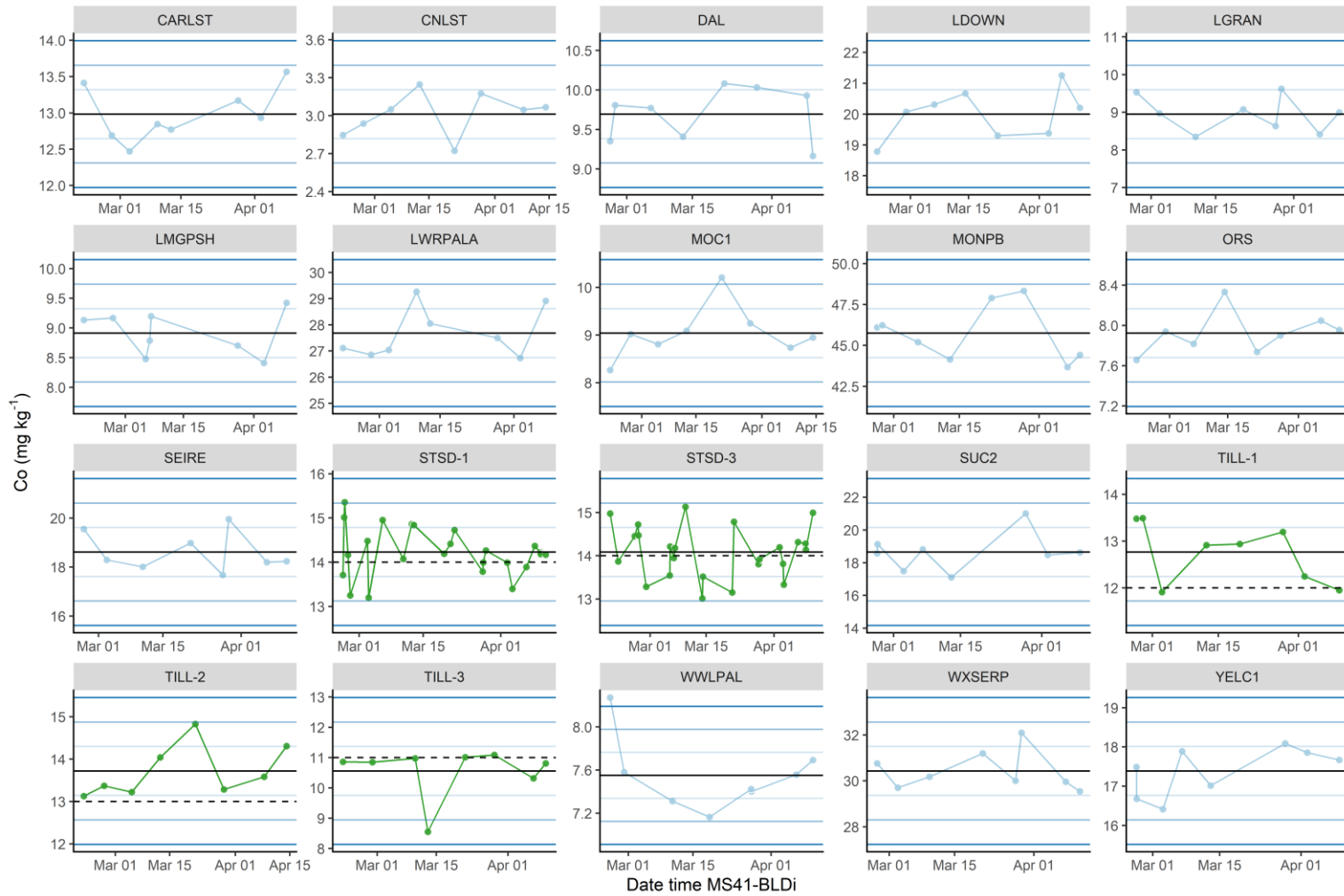
Cadmium (Cd) sample data IQR: 0.38–1.27  $\text{mg kg}^{-1}$

Cerium (Ce) MS41L-BLD



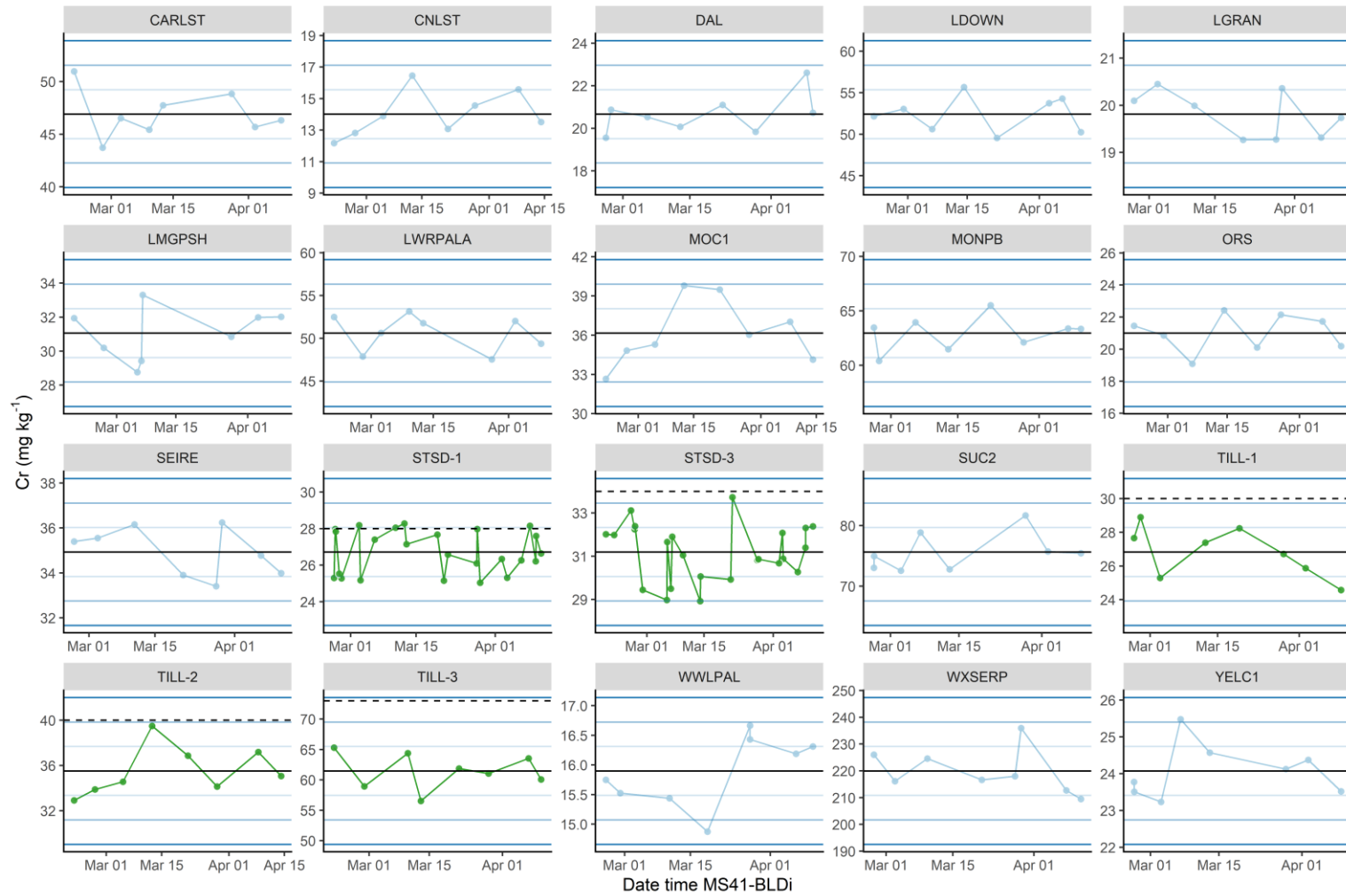
Cerium (Ce) sample data IQR: 15–35.1 mg kg<sup>-1</sup>

Cobalt (Co) MS41L-BLD



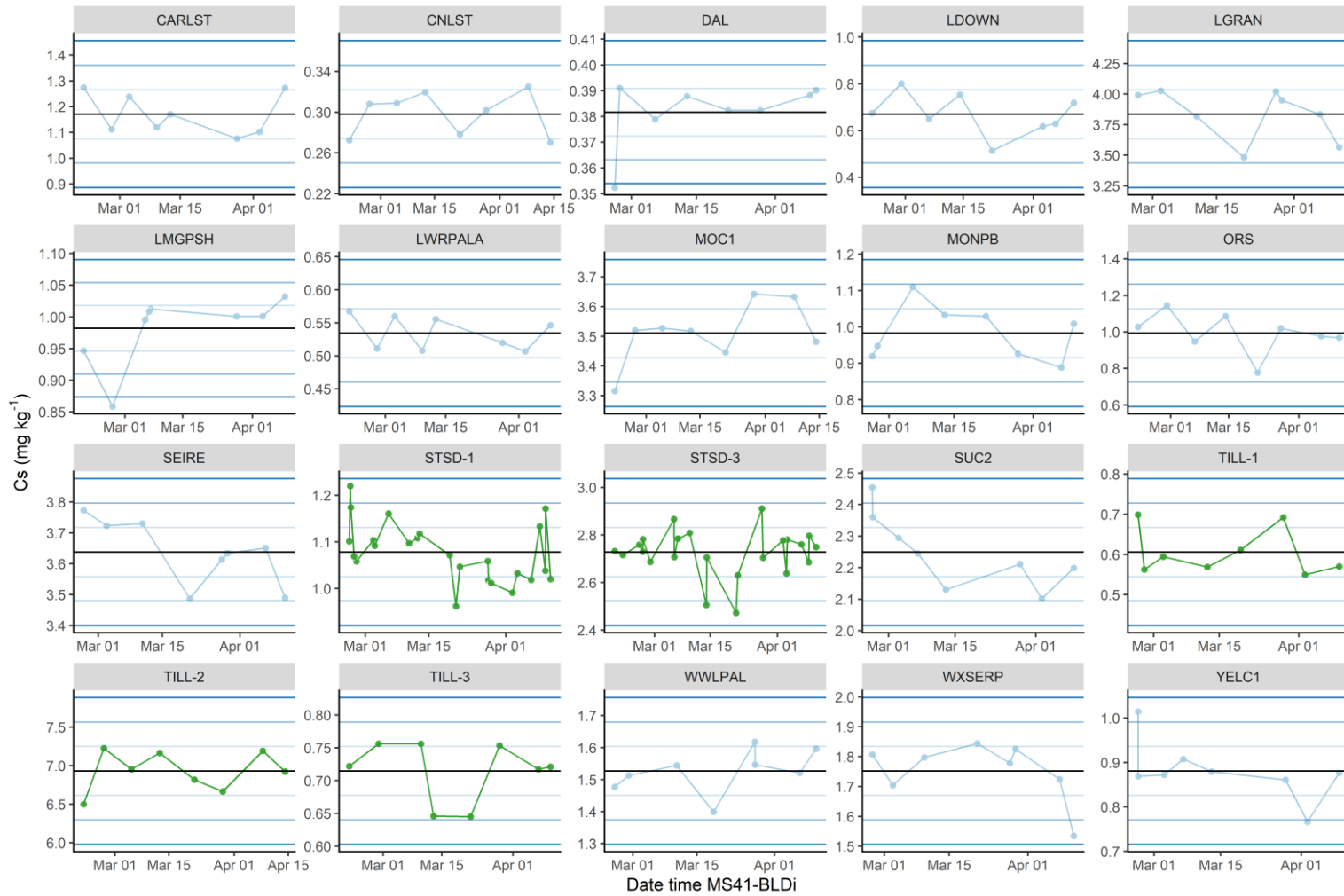
Cobalt (Co) sample data IQR: 2.87–9.53  $\text{mg kg}^{-1}$

Chromium (Cr) MS41L-BLD



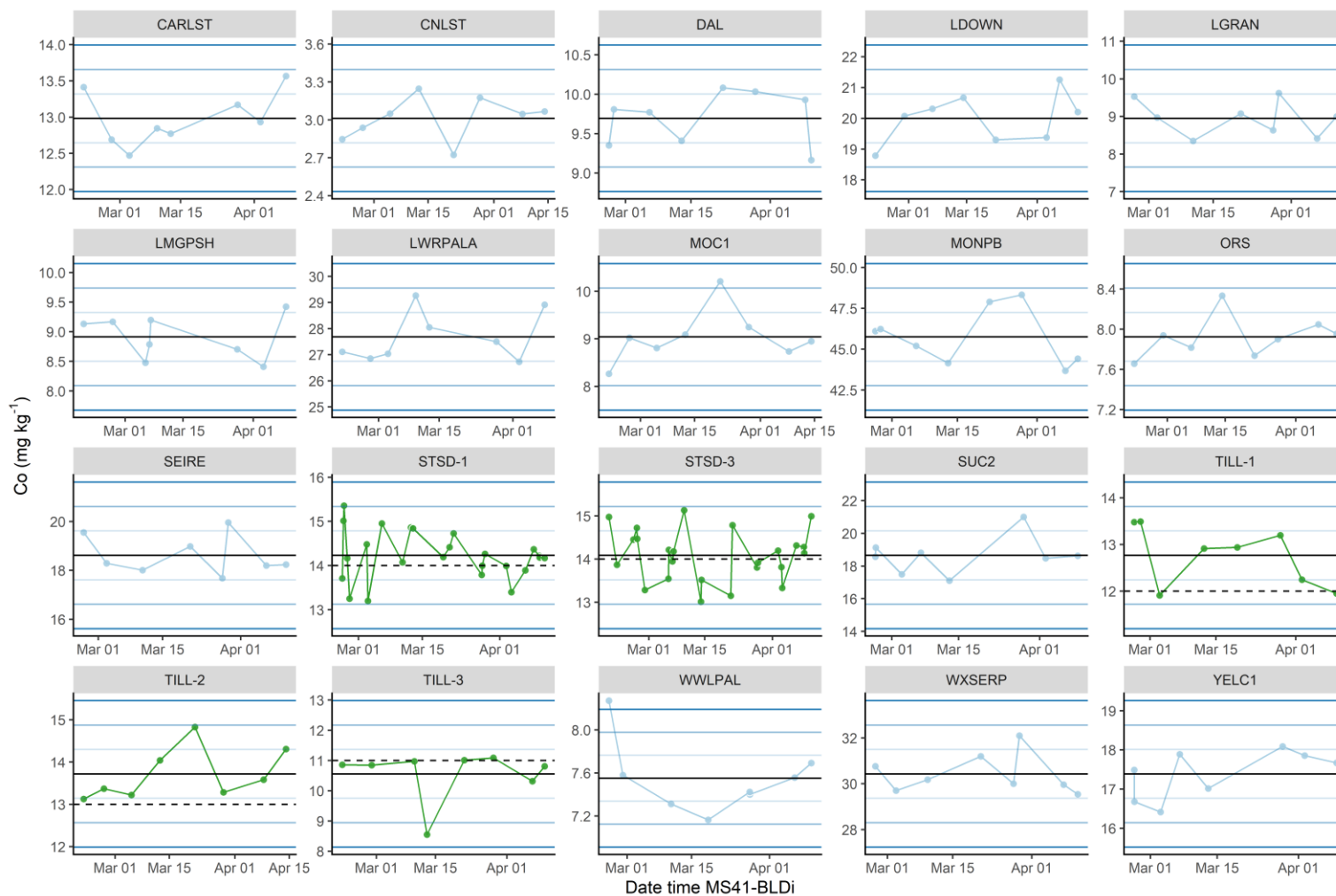
Chromium (Cr) sample data IQR: 10.1–25.3 mg kg<sup>-1</sup>

Caesium (Cs) MS41L-BLD



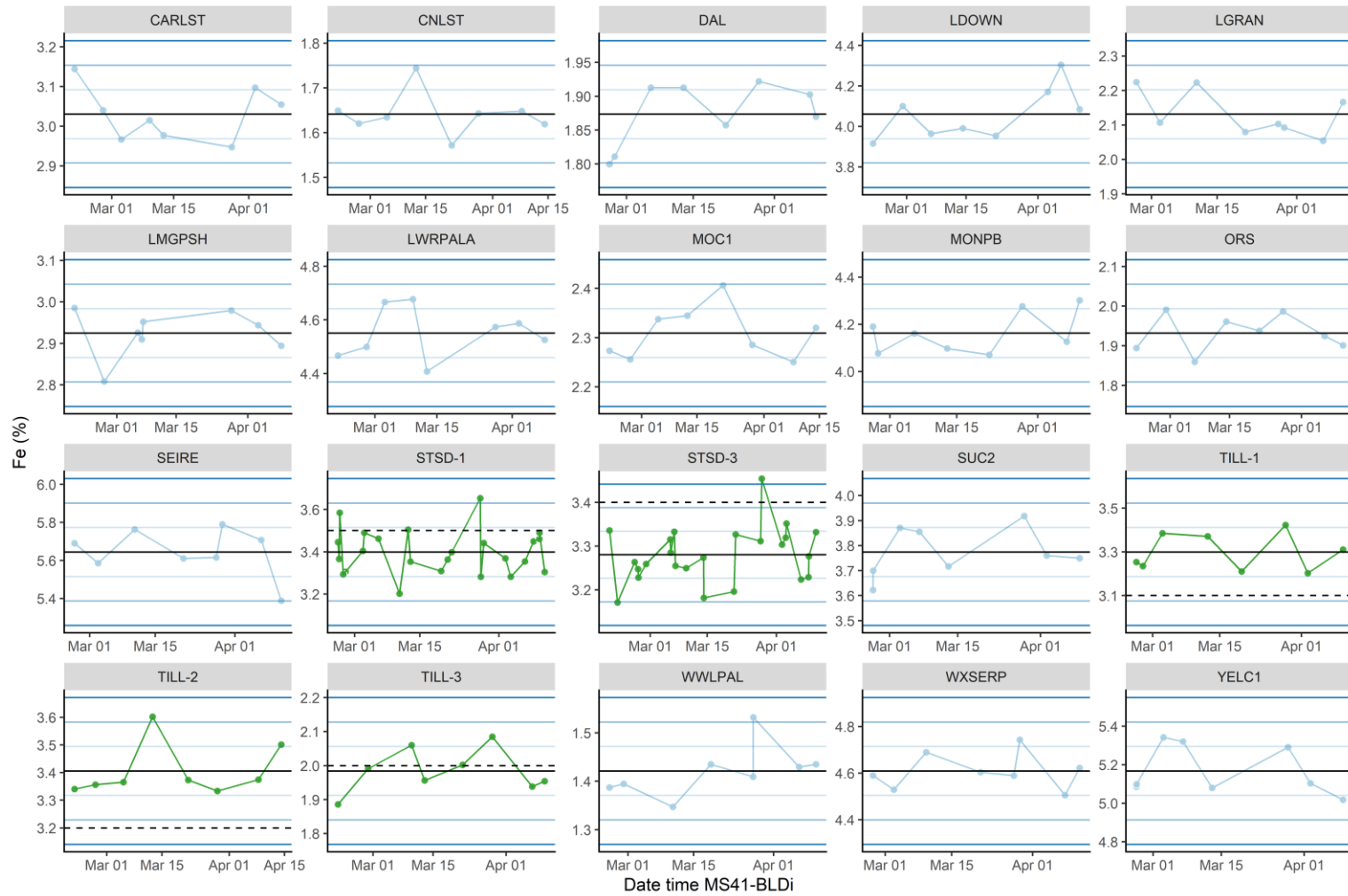
Caesium (Cs) sample data IQR: 0.354–0.923 mg kg<sup>-1</sup>

Copper (Cu) MS41L-BLD



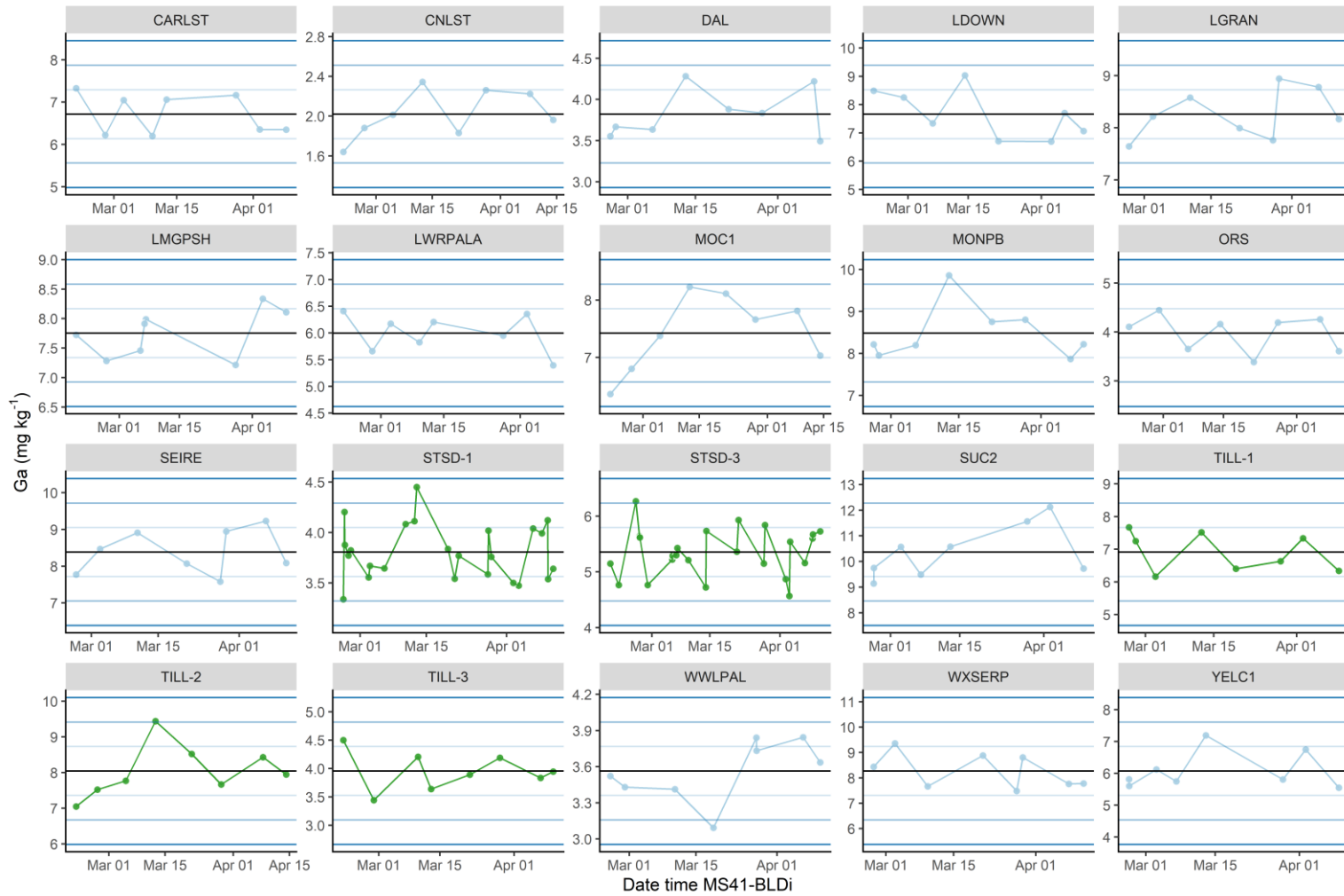
Copper (Cu) sample data IQR: 9.62–23.6 mg kg<sup>-1</sup>

Iron (Fe) MS41L-BLD



Iron (Fe) sample data IQR: 0.901–2.15%

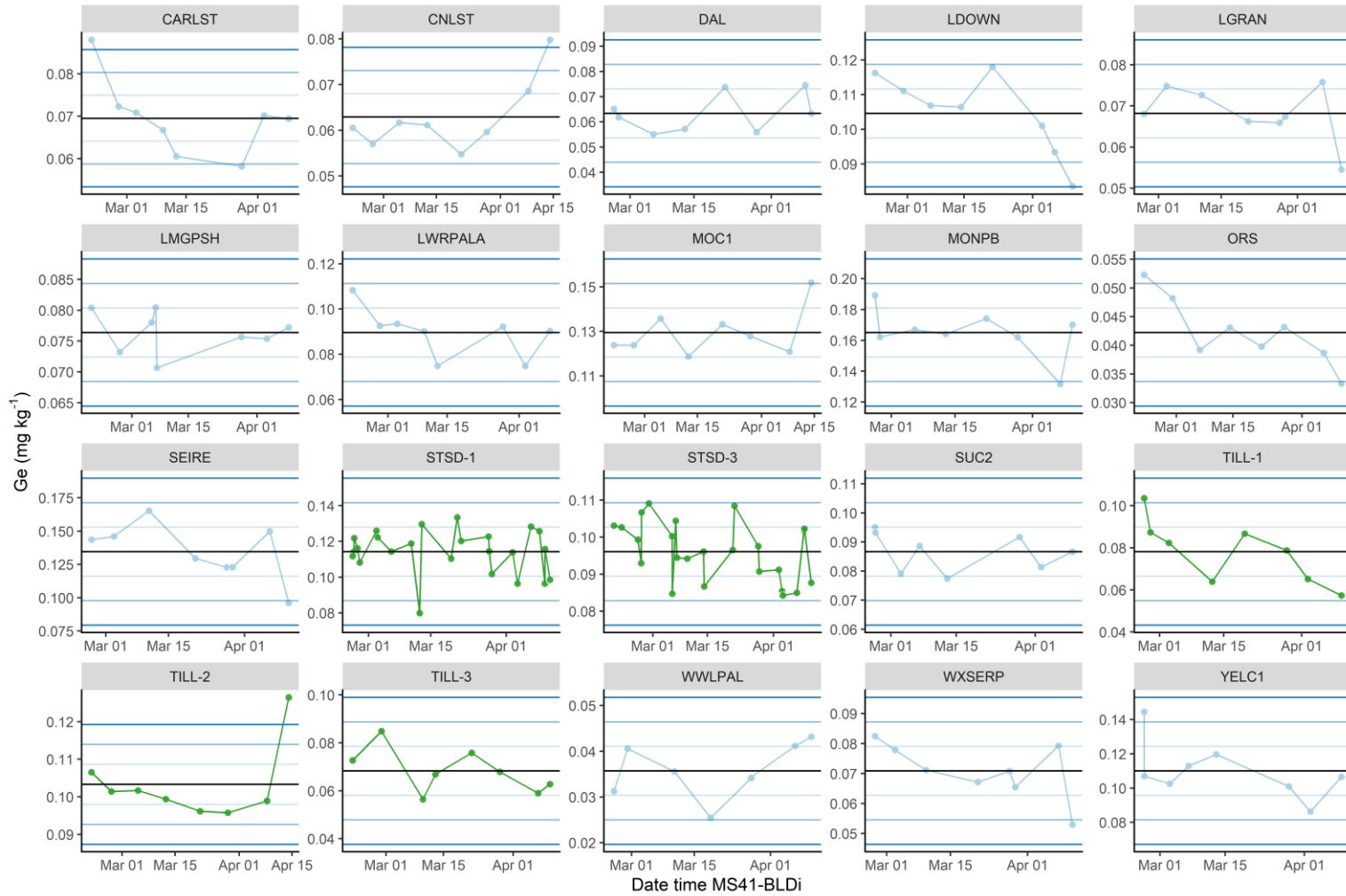
Gallium (Ga) MS41L-BLD



Gallium (Ga) sample data IQR:  $1.61\text{--}4.1 \text{ mg kg}^{-1}$

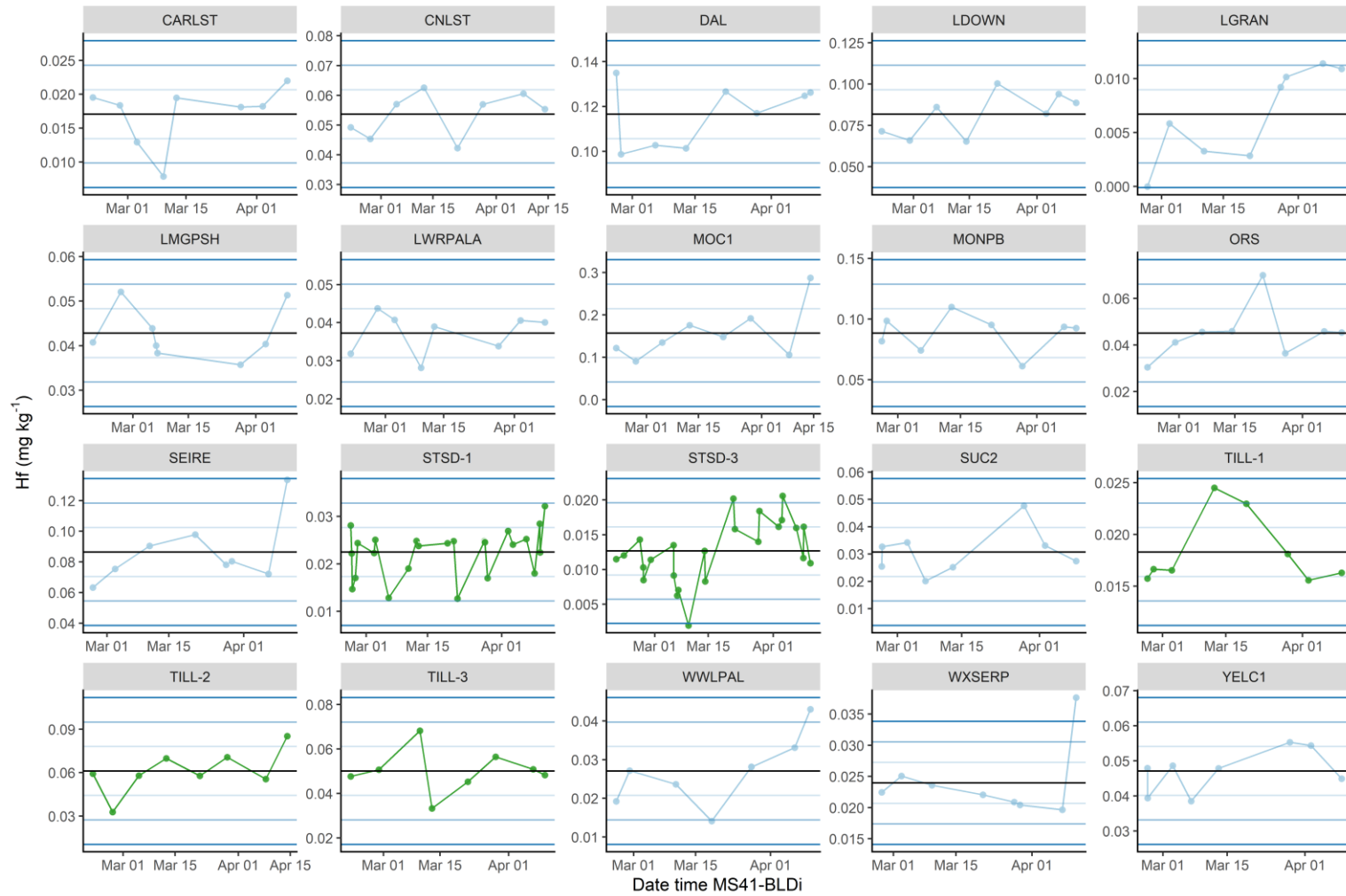


Germanium (Ge) MS41L-BLD



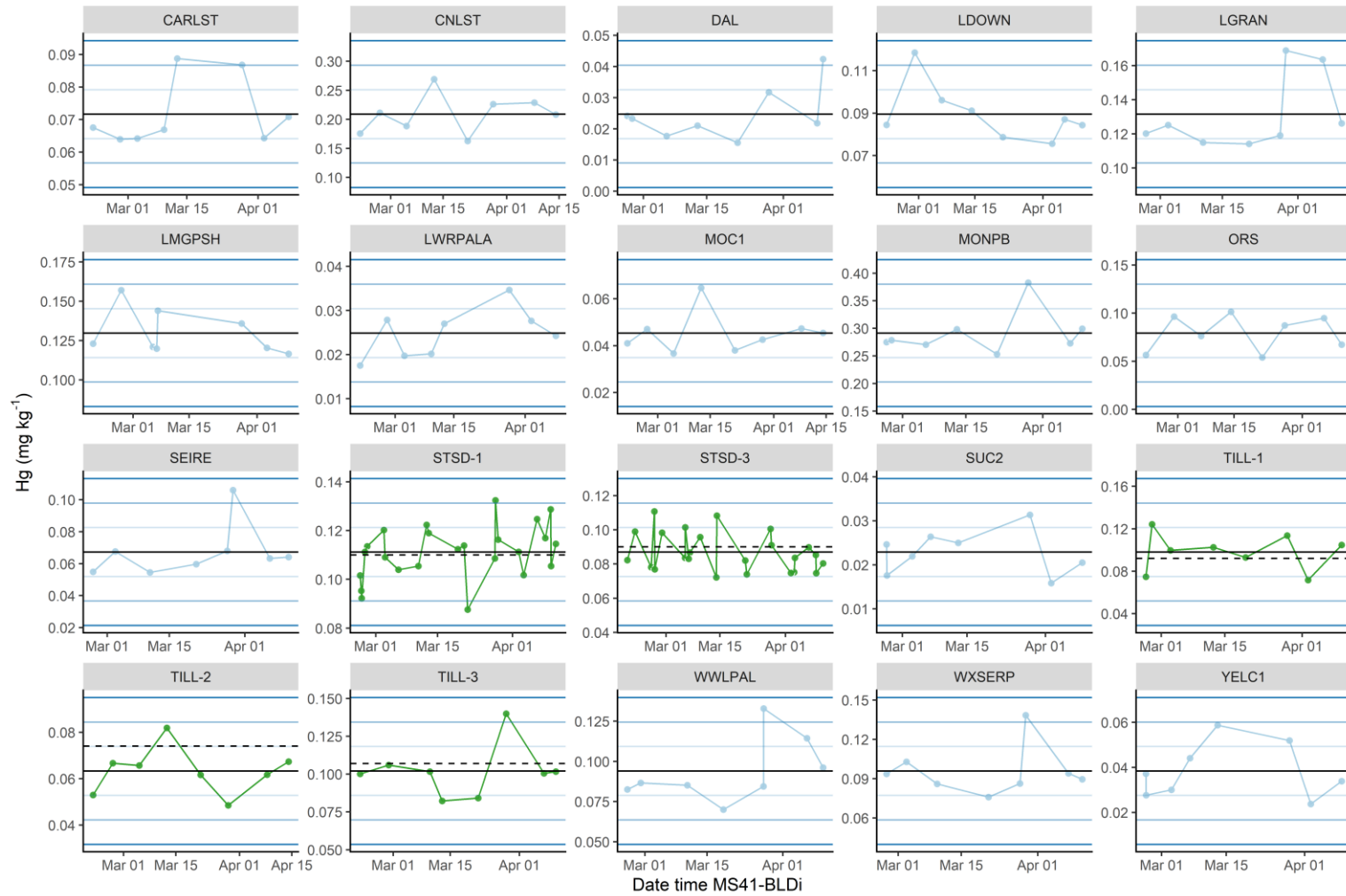
Germanium (Ge) sample data IQR: 0.0321-0.0591 mg kg<sup>-1</sup>

Hafnium (Hf) MS41L-BLD



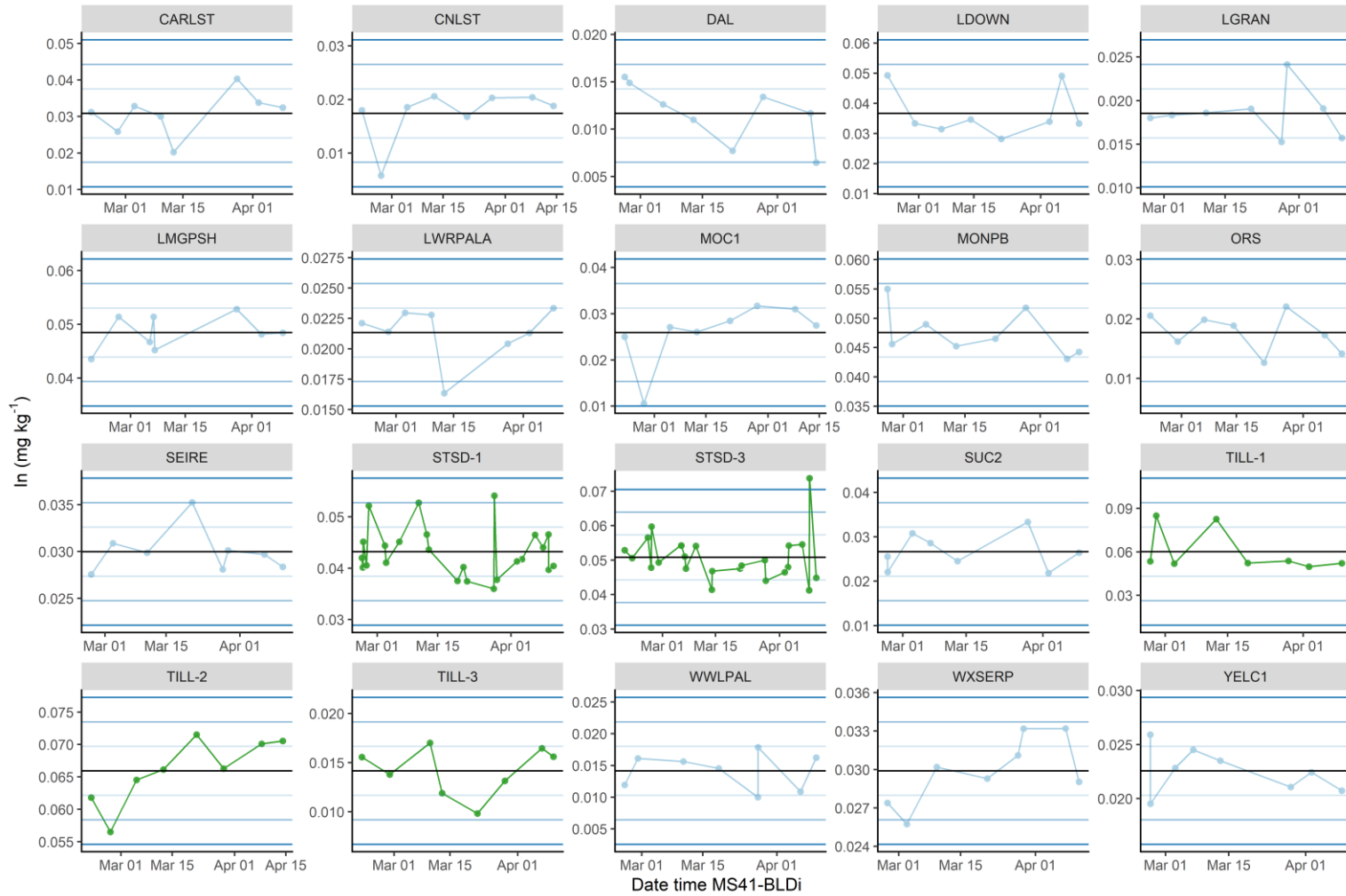
Hafnium (Hf) sample data IQR: 0.0221–0.0899mg kg<sup>-1</sup>

Mercury (Hg) MS41L-BLD



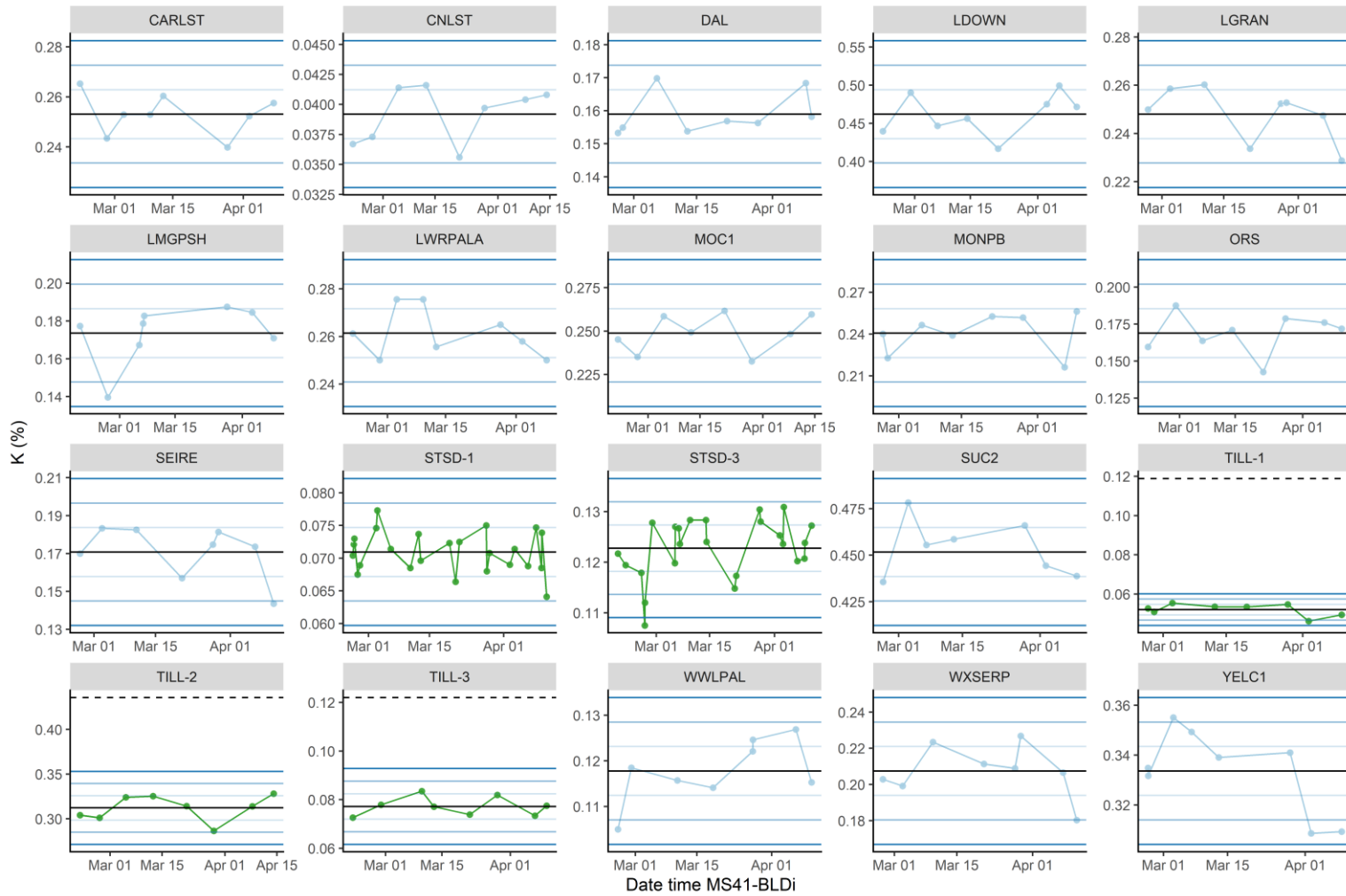
Mercury (Hg) sample data IQR: 0.0773–0.133  $\text{mg kg}^{-1}$

Indium (In) MS41L-BLD



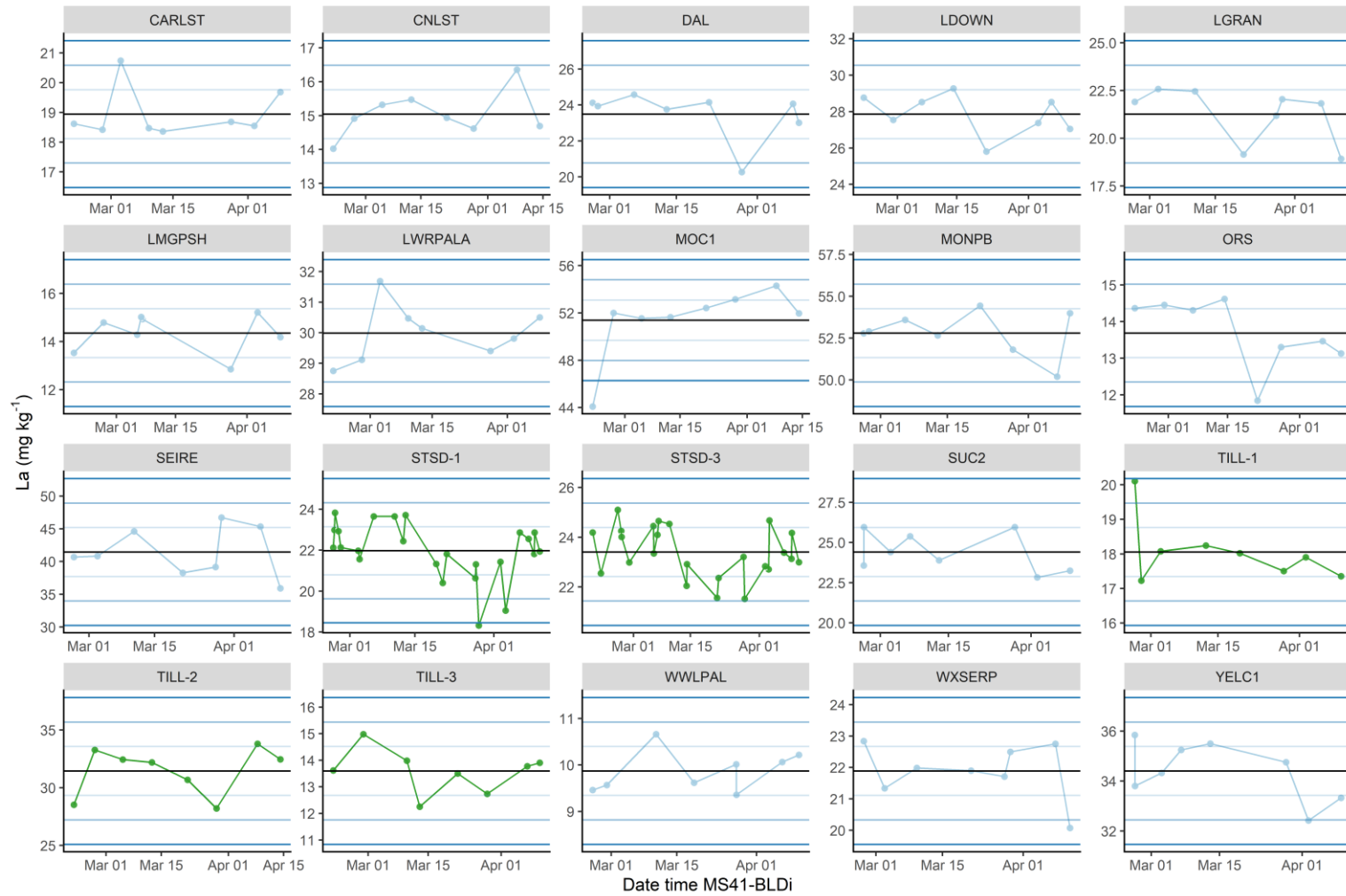
Indium (In) sample data IQR: 0.0118–0.0244  $\text{mg kg}^{-1}$

Potassium (K) MS41L-BLD



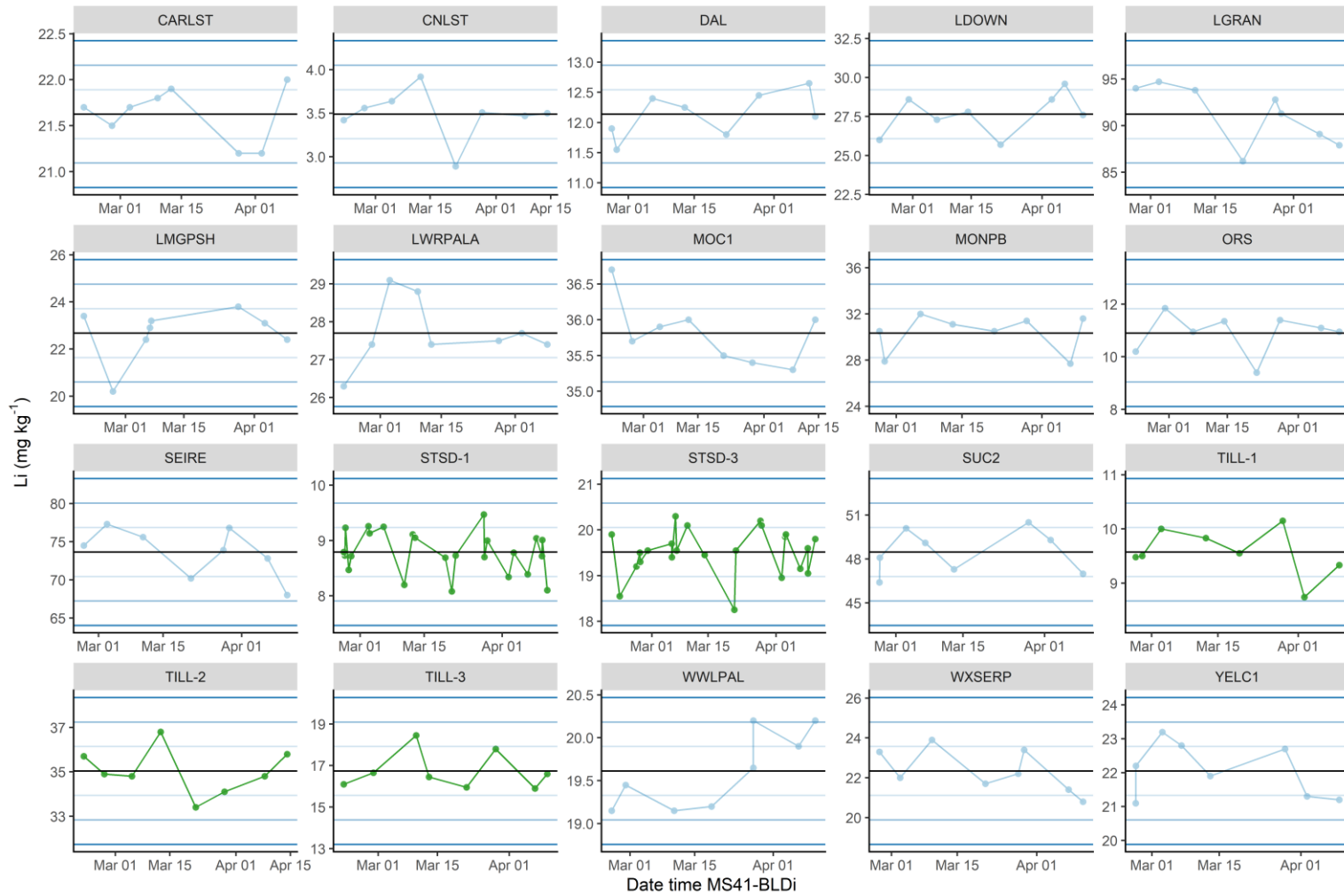
Potassium (K) sample data IQR: 0.0654–0.176 %

Lanthanum (La) MS41L-BLD



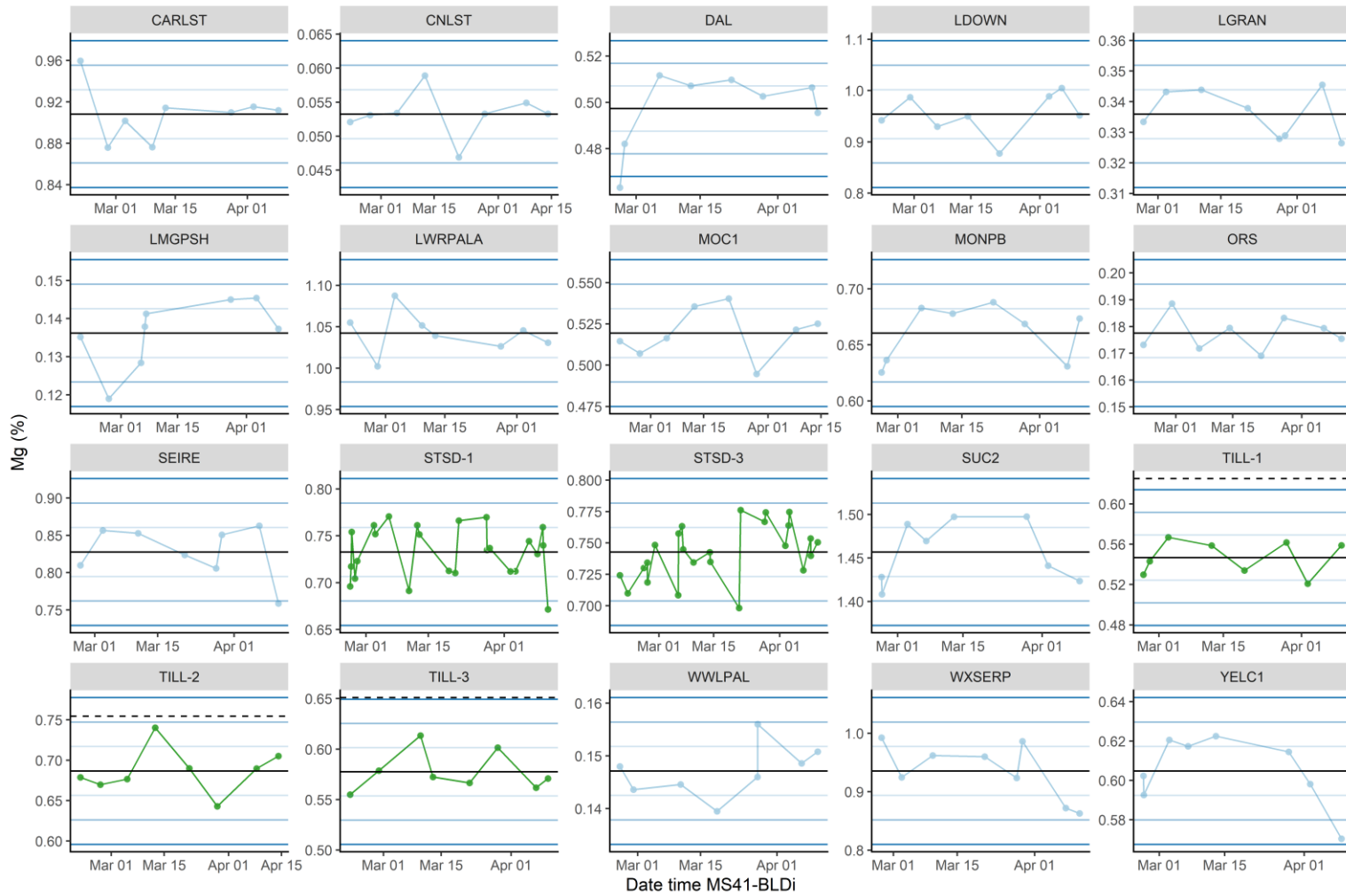
Lanthanum (La) sample data IQR: 7.56–17.7 mg kg<sup>-1</sup>

Lithium (Li) MS41L-BLD



Lithium (Li) sample data IQR: 4.14–13.8  $\text{mg kg}^{-1}$

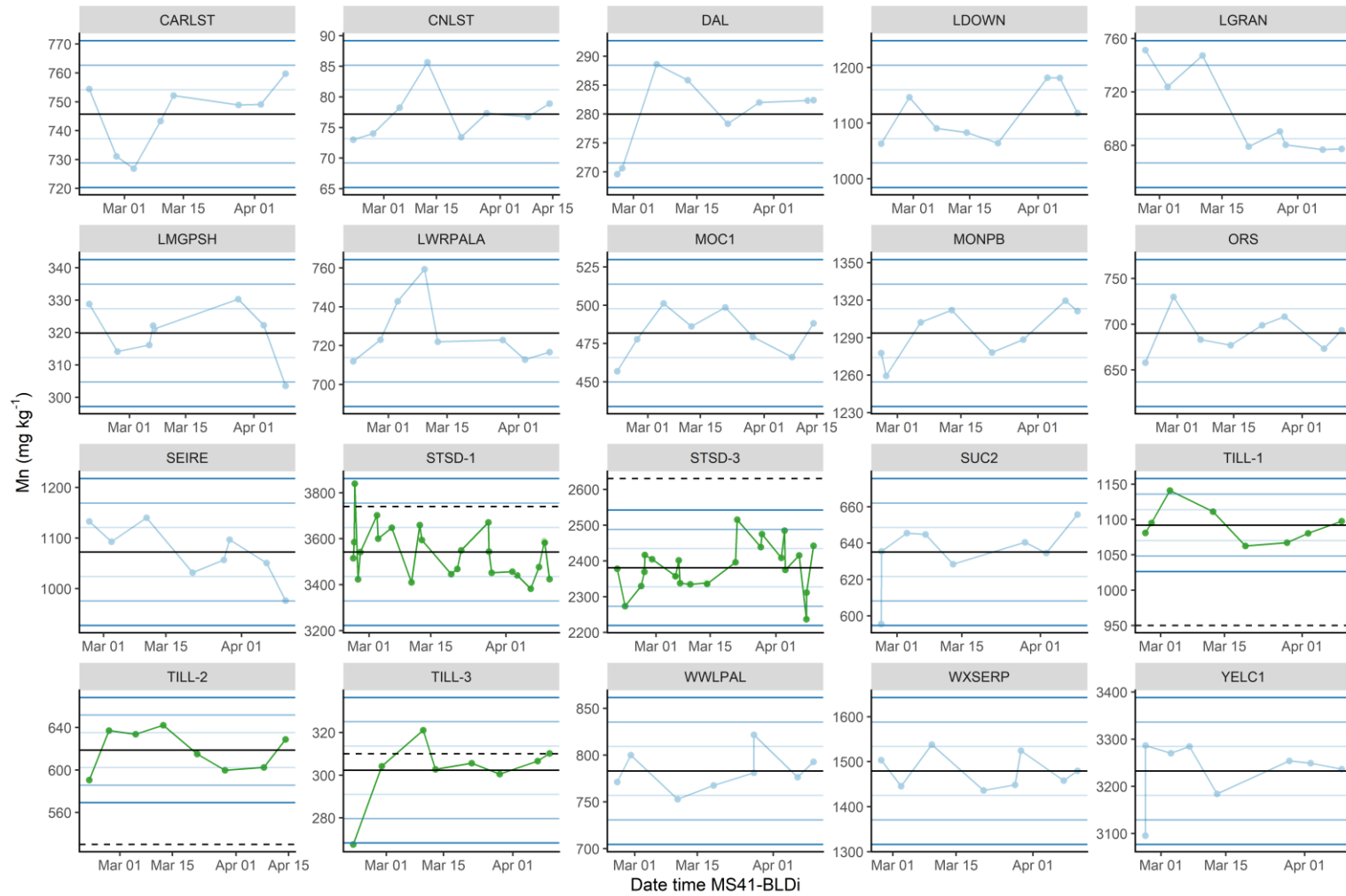
Magnesium (Mg) MS41L-BLD



Magnesium (Mg) sample data IQR: 0.0988–0.221 %

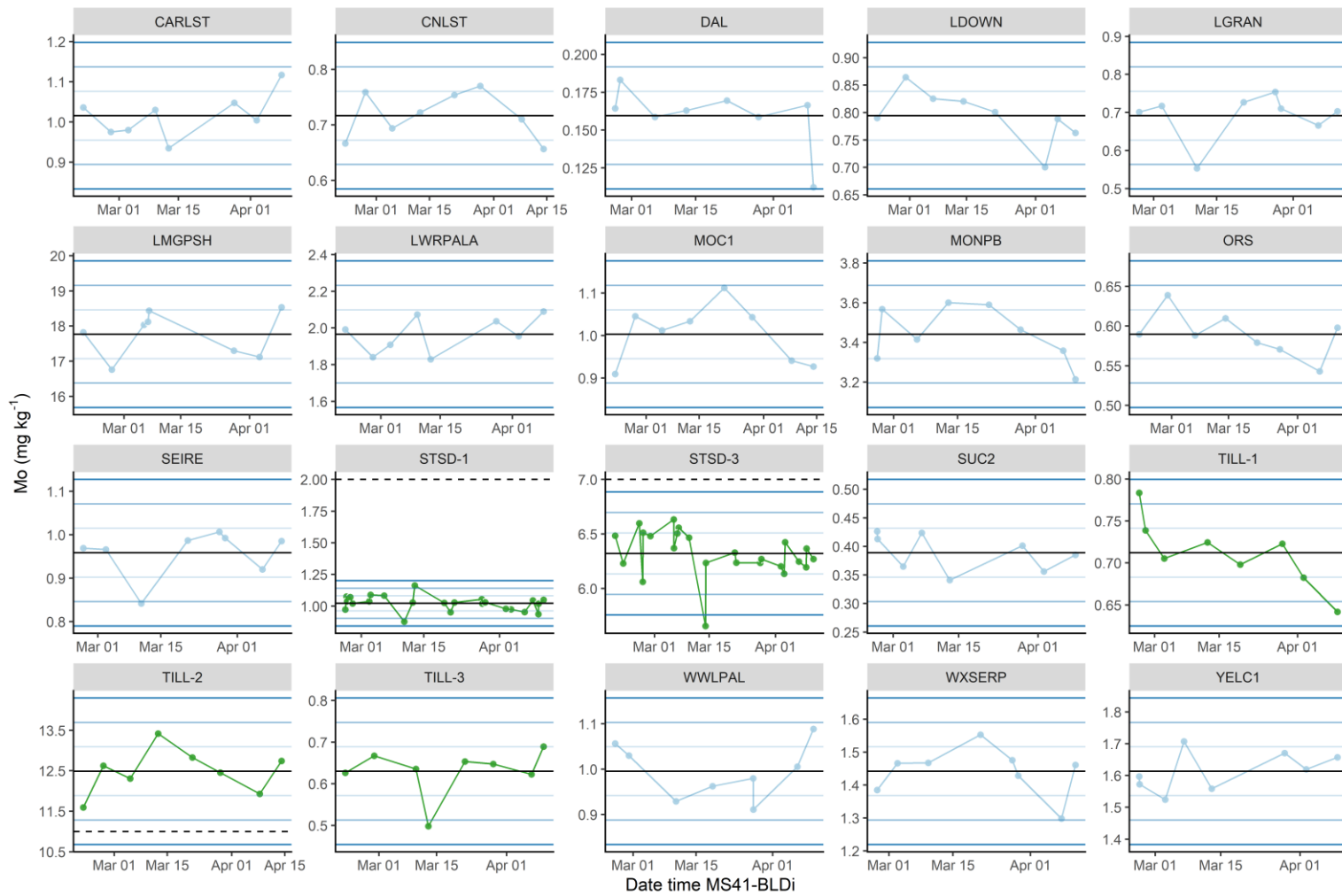


Manganese (Mn) MS41L-BLD



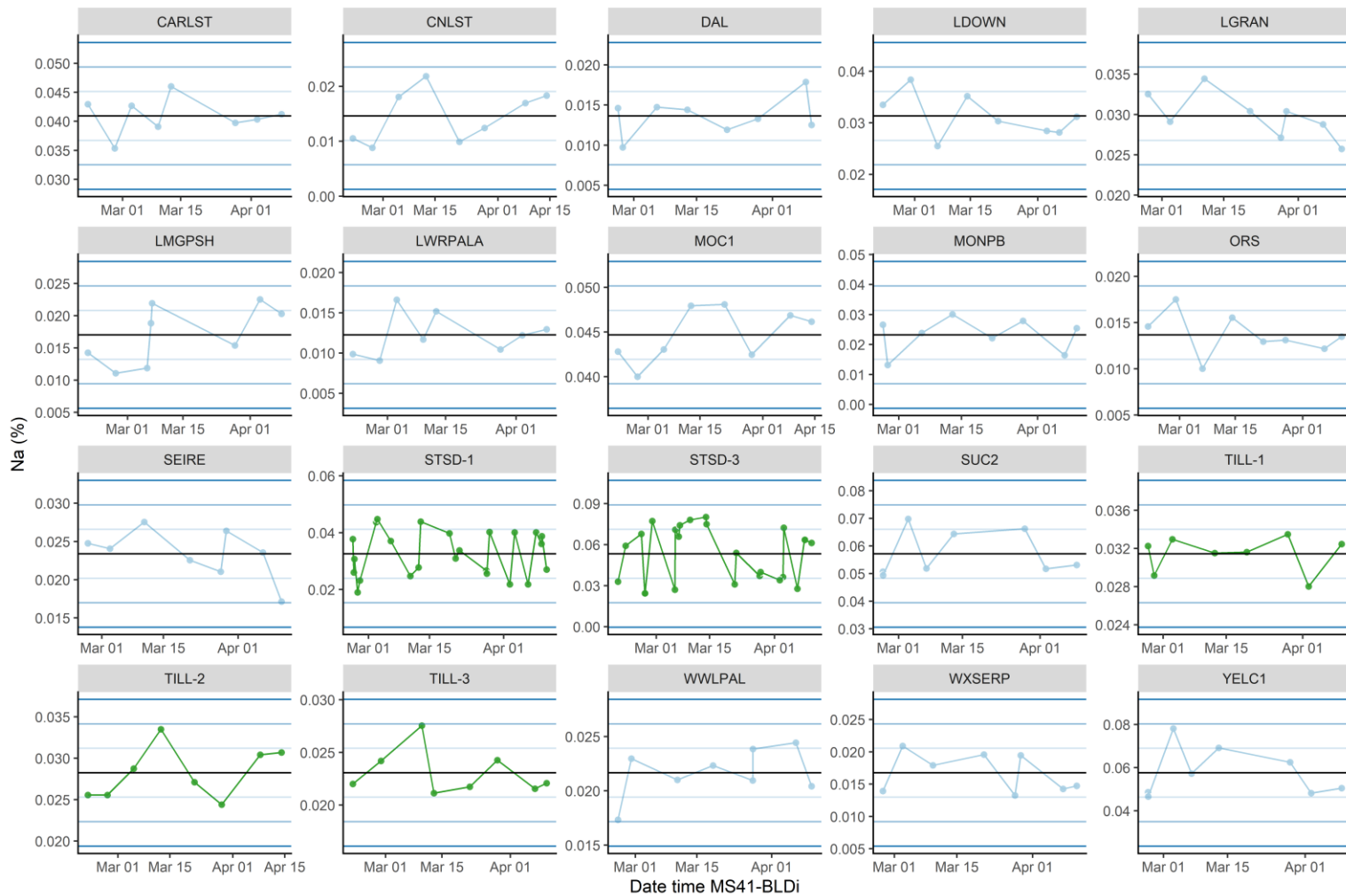
Manganese (Mn) sample data IQR: 159–902  $\text{mg kg}^{-1}$

Molybdenum (Mo) MS41L-BLD



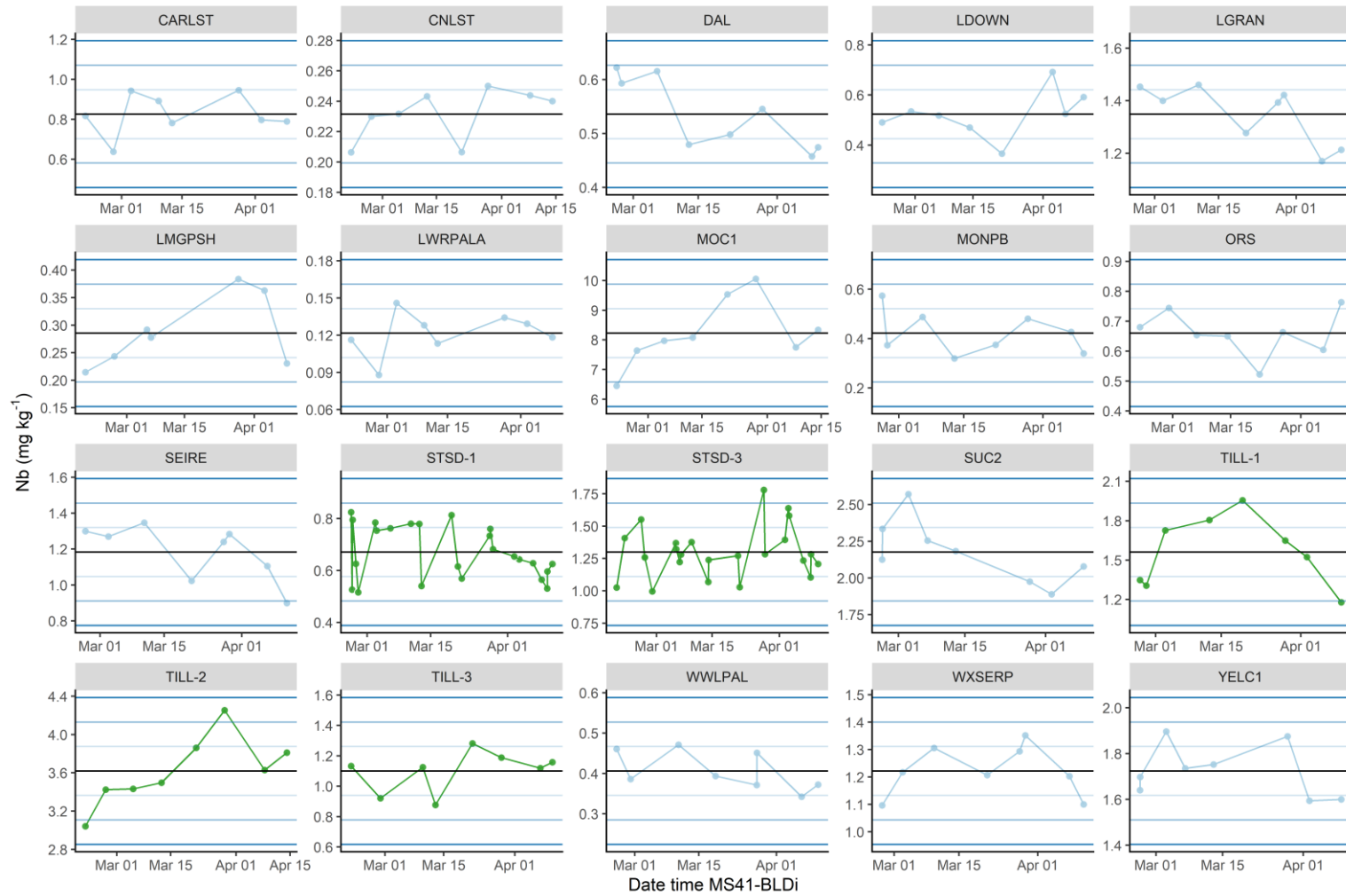
Molybdenum (Mo) sample data IQR: 0.601–1.57  $\text{mg kg}^{-1}$

Sodium (Na) MS41L-BLD



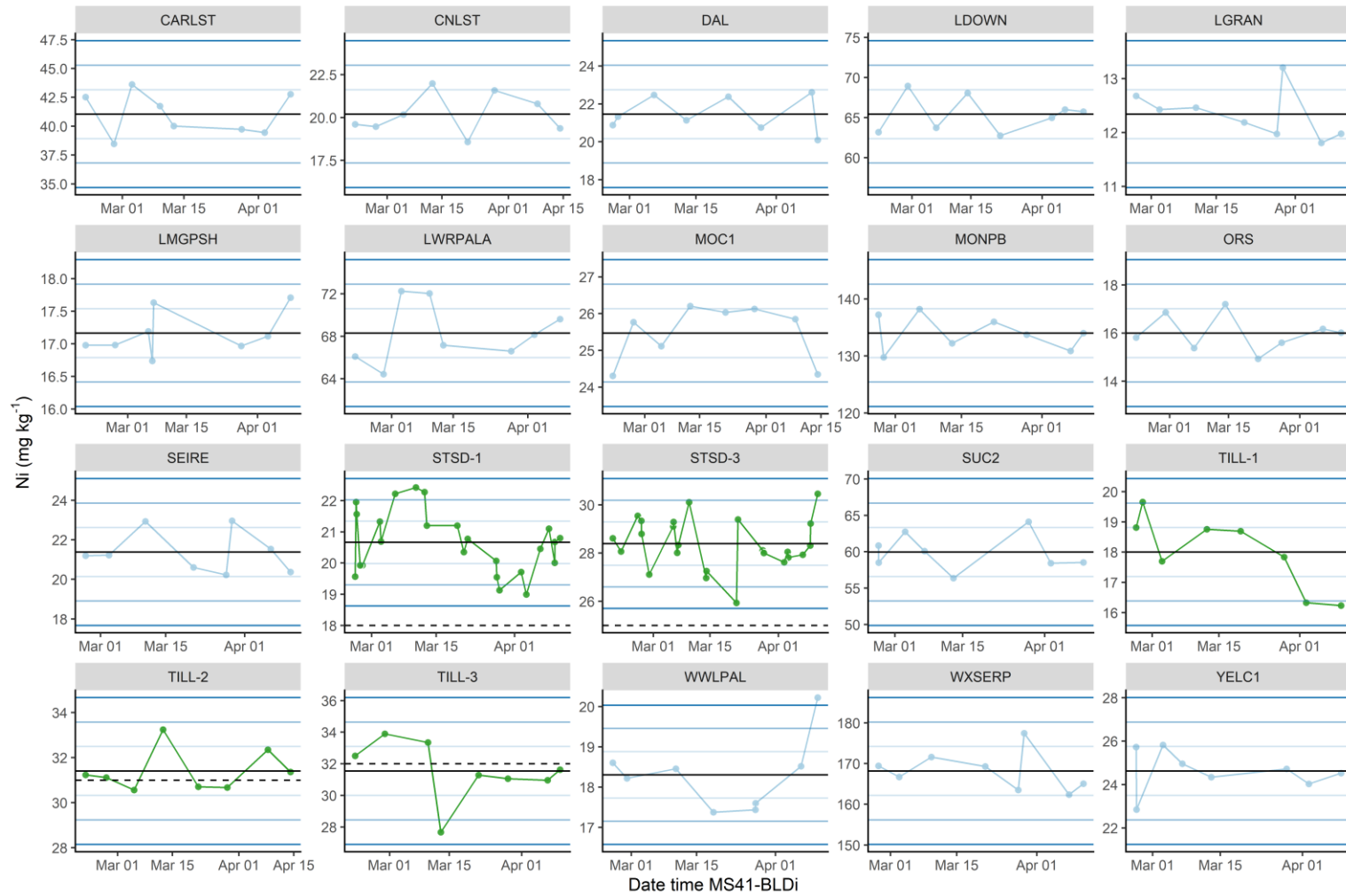
Sodium (Na) sample data IQR: 0.0156–0.0271 %

Niobium (Nb) MS41L-BLD



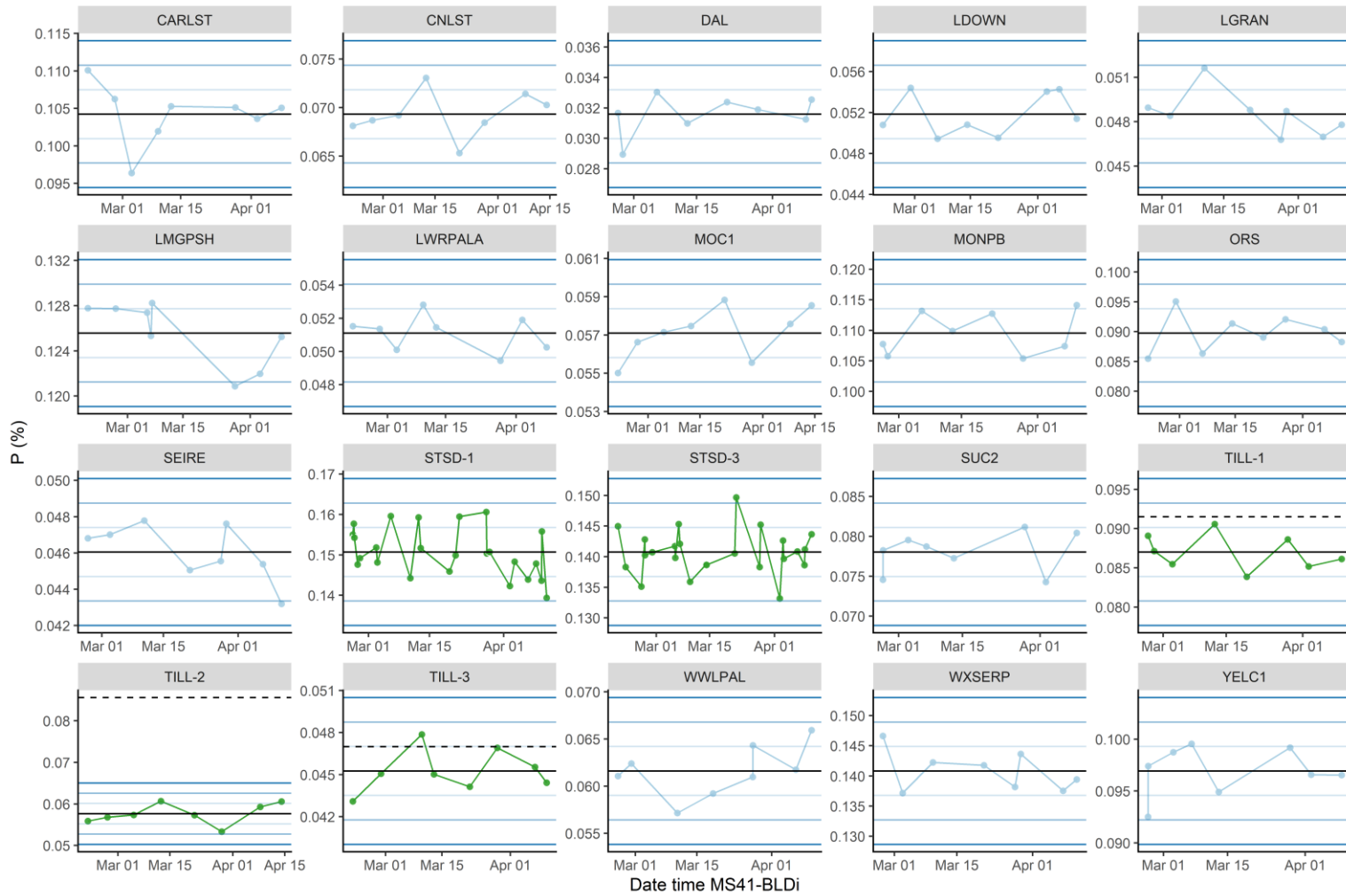
Niobium (Nb) sample data IQR: 0.172–0.384  $\text{mg kg}^{-1}$

Nickel (Ni) MS41L-BLD



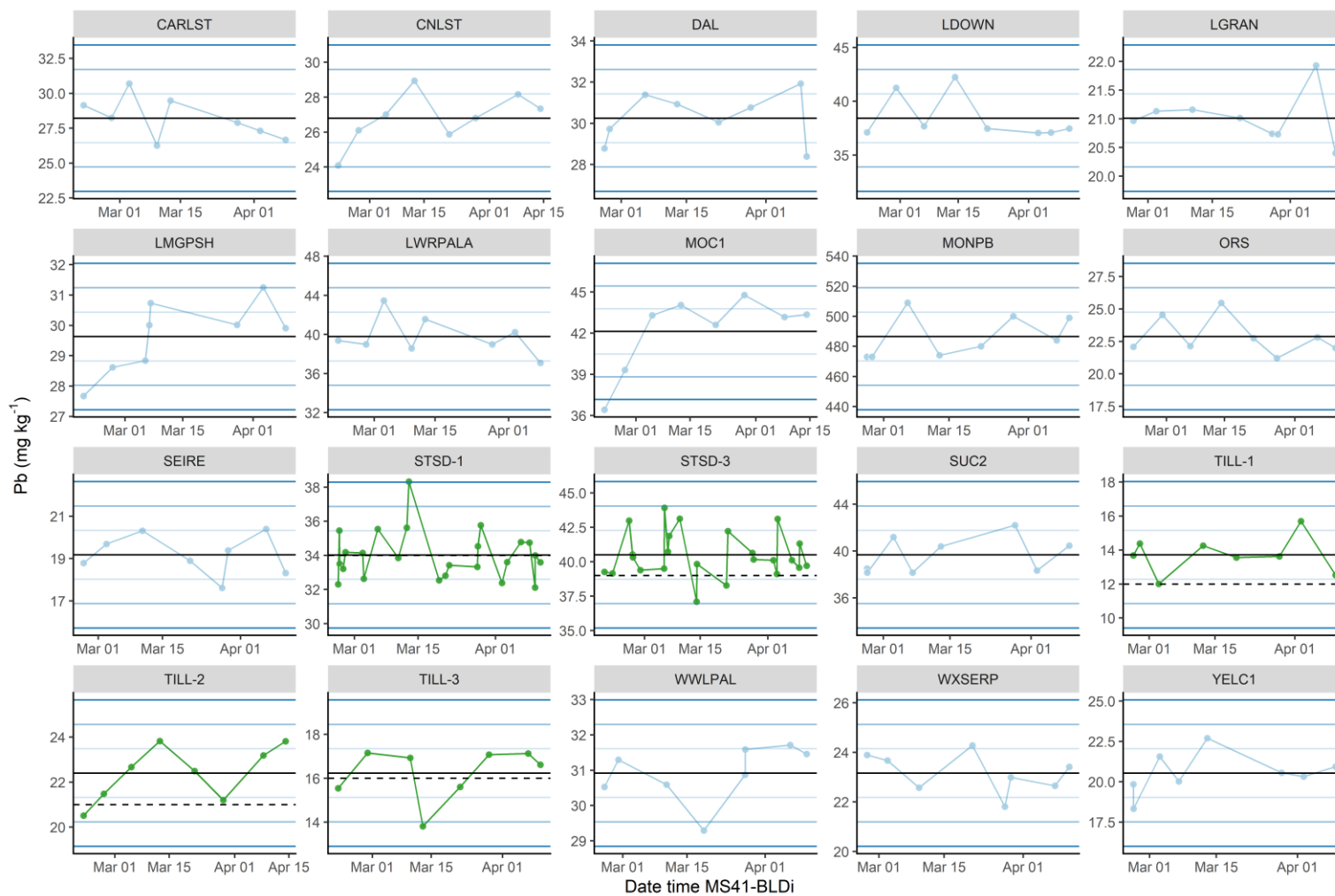
Nickel (Ni) sample data IQR: 10.3–34  $\text{mg kg}^{-1}$

Phosphorus (P) MS41L-BLD



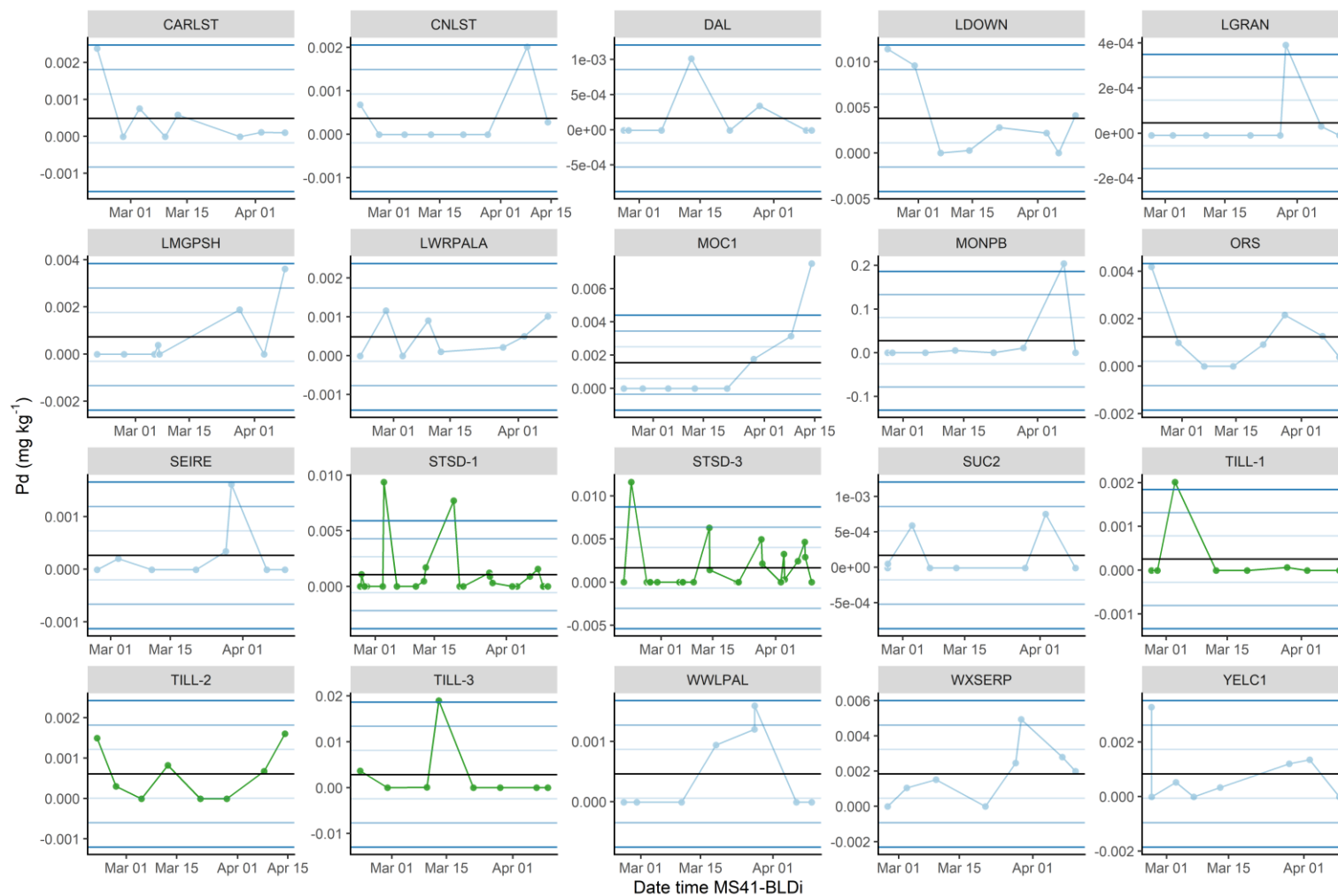
Phosphorus (P) sample data IQR: 626–1030 mg kg<sup>-1</sup>

Lead (Pb) MS41L-BLD



Lead (Pb) sample data IQR: 16.5–29  $\text{mg kg}^{-1}$

Palladium (Pd) MS41L-BLD



Palladium (Pd) sample data IQR: 0.0000181–0.0006 mg kg<sup>-1</sup>

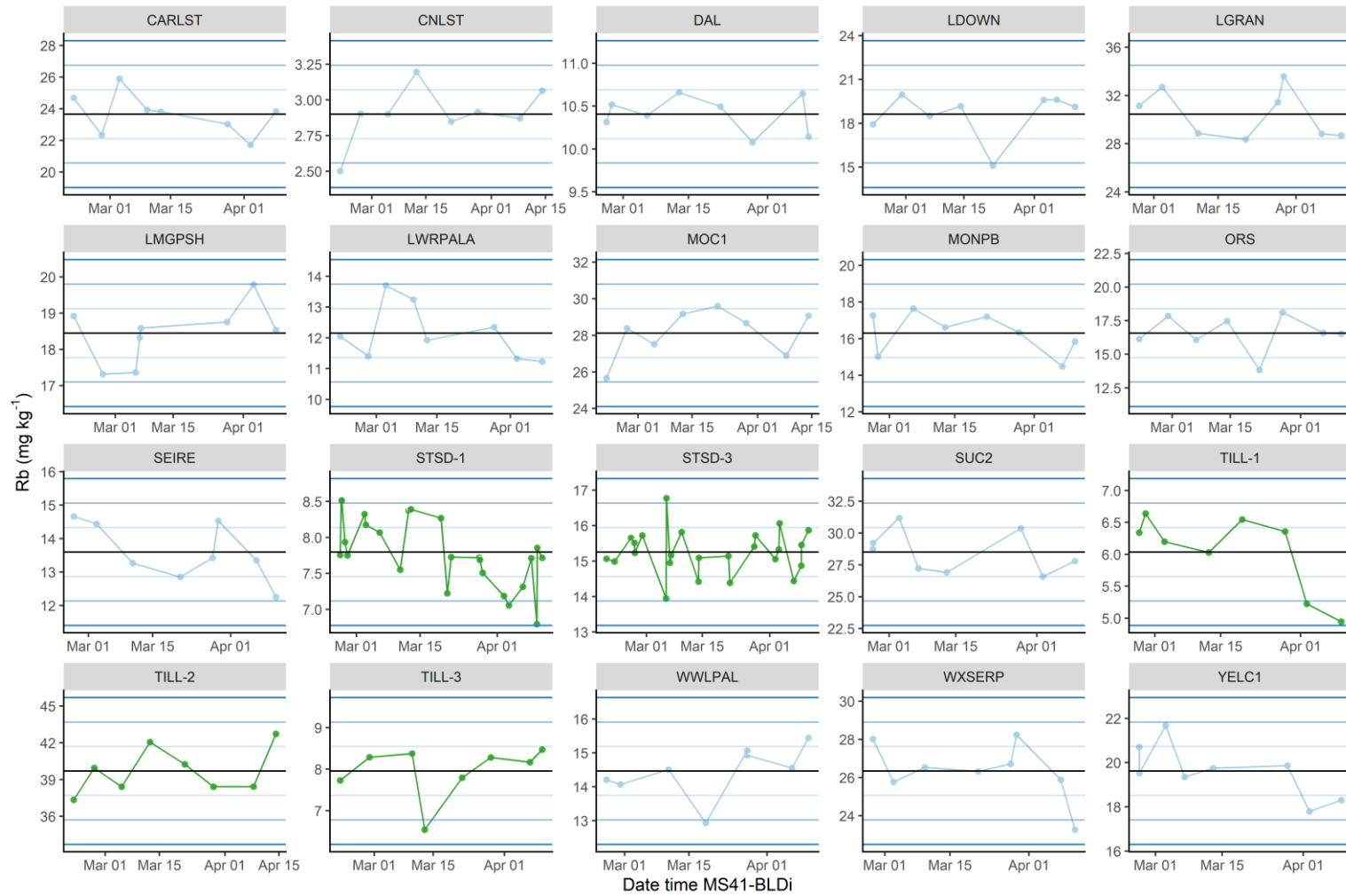


Platinum (Pt) MS41L-BLD



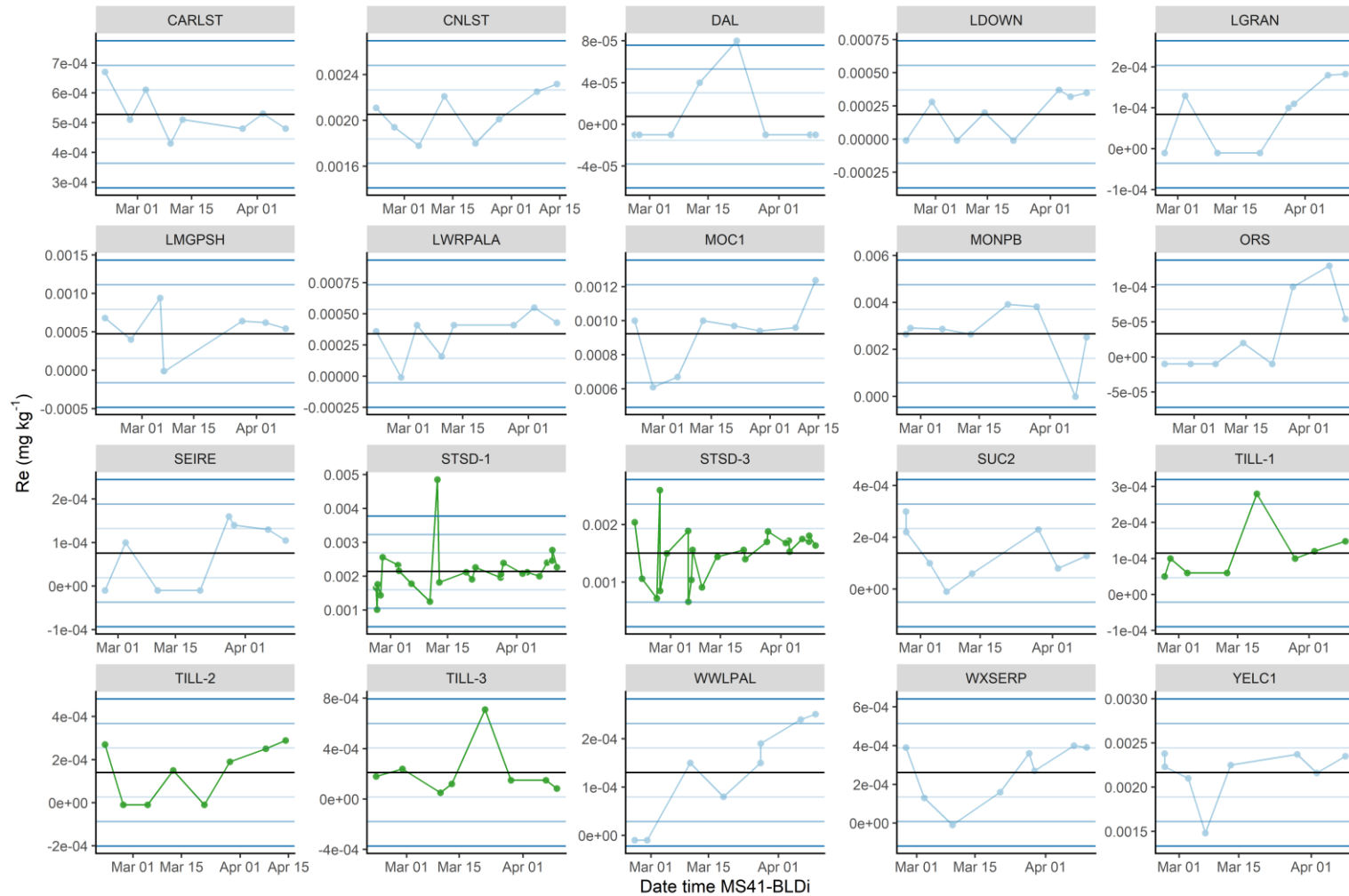
Platinum (Pt) sample data IQR: 0.00006–0.00127 mg kg<sup>-1</sup>

Rubidium (Rb) MS41L-BLD



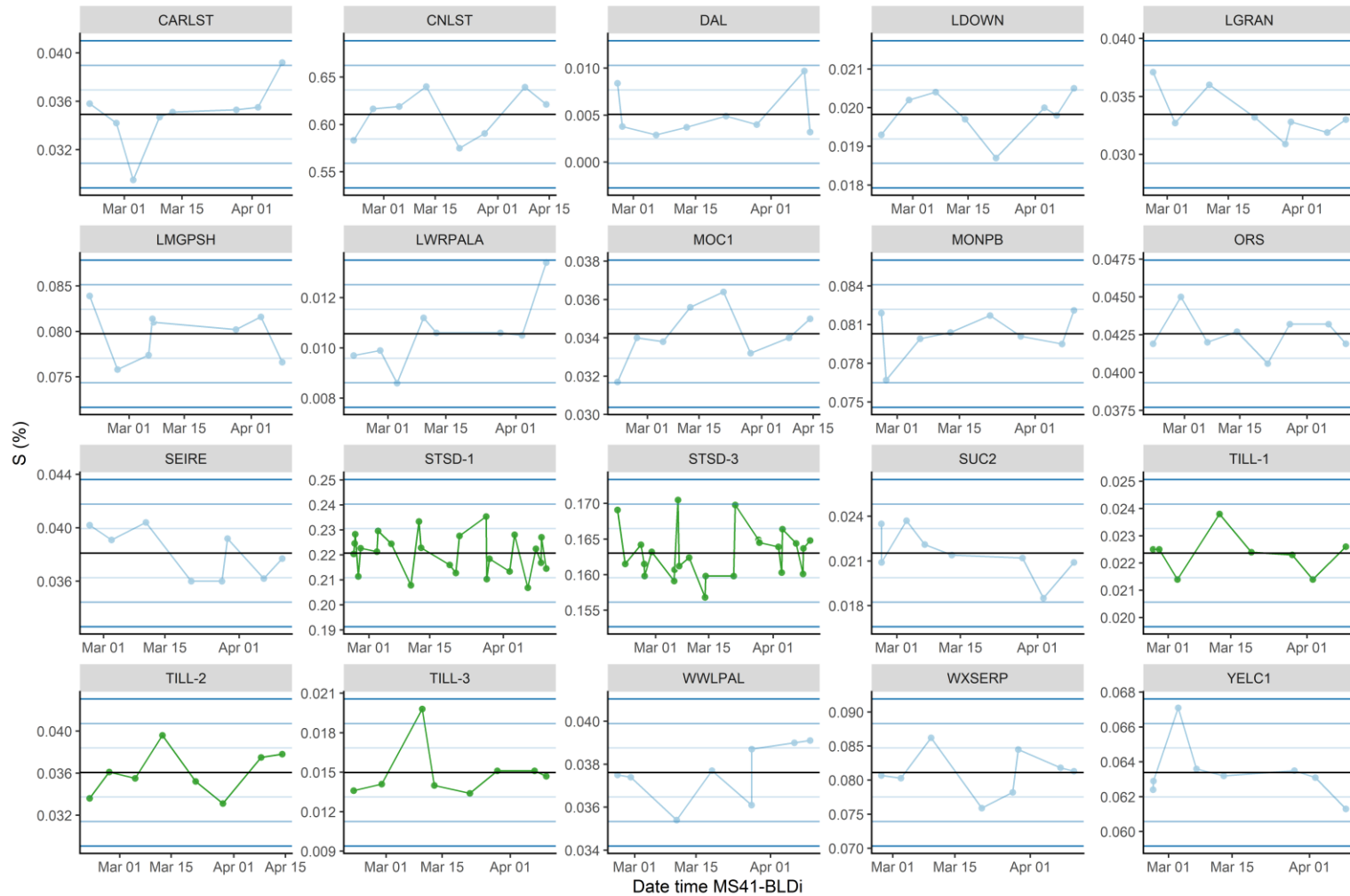
Rubidium (Rb) sample data IQR: 4.53–16.3 mg kg<sup>-1</sup>

Rhenium (Re) MS41L-BLD



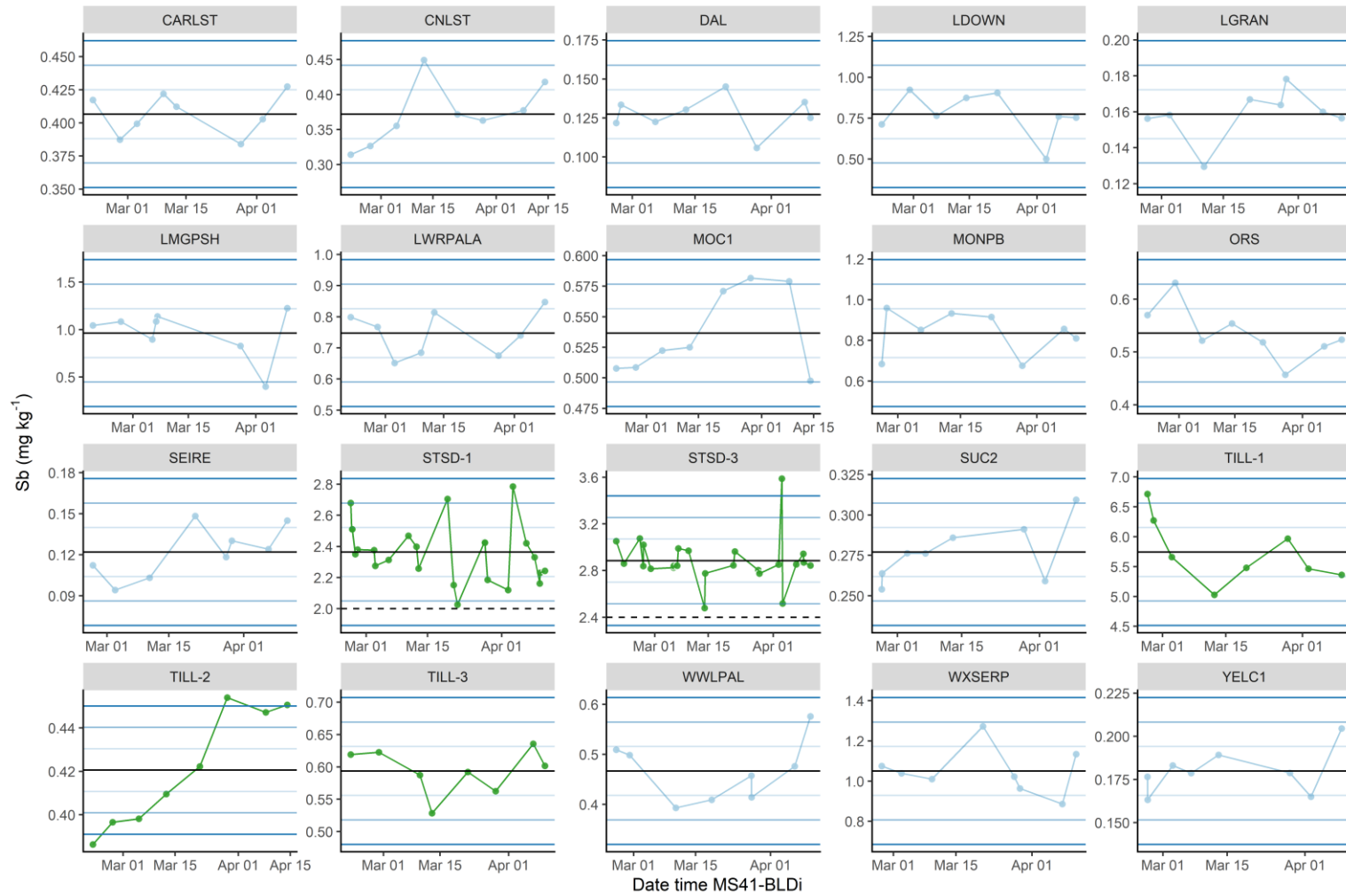
Rhenium (Re) sample data IQR: 0.00012–0.00077  $\text{mg kg}^{-1}$

Sulphur (S) MS41L-BLD



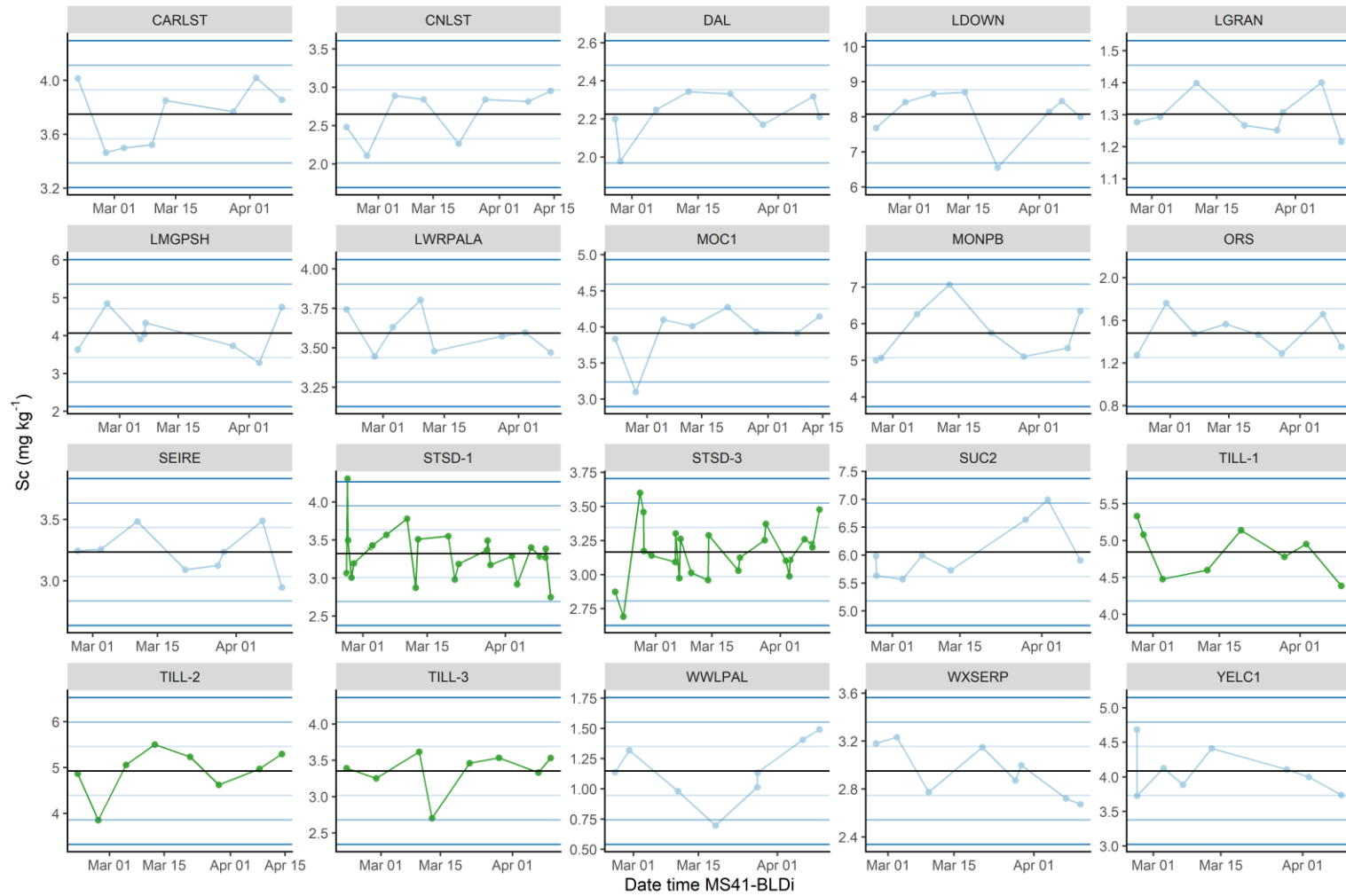
Sulphur (S) sample data IQR: 0.0535–0.181 %

Antimony (Sb) MS41L-BLD



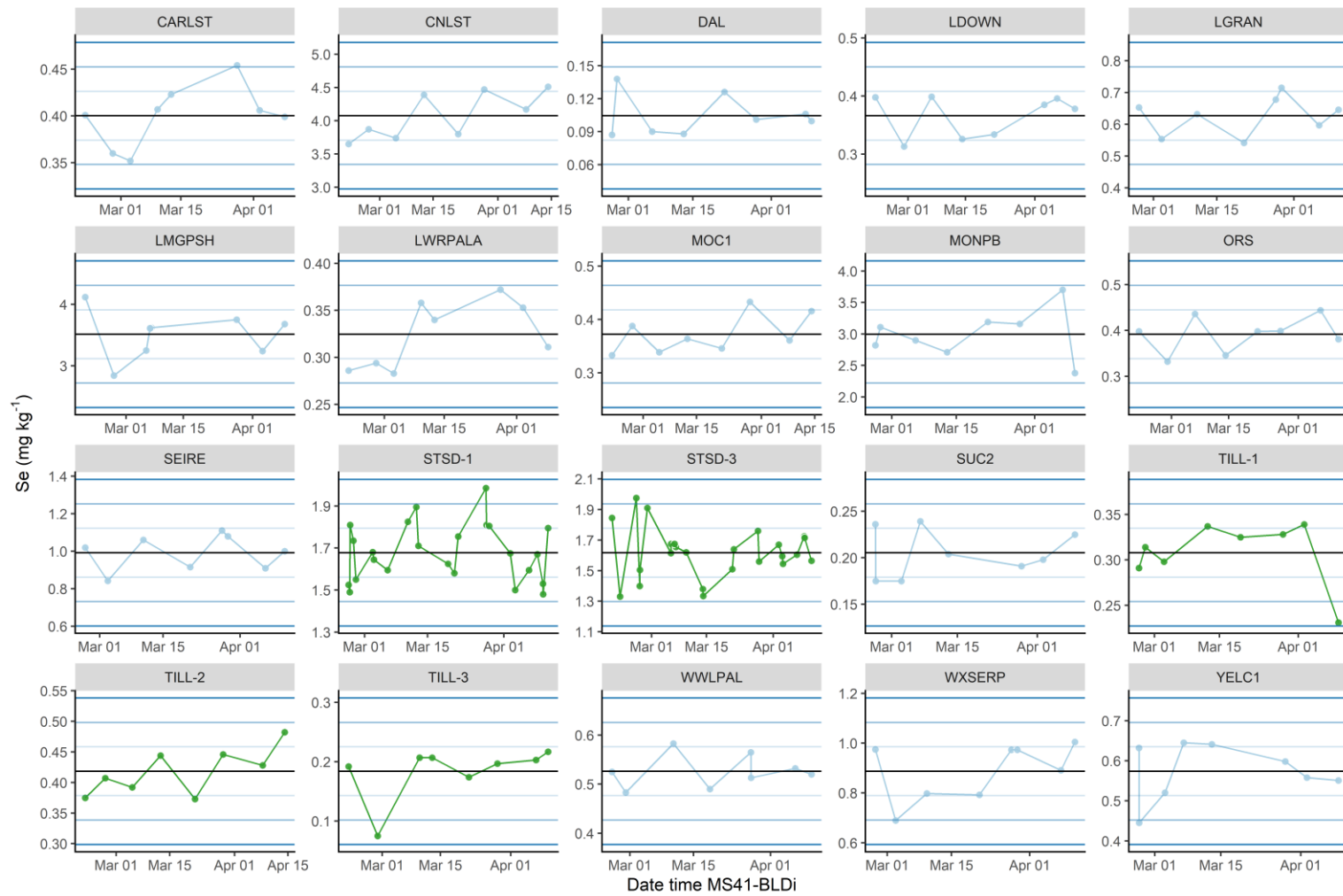
Antimony (Sb) sample data IQR: 0.267–0.589 mg kg<sup>-1</sup>

Scandium (Sc) MS41L-BLD



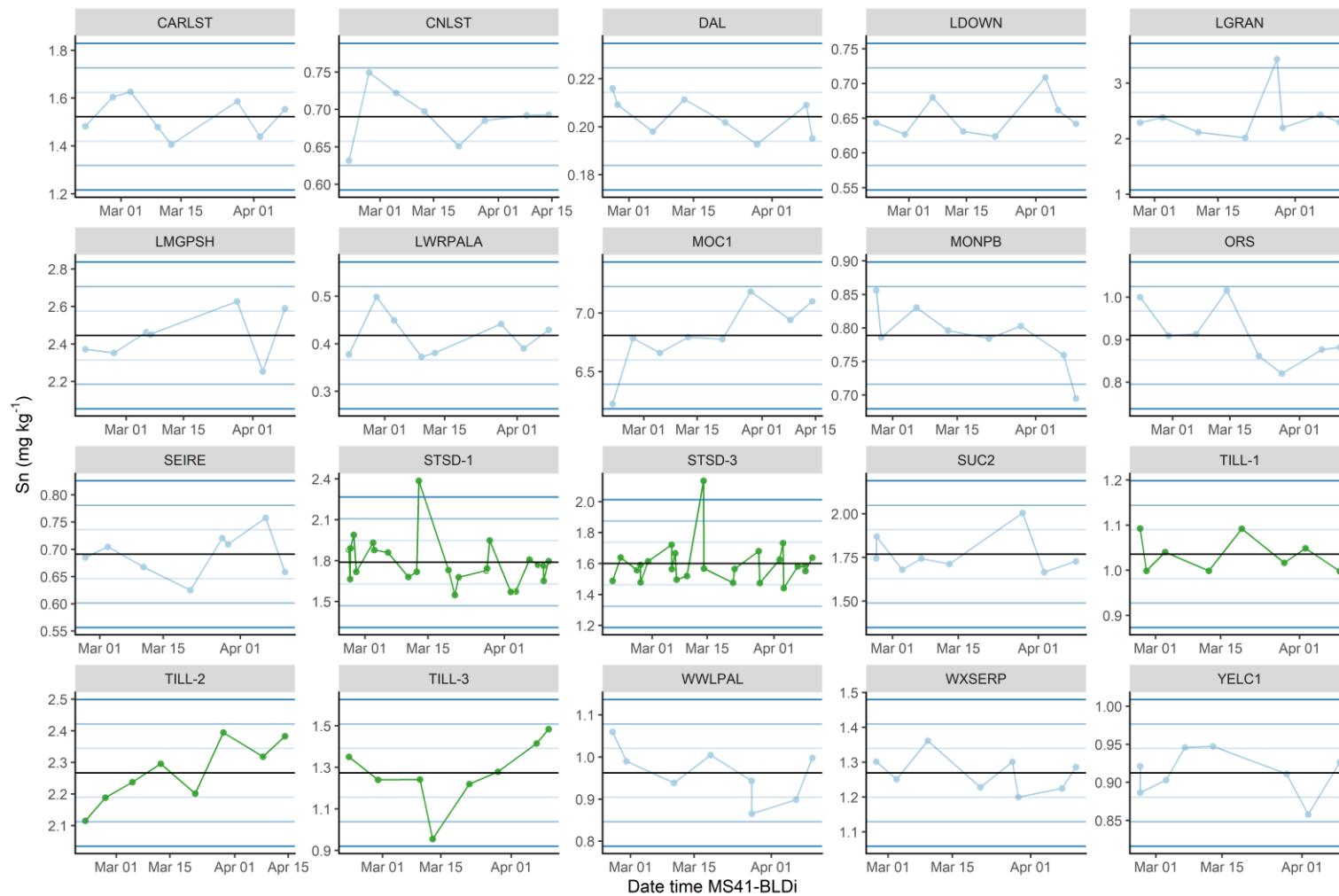
Scandium (Sc) sample data IQR: 0.958–3.16  $\text{mg kg}^{-1}$

Selenium (Se) MS41L-BLD



Selenium (Se) sample data IQR: 0.56–1.36  $\text{mg kg}^{-1}$

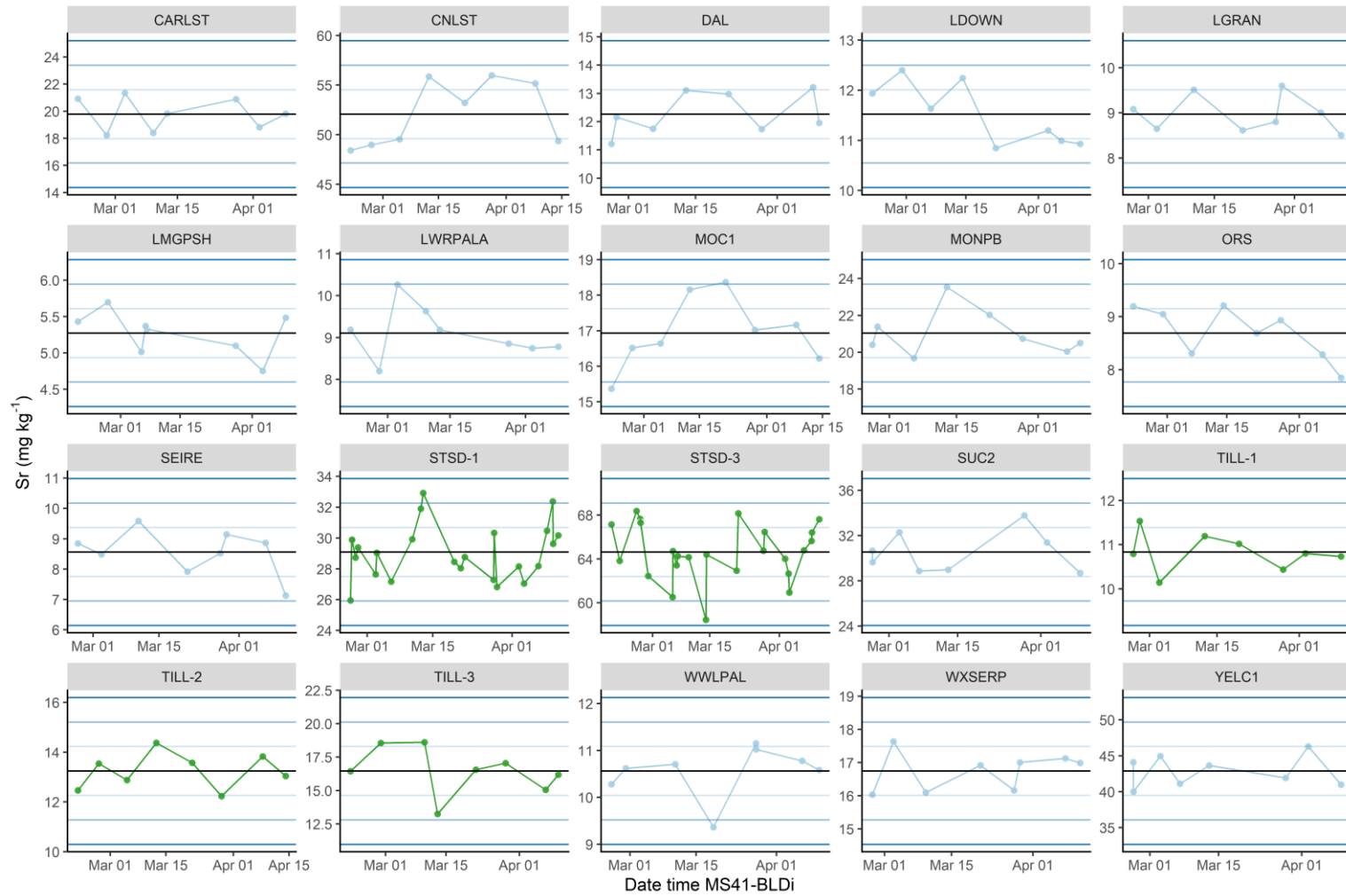
Tin (Sn) MS41L-BLD



Tin (Sn) sample data IQR: 0.525–0.876 mg kg<sup>-1</sup>

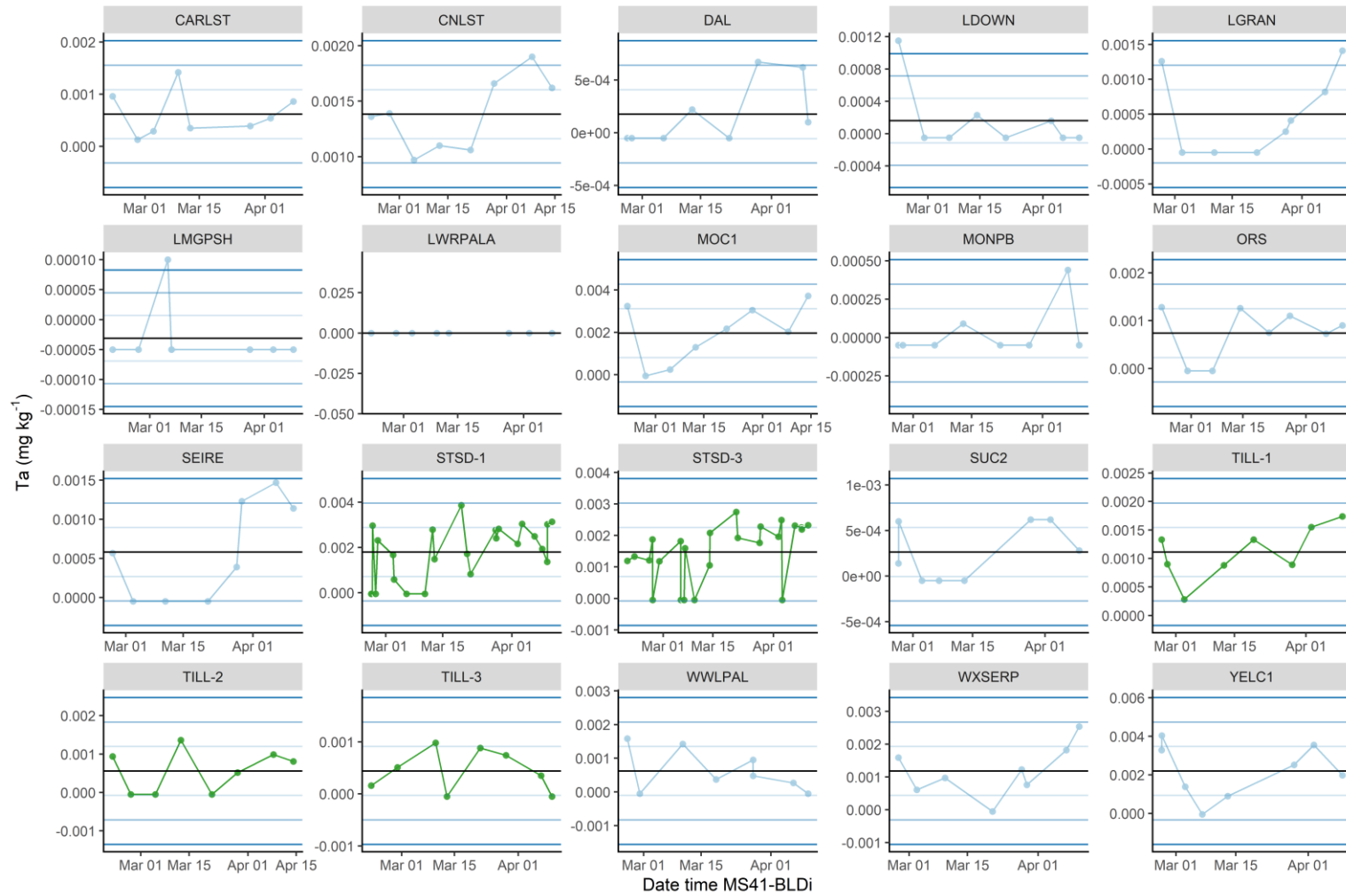


Strontium (Sr) MS41L-BLD



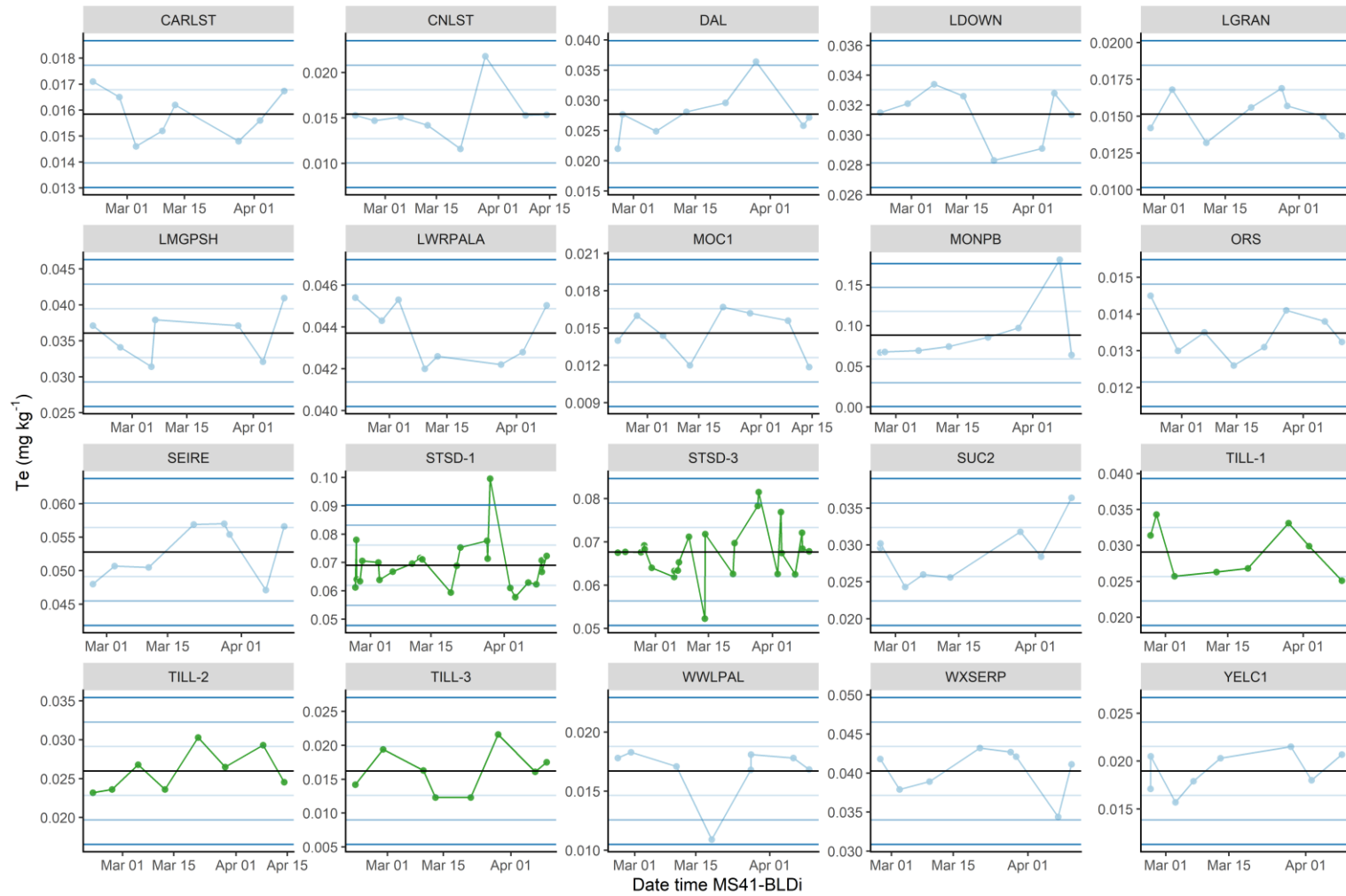
Strontium (Sr) sample data IQR: 15–31.1 mg kg<sup>-1</sup>

Tantalum (Ta) MS41L-BLD



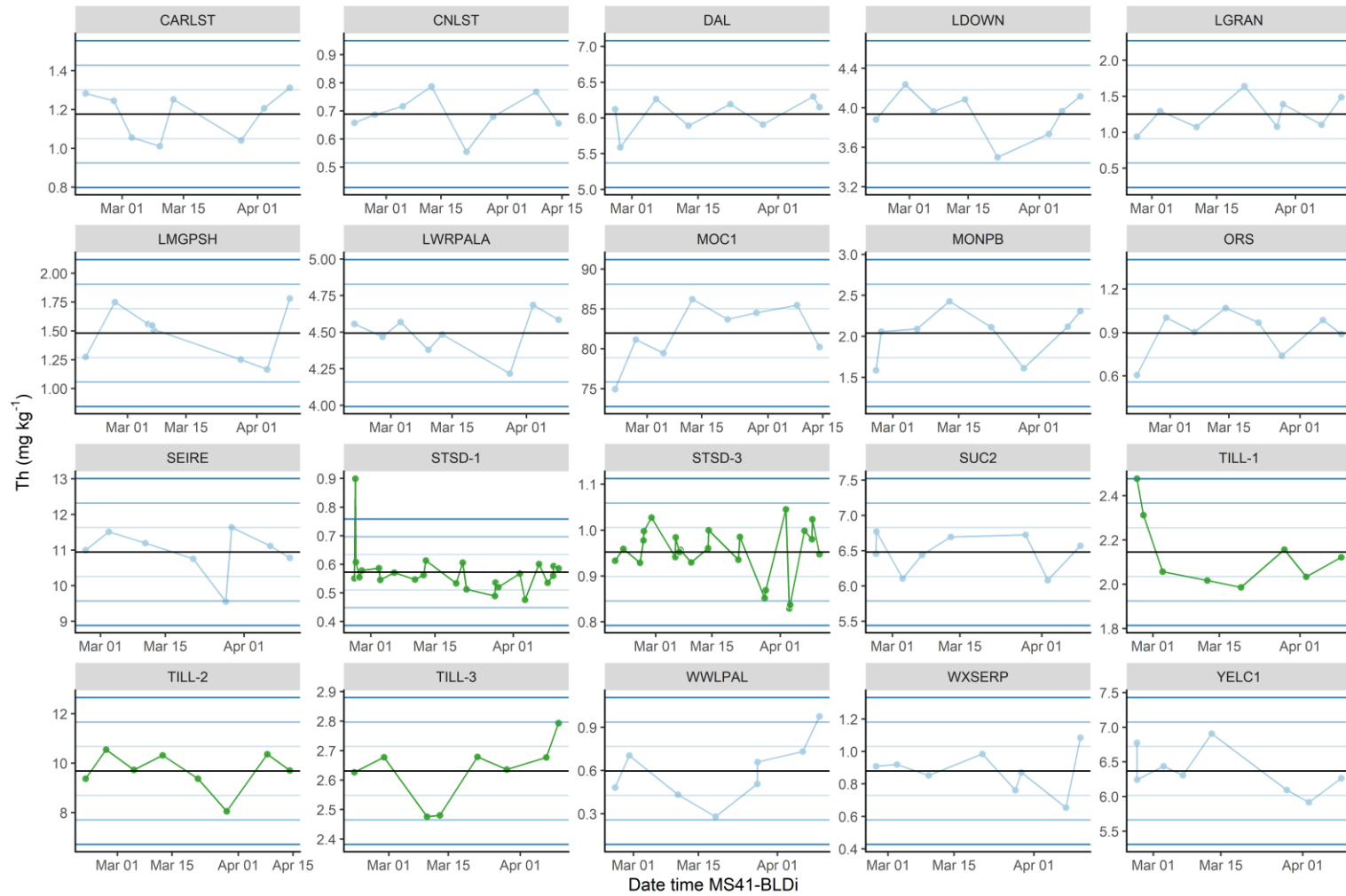
Tantalum (Ta) sample data IQR: 0.00007-0.00083 mg kg<sup>-1</sup>

Tellurium (Te) MS41L-BLD



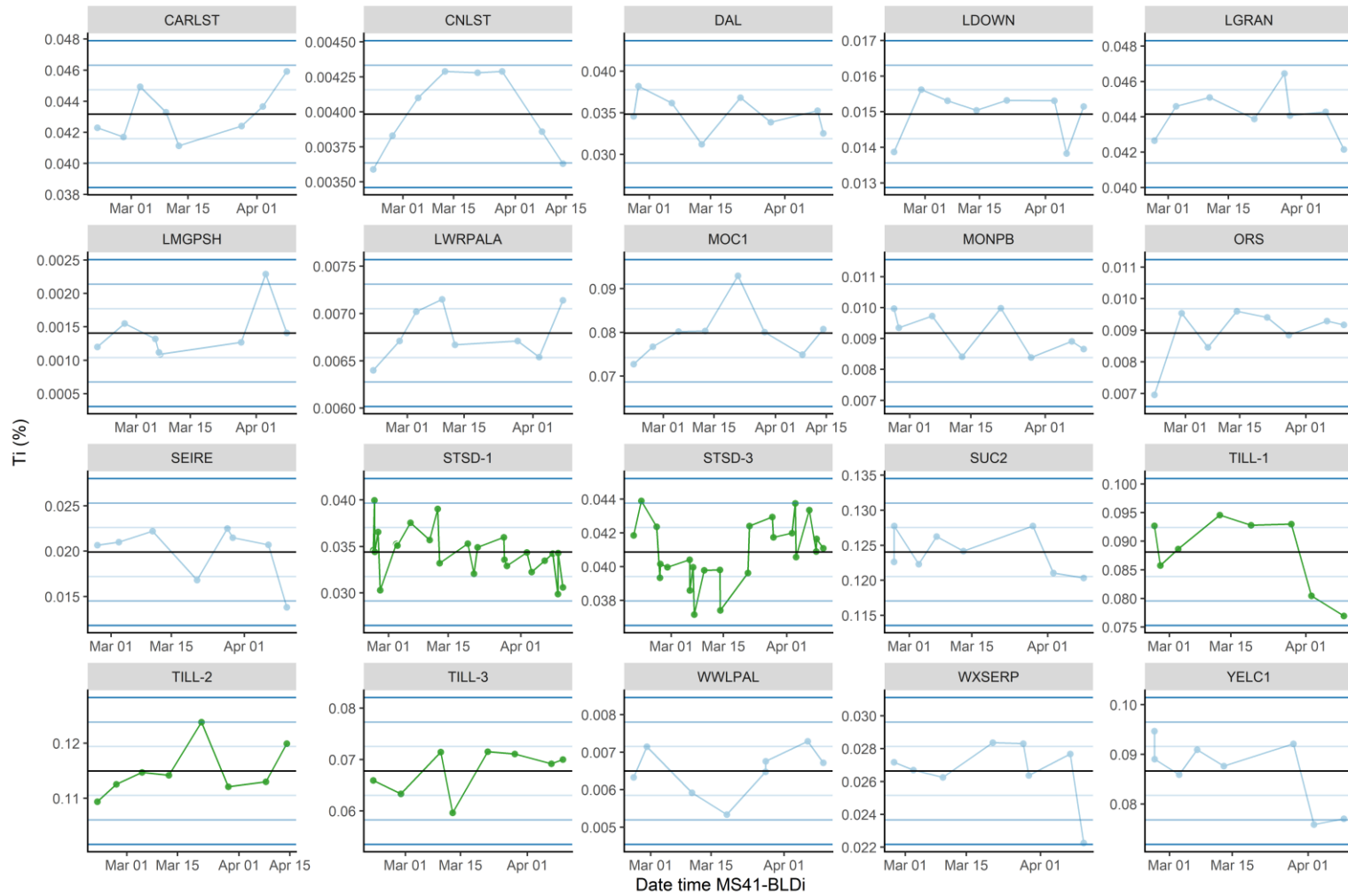
Tellurium (Te) sample data IQR: 0.0094-0.023  $\text{mg kg}^{-1}$

Thorium (Th) MS41L-BLD



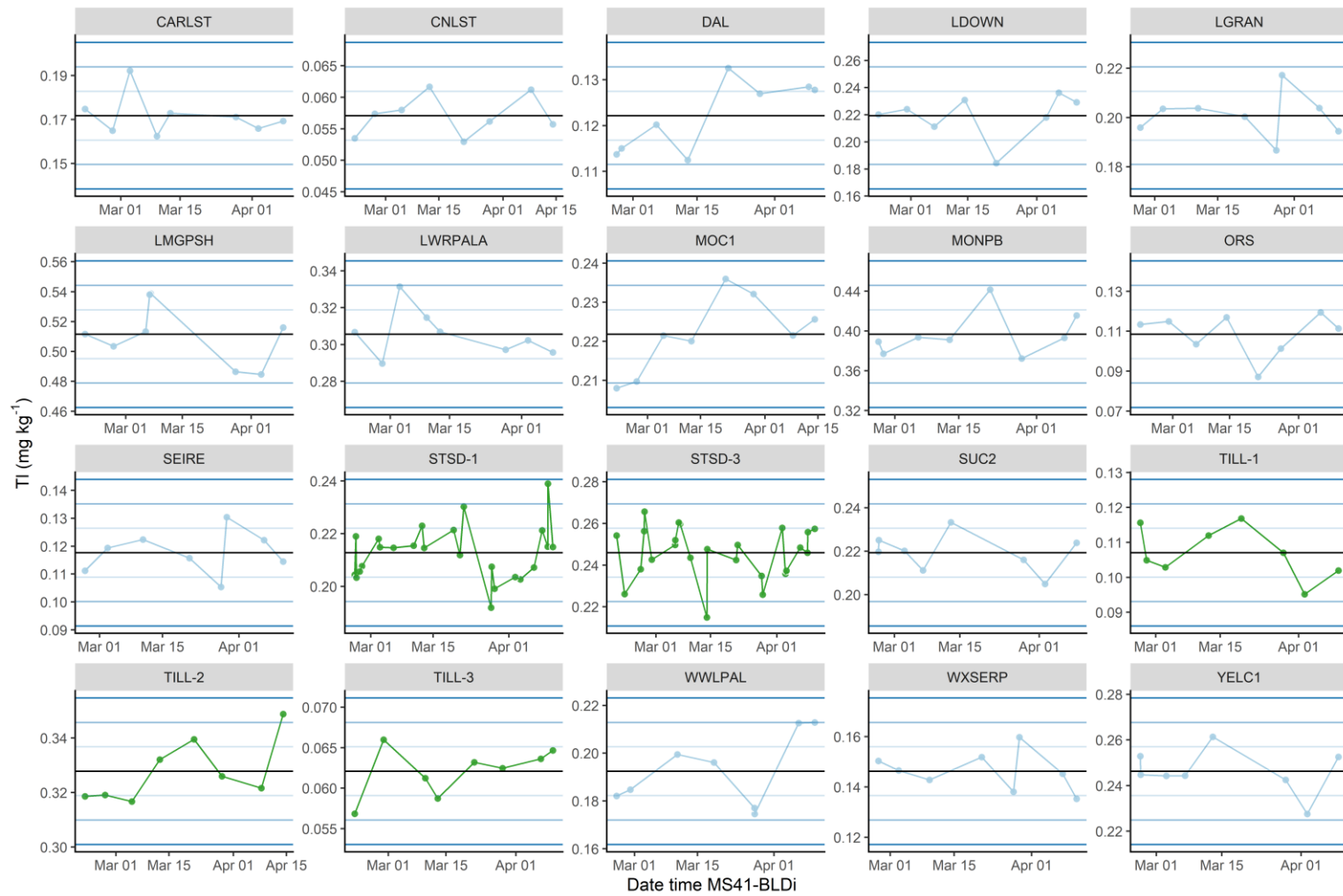
Thorium (Th) sample data IQR: 0.409–1.43 mg kg<sup>-1</sup>

Titanium (Ti) MS41L-BLD



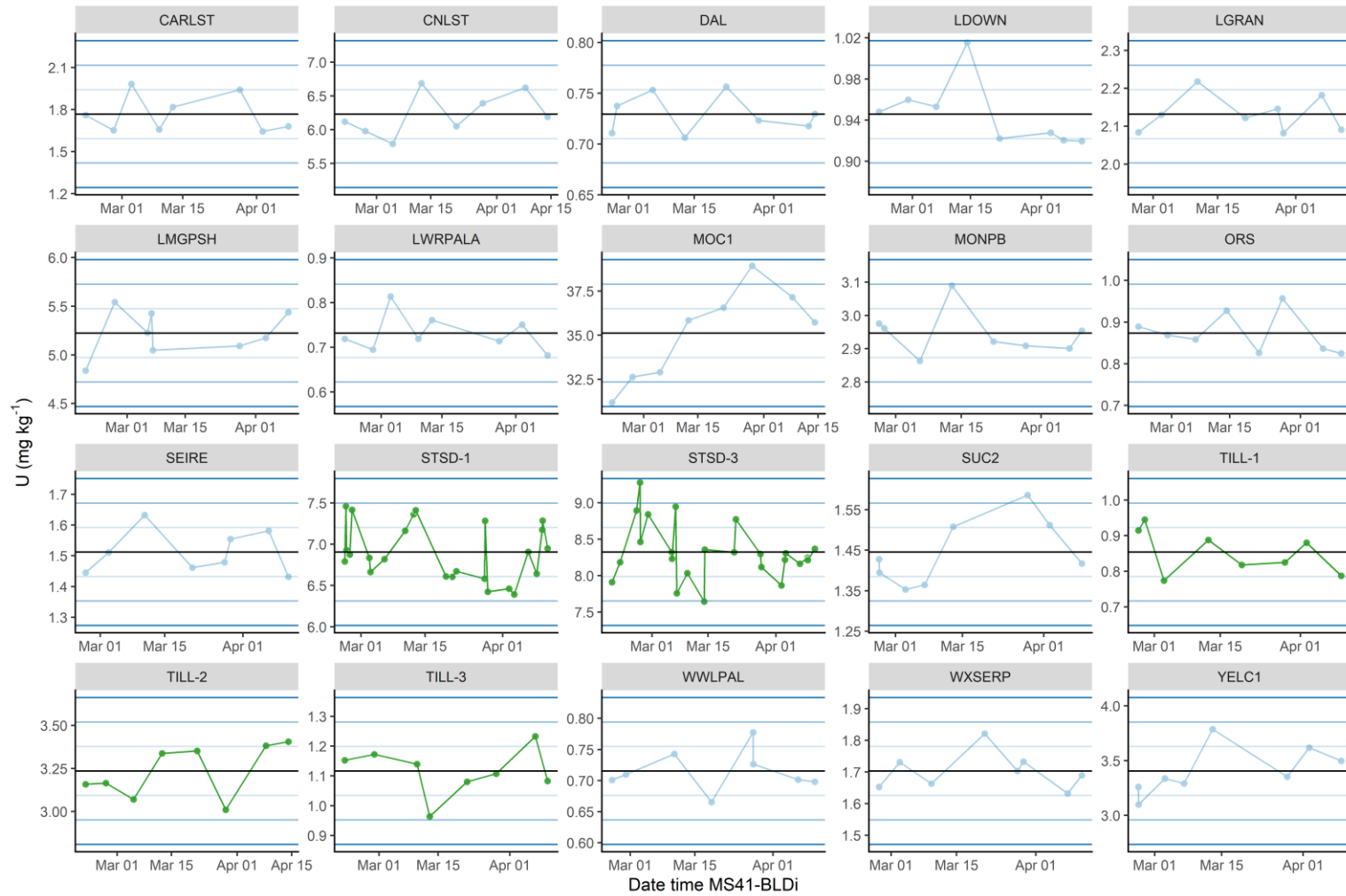
Titanium (Ti) sample data IQR: 0.00281-0.00607 %

Thallium (TI) MS41L-BLD



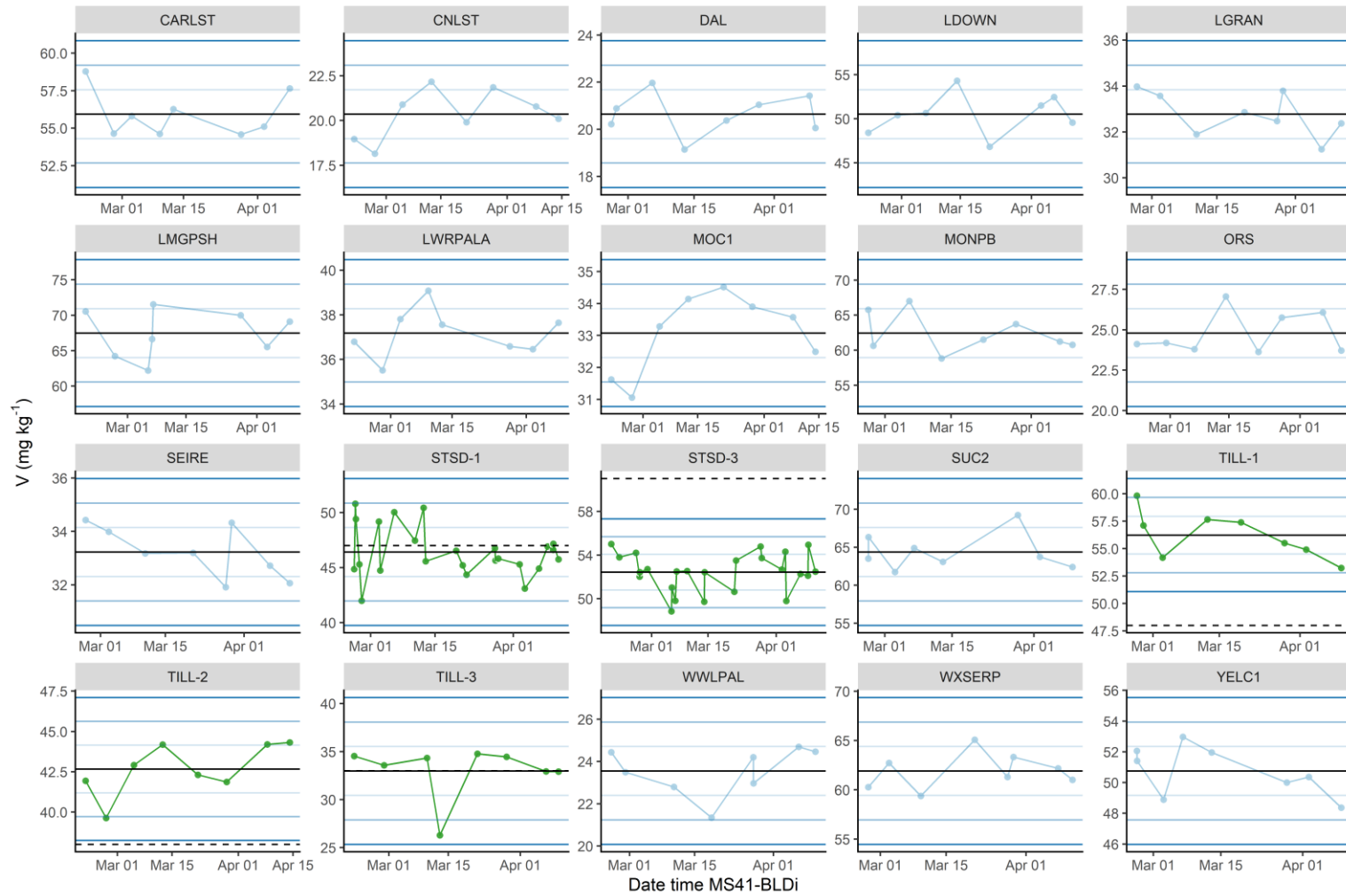
Thallium (TI) sample data IQR: 0.0981–0.251  $\text{mg kg}^{-1}$

Uranium (U) MS41L-BLD



Uranium (U) sample data IQR: 0.807–1.51  $\text{mg kg}^{-1}$

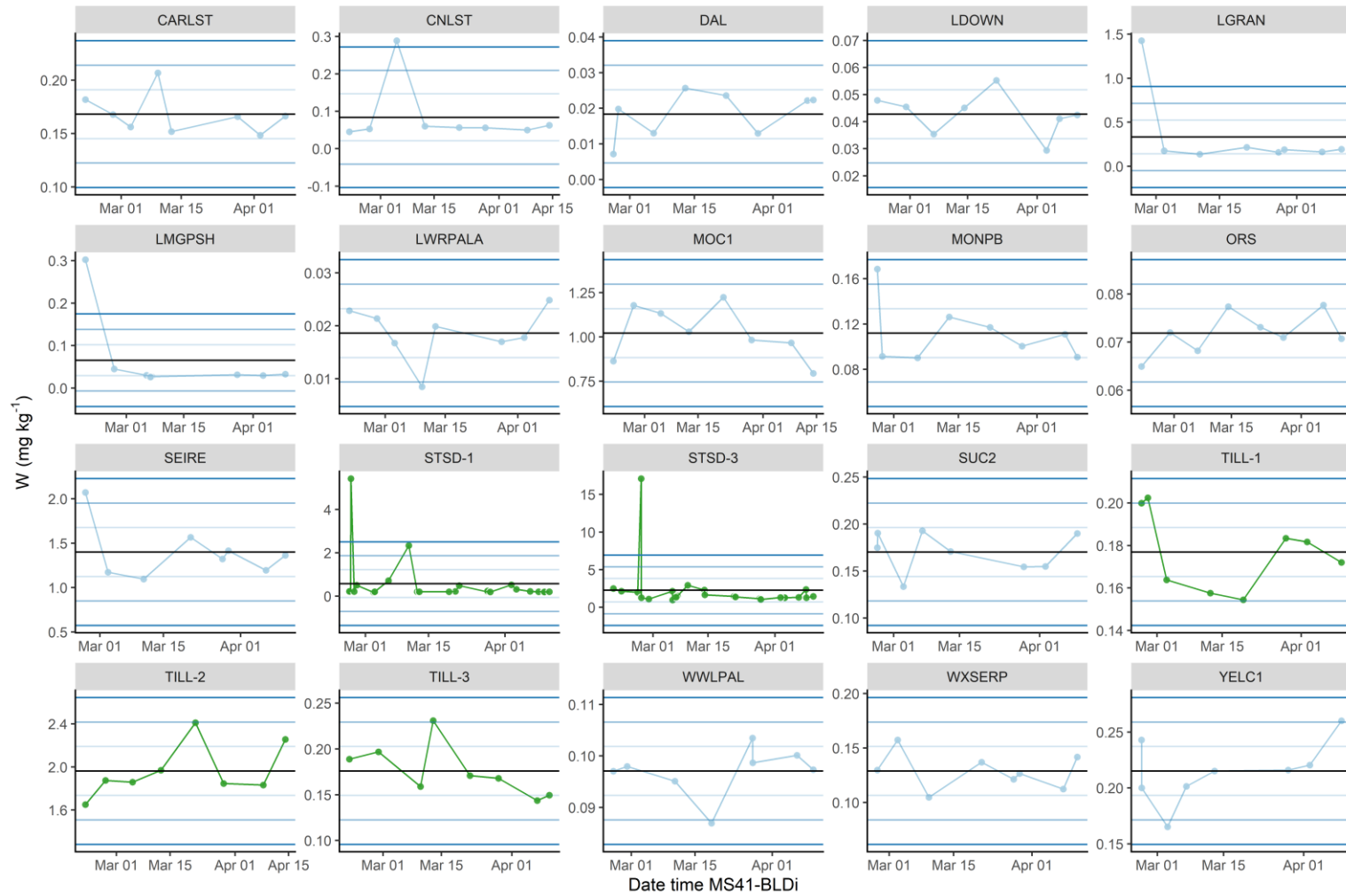
Vanadium (V) MS41L-BLD



Vanadium (V) sample data IQR: 15.8–37.2 mg kg<sup>-1</sup>

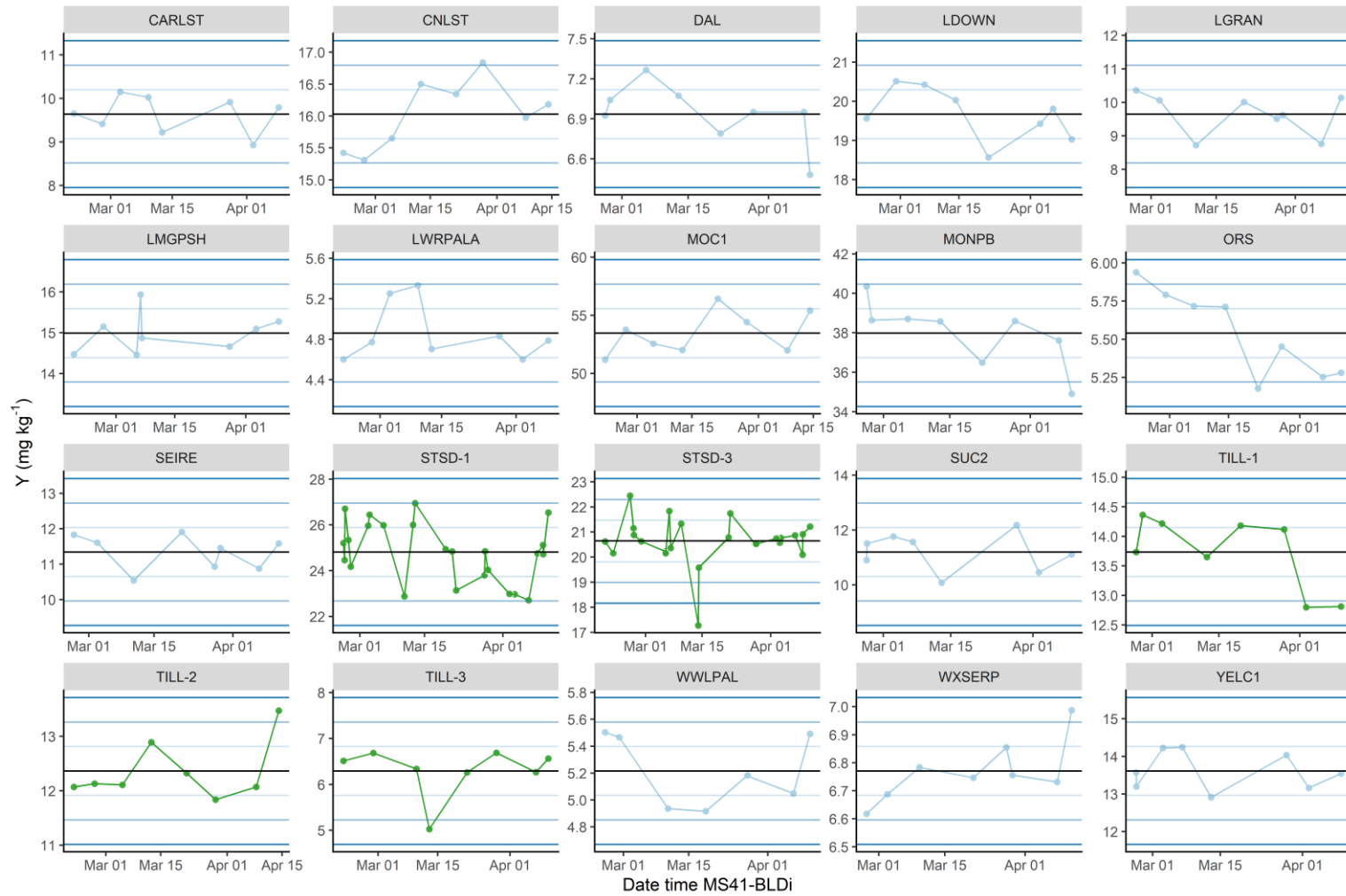


Tungsten (W) MS41L-BLD



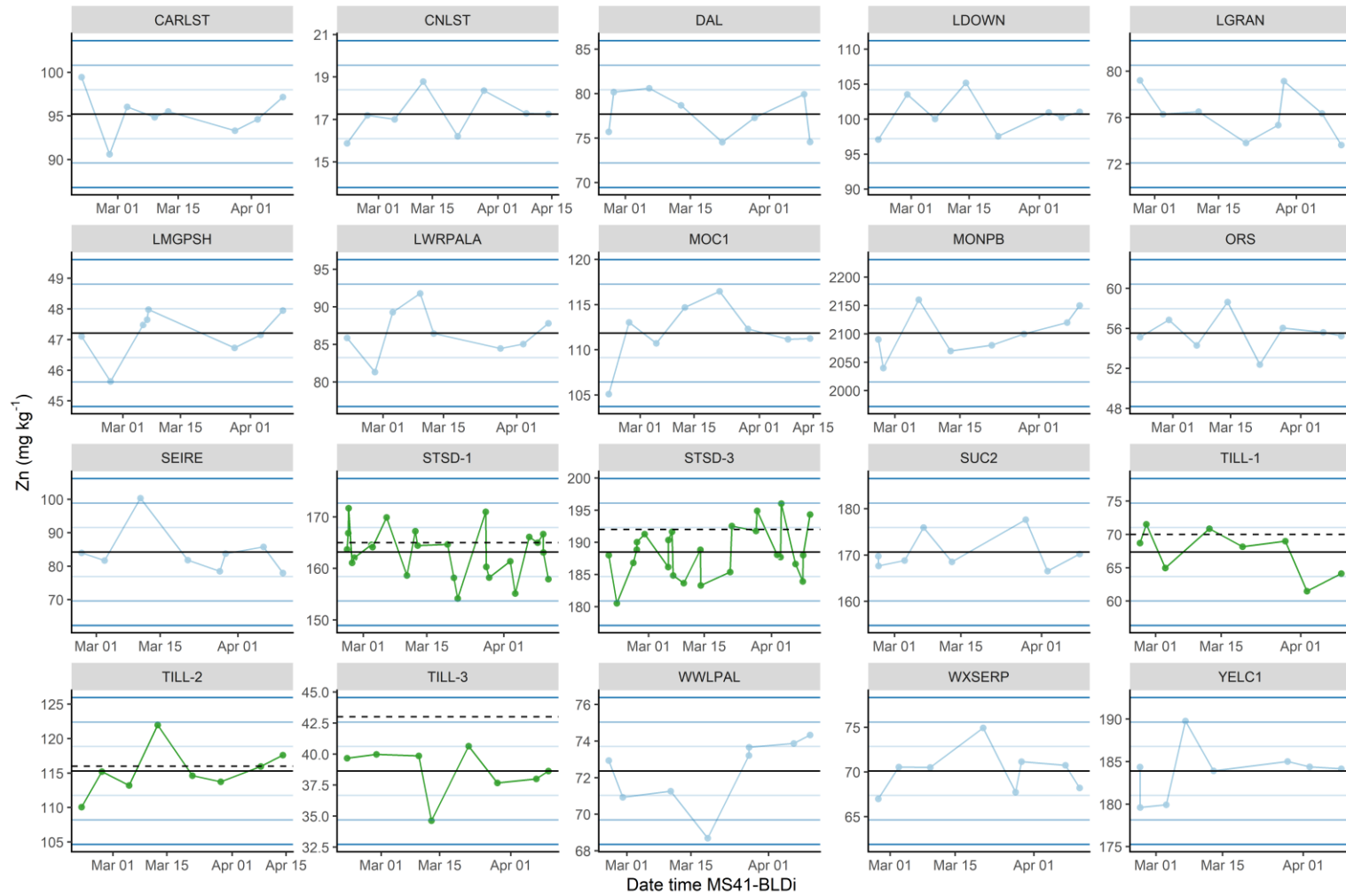
Tungsten (W) sample data IQR: 0.0394-0.0839  $\text{mg kg}^{-1}$

Yttrium (Y) MS41L-BLD



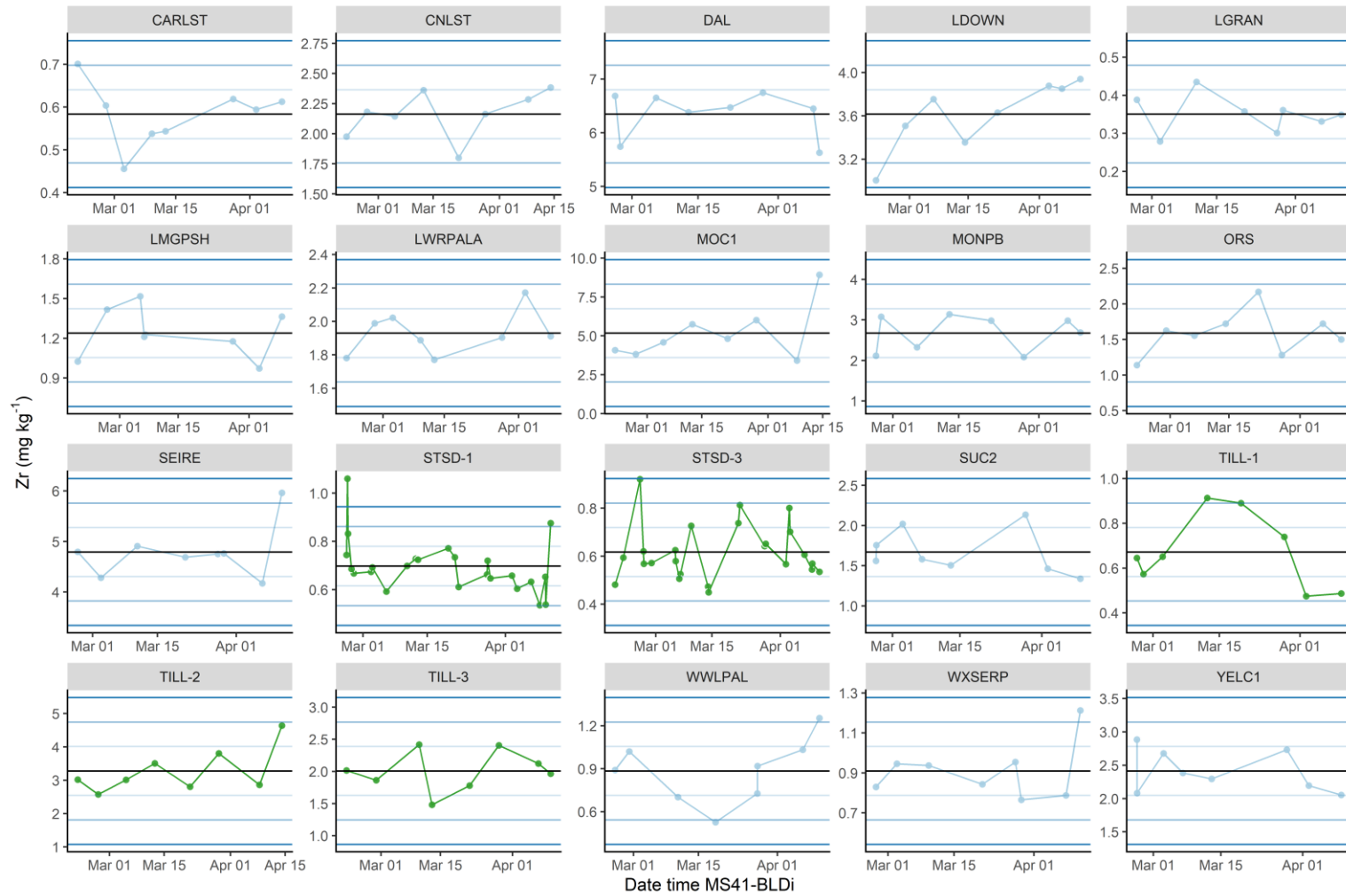
Yttrium (Y) sample data IQR: 5.04–19.1  $\text{mg kg}^{-1}$

Zinc (Zn) MS41L-BLD



Zinc (Zn) sample data IQR: 34.8–94.6 mg kg<sup>-1</sup>

Zirconium (Zr) MS41L-BLD



Zirconium (Zr) sample data IQR: 0.000326–0.000913  $\text{mg kg}^{-1}$

## 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):

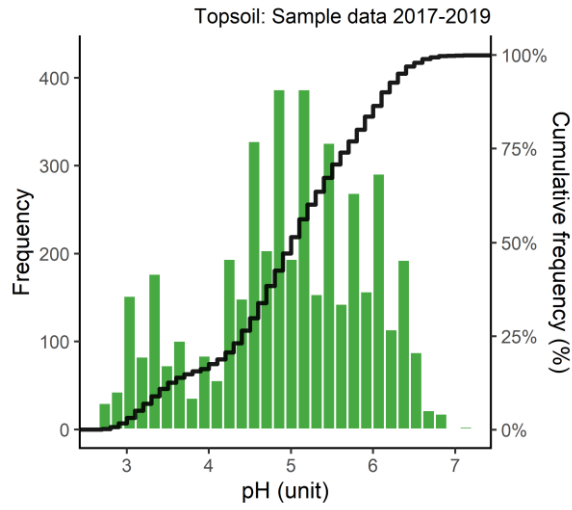
- The first chart (left) is the combined cumulative frequency and histogram. The histogram frequency (y axis left) and the cumulative frequency % (y axis right) are plotted against the analyte concentration (x axis).
- The second chart (right) is the same but data are  $\log_{10}$  transformed (an exception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

These data are censored. All “<LLD” values have been replaced with  $0.5 * \text{LLD}$  and for these shallow 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.

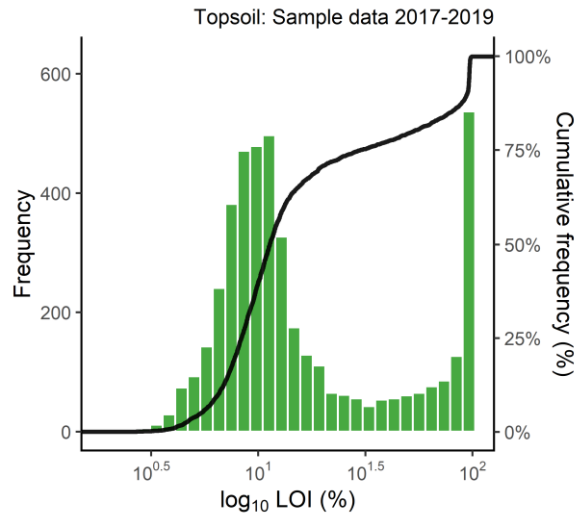
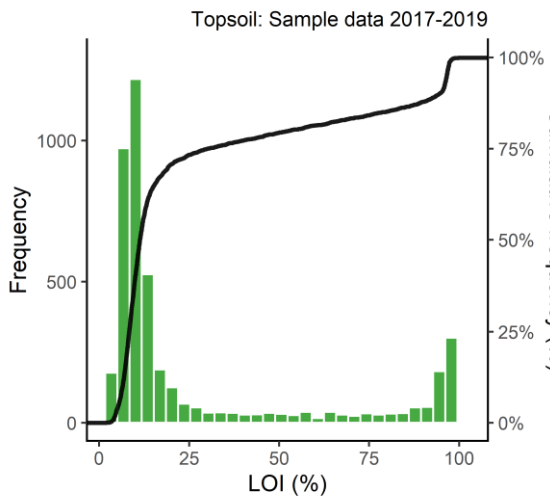
Typically a log transformation results in a less skewed distribution, and geochemical data are broadly log-normal. Censored data will sometimes display as an isolated histogram bar away from the normal data population above the LLD.

# pH and LOI sample site data

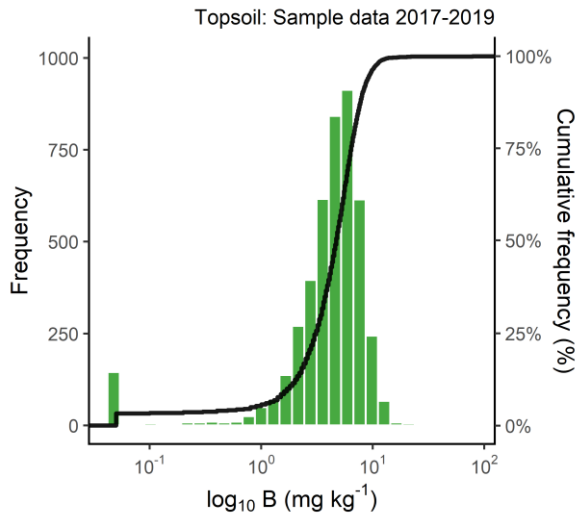
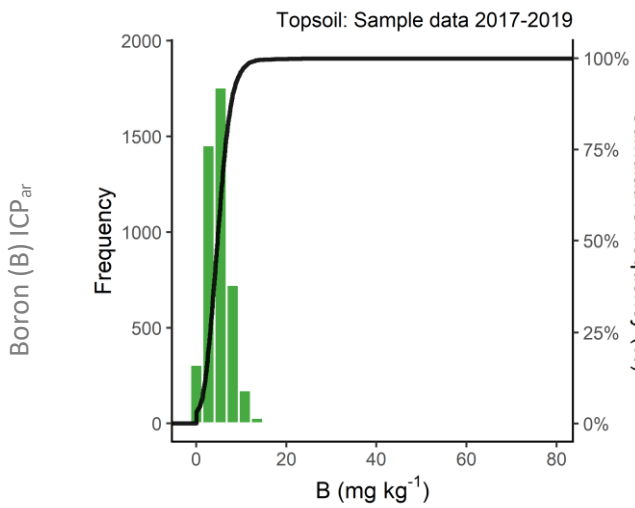
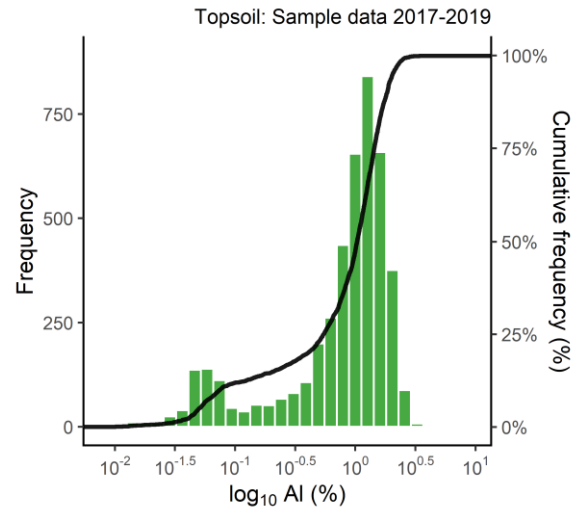
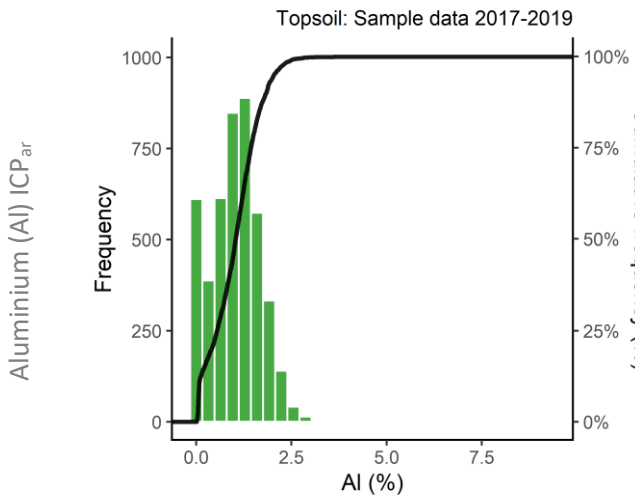
Soil pH (CaCl<sub>2</sub>)

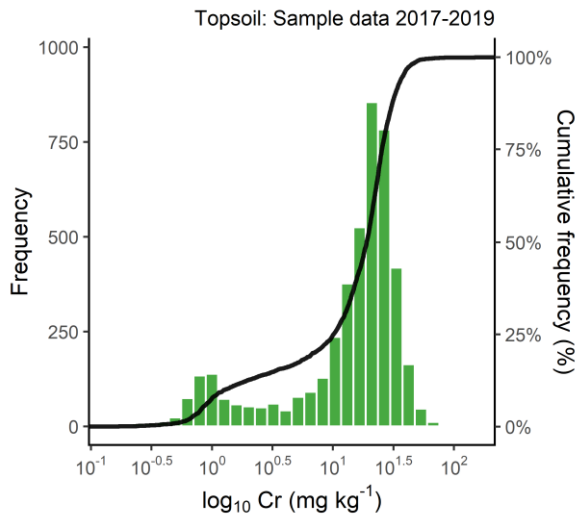
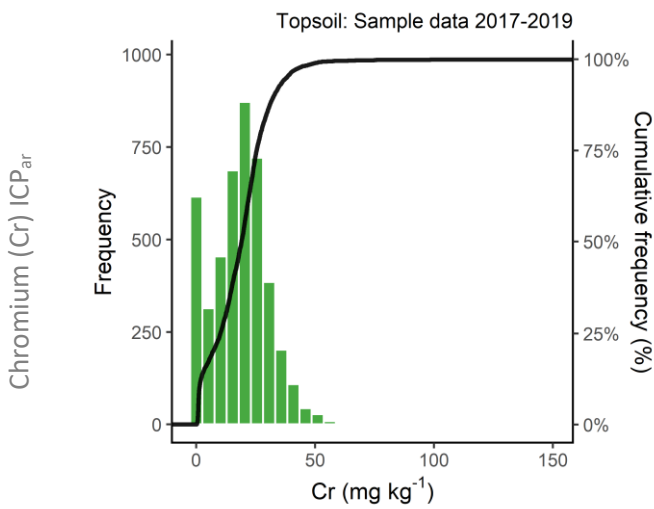
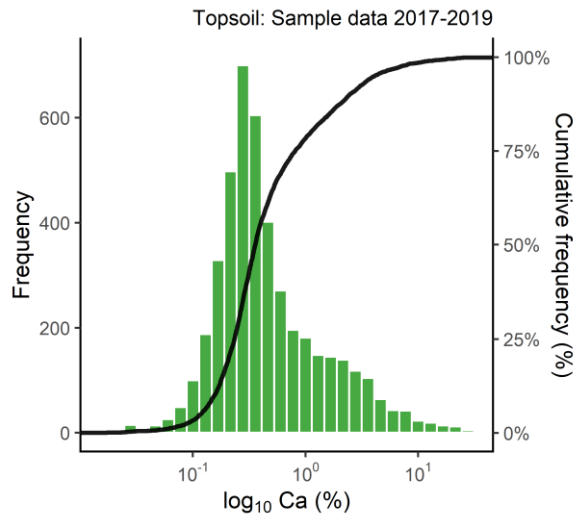
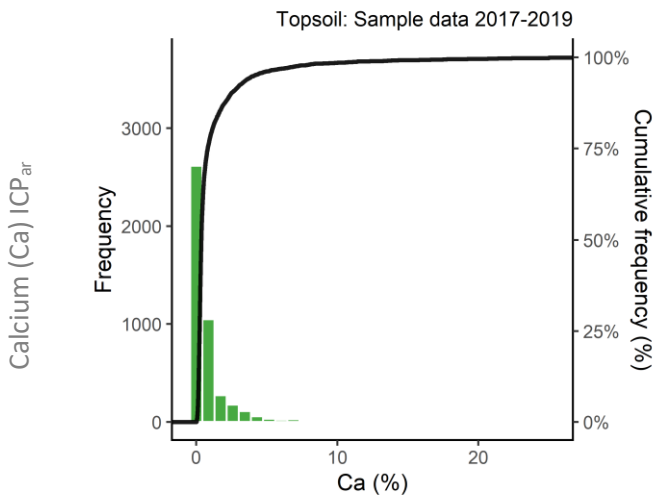
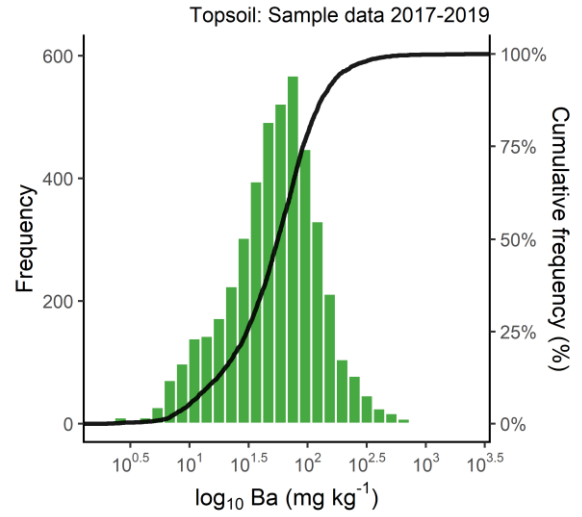
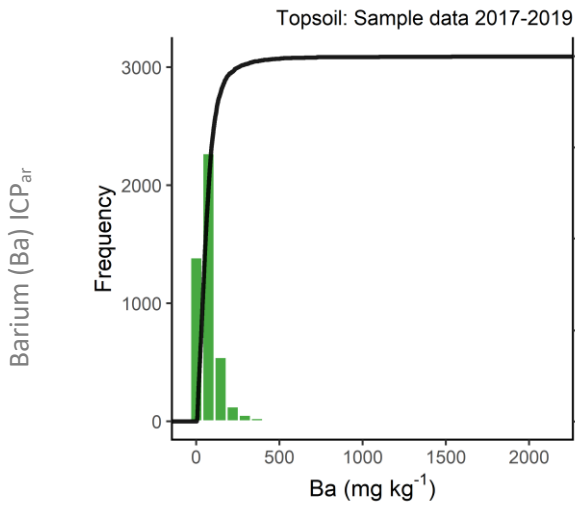


Soil loss-on-ignition (at 450C) %

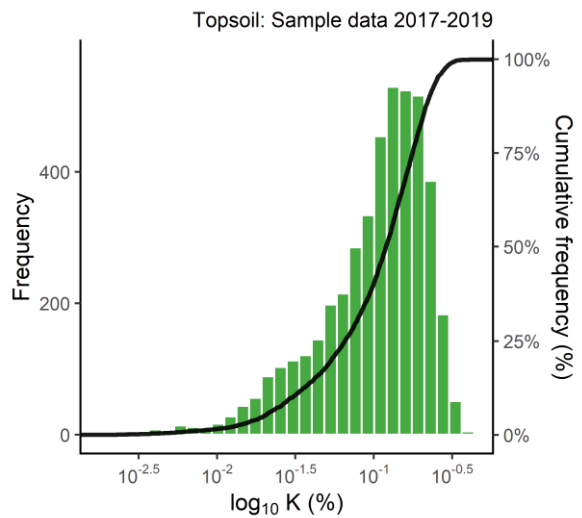
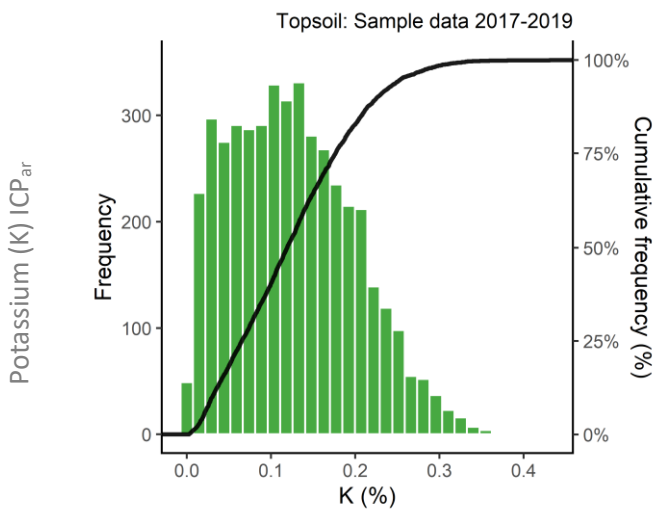
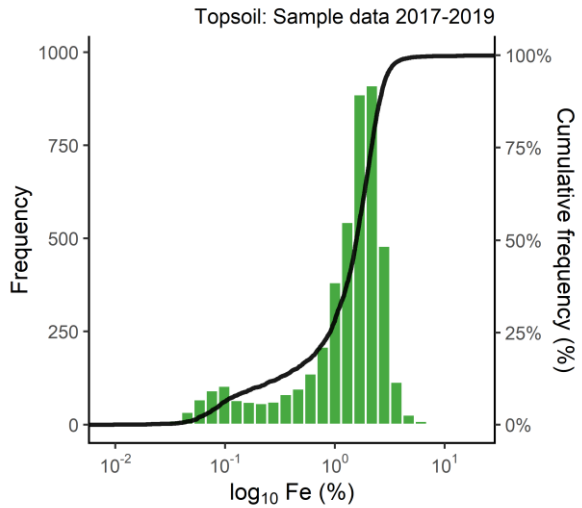
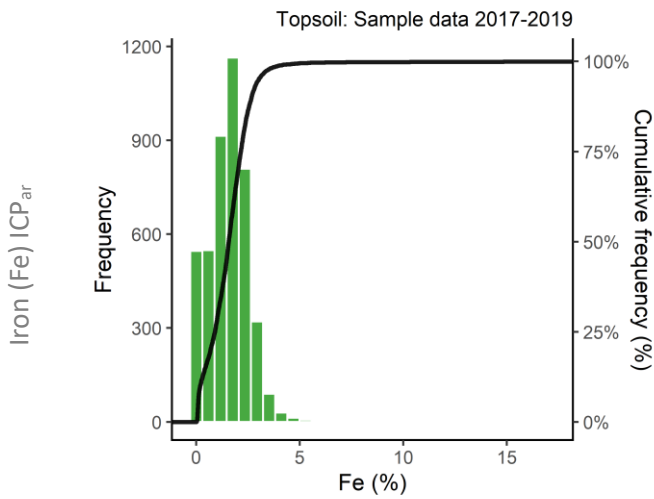
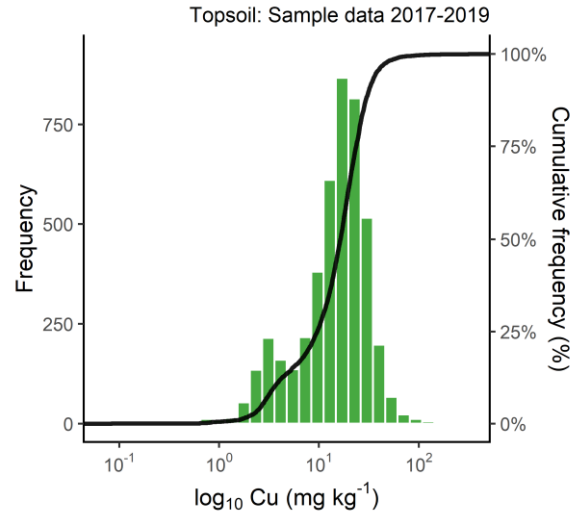
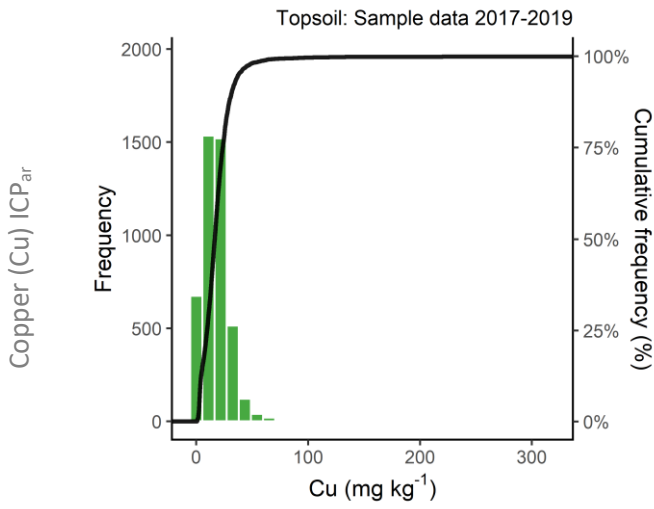


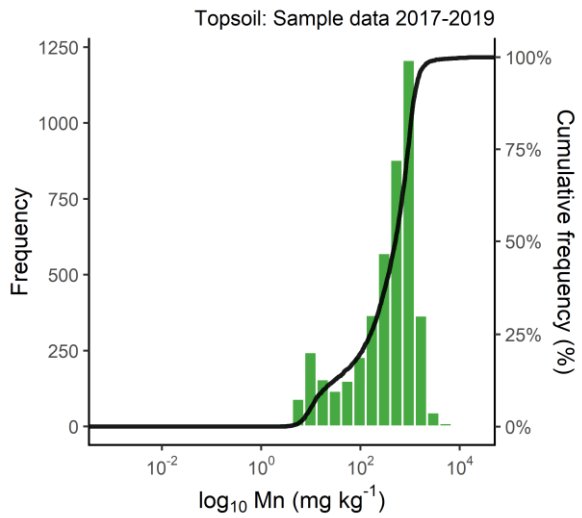
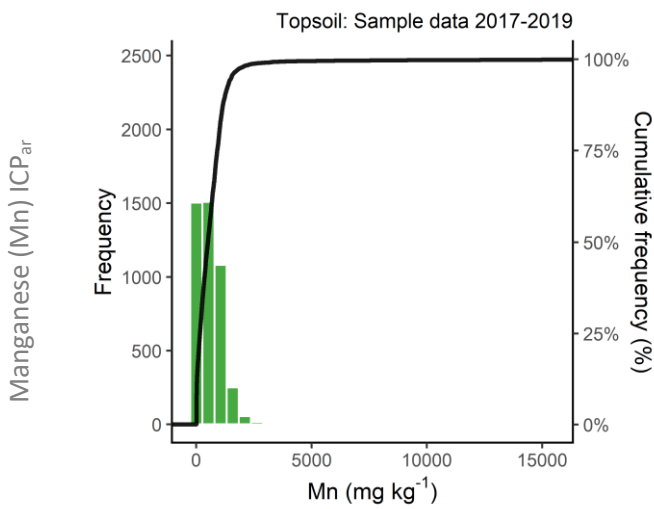
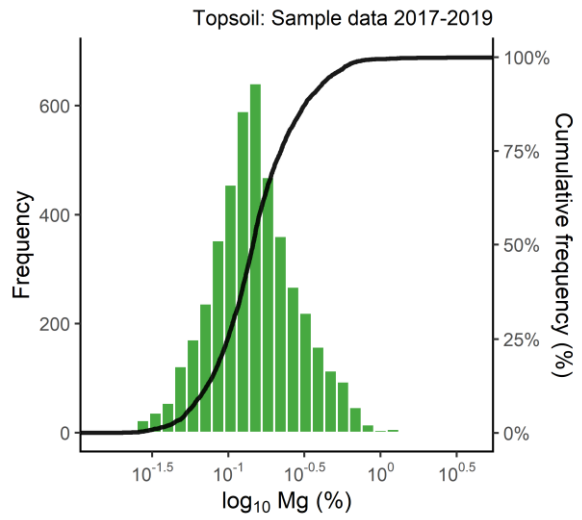
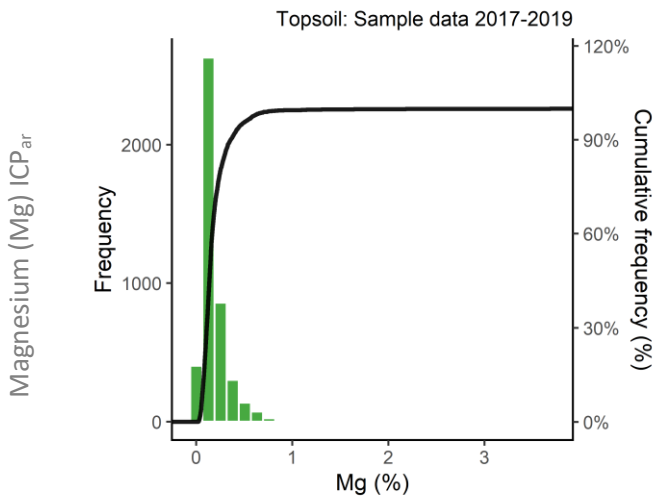
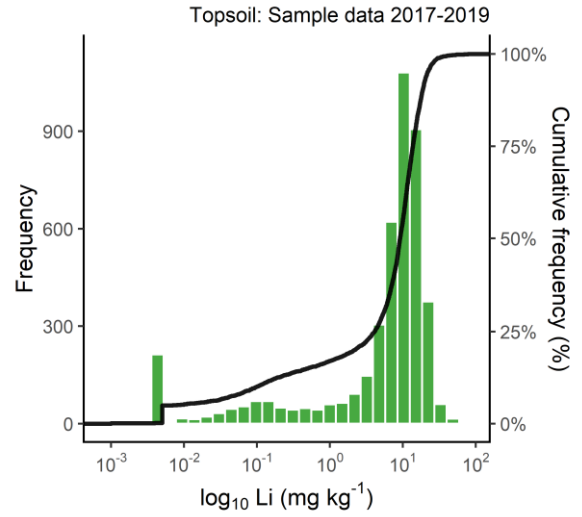
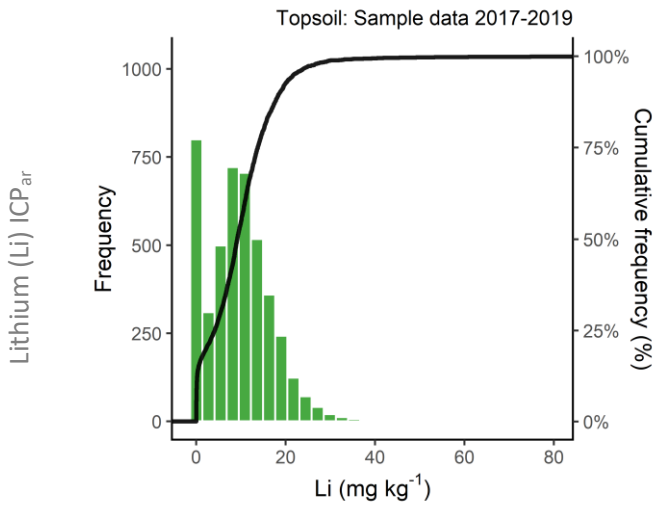
# ICP<sub>ar</sub> sample site data

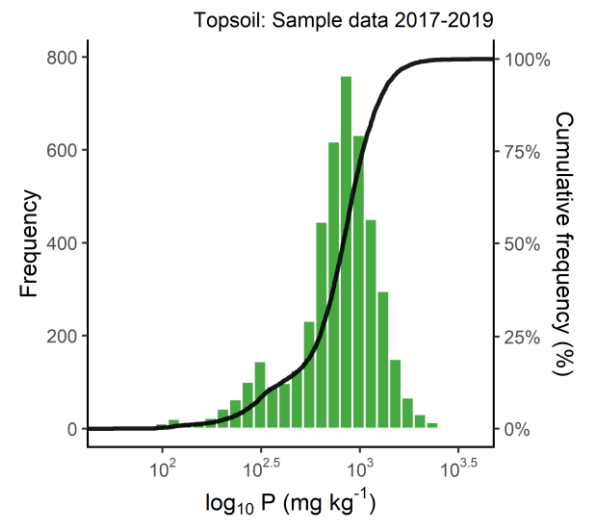
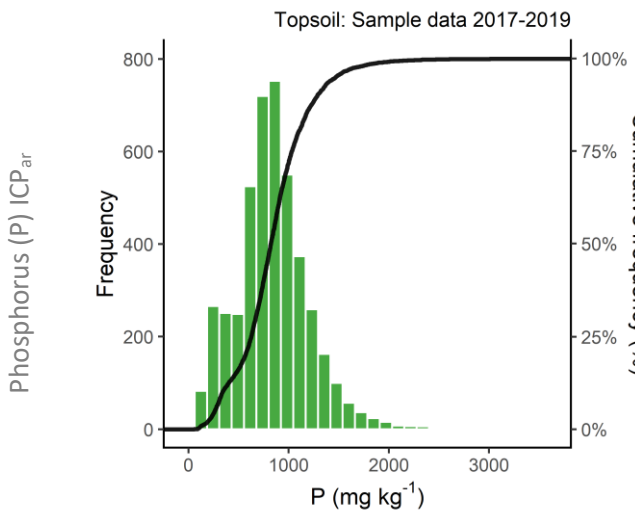
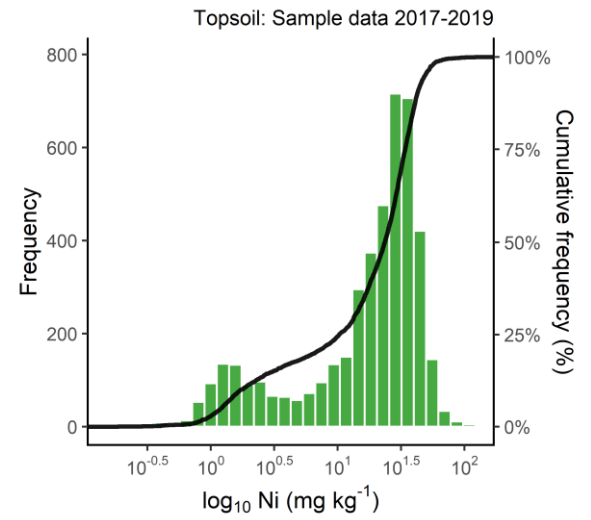
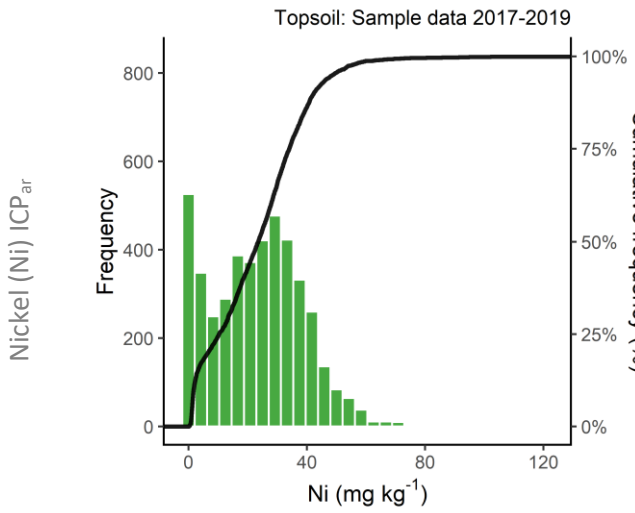
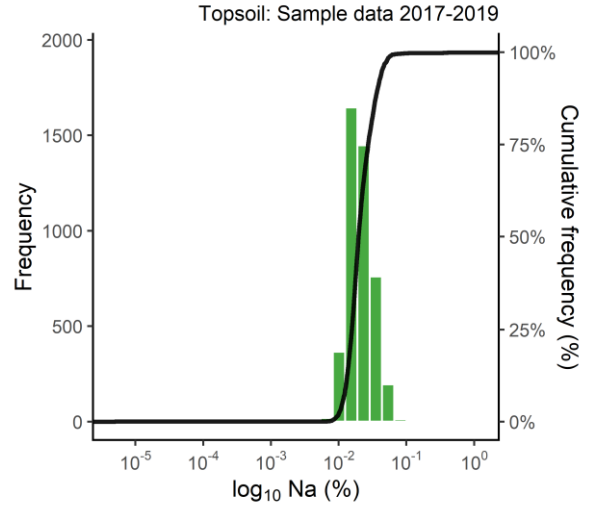
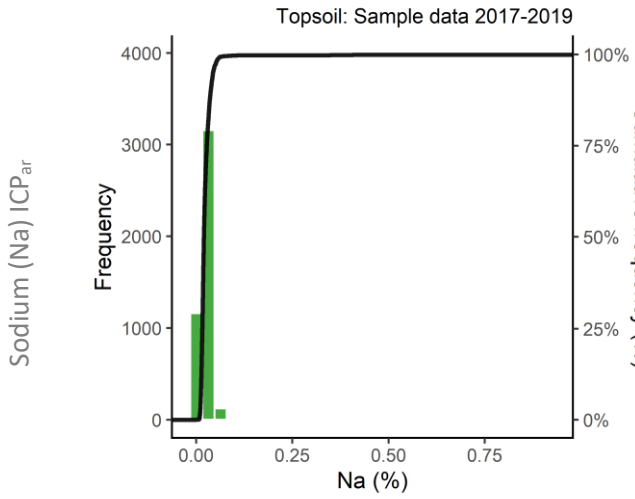


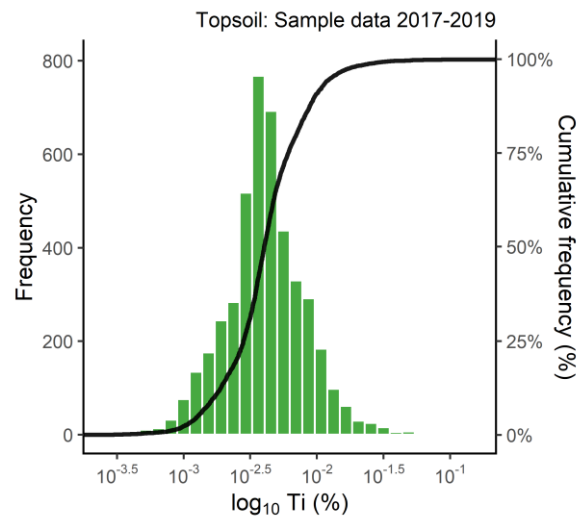
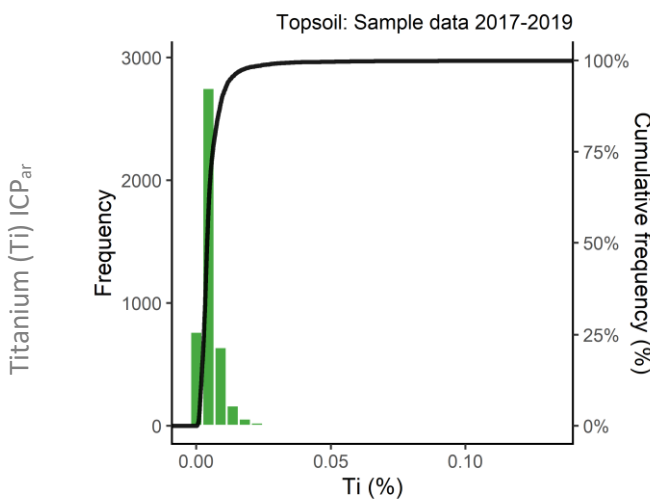
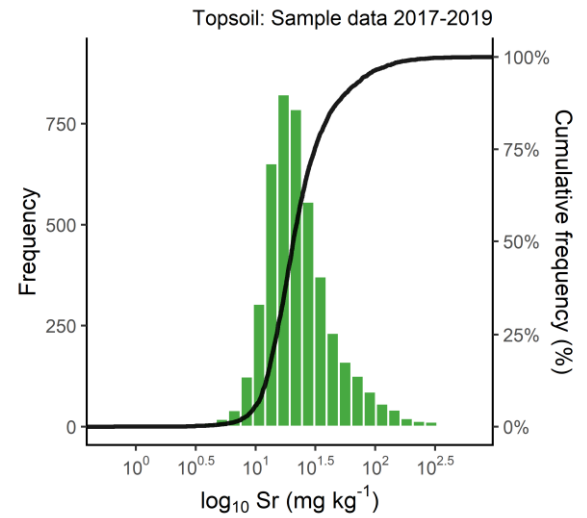
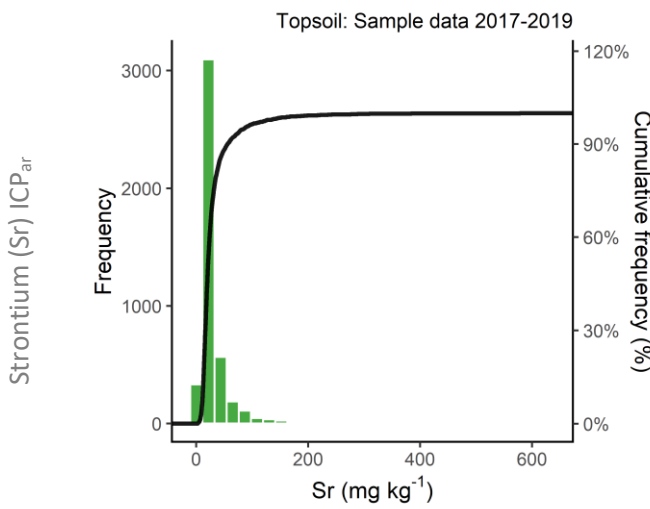
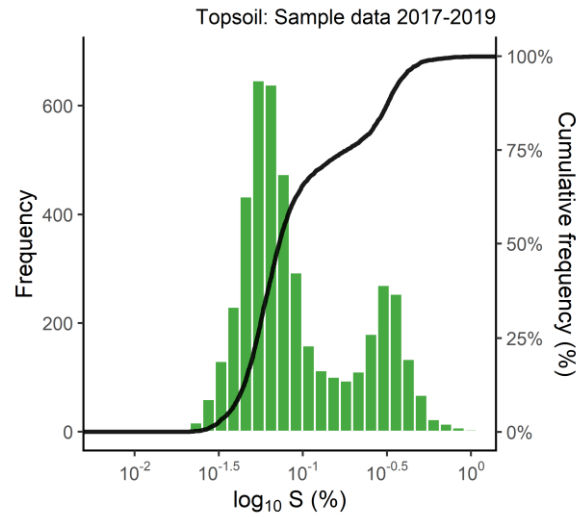
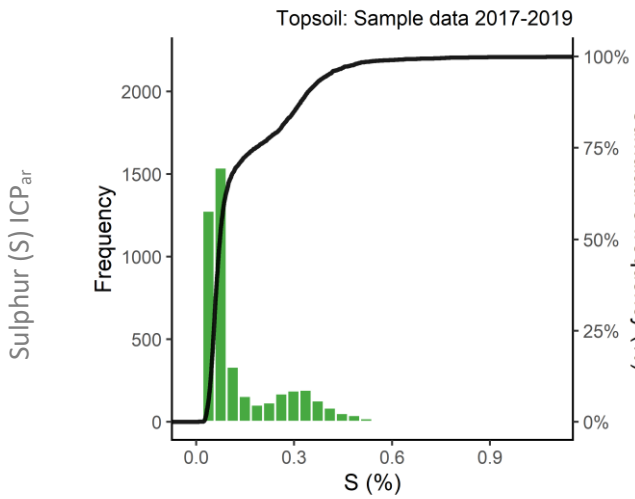


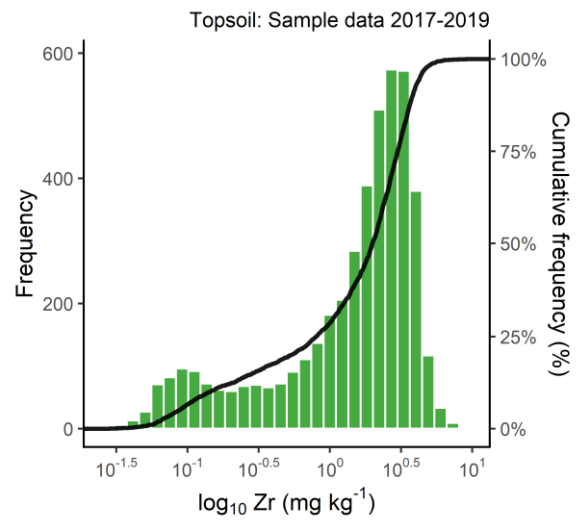
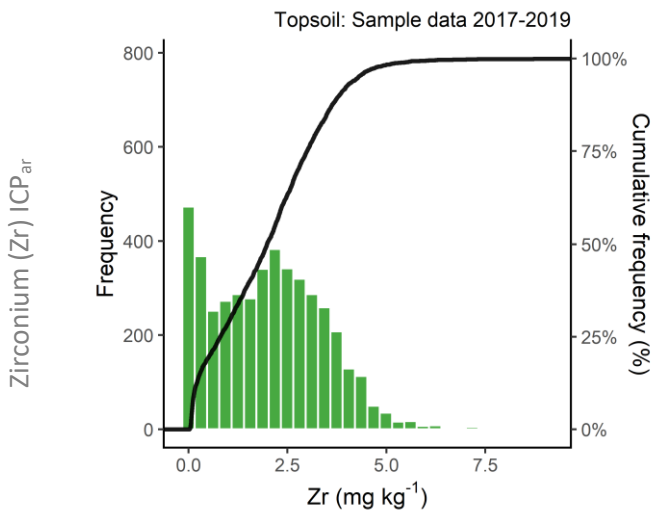
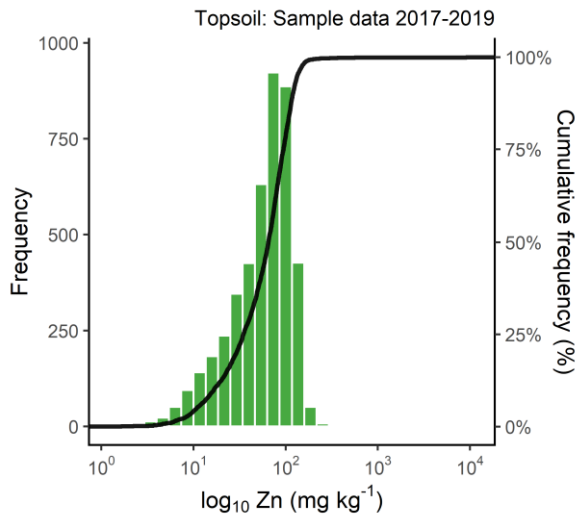
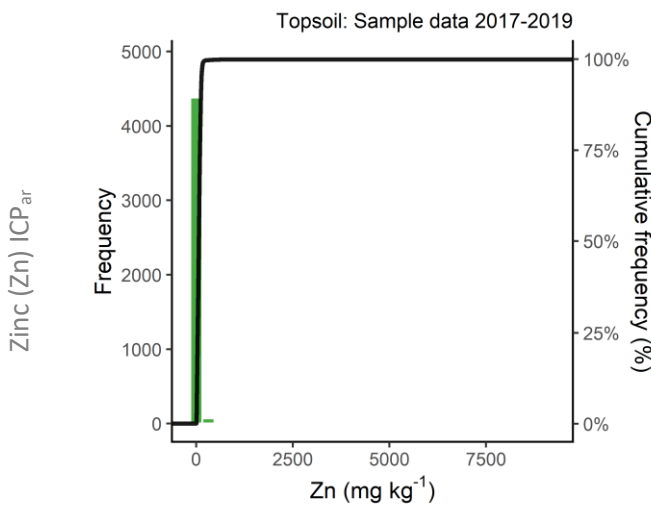
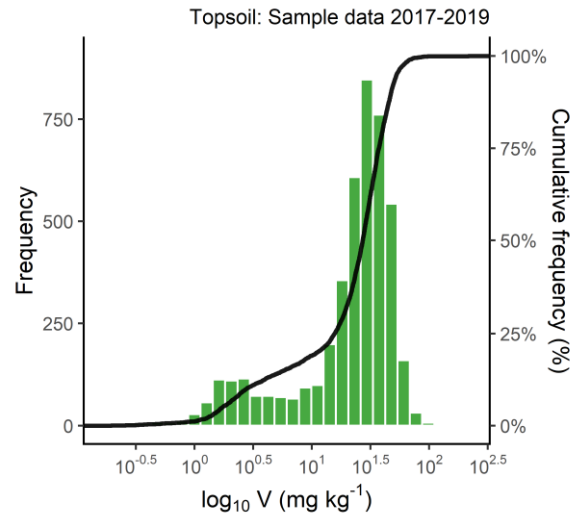
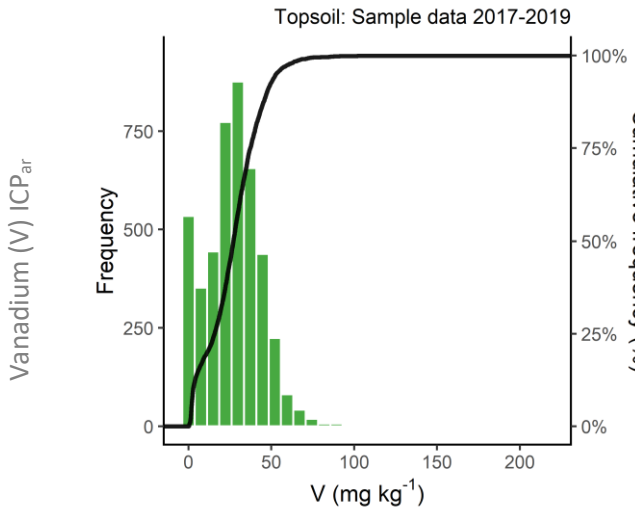


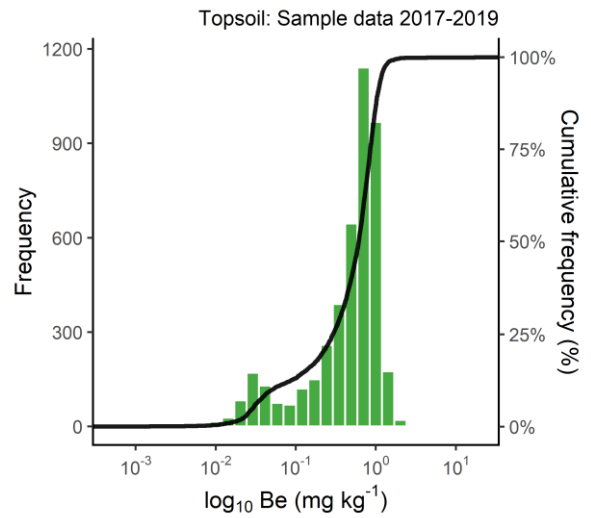
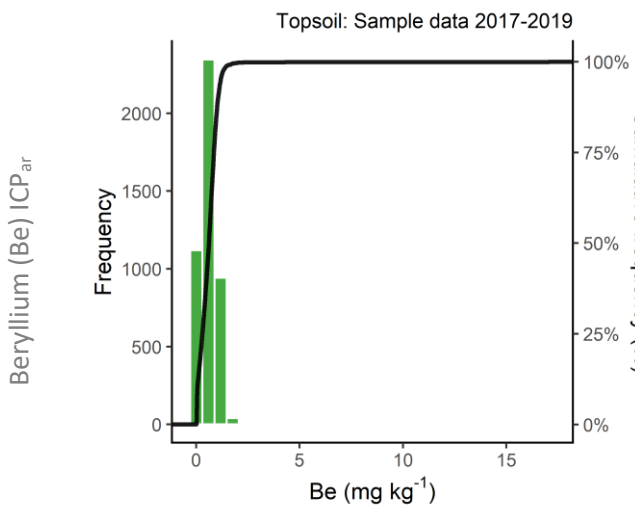
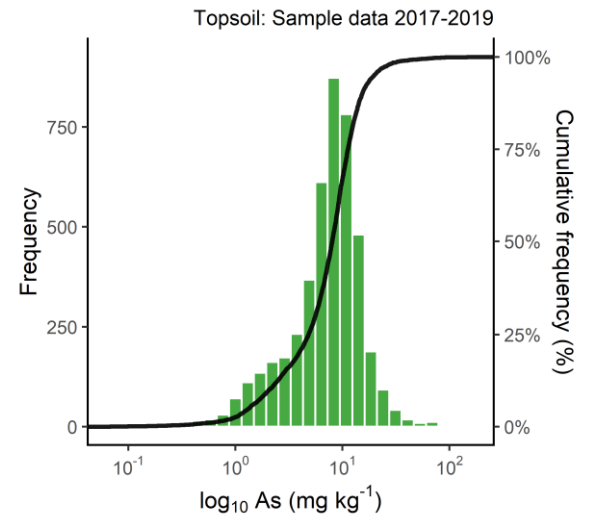
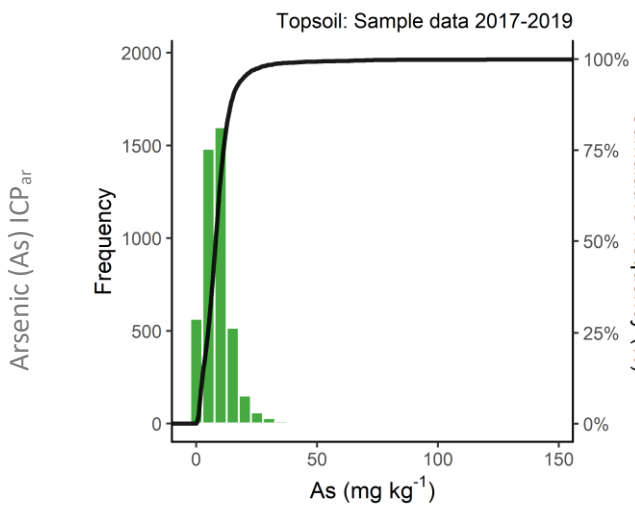
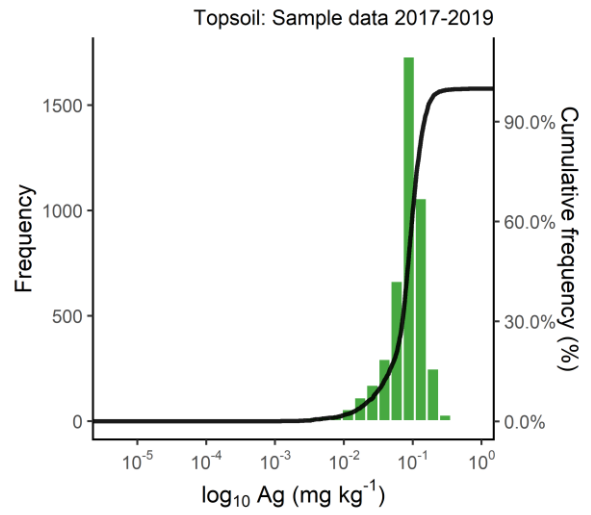
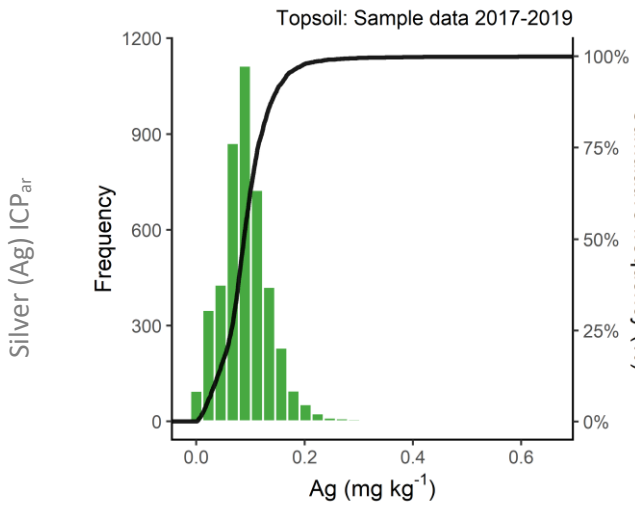


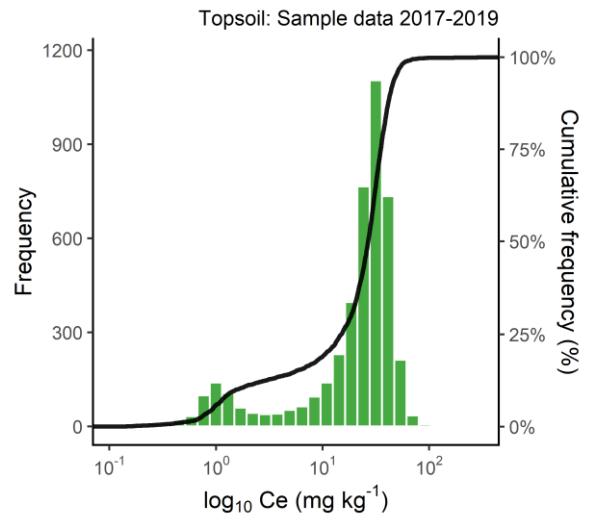
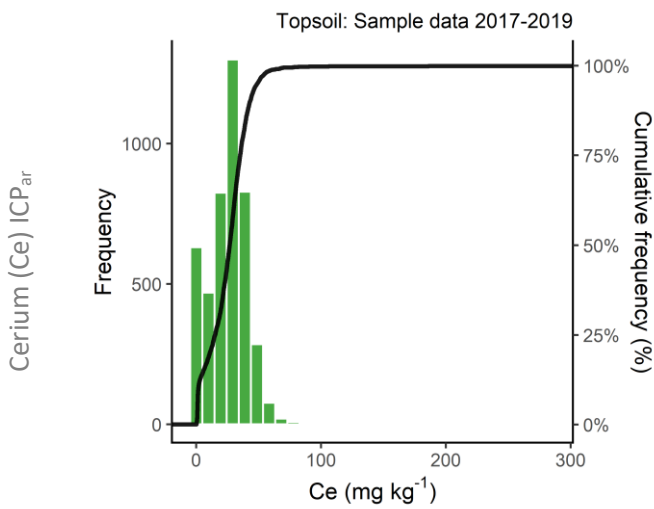
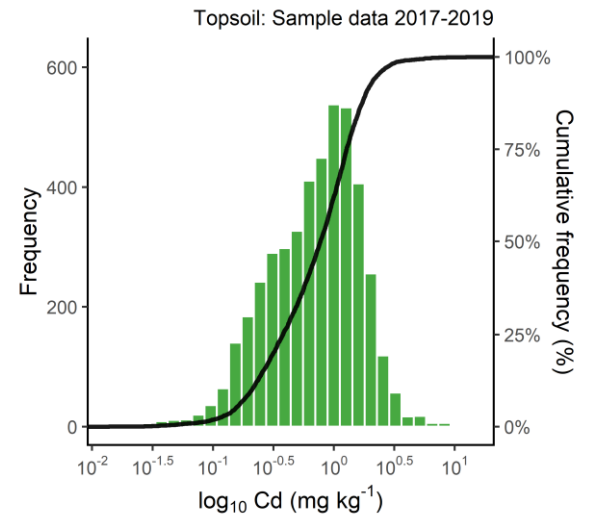
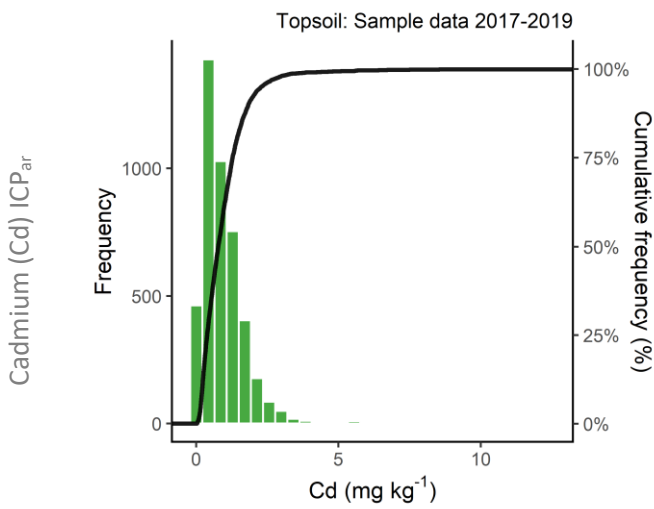
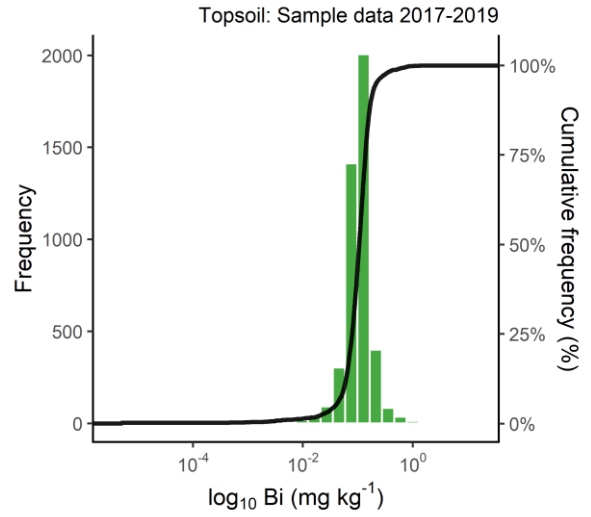
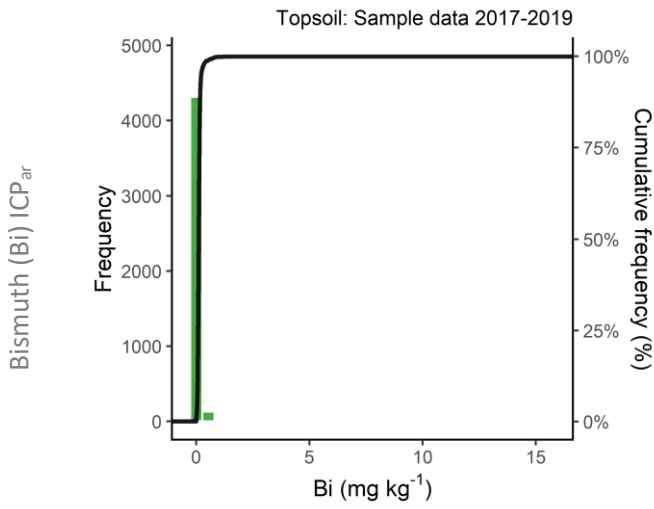


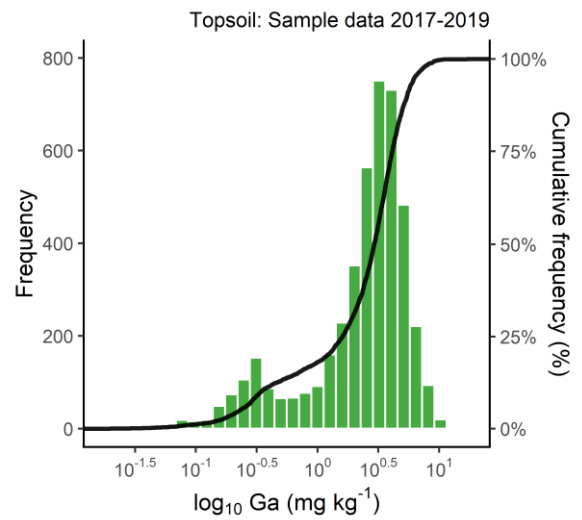
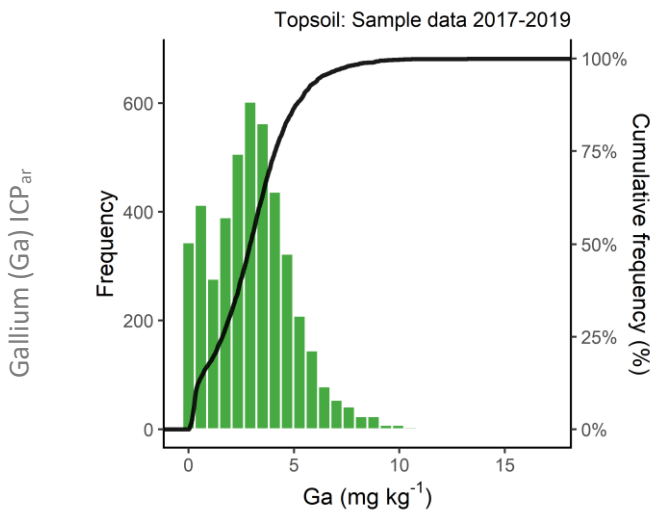
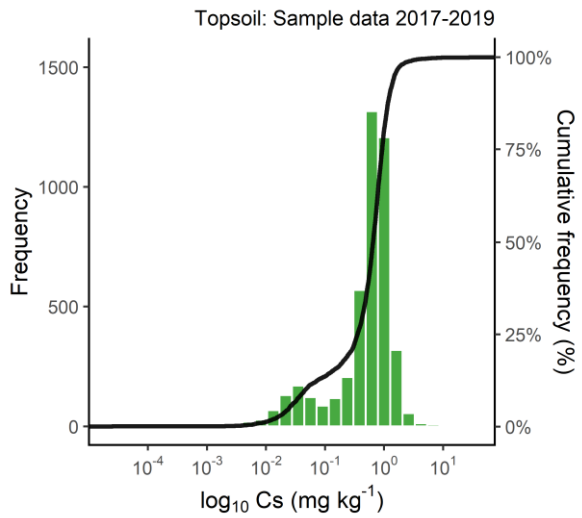
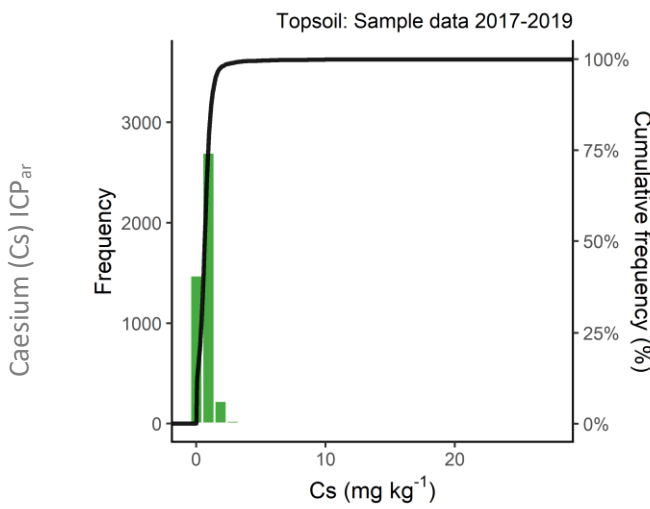
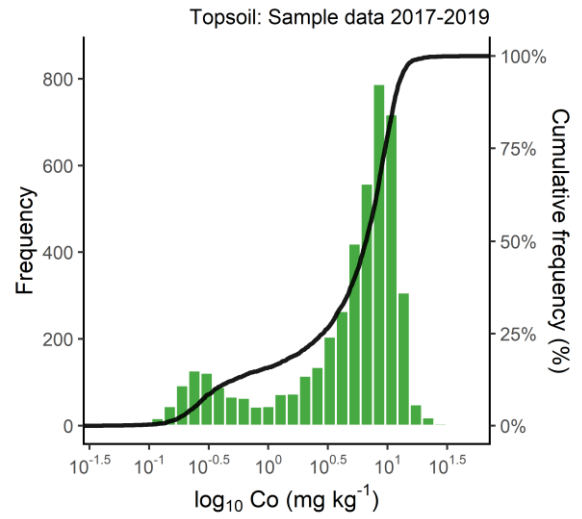
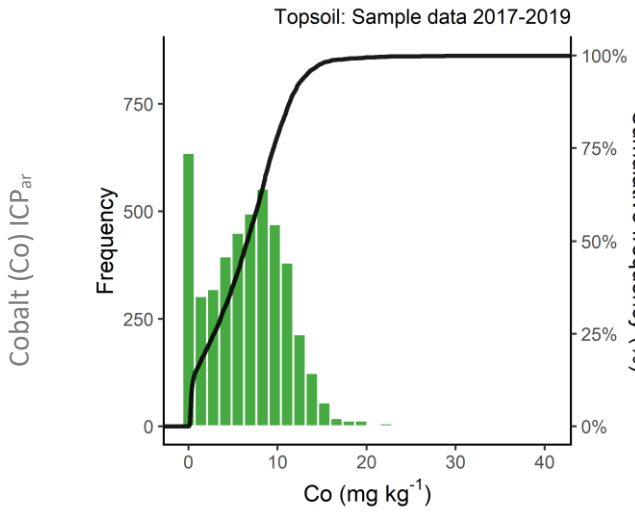




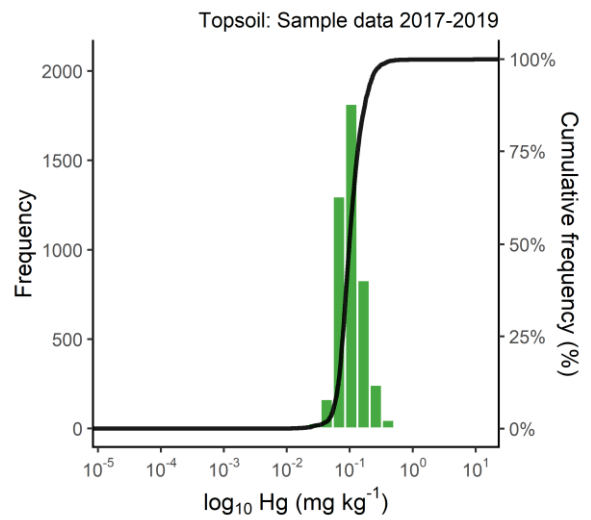
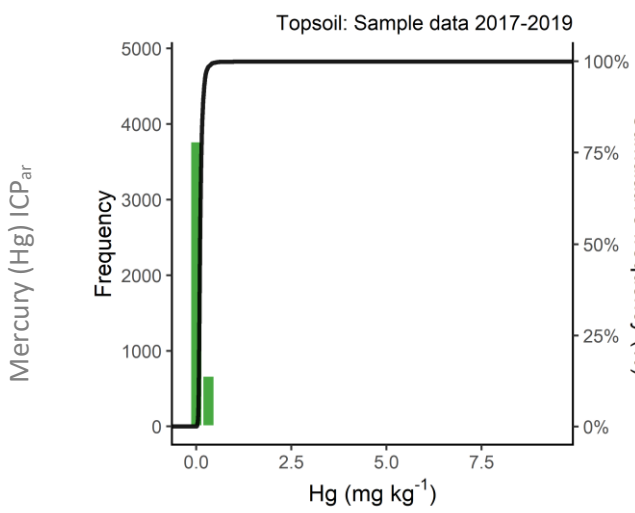
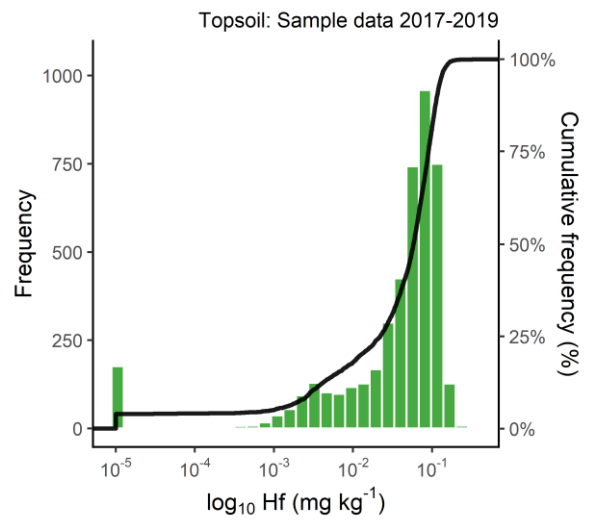
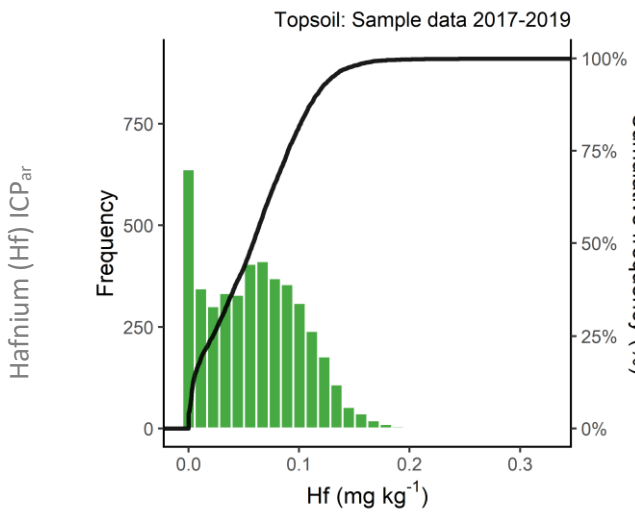
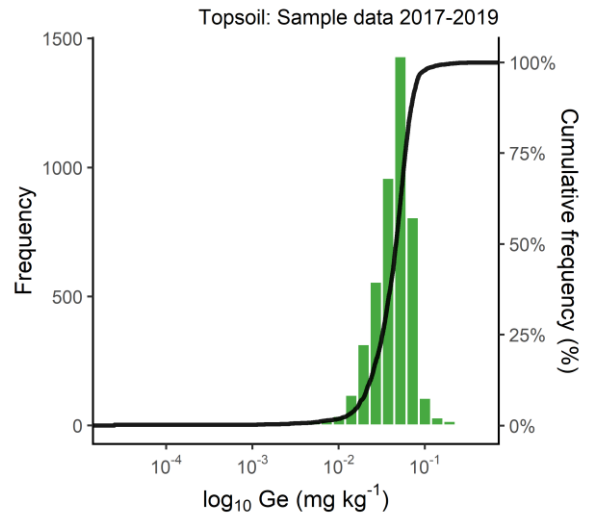
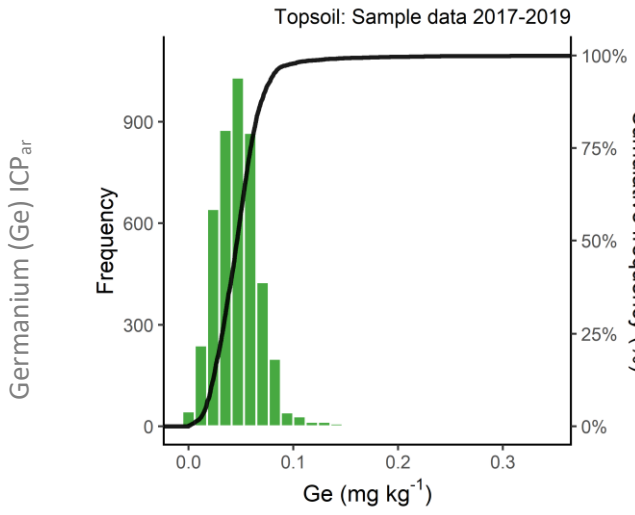


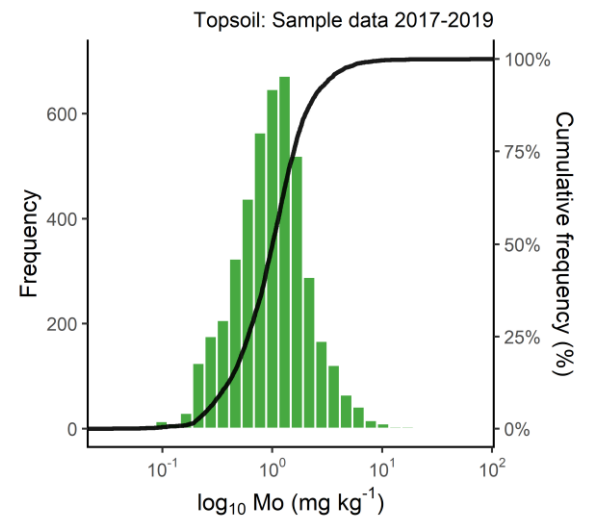
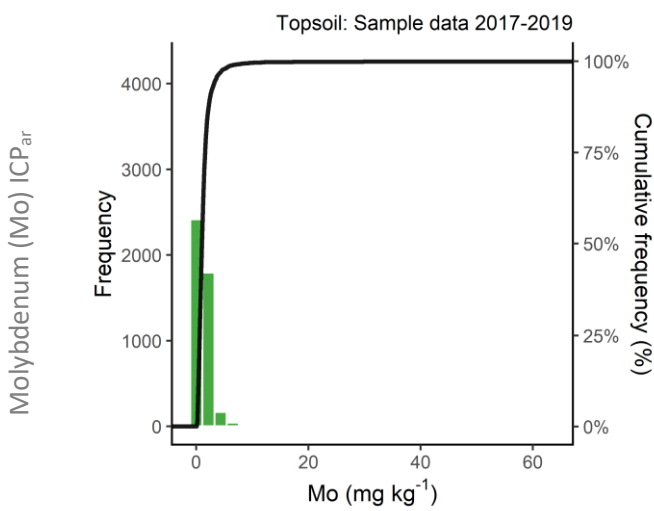
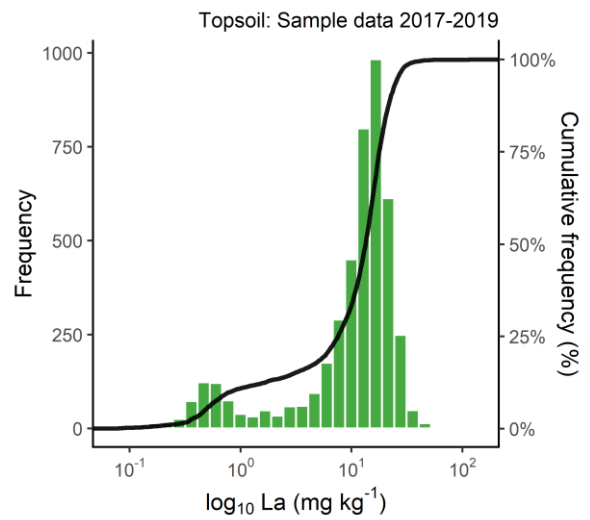
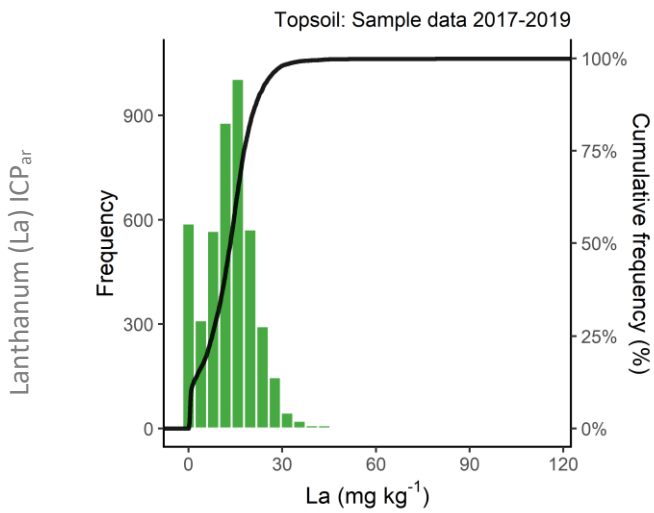
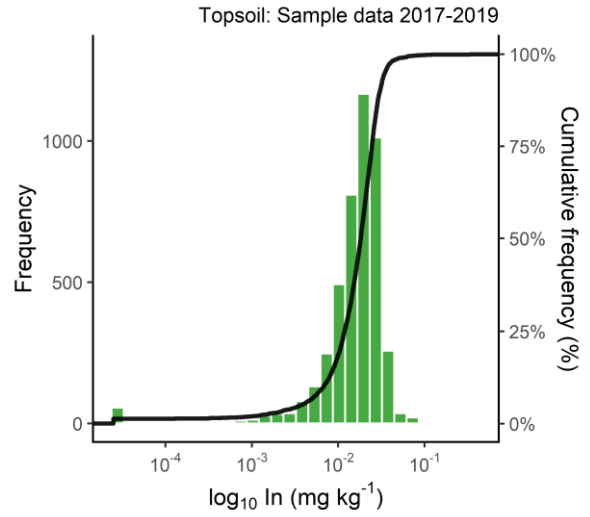
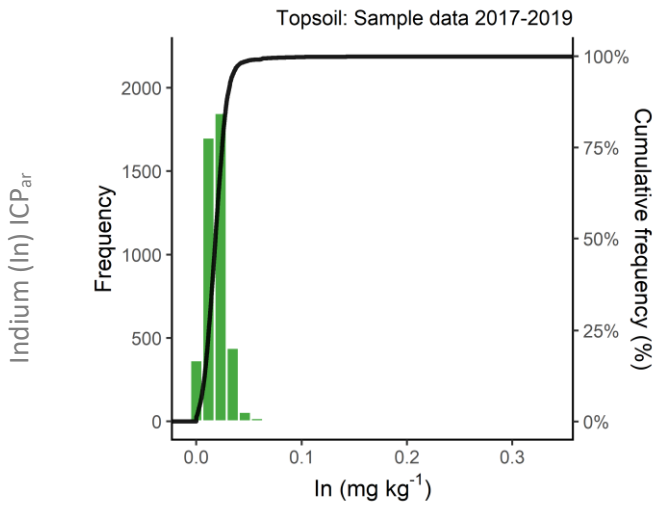


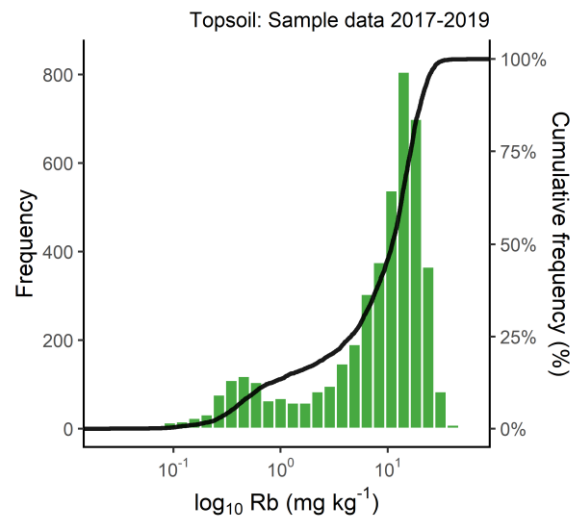
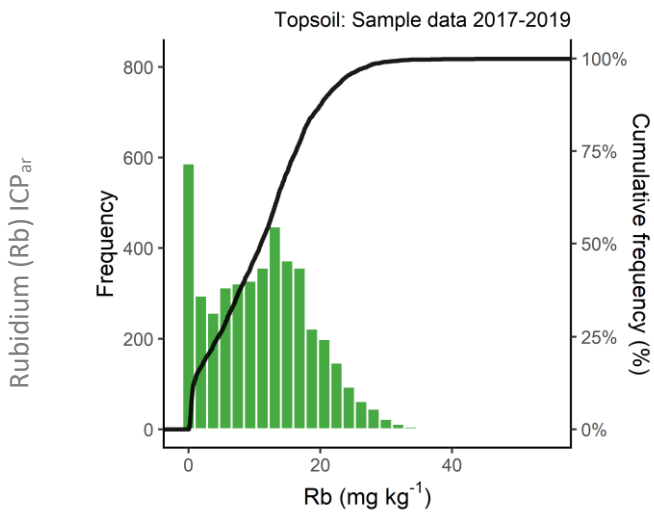
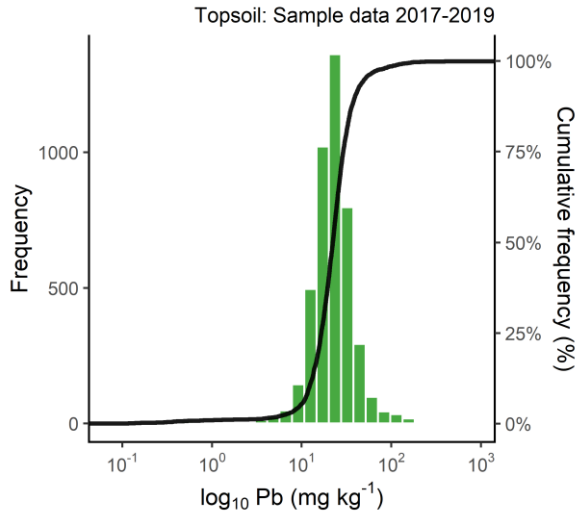
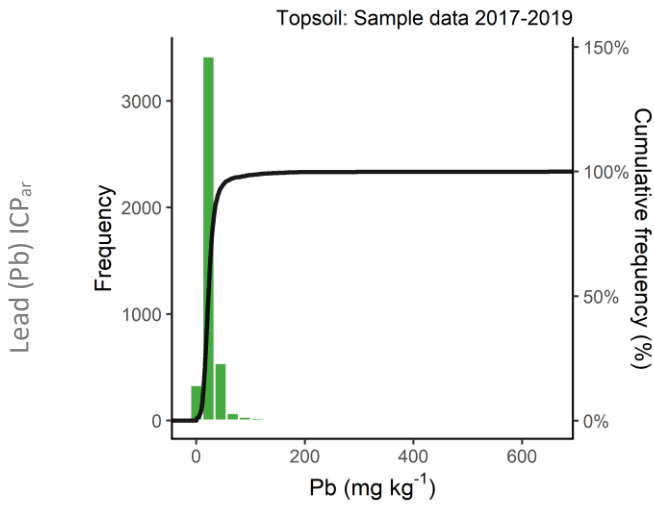
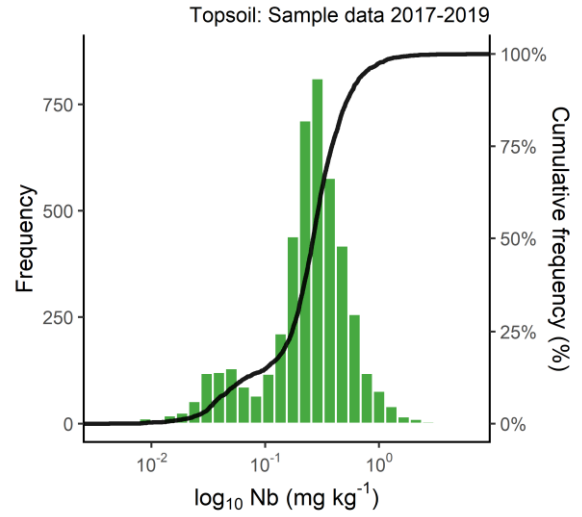
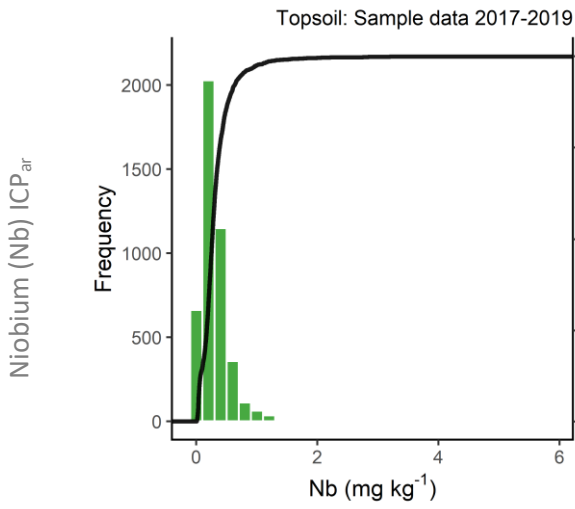




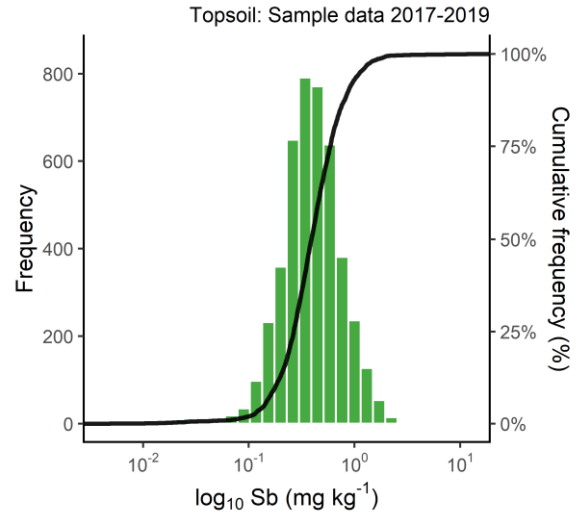
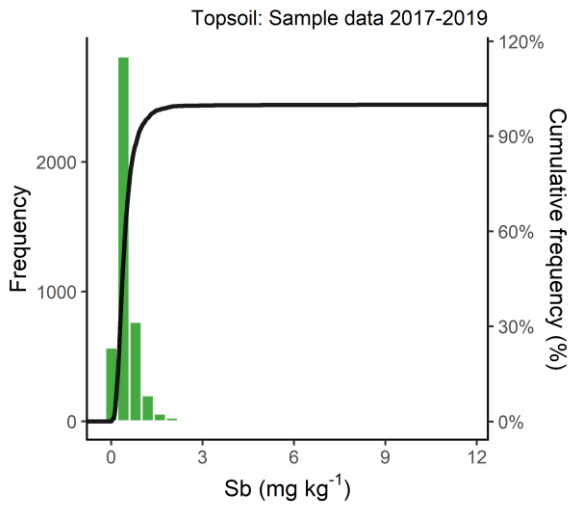




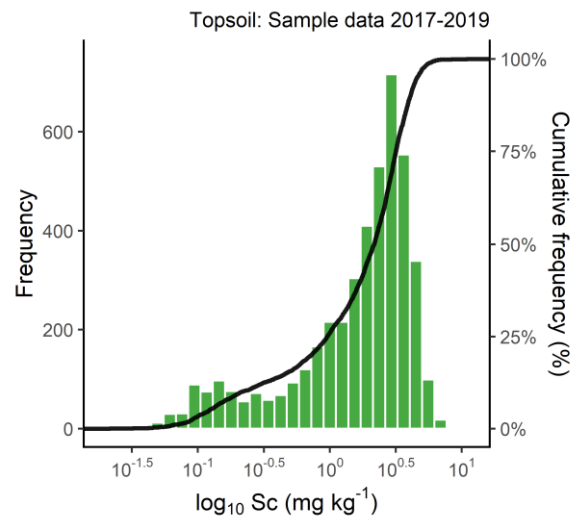
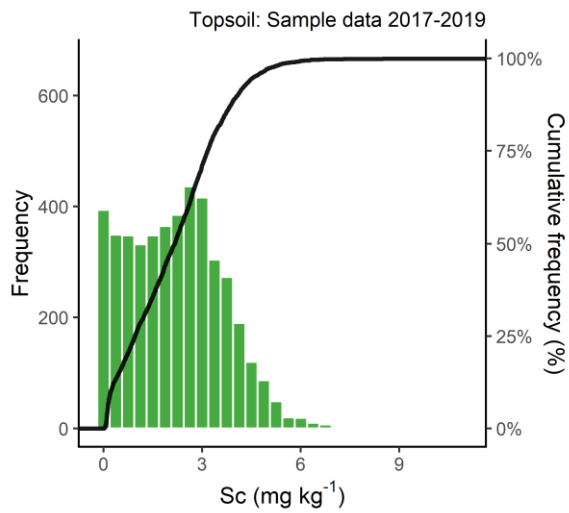




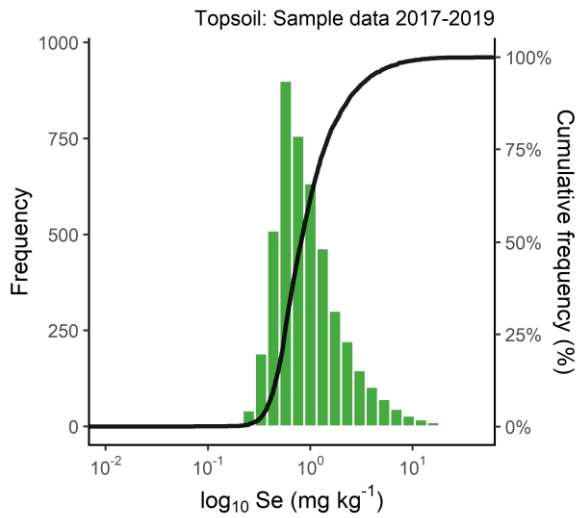
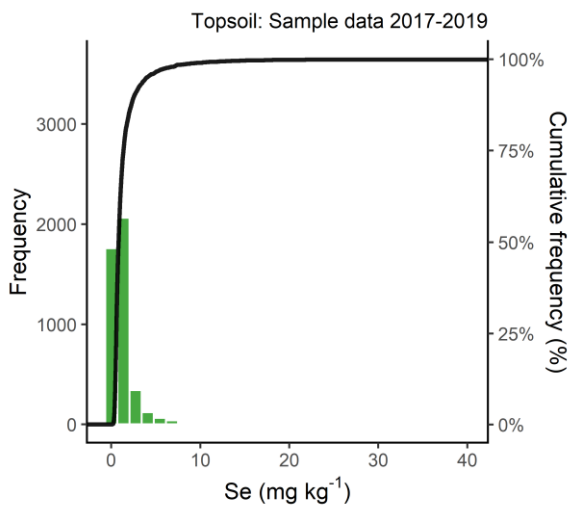
Antimony (Sb) ICP<sub>ar</sub>

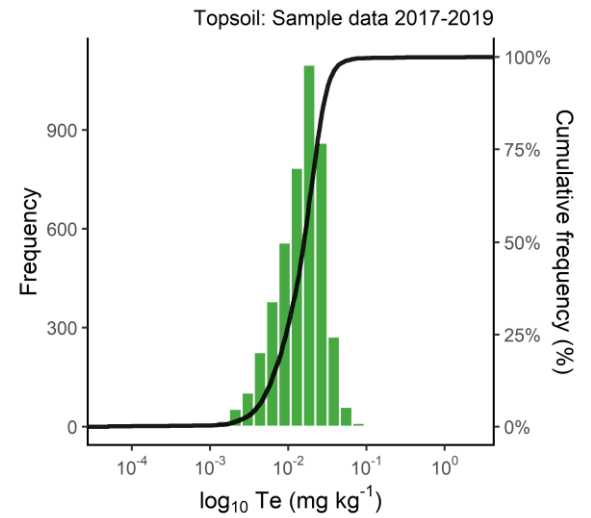
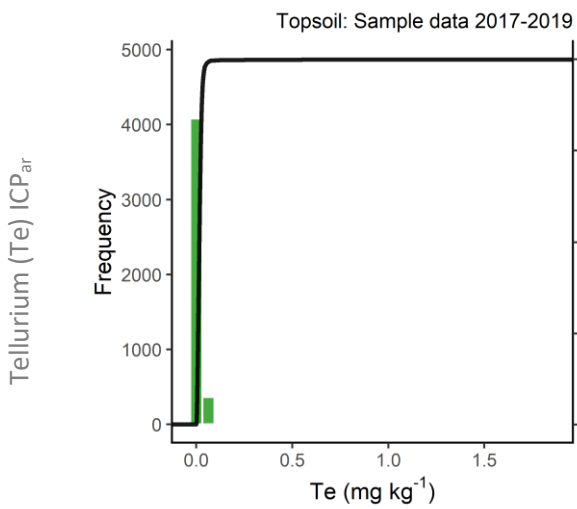
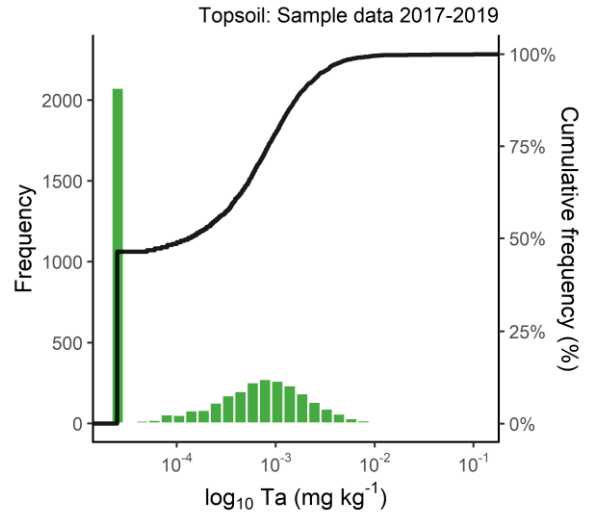
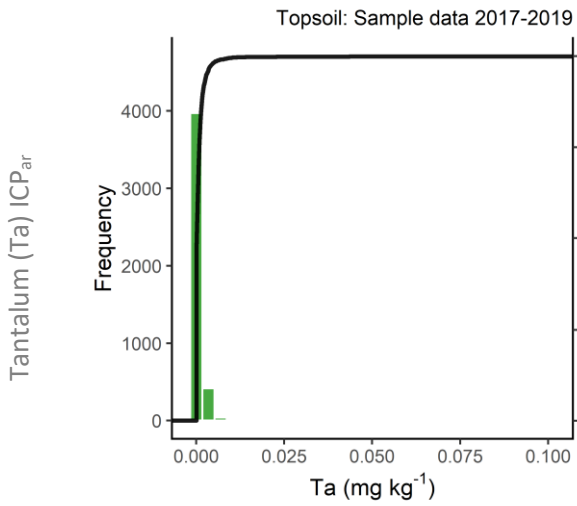
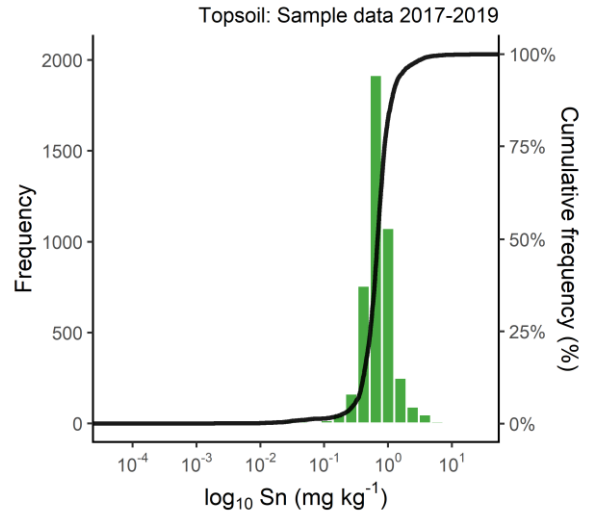
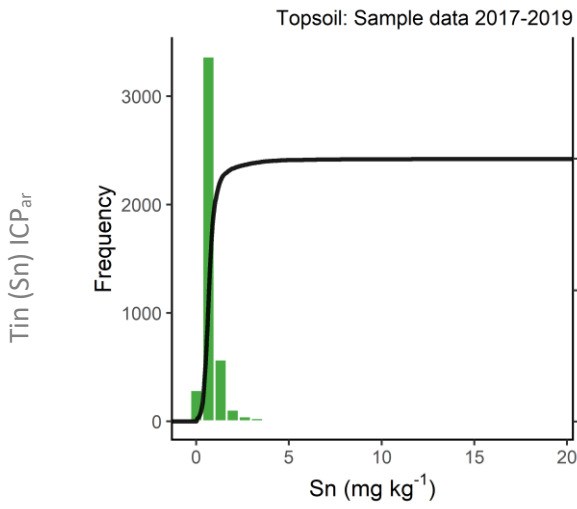


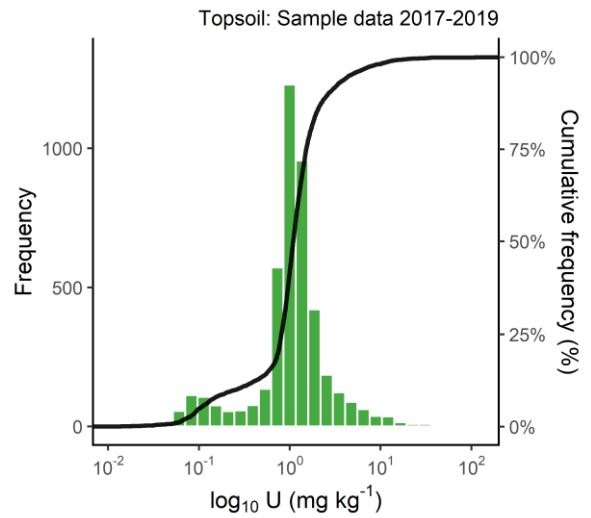
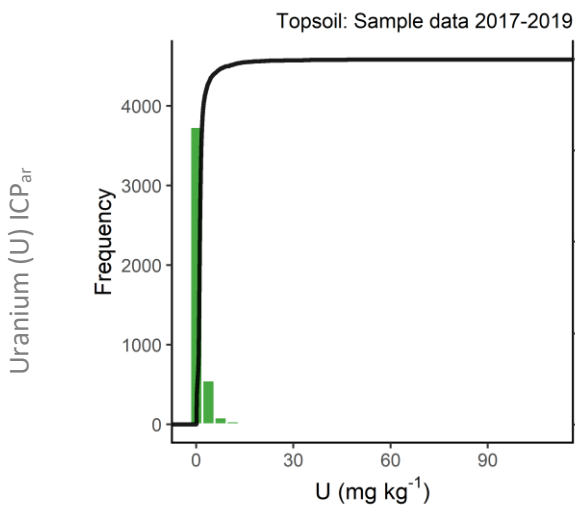
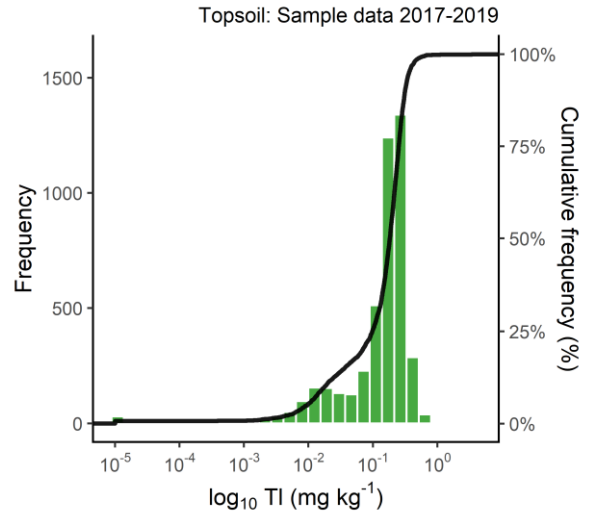
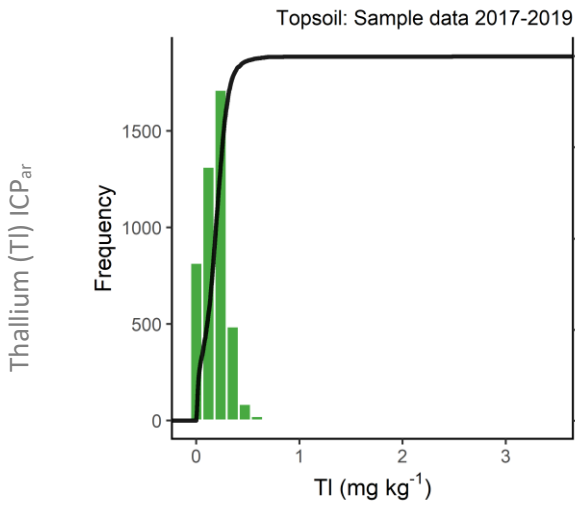
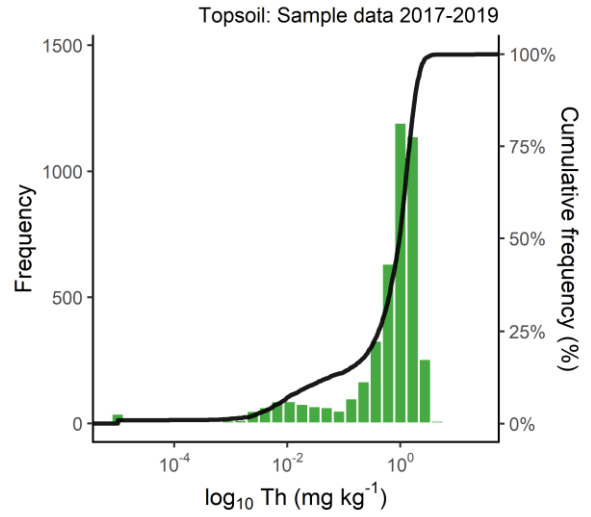
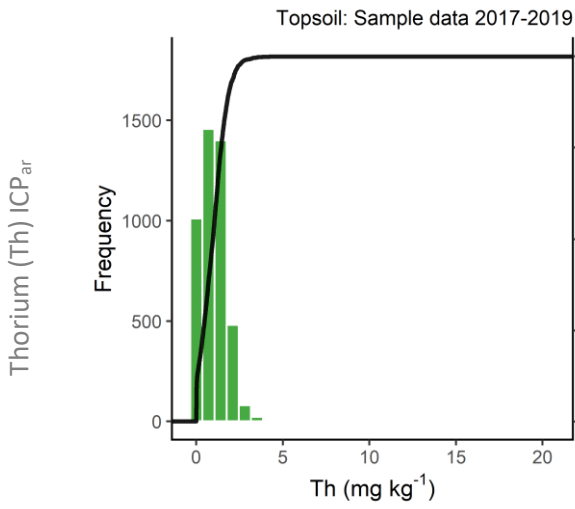
Scandium (Sc) ICP<sub>ar</sub>

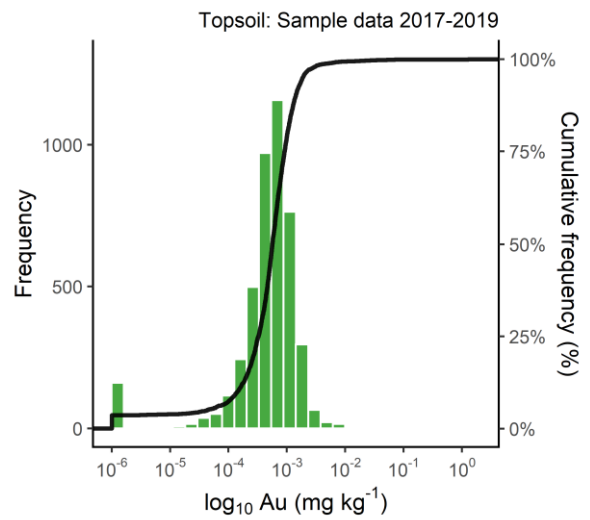
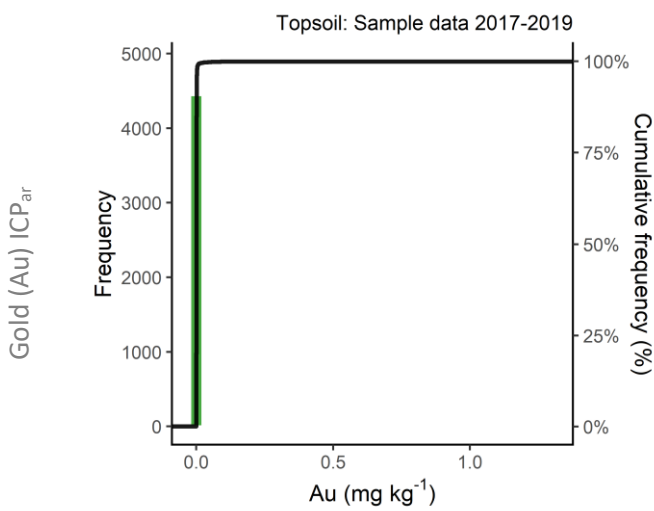
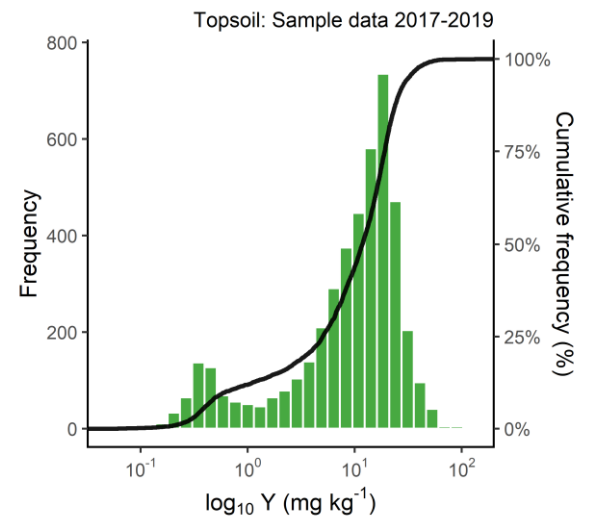
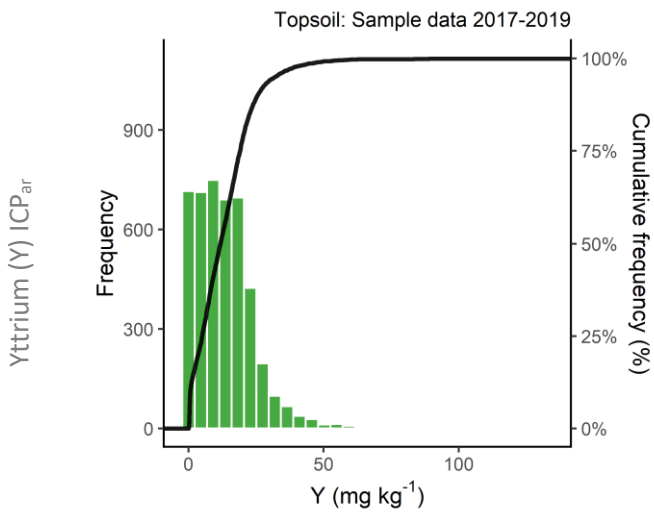
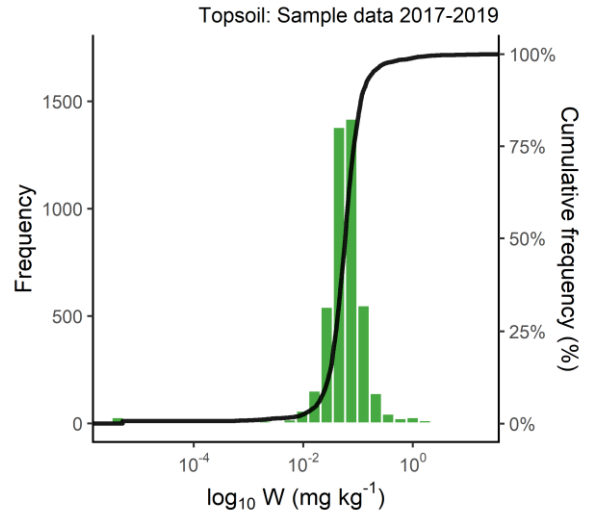
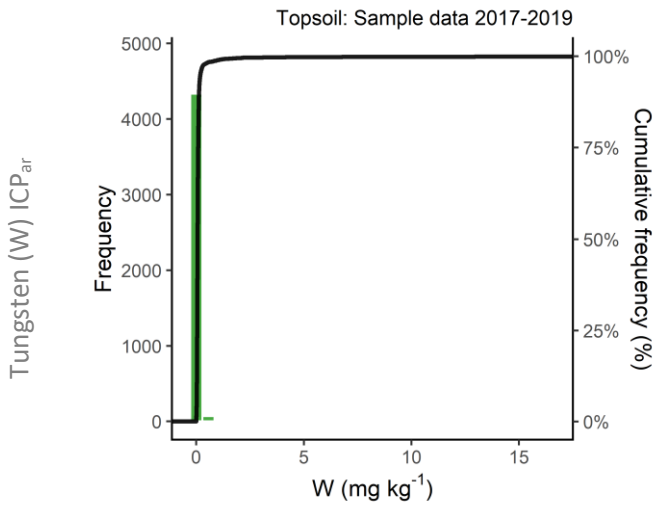


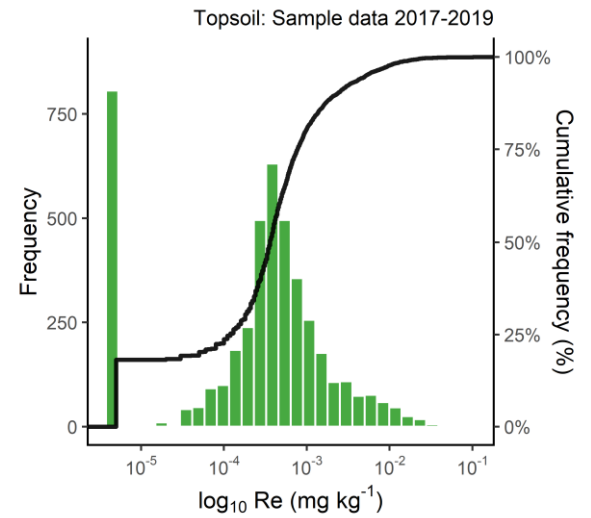
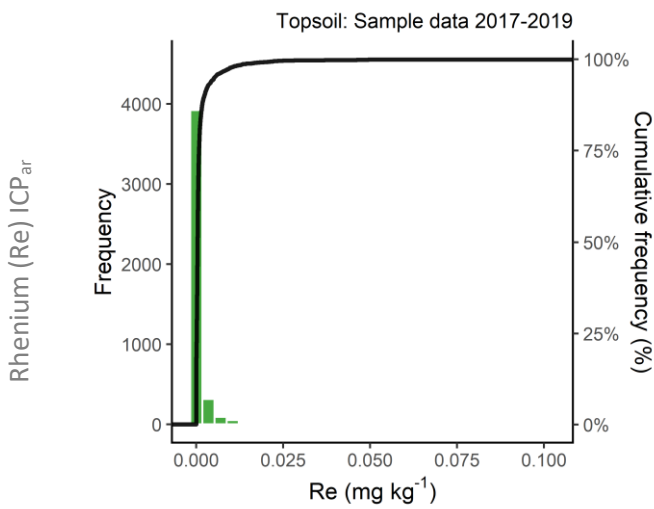
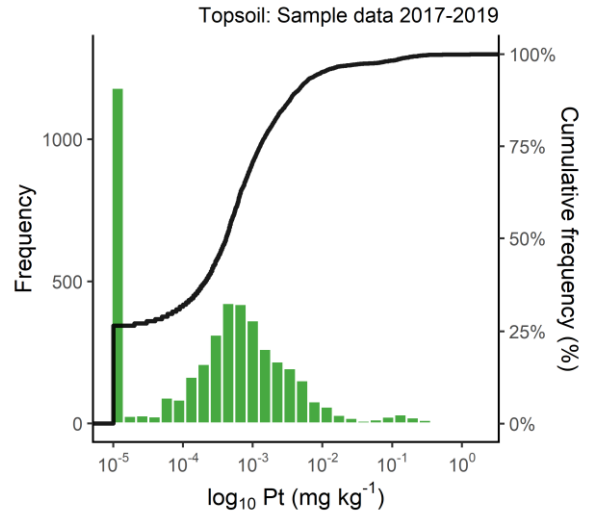
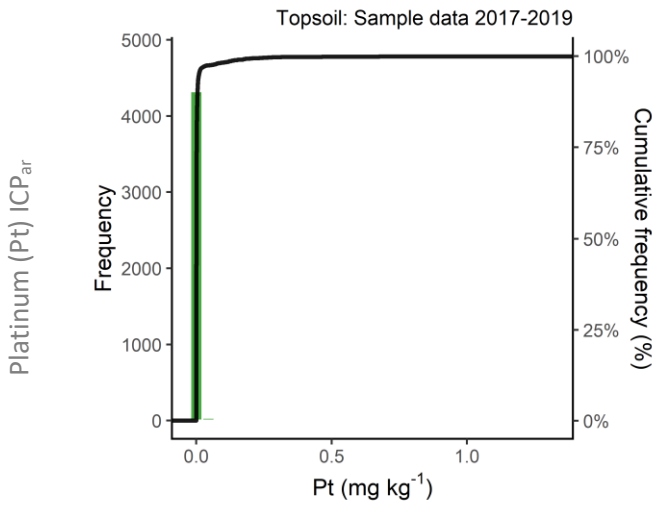
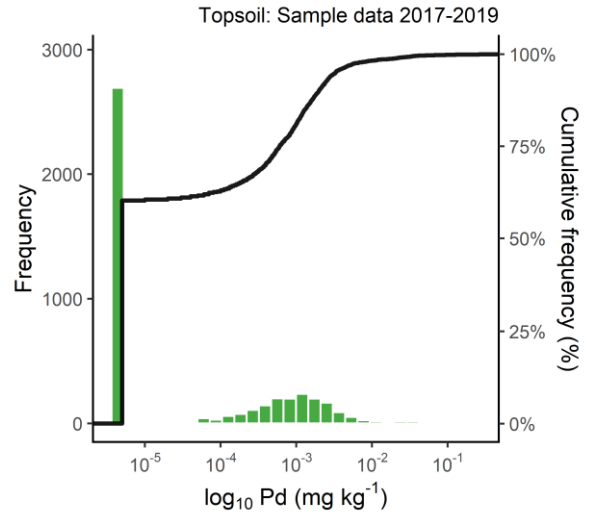
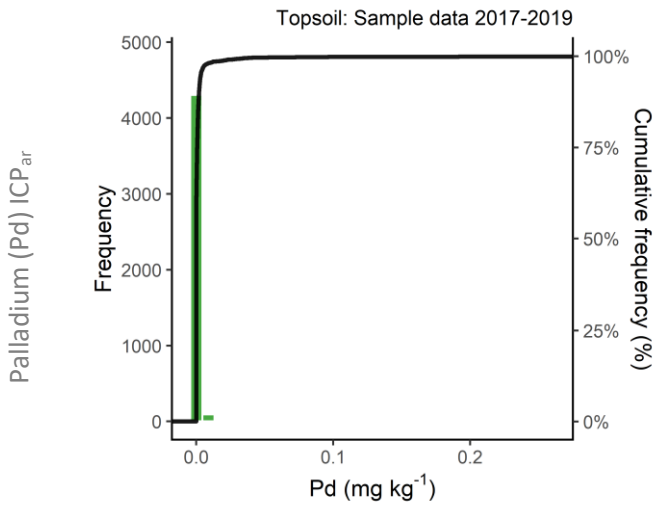
Selenium (Se) ICP<sub>ar</sub>













## 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:HNO<sub>3</sub>) 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 aluminosilicate 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.*

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
<b>Bismuth</b>	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
<b>Rhenium</b>	Re	ppm	0.0002	50
Sulphur	S	%	0.01	10
Antimony	Sb	ppm	0.005	10000
Scandium	Sc	ppm	0.005	10000
<b>Selenium</b>	Se	ppm	0.003	1000
Tin	Sn	ppm	0.01	500
Strontium	Sr	ppm	0.01	10000

ALS Minerals | Geochemistry IDA Business Park, Dublin Road, Loughrea, County Galway, H62 PN80, Ireland  
 Phone: 091-841741 Email: [www.alsglobal.com](http://www.alsglobal.com)

Page 2 of 3

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

### 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:

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

### 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 CaCl<sub>2</sub> 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

