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on behalf of Geological Survey Ireland

Tellus geochemical survey: QA-QC for deeper topsoil data from the Dublin urban area (G8 Block)

Report number: AES-24-G8S001

Document Information

Report title:	Tellus geochemical survey: QA-QC for deeper topsoil data from Dublin urban area (G8 Block)
Report number:	AES-24-G8S001
Current Document version:	3.0
Date:	18/07/2024

Prepared By	**Date**	**Comment**
V. Gallagher	29/02/2024 – 18/07/2024	Versions 1 - 3

Contributions/Review By	**Date**	**Comment**
V. Lowe	28/03/2024	Version 1.1
V. Lowe	28/03/2024	Version 2.1

Approved By	**Date**	**Comment**
J. Mather	18/07/2024	Final version

Version History

Ver. No.	**Ver. Date**	**Comment**	**Revised By**
1.1	28/03/2024	Minor edits and additional material	V. Lowe
1.2	03/04/2024	Minor edits and reformatting.	V. Gallagher
2.1	24/06/2024	Minor edits	V. Lowe
3.0	18/07/2024	Final version	V. Gallagher

Executive Summary

This report accompanies the publication of data and maps that present the inorganic geochemical data for deeper topsoil samples in the Dublin urban area. Samples were collected in 2021, as part of the Tellus geochemical survey project of Geological Survey Ireland.

Data are reported here for 877 sites distributed at a typical density of four sites per km^2 and covering an area of just over 200 km^2 (0.29 % of the country).

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

Acknowledgements

Aurum Exploration Ltd. gratefully acknowledges the successful award of *Provision of soil geochemical sampling and data QA/QC services for the Tellus programme* services tender by Geological Survey Ireland in April 2023.

This technical report is a data deliverable within this wider contract, compiled by Aurum Exploration Ltd. on behalf of our client Geological Survey Ireland, a division of the Department of Environment, Climate and Communications.

Aurum Exploration would like to express sincere appreciation to all those who contributed to the successful completion of this report, and in particular for the collaborative efforts between specialist contractors and client contributors, who dedicated their time, expertise and commitment to excellence to deliver this report and accompanying data and publications.

Furthermore, Aurum Exploration 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 associated with the Tellus programme.

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

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Introduction

Geological Survey Ireland is conducting a flagship project to sample and measure the geochemical characteristics of the surficial environment of Ireland. The Tellus project geochemistry workstream commenced in 2011. Its aim is to produce spatial data to determine the geochemical baseline of 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. At the time of publication national coverage of soil sample acquisition is set to be completed in 2024.

This report describes all aspects of data associated with deeper topsoil samples, denoted sample type 'S', collected from four survey sites per km^2 in the Dublin urban area. 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 analysis is confounded by uncertainty. Using reputable laboratories with accredited analytical and other procedures has been afforded the highest priority, yet it is still essential to assess the data in order to examine the reliability of the results and ensure that they are fit-for-purpose. To this end the geochemistry programme has employed a range of internal quality control (QC) procedures based on recommentations for comparable geochemical surveys (Plant *et al*., 1975). Broadly, these comprise:

- collection of field duplicate samples and preparation and analysis of field duplicate and analytical replicate samples;
- randomization 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 and
- use of analytical laboratory duplicates.

The trueness of the analytical results has been primarily assessed using certified reference materials, by reference to its accepted (statistically validated) element concentrations. 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 sample data is assessed using a series of randomly distributed duplicate and replicate samples to apportion the analytical variance to different sources.

Deeper topsoil samples

Sampling and sample summary

Survey design and sample locations

Maps displaying the survey extent and sample site locations of deeper topsoil samples are shown below (Map 1 and Map 2). The survey design is a systematic one based on a predefined fishnet of 500 m by 500 m 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 and 882 grid cells were defined for the Dublin urban area. Five of these did not yield samples, giving a total of 877 sample sites in the survey area, at a typical density of four samples per square kilometre.

In the urban environment it is difficult to adhere to the standard Tellus regional soils distance criteria (nominally >100 m from any mapped or observed minor feature and >200 m from more significant features such as dual carriageway roads and quarries). The following criteria were employed for urban 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 if possible be greater than 125 m from the edge of the 500 m by 500 m survey grid cell (except for coastal survey grid cells);
- samplers should seek to sample least disturbed, unbuilt ground available that is most central to the 500 m x 500 m survey grid cell and that best reflects the dominant land use represented by the wider survey grid cell;
- a soil sample site should not be directly under any trees or bushes or along the edges of an area of soil (e.g. beside paths, walls, railings, flower beds, etc.);
- a soil sample should not be taken from obviously imported or recently disturbed areas of soil (e.g. flower beds, raised beds, etc.;
- samples should not be taken across different areas of soil, even if they are proximal to one another and the same land use type;
- if space is limited, for example on a narrow grass verge, and samples cannot be collected in the normal format, i.e. auger holes arrayed in a square, then the auger holes should be distributed evenly, with GPS recording the location of the most central hole.

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

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

Details of the standard operating procedures and field sampling logistics have been documented internally by the client.

Summary of regular and control samples by field hundred batch

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

In each field batch of a hundred numbers, 84 were allocated to true soil sample site locations. The remaining 16 were set aside to be allocated to a variety of quality control samples (QCS). In summary:

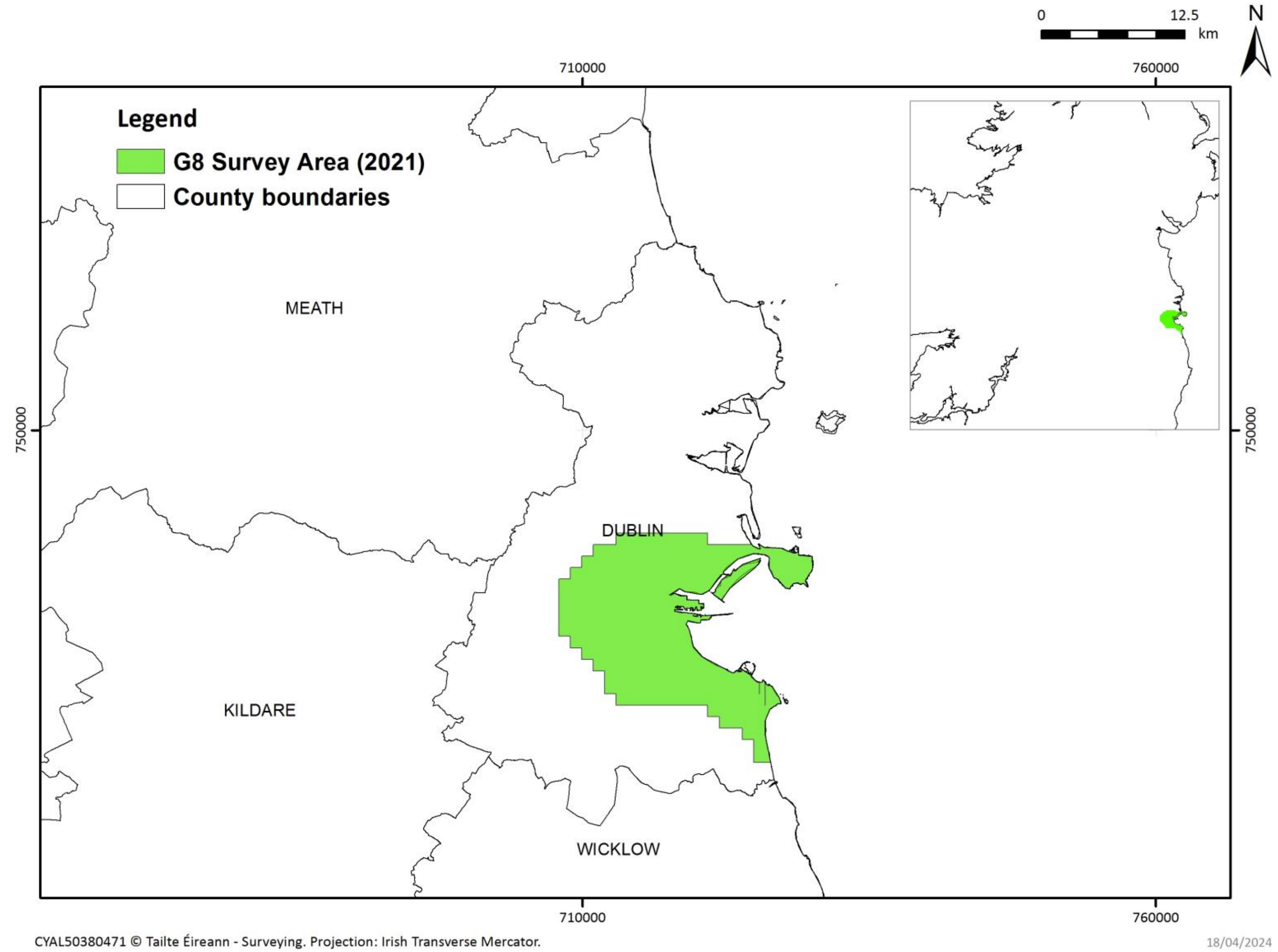
- Four sets of field duplicates (DUP) were collected in each batch, denoted duplicate pairs A-B, C-D, E-F and G-H, with each pair collected from a single site. DUPA, DUPC, DUPE and DUPG are treated as true samples for the purpose of the survey.
- Each duplicate site number has a corresponding replicate or subsample (SS) number; the duplicate sample was subsampled in the laboratory to create the replicate sample, which was analysed blindly to the analytical laboratories. These replicate samples are denoted SSA, SSB, SSC, SSD, SSE, SSF, SSG and SSH. For example, a quartet of DUPA, DUPB, SSA and SSB together provide four results from a single sample location. The data from duplicate and replicate samples are used to evaluate data variability.
- Four sample numbers are reserved for a selection of standards (STD or analytical reference materials, including certified reference materials (CRMs) and secondary reference materials (SRMs). These are used as quality control samples (QCS) for data quality assurance (QA) and quality control (QC) procedures.

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

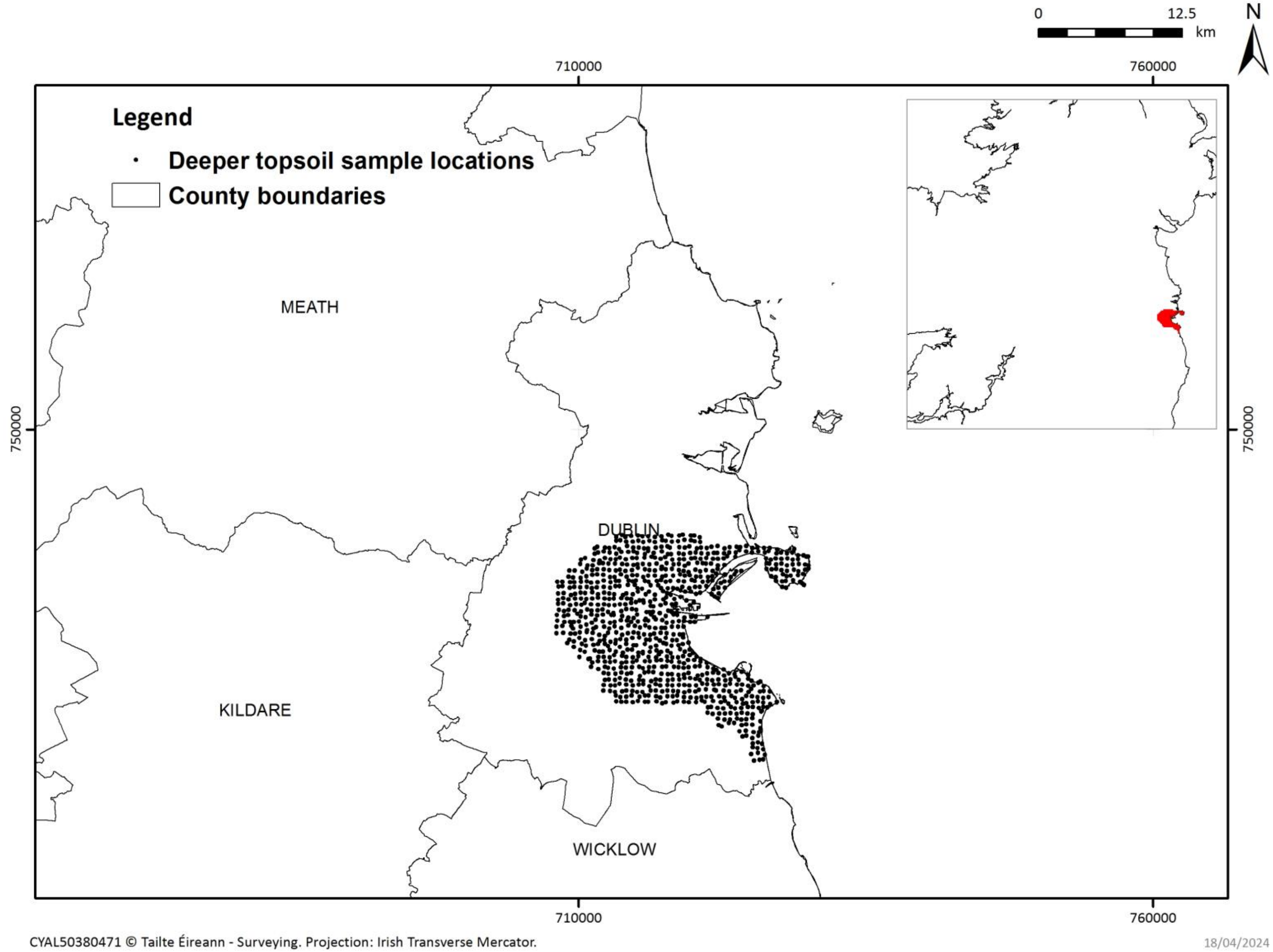
Table 1 Summary of QCS by field hundred batches.

(CRM numbers refer to ICPar analysis only – only SRMs were used for pH and LOI)

Random number checklist number	Field hundred batch	Sample ID range from	Sample ID range to	Sampling date from	Sampling date to	*n* samples in field hundred batch	*n* sample sites in field hundred batch	*n* blind CRMs	*n* blind SRMs	*n* DUP and SS QCS
1	6700xx	670001S	670100S	08/06/2021	05/07/2021	100	84	1	3	16
2	6701xx	670101S	670200S	14/06/2021	22/06/2021	100	84	1	3	16
3	6702xx	670201S	670300S	14/06/2021	07/07/2021	100	84	2	2	16
4	6703xx	670301S	670400S	21/06/2021	06/07/2021	100	84	1	3	16
5	6704xx	670401S	670500S	21/06/2021	19/07/2021	100	84	1	3	16
6	6705xx	670501S	670600S	29/06/2021	12/07/2021	100	84	2	2	16
1	6706xx	670601S	670700S	07/07/2021	28/07/2021	100	84	1	3	16
2	6707xx	670701S	670800S	05/07/2021	02/09/2021	100	84	1	3	16
3	6708xx	670801S	670900S	14/07/2021	03/09/2021	100	84	2	2	16
4	6709xx	670901S	671000S	21/07/2021	14/09/2021	100	84	1	3	16
5	6710xx	671001S	671099S	19/07/2021	16/09/2021	53	37	1	3	16



Map 1 Survey campaign area G8.



Map 2 Deeper topsoil sample locations for campaign area G8.

Soil sample preparation

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

Soil samples were collected in Rilsan® PA11 nylon resin bags, which were sealed with plastic ties. Samples were packaged into Euro stacking crates in numerical order and transported to the laboratory contracted to undertake sample preparation. Sample preparation was conducted at ALS Minerals Ltd. in Loughrea, Ireland.

Upon receipt, samples were logged into the laboratory's information management system (LIMS). Each sample was then removed from its bag and spread out into a large aluminium tray. Trays were placed in warming ovens to dry at c. 30 ˚C. The dried sample was then placed in a heavy-duty plastic bag and disaggregated using a wooden mallet, taking care not to break up lithic clasts. Disaggregation was completed, if required, using a ceramic mortar and pestle. Duplicate samples were riffle split to create replicate subsamples. The disaggregated material was cone-and-quartered to obtain a representative sub-sample of *c.* 30 - 35 g suitable for agate ball milling. Excess unmilled material was bagged, labelled and boxed. The sub-sample was milled in a Fritsch agate planetary ball mill with Ø 20 mm-sized agate grinding balls at 300 rpm for 40 minutes to produce a milled or pulped sample for chemical analyses so that nominally 99% of sample is <53 µm and 95% of sample is <32 µm. The mills are operated under conditions that cause minimal sample heating and that ensure a final product particle size of <32 µm. Cone-and-quartered sample splits of the milled material were prepared at the same time for the following analytical methods: LOI at 450°C, ICPar and XRFS. Sample splits of coarse fraction (<2 mm) fraction were also prepared for pH analyses.

Condition of samples submitted from the field contractor

A total of 877 survey grid cells were sampled from 08 June to 16 September 2021. Overall, the weather did not cause any significant issues in terms of sampling. Subsequent handling was made easier than was the case in Tellus campaigns prior to 2020 by the use of Rilsan® bags for collection, obviating the need for drying or significant rebagging by field teams before dispatch to GSI. All samples received by GSI were in an appropriate state for onward transfer to the preparation laboratory.

Sample splits prepared for analyses

Sample split prepared for pH analyses

Subsamples prepared for soil pH analyses were dried, disaggregated and sieved to <2 mm but not milled. Typically, just over 20 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 ICPar multi-element analyses

Subsamples of prepared (disaggregated, sieved and milled) samples and reference materials were prepared for ICPar multi-element analyses. Typically, 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.

Sample split prepared for XRFS multi-element analyses

Subsamples of prepared (disaggregated, sieved and milled) samples and reference materials were prepared for XRFS multi-element analyses. Typically, 13 g of sample mass were provided in a labelled securitainer, enough for the 12 g required to make a pressed pellet for analysis. 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, 3 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 within the randomized sequence of samples, as per instructions, for blind submission to the analytical laboratory.

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

Soil chemical analyses

Soil samples were analysed by several methods:

- soil loss-on-ignition at 450°C;
- soil pH by $CaCl_2$ slurry and
- multi-element analyses for a range of major, minor and trace elements by ICP following *aqua regia* digestion ("ICPar").

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

Tellus multi-element data are requested to be reported uncensored, *i.e.* without truncation or replacement by a fixed value below or above the limits of detection or reporting. A reported dataset commonly includes negative values. The advantages of this are manyfold for regional geochemical data. For Tellus, all interpolation spatial mapping makes use of uncensored data, which provide a continuous variable dataset. All statistical measures and data transformations cope better 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 have 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 weighed 1 g sample is combusted in a tared, pre-ignited crucible in a temperature-controlled Vecstar benchtop muffle furnace at 450°C for four hours. It is then cooled in a controlled (moisture-free) atmosphere and re-weighed. LOI is calculated as the proportionate mass difference before and after combustion.

Soil pH by $CaCl_2$ slurry

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

Method code OA-ELE07 is used for soil pH analyses of prepared (disaggregated and sieved) <2 mm fraction soil samples. A weighed 5 g sample is mixed with 12.5 mL of 0.01M $CaCl_2$ and placed on a reciprocal shaker for *c.* 5 minutes to form a slurry. In the case of hygroscopic soils and salts or other problematic matrices, a greater degree of dilution, standardized at 20 mL $CaCl_2$, may be applied. The soil suspension is allowed to settle for *c.* 1 hour. A pH electrode and automated titrator (794 Basic Titrino, Titrando 905 or Xylem TitroLine 7800) 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(-AES/-MS) analyses of 1 g prepared (milled) sub-sample after aqua regia extraction

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

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 1053 samples, including QCS, were submitted to ALS Minerals Ltd. in November 2021 for chemical analysis. Samples were analysed across five laboratory batches of *c.* 200 samples per batch (Table 2). Data for 1053 sample IDs by LOI were reported to GSI by 20/10/2023. Data for 1053 sample IDs by pH were reported to GSI by 17/10/2023. Data for 1053 sample IDs by ICPar were reported to GSI by 17/10/2023.

Table 2 Laboratory work orders for soil analyses

Analysis	ALS Work Order	Reporting date	Sample ID	
			From	To
ICPar	LR22272933	17/10/2023	670001S	670200S
ICPar	LR22265983	10/02/2023	670201S	670400S
ICPar	LR22252256	17/10/2023	670401S	670600S
ICPar	LR22249920	17/10/2023	670601S	670800S
ICPar	LR22286720	12/12/2022	670801S	671099S
LOI	LR22266120	20/10/2023	670001S	670200S
LOI	LR22286714	21/11/2022	670201S	670400S
LOI	LR22252262	20/10/2023	670401S	670600S
LOI	LR22249923	24/10/2022	670601S	670800S
LOI	LR22272930	20/10/2023	670801S	671099S
LOI	LR22327913	28/11/2022	670819S	670819S
pH	LR22272927	12/05/2023	670001S	670200S
pH	LR22265936	21/11/2022	670201S	670400S
pH	LR22252260	17/10/2023	670401S	670600S
pH	LR22249921	21/10/2022	670601S	670800S
pH	LR22286716	12/05/2023	670801S	671099S

Table 3 Deeper topsoil ICPar analytes, concentration units, methods, lower limits of detection and reporting (LLD/LRL), upper reporting limits (URL), accreditation statuses.

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

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

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

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

Table 4 Deeper topsoil pH ($CaCl_2$) and LOI (450°C) analytes, concentration units, methods, lower limits of detection and reporting (LLD/LRL), upper reporting limits (URL), accreditation statuses.

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

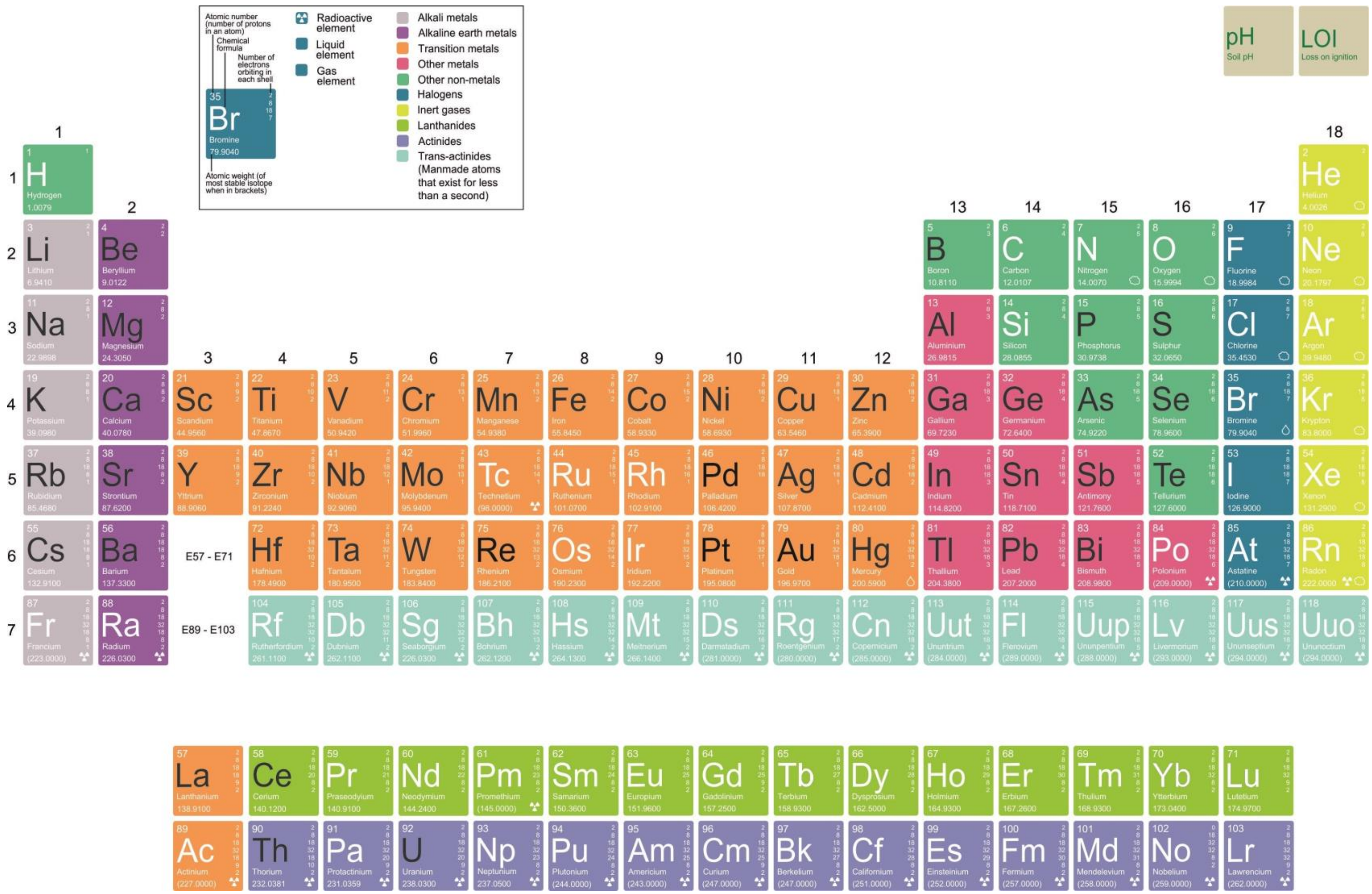


Figure 1 Graphic of the periodic table, with ICPar element analytes for deeper topsoil samples shown in black text, Soil pH ($CaCl_2$) and LOI (at 450°C) in green text. Adapted after http://www.sciencegeek.net/tables/PToE_basic.pdf

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, typically 20 m away from the original sampling location. It is used to assess the variability of the sampling process.
ii. **Replicate**: created in the laboratory by dividing a Duplicate sample into two identical parts, using a recognized subsampling method (e.g. riffle splitting). 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. For Tellus soil analysis, blanks are used by the laboratory for analytical quality control.

Randomization of sample identities

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

Randomization of sample identities allows the geochemist to check for quality concerns such as carry-over of high values (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. For the G8S samples, initial checks using QCS identified six separate incidences of sample switches. Most of these occurred during sample preparation but one switch involving LOI samples took place at the analytical stage. All errors were corrected and samples reanalysed as required, following which amended analytical certificates were issued..

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, four pairs of field duplicate samples (*i.e.* two samples collected from the same site) were collected: duplicate pairs A-B, C-D, E-F and G-H. 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 on what is considered the same site. There will necessarily be some compositional variance between the duplicate samples, and this will depend on soil type, geology and other factors, including anthropogenic influences.

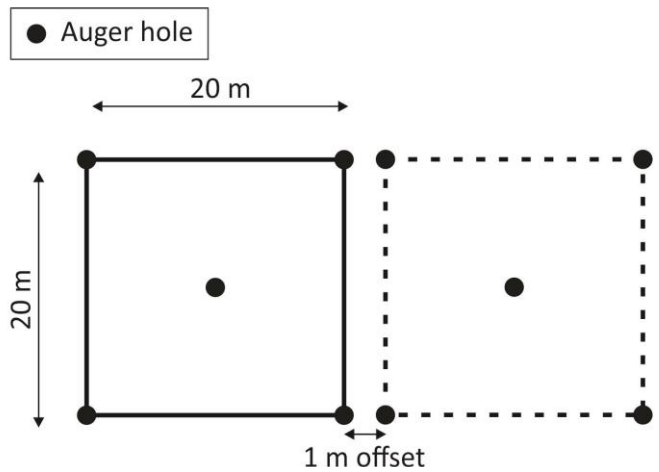


Figure 2 Diagrammatic plan for collection of a five-auger-hole composite soil sample and a field duplicate sample (indicated by dashed line pictogram).

For each of the samples denoted DUPA, DUPB, DUPC, DUPD, DUPE, DUPF, DUPG and DUPH, each sample was riffle split in half to produce two subsamples, one retaining the original DUP label (i.e. DUPA, DUPB, DUPC, DUPD, DUPE, DUPF, DUPG and DUPH), the second labelled as a replicate sample, denoted SSA, SSB, SSC, SSD, SSE, SSF, SSG and SSH.

The relationship between duplicate and replicate samples is displayed diagrammatically in Figure 3. The quartets of samples from the field duplicate sample sites are used to statistically evaluate the data variability (i) between sample sites, (ii) between samples on the same site and (iii) within individual samples.

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 not identified as control samples to the analytical laboratory.

Note that, for each duplicate pair in a field batch, by convention analytical data for DUPA, DUPC, DUPE and DUPG 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.

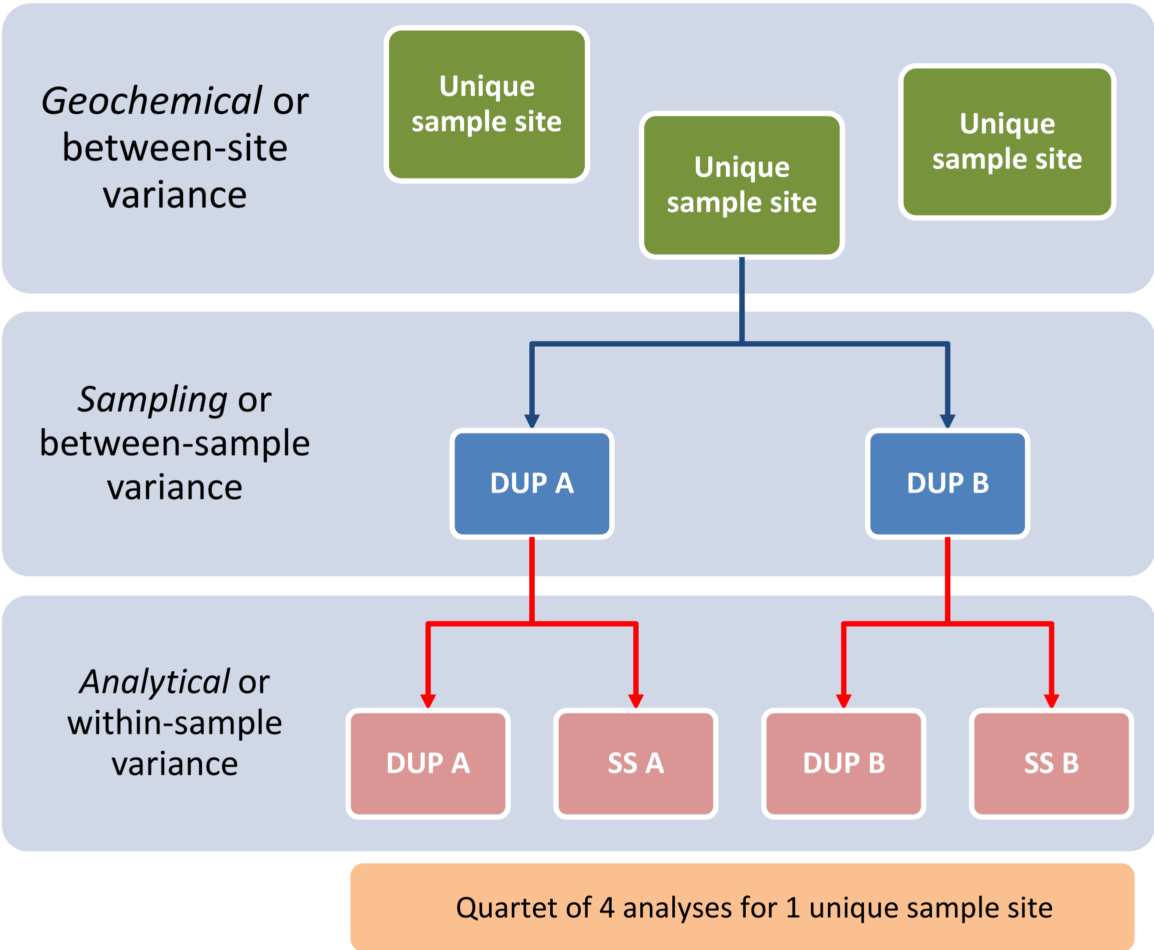


Figure 3 Diagram to show the relationship between field duplicates ("DUP") and replicate ("SS") samples, used to apportion data variance.

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. Mean paired relative difference (MPRD) values are also calculated for each DUP-DUP and DUP-SS pair, providing a numerical estimate of variation for each element within each duplicate site and within each duplicate sample, respectively.
- Data analysis using charts to visualize the data and to investigate anomalous data.

- Undertaking a hierarchical fully nested analysis of variance (after Sinclair, 1983) to quantify the proportions of data attributable to between-site, between-sample and within-sample variance.

A total of 176 samples of duplicates / replicates from 44 unique sample sites (quartets of data) across the survey area are available to assess in this way.

Review of conditionally-formatted and MPRD data for Duplicate-Replicate quartets

Data for Duplicate-Replicate quartets are conditionally formatted to flag quartet values that are greater or less than one standard deviation of the mean of that quartet. This allows an assessment of variation within quartets using measured concentrations, rather than relative (percentage) variations, which can be very large at low concentrations owing to analytical uncertainty. Sample misidentifications are normally readily identified using this approach since significant absolute variation in concentrations will generally be observed across the whole range of elements in the sample, rather than randomly among a limited number of elements as is typical of most samples. This approach also helps to flag potentially poor individual element analyses. For the G8S data, one DUP-REP quartet raised concerns. This includes samples 671063S(DUPC), 671072S (SSC), 6710052S (DUPD) and 671057S (SSD). The reported concentrations of several analytes in DUPC and DUPD are quite different, e.g. Ba, Ca, Cu, Mn and Pb, raising the possibility of a sample switch. As the compositions of the respective replicate samples (SSC and SSD) matched their duplicate counterparts, any such switch would have occurred prior to splitting of the duplicate sample to form the replicate sample. A detailed review of the samples was undertaken, involving examination of remaining sample splits and a full examination of the sampling records. Data for the G8A samples was also reviewed – these display similar if less pronounced compositional differences between DUPC and DUPD samples. No unambiguous evidence of sample misidentification was found and the observed variation between DUPC and DUPD data may best be ascribed to within-site variation in soil composition. Inspection of conditionally formatted data for the other 43 DUP-SS quartets did not identify any systematic data errors that could be attributed to sample misidentification or systematic analytical error.

MPRD % values are calculated for each DUP-DUP and DUP-REP pair and are an expression of the percentage variation from the mean of the pair. For example, for the DUPA – DUPB pair, the equation is ((DUPA-DUPB)/(mean DUPA-DUPB)*100). The within-sample (DUP-SS) MPRD % calculations for G8S reveal consistently large positive and negative values for some elements, for many or even most of the pairs: Au, B, Bi, Cs, Hg, In, Na, Pb, Pd, Pt, Re, Sb, Sn, Ta and W. The within-sample variation arises from the splitting of the original duplicate sample to form the replicate and the subsequent analysis of both. Elements such as Au, Na, Sn and W are prone to nugget effects and/or potentially incomplete digestion of host minerals in *aqua regia*, leading to potentially significant variation in measured concentrations between pairs. Elements such as Au, Hg, In, Pd, Pt, Re and Ta are present in very low concentrations so that analytical uncertainty can give rise to significant variation in measured concentration between samples in a DUP-REP pair.

There are numerous elements that have relatively large between-sample (DUP-DUP) MPRD % values for a range of sites: Au, Ag, As, Bi, Ca, Cu, Hg, In, Mn, Mo, Na, P, Pb, Pd, Pt, Re, S, Sb, Se, Sn, Sr, Ta, Ti, W, Zn. As with the within-sample MPRD %, for some elements the relatively large within-site MPRD reflects very low measured element concentrations and accompanying analytical uncertainty. For others, however, the data suggest significant degree of compositional variation within some individual sites: Ca, Cu, Mn, Pb, Sr and Zn.

Duplicate-Replicate data analysis using charts

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). Charts include (i) DUP-DUP and DUP-SS X-Y plots, faceted both by laboratory batch and field batch number, (ii) residual values (difference in concentration of DUP and corresponding DUP or SS sample), also faceted by laboratory and field batch numbers, and (iii) plots of MPRD % (DUP-DUP and DUP-SS). Each chart is inspected to identify samples that do not exhibit a close equality and to follow up on samples where a sample misidentification is suspected. For elements where the between-sample (or 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 there will be a greater scatter in duplicate-replicate (DUP-SS) relationships. The charts are a visual expression of the tabulated conditionally formatted data and MPRD % data. All are available to download from www.gsi.ie/tellus.

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, apart from pH, the data are log_{10}-transformed (since many geochemical datasets are log-normally distributed) and therefore it is a requirement that there are no zero or negative concentration values. Censored data distorts the ANOVA analysis and so any control quartet containing censored data (*i.e.* below detection data substituted by a constant value) was not used in the analysis. Any incomplete quartet cannot be used; for example if one of the four duplicate or replicate results is missing or not determined, the quartet is excluded. Since pH values are already in log_{10} form, they are excluded from the log_{10} transformation and ANOVA analysis is carried out on the original pH data.

Most variables had data above the LLD for each of the 44 duplicate-replicate quartets (Table 5). Exceptions were Pt (40 quartets) and Ta (36 quartets). In the case of Pd, ANOVA analysis could not be completed. Where the within-sample variance is >4 %, the results are highlighted pale orange: bismuth (Bi), tin (Sn), potassium (K), tungsten (W), chromium (Cr), titanium (Ti), platinum (Pt), gold (Au), pH, indium (In) and tantalum (Ta). Elements for which the between-site (geochemical) variance falls below 80 % include zinc (Zn), platinum (Pt), gold (Au), pH, indium (In) and tantalum (Ta).

ANOVA approach and results

The ANOVA test results based on all available duplicate site data for the survey area are presented in Table 5 and graphically in Chart 1.

Only six out of the 54 analytes reported for ANOVA in the survey area dataset have the proportion of variance that can be attributed to between-site variance below 80 %, indicating that the data are generally suitable for regional mapping. Between-sample variance, as measured by the difference between duplicate samples on the same site, is less than 16 % for all but four analytes (Zn, Au, pH and In). The within-sample variance, as measured by the difference between duplicate and corresponding replicate samples, is above 4 % for 11 out of 54 analytes, indicating a degree of sample heterogeneity. These analytes include elements that exhibit nugget effects (e.g. Au) or have low extraction rates in *aqua regia* (Sn, Ti, W) or are otherwise prone to significant analytical variability owing to their generally very low concentrations (Pt). In the case of pH, between-site variance accounts for 64.64 % of the total, which is relatively low compared to that estimated for earlier survey blocks (G8A, G7A), for which between-site variance accounted for more than 89 % of the total variance. This reflects a higher degree of both between-sample variance and within-sample variance for G8S samples. Data for reference materials (see below "Assessment of RMs data") suggest analytical variance may be a significant contributor to this.

Table 5 ANOVA results for all duplicate site deeper topsoil data.

Sorted by descending between-site variance component. Where the within-sample variance is >4%, the results are highlighted pale orange.

		Variance component (100% sum)			
Variable	Method	Between site (%)	Between sample (%)	Within sample (%)	*n* quartets
Li	ICPar	96.91	2.63	0.45	44
Zr	ICPar	95.56	3.37	1.08	44
Na	ICPar	95.32	2.69	1.99	44
Mo	ICPar	95.17	4.08	0.76	44
Y	ICPar	94.91	3.72	1.37	44
P	ICPar	94.82	4.85	0.34	44
Be	ICPar	94.68	4.83	0.49	44
As	ICPar	94.43	4.50	1.06	44
Mg	ICPar	94.15	5.40	0.45	44
Cs	ICPar	94.07	4.47	1.46	44
V	ICPar	93.51	3.91	2.59	44
Sc	ICPar	93.32	3.96	2.72	44
Ni	ICPar	93.26	5.76	0.98	44
U	ICPar	92.56	6.84	0.60	44
Th	ICPar	92.11	6.17	1.72	44
Ca	ICPar	92.06	7.86	0.08	44
Sr	ICPar	91.36	8.43	0.21	44
LOI	LOI at 450˚C	91.28	7.74	0.98	44
Fe	ICPar	91.09	7.80	1.11	44
Ge	ICPar	90.89	5.74	3.37	44
Re	ICPar	90.85	7.28	1.87	44
Hf	ICPar	90.71	6.84	2.45	44
Te	ICPar	90.62	6.37	3.00	44
Mn	ICPar	90.60	8.52	0.88	44

Variable	Method	Variance component (100% sum)			*n* quartets
		Between site (%)	Between sample (%)	Within sample (%)	
Pb	ICPar	90.43	7.96	1.61	44
S	ICPar	90.19	9.36	0.45	44
Co	ICPar	90.16	8.43	1.41	44
Nb	ICPar	89.70	8.13	2.17	44
Ag	ICPar	89.26	9.06	1.68	44
B	ICPar	89.20	8.81	1.99	44
Sb	ICPar	88.75	7.43	3.82	44
Cd	ICPar	88.68	9.34	1.98	44
Ga	ICPar	88.49	8.12	3.39	44
Al	ICPar	88.22	7.82	3.95	44
La	ICPar	88.15	8.80	3.05	44
Bi	ICPar	87.26	8.53	4.20	44
Tl	ICPar	87.26	9.60	3.14	44
Ce	ICPar	87.05	9.37	3.58	44
Sn	ICPar	87.03	8.40	4.57	44
Rb	ICPar	86.95	9.14	3.90	44
Se	ICPar	85.91	10.15	3.94	44
Cu	ICPar	84.32	14.30	1.38	44
K	ICPar	84.14	10.02	5.84	44
Hg	ICPar	84.13	13.22	2.65	44
W	ICPar	83.76	9.55	6.68	44
Ba	ICPar	83.48	15.56	0.96	44
Cr	ICPar	82.54	10.76	6.70	44
Ti	ICPar	81.98	10.13	7.90	44
Zn	ICPar	79.95	18.45	1.61	44
Pt	ICPar	73.40	10.88	15.72	40
Au	ICPar	69.84	17.91	12.25	44
pH	pH $CaCl_2$	69.64	18.23	12.14	44
In	ICPar	61.86	16.52	21.62	44
Ta	ICPar	61.83	13.43	24.73	36

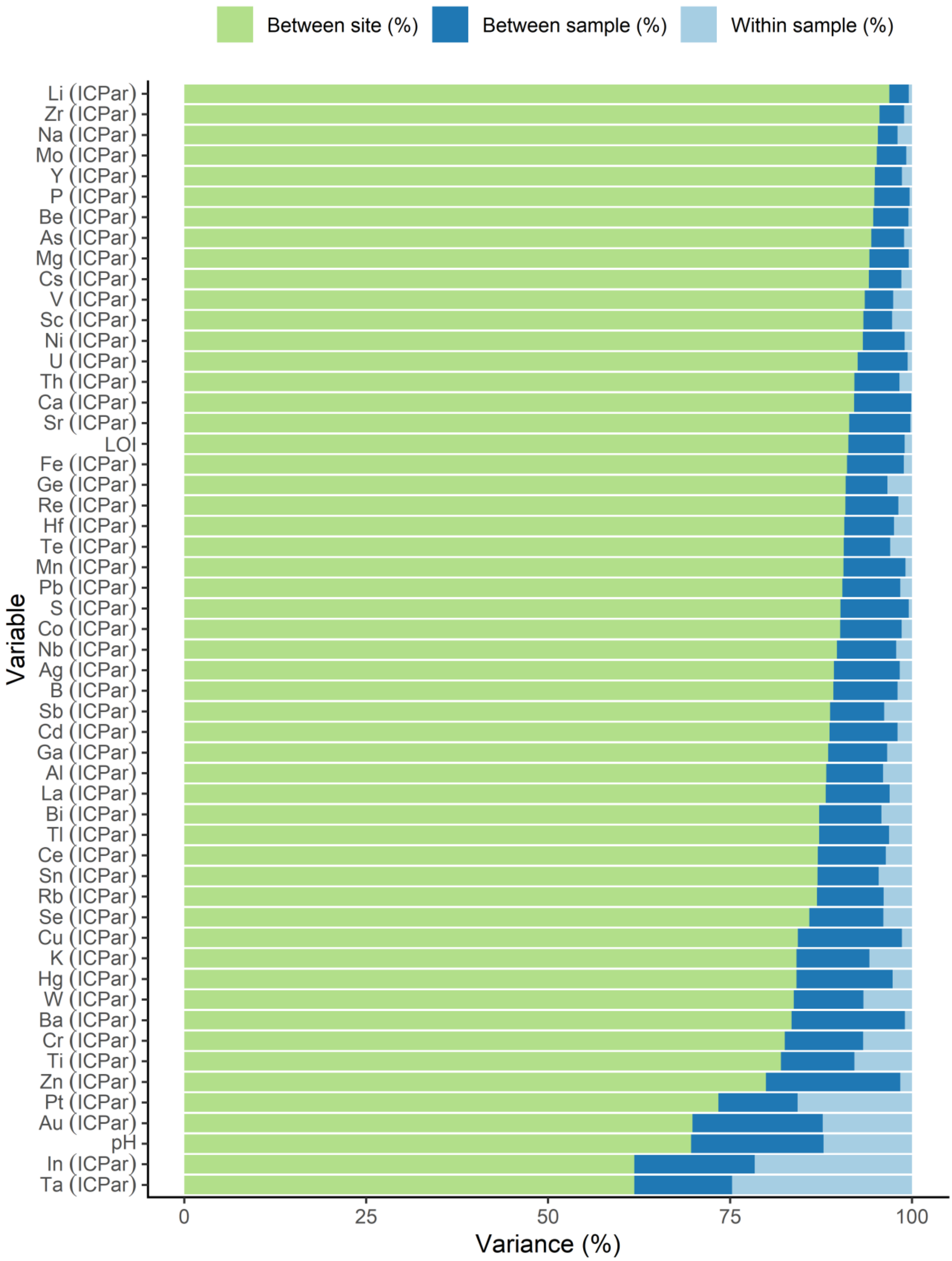


Chart 1 Stacked bar chart to display ANOVA results for all duplicate site deeper topsoil data.

Reference materials data

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

RMs comprise primary or certified reference materials (CRMs), purchased from suppliers with an accompanying certificate of elemental analyses, and secondary reference materials (SRMs) produced and used by the geochemical mapping programme. All are submitted blindly to the laboratory in order to assess the results without bias. In addition to these control samples, the laboratory has used its own "in-house" selection of blank sample material and CRMs. Together the RMs are a critical tool to evaluate data quality, not only for a given dataset, but also to tie together multiple datasets that may span years or decades and more than one analytical facility.

Concentration data for all RMs 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 6 and Table 7).

Table 6 In-house CRMs used for multi-element ICPar analyses

CRM name	CRM Manufacturer	Description
MRGeo08	ORE Research & Exploration	Blend of copper, zinc, nickel, molybdenum and lead concentrate mixed with granite, Australia.
GBM908-10	Geostats Pty Ltd.	Copper-gold oxide ore
OREAS 45f	ORE Research & Exploration	Blend of mineralized lateritic soil, barren lateritic soil and minor additions of gold and nickel ores, 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 7 In-house CRMs used for soil LOI analyses

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

Randomized and blind-to-laboratory RMs

A range of reference materials (RMs) was used, comprising CRMs and SRMs submitted blind to the analyst (Table 8 and Table 9**,** respectively) in a randomized order amongst other QCS and regular site samples.

Certified reference materials (CRMs)

Table 8 Blind CRMs used for ICPar 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, 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 developed from soil and stream sediment collected on the island of Ireland (Table 9). Bulk soil samples CARLST, CNLST, LDOWN, LGRAN, LMGPSH, MONPB, ORS, WWLPAL and WXSERP were collected in 2015 as part of a joint GSI-BGS initiative. YELC1 is a bulk stream sediment sample collected by GSI in 2017. APT, AST, SPT and SST are soil samples derived from several thousand individual Tellus site samples that were initially prepared by BGS and then discarded owing to collection-related QC failures. They were subsequently repurposed by BGS as SRMs for the Tellus project. The original 2 mm and milled A and S samples were sorted by visual inspection into silty (or mineral-rich) and peaty (or organic-rich) fractions, combined and then homogenized. These RMs are used for QA-QC of pH and LOI analyses.

Table 9 Blind SRMs used for ICPar multi-element, LOI and pH analyses

SRM name	Location co-ordinates (ITM)	Material type	Primary land uses	Stream order	Description	Stream drainage type
CARLST	722923E 807165N	Topsoil	Potato crop field (BDC1)		Silty soil derived from Lr Palaeozoic sandstone and shale till, overlying Carboniferous limestone	
CNLST	638777E 817560N	Topsoil	Grass moor/rough grazing (AC00)		Silty soil derived from alluvial deposit, overlying Carboniferous shale and limestone	
LDOWN	689129E 798798N	Topsoil	Arable land (BD00)		Silty soil derived from Lr Palaeozoic sandstone and shale till, overlying Silurian greywacke	

SRM name	Location co-ordinates (ITM)	Material type	Primary land uses	Stream order	Description	Stream drainage type
LGRAN	697129E 695189N	Topsoil	Pasture (BAB0) and agricultural grassland (BA00)		Sandy soil derived from granite till, overlying quartz diorite	
LMGPSH	603645E 827212N	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	
MONPB	687223E 824492N	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	
ORS	582724E 600936N	Topsoil	Agricultural grassland (BA00). Teagasc Moorpark agricultural research grassland, field 38C		Silty soil derived from Devonian sandstone (ORS) till, overlying Carboniferous Waulsortian limestone	
WWLPAL	696954E 708922N	Topsoil	Ploughed field. Arable land (BD00)		Till derived from Lr Palaeozoic sandstone and shale overlying granite	
WXSERP	706259E 666211N	Topsoil	Grass moor/rough grazing (AC00)		Silty clay topsoil overlying serpentinite and Ordovician slate and phyllite	
YELC1	533754E 809611N	Stream sediment <150 µm	Grass moor/rough grazing (AC00) to east with no livestock present. Coniferous woodland – established	Yellow River. 2^{nd} order.	Stream sediment overlying equigranular granodiorite	Small stream <3 m wide

SRM name	Location co-ordinates (ITM)	Material type	Primary land uses	Stream order	Description	Stream drainage type
			(AEBB) to the west of site and deciduous woodland – established (AEAB) along stream bank			
APT	n/a	Topsoil	Diverse land uses in North Midlands region		Peaty soil, mainly overlying Lr Carboniferous limestone and clastic rocks	
AST	n/a	Topsoil	Diverse land uses in North Midlands region		Silty soil, mainly overlying Lr Carboniferous limestone and clastic rocks	
SPT	n/a	Topsoil	Diverse land uses in North Midlands region		Peaty soil, mainly overlying Lr Carboniferous limestone and clastic rocks	
SST	n/a	Topsoil	Diverse land uses in North Midlands region		Silty soil, mainly overlying Lr Carboniferous limestone and clastic rocks	

Assessment of RMs data

Data are monitored by statistically summarizing and charting data batches.

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

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

A well-homogenized reference material would be expected to display a normal distribution of results around an accepted reference value, for each determinand. To verify this assumption, a histogram of all results is plotted for each RM to evaluate the spread of analytical data. Moreover, the control charts display warning limits. In a statistically normal dataset, approximately 5% of samples will fall outside of the warning limits and, 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 less-than (“<”) the LLD are plotted as “-LLD” and are essentially disregarded.

Control charts

Shewhart-style control charts (Shewhart, 1931) have been created for all blind and laboratory in-house RM data where date and time stamp data are available, i.e. for ICPar and pH data but not LOI data. The G8 soil samples were collected in 11 field batches, thus giving a total of 44 blind RMs, since each field batch allows for four RM insertions. For ICPar analyses, these were split between 14 CRM samples and 30 SRM samples; for pH only SRMs were used. As the Tellus RMs utilized for the QC programme for ICPar analyses include five individual CRMs and 10 individual SRMs (Table 8 and Table 9), the 44 RM insertions allowed for only a limited number of samples of each RM to be inserted, thus restricting the scope and utility of the QC data. To mitigate this, data for RMs inserted into the field batches for the G7 survey, for which laboratory analyses were carried out directly before the G8 analyses, have been combined with the G8 RM data to provide an adequate number of analyses for each RM. The G7 soil samples were collected in 12 field batches, giving 48 blind RM samples. These were split between 16 CRM and 32 SRM samples. Thus, combining the ICPar data for G7 with that for G8 gives a total of 92 RM analyses, of which 30 are CRM analyses and 62 SRM analyses. Multiple analyses of five in-house CRMs were carried out by the laboratory as part of each analytical batch, giving a total of 142 analyses of in-house CRMs. For pH analyses, 44 SRM analyses, eleven each of four individual SRMs, were completed for G8S.

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

A normal data distribution is not required in the calculation of control limits and these control charts are robust for non-homogenous samples. Infrequent, one-off exceedances of the upper and lower control limits (process mean ± 3 sequential deviations, dark blue horizontal lines on control chart) are termed failures but are statistically acceptable. Exceedances of the warning limits (process mean ± 2 sequential deviations, medium blue horizontal lines) are more common. One exceedance constitutes a warning, while two or more consecutive data points lying outside a limit constitute a failure. The lightest blue horizontal lines on the control charts are process mean ± 1 sequential deviation. They are useful reference lines against which drift and shift can be observed but do not constitute a formal limit used for monitoring of the analytical process quality. These control charts are inspected for trends in the sequence and/or multiple analytes exhibiting patterns of behaviour. The main quality checks are for multiple analytes of the same sample presenting warning or failures and the periods of time for the analyses where multiple sample warnings or failures are seen. If the method LLD is ≥ upper control limit then any description of control failures is meaningless. These are not described in this report. However, it is still useful to assess the reproducibility of data results below the LLD in an uncensored dataset. A summary of flagged quality issues for ICPar analyses is presented in Table 10 (blind RMs) and Table 11(in-house CRMs) below.

Blind RMs: ICPar analyses

Most of the observed violations (Table 10) are classed as single analyte failures/warnings or multiple analyte 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. Five such events were recorded where at least two analytes fell outside of lower/upper control limits (type 1_{3S} violation) or successive analyses breached warning limits (type 2_{2S} violation). In some cases the recorded failures were observed for analytes present in generally low concentrations (Pd, Pt), typically close to or below the method LLD, and where greater variability is therefore to be expected. For others, the failures appear to reflect significant analytical variation that has given rise to relatively high or low concentrations for numerous analytes. Two observed events raise caution about potential implications for data quality within certain data ranges. These events do not invalidate reported data but caution users that confidence is somewhat lower than for the rest of the data. This increased uncertainty is not quantified. Users are cautioned to treat affected data accordingly.

- Between 20.36 on 25/02/2022 and 01.53 on 26/02/2022 three consecutive, multiple element failures and warnings occurred. Sodium (Na) failed or exceeded warning limits in three instances, while Se and V failed in one instance. This period was also flagged for failures in in-house RMs (see below). Affected batch: LR22026808, involving G7S samples only. Possible cause: poor analytical performance.
- Between 16.34 and 17.08 on 11/06/2022 element failures (positive type 1_{3S} violations) were recorded for silver (Ag) and cerium (Ce) and there were multiple-element warnings (positive type 2_{2S} violations) among several RMs for antimony (Sb), arsenic (As), caesium (Cs), lanthanum (La), lead (Pb), mercury (Hg), molybdenum (Mo), rhenium (Re), silver (Ag), tantalum (Ta), tellurium (Te), thorium (Th), titanium (Ti), thallium (Tl), vanadium (V) and yttrium (Y). Several other elements also display relatively high concentrations for this period without breaching warning limits. This period was also flagged for failures in in-house RMs (see below). Affected batch: LR22136773, involving G7S samples. Possible cause: poor analytical performance.

Blind RMs: pH analyses

The rationale for combining G7S and G8S RM data for ICPar analyses, i.e. the relative lack of data for individual RMs, does not apply to pH RMs as there are only four of these distributed among the 44 SRM insertions. There are thus more than sufficient G8S data to generate a useful control chart for each SRM.

The blind SRMs included for pH analysis have, like pH samples themselves, been sieved to ≤ 2 mm. They are relatively heterogeneous compared to milled samples used for ICPar and LOI analysis. This contributes to the significant imprecision or scatter generally observed in pH SRM data. This in turn results in relatively high standard deviations about the mean and, thus, relatively wide control limits. An added complication for G8S data is that the pH samples and SRMs were analysed over two distinct periods, in October 2022 and March 2023. Data for AST and SST are very similar for both periods but data for APT and SPT, the peaty material, differ significantly. For October 2022, the mean pH value for both APT and SPT is 3.58; for March 2023, the mean pH values for APT and SPT are 4.02 and 4.06, respectively. Over 90 % of the G8S samples have measured pH values of 6.0 or above so this observed variation in pH values for peaty SRMs between the different measurement periods may have limited relevance for most G8S sample data. Despite this variation and the general imprecision of the pH data, control charts for the four pH SRMs (Appendix A) display only one failure (type 1_{3s} violation for APT) and four warnings (APT, SPT (2) and AST) (Table 10). None of these, in itself, raises concerns about the pH data.

A plot of Tellus pH SRM data collected to date (Figure 4), analysed for both A and S sample campaigns, indicates that the reported data for G8 are significantly higher than those for previous survey blocks, including G7, for the silty material, AST and SST. This is reflected in the relatively high mean pH value (AST and SST combined) for the G8 survey block (6.71) compared to that for G3 (mean pH = 5.94), G5 (6.24), G6 (6.29) and G7 (6.34). Mapping of G8S regular sample data indicates that these, too, are higher than expected by comparison with adjacent survey blocks (G6 and G7). The reason for this difference is unclear but, given that both RMs and regular samples are affected, the most likely cause is analytical variation, rather than, for example, heterogeneity among the SRM batches. An important consequence of the higher recorded pH concentrations for G8 is that merging the G8 pH data with that of the other blocks will require data levelling. In the absence of CRMs for pH, one approach is to use the mean values of each of the SRMs (APT, AST, SPT, SST) for previous survey blocks, e.g. G3 to G6, as the accepted values for these RMs, in order to provide reference values for regression analysis.

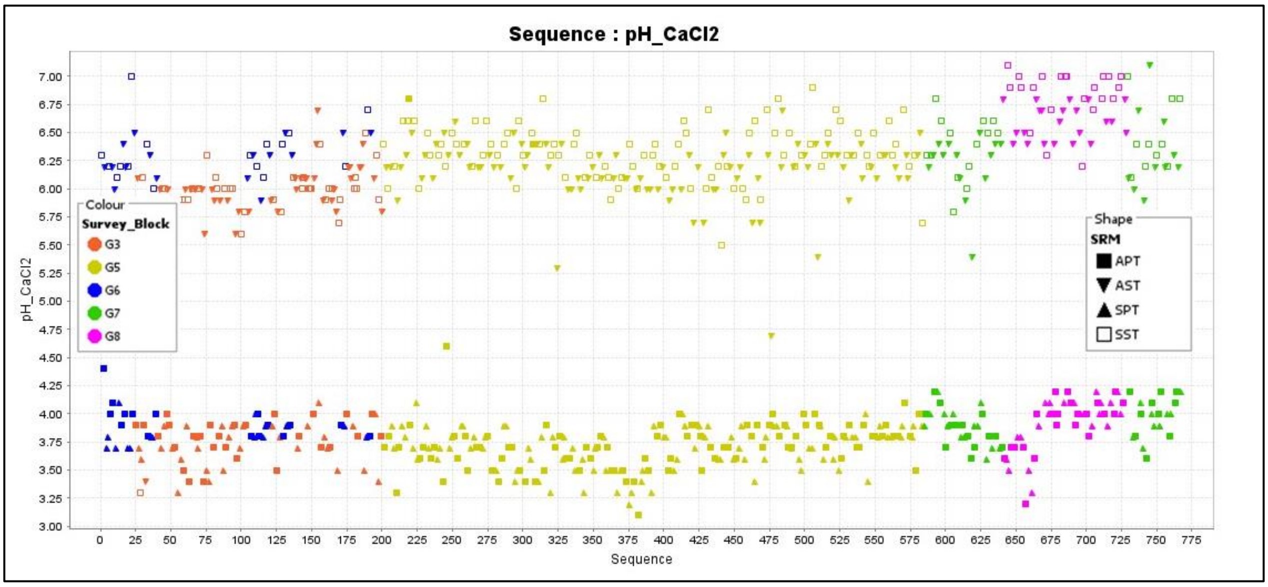


Figure 4 Tellus SRM pH data for survey blocks G3 to G8, plotted in order of analysis (oldest analyses on left).

In-house RMs: ICPar analyses

Several observed events raise caution about potential implications for data quality within certain data ranges. These events do not invalidate reported data but caution users that confidence is somewhat lower than for the rest of the data. This increased uncertainty is not quantified. Users are cautioned to treat affected data accordingly.

- Between 16.59 and 19.02 on 06/02/2022 multiple element failures and warnings occurred. Boron (B) failed in two instances and single failures were recorded for Na, Nb, Te and Se. Affected batch: LR2201396, involving G7S samples. Possible cause: poor analytical performance.
- Between 16.38 and 16.46 on 19/02/2022 multiple element failures and warnings occurred. Tellurium (Te) failed in two instances and single failures were recorded for Ba, S, Sc and Se. Affected batch: LR2201396, involving G7S samples. Possible cause: poor analytical performance.
- Between 25/02/2022 and 27/02/2022 four instances of multiple element failures occurred. Sodium (Na) failed in three instances and Th in two. Failures were also recorded for Al, Ba, Be, Hf, Pb, Sc and U. This period was also flagged for failures in blind RMs. Affected batch: LR22026808 (G7S samples). Possible cause: poor analytical performance.
- Between 06.04 and 08.18 on 26/04/2022 two instances of multiple element failures occurred. Failures were recorded for Ba, Cu, In, Mg, Pd and Se. Multiple analyte warnings were also recorded

for Al, As, Ba, Cr, Cs, La, Mg, Nb, Se and Zn. Affected batch: LR22052675 (G7S samples). Possible cause: poor analytical performance.

- Between 30/04/2022 and 01/05/2022 four instances of multiple element failures occurred. Tungsten (W) failed in three instances and Mg, Nb and Ta failed in two. Failures were also recorded for Au, Cu, In and Te, along with multiple warnings: B, Cu, Co, Fe, Ni, P, Rb, Sr, Ta, Ti, W, Y, Zr. Affected batch: LR22026808 (G7S samples). Possible cause: poor analytical performance.
- Between 09/06/2022 and 11/06/2022 five instances of multiple element failures occurred. Cs, Ge, Re, Se and Y failed in two instances. Failures were also recorded for Au, Pt, S, Sn, and Zn, along with multiple warnings: B, Cu, Co, Fe, Ni, P, Rb, Sr, Ta, Ti, W, Y, Zr. This period was also flagged for failures in blind RMs. Affected batch: LR22136773 (G7S samples). Possible cause: poor analytical performance.
- Between 12.45 and 14.45 on 22/06/2022 two instances of multiple element failures occurred. Failures were recorded twice for Ba, Ge and Sc and once for Hg and Zn. Affected batch: LR22136773 (G7S samples). Possible cause: poor analytical performance.
- Between 06.39 and 08.56 on 15/09/2022 three instances of multiple element failures occurred. Failures were recorded twice for Pb, Se and Ti and once for Bi, K and Re. Affected batch: LR22249920 (G8S samples). Possible cause: poor analytical performance.
- Between 10.03 and 12.23 on 16/10/2022 three instances of multiple element failures occurred. Failures were recorded twice for As, Sn and Sr and once for Ge, Pb, V, Zn, along with multiple warnings: Cd, Ce, Cs, Ge, Hf, Hg, In, La Mo, Na, Ni, Rb, Re, Se, Sr, U, Y, Zr. Affected batch: LR22265983 (G8S samples). Possible cause: poor analytical performance.
- Between 08/11/2022 and 10/11/2022 four instances of multiple element failures occurred. Cu, Mn and P failed three times, Li and Zn twice. Failures were also recorded for Al, Ge, Mo, W, Hg, Cr, Ni, Pb, along with multiple warnings: Al, Ba, Be, Ca, Cd, Cs, Cu, Fe, Ga, Ge, In, K, Li, Mg, Mn, Ni, P, Pb, Rb, S, Sb, Sc, Ti, Tl, V, Zn. Affected batches: LR22272933 and LR22286720 (G8A samples). Possible cause: poor analytical performance.
- Between 23.53 on 24/11/2022 and 00.11 on 25/11/2022 two instances of multiple element failures occurred. Failures were recorded Ge, K, Na and Sn, along with multiple warnings: Al, Ba, Pb and Te. Affected batch: LR22286720 (G8S samples). Possible cause: poor analytical performance.

Table 10. Summary of data quality issues observed by control charts for ICPar analyses of Tellus CRMs (G7S and G8S) and pH analyses of SRMs (G8S).

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
LDOWN	617512S	LR22013935	ICP-MS	04/02/2022 23:46	Multiple analyte warnings: Ce, Pd	Outwith upper warning limit
CNLST	617613S	LR22013936	ICP-MS	06/02/2022 16:09	Multiple analyte warnings: Na, Nb, Pt	Outwith upper/lower warning limits
CARLST	617639S	LR22013936	ICP-MS	06/02/2022 17:28	Single analyte failure (Na) and multiple analyte warnings (Cu, Se, Sr, Tl)	Outwith upper control and lower warning limits
STSD-1	617661S	LR22013936	ICP-MS	06/02/2022 18:09	Single analyte failure (Na) and single analyte warning (Li)	Outwith upper control and warning limits
WWLPAL	617685S	LR22013936	ICP-MS	06/02/2022 19:23	Single analyte failure (S)	Outwith upper control limit
LMGPSH	617537S	LR22013935	ICP-MS	10/02/2022 10:51	Multiple analyte failures: Au, Na	Outwith upper control limits
CARLST	617563S	LR22013935	ICP-MS	10/02/2022 11:30	Multiple analyte warnings: B, Li, Na, P, Rb, Sc, Th, Ti	Outwith upper/lower warning limits
STSD-3	617588S	LR22013935	ICP-MS	10/02/2022 13:12	Single analyte failure (Pt) and multiple analyte warnings (Al, Na)	Outwith upper warning limits
WXSERP	617914S	LR22026801	ICP-MS	14/02/2022 21:49	Single analyte failure (Na) and multiple analyte warnings (In, Ti, V)	Outwith upper control and lower warning limits
YELC1	617938S	LR22026801	ICP-MS	14/02/2022 23:00	Multiple analyte warnings: Na, Nb	Outwith upper/lower warning limits
TILL-2	617961S	LR22026801	ICP-MS	14/02/2022 23:39	Single analyte warning (Na)	Outwith upper warning limit
WXSERP	617987S	LR22026801	ICP-MS	15/02/2022 00:48	Single analyte failure (Na) and multiple analyte warnings (Cr, Ta)	Outwith upper control and upper/lower warning limits
STSD-1	618015S	LR22026808	ICP-MS	25/02/2022 20:36	Multiple analyte failures (Na, Pd) and multiple analyte warnings (U, Y)	Outwith upper control and upper/lower warning limits
WWLPAL	618037S	LR22026808	ICP-MS	25/02/2022 21:58	Multiple analyte warnings: Cu, Na, Pd	Outwith upper/lower warning limits

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
STSD-3	618064S	LR22026808	ICP-MS	26/02/2022 00:44	Multiple analyte failures: Na, Pt	Outwith upper control and upper warning limits
ORS	618088S	LR22026808	ICP-MS	26/02/2022 01:53	Multiple analyte failures (Se, V) and multiple analyte warnings (Cu, Na, Ni)	Outwith upper/lower control and warning limits
LMGPSH	617735S	LR22025685	ICP-MS	07/03/2022 11:47	Single analyte failure (Na) and single analyte warning (Ca)	Outwith upper control and upper warning limits
TILL-3	617760S	LR22025685	ICP-MS	07/03/2022 12:25	Multiple analyte warnings: Ge, Mo	Outwith upper/lower warning limits
STSD-1	617784S	LR22025685	ICP-MS	07/03/2022 13:34	Multiple analyte warnings: B, Cd, Nb	Outwith upper/lower warning limits
MONPB	617714S	LR22025685	ICP-MS	07/03/2022 15:02	Multiple analyte warnings: Na, Sr, Tl	Outwith upper/lower warning limits
LMGPSH	618335S	LR22052675	ICP-MS	26/04/2022 05:20	Single analyte failure (Pd)	Outwith upper control limit
LGRAN	618415S	LR22052675	ICP-MS	26/04/2022 07:42	Single analyte failure (Pd) and multiple analyte warnings (Ag, Ba, Ge, Se, Sn, Tl)	Outwith upper control and lower warning limits
ORS	618437S	LR22052675	ICP-MS	30/04/2022 09:35	Multiple analyte warnings: Nb, Pb, Pd	Outwith upper/lower warning limits
TILL-1	618459S	LR22052675	ICP-MS	30/04/2022 10:08	Multiple analyte warnings: As, Au	Outwith upper/lower warning limits
LMGPSH	618137S	LR22046830	ICP-MS	30/04/2022 12:57	Multiple analyte warnings: Ce, K, Li, Ti	Outwith upper warning limits
STSD-3	618188S	LR22046830	ICP-MS	30/04/2022 14:22	Single analyte warning: Pd	Outwith upper warning limit
CARLST	618163S	LR22046830	ICP-MS	01/05/2022 10:54	Single analyte failure (Pd) and single analyte warning (Pb)	Outwith upper control and lower warning limits
LGRAN	617815S	LR22025686	ICP-MS	02/05/2022 10:59	Single analyte failure: Tl	Outwith lower warning limit (consecutive)
ORS	617837S	LR22025686	ICP-MS	02/05/2022 11:32	Single analyte warning: Al	Outwith lower warning limit

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
LGRAN	617884S	LR22025686	ICP-MS	02/05/2022 15:28	Single analyte warning: Sb	Outwith upper warning limit
WXSERP	618514S	LR22136773	ICP-MS	09/06/2022 22:54	Multiple analyte warnings: Cd, Hf, Nb, Th	Outwith upper warning limits
WXSERP	618587S	LR22136773	ICP-MS	10/06/2022 01:01	Multiple analyte warnings: Ag, B, Sc, Se	Outwith upper/lower warning limits
STSD-1	618615S	LR22136773	ICP-MS	11/06/2022 16:34	Multiple analyte failures (Ag, Ce) and multiple analyte warnings (As, Cs, Hg, La, Ni, Pb, Re, Sb, Ta, Te, Th, Ti, Tl, V)	Outwith upper control and upper/lower warning limits
WWLPAL	618637S	LR22136773	ICP-MS	11/06/2022 16:51	Multiple analyte warnings: As, Cs, Mo, Ni, V, Y	Outwith upper warning limits
STSD-3	618664S	LR22136773	ICP-MS	11/06/2022 17:08	Multiple analyte warnings: As, Ce, La, Ni, Re	Outwith upper/lower warning limits
CARLST	670634S	LR22249920	ICP-MS	15/09/2022 02:55	Multiple analyte warnings: Na, U	Outwith upper/lower warning limits
CARLST	670720S	LR22249920	ICP-MS	15/09/2022 06:50	Multiple analyte warnings: Ag, As, Nb, Re	Outwith upper/lower warning limits
LMGPSH	670684S	LR22249920	ICP-MS	15/09/2022 08:30	Single analyte warning: Na	Outwith lower warning limit
STSD-1	670795S	LR22249920	ICP-MS	17/09/2022 12:41	Multiple analyte warnings: Au, Pt	Outwith upper warning limits
WXSERP	670442S	LR22252256	ICP-MS	17/09/2022 13:49	Single analyte failure: U	Outwith upper warning limit (consecutive)
WXSERP	670468S	LR22252256	ICP-MS	17/09/2022 15:07	Single analyte failure: U	Outwith lower warning limit (consecutive)
STSD-3	670557S	LR22252256	ICP-MS	26/09/2022 23:39	Single analyte warning: Bi	Outwith upper warning limit
WWLPAL	670531S	LR22252256	ICP-MS	27/09/2022 01:18	Multiple analyte warnings: Ag, In, Te	Outwith upper/lower warning limits
ORS	670582S	LR22252256	ICP-MS	27/09/2022 02:15	Single analyte warning: In	Outwith lower warning limit
STSD-1	670221S	LR22265983	ICP-MS	05/10/2022 14:16	Multiple analyte warnings: Rb, Sn, Sr	Outwith lower warning limits

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
LGRAN	670308S	LR22265983	ICP-MS	11/10/2022 15:34	Single analyte warning: Sb	Outwith upper warning limit
STSD-3	670009S	LR22272933	ICP-MS	13/10/2022 10:23	Multiple analyte warnings: Pt, U	Outwith lower warning limits
CARLST	670034S	LR22272933	ICP-MS	08/11/2022 06:25	Multiple analyte warnings: Co, Ni	Outwith upper warning limits
LDOWN	670059S	LR22272933	ICP-MS	08/11/2022 07:42	Multiple analyte warnings: Au, Y	Outwith upper warning limits
LMGPSH	670084S	LR22272933	ICP-MS	08/11/2022 08:47	Single analyte failure: Sn	Outwith upper warning limit (consecutive)
CARLST	670120S	LR22272933	ICP-MS	08/11/2022 10:17	Single analyte failure (Sb) and multiple analyte warnings (Cs, Cu, Ge, Hf)	Outwith upper control and warning limits
CNLST	670145S	LR22272933	ICP-MS	09/11/2022 22:27	Multiple analyte warnings: Al, Be	Outwith lower warning limits
STSD-1	670195S	LR22272933	ICP-MS	10/11/2022 00:39	Single analyte warning: W	Outwith upper warning limit
STSD-1	670821S	LR22286720	ICP-MS	10/11/2022 02:01	Single analyte failure (Hf) and multiple analyte warnings (Th, Zr)	Outwith upper control and warning limits
LMGPSH	670847S	LR22286720	ICP-MS	10/11/2022 05:34	Single analyte failure (Sn) and single analyte warning (V)	Outwith lower warning limits
TILL-1	670932S	LR22286720	ICP-MS	11/11/2022 01:52	Single analyte warning: Ag	Outwith lower warning limit
ORS	670983S	LR22286720	ICP-MS	11/11/2022 06:03	Multiple analyte warnings: As, V	Outwith upper/lower warning limits
WXSERP	671042S	LR22286720	ICP-MS	11/11/2022 07:38	Single analyte failure (B) and single analyte warning (P)	Outwith lower warning limits (consecutive)
WXSERP	671068S	LR22286720	ICP-MS	11/11/2022 07:58	Single analyte failure (B) and single analyte warning (Zr)	Outwith lower warning limits (consecutive)
TILL-2	671092S	LR22286720	ICP-MS	11/11/2022 09:35	Multiple analyte warnings: Hf, Mo, Zn	Outwith upper/lower warning limits
LGRAN	618484S	LR22052675	ICP-MS	16/08/2023 17:43	Single analyte failure (Mo) and multiple analyte warnings (K, Sn, Tl)	Outwith upper control and warning limits

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
APT_pH	670221S	LR22265936	pH CaCl2	05/10/2022 13:31		Outwith lower control limit
APT_pH	671019S	LR22286716	pH CaCl2	13/03/2023 20:01		Outwith upper warning limit
SPT_pH	670308S	LR22265936	pH CaCl2	06/10/2022 01:28		Outwith lower warning limit
SPT_pH	671068S	LR22286716	pH CaCl2	20/03/2023 12:00		Outwith upper warning limit
SST_pH	670894S	LR22286716	pH CaCl2	13/03/2023 13:19		Outwith lower warning limit

Table 11 Summary of data quality issues observed by control charts for ICPar analyses of laboratory in-house CRMs.

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS 46	LR22013935	RR22291884-015	ICP-MS	04/02/2022 23:48	Single analyte failure (Sc) and single analyte warning (Se)	Outwith upper warning limit (consecutive) and outwith upper warning limit
MRGeo08	LR22013935	RR22291884-040	ICP-MS	05/02/2022 00:28	Single analyte failure (Na) and single analyte warning (Th)	Outwith upper control and lower warning limits
OREAS-45f	LR22013935	RR22291885-032	ICP-MS	10/02/2022 11:32	Single analyte failure (B) and multiple analyte warnings (Nb, Sb, Se, Te)	Outwith upper warning limit (consecutive) and outwith upper/lower warning limits
GBM908-10	LR22013935	RR22291885-040	ICP-MS	10/02/2022 12:04	Single analyte failure (Pt) and multiple analyte warnings (Hf, Sr, U, Zn)	Outwith upper warning limit (consecutive) and outwith upper warning limits
OREAS 46	LR22013935	RR22291886-009	ICP-MS	10/02/2022 12:35	Single analyte failure (Ag) and multiple analyte warnings (Cd, Sb)	Outwith upper control and upper/lower warning limits
MRGeo08	LR22013935	RR22291886-040	ICP-MS	10/02/2022 13:41	Multiple analyte failures (Na, Rb) and multiple analyte warnings (Ga, Mn)	Outwith upper control, upper warning (consecutive) and upper/lower warning limits
OREAS-45f	LR22013936	RR22291887-028	ICP-MS	06/02/2022 16:32	Single analyte warning (Pt)	Outwith upper warning limit
GBM908-10	LR22013936	RR22291887-040	ICP-MS	06/02/2022 16:59	Multiple analyte failures (B, Te) and single analyte warning (Rb)	Outwith upper control and lower warning limits
OREAS 46	LR22013936	RR22291888-003	ICP-MS	06/02/2022 17:22	Single analyte failure (Sc) and single analyte warning (Ga)	Outwith lower warning limit (consecutive) and outwith lower warning limit
MRGeo08	LR22013936	RR22291888-040	ICP-MS	06/02/2022 18:27	Multiple analyte failures (Na, Nb) and multiple analyte warnings (Co, Li)	Outwith upper/lower control and upper/lower warning limits
OREAS-45f	LR22013936	RR22291890-010	ICP-MS	06/02/2022 19:02	Multiple analyte failures (B, Se) and multiple analyte warnings (Ba, P, Y)	Outwith upper/lower warning limits (consecutive) and upper/lower warning limits
GBM908-10	LR22013936	RR22291890-035	ICP-MS	06/02/2022 19:49	Single analyte failure (Pt) and multiple analyte warnings (Ba, K, Mo)	Outwith upper warning limit (consecutive) and upper/lower warning limits
OREAS 46	LR22013936	RR22353233-005	ICP-MS	19/02/2022 16:38	Multiple analyte failures (Se, Te) and single analyte warning (Re)	Outwith upper/lower control and upper warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
MRGeo08	LR22013936	RR22353233-009	ICP-MS	19/02/2022 16:46	Multiple analyte failures (Ba, S, Sc, Te) and multiple analyte warnings (Hf, La, Mn, Y)	Outwith upper/lower control, upper warning (consecutive) and upper warning limits
OREAS 46	LR22025685	RR22458109-005	ICP-MS	07/03/2022 11:44	Single analyte failure (Mo) and multiple analyte warnings (V, Zn)	Outwith lower control and upper warning limits
MRGeo08	LR22025685	RR22458109-040	ICP-MS	07/03/2022 12:46	Multiple analyte failures (Al, Ba, Na, V) and multiple analyte warnings (Be, Ca, Cu, Fe, Li, Ni, Pb, Se, Zn)	Outwith upper warning (consecutive) and upper warning limits
OREAS-45f	LR22025685	RR22458110-010	ICP-MS	07/03/2022 13:15	Multiple analyte warnings (K, Li, Na)	Outwith upper/lower warning limits
GBM908-10	LR22025685	RR22458110-039	ICP-MS	07/03/2022 14:09	Single analyte failure (Ni) and single analyte warning (Pb)	Outwith upper warning (consecutive) and upper warning limits
OREAS-45f	LR22025685	RR22458108-029	ICP-MS	07/03/2022 15:20	Single analyte failure (Na) and multiple analyte warnings (Fe, W)	Outwith upper control and upper/lower warning limits
GBM908-10	LR22025685	RR22458108-040	ICP-MS	07/03/2022 15:38	Single analyte failure (Ni) and single analyte warning (Fe)	Outwith upper warning (consecutive) and upper warning limits
OREAS 46	LR22025686	RR22762119-017	ICP-MS	01/05/2022 12:23	Multiple analyte warnings: Al, Fe, Zn	Outwith lower warning limits
MRGeo08	LR22025686	RR22761858-040	ICP-MS	02/05/2022 11:56	Single analyte failure (Ni) and multiple analyte warnings (Cd, Co, Fe, Ga, La, Pb, Pd, S, Sc, Tl, U, Y, Zn)	Outwith upper warning (consecutive) and upper/lower warning limits
OREAS 46	LR22025686	RR22762134-025	ICP-MS	02/05/2022 15:59	Multiple analyte warnings: Nb, Ta	Outwith upper/lower warning limits
MRGeo08	LR22025686	RR22762134-031	ICP-MS	02/05/2022 16:09	Single analyte warning: Zn	Outwith upper warning limit
GBM908-10	LR22025686	RR22762118-040	ICP-MS	03/05/2022 07:30	Multiple analyte warnings: Au, Be, Ca, K, Na	Outwith upper/lower warning limits
OREAS 46	LR22025686	RR22856440-007	ICP-MS	11/05/2022 03:54	Multiple analyte failures (Cs, Y) and single analyte warning (Bi)	Outwith upper warning (consecutive) and upper warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
GBM908-10	LR22026801	RR22336880-040	ICP-MS	14/02/2022 21:13	Single analyte warning: Na	Outwith upper warning limit
OREAS-45f	LR22026801	RR22336880-014	ICP-MS	14/02/2022 21:55	Single analyte failure (Na) and single analyte warning (Ti)	Outwith upper control and lower warning limits
OREAS 46	LR22026801	RR22336881-024	ICP-MS	14/02/2022 23:27	Multiple analyte warnings: Ge, V, Y, Zn, Zr	Outwith upper/lower warning limits
MRGeo08	LR22026801	RR22336881-040	ICP-MS	14/02/2022 23:54	Multiple analyte failures (Ba, Na) and single analyte warning (Mg)	Outwith upper control, upper warning (consecutive) and upper warning limits
OREAS-45f	LR22026801	RR22336882-019	ICP-MS	15/02/2022 00:40	Single analyte failure (Na)	Outwith upper control limit
GBM908-10	LR22026801	RR22336882-038	ICP-MS	15/02/2022 01:12	Multiple analyte warnings: In, Ta, Ti	Outwith upper/lower warning limits
OREAS-45f	LR22026808	RR22372642-008	ICP-MS	25/02/2022 20:18	Multiple analyte failures (Hf, Na)	Outwith upper/lower control limits
GBM908-10	LR22026808	RR22372642-040	ICP-MS	25/02/2022 21:32	Multiple analyte warnings: Co, Hf, Na, Pd	Outwith upper/lower warning limits
OREAS 46	LR22026808	RR22372643-034	ICP-MS	26/02/2022 00:46	Multiple analyte failures (Pb, U) and multiple analyte warnings (Ca, In, Th)	Outwith lower control and upper/lower warning limits
MRGeo08	LR22026808	RR22372643-040	ICP-MS	26/02/2022 00:57	Multiple analyte failures (Sc, Th) and multiple analyte warnings (Ge, Rb, Sr)	Outwith upper warning (consecutive) and upper/lower warning limits
OREAS-45f	LR22026808	RR22372644-015	ICP-MS	26/02/2022 01:38	Single analyte failure (Na) and multiple analyte warnings (Pd, Sc, Tl)	Outwith upper control and upper/lower warning limits
GBM908-10	LR22026808	RR22372644-038	ICP-MS	26/02/2022 02:16	Multiple analyte warnings: Au, Ga, Ge, S, Ti	Outwith lower warning limits
OREAS 46	LR22026808	RR22430633-003	ICP-MS	27/02/2022 15:02	Multiple analyte warnings: Ge, Te	Outwith upper/lower warning limits
MRGeo08	LR22026808	RR22430633-006	ICP-MS	27/02/2022 15:08	Multiple analyte failures (Al, Ba, Be, Na, Th) and single analyte warning (Ta)	Outwith upper control, upper/lower warning (consecutive) and upper warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS 46	LR22046830	RR22761852-013	ICP-MS	30/04/2022 11:58	Single analyte failure (Ca) and single analyte warning (Mg)	Outwith lower warning (consecutive) and lower warning limits
MRGeo08	LR22046830	RR22761852-040	ICP-MS	30/04/2022 13:01	Multiple analyte failures (Mg, Nb, Ta, W) and single analyte warning (Ti)	Outwith lower control, upper warning (consecutive) and upper warning limits
OREAS 46	LR22046830	RR22761854-025	ICP-MS	30/04/2022 14:31	Single analyte warning	Outwith lower warning limit
MRGeo08	LR22046830	RR22761854-040	ICP-MS	30/04/2022 14:55	Multiple analyte failures (Mg, Nb, Ta, W)	Outwith upper control and upper/lower warning (consecutive) limits
OREAS-45f	LR22046830	RR22762116-010	ICP-MS	01/05/2022 10:24	Multiple analyte failures (Cu, In) and multiple analyte warnings (B, Co, Fe, Ni, P, Rb, Sr, W, Y, Zr)	Outwith upper control, upper warning (consecutive) and upper/lower warning limits
GBM908-10	LR22046830	RR22762116-040	ICP-MS	01/05/2022 11:41	Multiple analyte warnings: Ag, Al, As	Outwith lower warning limits
OREAS 46	LR22046830	RR22762117-017	ICP-MS	01/05/2022 17:43	Multiple analyte failures (Au, Te, W) and single analyte warning (Ta)	Outwith upper/lower control and lower warning limits
MRGeo08	LR22046830	RR22762117-040	ICP-MS	01/05/2022 18:20	Single analyte failure (Ni) and single analyte warning (Ca)	Outwith upper warning (consecutive) and lower warning limits
OREAS 46	LR22046830	RR22762115-004	ICP-MS	02/05/2022 12:16	Single analyte failure: B	Outwith upper control limit
MRGeo08	LR22046830	RR22762115-040	ICP-MS	02/05/2022 14:54	Single analyte warning: Li	Outwith lower warning limit
OREAS-45f	LR22046830	RR22762118-035	ICP-MS	03/05/2022 07:18	Multiple analyte warnings: Ca, Ge	Outwith upper/lower warning limits
MRGeo08	LR22046830	RR22856440-012	ICP-MS	11/05/2022 04:06	Multiple analyte failures (Cs, Re, Y) and single analyte warning (Pd)	Outwith upper control and upper warning limits
OREAS 46	LR22052675	RR22542880-032	ICP-MS	23/03/2022 08:22	Single analyte warning: Na	Outwith upper warning limit

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
MRGeo08	LR22052675	RR22542880-040	ICP-MS	23/03/2022 08:50	Multiple analyte failures (Fe, Li, Ta, V) and multiple analyte warnings (B, Pb, Pd, Ti)	Outwith upper control, lower warning (consecutive) and upper/lower warning limits
OREAS 46	LR22052675	RR22761848-019	ICP-MS	26/04/2022 04:16	Single analyte failure (Mg) and multiple analyte warnings (As, B, Be, Ca, P, Ti)	Outwith lower control and upper/lower warning limits
MRGeo08	LR22052675	RR22761848-040	ICP-MS	26/04/2022 04:57	Single analyte failure (Li) and multiple analyte warnings (Cu, Ge, Se)	Outwith upper warning (consecutive) and upper/lower warning limits
OREAS 46	LR22052675	RR22762113-029	ICP-MS	26/04/2022 06:04	Multiple analyte failures (Mg, Pd) and multiple analyte warnings (Al, Cr)	Outwith upper control, lower warning (consecutive) and lower warning limits
MRGeo08	LR22052675	RR22762113-040	ICP-MS	26/04/2022 06:23	Multiple analyte warnings: As, Ba, Cr, La, Mg	Outwith upper control, lower warning (consecutive) and upper/lower warning limits
OREAS-45f	LR22052675	RR22762114-029	ICP-MS	26/04/2022 08:00	Multiple analyte failures (Ba, Cu, In, Se) and multiple analyte warnings (Cs, Zn)	Outwith upper/lower control, lower warning (consecutive) and lower warning limits
GBM908-10	LR22052675	RR22762114-040	ICP-MS	26/04/2022 08:18	Multiple analyte warnings: Mg, Nb, Se	Outwith upper/lower warning limits
OREAS 46	LR22052675	RR22761850-005	ICP-MS	30/04/2022 09:32	Single analyte failure (Co) and single analyte warning (Mg)	Outwith lower control and upper warning limits
MRGeo08	LR22052675	RR22761850-040	ICP-MS	30/04/2022 11:22	Multiple analyte warnings: Bi, Mo, Ni, Pd, S, U	Outwith upper/lower warning limits
OREAS 46	LR22136773	RR23047075-016	ICP-MS	09/06/2022 22:48	Multiple analyte failures (Cs, Pt, Y) and multiple analyte warnings (Ga, Ta, Te, Zr)	Outwith upper control, upper warning (consecutive) and upper warning limits
MRGeo08	LR22136773	RR23047075-040	ICP-MS	09/06/2022 23:46	Multiple analyte failures (Cs, Re, Se, Y) and multiple analyte warnings (Ag, Sn, Zr)	Outwith upper/lower warning (consecutive) and upper warning limits
OREAS 46	LR22136773	RR23047077-022	ICP-MS	10/06/2022 00:57	Single analyte failure (S) and multiple analyte warnings (Cd, Cr, Ge, Rb, Sn)	Outwith upper control and upper warning limits
MRGeo08	LR22136773	RR23047077-040	ICP-MS	10/06/2022 02:47	Single analyte failure (Se)	Outwith lower warning (consecutive) limit

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS 46	LR22136773	RR23047079-018	ICP-MS	11/06/2022 12:08	Multiple analyte warnings: La, Nb, Sb	Outwith upper/lower warning limits
MRGeo08	LR22136773	RR23047079-040	ICP-MS	11/06/2022 13:09	Multiple analyte failures (Au, Re) and multiple analyte warnings (Ag, Bi, Ce, Cs, Hf, La, Mo, Pd, Sn, Th, Tl, W, Y, Zr)	Outwith upper control and upper warning limits
OREAS-45f	LR22136773	RR23048314-005	ICP-MS	11/06/2022 16:26	Multiple analyte failures (Ge, Sn) and multiple analyte warnings (Ca, Cu, Sr, Y)	Outwith lower control, lower warning (consecutive) and lower warning limits
MRGeo08	LR22136773	RR23048314-040	ICP-MS	11/06/2022 17:24	Multiple analyte failures (Ge, Zn) and multiple analyte warnings (Mg, Ta)	Outwith upper/lower warning (consecutive) and upper/lower warning limits
OREAS-45f	LR22136773	RR23119671-023	ICP-MS	22/06/2022 12:45	Multiple analyte failures (B, Ge, Hg) and single analyte warning (Be)	Outwith lower control, lower warning (consecutive) and upper warning limits
MRGeo08	LR22136773	RR23119671-040	ICP-MS	22/06/2022 13:27	Multiple analyte failures (B, Ge, Sc, Zn) and single analyte warning (Be)	Outwith lower control, upper warning (consecutive) and upper warning limits
OREAS 46	LR22136773	RR23125603-003	ICP-MS	22/06/2022 14:36	Multiple analyte warnings: Cs, V	Outwith lower warning limits
MRGeo08	LR22136773	RR23125603-008	ICP-MS	22/06/2022 14:45	Single analyte failure (Sc) and single analyte warning (Sb)	Outwith upper warning (consecutive) and upper warning limits
OREAS 46	LR22249920	RR23654872-014	ICP-MS	15/09/2022 02:50	Single analyte failure (K)	Outwith upper warning (consecutive) limit
MRGeo08	LR22249920	RR23654872-040	ICP-MS	15/09/2022 04:43	Single analyte failure (Sc) and multiple analyte warnings (Ba, Fe)	Outwith lower control and upper/lower warning limits
OREAS 46	LR22249920	RR23654874-024	ICP-MS	15/09/2022 06:39	Multiple analyte failures (Bi, K, Pb, Se) and single analyte warning (Ce)	Outwith lower control, upper/lower warning (consecutive) and upper warning limits
MRGeo08	LR22249920	RR23654874-040	ICP-MS	15/09/2022 07:05	Multiple analyte failures (Re, Ti) and single analyte warning (Pt)	Outwith lower control, lower warning (consecutive) and upper warning limits
OREAS 46	LR22249920	RR23654879-018	ICP-MS	15/09/2022 08:10	Multiple analyte failures (Pb, Se) and multiple analyte warnings (Cd, Hf)	Outwith upper control, lower warning (consecutive) and upper warning limits
MRGeo08	LR22249920	RR23654879-040	ICP-MS	15/09/2022 08:56	Single analyte failure (Ti) and multiple analyte warnings (Au, Cd, S)	Outwith lower warning (consecutive) and upper/lower warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS-45f	LR22249920	RR23654878-007	ICP-MS	16/09/2022 18:40	Single analyte failure (Pd) and single analyte warning (Ce)	Outwith lower control and upper warning limits
MRGeo08	LR22249920	RR23654878-040	ICP-MS	16/09/2022 19:40	Multiple analyte warnings: Ga, W	Outwith upper/lower warning limits
OREAS 46	LR22249920	RR23670685-024	ICP-MS	17/09/2022 16:52	Single analyte failure (Hg)	Outwith upper warning (consecutive) limit
OREAS 46	LR22252256	RR23663655-004	ICP-MS	17/09/2022 13:41	Multiple analyte failures (Hg, Pd) and single analyte warning (Na)	Outwith upper control, upper warning (consecutive) and upper warning limits
OREAS 46	LR22252256	RR23671701-034	ICP-MS	18/09/2022 11:40	Single analyte failure (Sb) and multiple analyte warnings (Co, Ta, Y)	Outwith upper control and lower warning limits
MRGeo08	LR22252256	RR23671701-040	ICP-MS	18/09/2022 12:02	Single analyte warning: Ta	Outwith lower warning limit
OREAS 46	LR22252256	RR23670687-027	ICP-MS	19/09/2022 11:03	Multiple analyte warnings: Be, Ca, Ge, Mg, Ti	Outwith upper/lower warning limits
MRGeo08	LR22252256	RR23670687-040	ICP-MS	19/09/2022 11:37	Multiple analyte warnings: Nb, Pt	Outwith lower warning limits
MRGeo08	LR22252256	RR23671702-040	ICP-MS	27/09/2022 00:25	Multiple analyte warnings: Bi, Ga, V	Outwith lower warning limits
OREAS 46	LR22252256	RR23663657-025	ICP-MS	27/09/2022 01:20	Single analyte failure (In)	Outwith upper control warning limit
OREAS 46	LR22252256	RR23663659-013	ICP-MS	27/09/2022 03:00	Single analyte warning (Au)	Outwith upper warning limit
MRGeo08	LR22252256	RR23663657-040	ICP-MS	29/09/2022 08:26	Multiple analyte warnings: Ca, K, Li, Mg, P, Pb, S	Outwith upper warning limits
MRGeo08	LR22252256	RR23663659-024	ICP-MS	29/09/2022 08:47	Single analyte failure (Ta)	Outwith lower control limit
MRGeo08	LR22252256	RR23792154-040	ICP-MS	05/10/2022 16:49	Single analyte failure (Pt)	Outwith upper warning (consecutive) limit

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS 46	LR22265983	RR23792154-017	ICP-MS	05/10/2022 14:04	Multiple analyte failures (Co, Pd, Sc) and multiple analyte warnings (Cr, Y, Zr)	Outwith upper/lower control, lower warning (consecutive) and lower warning limits
OREAS-45f	LR22265983	RR23824669-008	ICP-MS	11/10/2022 15:43	Multiple analyte warnings: Bi, Co	Outwith lower warning limits
MRGeo08	LR22265983	RR23824669-040	ICP-MS	11/10/2022 16:41	Single analyte failure (Ta) and multiple analyte warnings (Co, Cu, V)	Outwith upper control and upper/lower warning limits
OREAS-45f	LR22265983	RR23830998-025	ICP-MS	13/10/2022 10:12	Multiple analyte warnings: Ca, Co, Li, Pd, Rb, Te, Th	Outwith upper/lower warning limits
MRGeo08	LR22265983	RR23830998-040	ICP-MS	13/10/2022 11:15	Multiple analyte warnings: Be, Na	Outwith lower warning limits
OREAS 46	LR22265983	RR23824670-010	ICP-MS	13/10/2022 11:48	Multiple analyte failures (Co, V, Zn) and single analyte warning (Ti)	Outwith upper warning (consecutive) and upper warning limits
MRGeo08	LR22265983	RR23824670-040	ICP-MS	13/10/2022 12:45	Single analyte failure (Sn)	Outwith lower warning (consecutive) limit
OREAS-45f	LR22265983	RR23824667-021	ICP-MS	16/10/2022 10:03	Multiple analyte failures (As, Pb) and multiple analyte warnings (Ge, Mo, Na, Sr)	Outwith upper control and upper/lower warning limits
MRGeo08	LR22265983	RR23824667-040	ICP-MS	16/10/2022 10:48	Multiple analyte failures (Sn, Sr) and multiple analyte warnings (Cs, Hf, In, Re, U, Y, Zr)	Outwith upper control, upper warning (consecutive) and upper warning limits
OREAS 46	LR22265983	RR23824668-004	ICP-MS	16/10/2022 11:11	Multiple analyte failures (As, Ge, Sn, Sr, V, Zn) and multiple analyte warnings (Cd, Ce, Cs, Hf, Hg, La, Ni, Rb, Se, U, Y)	Outwith upper/lower control, upper warning (consecutive) and upper warning limits
MRGeo08	LR22265983	RR23824668-040	ICP-MS	16/10/2022 12:23	Single analyte failure (Sb)	Outwith lower control limit
OREAS 46	LR22272933	RR23995060-022	ICP-MS	08/11/2022 06:28	Single analyte warning (Co)	Outwith upper warning limit
OREAS-45f	LR22272933	RR23995061-002	ICP-MS	08/11/2022 07:29	Multiple analyte warnings: Bi, Sn	Outwith upper warning limits
OREAS 920	LR22272933	RR23995061-040	ICP-MS	08/11/2022 08:55	Single analyte warning (Ga)	Outwith upper warning limit

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS 46	LR22272933	RR23995062-035	ICP-MS	08/11/2022 10:19	Multiple analyte failures (Al, Cu, Ge, Mo, P, W) and multiple analyte warnings (Ba, Be, Ca, Cd, Fe, In, K, Li, Mg, Mn, Ni, Pb, Sb, Tl, V, Zn)	Outwith upper control and upper/lower warning limits
MRGeo08	LR22272933	RR23995062-040	ICP-MS	08/11/2022 10:28	Multiple analyte warnings: Sb, Ti	Outwith upper/lower warning limits
OREAS-45f	LR22272933	RR23995063-037	ICP-MS	09/11/2022 23:08	Multiple analyte failures (Cu, Hg, Mn, P) and multiple analyte warnings (Cs, S)	Outwith upper/lower control, lower warning (consecutive) and upper/lower warning limits
OREAS 920	LR22272933	RR23995063-040	ICP-MS	09/11/2022 23:14	Single analyte warning (Ni)	Outwith upper warning limit
MRGeo08	LR22272933	RR23995064-040	ICP-MS	10/11/2022 00:42	Multiple analyte failures (Li, Mn, Zn) and single analyte warning (Ge)	Outwith lower warning (consecutive) and upper warning limits
OREAS 920	LR22272933	RR23995065-040	ICP-MS	10/11/2022 02:23	Multiple analyte warnings: Al, Nb, P, Rb, Ti	Outwith upper/lower warning limits
OREAS 46	LR22272933	RR24104857-003	ICP-MS	22/11/2022 22:11	Single analyte failure (Re) and single analyte warning (Ta)	Outwith upper control and upper warning limits
OREAS-45f	LR22286720	RR23995065-033	ICP-MS	10/11/2022 02:10	Multiple analyte failures (Cr, Cu, Mn, Ni, P) and multiple analyte warnings (Ga, LI, Sc, V)	Outwith lower control, lower warning (consecutive) and lower warning limits
MRGeo08	LR22286720	RR23995066-040	ICP-MS	10/11/2022 06:54	Multiple analyte failures (Li, Mn, Pb, Zn) and multiple analyte warnings (Al, Ba, Ca, Cu, P, Rb, S, Ti)	Outwith lower control and lower warning limits
OREAS-45f	LR22286720	RR23995067-023	ICP-MS	10/11/2022 22:52	Multiple analyte warnings: Ge, Re	Outwith upper warning limits
OREAS 920	LR22286720	RR23995067-040	ICP-MS	10/11/2022 23:58	Single analyte failure (Pd) and multiple analyte warnings (Bi, La)	Outwith upper control and upper warning limits
OREAS 46	LR22286720	RR23995068-016	ICP-MS	11/11/2022 00:37	Single analyte failure (Au)	Outwith upper control limit
OREAS-45f	LR22286720	RR23995069-036	ICP-MS	11/11/2022 03:43	Single analyte warning (Ge)	Outwith upper warning limit

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS 920	LR22286720	RR23995069-040	ICP-MS	11/11/2022 03:50	Multiple analyte warnings: Th, Ti	Outwith upper warning limits
OREAS-45f	LR22286720	RR24022804-009	ICP-MS	11/11/2022 06:00	Multiple analyte failures: Ge, Tl	Outwith upper control and upper warning (consecutive) limits
OREAS 920	LR22286720	RR24022804-040	ICP-MS	11/11/2022 07:03	Single analyte warning (Y)	Outwith lower warning limit
OREAS 46	LR22286720	RR24022805-006	ICP-MS	11/11/2022 07:29	Single analyte failure (Au) and multiple analyte warnings (Ce, Hg)	Outwith upper warning (consecutive) and upper/lower warning limits
MRGeo08	LR22286720	RR24022805-040	ICP-MS	11/11/2022 09:08	Single analyte warning (Ce)	Outwith lower warning limit
OREAS-45f	LR22286720	RR24022806-004	ICP-MS	11/11/2022 09:32	Multiple analyte failures (Ge, Sn, Tl) and multiple analyte warnings (As, Ta)	Outwith upper control, upper warning (consecutive) and upper warning limits
OREAS-45f	LR22286720	RR24124085-004	ICP-MS	24/11/2022 23:53	Multiple analyte failures (Ge, Sn) and single analyte warning (Pb)	Outwith upper control, upper warning (consecutive) and lower warning limits
OREAS 920	LR22286720	RR24124085-007	ICP-MS	25/11/2022 00:11	Multiple analyte failures (K, Na) and multiple analyte warnings (Al, Ba, Te)	Outwith upper control and upper/lower warning 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. Since all analyses reported here were carried out following *aqua regia* extraction, available certified values are reported for *aqua regia* or other incomplete extractions where available and are referred to as 'partial' digestions. Where certified values obtained through 'partial' digestions are not available, 'total' digestion values are used instead to carry out regression analysis. The methodology for 'total' digestions varies between different CRMs but certified values for such extractions are typically significantly higher than those recorded for *aqua regia* extractions. In these cases, the utility of the regression analysis is limited and the user is advised to interpret the resultant plots accordingly. For the ICPar analytes five CRMs are available: STSD 1, STSD 3, TILL 1, TILL 2 and TILL 3. Each regression line and its equation are based on up to five data points. For the LOI and pH analyses there are no CRMs but a series of project SRMs were used: APT, AST, SPT and SST. Unlike the ICPar RMs, for which data from the G7S and G8S surveys are combined, data for the LOI and pH SRMs are derived solely from the G8S survey. The reference concentrations employed for the regression analysis of measured LOI and pH data are the means of previous analyses of the SRMs carried out for preceding survey blocks up to and including G6 block data.

A summary of the linear regression relationships for the ICPar analytes is presented in Table 12 for Tellus CRM data and in Table 14 for in-house CRM data. Table 13 displays the regression relationship for LOI and pH data. Regression curves for analytes for which certified values obtained through 'partial' digestions are available generally display a very good fit to the data points and, in turn, the measured values are generally a good match for certified values. In some cases (Ag, Be, Fe, K, Na), the good fit obtained is at least partly a reflection of clustering of data at either end of the data range, yielding a near-two-point regression curve. For a few analytes such as Be, K and Na, measured values are a poor match for certified values, possibly reflecting the different partial extraction methodology used for the CRMs rather than any analytical issues.

Some regression curves for analytes for which only certified values obtained through 'total' digestions are available display good fits to the data (Ce, Cs, Li, U) but, with the exception of U, measured and certified values for these analytes are generally poorly matched. Regression curves for analytes such as Au, Hf, Nb, Sc, Sr, Ta, Ti and Zr display poor fits to the measured data as well as a very poor match for certified values. This is unsurprising in the case of elements such Au that display a strong "nugget" effect in soil samples, given the small quantity of sample analysed. In the case of other elements, *aqua regia* extracts from soil a small proportion of the total concentration of element present in the sample (e.g. c. 1 % of Hf or Zr: Reimann *et al*. 2014), so a significant mismatch between certified and analytical values is to be expected. Regression plots were not constructed for Bi, Ga, Ge, In, Pd, Pt, Re, Se, Sn, Te, Tl and W due to insufficient certified data. No ICPar data are recommended to be conditioned.

In the case of pH, as noted above, reported G8S data are generally higher than those for adjacent survey blocks. Consequently, the G8S data require conditioning, or levelling, if they are to be mapped together with data for other blocks. The linear regression relationship between the G8S data and the mean values for the pH SRMs for blocks up to G6 (Table 13) provides a means of conditioning the data in this case. Data for each block should be reviewed on an Individual basis but a similar approach to conditioning of pH data may be appropriate in future if required.

Table 12 Linear regression relationships for ICPar analytes.

Analyte	CRMs	Digestion	Linear regression relationships		
			Intercept	Slope	R squared
Ag (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	0.0327	1.01	1
Al (%)	TILL-1, TILL-2, TILL-3	partial	0.369	0.71	0.999
As (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	4.28	0.986	0.998
Au (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-0.0066	1.53	0.681

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R squared
B (mg kg^{-1})	STSD-1, STSD-3	total	-26.2	0.395	1
Ba (mg kg^{-1})	TILL-1, TILL-2, TILL-3	partial	-4.43	1.03	1
Be (mg kg^{-1})	TILL-1, TILL-2, TILL-3	partial	-0.434	9.1	0.989
Bi (mg kg^{-1})					
Ca (%)	TILL-1, TILL-2, TILL-3	partial	-0.0221	0.833	0.998
Cd (mg kg^{-1})	TILL-1, TILL-2, TILL-3	partial	-0.0161	1.17	1
Ce (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-0.47	0.698	0.958
Co (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	0.108	1.01	0.984
Cr (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	3.95	0.803	0.996
Cs (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	0.0053	0.547	0.996
Cu (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	0.849	0.969	0.999
Fe (%)	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	0.277	0.89	0.921
Ga (mg kg^{-1})					
Ge (mg kg^{-1})					
Hf (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	0.0159	0.00202	0.0934
Hg (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	-0.0191	1.14	0.875
In (mg kg^{-1})					
K (%)	TILL-1, TILL-2, TILL-3	partial	-0.0273	0.768	0.991
La (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-	total	4.29	0.524	0.89
Li (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-	total	1.23	0.72	0.974
Mg (%)	TILL-1, TILL-2, TILL-3	partial	-0.197	1.17	0.993
Mn (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	91.6	0.923	0.997
Mo (mg kg^{-1})	TILL-1, TILL-2, TILL-3	partial	-1.69	1.23	0.987
Na (%)	TILL-1, TILL-2, TILL-3	partial	0.0117	0.38	0.885
Nb (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-0.156	0.163	0.898
Ni (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	3.07	0.958	0.916
P (%)	TILL-1, TILL-2, TILL-3	partial	0.0121	0.683	0.635
Pb (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	2.5	0.969	0.996
Pd (mg kg^{-1})					
Pt (mg kg^{-1})					
Rb (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-2.1	0.263	0.942
Re (mg kg^{-1})					
S (%)	STSD-1, STSD-3	total	-0.0507	1.52	1
Sb (mg kg^{-1})	STSD-1, STSD-3	partial	-0.686	1.47	1
Sc (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	4.45	-0.033	0.00529
Se (mg kg^{-1})					
Sn (mg kg^{-1})					

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R squared
Sr (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	33.4	-0.00721	3.91E-04
Ta (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2	total	0.00225	-3.18E-04	0.123
Te (mg kg^{-1})					
Th (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-1.3	0.504	0.792
Ti (%)	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	0.0458	0.0126	0.589
Tl (mg kg^{-1})					
U (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-1.04	0.916	0.96
V (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	17.6	0.617	0.767
W (mg kg^{-1})					
Y (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-3.1	0.566	0.546
Zn (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	-3.61	1.01	1
Zr (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	0.652	0.0022	0.063

Table 13 Linear regression relationships for LOI at 450°C and pH $CaCl_2$.

	Linear regression relationships		
Analyte	Intercept	Slope	R squared
LOI at 450°C (%)	0.394	1	1
pH $CaCl_2$	-0.641	1.19	0.998

Table 14 Linear regression relationship for laboratory in-house ICPar analytes

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R^2
Ag (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00251	0.987	1
Al (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0214	1.01	1
As (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.118	1.05	1
Au (mg kg^{-1})	OREAS45f, MRGeo08	partial	1.92E-04	0.938	1
B (mg kg^{-1})					
Ba (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-1.9	0.998	1
Be (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.00237	0.957	0.998
Bi (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00659	1	0.996
Ca (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.00951	0.98	1
Cd (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00583	1.03	1
Ce (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.758	0.992	1
Co (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.452	0.971	0.998
Cr (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	1.18	0.993	1
Cs (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0421	0.994	1
Cu (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.879	1.01	1

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R^2
Fe (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0652	1.02	1
Ga (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.38	1.04	0.999
Ge (mg kg^{-1})	OREAS45f, OREAS46, MRGeo08	partial	0.0232	0.863	0.879
Hf (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.00914	0.945	0.995
Hg (mg kg^{-1})	OREAS45f, OREAS46, MRGeo08	partial	0.00158	0.98	0.999
In (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00136	0.989	1
K (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00883	1.03	1
La (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.478	1.01	0.996
Li (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.122	1.01	1
Mg (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0391	1.05	0.999
Mn (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-6.96	1.01	0.999
Mo (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0737	1.01	1
Na (%)	OREAS45f, OREAS46, MRGeo08	partial	0.00287	1.02	1
Nb (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.259	1.28	0.998
Ni (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-2.52	1.03	1
P (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-2.52E-04	1.01	1
Pb (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.144	1	1
Pd (mg kg^{-1})	OREAS45f, MRGeo08	partial	-0.00405	1.07	1
Pt (mg kg^{-1})	OREAS45f, MRGeo08	partial	-6.39E-04	0.997	1
Rb (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.357	1	1
Re (mg kg^{-1})					
S (%)	OREAS45f, OREAS920, MRGeo08	partial	2.14E-04	0.99	1
Sb (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	0.00701	0.94	1
Sc (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.111	1.03	1
Se (mg kg^{-1})	OREAS920, MRGeo08	partial	-0.647	1.01	1
Sn (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0473	1	0.999
Sr (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-1.08	1.01	1
Ta (mg kg^{-1})					
Te (mg kg^{-1})	OREAS46, MRGeo08	partial	-0.00847	1.42	1
Th (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0485	0.98	1
Ti (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.00344	0.976	1
Tl (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00637	0.989	1
U (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.044	1.01	1
V (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	1.37	0.987	0.999
W (mg kg^{-1})	OREAS46, MRGeo08	partial	0.00251	0.952	1
Y (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.177	0.97	0.996
Zn (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.49	1.01	1

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R^2
Zr (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.177	0.991	0.998

Beryllium (Be) by ICPar (MS41L-BLD)

Beryllium concentrations measured by the MS41L-BLD method do not fit well to certified concentrations in the CRMs, being significantly lower in each case. The regression line is nevertheless broadly parallel to the 1:1 line, indicating a consistent rate of extraction of Be in *aqua regia* across the range of CRMs. This data should be used with caution. No data conditioning is recommended.

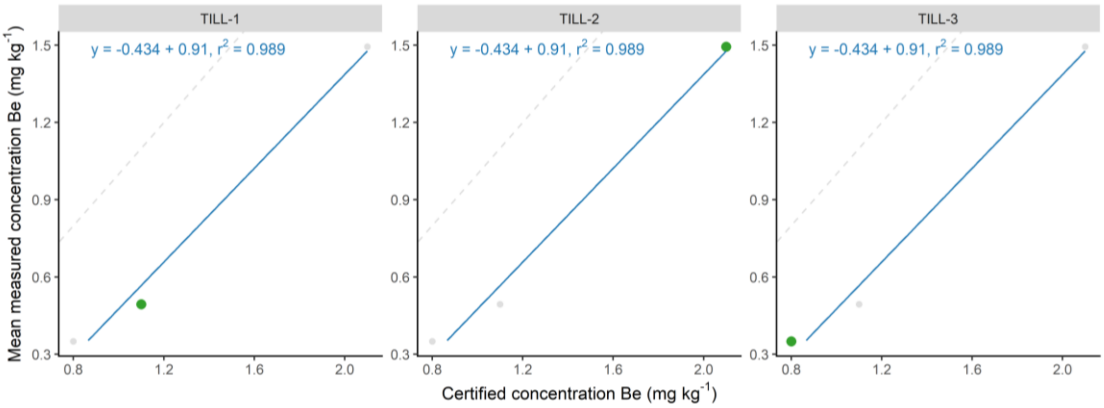


Chart 2 Beryllium (Be) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is visible to the left of the regression line.

Potassium (K) by ICPar (MS41L-BLD)

Potassium concentrations measured by the MS41L-BLD method do not fit well to certified concentrations in the CRMs, being significantly lower in each case. The regression line is nevertheless broadly parallel to the 1:1 line, indicating a consistent rate of extraction of K in *aqua regia* across the range of CRMs. This data should be used with caution. No data conditioning is recommended.

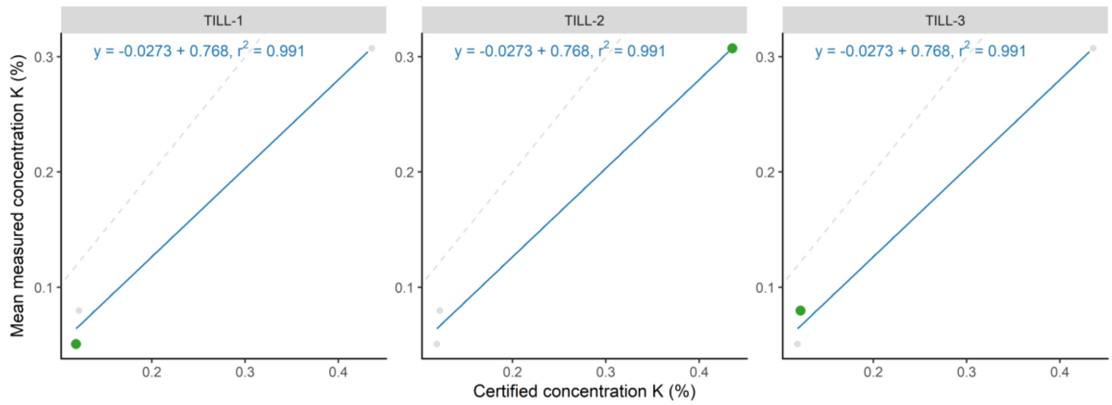


Chart 3 Potassium (K) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Sodium (Na) by ICPar (MS41L-BLD)

Sodium concentrations measured in CRMs by the MS41L-BLD method are significantly lower than corresponding certified concentrations in each case. Use of this data is not recommended. No data conditioning is recommended.

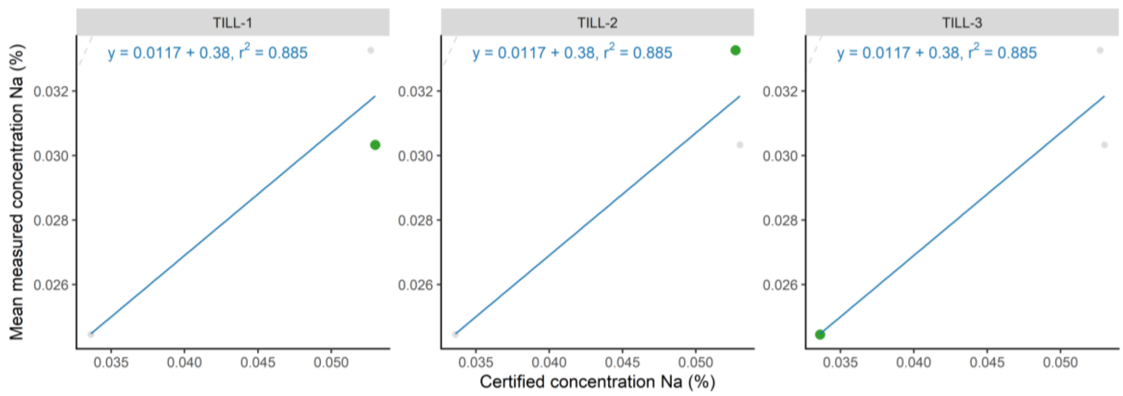


Chart 4 Sodium (Na) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is not visible but lies to the left of the chart area.

Phosphorus (P) by ICPar (MS41L-BLD)

Phosphorus concentrations measured by the MS41L-BLD method are generally good but yield a poorly-fitting regression curve owing to apparently poor data for one CRM (TILL-2). Some caution is required given that the "partial" extraction method used for the CCRMP till CRMs is not an exact match for *aqua regia* digestion. No data conditioning is recommended.

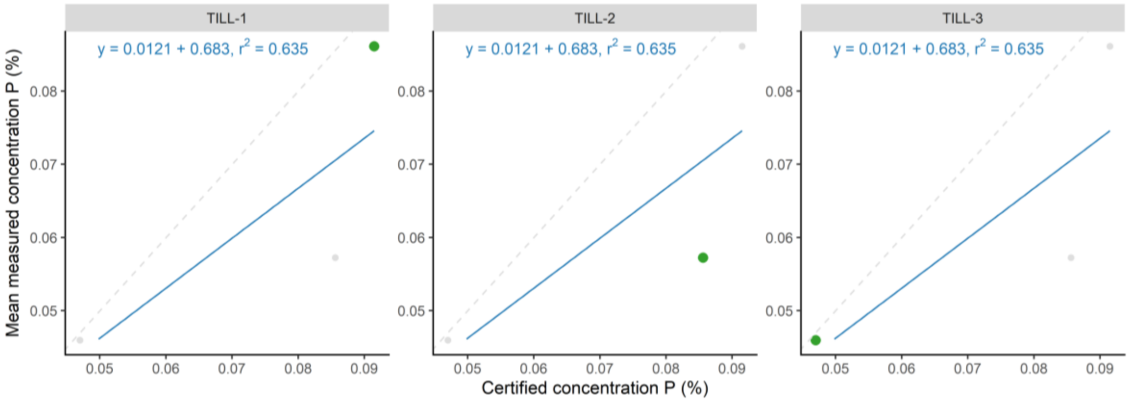


Chart 5 Phosphorus (P) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

Vanadium (V) by ICPar (MS41L-BLD)

Vanadium concentrations measured by the MS41L-BLD method are generally good but yield a somewhat poorly-fitting regression curve. No data conditioning is recommended.

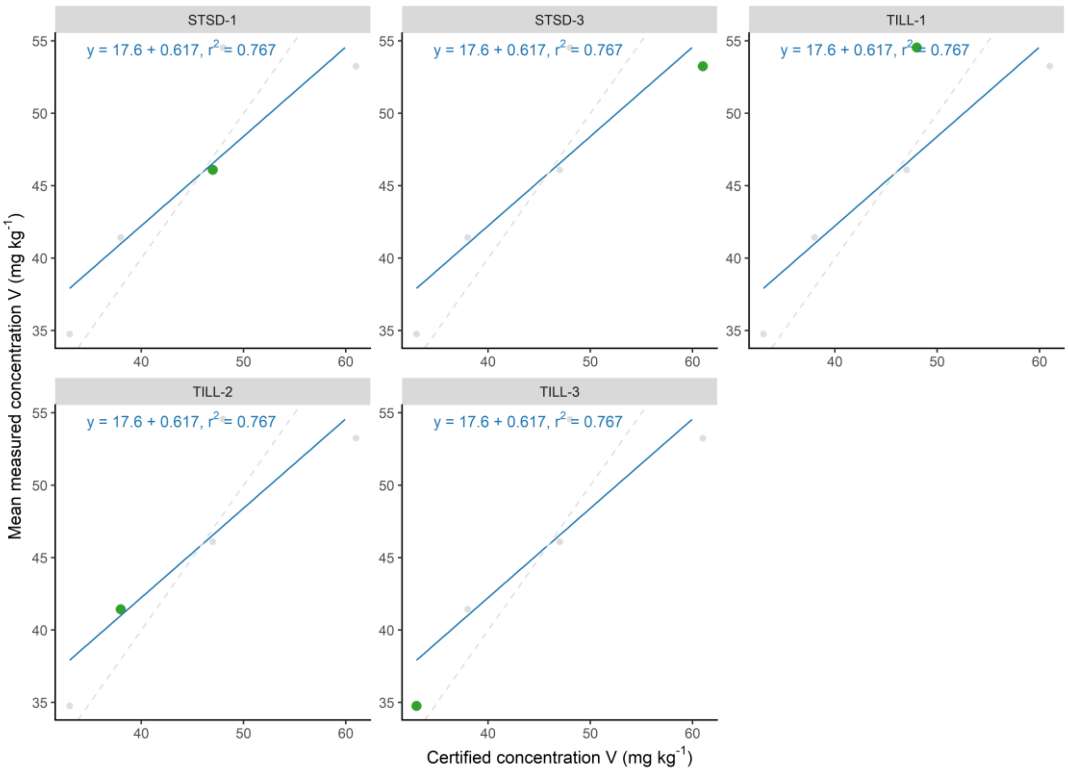


Chart 6 Vanadium (V) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

pH $CaCl_2$

Reported pH values for SRMs for G8S are generally higher than reported for adjacent survey blocks. Thus, regression of the data against mean values for Tellus survey blocks up to G6 yields a regression curve that is distinctly offset from the 1:1 line. For mapping purposes, in order to level data against adjacent survey blocks (G6 and G7), data conditioning is recommended using the equation for the regression curve (Table 13).

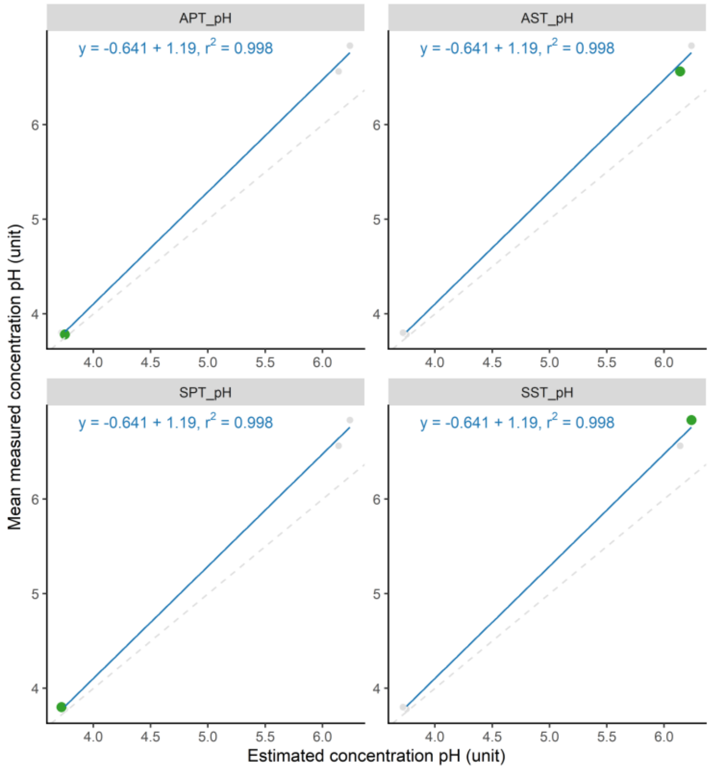


Chart 7 pH CaCl2 in blind SRMs, faceted by SRM name. The 1:1 equality line is shown as a feint dashed grey line.

Calculating relative bias

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

Equation 1 Relative bias %.

The relative bias of each analyte relative to the certified concentration in each of the CRMs analysed (STSD-1; STSD-3; TILL-1; TILL-2 and TILL-3) has been calculated according to Equation 1 (above). The results are presented in Table 15, Table 16, Table 17, Table 18 and Table 19. Certified concentrations for partial extractions are used where available but otherwise certified "total" concentrations have been used. The latter can be expected to differ significantly, in the case of some elements, from concentrations measured following partial extraction in *aqua regia*, potentially leading to large negative bias estimates for those elements with low extraction rates.

Table 15 Summary of relative bias ("Bias %") calculated for STSD-1 CRM data (n=11) analysed by ICPar method MS41L-BLD.

"N/A" indicates no reference concentration value is available. "Cert" indicates whether reference values were derived from "Total" or "Partial" extraction methods. "LLD" is the lower limit of detection for the analytical method.

	Au ($mgkg^{-1}$)	Ag ($mgkg^{-1}$)	Al (%)	As ($mgkg^{-1}$)	B ($mgkg^{-1}$)	Ba ($mgkg^{-1}$)	Be ($mgkg^{-1}$)	Bi ($mgkg^{-1}$)	Ca (%)	Cd ($mgkg^{-1}$)	Ce ($mgkg^{-1}$)	Co ($mgkg^{-1}$)
Bias %	-60.72%	12.29%	-75.97%	22.65%	-89.96%	-55.32%	-74.47%	N/A	-35.36%	15.55%	-30.45%	0.99%
Cert	Total	Partial	Total	Partial	Total	Total	Total	N/A	Total	Partial	Total	Partial
% < 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%
	Cr ($mgkg^{-1}$)	Cs ($mgkg^{-1}$)	Cu ($mgkg^{-1}$)	Fe (%)	Ga ($mgkg^{-1}$)	Ge ($mgkg^{-1}$)	Hf ($mgkg^{-1}$)	Hg ($mgkg^{-1}$)	In ($mgkg^{-1}$)	K (%)	La ($mgkg^{-1}$)	Li ($mgkg^{-1}$)
Bias %	-4.06%	-38.69%	0.44%	-4.45%	N/A	N/A	-99.58%	-6.63%	N/A	-92.64%	-29.26%	-18.77%
Cert	Partial	Total	Partial	Partial	N/A	N/A	Total	Partial	N/A	Total	Total	Total
% < 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 (%)	Mn ($mgkg^{-1}$)	Mo ($mgkg^{-1}$)	Na (%)	Nb ($mgkg^{-1}$)	Ni ($mgkg^{-1}$)	P (%)	Pb ($mgkg^{-1}$)	Pd ($mgkg^{-1}$)	Pt ($mgkg^{-1}$)	Rb ($mgkg^{-1}$)	Re ($mgkg^{-1}$)
Bias %	-44.66%	-4.34%	-51.28%	-97.25%	-86.04%	15.03%	-10.43%	2.10%	N/A	N/A	-73.60%	N/A
Cert	Total	Partial	Partial	Total	Total	Partial	Total	Partial	N/A	N/A	Total	N/A
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	81.8%	36.4%	0.0%	0.0%
	S (%)	Sb ($mgkg^{-1}$)	Sc ($mgkg^{-1}$)	Se ($mgkg^{-1}$)	Sn ($mgkg^{-1}$)	Sr ($mgkg^{-1}$)	Ta ($mgkg^{-1}$)	Te ($mgkg^{-1}$)	Th ($mgkg^{-1}$)	Ti (%)	Tl ($mgkg^{-1}$)	U ($mgkg^{-1}$)
Bias %	24.31%	12.45%	-72.82%	N/A	-57.22%	-82.98%	-99.41%	N/A	-82.58%	-91.96%	N/A	-14.06%
Cert	Total	Partial	Total	N/A	Total	Total	Total	N/A	Total	Total	N/A	Total
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	9.1%	0.0%	0.0%	0.0%	0.0%	0.0%
	V ($mgkg^{-1}$)	W ($mgkg^{-1}$)	Y ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Zr ($mgkg^{-1}$)							
Bias %	-1.92%	N/A	-44.50%	-0.56%	-99.65%							
Cert	Partial	N/A	Total	Partial	Total							
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%							

Table 16 Summary of relative bias ("Bias %") calculated for STSD-3 CRM data (n=7) analysed by ICPar method MS41L-BLD.

"N/A" indicates no reference concentration value is available. "Cert" indicates whether reference values were derived from "Total" or "Partial" extraction methods. "LLD" is the lower limit of detection for the analytical method.

	Au (mgkg^{-1})	Ag (mgkg^{-1})	Al (%)	As (mgkg^{-1})	B (mgkg^{-1})	Ba (mgkg^{-1})	Be (mgkg^{-1})	Bi (mgkg^{-1})	Ca (%)	Cd (mgkg^{-1})	Ce (mgkg^{-1})	Co (mgkg^{-1})
Bias %	-62.85%	9.45%	-72.67%	25.27%	-92.47%	-56.42%	-57.75%	N/A	-46.94%	14.96%	-37.53%	1.49%
Cert	Total	Partial	Total	Partial	Total	Total	Total	N/A	Total	Partial	Total	Partial
% < 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%
	Cr (mgkg^{-1})	Cs (mgkg^{-1})	Cu (mgkg^{-1})	Fe (%)	Ga (mgkg^{-1})	Ge (mgkg^{-1})	Hf (mgkg^{-1})	Hg (mgkg^{-1})	In (mgkg^{-1})	K (%)	La (mgkg^{-1})	Li (mgkg^{-1})
Bias %	-6.63%	-47.82%	2.74%	-5.99%	N/A	N/A	-99.69%	-1.51%	N/A	-91.74%	-41.19%	-14.57%
Cert	Partial	Total	Partial	Partial	N/A	N/A	Total	Partial	N/A	Total	Total	Total
% < 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 (%)	Mn (mgkg^{-1})	Mo (mgkg^{-1})	Na (%)	Nb (mgkg^{-1})	Ni (mgkg^{-1})	P (%)	Pb (mgkg^{-1})	Pd (mgkg^{-1})	Pt (mgkg^{-1})	Rb (mgkg^{-1})	Re (mgkg^{-1})
Bias %	-43.21%	-8.15%	-10.43%	-94.38%	-88.61%	17.24%	-18.76%	5.66%	N/A	N/A	-76.60%	N/A
Cert	Total	Partial	Partial	Total	Total	Partial	Total	Partial	N/A	N/A	Total	N/A
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	71.4%	0.0%	0.0%	0.0%
	S (%)	Sb (mgkg^{-1})	Sc (mgkg^{-1})	Se (mgkg^{-1})	Sn (mgkg^{-1})	Sr (mgkg^{-1})	Ta (mgkg^{-1})	Te (mgkg^{-1})	Th (mgkg^{-1})	Ti (%)	Tl (mgkg^{-1})	U (mgkg^{-1})
Bias %	16.26%	18.17%	-73.04%	N/A	-60.65%	-70.79%	-99.76%	N/A	-88.86%	-90.16%	N/A	-21.93%
Cert	Total	Partial	Total	N/A	Total	Total	Total	N/A	Total	Total	N/A	Total
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	14.3%	0.0%	0.0%	0.0%	0.0%	0.0%
	V (mgkg^{-1})	W (mgkg^{-1})	Y (mgkg^{-1})	Zn (mgkg^{-1})	Zr (mgkg^{-1})							
Bias %	-12.70%	N/A	-42.80%	-0.79%	-99.64%							
Cert	Partial	N/A	Total	Partial	Total							
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%							

Table 17 Summary of relative bias ("Bias %") calculated for TILL-1 CRM data (n=4) analysed by ICPar method MS41L-BLD.

"N/A" indicates no reference concentration value is available. "Cert" indicates whether reference values were derived from "Total" or "Partial" extraction methods. "LLD" is the lower limit of detection for the analytical method.

	Au ($mgkg^{-1}$)	Ag ($mgkg^{-1}$)	Al (%)	As ($mgkg^{-1}$)	B ($mgkg^{-1}$)	Ba ($mgkg^{-1}$)	Be ($mgkg^{-1}$)	Bi ($mgkg^{-1}$)	Ca (%)	Cd ($mgkg^{-1}$)	Ce ($mgkg^{-1}$)	Co ($mgkg^{-1}$)
Bias %	14.3%	14.3%	14.3%	14.3%	N/A	-1.45%	349.32%	N/A	-24.40%	N/A	-27.07%	4.11%
Cert	Total	Partial	Partial	Partial	N/A	Partial	Partial	N/A	Partial	N/A	Total	Partial
% < LLD	0.0%	0.0%	0.0%	0.0%	100%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Cr ($mgkg^{-1}$)	Cs ($mgkg^{-1}$)	Cu ($mgkg^{-1}$)	Fe (%)	Ga ($mgkg^{-1}$)	Ge ($mgkg^{-1}$)	Hf ($mgkg^{-1}$)	Hg ($mgkg^{-1}$)	In ($mgkg^{-1}$)	K (%)	La ($mgkg^{-1}$)	Li ($mgkg^{-1}$)
Bias %	-11.74%	-41.73%	-5.95%	5.84%	N/A	N/A	-99.88%	1.40%	N/A	-57.20%	-35.02%	-35.83%
Cert	Partial	Total	Partial	Partial	N/A	N/A	Total	Partial	N/A	Partial	Total	Total
% < 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 (%)	Mn ($mgkg^{-1}$)	Mo ($mgkg^{-1}$)	Na (%)	Nb ($mgkg^{-1}$)	Ni ($mgkg^{-1}$)	P (%)	Pb ($mgkg^{-1}$)	Pd ($mgkg^{-1}$)	Pt ($mgkg^{-1}$)	Rb ($mgkg^{-1}$)	Re ($mgkg^{-1}$)
Bias %	-15.20%	14.82%	N/A	-42.77%	-85.04%	-3.66%	-5.89%	20.41%	N/A	N/A	-86.44%	N/A
Cert	Partial	Partial	N/A	Partial	Total	Partial	Partial	Partial	N/A	N/A	Total	N/A
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	75.0%	50.0%	0.0%	0.0%
	S (%)	Sb ($mgkg^{-1}$)	Sc ($mgkg^{-1}$)	Se ($mgkg^{-1}$)	Sn ($mgkg^{-1}$)	Sr ($mgkg^{-1}$)	Ta ($mgkg^{-1}$)	Te ($mgkg^{-1}$)	Th ($mgkg^{-1}$)	Ti (%)	Tl ($mgkg^{-1}$)	U ($mgkg^{-1}$)
Bias %	N/A	-27.28%	-61.84%	N/A	N/A	-96.31%	-99.85%	N/A	-60.05%	-85.51%	N/A	-62.45%
Cert	N/A	Total	Total	N/A	N/A	Total	Total	N/A	Total	Total	N/A	Total
% < 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%
	V ($mgkg^{-1}$)	W ($mgkg^{-1}$)	Y ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Zr ($mgkg^{-1}$)							
Bias %	13.64%	N/A	-64.72%	-4.75%	-99.88%							
Cert	Partial	N/A	Total	Partial	Total							
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%							

Table 18 Summary of relative bias ("Bias %") calculated for TILL-2 CRM data (n=4) analysed by ICPar method MS41L-BLD.

"N/A" indicates no reference concentration value is available. "Cert" indicates whether reference values were derived from "Total" or "Partial" extraction methods. "LLD" is the lower limit of detection for the analytical method.

	Au (mgkg^{-1})	Ag (mgkg^{-1})	Al (%)	As (mgkg^{-1})	B (mgkg^{-1})	Ba (mgkg^{-1})	Be (mgkg^{-1})	Bi (mgkg^{-1})	Ca (%)	Cd (mgkg^{-1})	Ce (mgkg^{-1})	Co (mgkg^{-1})
Bias %	-38.16%	20.04%	-18.04%	11.83%	N/A	-1.79%	611.31%	17.84%	-25.57%	10.57%	-29.51%	1.55%
Cert	Total	Partial	Partial	Partial	N/A	Partial	Partial	Partial	Partial	Partial	Total	Partial
% < LLD	0.0%	0.0%	0.0%	0.0%	25.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

	Cr (mgkg^{-1})	Cs (mgkg^{-1})	Cu (mgkg^{-1})	Fe (%)	Ga (mgkg^{-1})	Ge (mgkg^{-1})	Hf (mgkg^{-1})	Hg (mgkg^{-1})	In (mgkg^{-1})	K (%)	La (mgkg^{-1})	Li (mgkg^{-1})
Bias %	-11.62%	-44.56%	-2.55%	2.81%	N/A	N/A	-99.45%	-23.71%	N/A	-29.45%	-34.83%	-27.55%
Cert	Partial	Total	Partial	Partial	N/A	N/A	Total	Partial	N/A	Partial	Total	Total
% < 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 (%)	Mn (mgkg^{-1})	Mo (mgkg^{-1})	Na (%)	Nb (mgkg^{-1})	Ni (mgkg^{-1})	P (%)	Pb (mgkg^{-1})	Pd (mgkg^{-1})	Pt (mgkg^{-1})	Rb (mgkg^{-1})	Re (mgkg^{-1})
Bias %	-9.01%	13.76%	14.13%	-36.87%	-82.90%	1.77%	-33.13%	9.52%	N/A	N/A	-74.36%	N/A
Cert	Partial	Partial	Partial	Partial	Total	Partial	Partial	Partial	N/A	N/A	Total	N/A
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	25.0%	0.0%	0.0%

	S (%)	Sb (mgkg^{-1})	Sc (mgkg^{-1})	Se (mgkg^{-1})	Sn (mgkg^{-1})	Sr (mgkg^{-1})	Ta (mgkg^{-1})	Te (mgkg^{-1})	Th (mgkg^{-1})	Ti (%)	Tl (mgkg^{-1})	U (mgkg^{-1})
Bias %	N/A	-46.43%	-58.36%	N/A	N/A	-90.80%	-99.91%	N/A	-51.39%	-97.88%	N/A	-45.99%
Cert	N/A	Total	Total	N/A	N/A	Total	Total	N/A	Total	Total	N/A	Total
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100%	0.0%	0.0%	0.0%	0.0%	0.0%

	V (mgkg^{-1})	W (mgkg^{-1})	Y (mgkg^{-1})	Zn (mgkg^{-1})	Zr (mgkg^{-1})
Bias %	9.04%	-62.96%	-71.16%	-2.38%	-99.16%
Cert	Partial	Total	Total	Partial	Total
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%

Table 19 Summary of relative bias (“Bias %”) calculated for TILL-3 CRM data (n=4) analysed by ICPar method MS41L-BLD.

“N/A” indicates no reference concentration value is available. “Cert” indicates whether reference values were derived from “Total” or “Partial” extraction methods. “LLD” is the lower limit of detection for the analytical method.

	Au ($mgkg^{-1}$)	Ag ($mgkg^{-1}$)	Al (%)	As ($mgkg^{-1}$)	B ($mgkg^{-1}$)	Ba ($mgkg^{-1}$)	Be ($mgkg^{-1}$)	Bi ($mgkg^{-1}$)	Ca (%)	Cd ($mgkg^{-1}$)	Ce ($mgkg^{-1}$)	Co ($mgkg^{-1}$)
Bias %	-61.53%	2.93%	3.40%	3.47%	N/A	-7.27%	337.19%	N/A	-19.40%	N/A	-25.61%	-0.37%
Cert	Total	Partial	Partial	Partial	N/A	Partial	Partial	N/A	Partial	N/A	Total	Partial
% < 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%

	Cr ($mgkg^{-1}$)	Cs ($mgkg^{-1}$)	Cu ($mgkg^{-1}$)	Fe (%)	Ga ($mgkg^{-1}$)	Ge ($mgkg^{-1}$)	Hf ($mgkg^{-1}$)	Hg ($mgkg^{-1}$)	In ($mgkg^{-1}$)	K (%)	La ($mgkg^{-1}$)	Li ($mgkg^{-1}$)
Bias %	-14.15%	-55.65%	-5.75%	-1.40%	N/A	N/A	-99.24%	-1.18%	N/A	-34.65%	-31.25%	-18.15%
Cert	Partial	Total	Partial	Partial	N/A	N/A	Total	Partial	N/A	Partial	Total	Total
% < 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 (%)	Mn ($mgkg^{-1}$)	Mo ($mgkg^{-1}$)	Na (%)	Nb ($mgkg^{-1}$)	Ni ($mgkg^{-1}$)	P (%)	Pb ($mgkg^{-1}$)	Pd ($mgkg^{-1}$)	Pt ($mgkg^{-1}$)	Rb ($mgkg^{-1}$)	Re ($mgkg^{-1}$)
Bias %	-11.80%	1.63%	N/A	-27.25%	-80.94%	2.72%	-2.21%	12.22%	N/A	N/A	-84.57%	N/A
Cert	Partial	Partial	N/A	Partial	Total	Partial	Partial	Partial	N/A	N/A	Total	N/A
% < LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	50.0%	0.0%	0.0%	100%

	S (%)	Sb ($mgkg^{-1}$)	Sc ($mgkg^{-1}$)	Se ($mgkg^{-1}$)	Sn ($mgkg^{-1}$)	Sr ($mgkg^{-1}$)	Ta ($mgkg^{-1}$)	Te ($mgkg^{-1}$)	Th ($mgkg^{-1}$)	Ti (%)	Tl ($mgkg^{-1}$)	U ($mgkg^{-1}$)
Bias %	N/A	-29.21%	-63.62%	N/A	N/A	-94.00%	N/A	N/A	-42.18%	-75.68%	N/A	-44.00%
Cert	N/A	Total	Total	N/A	N/A	Total	N/A	N/A	Total	Total	N/A	Total
% < 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%

	V ($mgkg^{-1}$)	W ($mgkg^{-1}$)	Y ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Zr ($mgkg^{-1}$)
Bias %	5.36%	N/A	-61.25%	-5.69%	-99.02%
Cert	Partial	N/A	Total	Partial	Total
% < 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.

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

Analytes of concern and carry-over contamination investigated

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

It is very important to assess the blank sample concentrations in the context of the real sample site data. If the blank samples are reported to contain a measurable analyte above its LLD, and even some way above it, but that concentration is quantifiably low compared to the concentrations reported for actual samples, then there is really no need to reject the data in the application for regional geochemical mapping. However, if 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 ICPar

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), yielding a total of 36 blank analyses for the G8 S dataset. These data are compiled and summarily reported at the end of each analytical batch as 'Blanks'. Blank data for methods ME-MS41L and MS41L-BLD are summarized in Table 20 and Table 21. In a standard, left-censored dataset baseline observations for a number of elements typically occurring close to the certified LLD can be lost. To understand better the behaviour of these elements at the low end of the distribution, the data were originally reported to an arbitrary limit lower by a factor of 100 than the certified LLD, thus producing the MS41L-BLD dataset. Data records in the MS41L-BLD dataset were then censored to the certified LLDs to produce the certified ME-MS41L dataset. It is therefore expected that frequent blank data exceedances will be observed in the BLD dataset, given its very low detection limits, and the user is cautioned to interpret these data in this context.

For the ME-MS41L dataset, blank data for twelve elements contained exceedances of the LLD concentrations: Bi (two exceedances of the LLD across two laboratory analytical batches), Cd (three exceedances across two batches), Co (one exceedance), Ga (one exceedance), Hg (three exceedances across two batches), Li (three exceedances across two batches), Na (one exceedance), Pb (one exceedance), Re (one exceedance), Sb (two exceedances across two batches), Tl (one exceedance) and W (two exceedances across two batches). These exceedances are not systematic, indicating random deviations. The LLDs for these elements range from 0.0002 to 0.005 mg/kg, except for Li (0.1 mg/kg), and the exceedances reported were ≤ 2*LLD (Bi, Co, Ga, Pb, Re) or ≤ 3*LLD (Cd, Hg, Tl). Exceptions were Li (max blank value of 0.4 mg/kg = 4*LLD), , Na (max blank value of 0.005 mg/kg = 5*LLD), Sb (max blank value of 0.031 mg/kg = 6*LLD), and W (max blank value of 0.008 mg/kg = 8*LLD). For Bi, Cd, Co, Ga, Pb, Sb, Tl and W, the minimum reported concentration in the dataset was much higher than the maximum reported blank concentration so the observed blank exceedances for these eight elements do not have material significance for the sample dataset. For Hg, the two blank exceedances in batch LR22249920 were reported as 0.005 and 0.009 mg/kg and the blank exceedance in batch LR22286720 was reported as 0.005 mg/kg - only one sample in the sample dataset has been reported as ≤ 0.009 mg/kg, with a concentration of 0.004 mg/kg. In the case of Li, the two blank exceedances in batch LR22286720 were reported as 0.004 and 0.003 mg/kg and the blank exceedance in batch LR22272933 was reported as 0.004 mg/kg – one sample in the sample dataset was reported as 0.4 mg/kg so user caution is thus advised when interpreting data at the lower end of the concentration spectrum for Li. For Na, the single observed exceedance of the LLD for blank samples was reported as 0.005 mg/kg – the minimum reported value for samples is 0.007 mg/kg so this exceedance does not give rise to concern. In the case of Re, the blank exceedance in batch LR22249920 was reported as 0.0003 mg/kg. This concentration overlaps measured concentrations reported for 45 samples, including 21 for which the reported concentration is below the LLD (0.0002), and user caution is thus advised when interpreting data at the lower end of the concentration spectrum for Re.

Table 20 Summary of above-method-LLD ("LLD") detectable ICPar ME-MS41L data in blank reference material. Analytes with >5% of data above the LLD are highlighted in orange.

	Au mg kg^{-1}	Ag mg kg^{-1}	Al %	As mg kg^{-1}	B mg kg^{-1}	Ba mg kg^{-1}	Be mg kg^{-1}	Bi mg kg^{-1}	Ca %	Cd mg kg^{-1}
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	0	0	0	0	0	0	0	2	0	3
% > LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	5.6%	0.0%	8.3%
	Ce mg kg^{-1}	Co mg kg^{-1}	Cr mg kg^{-1}	Cs mg kg^{-1}	Cu mg kg^{-1}	Fe %	Ga mg kg^{-1}	Ge mg kg^{-1}	Hf mg kg-1	Hg mg kg-1
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	0	1	0	0	0	0	1	0	0	3
% > LLD	0.0%	2.8%	0.0%	0.0%	0.0%	0.0%	2.8%	0.0%	0.0%	8.3%
	In mg kg^{-1}	K %	La mg kg^{-1}	Li mg kg^{-1}	Mg mg kg^{-1}	Mn mg kg^{-1}	Mo mg kg^{-1}	Na mg kg^{-1}	Nb mg kg^{-1}	Ni mg kg^{-1}
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	0	0	0	3	0	0	0	1	0	0
% > LLD	0.0%	0.0%	0.0%	8.3%	0.0%	0.0%	0.0%	2.8%	0.0%	0.0%
	P %	Pb mg kg^{-1}	Pd µg L-1	Pt mg kg-1	Rb mg kg^{-1}	Re mg kg^{-1}	S %	Sb mg kg^{-1}	Sc mg kg^{-1}	Se mg kg^{-1}
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	0	1	0	0	0	1	0	2	0	0
% > LLD	0.0%	2.8%	0.0%	0.0%	0.0%	2.8%	0.0%	5.6%	0.0%	0.0%
	Sn mg kg^{-1}	Sr mg kg^{-1}	Ta mg kg^{-1}	Te mg kg^{-1}	Th mg kg^{-1}	Ti %	Tl mg kg^{-1}	U mg kg^{-1}	V mg kg^{-1}	W mg kg^{-1}
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	0	0	0	0	0	0	1	0	0	2
% > LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	2.8%	0.0%	0.0%	5.6%
	Y mg kg^{-1}	Zn mg kg^{-1}	Zn mg kg^{-1}							
Count	36	36	36							
Count > LLD	0	0	0							
% > LLD	0.0%	0.0%	0.0%							

Table 21 Summary of above-method-LLD detectable ICPar MS41L-BLD data in blank reference material. Analytes with >5% of data above the LLD are highlighted in orange.

	Au mg kg^{-1}	Ag mg kg^{-1}	Al %	As mg kg^{-1}	B mg kg^{-1}	Ba mg kg^{-1}	Be mg kg^{-1}	Bi mg kg^{-1}	Ca %	Cd mg kg^{-1}
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	10	18	12	17	11	6	8	26	17	28
% > LLD	27.8%	50.0%	33.3%	47.2%	30.6%	16.7%	22.2%	72.2%	47.2%	77.8%
	Ce mg kg^{-1}	Co mg kg^{-1}	Cr mg kg^{-1}	Cs mg kg^{-1}	Cu mg kg^{-1}	Fe %	Ga mg kg^{-1}	Ge mg kg^{-1}	Hf mg kg-1	Hg mg kg-1
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	14	27	29	11	23	10	26	25	16	32
% > LLD	38.9%	75.0%	80.6%	30.6%	63.9%	27.8%	72.2%	69.4%	44.4%	88.9%
	In mg kg^{-1}	K %	La mg kg^{-1}	Li mg kg^{-1}	Mg mg kg^{-1}	Mn mg kg^{-1}	Mo mg kg^{-1}	Na mg kg^{-1}	Nb mg kg^{-1}	Ni mg kg^{-1}
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	18	3	14	13	5	21	22	17	19	21
% > LLD	50.0%	8.3%	38.9%	36.1%	13.9%	58.3%	61.1%	47.2%	52.8%	58.3%
	P %	Pb mg kg^{-1}	Pd µg L^{-1}	Pt mg kg^{-1}	Rb mg kg^{-1}	Re mg kg^{-1}	S %	Sb mg kg^{-1}	Sc mg kg^{-1}	Se mg kg^{-1}
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	23	19	21	6	19	13	12	25	16	21
% > method LLD	63.9%	52.8%	58.3%	16.7%	52.8%	36.1%	33.3%	69.4%	44.4%	58.3%
	Sn mg kg^{-1}	Sr mg kg^{-1}	Ta mg kg^{-}	Te mg kg^{-1}	Th mg kg^{-1}	Ti %	Tl mg kg^{-1}	U mg kg-1	V mg kg^{-1}	W mg kg^{-1}
Count	36	36	36	36	36	36	36	36	36	36
Count > LLD	20	23	32	13	18	0	15	7	17	19
% > LLD	55.6%	63.9%	88.9%	36.1%	50.0%	0.0%	41.7%	19.4%	47.2%	52.8%
	Y mg kg^{-1}	Zn mg kg^{-1}	Zn mg kg^{-1}							
Count	36	36	36							
Count > LLD	10	20	18							
% > LLD	27.8%	55.6%	50.0%							

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 through better processing and correction of data. 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 ICPar interferences

The analytical laboratory is primarily responsible for checking and where possible correcting for analytical interferences. No instances of interference were reported by the laboratory.

Univariate statistical summaries

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

When published by GSI, all geochemical data are censored, so that results below the lower reporting (detection) limit are reported as one half the stated lower limit of detection. Dealing statistically with non-detects and data truncated to both a lower and upper reporting limit is challenging, as numerically there needs to be a systematic and robust way of including these data. Representing censored data on a map can be managed by statistically classifying the data, based on percentile breaks in the data. Below is a statistical summary of the data (Table 22, Table 23 and Table 24) including both ICP-MS methods. These statistical summaries are calculated using the R program (R Core Team, 2013) employing 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.

Note that data used for the percentile calculations for the MS41L-BLD and ME-MS41L datasets are only right-censored (URL) and not-left censored (LLD), so that the percentile values represent points calculated for the entire data population, including values below the LLD. For analytes for which a proportion of data fall below the LLD, the calculated 0^{th} percentile does not always match with the minimum value of the entire data population because the calculation of the 0^{th} percentile value involves discounting values below the LLD.

Three methods for robust estimators of descriptive statistics (median, mean and standard deviation) are employed and colour coded accordingly (Table 25, Table 26 and Table 27). For those elements with ≤50% of censored data, the Kaplan-Meier estimator method was used to estimate the median, mean and standard deviation of the data (Kaplan and Meier, 1958). For those elements where >50% and ≤80% of the data are censored, the maximum likelihood estimation (MLE) method was used to estimate the median, mean and standard deviation. Where >80% of the data were censored the median, mean and standard deviation are estimated using a regression on order statistics (ROS) method (Helsel, 2005). This follows some recommendations of the NADA package and of Antweiler and Taylor (2008) on estimators of environmental datasets.

Table 22 Univariate summary statistics for deeper topsoil pH ($CaCl_2$) and LOI (450°C) sample data.

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
pH	0.1	pH unit	877	0	0	3.3	5.9	6.3	6.4	6.5	6.8	7	7	7.1	7.2	7.4	7.4	7.5	7.7
LOI (450°C)	0.01	%	877	0	0	0.38	4.69	5.39	5.84	6.71	8.32	9.58	9.99	10.4	11.8	13.5	14.9	17.5	25.1

Table 23 Univariate summary statistics for deeper topsoil ICPar sample data calculated for MS41L-BLD method.

Variable	LLD	Unit	*n*	*n* < LLD	% < LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
Ag	0.00001	mg kg^{-1}	877	0	0	0.0162	0.11	0.14	0.157	0.183	0.25	0.346	0.386	0.433	0.608	0.813	0.997	1.55	9.46
Al	0.0001	%	877	0	0	0.118	0.773	0.868	0.923	0.972	1.06	1.14	1.16	1.19	1.26	1.33	1.44	1.56	1.72
As	0.0001	mg kg^{-1}	877	0	0	2.27	12.4	14	15	16.3	18.7	21.6	23	24.3	31.1	38.2	48.5	73.5	1020
B	0.1	mg kg^{-1}	877	1	0.114	1.3	3.2	4.1	4.7	5.5	6.8	7.8	8.1	8.4	9.6	10.9	12.8	16.7	33.2
Ba	0.005	mg kg^{-1}	877	0	0	9.27	66.8	79.5	84.7	93.9	112	131	139	146	186	233	303	405	1520
Be	0.0001	mg kg^{-1}	877	0	0	0.0815	0.651	0.878	0.962	1.04	1.17	1.3	1.34	1.39	1.6	1.82	2.11	2.49	4.6
Bi	0.000005	mg kg^{-1}	877	0	0	0.0155	0.132	0.153	0.166	0.181	0.219	0.265	0.286	0.307	0.394	0.475	0.599	0.917	3.26
Ca	0.0001	%	877	0	0	0.0349	0.347	0.718	1.08	1.78	3.47	4.87	5.19	5.63	6.59	7.75	8.69	9.66	12.9
Cd	0.00001	mg kg^{-1}	877	0	0	0.0398	0.64	1.1	1.31	1.6	1.98	2.22	2.28	2.36	2.56	2.78	3.04	3.45	8.01
Ce	0.00003	mg kg^{-1}	877	0	0	4.4	19	21.2	22.2	23.6	25.9	27.6	28.2	28.8	30.3	32.1	33.3	37.4	44.5
Co	0.00001	mg kg^{-1}	877	0	0	0.308	6.83	8.83	9.53	10.4	11.7	12.8	13.2	13.5	15	16.1	18.1	19.4	27.7
Cr	0.0001	mg kg^{-1}	877	0	0	3.06	15.5	18.3	19.3	20.2	22	23.3	23.7	24.2	25.8	27.8	29.4	32.9	57.7
Cs	0.00005	mg kg^{-1}	877	0	0	0.192	0.358	0.394	0.413	0.448	0.525	0.618	0.663	0.722	0.941	1.17	1.39	2.17	3.15
Cu	0.0001	mg kg^{-1}	877	0	0	1.48	21.7	28	30.9	35.7	46.4	57.7	62	68.9	94.4	130	172	227	2850
Fe	0.00001	%	877	0	0	0.176	1.66	2	2.1	2.2	2.4	2.55	2.59	2.64	2.84	3.04	3.36	3.78	6.31

Variable	LLD	Unit	*n*	*n* < LLD	% < 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
Ga	0.00004	mg kg^{-1}	877	0	0	0.413	2.26	2.5	2.68	2.86	3.24	3.57	3.68	3.77	4.1	4.55	4.95	5.31	8.74
Ge	0.00005	mg kg^{-1}	877	0	0	0.0097	0.0418	0.0481	0.0502	0.0537	0.0611	0.0675	0.0695	0.072	0.0814	0.0936	0.107	0.15	0.392
Hf	0.00002	mg kg^{-1}	877	0	0	0.0043	0.0443	0.0606	0.0683	0.0781	0.0926	0.104	0.107	0.109	0.118	0.124	0.129	0.135	0.17
Hg	0.00004	mg kg^{-1}	877	0	0	0.0039	0.0771	0.1	0.115	0.155	0.266	0.401	0.458	0.548	0.953	1.43	2.17	3.2	29.3
In	0.00005	mg kg^{-1}	877	6	0.68	0.0011	0.0108	0.0156	0.0182	0.021	0.0244	0.0268	0.0278	0.0288	0.0312	0.0339	0.0388	0.0438	0.109
K	0.0001	%	877	0	0	0.0278	0.0969	0.105	0.11	0.118	0.132	0.142	0.145	0.149	0.161	0.171	0.18	0.189	0.232
La	0.00002	mg kg^{-1}	877	0	0	2.1	9.6	10.8	11.3	12	13	13.9	14.1	14.4	15.2	15.9	16.6	18.3	23.2
Li	0.001	mg kg^{-1}	877	0	0	0.354	8.72	9.86	10.6	11.4	13.9	16.5	17.5	18.6	22.8	27.1	31	36.1	62.8
Mg	0.0001	%	877	0	0	0.025	0.168	0.184	0.198	0.214	0.254	0.292	0.302	0.315	0.36	0.412	0.461	0.535	1.43
Mn	0.001	mg kg^{-1}	877	0	0	9.83	544	739	815	916	1180	1400	1450	1520	1740	1970	2330	2450	3510
Mo	0.0001	mg kg^{-1}	877	0	0	0.0752	1.44	1.93	2.22	2.57	3.24	3.69	3.79	3.95	4.35	4.89	5.38	6.48	17
Na	0.00001	%	877	0	0	0.0072	0.0125	0.0135	0.0143	0.0154	0.0177	0.0201	0.021	0.0227	0.0273	0.0348	0.0463	0.0652	0.181
Nb	0.00002	mg kg^{-1}	877	0	0	0.0736	0.216	0.244	0.264	0.291	0.342	0.388	0.404	0.423	0.5	0.588	0.649	0.803	1.53
Ni	0.0004	mg kg^{-1}	877	0	0	2.53	22.3	30.4	34.4	38.9	46.2	50.6	51.9	53.4	57.1	61.2	66.7	75.5	101
P	0.00001	mg kg^{-1}	877	0	0	104	461	560	619	694	864	1030	1090	1190	1500	1840	2150	2610	3380
Pb	0.00005	mg kg^{-1}	877	0	0	4.9	34.4	42.5	48.8	59.8	93.2	141	161	183	274	417	623	812	2020
Rb	0.00005	mg kg^{-1}	877	0	0	2.17	7.01	7.55	7.87	8.37	9.37	10.3	10.7	11.1	12.4	14.2	15.6	16.8	21.7
Re	0.000002	mg kg^{-1}	877	2	0.23	0.000051	0.000338	0.000529	0.000703	0.000878	0.00132	0.00166	0.00179	0.00191	0.0023	0.00268	0.00307	0.00355	0.0055
S	0.0001	%	877	0	0	0.0099	0.03	0.0362	0.04	0.0452	0.0578	0.0675	0.071	0.0742	0.0848	0.0956	0.109	0.133	0.324
Sb	0.00005	mg kg^{-1}	877	0	0	0.0646	0.615	0.84	0.939	1.1	1.52	1.92	2.05	2.22	2.94	3.87	4.83	8.37	30.6
Sc	0.00005	mg kg^{-1}	877	0	0	0.566	2.02	2.72	2.99	3.3	3.74	4.03	4.11	4.21	4.45	4.69	4.91	5.28	7.58
Se	0.00003	mg kg^{-1}	877	0	0	0.0284	0.518	0.636	0.704	0.799	0.978	1.1	1.14	1.18	1.32	1.48	1.59	1.76	6.15
Sn	0.0001	mg kg^{-1}	877	0	0	0.196	0.983	1.28	1.63	2.33	4.27	7.67	9.2	11.4	19.2	33.6	48.6	69.9	327
Sr	0.0001	mg kg^{-1}	877	0	0	5.39	21.6	30.7	40.9	59.8	102	142	153	166	193	233	268	307	401

Variable	LLD	Unit	*n*	*n* < LLD	% < 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
Ta	0.00005	mg kg^{-1}	877	107	12.20	0.0000518	0.000129	0.000173	0.000204	0.00036	0.00065	0.00086	0.00092	0.00099	0.00122	0.00157	0.00206	0.00363	0.0233
Te	0.00003	mg kg^{-1}	877	0	0	0.0014	0.0159	0.0211	0.0236	0.0263	0.0313	0.0353	0.0364	0.0379	0.0416	0.0463	0.0495	0.0538	0.106
Th	0.00002	mg kg^{-1}	877	0	0	0.46	0.942	1.06	1.12	1.24	1.43	1.58	1.63	1.67	1.79	1.93	2.1	2.21	5.72
Ti	0.00001	%	877	0	0	0.00021	0.00292	0.00333	0.00361	0.00408	0.00525	0.00671	0.00712	0.00779	0.0106	0.0144	0.0174	0.024	0.0535
Tl	0.00001	mg kg^{-1}	877	0	0	0.0223	0.13	0.169	0.185	0.203	0.227	0.245	0.251	0.257	0.274	0.294	0.31	0.343	1.15
U	0.00005	mg kg^{-1}	877	0	0	0.145	0.603	0.712	0.756	0.825	0.927	1.02	1.05	1.08	1.2	1.29	1.55	1.92	2.96
V	0.001	mg kg^{-1}	877	0	0	3.24	25.4	31.2	32.7	34.6	38.6	41.5	42.2	43.1	46	49.3	52.7	60.2	90.3
W	0.00001	mg kg^{-1}	877	0	0	0.0343	0.0659	0.0762	0.0815	0.0875	0.113	0.144	0.159	0.175	0.246	0.33	0.476	1.27	27.4
Y	0.00003	mg kg^{-1}	877	0	0	1.17	7.82	11.4	12.9	14.5	16.3	17.6	18	18.4	19.3	20.4	21.3	22.7	30.5
Zn	0.001	mg kg^{-1}	877	0	0	9.49	80.8	99.5	108	119	140	167	181	193	252	310	428	674	6420
Zr	0.0001	mg kg^{-1}	877	0	0	0.183	1.49	2.08	2.37	2.67	3.16	3.48	3.59	3.68	3.96	4.19	4.33	4.53	6.16
Au	0.000002	mg kg^{-1}	877	1	0.114	0.0001	0.00117	0.00156	0.00179	0.00222	0.00326	0.00419	0.00455	0.00504	0.00695	0.00971	0.0131	0.0206	0.105
Pd	0.00001	mg kg^{-1}	877	718	81.87	<LLD	<LLD	<LLD	<LLD	<LLD	0.0000328	0.000114	0.000162	0.000233	0.00122	0.00331	0.00487	0.00592	0.0234
Pt	0.00002	mg kg^{-1}	877	33	3.76	0.00003	0.000128	0.000206	0.00031	0.00047	0.00068	0.000882	0.00096	0.00103	0.00138	0.0017	0.00224	0.00464	0.0255

Table 24 Univariate summary statistics for deeper topsoil ICPar sample data calculated for ME-MS41L method.

Variable	LLD	Unit	*n*	*n* < LLD	% < LLD	0th percentile	5th percentile	10th percentile	15th percentile	25th percentile	50th percentile	70th percentile	75th percentile	80th percentile	90th percentile	95th percentile	97.5th percentile	99th percentile	100th percentile
Ag	0.001	mg kg^{-1}	877	0	0	0.016	0.111	0.14	0.157	0.183	0.25	0.346	0.386	0.433	0.608	0.813	0.997	1.55	9.46
Al	0.01	%	877	0	0	0.12	0.77	0.87	0.92	0.97	1.06	1.14	1.16	1.19	1.26	1.33	1.43	1.55	1.72
As	0.01	mg kg^{-1}	877	0	0	2.27	12.4	14	15	16.3	18.8	21.6	23	24.3	31.1	38.2	48.5	73.5	1020
B	10	mg kg^{-1}	877	158	18.02	8.41	9.1	9.29	9.41	10	10	10	10	10	10	10	10	20	30
Ba	0.5	mg kg^{-1}	877	0	0	9.3	66.9	79.5	84.6	93.9	112	132	138	146	186	233	303	405	1520
Be	0.01	mg kg^{-1}	877	0	0	0.08	0.648	0.88	0.96	1.04	1.17	1.3	1.34	1.39	1.61	1.82	2.11	2.49	4.6
Bi	0.0005	mg kg^{-1}	877	0	0	0.0155	0.133	0.153	0.166	0.18	0.219	0.265	0.286	0.307	0.394	0.475	0.599	0.917	3.26
Ca	0.01	%	877	0	0	0.03	0.35	0.716	1.08	1.78	3.47	4.87	5.19	5.63	6.59	7.75	8.7	9.66	12.8
Cd	0.001	mg kg^{-1}	877	0	0	0.04	0.64	1.09	1.31	1.6	1.98	2.22	2.28	2.36	2.56	2.78	3.04	3.45	8.01
Ce	0.003	mg kg^{-1}	877	0	0	4.4	19	21.2	22.1	23.6	25.9	27.6	28.2	28.8	30.3	32	33.3	37.4	44.5
Co	0.001	mg kg^{-1}	877	0	0	0.308	6.83	8.84	9.53	10.4	11.7	12.8	13.2	13.5	15	16.2	18.1	19.4	27.7
Cr	0.01	mg kg^{-1}	877	0	0	3.06	15.5	18.3	19.3	20.2	22	23.3	23.7	24.2	25.8	27.8	29.4	32.9	57.7
Cs	0.005	mg kg^{-1}	877	0	0	0.192	0.358	0.394	0.413	0.448	0.525	0.618	0.663	0.722	0.941	1.17	1.39	2.16	3.15
Cu	0.01	mg kg^{-1}	877	0	0	1.48	21.7	28	30.9	35.7	46.4	57.7	62	68.9	94.4	130	172	227	2850
Fe	0.001	%	877	0	0	0.176	1.66	2	2.09	2.2	2.4	2.55	2.59	2.64	2.84	3.04	3.36	3.78	6.31
Ga	0.004	mg kg^{-1}	877	0	0	0.413	2.26	2.5	2.68	2.86	3.24	3.57	3.68	3.77	4.11	4.55	4.95	5.31	8.74
Ge	0.005	mg kg^{-1}	877	0	0	0.01	0.042	0.048	0.05	0.054	0.061	0.068	0.069	0.072	0.081	0.0932	0.107	0.149	0.392
Hf	0.002	mg kg^{-1}	877	0	0	0.004	0.044	0.0606	0.068	0.078	0.093	0.104	0.107	0.109	0.118	0.124	0.129	0.135	0.17
Hg	0.004	mg kg^{-1}	877	0	0	0.004	0.0768	0.1	0.115	0.155	0.266	0.401	0.458	0.549	0.953	1.43	2.17	3.2	29.3
In	0.005	mg kg^{-1}	877	16	1.82	0.005	0.0114	0.016	0.018	0.021	0.024	0.027	0.028	0.029	0.031	0.034	0.039	0.044	0.109
K	0.01	%	877	0	0	0.03	0.1	0.11	0.11	0.12	0.13	0.14	0.15	0.15	0.16	0.17	0.18	0.19	0.23
La	0.002	mg kg^{-1}	877	0	0	2.1	9.6	10.8	11.3	11.9	13	13.9	14.2	14.3	15.2	16	16.6	18.3	23.2
Li	0.1	mg kg^{-1}	877	0	0	0.4	8.7	9.9	10.6	11.5	14	16.5	17.5	18.7	22.8	27.1	31	36.1	62.8
Mg	0.01	%	877	0	0	0.03	0.17	0.18	0.2	0.21	0.25	0.29	0.3	0.318	0.36	0.41	0.461	0.54	1.43

Variable	LLD	Unit	*n*	*n* < LLD	% < 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
Mn	0.1	mg kg^{-1}	877	0	0	9.8	544	739	815	916	1180	1400	1450	1520	1740	1970	2330	2450	3510
Mo	0.01	mg kg^{-1}	877	0	0	0.08	1.44	1.93	2.22	2.57	3.24	3.69	3.79	3.95	4.35	4.89	5.38	6.48	17
Na	0.001	%	877	0	0	0.007	0.013	0.014	0.014	0.015	0.018	0.02	0.021	0.023	0.027	0.035	0.0461	0.0652	0.182
Nb	0.002	mg kg^{-1}	877	0	0	0.074	0.217	0.244	0.264	0.291	0.342	0.388	0.404	0.423	0.5	0.588	0.649	0.803	1.53
Ni	0.04	mg kg^{-1}	877	0	0	2.53	22.3	30.4	34.4	38.9	46.2	50.6	51.9	53.4	57.1	61.3	66.7	75.5	101
P	0.001	mg kg^{-1}	877	0	0	100	460	560	620	690	860	1030	1090	1190	1490	1840	2150	2610	3380
Pb	0.005	mg kg^{-1}	877	0	0	4.9	34.4	42.5	48.8	59.8	93.2	142	161	183	274	417	623	812	2020
Rb	0.005	mg kg^{-1}	877	0	0	2.17	7.02	7.56	7.87	8.37	9.37	10.3	10.7	11.1	12.4	14.2	15.6	16.8	21.7
Re	0.0002	mg kg^{-1}	877	21	2.395	0.0002	0.000378	0.0005	0.0007	0.0009	0.0013	0.0017	0.0018	0.0019	0.0023	0.0027	0.0031	0.00352	0.0055
S	0.01	%	877	0	0	0.01	0.03	0.04	0.04	0.05	0.06	0.07	0.07	0.07	0.08	0.1	0.11	0.132	0.32
Sb	0.005	mg kg^{-1}	877	0	0	0.065	0.615	0.84	0.938	1.1	1.52	1.92	2.05	2.22	2.94	3.87	4.83	8.37	30.6
Sc	0.005	mg kg^{-1}	877	0	0	0.566	2.02	2.72	2.99	3.3	3.74	4.03	4.11	4.21	4.45	4.69	4.91	5.28	7.58
Se	0.003	mg kg^{-1}	877	0	0	0.028	0.518	0.636	0.704	0.799	0.978	1.1	1.14	1.18	1.32	1.48	1.59	1.76	6.15
Sn	0.01	mg kg^{-1}	877	0	0	0.2	0.98	1.28	1.63	2.33	4.27	7.66	9.2	11.4	19.2	33.6	48.6	69.9	327
Sr	0.01	mg kg^{-1}	877	0	0	5.39	21.7	30.7	40.9	59.8	102	142	153	166	193	233	268	307	401
Ta	0.005	mg kg^{-1}	877	871	99.32	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.023
Te	0.003	mg kg^{-1}	877	13	1.482	0.003	0.016	0.021	0.024	0.026	0.031	0.035	0.036	0.038	0.042	0.046	0.05	0.054	0.106
Th	0.002	mg kg^{-1}	877	0	0	0.46	0.943	1.05	1.12	1.24	1.43	1.58	1.62	1.66	1.79	1.93	2.1	2.21	5.72
Ti	0.001	%	877	1	0.114	0.0012	0.003	0.003	0.004	0.004	0.005	0.007	0.007	0.008	0.011	0.0142	0.0171	0.0242	0.053
Tl	0.001	mg kg^{-1}	877	0	0	0.022	0.13	0.17	0.185	0.203	0.227	0.245	0.251	0.257	0.274	0.294	0.31	0.343	1.15
U	0.005	mg kg^{-1}	877	0	0	0.145	0.603	0.713	0.756	0.825	0.927	1.02	1.05	1.08	1.2	1.29	1.55	1.92	2.96
V	0.1	mg kg^{-1}	877	0	0	3.2	25.4	31.2	32.7	34.6	38.6	41.5	42.2	43.1	45.9	49.2	52.7	60.2	90.3
W	0.001	mg kg^{-1}	877	0	0	0.034	0.066	0.076	0.082	0.088	0.113	0.144	0.159	0.175	0.246	0.33	0.477	1.27	27.4
Y	0.003	mg kg^{-1}	877	0	0	1.17	7.82	11.3	12.9	14.4	16.3	17.6	18.1	18.4	19.3	20.4	21.3	22.7	30.5

Variable	LLD	Unit	*n*	*n* < LLD	% < 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
Zn	0.1	mg kg^{-1}	877	0	0	9.5	80.8	99.5	108	119	140	167	181	193	252	310	428	674	6420
Zr	0.01	mg kg^{-1}	877	0	0	0.18	1.5	2.08	2.37	2.67	3.16	3.48	3.59	3.68	3.96	4.19	4.33	4.53	6.16
Au	0.0002	mg kg^{-1}	877	4	0.46	0.0002	0.0012	0.0016	0.0018	0.0022	0.0033	0.0042	0.0045	0.005	0.0069	0.0097	0.013	0.0207	0.105
Pd	0.001	mg kg^{-1}	877	748	85.29	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.001	0.003	0.005	0.006	0.023
Pt	0.002	mg kg^{-1}	877	807	92.02	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.002	0.002	0.00424	0.026

Table 25 Univariate summary statistics including best fits based on proportions of pH (CaC2) and LOI (450°C) data below the LLD.

Variable	LLD	Unit	*n*	*n* < LLD	% < 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	0.1		877	0	0	6.73	6.7	0.297	5.75	7.25	6.8	6.8	6.7	6.73	6.73	6.73	0.532	0.532	0.611
LOI	0.01	%	877	0	0	8.51	7.97	2.42	1.79	11.6	8.32	8.32	7.97	8.51	8.51	8.62	2.89	2.89	3.56

Table 26 Univariate summary statistics including best fits based on proportions of ICPar data below the MS41L-BLD LLD.

Variable	LLD	Unit	*n*	*n* < LLD	% < LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
Ag	0.00001	mg kg^{-1}	877	0	0	0.35	0.267	0.125	-0.12	0.487	0.25	0.25	0.267	0.35	0.35	0.336	0.513	0.513	0.258
Al	0.0001	%	877	0	0	1.05	1.02	0.139	0.692	1.25	1.06	1.06	1.02	1.05	1.05	1.07	0.207	0.207	0.308
As	0.0001	mg kg^{-1}	877	0	0	22.9	19.5	4.44	6.28	26.4	18.7	18.7	19.5	22.9	22.9	21.7	38.5	38.5	10.5
B	0.1	mg kg^{-1}	877	1	0.114	7	6.51	1.93	1.6	9.4	6.8	6.8	6.48	6.99	6.99	7.06	2.83	2.82	3.07
Ba	0.005	mg kg^{-1}	877	0	0	129	114	31.6	26.9	161	112	112	114	129	129	129	92.9	92.9	68.9
Be	0.0001	mg kg^{-1}	877	0	0	1.21	1.13	0.215	0.59	1.49	1.17	1.17	1.13	1.21	1.21	1.23	0.397	0.397	0.541
Bi	0.000005	mg kg^{-1}	877	0	0	0.259	0.227	0.0666	0.0231	0.338	0.219	0.219	0.227	0.259	0.259	0.257	0.192	0.192	0.136

Variable	LLD	Unit	*n*	*n* < LLD	% < 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
Ca	0.0001	%	877	0	0	3.66	2.69	2.54	-3.33	6.89	3.47	3.47	2.69	3.66	3.66	4.23	2.31	2.31	5.14
Cd	0.00001	mg kg^{-1}	877	0	0	1.9	1.69	0.492	0.576	2.62	1.98	1.98	1.69	1.9	1.9	2.07	0.674	0.674	1.45
Ce	0.00003	mg kg^{-1}	877	0	0	25.6	25.1	3.43	16.6	30.5	25.9	25.9	25.1	25.6	25.6	25.7	4.6	4.6	5.84
Co	0.00001	mg kg^{-1}	877	0	0	11.7	11.1	2.06	6.29	14.6	11.7	11.7	11.1	11.7	11.7	12	3.01	3.01	4.92
Cr	0.0001	mg kg^{-1}	877	0	0	21.9	21.3	2.57	15	25.5	22	22	21.3	21.9	21.9	22	4.59	4.59	5.86
Cs	0.00005	mg kg^{-1}	877	0	0	0.614	0.566	0.14	0.125	0.771	0.525	0.525	0.566	0.614	0.614	0.607	0.309	0.309	0.234
Cu	0.0001	mg kg^{-1}	877	0	0	62.3	47	18.5	-3.78	75.2	46.4	46.4	47	62.3	62.3	59.2	134	134	45.2
Fe	0.00001	%	877	0	0	2.39	2.3	0.291	1.62	2.78	2.4	2.4	2.3	2.39	2.39	2.42	0.544	0.544	0.788
Ga	0.00004	mg kg^{-1}	877	0	0	3.27	3.15	0.59	1.63	4.09	3.24	3.24	3.15	3.27	3.27	3.3	0.79	0.79	1.03
Ge	0.00005	mg kg^{-1}	877	0	0	0.0642	0.0611	0.0112	0.03	0.0773	0.0611	0.0611	0.0611	0.0642	0.0642	0.0641	0.0242	0.0242	0.0206
Hf	0.00002	mg kg^{-1}	877	0	0	0.0902	0.0854	0.021	0.0351	0.121	0.0926	0.0926	0.0854	0.0902	0.0902	0.092	0.0242	0.0242	0.0367
Hg	0.00004	mg kg^{-1}	877	0	0	0.483	0.281	0.196	-0.299	0.61	0.266	0.266	0.281	0.483	0.483	0.438	1.18	1.18	0.526
In	0.00005	mg kg^{-1}	877	6	0.68	0.0242	0.0228	0.00494	0.0112	0.0311	0.0244	0.0244	0.0218	0.0241	0.0241	0.0269	0.00785	0.00772	0.0194
K	0.0001	%	877	0	0	0.132	0.129	0.0202	0.0773	0.159	0.132	0.132	0.129	0.132	0.132	0.132	0.0244	0.0244	0.0283
La	0.00002	mg kg^{-1}	877	0	0	12.9	12.6	1.61	8.72	15.2	13	13	12.6	12.9	12.9	13	2.29	2.29	3.01
Li	0.001	mg kg^{-1}	877	0	0	15.2	14.1	4.23	2.37	20.5	14	13.9	14.1	15.2	15.2	15.3	6.12	6.12	6.55
Mg	0.0001	%	877	0	0	0.266	0.254	0.0638	0.0826	0.346	0.254	0.254	0.254	0.266	0.266	0.267	0.0877	0.0877	0.0862
Mn	0.001	mg kg^{-1}	877	0	0	1200	1090	396	112	1720	1180	1180	1090	1200	1200	1270	455	455	749
Mo	0.0001	mg kg^{-1}	877	0	0	3.22	2.91	0.915	0.737	4.4	3.24	3.24	2.91	3.22	3.22	3.41	1.22	1.22	2.08
Na	0.00001	%	877	0	0	0.0203	0.0188	0.004	0.00697	0.0238	0.0177	0.0177	0.0188	0.0203	0.0203	0.0199	0.0122	0.0122	0.00691
Nb	0.00002	mg kg^{-1}	877	0	0	0.362	0.345	0.08	0.122	0.461	0.342	0.342	0.345	0.362	0.362	0.362	0.125	0.125	0.112
Ni	0.0004	mg kg^{-1}	877	0	0	44.7	41.8	9.5	19.3	58.5	46.2	46.2	41.8	44.7	44.7	46	12.5	12.5	21.2
P	0.00001	mg kg^{-1}	877	0	0	956	867	283	97.9	1290	864	864	867	956	956	962	446	446	463
Pb	0.00005	mg kg^{-1}	877	0	0	143	101	62.1	-91.7	211	93.2	93.2	101	143	143	139	165	165	132
Rb	0.00005	mg kg^{-1}	877	0	0	9.68	9.36	1.62	4.87	11.9	9.37	9.37	9.36	9.68	9.68	9.71	2.38	2.38	2.67

Variable	LLD	Unit	*n*	*n* < LLD	% < 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
Re	0.000002	mg kg^{-1}	877	2	0.23	0.00139	0.00117	0.000681	-0.000489	0.00225	0.00132	0.00132	0.00115	0.00139	0.00139	0.00152	0.000743	0.000743	0.00131
S	0.0001	%	877	0	0	0.0598	0.0558	0.019	0.0065	0.0839	0.0578	0.0578	0.0558	0.0598	0.0598	0.06	0.0231	0.0231	0.0236
Sb	0.00005	mg kg^{-1}	877	0	0	1.84	1.5	0.687	-0.337	2.53	1.52	1.52	1.5	1.84	1.84	1.83	1.79	1.79	1.29
Sc	0.00005	mg kg^{-1}	877	0	0	3.64	3.5	0.592	2.09	4.51	3.74	3.74	3.5	3.64	3.64	3.68	0.834	0.834	1.19
Se	0.00003	mg kg^{-1}	877	0	0	0.978	0.9	0.254	0.288	1.31	0.978	0.978	0.9	0.978	0.978	1.02	0.347	0.347	0.554
Sn	0.0001	mg kg^{-1}	877	0	0	9.31	4.73	3.71	-7.99	12.6	4.27	4.27	4.73	9.31	9.31	8.46	19.3	19.3	12.5
Sr	0.0001	mg kg^{-1}	877	0	0	111	89.3	67.8	-80	200	102	102	89.3	111	111	116	67.1	67.1	97.6
Ta	0.00005	mg kg^{-1}	877	107	12.20	0.000836	0.000657	0.000356	-0.00028	0.00122	0.00065	0.00065	0.000453	0.000741	0.000753	0.000915	0.00101	0.00101	0.0016
Te	0.00003	mg kg^{-1}	877	0	0	0.0314	0.0291	0.00756	0.0111	0.0415	0.0313	0.0313	0.0291	0.0314	0.0314	0.0326	0.00986	0.00986	0.0165
Th	0.00002	mg kg^{-1}	877	0	0	1.44	1.4	0.289	0.653	1.82	1.43	1.43	1.4	1.44	1.44	1.44	0.334	0.334	0.332
Ti	0.00001	%	877	0	0	0.00647	0.00562	0.00209	-0.00048	0.00864	0.00525	0.00525	0.00562	0.00647	0.00647	0.00636	0.00449	0.00449	0.00337
Tl	0.00001	mg kg^{-1}	877	0	0	0.223	0.213	0.0362	0.13	0.276	0.227	0.227	0.213	0.223	0.223	0.226	0.0603	0.0603	0.0811
U	0.00005	mg kg^{-1}	877	0	0	0.948	0.908	0.171	0.489	1.16	0.927	0.927	0.908	0.948	0.948	0.954	0.27	0.27	0.308
V	0.001	mg kg^{-1}	877	0	0	38.2	36.9	5.54	23.1	46	38.6	38.6	36.9	38.2	38.2	38.6	8.36	8.36	11.6
W	0.00001	mg kg^{-1}	877	0	0	0.22	0.127	0.0423	-0.0197	0.195	0.113	0.113	0.127	0.22	0.22	0.153	1.21	1.21	0.103
Y	0.00003	mg kg^{-1}	877	0	0	15.7	14.8	2.66	9.07	19.8	16.3	16.3	14.8	15.7	15.7	16	3.87	3.87	6.55
Zn	0.001	mg kg^{-1}	877	0	0	173	145	40	25.6	212	140	140	145	173	173	169	244	244	99.6
Zr	0.0001	mg kg-1	877	0	0	3.06	2.91	0.675	1.3	4.04	3.16	3.16	2.91	3.06	3.06	3.11	0.8	0.8	1.17
Au	0.000002	mg kg-1	877	1	0.114	0.00423	0.00323	0.00167	-0.00129	0.00572	0.00326	0.00326	0.0032	0.00423	0.00423	0.00421	0.00556	0.00556	0.0036
Pd	0.00001	mg kg-1	877	718	81.87	0.00239	0.00129	0.00165	-0.00392	0.00519	NA	0.0000328	1.31E-08	0.000457	0.000476	39600	0.00147	0.00147	1.2E+17
Pt	0.00002	mg kg-1	877	33	3.76	0.000887	0.000659	0.000341	-0.000245	0.00122	0.00068	0.00068	0.000572	0.000855	0.000858	0.000962	0.00128	0.00128	0.0013

Table 27 Univariate summary statistics including best fits based on proportions of ICPar data below the ME-MS41L LLD.

Variable	LLD	Unit	*n*	*n* below LLD	% below LLD	Arithmetic mean	Geometric mean	MAD	Lower fence	Upper fence	K-M median	ROS median	MLE median	K-M mean	ROS mean	MLE mean	K-M SD	ROS SD	MLE SD
Ag	0.001	mg kg^{-1}	877	0	0	0.35	0.267	0.125	-0.121	0.487	0.25	0.25	0.267	0.35	0.35	0.336	0.513	0.513	0.258
Al	0.01	%	877	0	0	1.05	1.02	0.133	0.685	1.25	1.06	1.06	1.02	1.05	1.05	1.07	0.207	0.207	0.307
As	0.01	mg kg^{-1}	877	0	0	22.9	19.5	4.45	6.25	26.4	18.8	18.8	19.5	22.9	22.9	21.7	38.5	38.5	10.5
B	10	mg kg^{-1}	877	158	18.02	10.2	10.2	0	10	10	10	10	3.77	10.2	10	37.4	1.54	1.59	370
Ba	0.5	mg kg^{-1}	877	0	0	129	114	31.9	27	161	112	112	114	129	129	129	92.9	92.9	68.9
Be	0.01	mg kg^{-1}	877	0	0	1.21	1.13	0.222	0.59	1.49	1.17	1.17	1.13	1.21	1.21	1.24	0.397	0.397	0.542
Bi	0.0005	mg kg^{-1}	877	0	0	0.259	0.227	0.0667	0.0223	0.339	0.219	0.219	0.227	0.259	0.259	0.257	0.192	0.192	0.136
Ca	0.01	%	877	0	0	3.66	2.69	2.54	-3.33	6.9	3.47	3.47	2.69	3.66	3.66	4.24	2.31	2.31	5.15
Cd	0.001	mg kg^{-1}	877	0	0	1.9	1.69	0.497	0.58	2.62	1.97	1.98	1.69	1.9	1.9	2.07	0.674	0.674	1.45
Ce	0.003	mg kg^{-1}	877	0	0	25.6	25.1	3.41	16.7	30.5	25.9	25.9	25.1	25.6	25.6	25.7	4.6	4.6	5.84
Co	0.001	mg kg^{-1}	877	0	0	11.7	11.1	2.08	6.28	14.5	11.7	11.7	11.1	11.7	11.7	12	3.01	3.01	4.92
Cr	0.01	mg kg^{-1}	877	0	0	21.9	21.3	2.52	14.9	25.4	22	22	21.3	21.9	21.9	22	4.59	4.59	5.86
Cs	0.005	mg kg^{-1}	877	0	0	0.614	0.566	0.139	0.126	0.77	0.525	0.525	0.566	0.614	0.614	0.607	0.309	0.309	0.234
Cu	0.01	mg kg^{-1}	877	0	0	62.3	47	18.5	-3.75	75.2	46.4	46.4	47	62.3	62.3	59.2	134	134	45.2
Fe	0.001	%	877	0	0	2.39	2.3	0.297	1.62	2.78	2.4	2.4	2.3	2.39	2.39	2.42	0.544	0.544	0.788
Ga	0.004	mg kg^{-1}	877	0	0	3.27	3.15	0.593	1.63	4.09	3.24	3.24	3.15	3.27	3.27	3.3	0.79	0.79	1.03
Ge	0.005	mg kg^{-1}	877	0	0	0.0642	0.0611	0.0119	0.0315	0.0765	0.061	0.061	0.0611	0.0642	0.0642	0.0641	0.0242	0.0242	0.0206
Hf	0.002	mg kg^{-1}	877	0	0	0.0902	0.0854	0.0208	0.0345	0.121	0.093	0.093	0.0854	0.0902	0.0902	0.092	0.0242	0.0242	0.0367
Hg	0.004	mg kg^{-1}	877	0	0	0.483	0.281	0.196	-0.3	0.61	0.266	0.266	0.281	0.483	0.483	0.438	1.18	1.18	0.526
In	0.005	mg kg^{-1}	877	16	1.82	0.0245	0.0233	0.00445	0.0105	0.0315	0.024	0.024	0.0208	0.0241	0.0242	0.0313	0.00772	0.0075	0.0352
K	0.01	%	877	0	0	0.132	0.129	0.0148	0.075	0.165	0.13	0.13	0.129	0.132	0.132	0.132	0.0247	0.0247	0.0287
La	0.002	mg kg^{-1}	877	0	0	12.9	12.6	1.63	8.65	15.2	13	13	12.6	12.9	12.9	13	2.29	2.29	3.01
Li	0.1	mg kg^{-1}	877	0	0	15.2	14.1	4.3	2.5	20.5	14	14	14.1	15.2	15.2	15.4	6.12	6.12	6.53

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
Mg	0.01	%	877	0	0	0.266	0.254	0.0593	0.075	0.345	0.25	0.25	0.254	0.266	0.266	0.267	0.0879	0.0879	0.0855
Mn	0.1	mg kg^{-1}	877	0	0	1200	1090	394	115	1720	1180	1180	1090	1200	1200	1270	455	455	749
Mo	0.01	mg kg^{-1}	877	0	0	3.22	2.91	0.919	0.74	4.4	3.24	3.24	2.91	3.22	3.22	3.4	1.22	1.22	2.08
Na	0.001	%	877	0	0	0.0203	0.0188	0.00445	0.006	0.024	0.018	0.018	0.0188	0.0203	0.0203	0.0199	0.0122	0.0122	0.00693
Nb	0.002	mg kg^{-1}	877	0	0	0.362	0.345	0.0801	0.121	0.461	0.342	0.342	0.345	0.362	0.362	0.362	0.125	0.125	0.112
Ni	0.04	mg kg^{-1}	877	0	0	44.7	41.8	9.49	19.4	58.4	46.2	46.2	41.8	44.7	44.7	46	12.5	12.5	21.2
P	0.001	mg kg^{-1}	877	0	0	957	867	282	90	1290	860	860	867	957	957	962	446	446	463
Pb	0.005	mg kg^{-1}	877	0	0	143	101	62	-92	212	93.2	93.2	101	143	143	139	165	165	132
Rb	0.005	mg kg^{-1}	877	0	0	9.68	9.36	1.62	4.87	11.9	9.37	9.37	9.36	9.68	9.68	9.71	2.38	2.38	2.67
Re	0.0002	mg kg^{-1}	877	21	2.395	0.00142	0.00124	0.000593	-0.00045	0.00225	0.0013	0.0013	0.00106	0.00139	0.0014	0.00206	0.000739	0.000735	0.00344
S	0.01	%	877	0	0	0.0599	0.0557	0.0148	0.02	0.08	0.06	0.06	0.0557	0.0599	0.0599	0.0602	0.0233	0.0233	0.0245
Sb	0.005	mg kg^{-1}	877	0	0	1.84	1.5	0.689	-0.325	2.52	1.52	1.52	1.5	1.84	1.84	1.83	1.79	1.79	1.29
Sc	0.005	mg kg^{-1}	877	0	0	3.64	3.5	0.593	2.08	4.52	3.74	3.74	3.5	3.64	3.64	3.68	0.834	0.834	1.19
Se	0.003	mg kg^{-1}	877	0	0	0.978	0.9	0.254	0.288	1.31	0.978	0.978	0.9	0.978	0.978	1.02	0.347	0.347	0.554
Sn	0.01	mg kg^{-1}	877	0	0	9.31	4.73	3.71	-7.97	12.6	4.27	4.27	4.73	9.31	9.31	8.46	19.3	19.3	12.5
Sr	0.01	mg kg^{-1}	877	0	0	111	89.3	67.8	-80	200	102	102	89.3	111	111	116	67	67	97.6
Ta	0.005	mg kg^{-1}	877	871	99.32	0.00917	0.00784	0.00148	0.00338	0.00863	NA	0.0000104	2.88E-20	0.00503	0.00016	3.79E+24	0.00068	0.000959	5.01E+68
Te	0.003	mg kg^{-1}	877	13	1.482	0.0318	0.0304	0.00741	0.012	0.042	0.031	0.031	0.0274	0.0314	0.0316	0.0415	0.00981	0.00943	0.0474
Th	0.002	mg kg^{-1}	877	0	0	1.44	1.4	0.289	0.65	1.82	1.43	1.43	1.4	1.44	1.44	1.44	0.334	0.334	0.332
Ti	0.001	%	877	1	0.114	0.0065	0.00565	0.00148	-0.0005	0.0085	0.005	0.005	0.00561	0.00649	0.00649	0.00647	0.00448	0.00448	0.00372
Tl	0.001	mg kg^{-1}	877	0	0	0.223	0.213	0.0356	0.131	0.275	0.227	0.227	0.213	0.223	0.223	0.226	0.0603	0.0603	0.081
U	0.005	mg kg^{-1}	877	0	0	0.948	0.908	0.17	0.487	1.16	0.927	0.927	0.908	0.948	0.948	0.954	0.27	0.27	0.307
V	0.1	mg kg^{-1}	877	0	0	38.2	36.9	5.49	23.2	46	38.6	38.6	36.9	38.2	38.2	38.6	8.36	8.36	11.6
W	0.001	mg kg^{-1}	877	0	0	0.22	0.127	0.043	-0.0185	0.195	0.113	0.113	0.127	0.22	0.22	0.153	1.21	1.21	0.103
Y	0.003	mg kg^{-1}	877	0	0	15.7	14.8	2.67	9.05	19.9	16.3	16.3	14.8	15.7	15.7	16	3.87	3.87	6.55

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	0.1	mg kg^{-1}	877	0	0	173	145	40	26	212	140	140	145	173	173	169	244	244	99.6
Zr	0.01	mg kg^{-1}	877	0	0	3.06	2.91	0.682	1.29	4.05	3.16	3.16	2.91	3.06	3.06	3.11	0.799	0.799	1.17
Au	0.0002	mg kg^{-1}	877	4	0.46	0.00425	0.00326	0.00163	-0.0014	0.0058	0.0033	0.0033	0.00316	0.00423	0.00423	0.00448	0.00556	0.00556	0.00453
Pd	0.001	mg kg^{-1}	877	748	85.29	0.00298	0.00224	0.00148	-0.0035	0.0055	NA	0.000169	1.19E-09	0.00129	0.00062	144000000	0.00127	0.00145	1.75E+25
Pt	0.002	mg kg^{-1}	877	807	92.02	0.00333	0.00262	0	0.000875	0.00313	NA	0.000215	4.6E-11	0.00211	0.000545	432000000	0.0011	0.00135	4.07E+27

Regional-scale mapping and interpolation of sample data recommendations

All geochemical data have been assessed to see if the data are suitable to map, primarily as single-element interpolated or point geochemical maps. Tellus produces a series of geochemical maps available to download from www.gsi.ie/tellus and/or viewed on the GSI web map viewer. They will be added 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. Suggested interpolated mapping parameters for the G8 urban geochemical data (collected on a 500 x 500 m grid) are given in Table 28. 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, so the greater the distance the less influence the sample data point has on the output cell value.

Table 28 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)	500	Fixed	2	75	1:100,000

The inverse distance weighted (IDW) interpolation was performed on all geochemical data for the G8 block. These parameters were selected to account for the typical inter-sample distances across the urban survey area only. It is acknowledged that alternative 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 concentration values that are 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 estimates of average or typical values over an area may be obtained at lower levels of concentration. Thus, meaningful spatial distribution patterns may be recognized for some elements at levels lower than the reported LLD/LRL. For geochemical mapping, the optimum is to use uncensored data, i.e. data that are not truncated to the LLD, in the mapping process in order to present the data in such a way that the lower concentrations are not unduly emphasized numerically and to describe below-LLD values as such in the classification. Reliability also decreases above the URL but results do, nevertheless, give an indication of the concentration in the sample. Results outside the lower detection / upper reporting limits were therefore reported and entered into the database.

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 due to a very high proportion of data below the certified ME-MS41L method LLD (rendering this presentation meaningless).

However, they can be represented as interpolated maps by using data for the MS41L-BLD method but the user is cautioned that these data are obtained through a non-accredited method.

Table 29 Deeper topsoil analytes where mapping of the certified ME-MS41L dataset is not recommended.

Variable	Method	Issue	Recommendation
Ta	ICP-MS (ME-MS41L)	99.3 % data <LLD.	Better presented as proportional colour/symbol point map.
Pd	ICP-MS (ME-MS41L)	85.3 % data <LLD.	Perhaps better presented as proportional colour/symbol point map.
Pt	ICP-MS (ME-MS41L)	92.0 % data <LLD.	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 used in geochemistry field database.
GIS	Geographical Information System	Digital mapping software environment.
GSI	Geological Survey Ireland	Irish national geological agency. The contracting and project-leading authority.
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer	Analytical instrument which utilizes an inductively-generated plasma flame that ionizes analytes which are then separated according to their mass and quantified by mass spectrometer.
IDW	Inverse distance weighted	Spatial data interpolation method.
IQR	Interquartile range	Statistical dispersion of distribution between the 25^{th} and 75^{th} percentile. Represents 50% of the data set.
K-M	Kaplan-Meier	Non-parametric method 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 exceeds the lower calibration range of an analytical run or instrument.
MAD	Median absolute deviation	Parametric method of calculating summary statistics with a moderate proportion of data below the LLD.
MLE	Maximum likelihood estimation	Parametric method that fits a distribution curve, with non-detects included and represented proportionally in the observation population.
OES	Optical Emission Spectrometer	Analytical instrument/detector.
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 utilized 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.
TE	Táilte Eireann	Irish topographic mapping agency and map publisher (paper and digital).
URL	Upper reporting limit	Concentration at which analyte is exceeding upper calibration range of an analytical run or instrument.

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

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

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

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Appendices

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

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

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

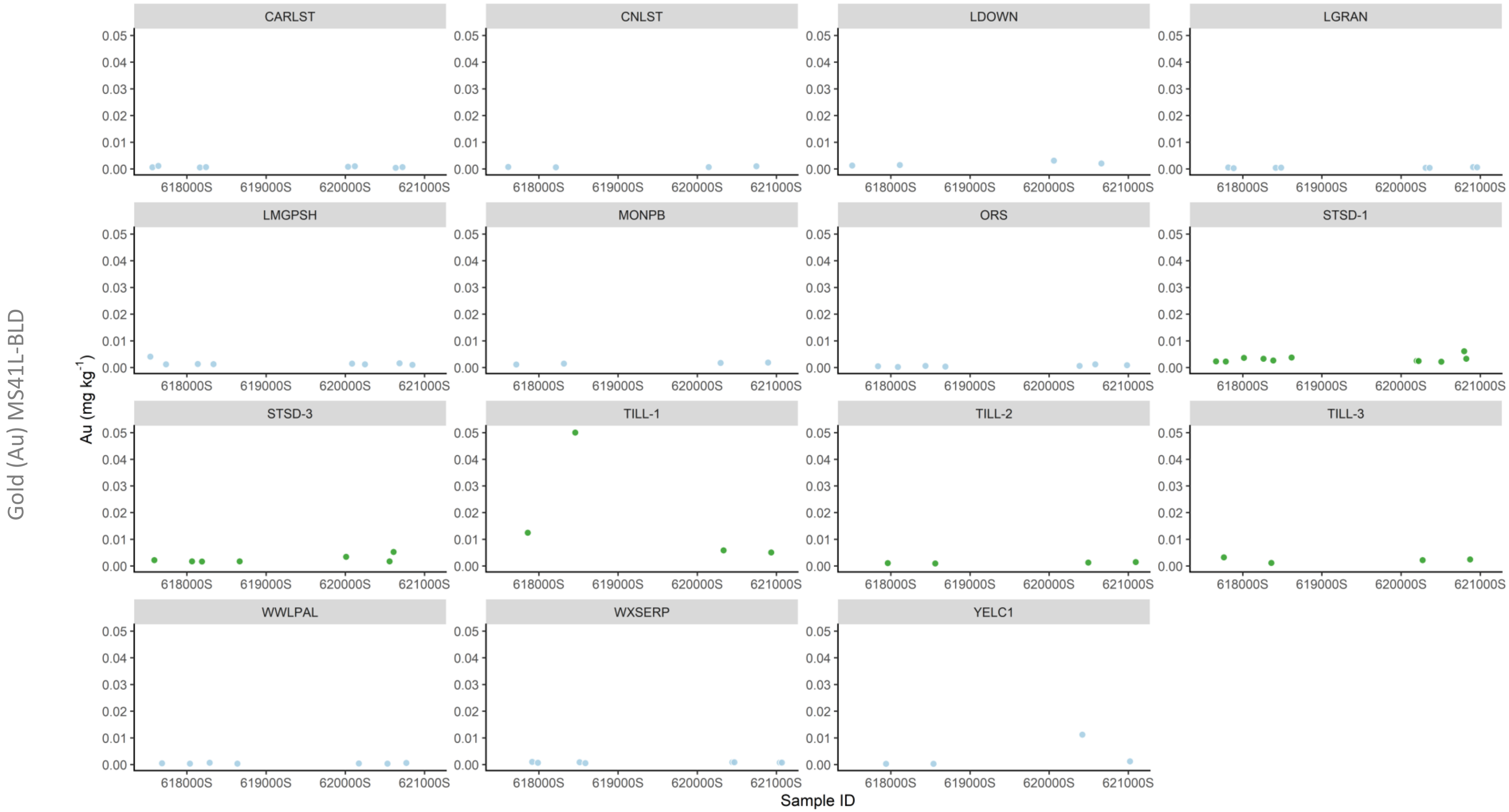
A. RMs data QCS charts

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

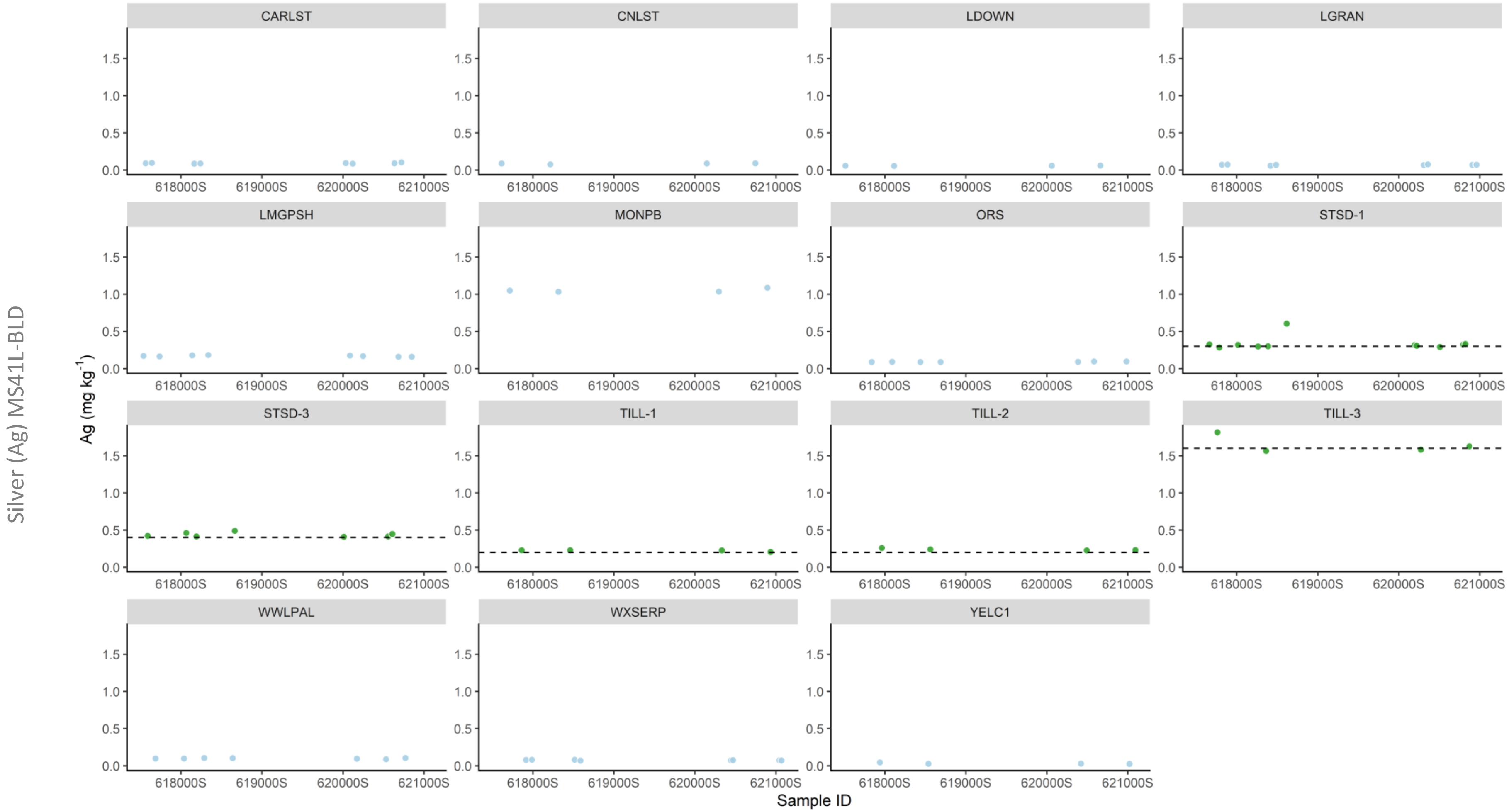
- The first chart is of analyte concentration (y axis) against the sample ID (x axis), faceted by the reference material (name in the grey banner at the top). With the assumption that all samples are run in the numerical order as required and directed, each chart displays the repeatability of the reference material across the laboratory analytical batches. The dashed horizontal line denotes the CRM reference value (certified, information or provisional) for the appropriate partial extraction method, where available.
- The second is a control chart of analyte concentration (y axis) against the measurement date and time (x axis) for each reference material (CRM and SRM). Each control chart displays the process mean of the data (central horizontal black line) and a series of control limits at 1, 2 and 3 times the process mean ± the sequential deviation (shown as light, medium and dark blue horizontal lines respectively. Each date point is connected by a line to show the sequence of analyses. The dashed horizontal line denotes the CRM reference value (certified, information or provisional) for the appropriate partial extraction method, where available. For some elements this value is sufficiently different to the reported values for the analysed material that it is not possible to display it on the chart without severely compressing the vertical axis of the chart – in such cases the reference value is omitted.

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.

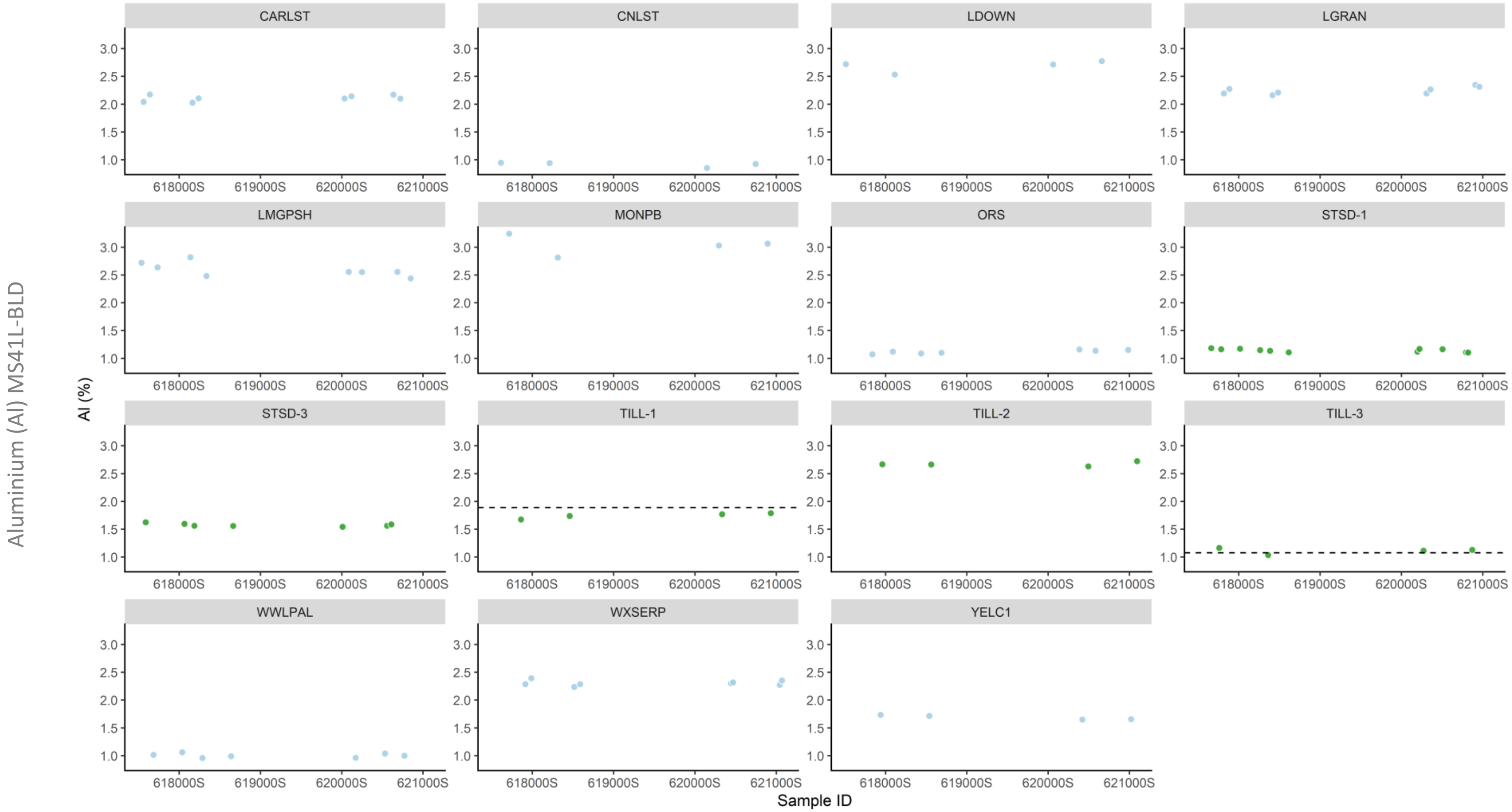
ICPar RMs data by ALS Minerals Ltd method code MS41L-BLD



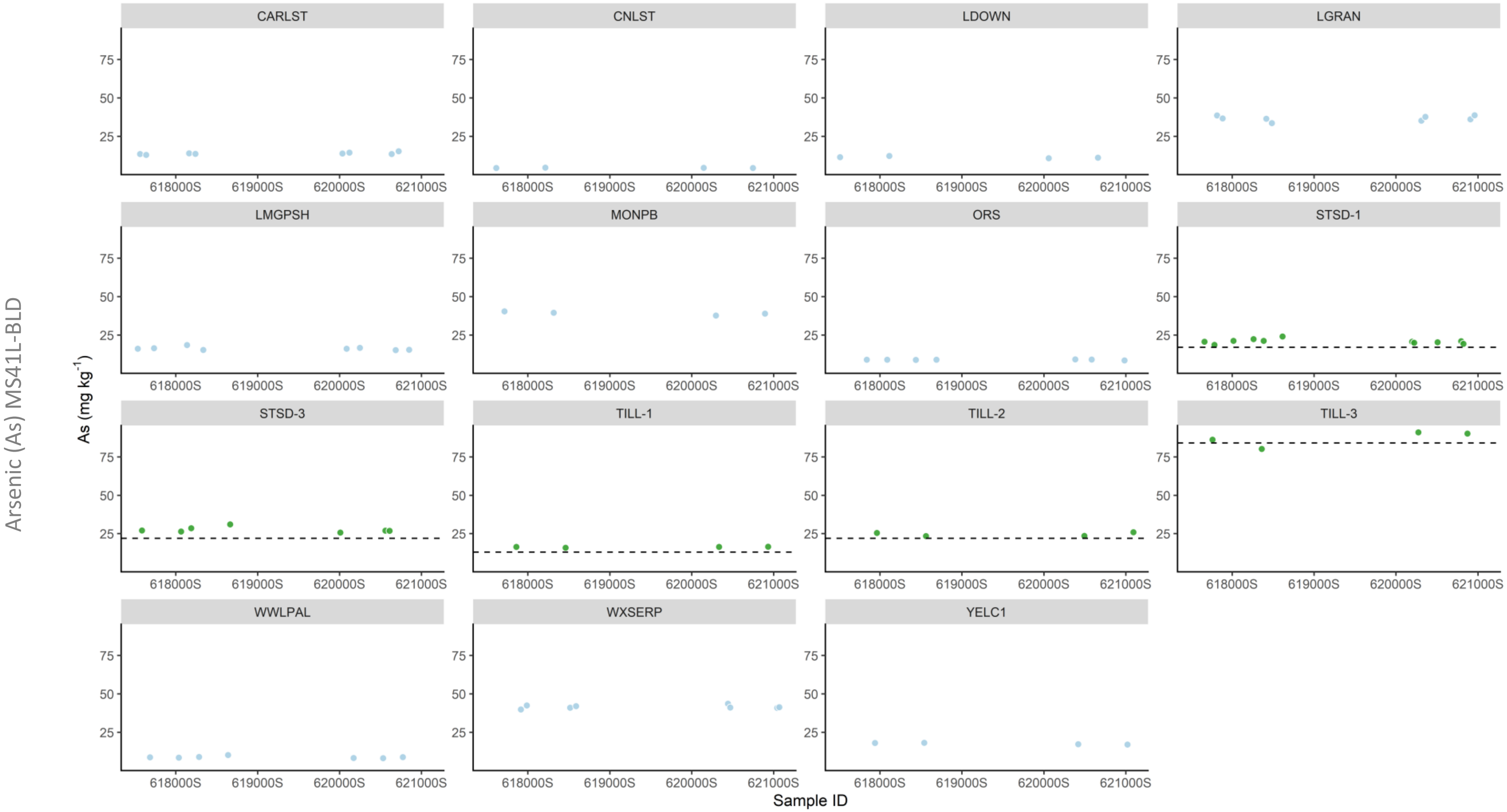
Gold (Au) sample data IQR: 0.00222–0.00455 mg kg^{-1}



Silver (Ag) sample data IQR: 0.183–0.386 mg kg^{-1}

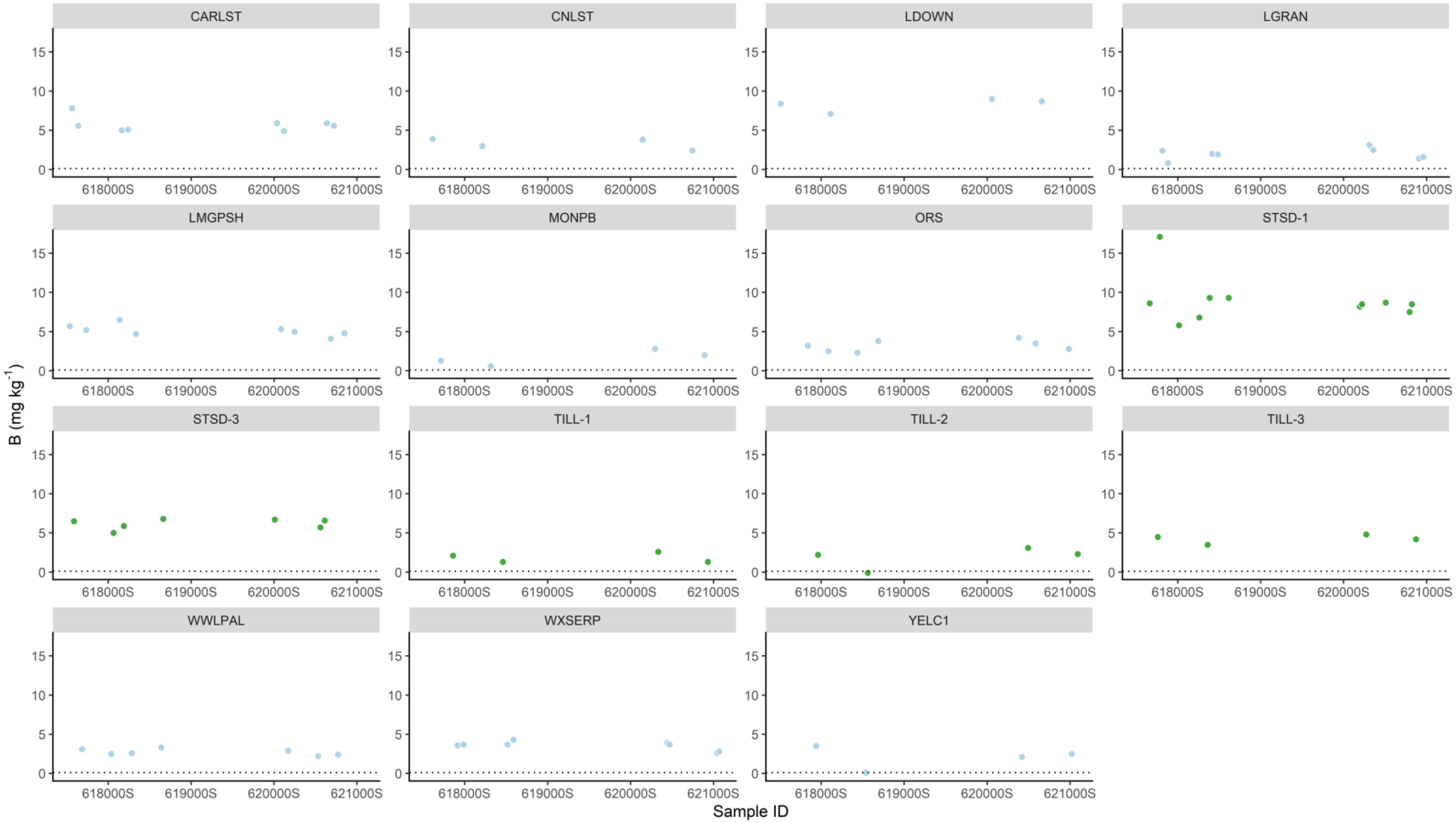


Aluminium (Al) sample data IQR: 0.972–1.16 %



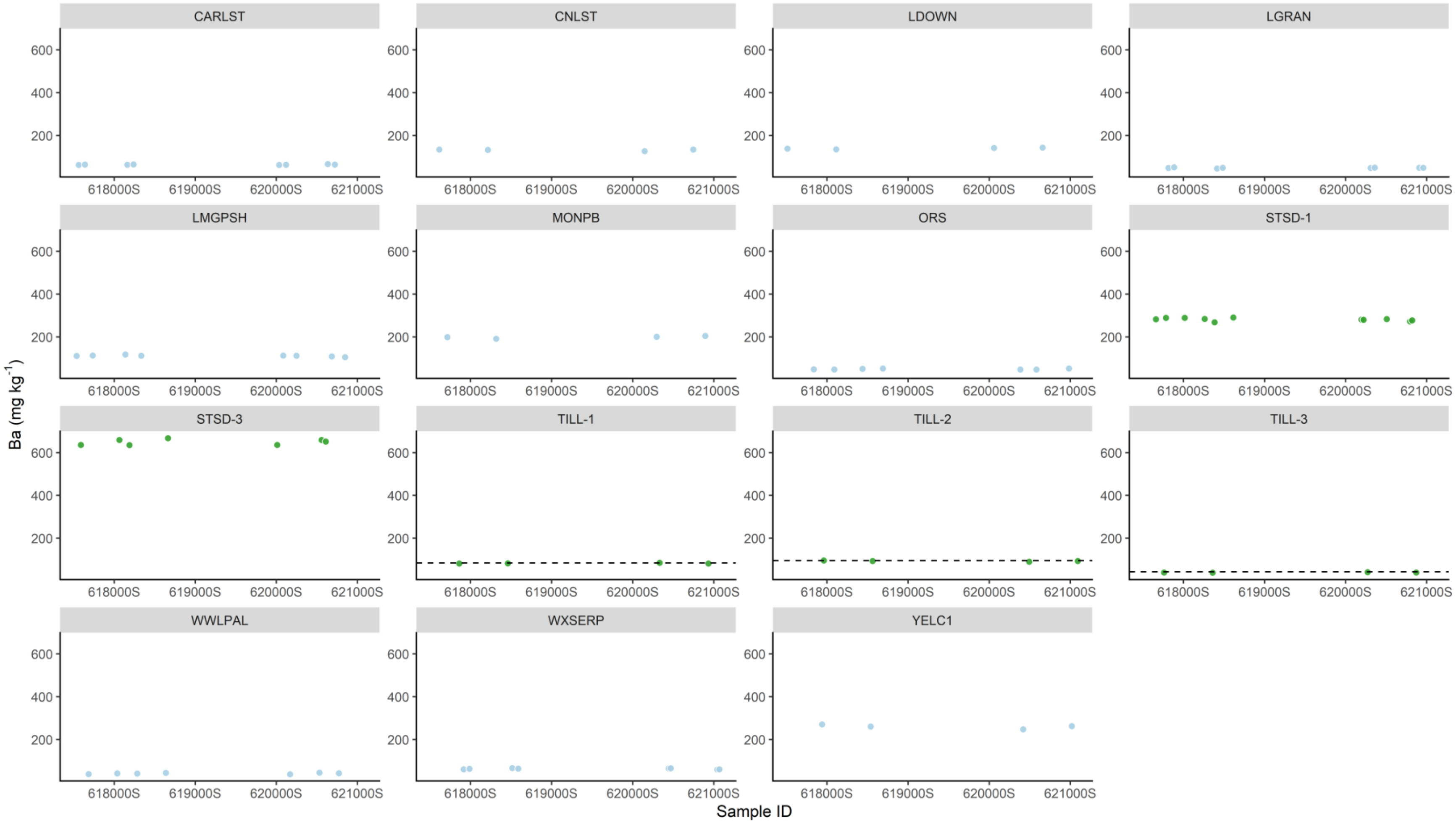
Arsenic (As) sample data IQR: 16.3–23.0 mg kg^{-1}

Boron (B) MS41L-BLD

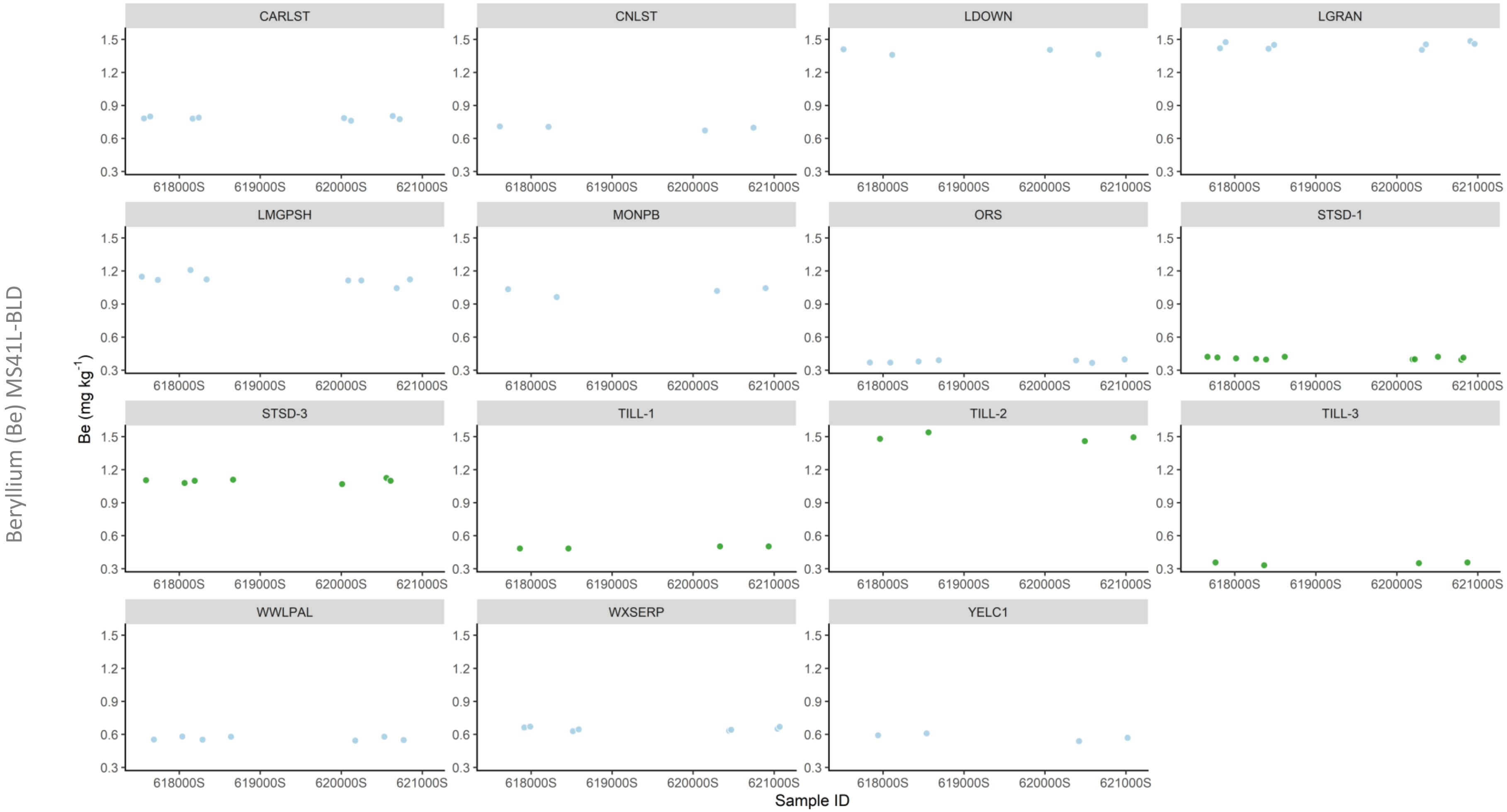


Boron (B) sample data IQR: 5.5 -8.1 mg kg^{-1}

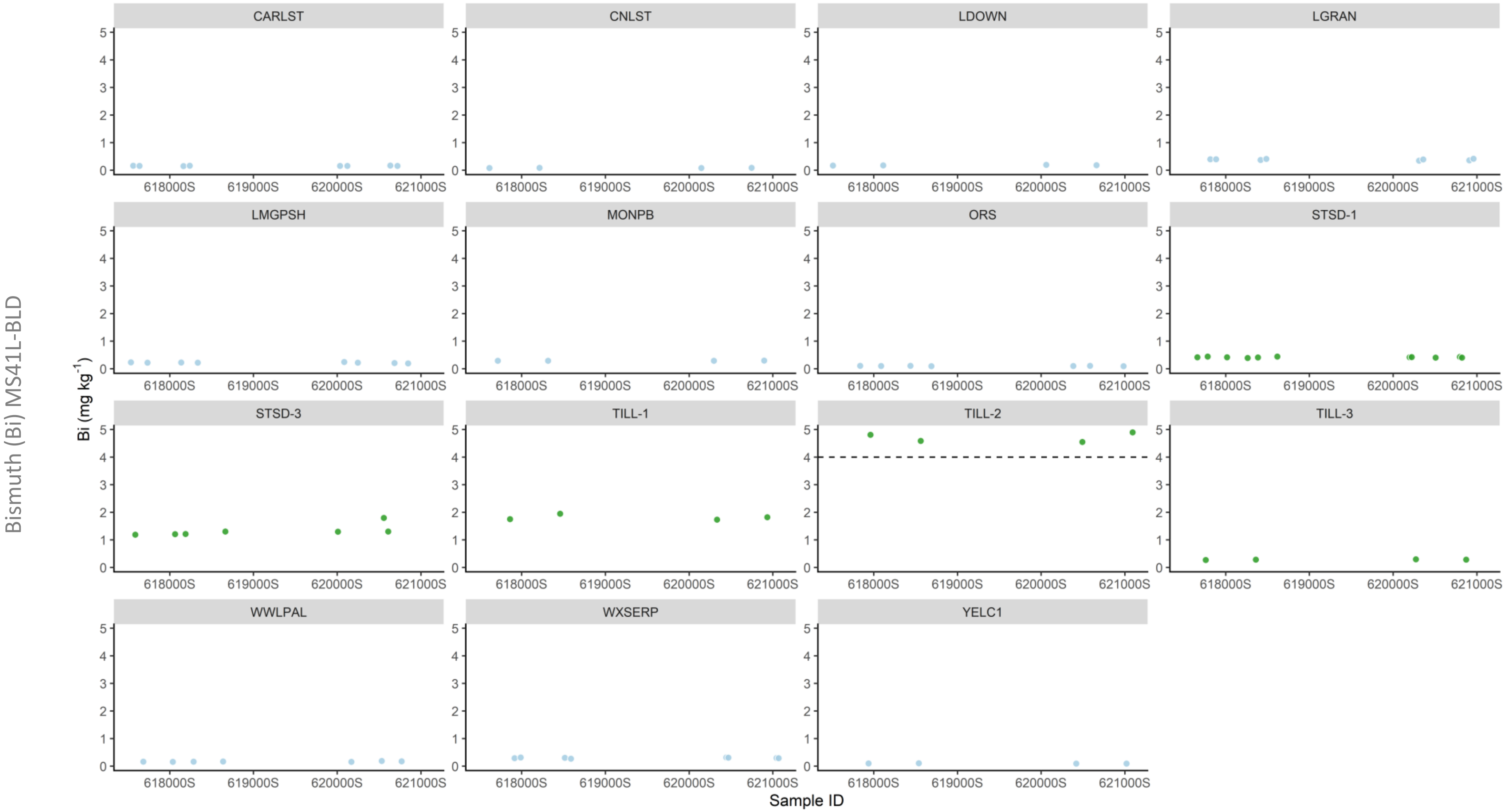
Barium (Ba) MS41L-BLD



Barium (Ba) sample data IQR: 93.9–139 mg kg^{-1}

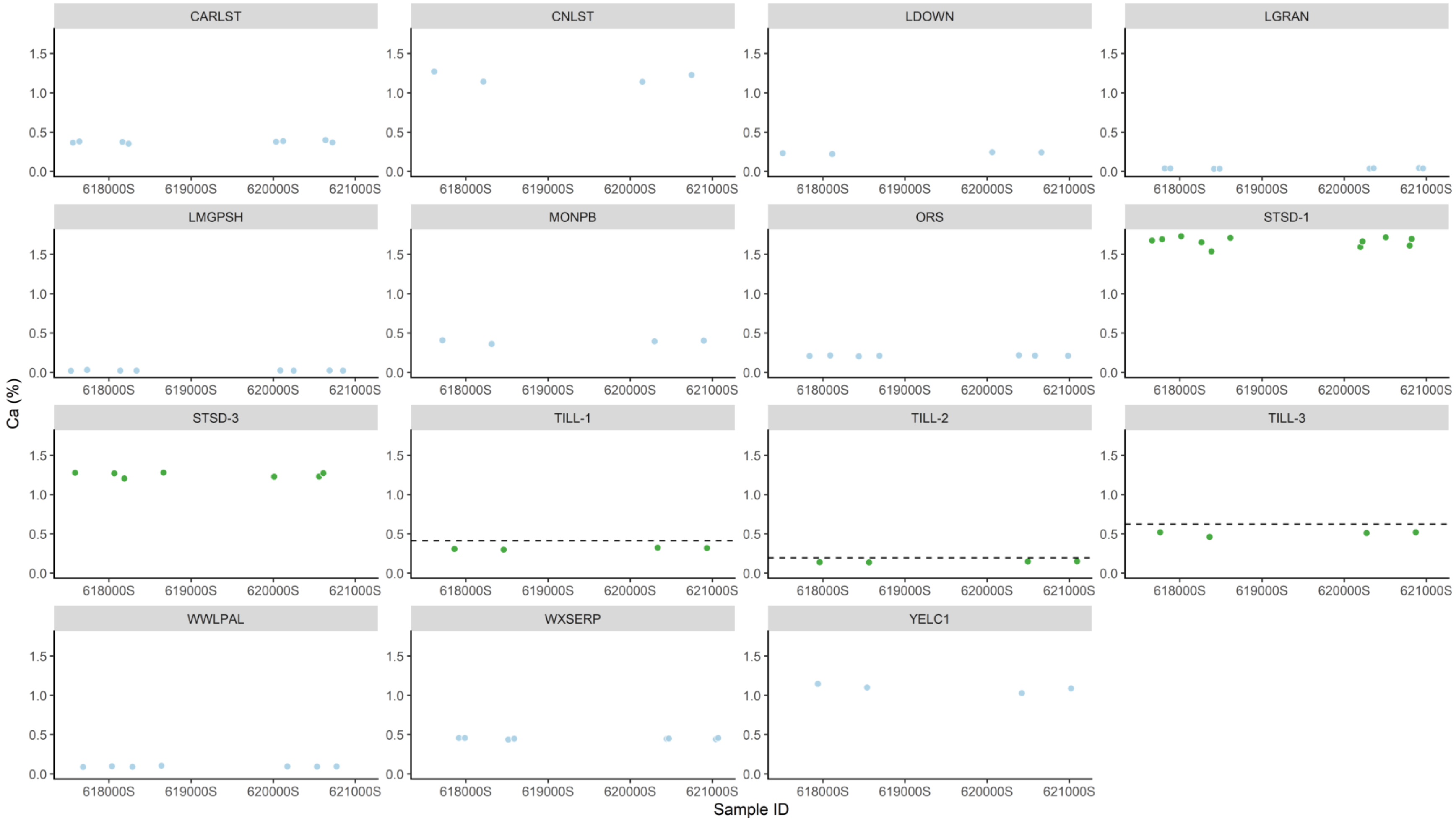


Beryllium (Be) sample data IQR: 1.04–1.34 mg kg^{-1}



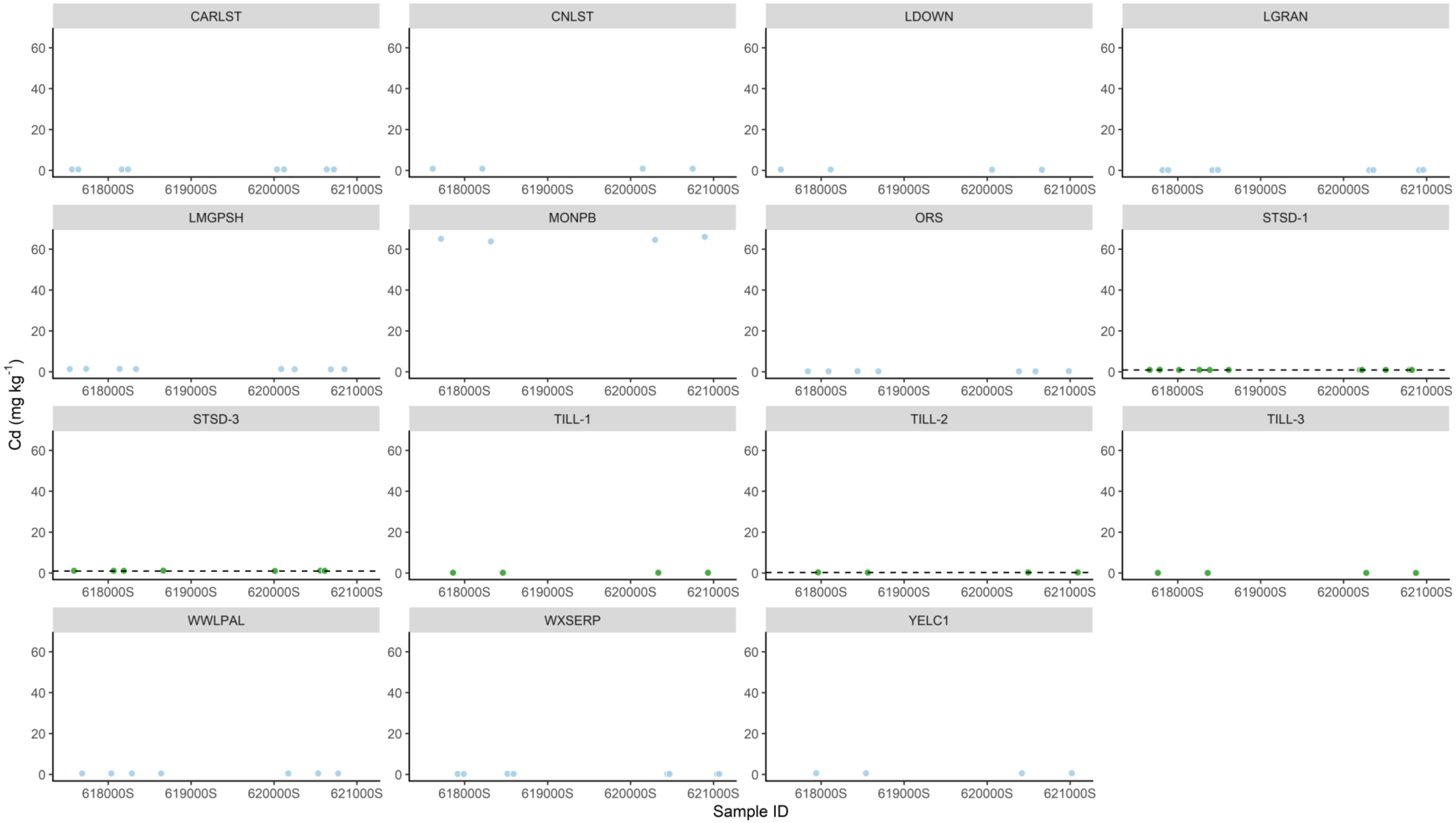
Bismuth (Bi) sample data IQR: 0.181–0.286 mg kg^{-1}

Calcium (Ca) MS41L-BLD



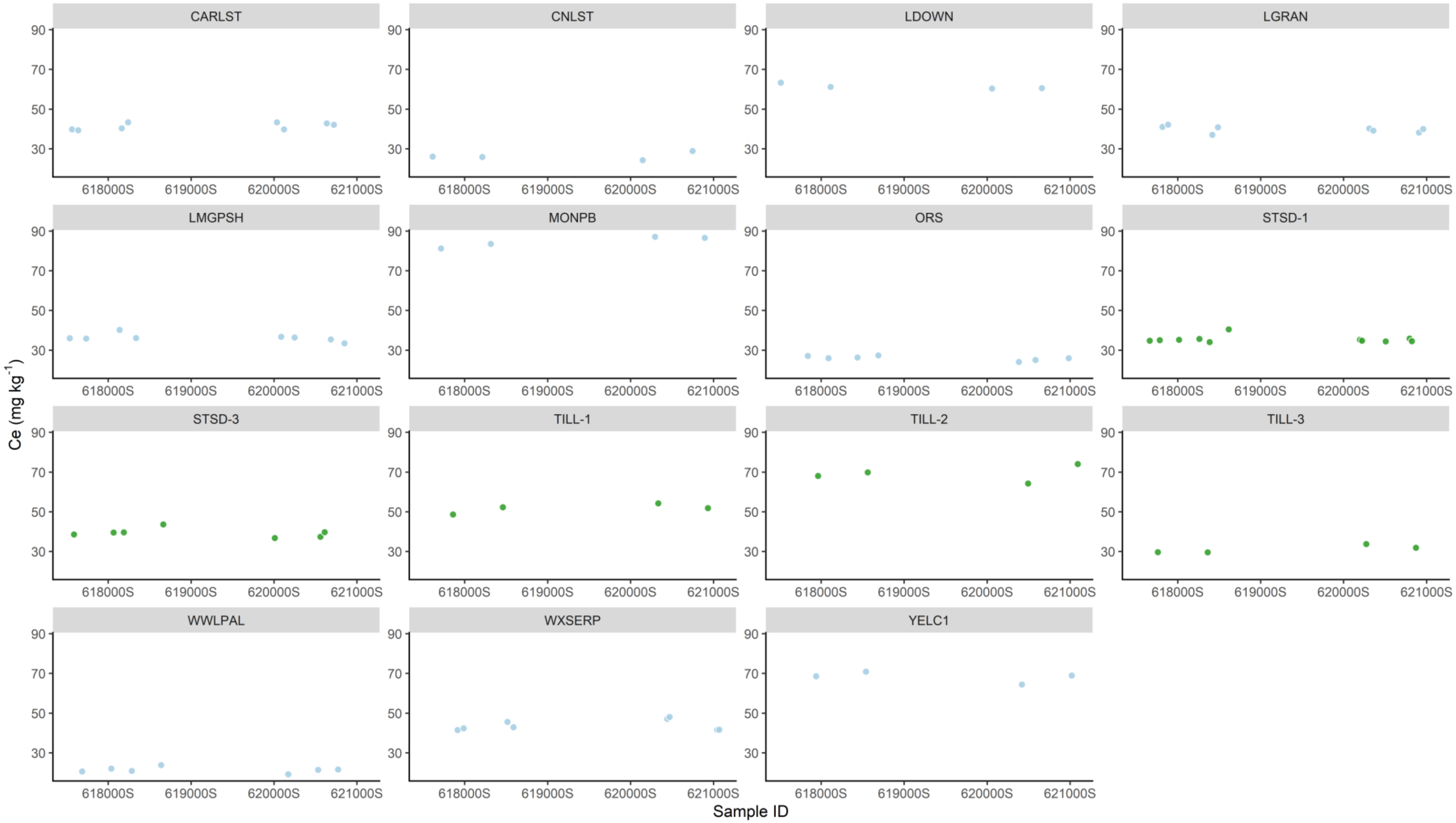
Calcium (Ca) sample data IQR: 1.78–5.19 %

Cadmium (Cd) MS41L-BLD



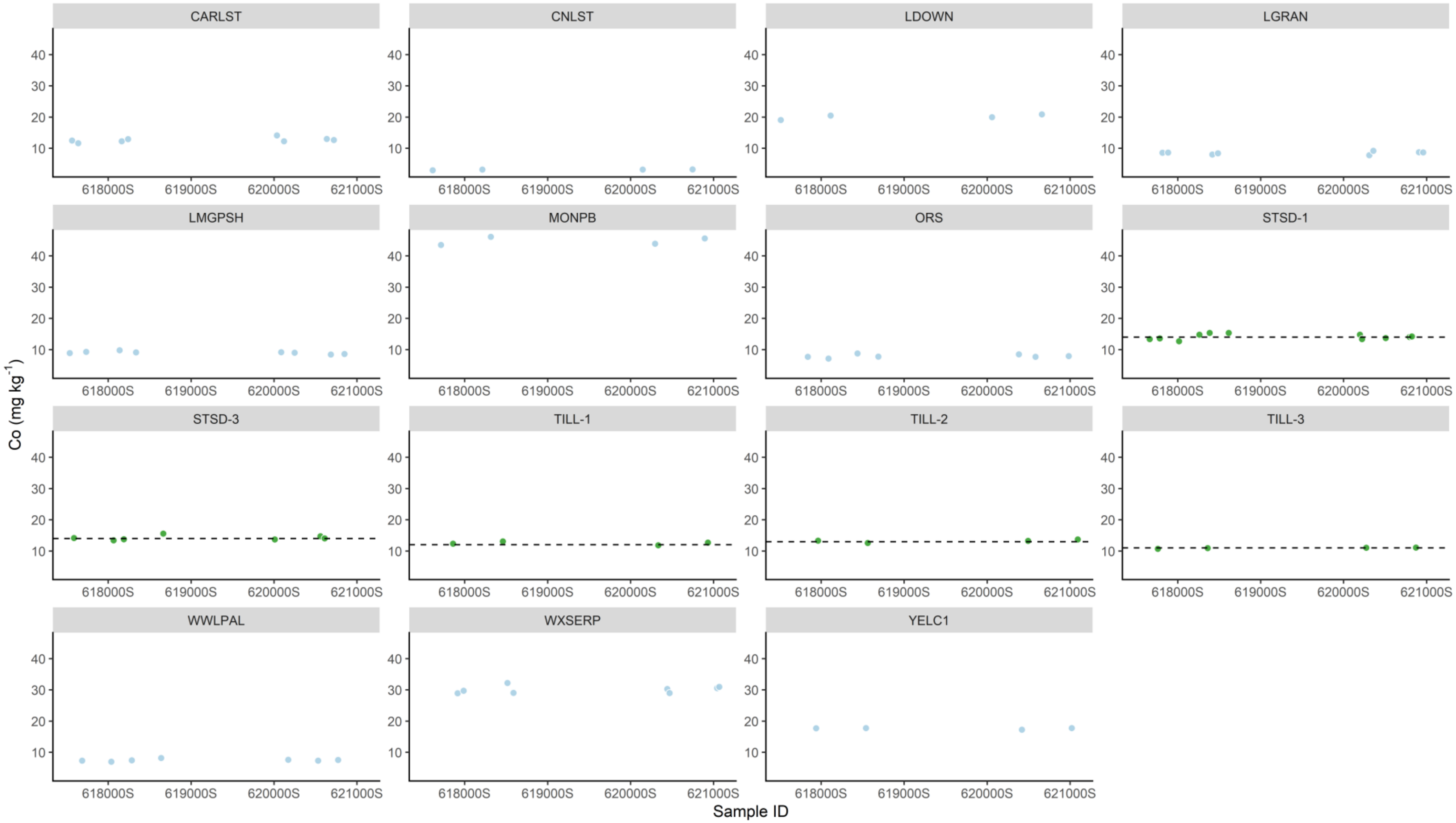
Cadmium (Cd) sample data IQR: 1.6–2.28 mg kg^{-1}

Cerium (Ce) MS41L-BLD

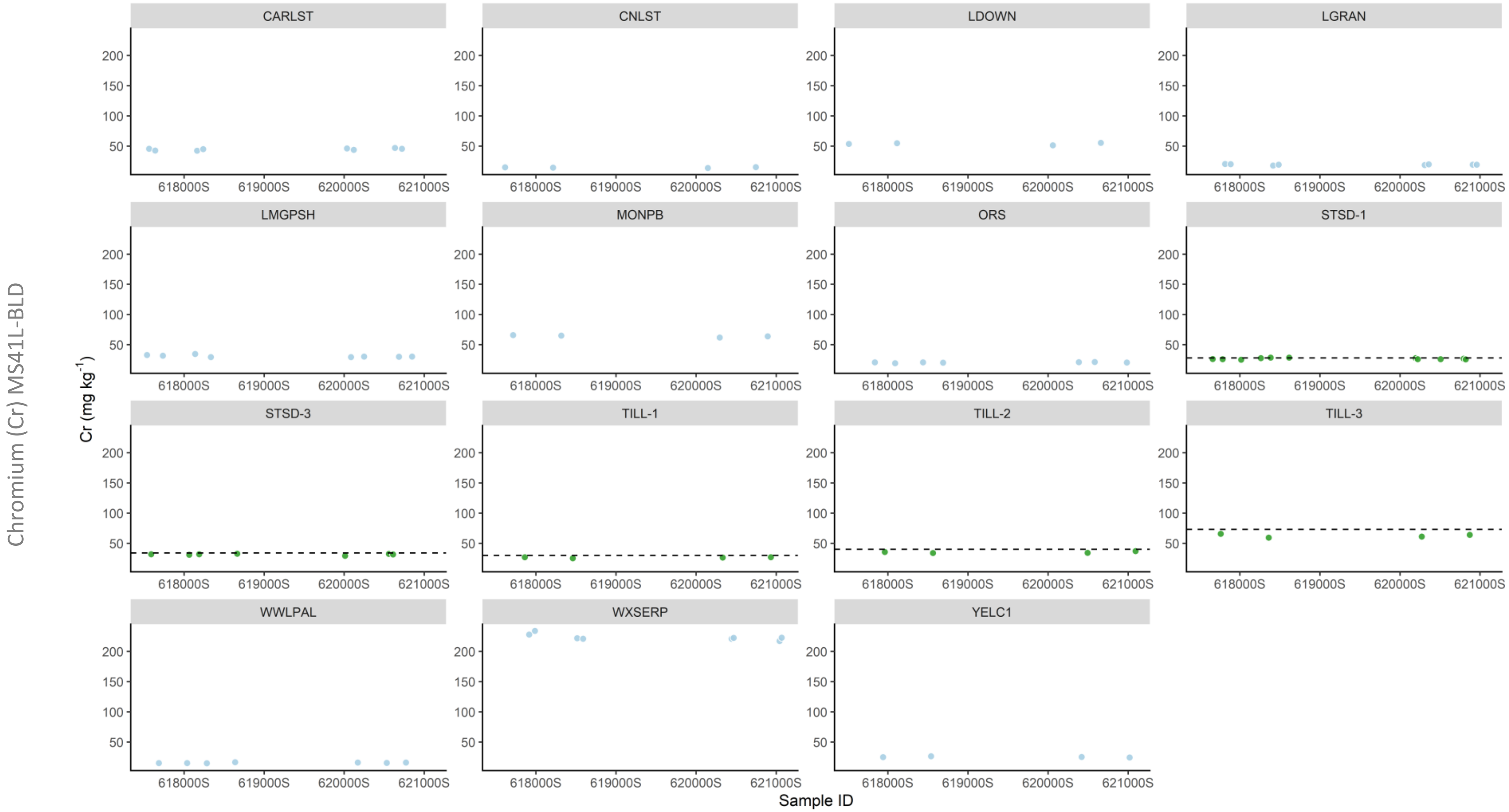


Cerium (Ce) sample data IQR: 23.6–28.2 mg kg^{-1}

Cobalt (Co) MS41L-BLD

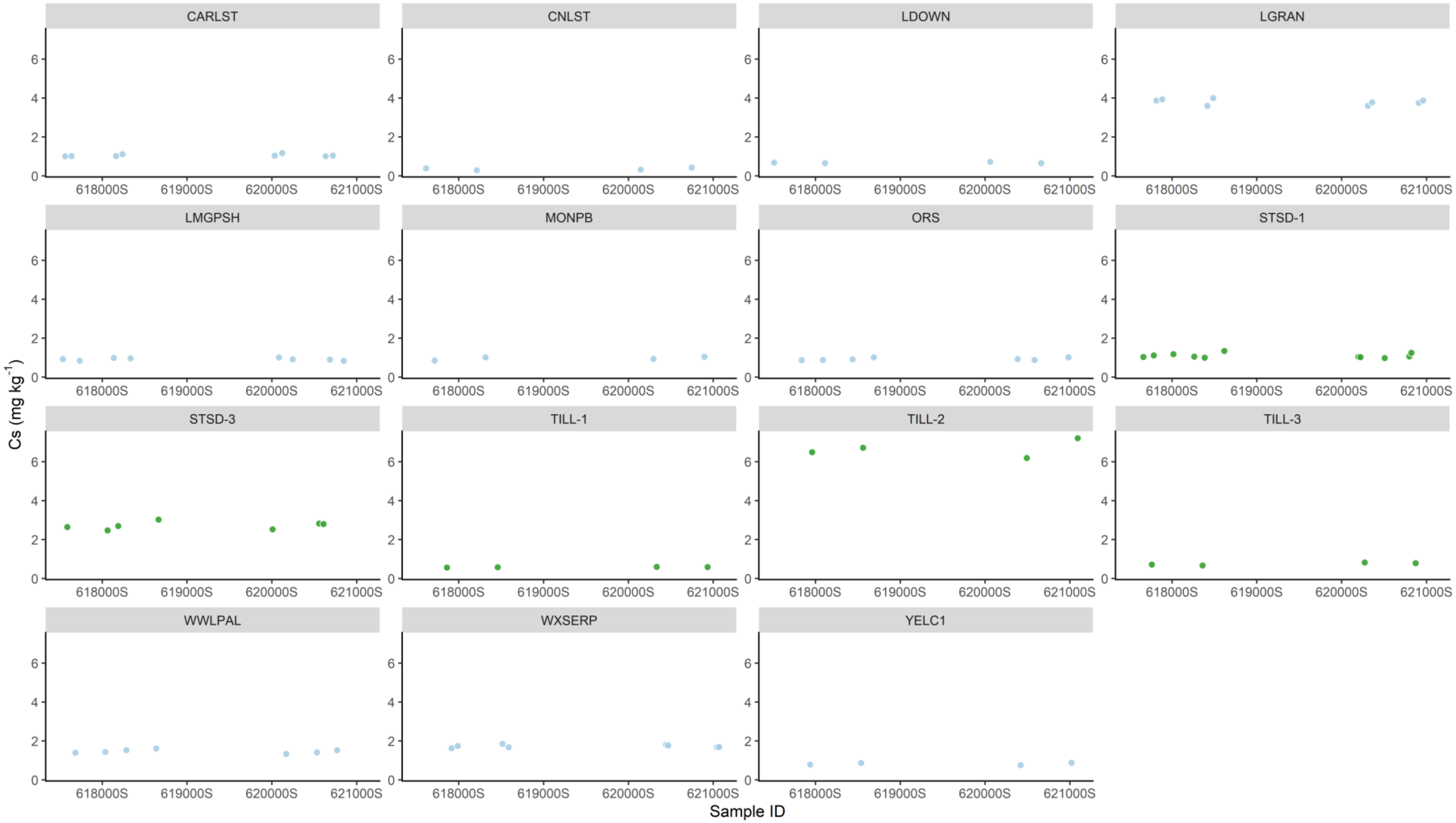


Cobalt (Co) sample data IQR: 10.4–13.2 mg kg^{-1}

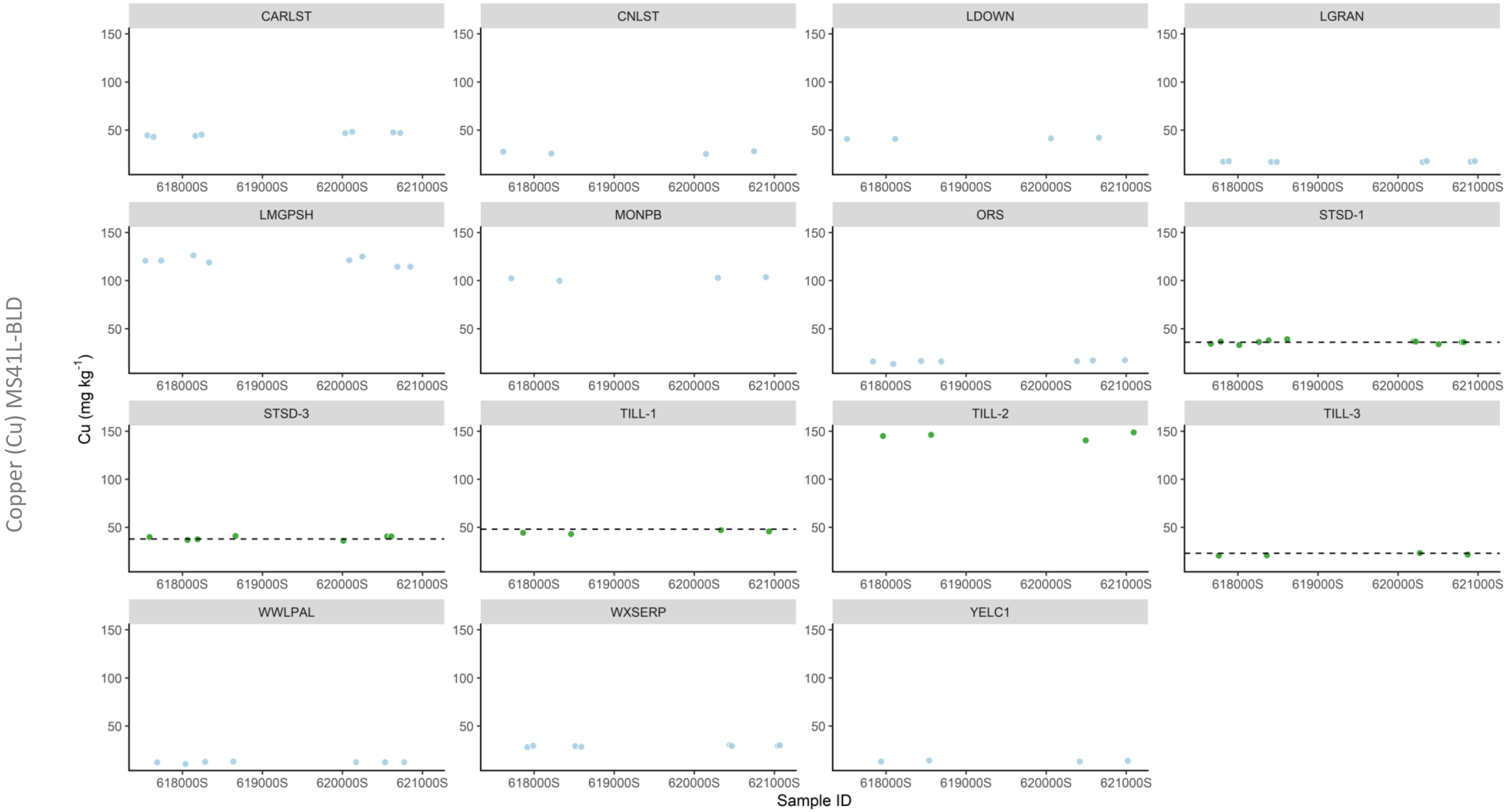


Chromium (Cr) sample data IQR: 20.2–23.7 mg kg^{-1}

Caesium (Cs) MS41L-BLD

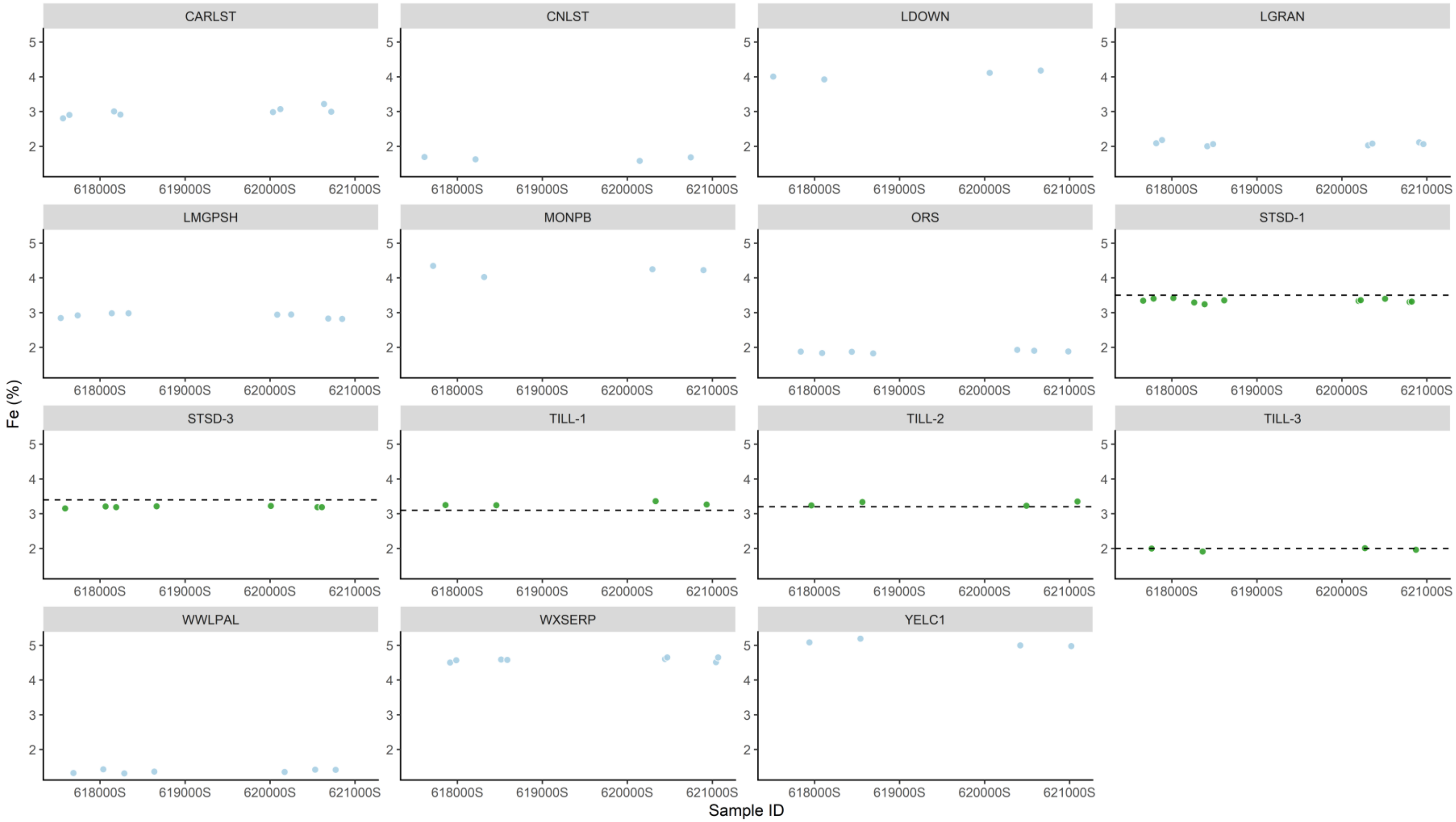


Caesium (Cs) sample data IQR: 0.448–0.663 mg kg^{-1}



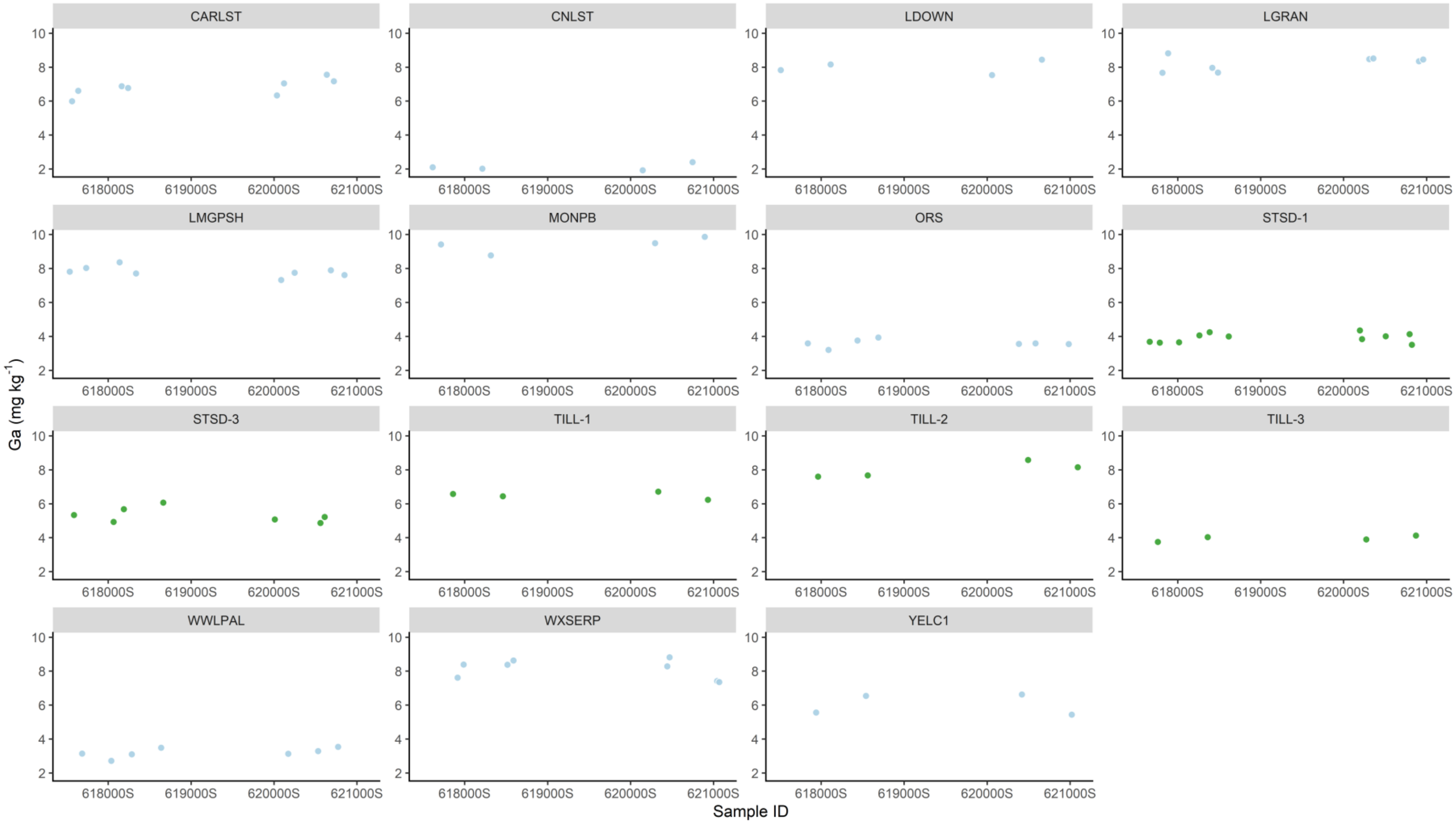
Copper (Cu) sample data IQR: 35.7–62.0 mg kg^{-1}

Iron (Fe) MS41L-BLD



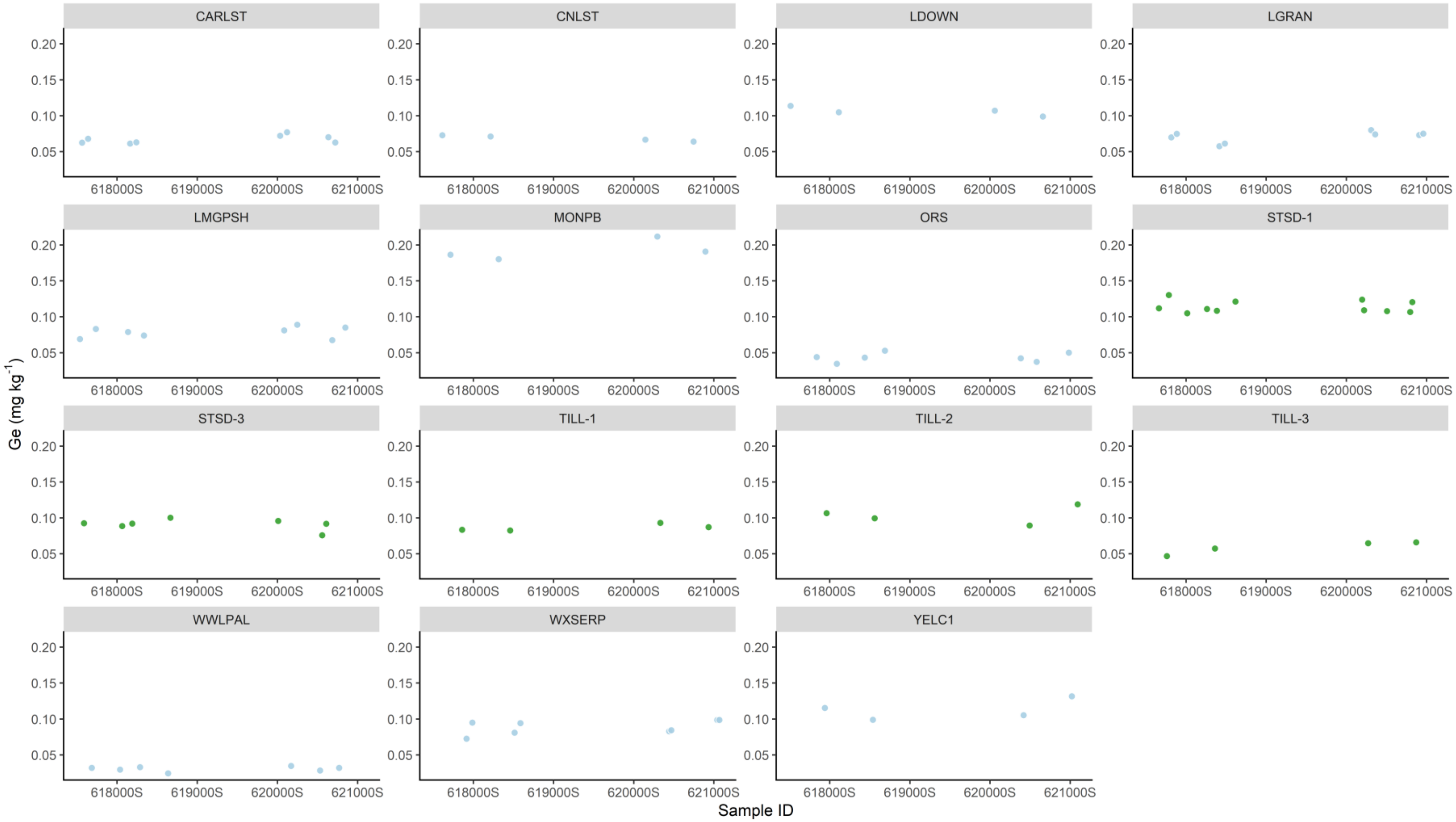
Iron (Fe) sample data IQR: 2.20–2.59 %

Gallium (Ga) MS41L-BLD



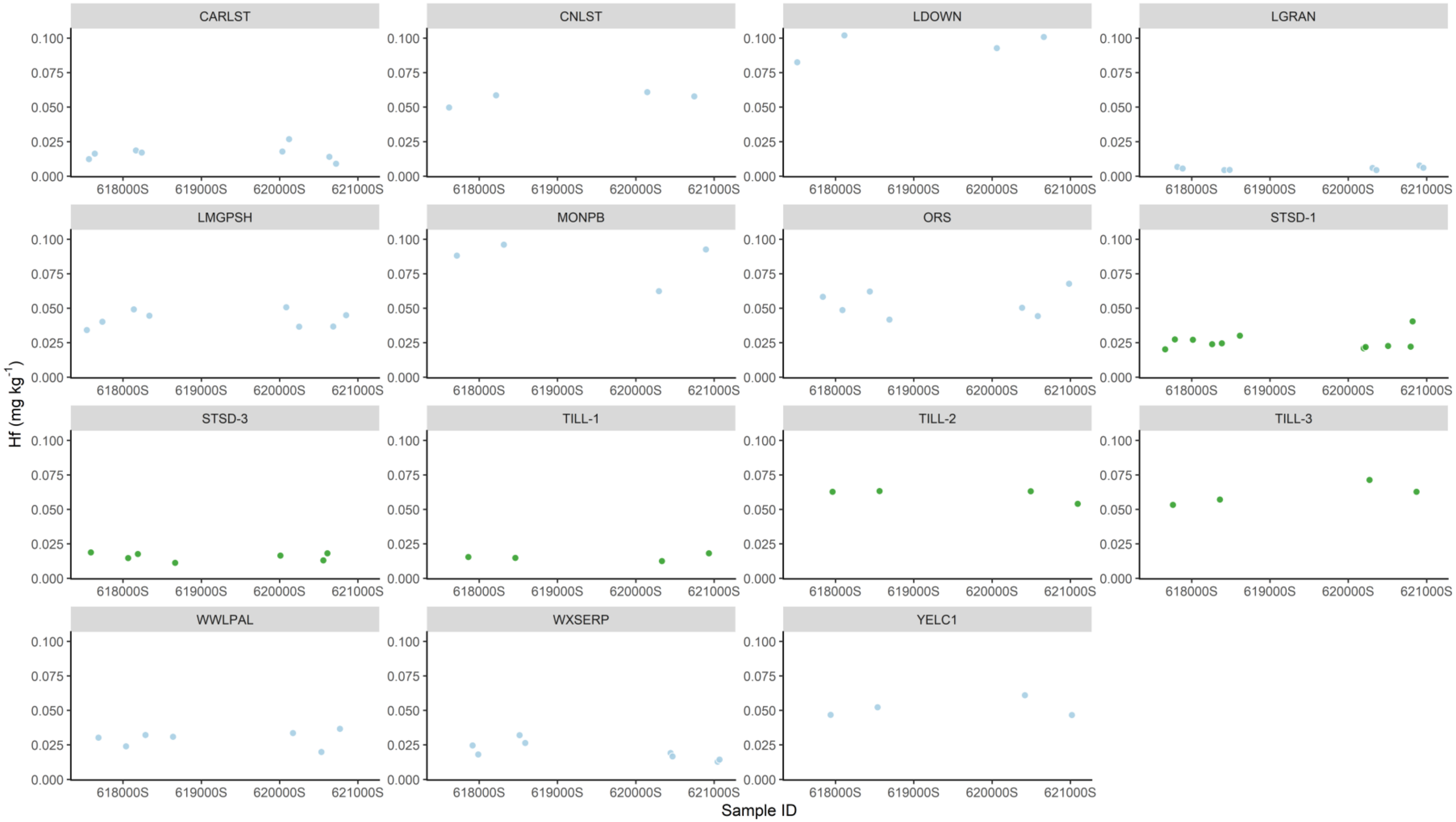
Gallium (Ga) sample data IQR: 2.86–3.68 mg kg^{-1}

Germanium (Ge) MS41L-BLD

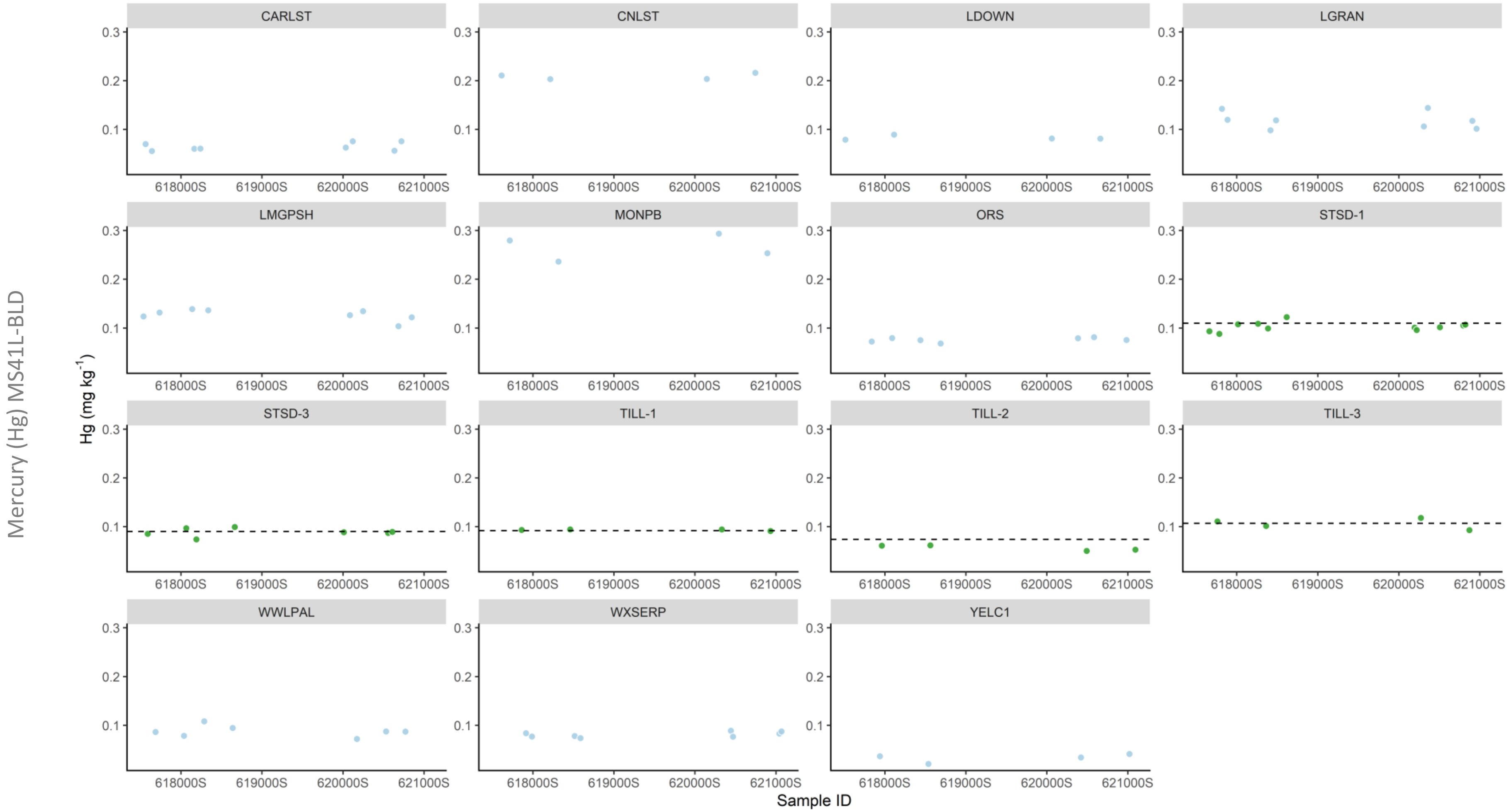


Germanium (Ge) sample data IQR: 0.0537-0.0695 mg kg^{-1}

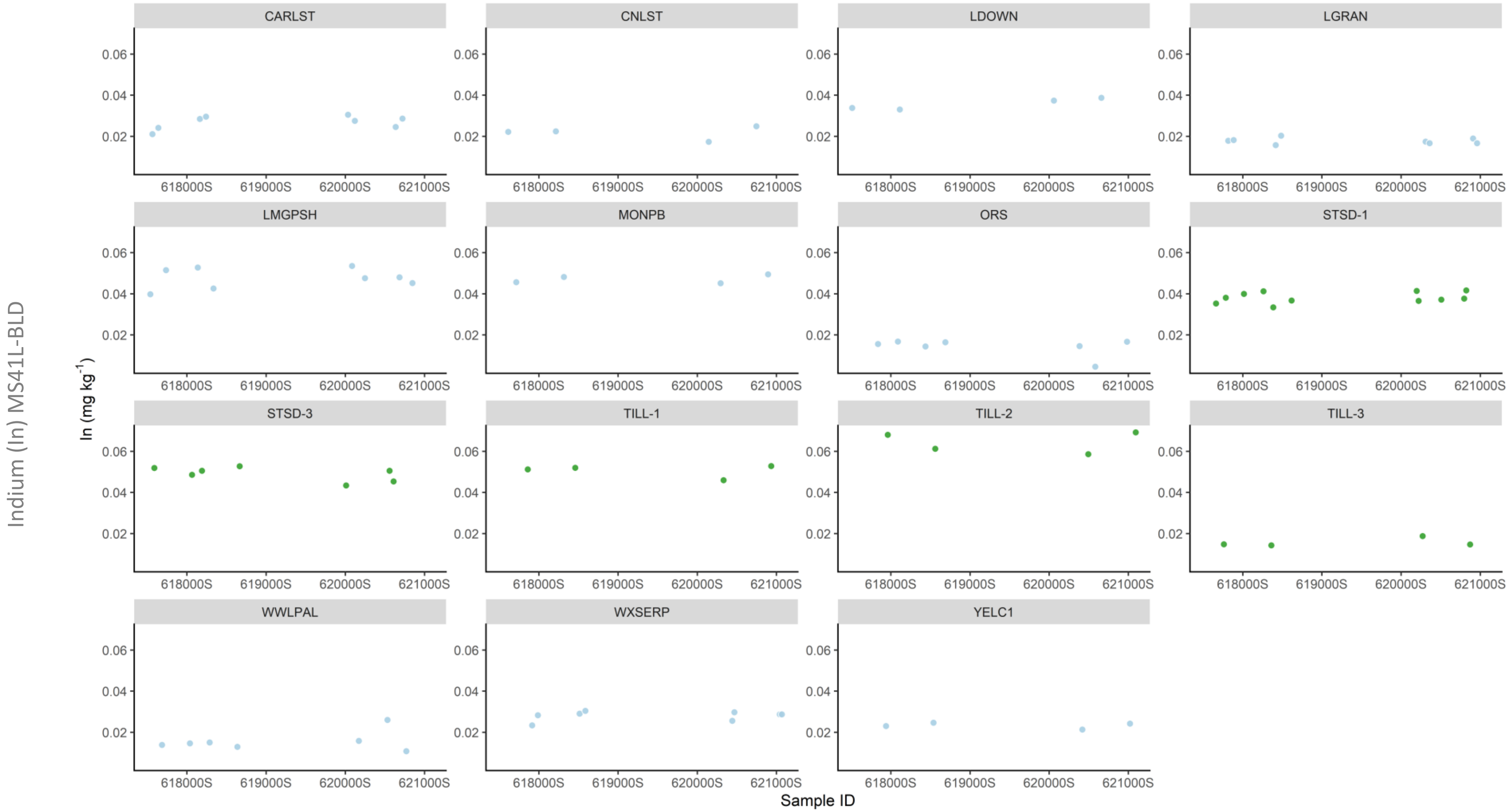
Hafnium (Hf) MS41L-BLD



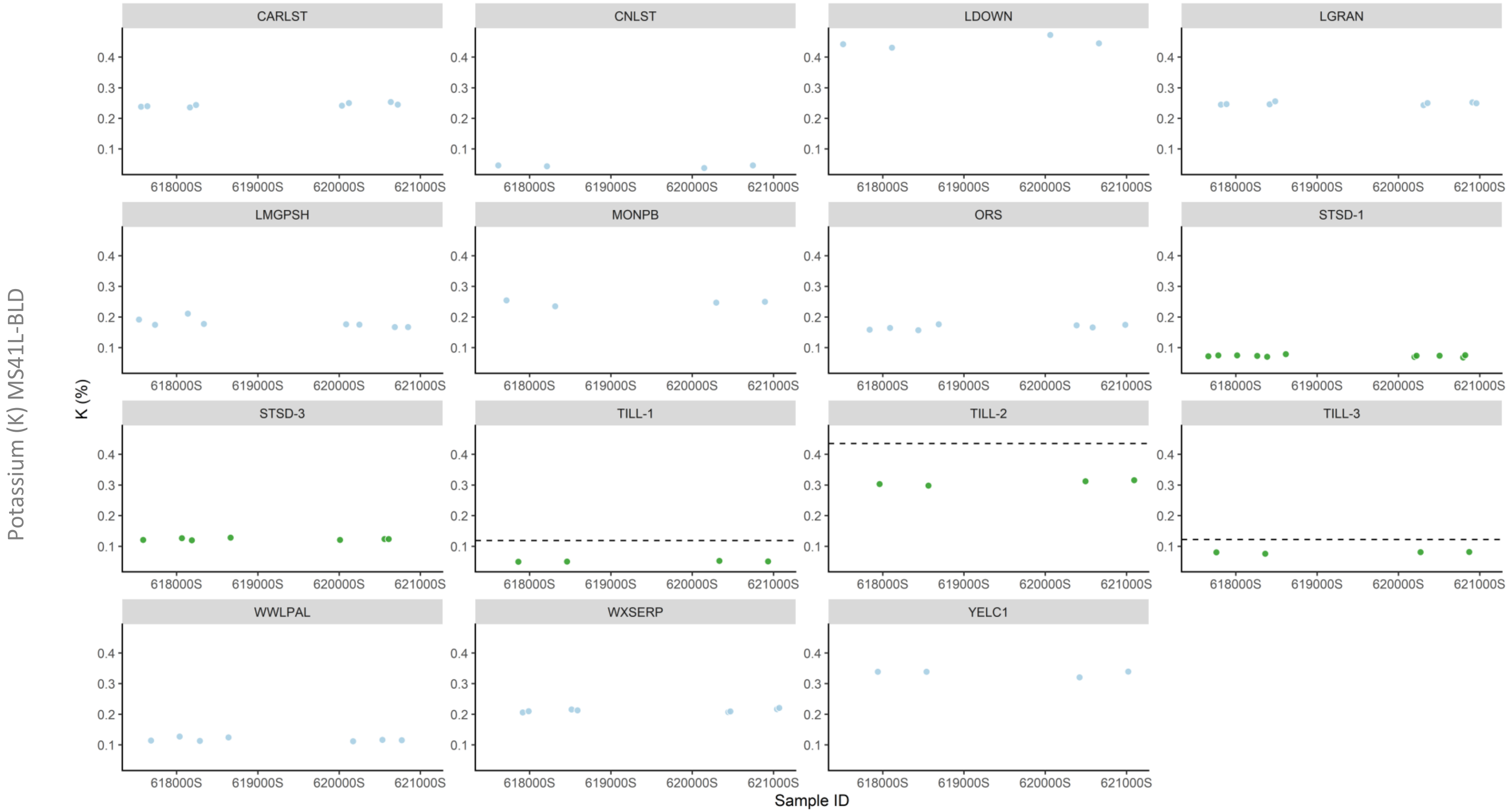
Hafnium (Hf) sample data IQR: 0.0781–0.107 mg kg^{-1}



Mercury (Hg) sample data IQR: 0.155–0.458 mg kg^{-1}

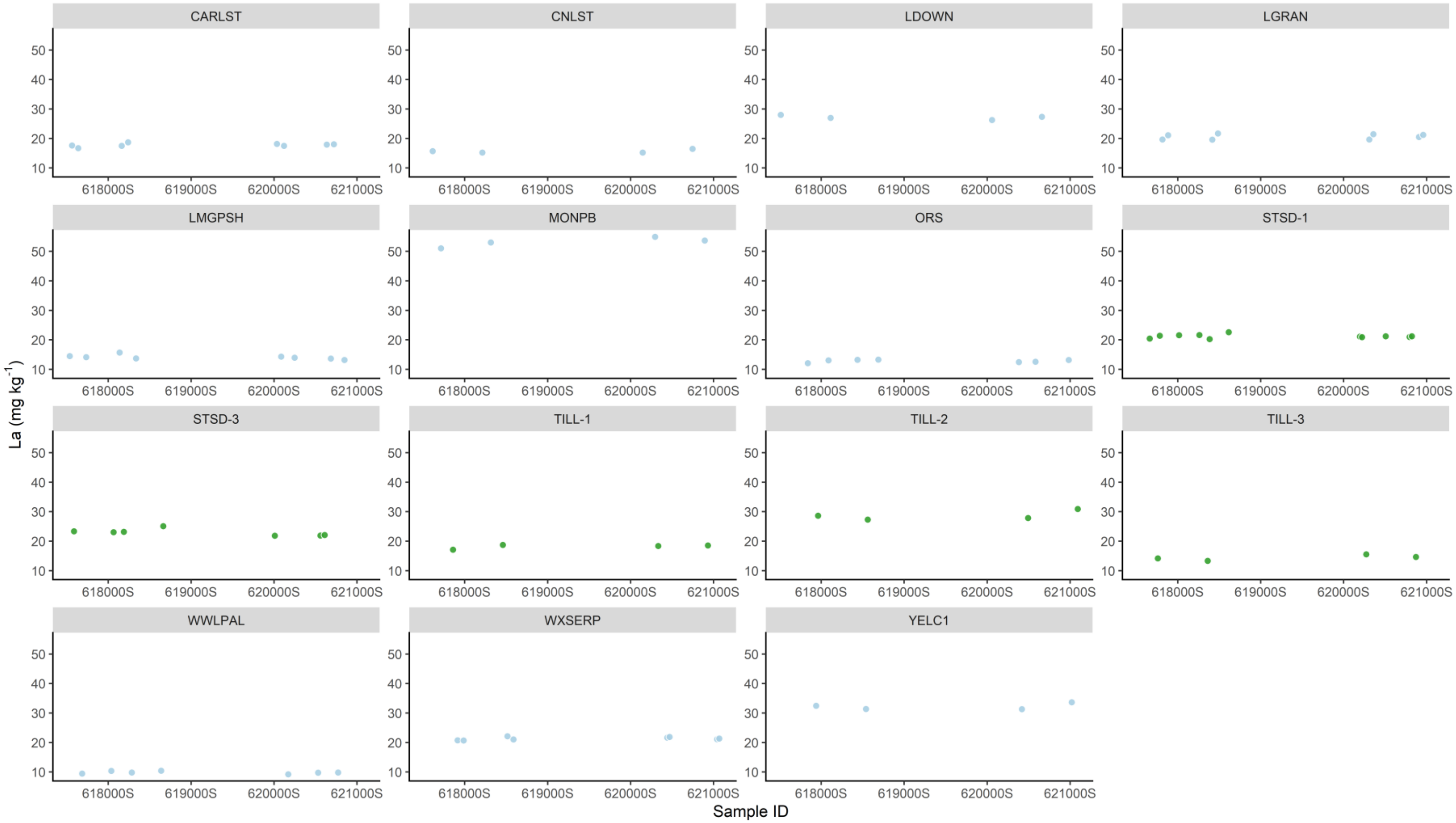


Indium (In) sample data IQR: 0.0210–0.0278 mg kg^{-1}



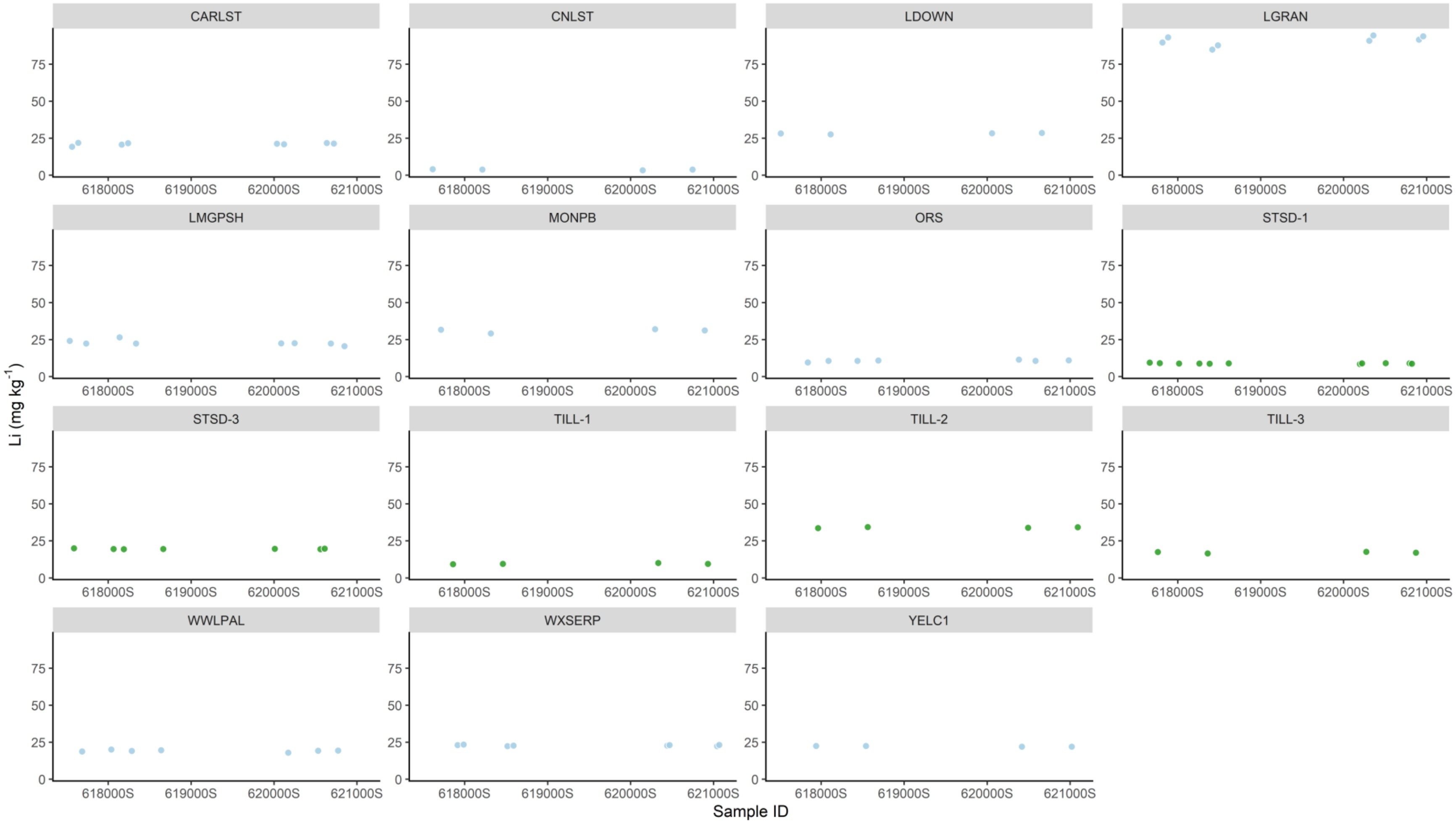
Potassium (K) sample data IQR: 0.118–0.145 %

Lanthanum (La) MS41L-BLD

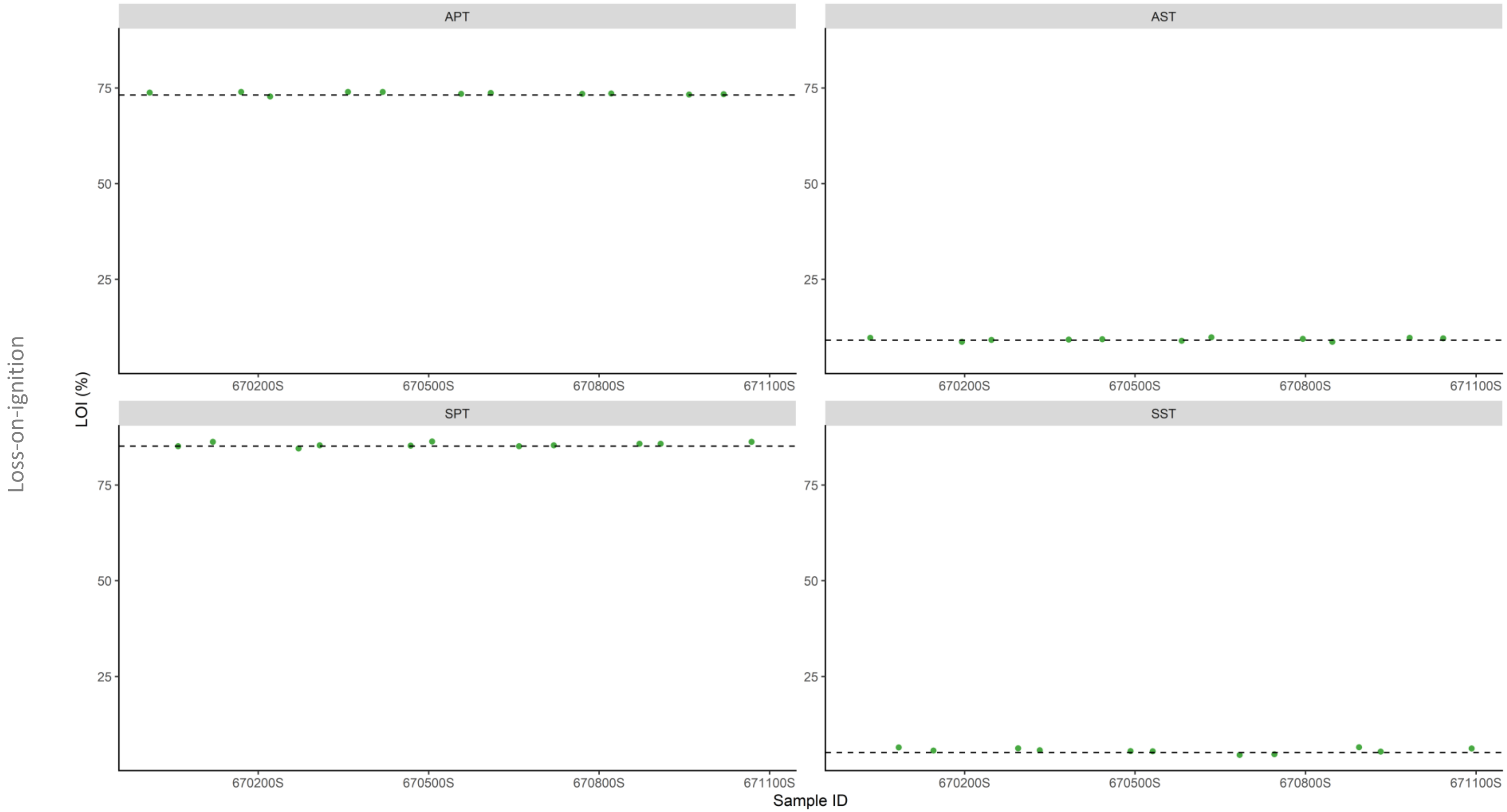


Lanthanum (La) sample data IQR: 12.0–14.1 mg kg^{-1}

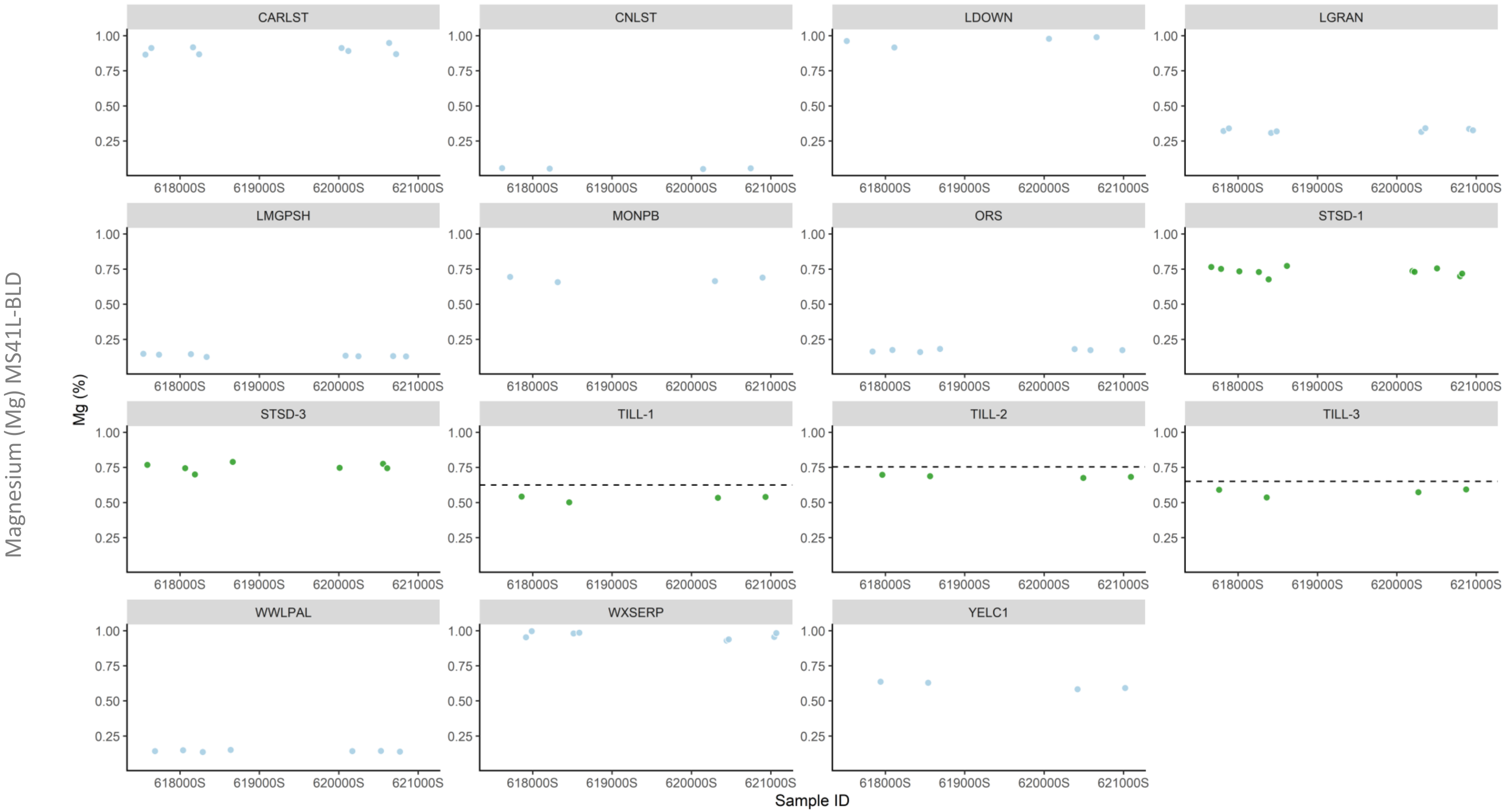
Lithium (Li) MS41L-BLD



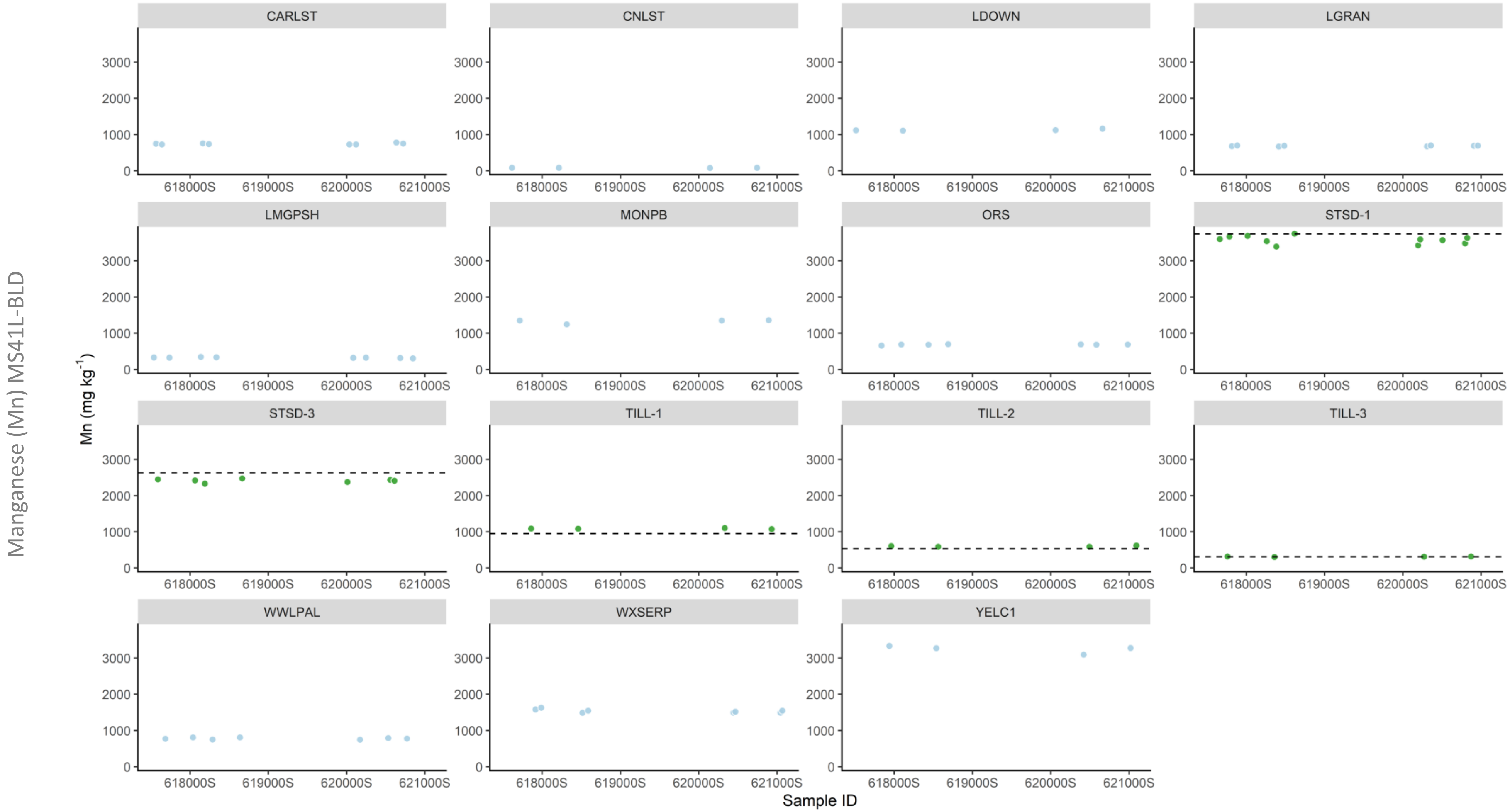
Lithium (Li) sample data IQR: 11.4–17.5 mg kg^{-1}



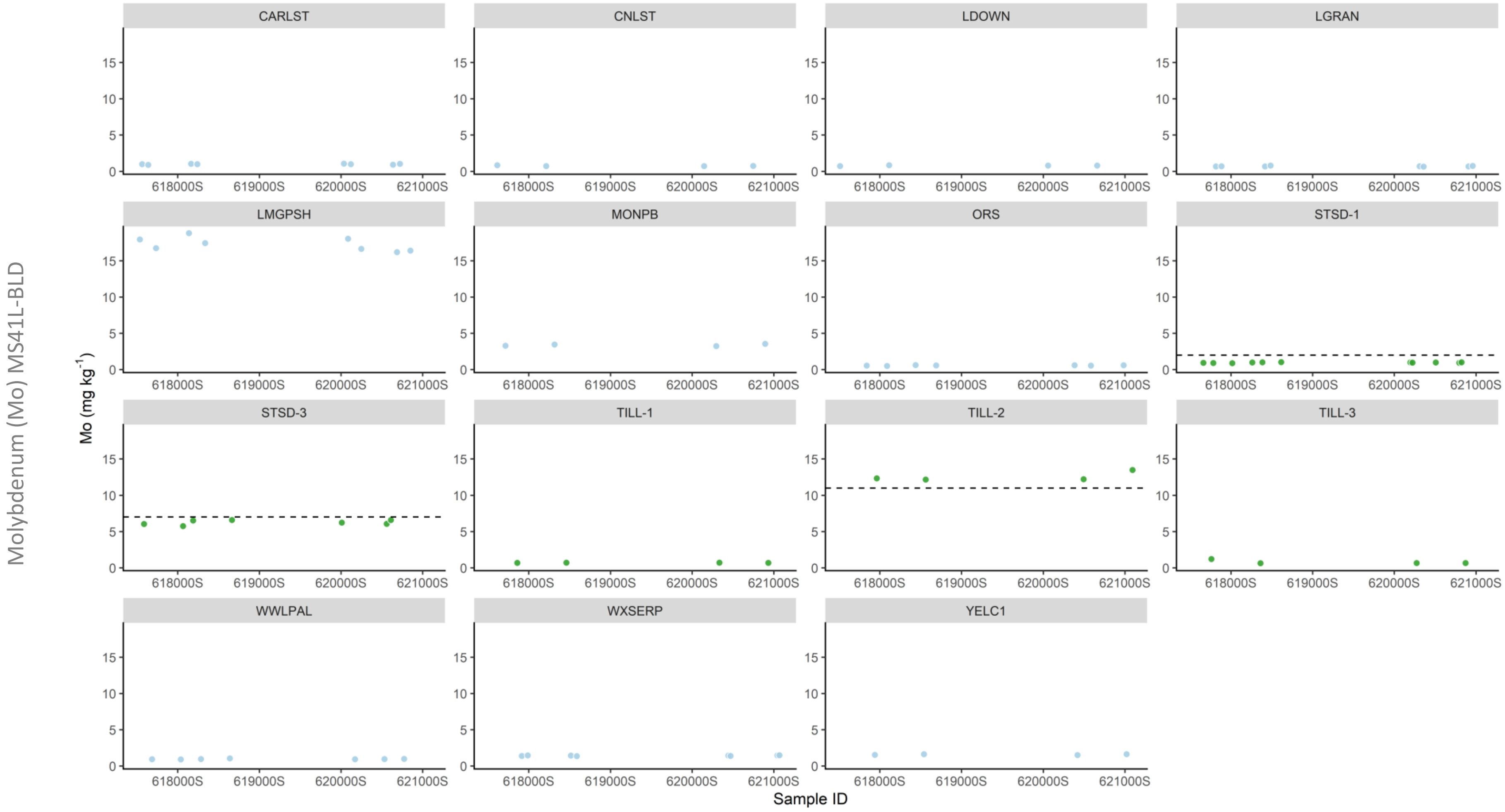
Loss on ignition (LOI) sample data IQR: 6.71–9.99 %



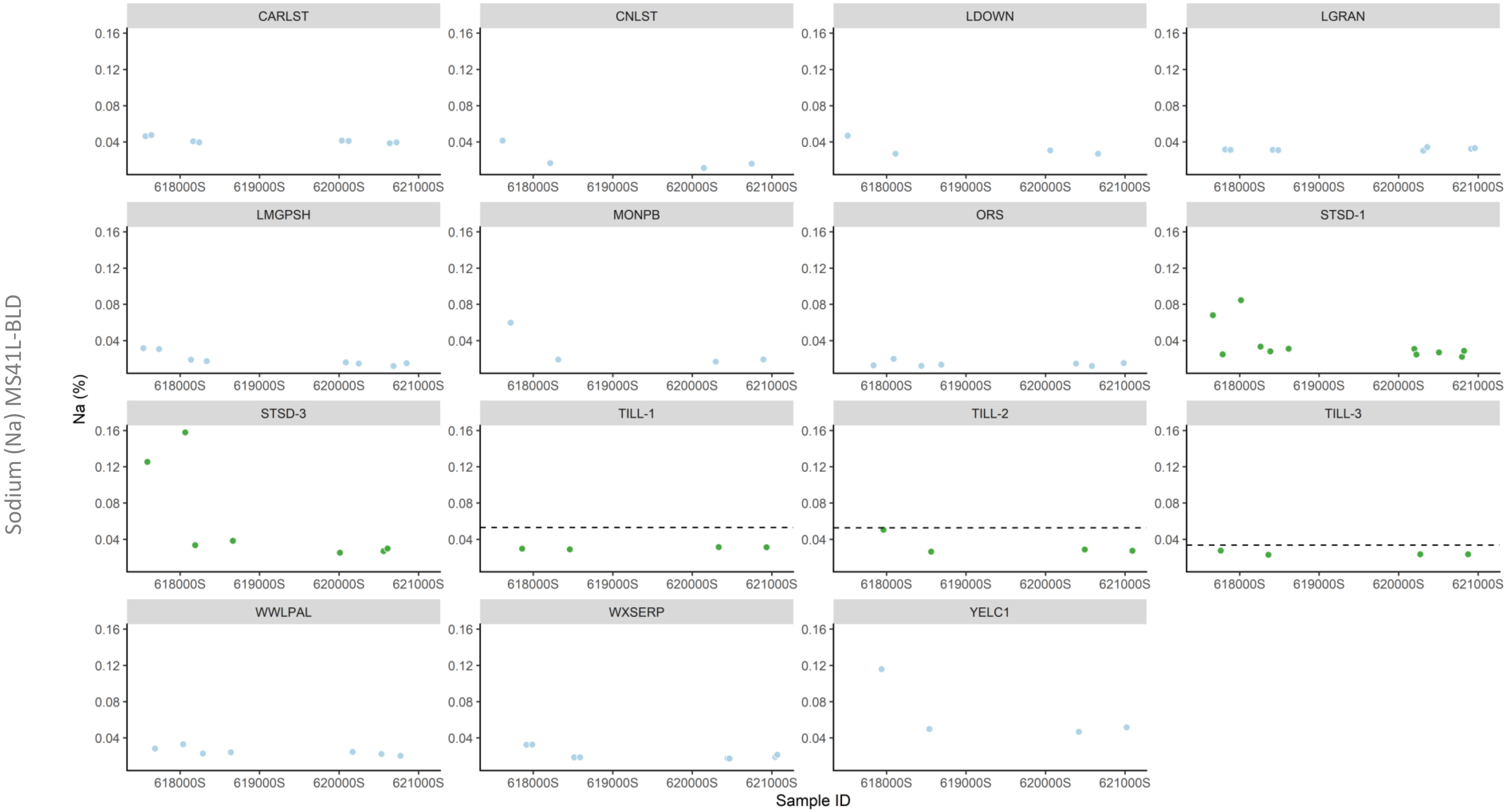
Magnesium (Mg) sample data IQR: 0.214–0.302 %



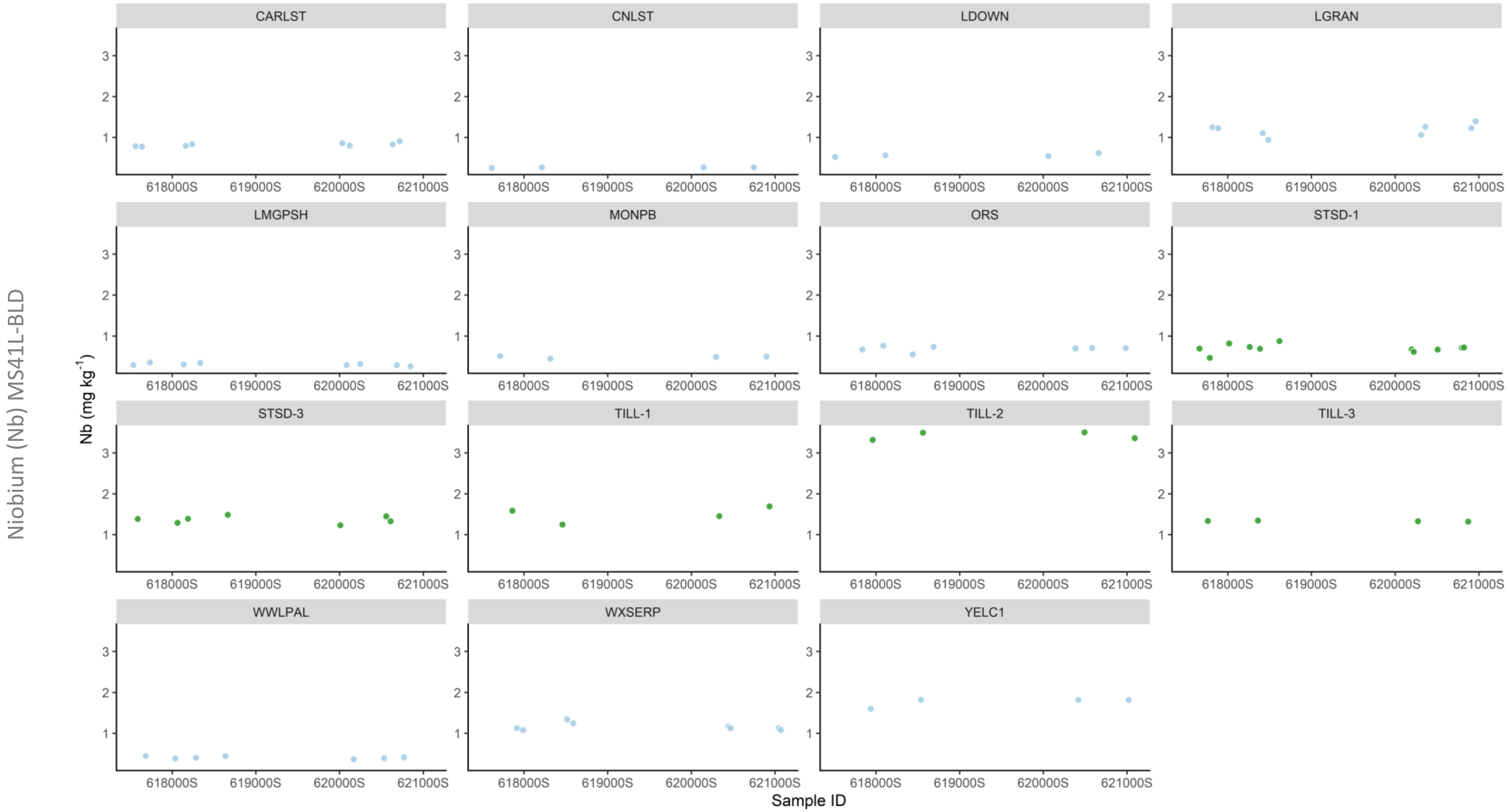
Manganese (Mn) sample data IQR: 916–1450 mg kg^{-1}



Molybdenum (Mo) sample data IQR: 2.57–3.79 mg kg^{-1}

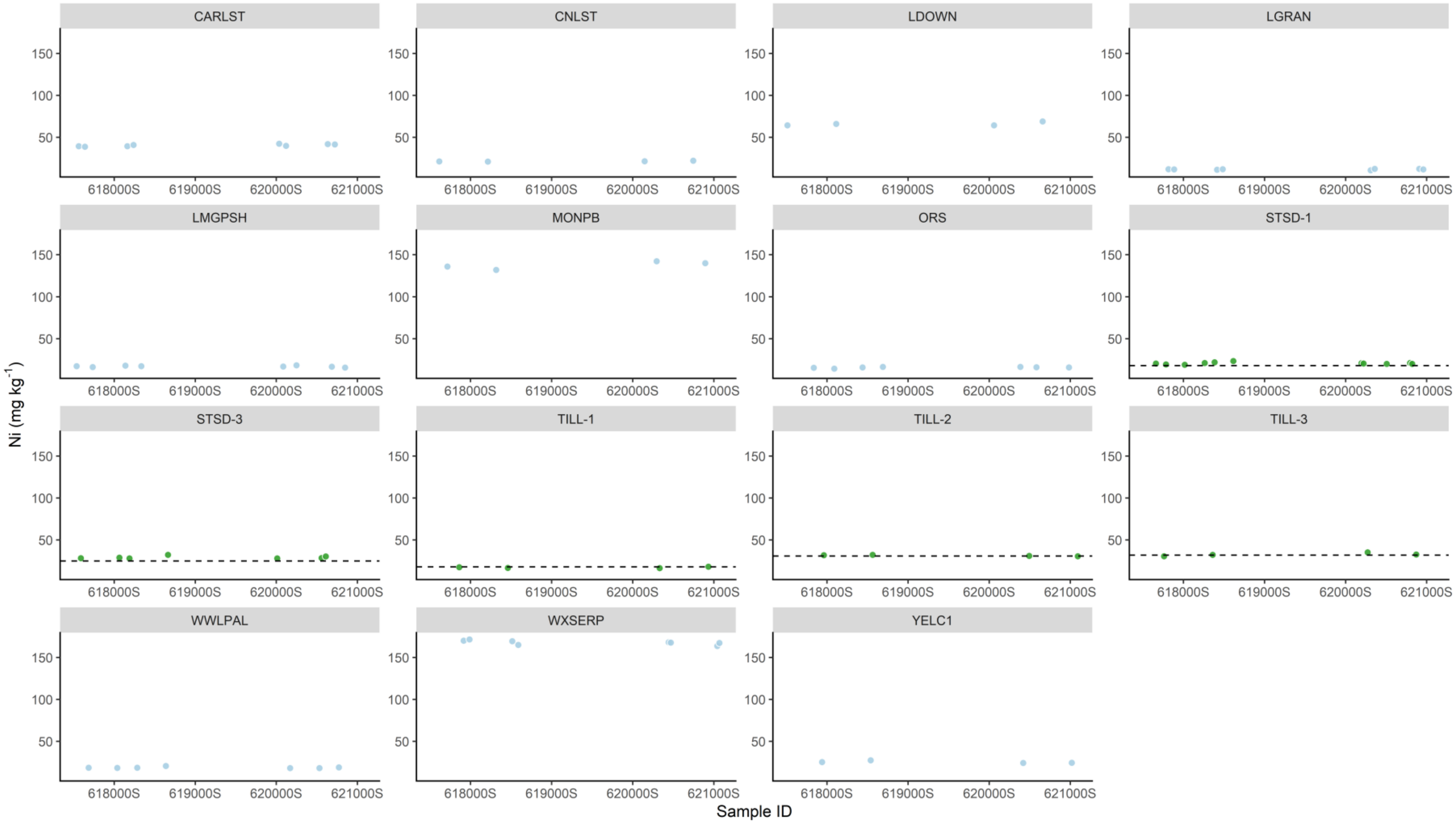


Sodium (Na) sample data IQR: 0.0154–0.0210 %

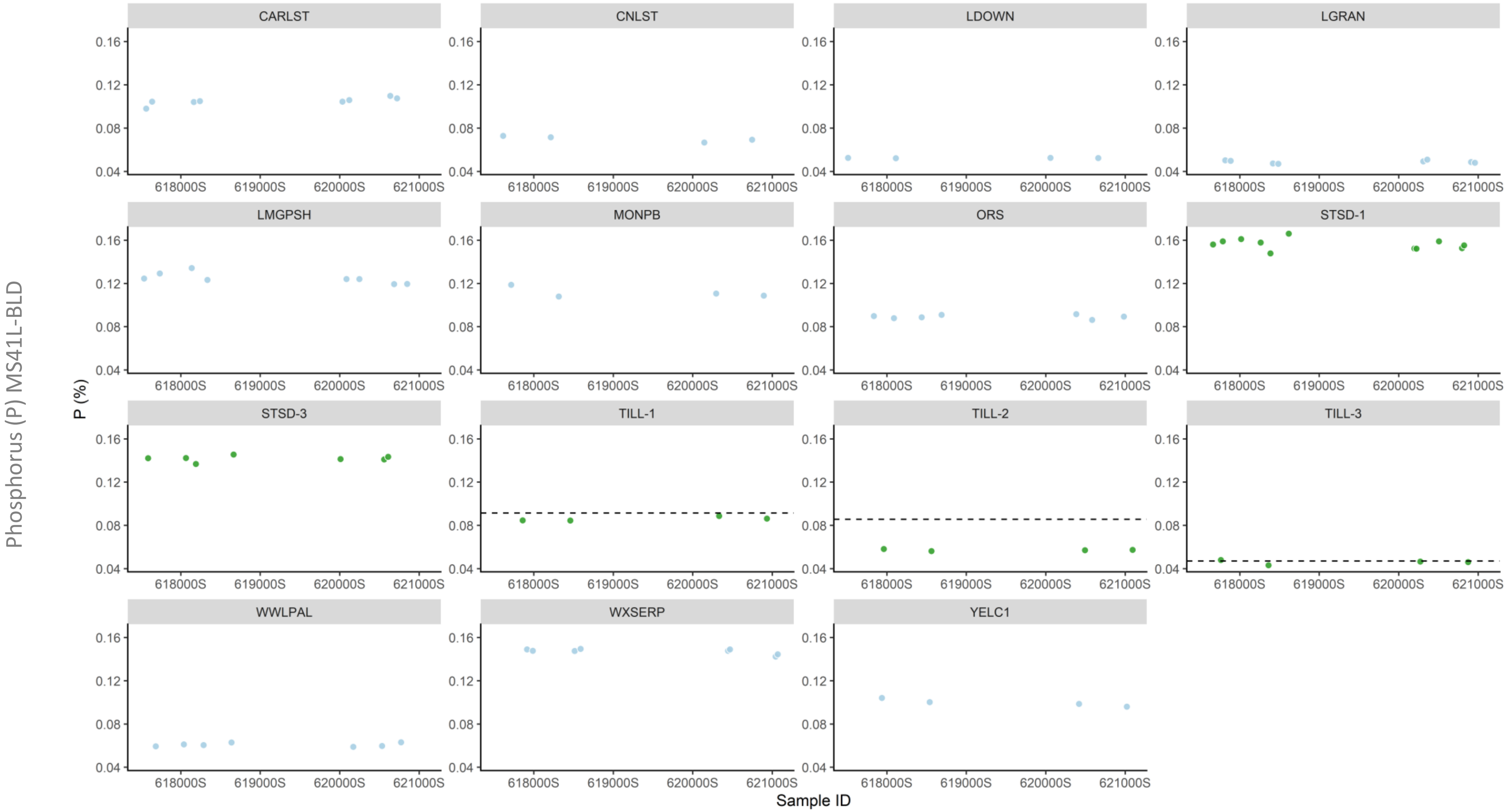


Niobium (Nb) sample data IQR: 0.291–0.404 mg kg^{-1}

Nickel (Ni) MS41L-BLD

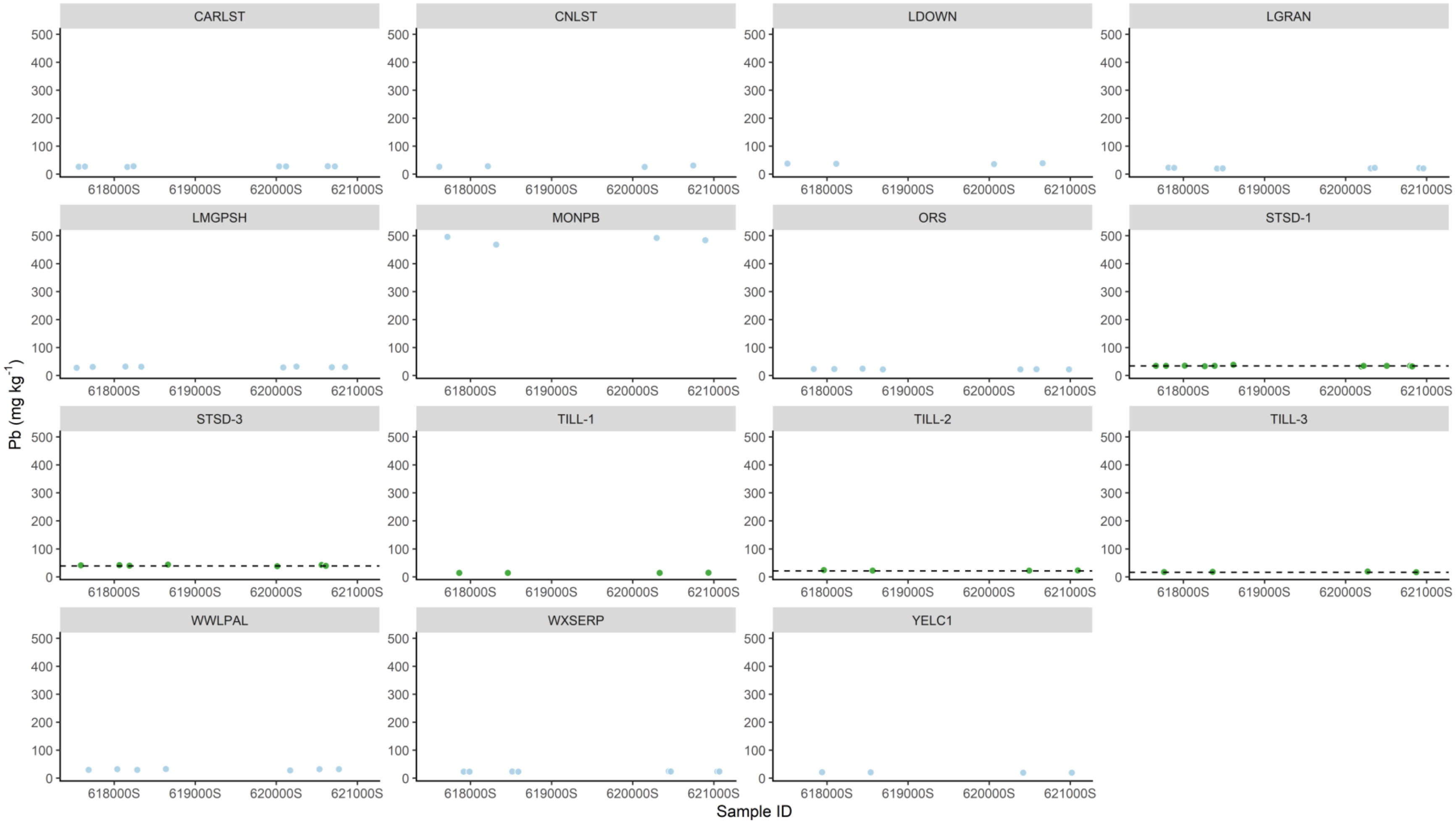


Nickel (Ni) sample data IQR: 38.9–51.9 mg kg^{-1}



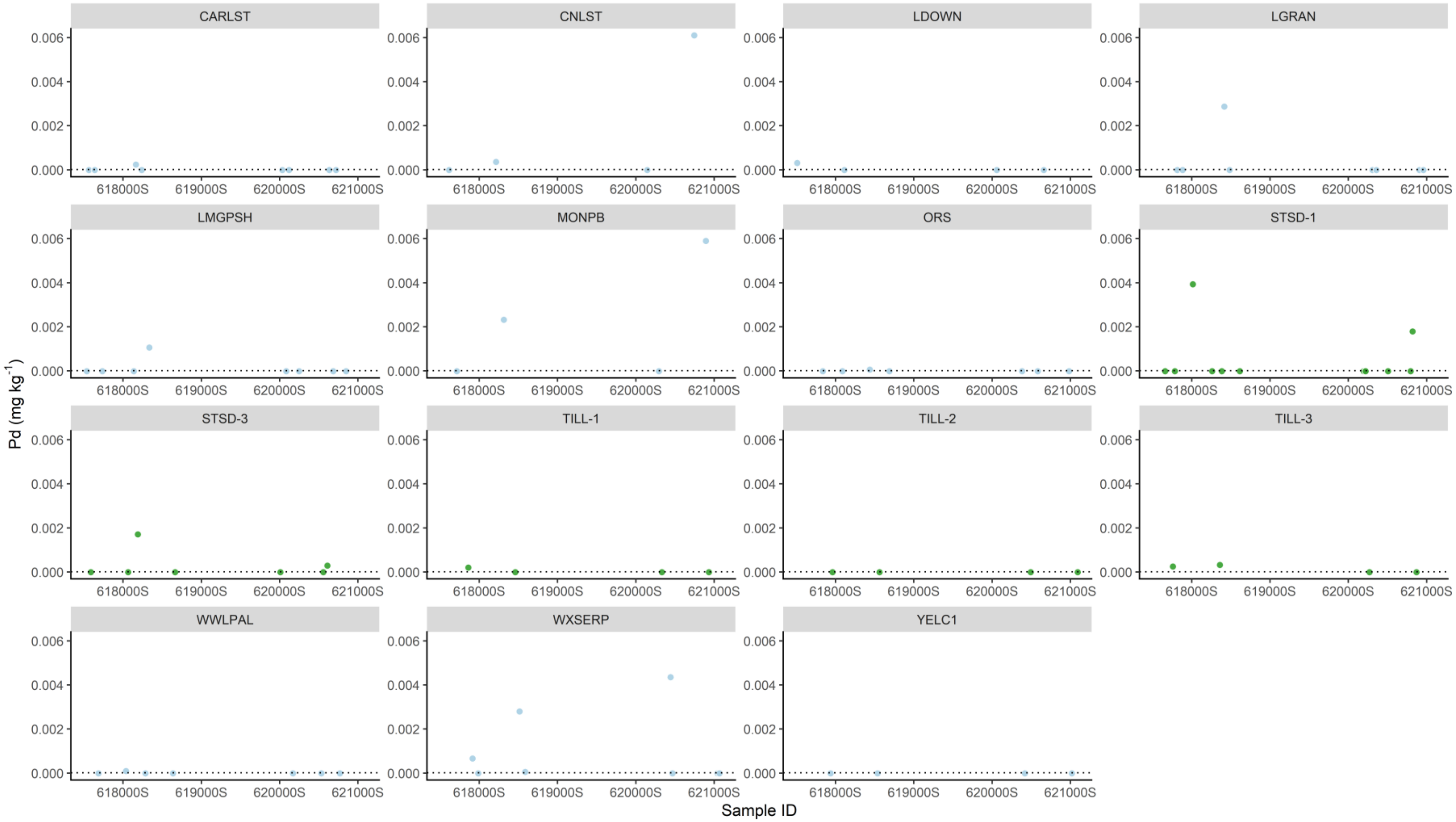
Phosphorus (P) sample data IQR: 694–1090 mg kg^{-1}

Lead (Pb) MS41L-BLD



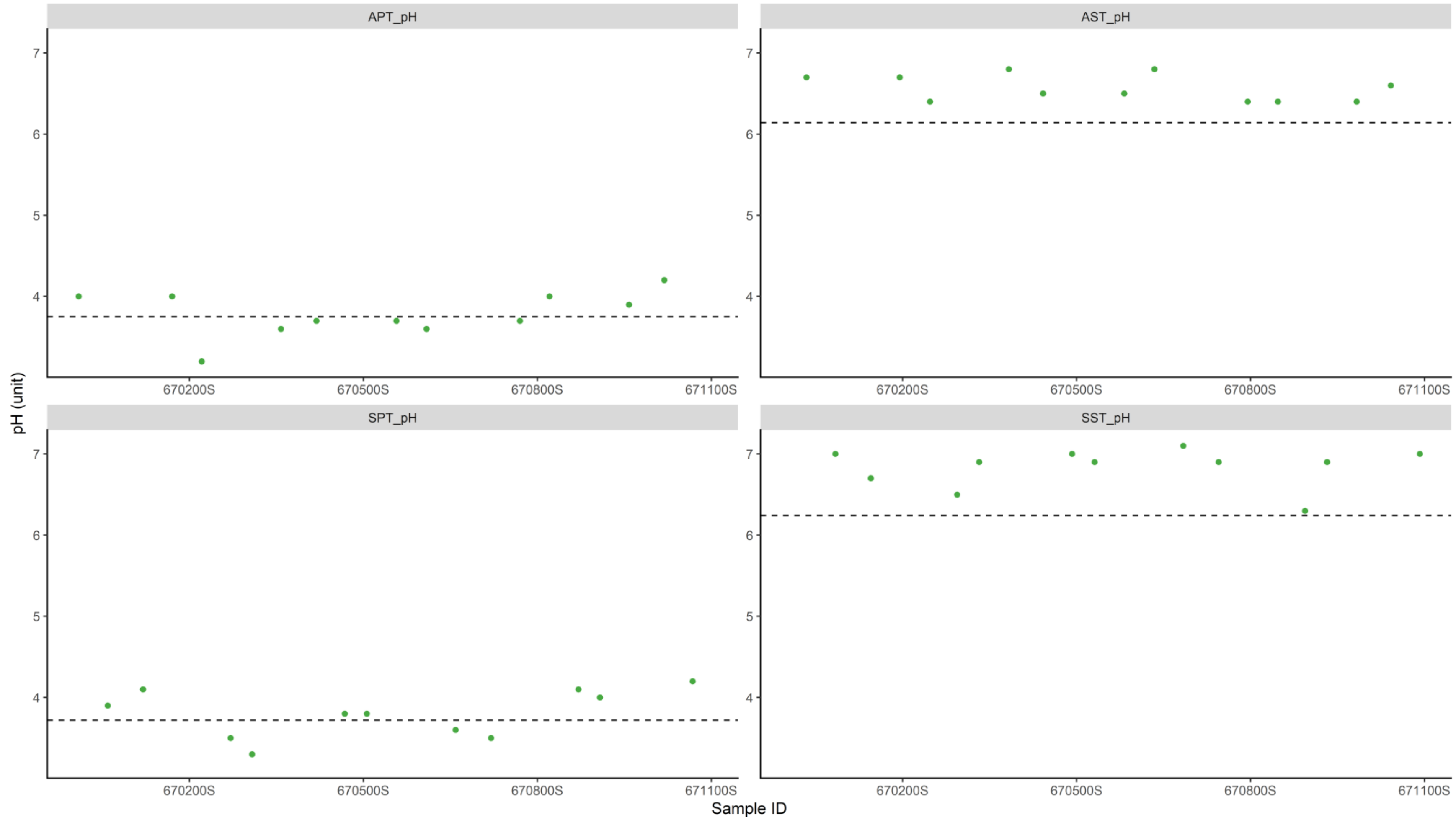
Lead (Pb) sample data IQR: 59.8–161 mg kg^{-1}

Palladium (Pd) MS41L-BLD



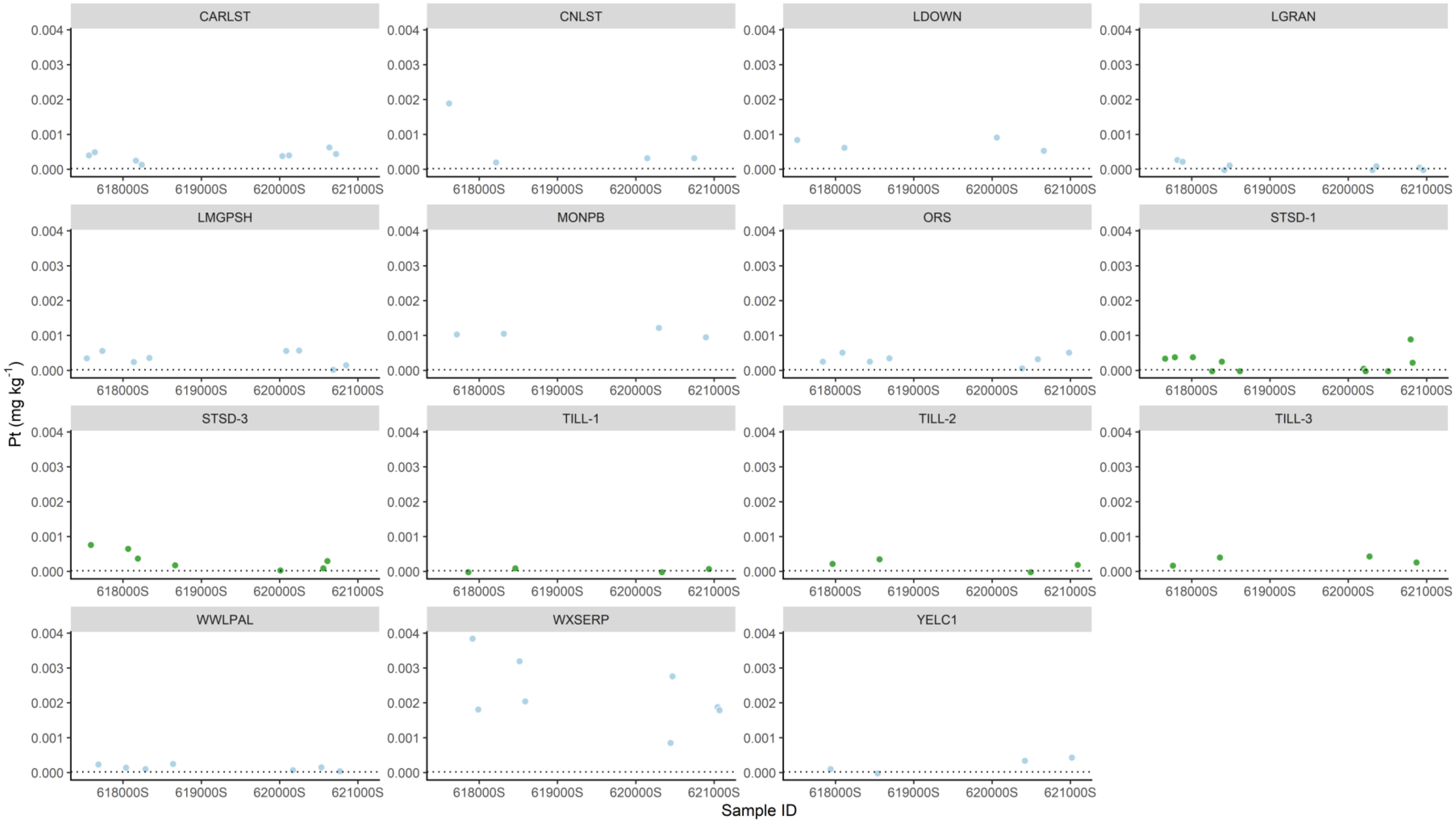
Palladium (Pd) sample data IQR: 0.00000612–0.000162 mg kg^{-1}

pH $CaCl_2$

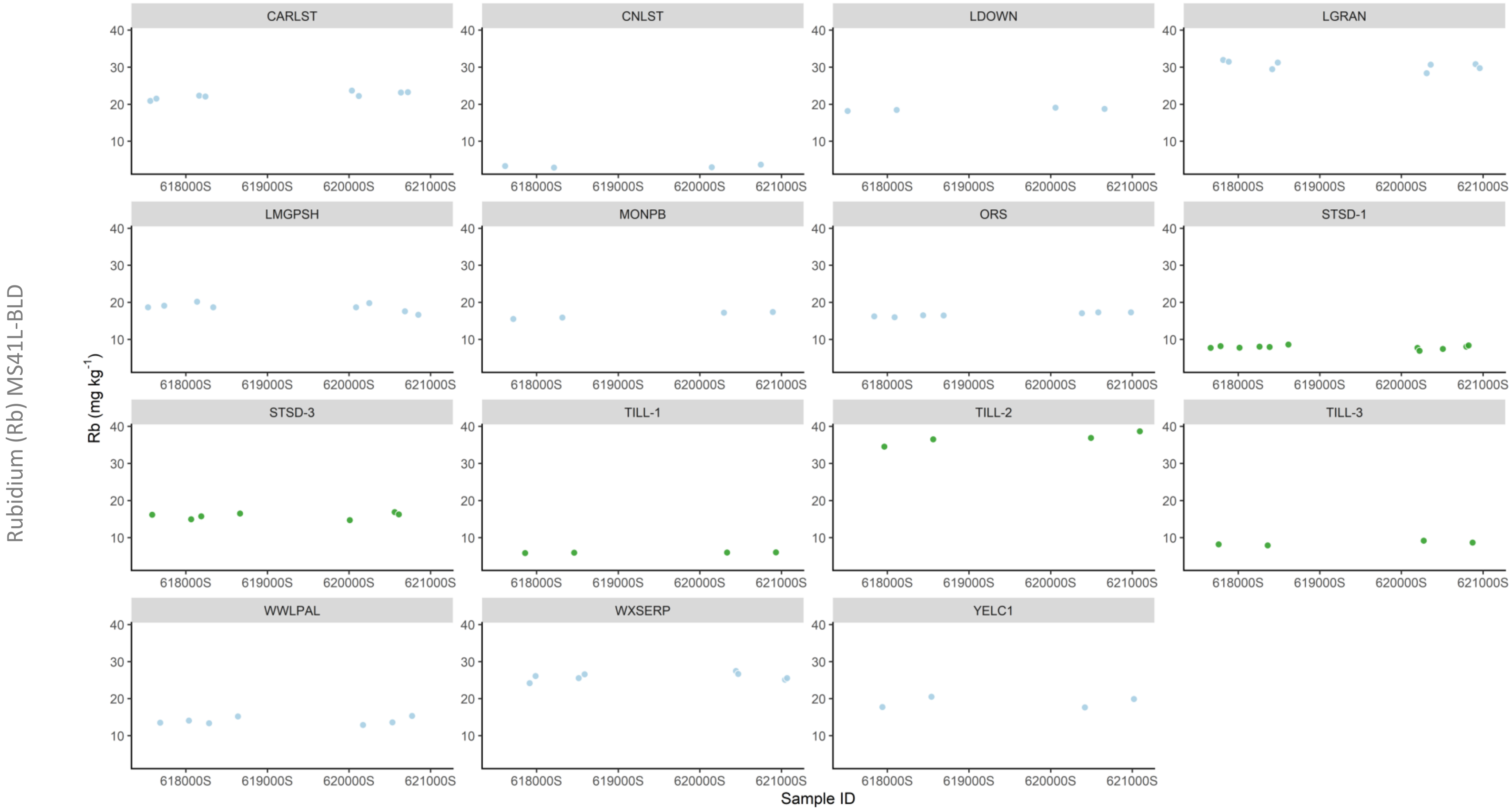


pH $CaCl_2$ sample data IQR: 6.5–7.0

Platinum (Pt) MS41L-BLD

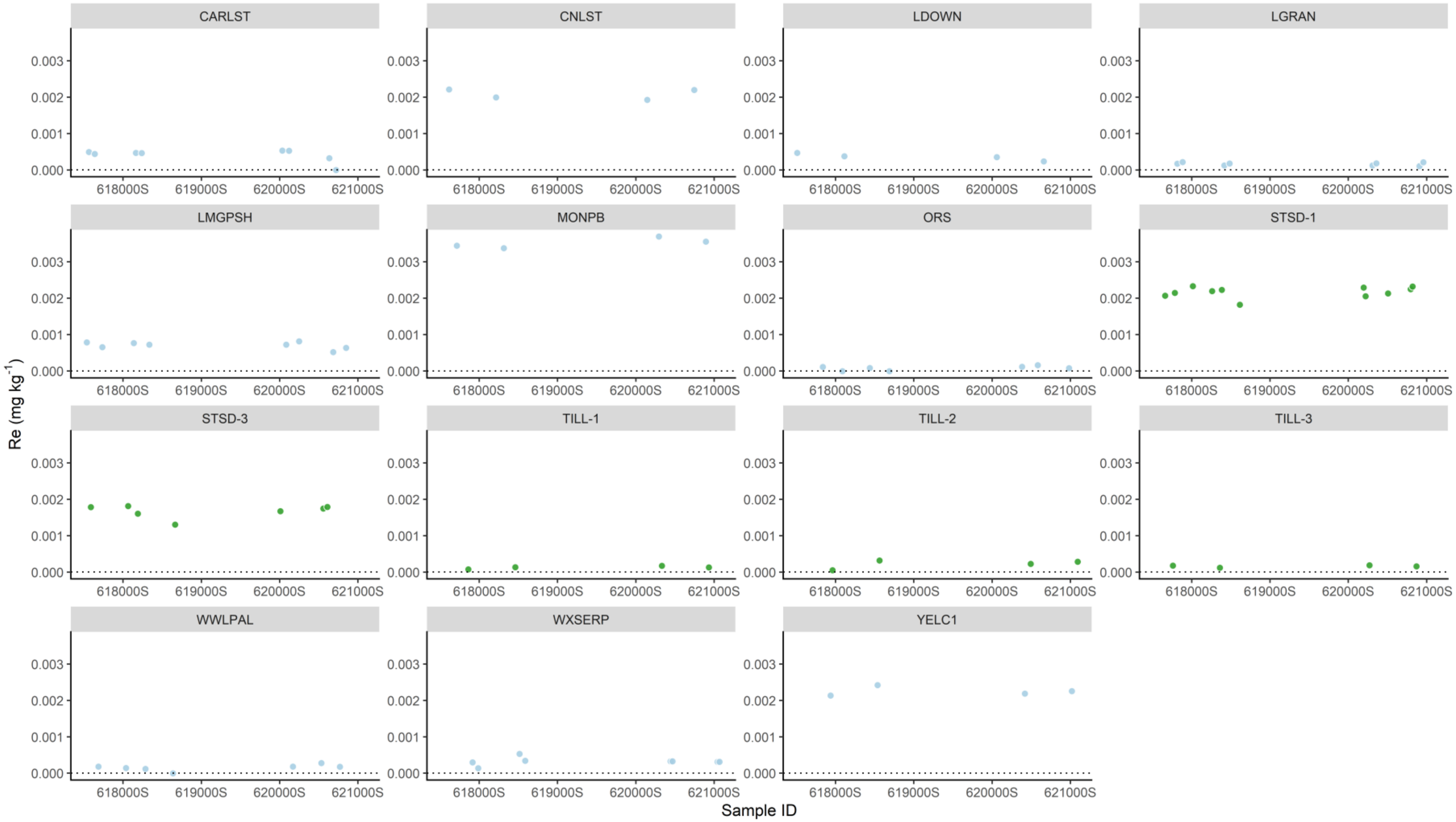


Platinum (Pt) sample data IQR: 0.00047–0.00096 mg kg^{-1}

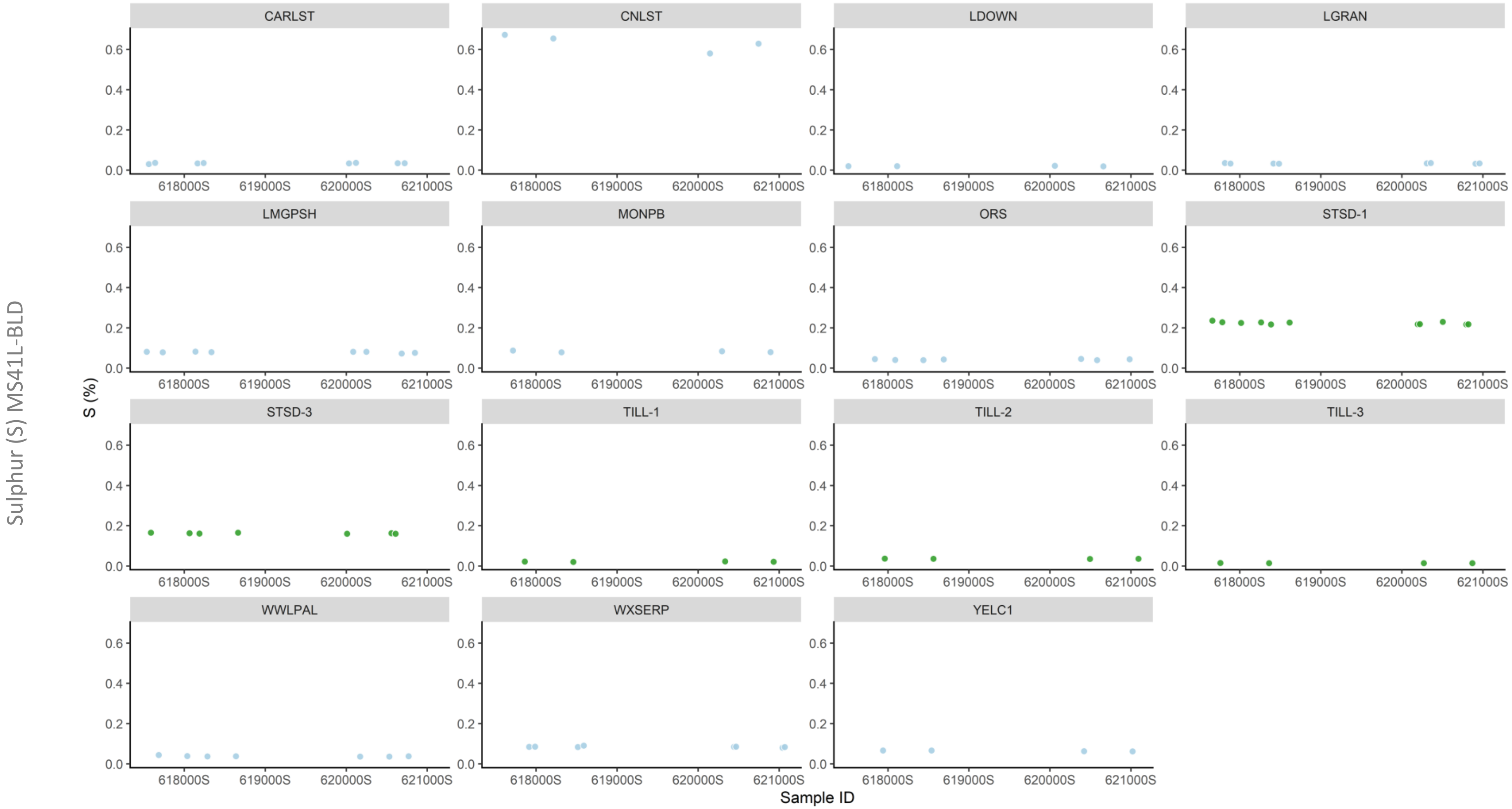


Rubidium (Rb) sample data IQR: 8.37–10.7 mg kg^{-1}

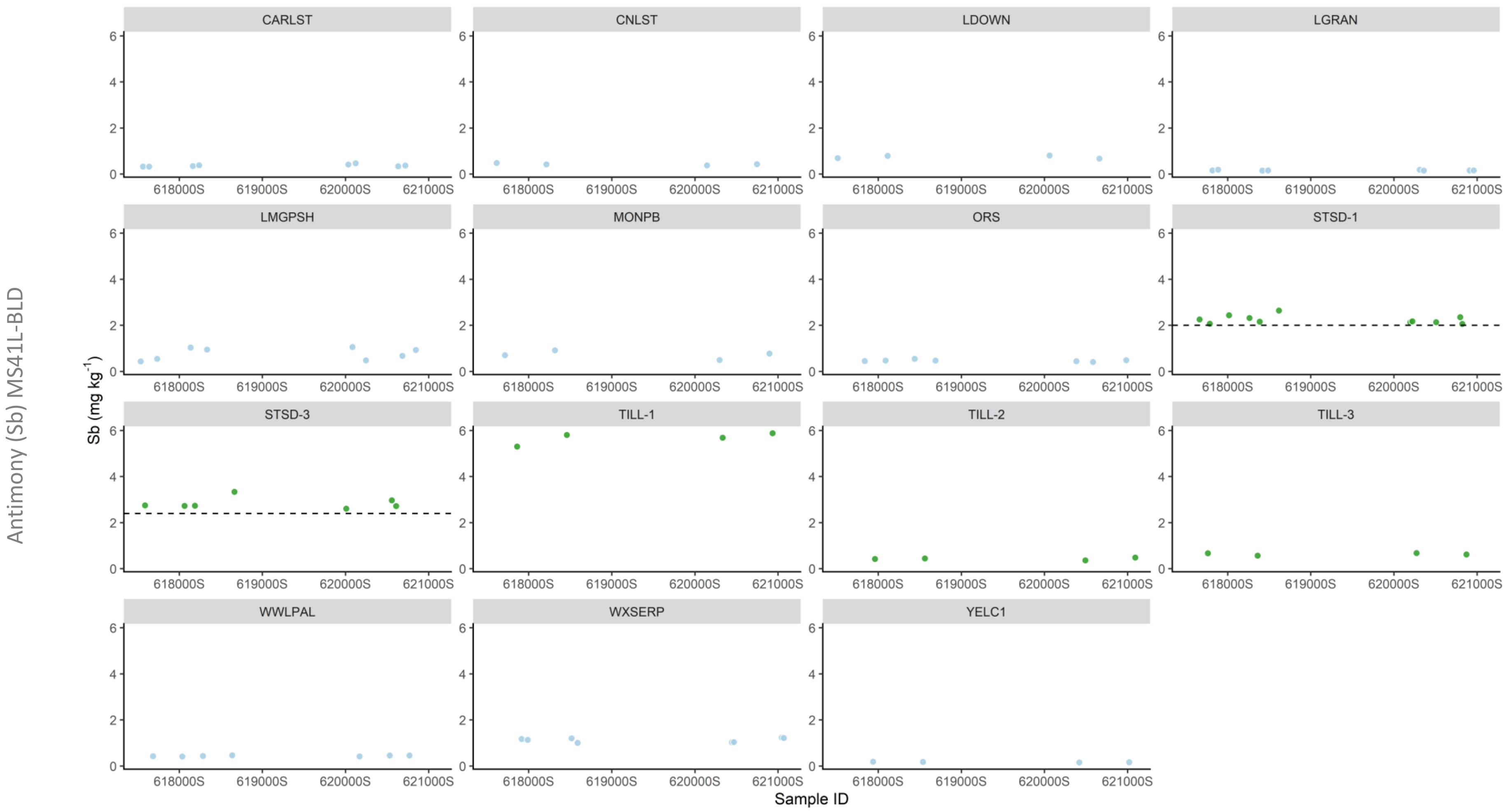
Rhenium (Re) MS41L-BLD



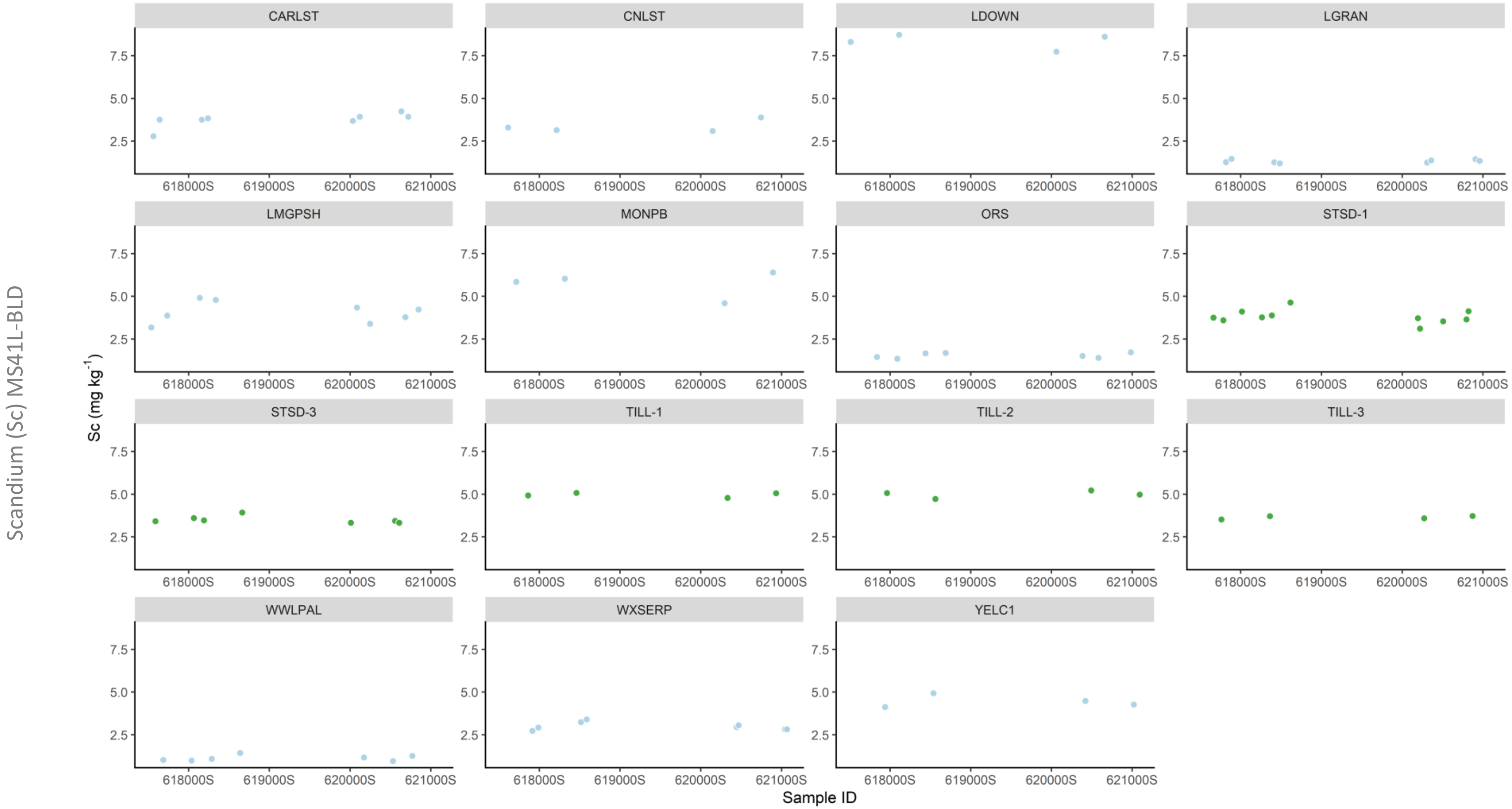
Rhenium (Re) sample data IQR: 0.000878–0.00179 mg kg^{-1}



Sulphur (S) sample data IQR: 0.0452–0.071 %

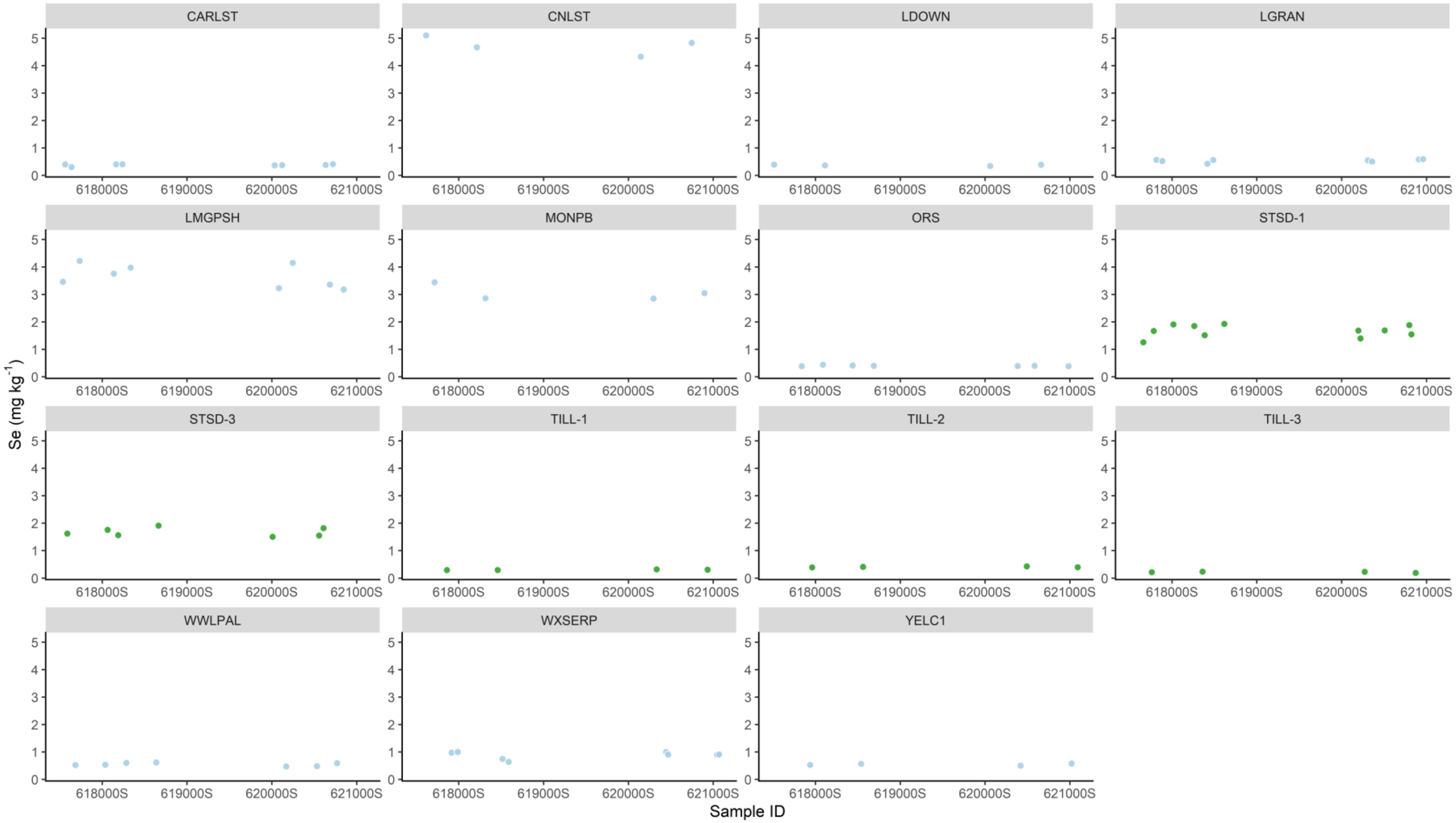


Antimony (Sb) sample data IQR: 1.10–2.05 mg kg^{-1}



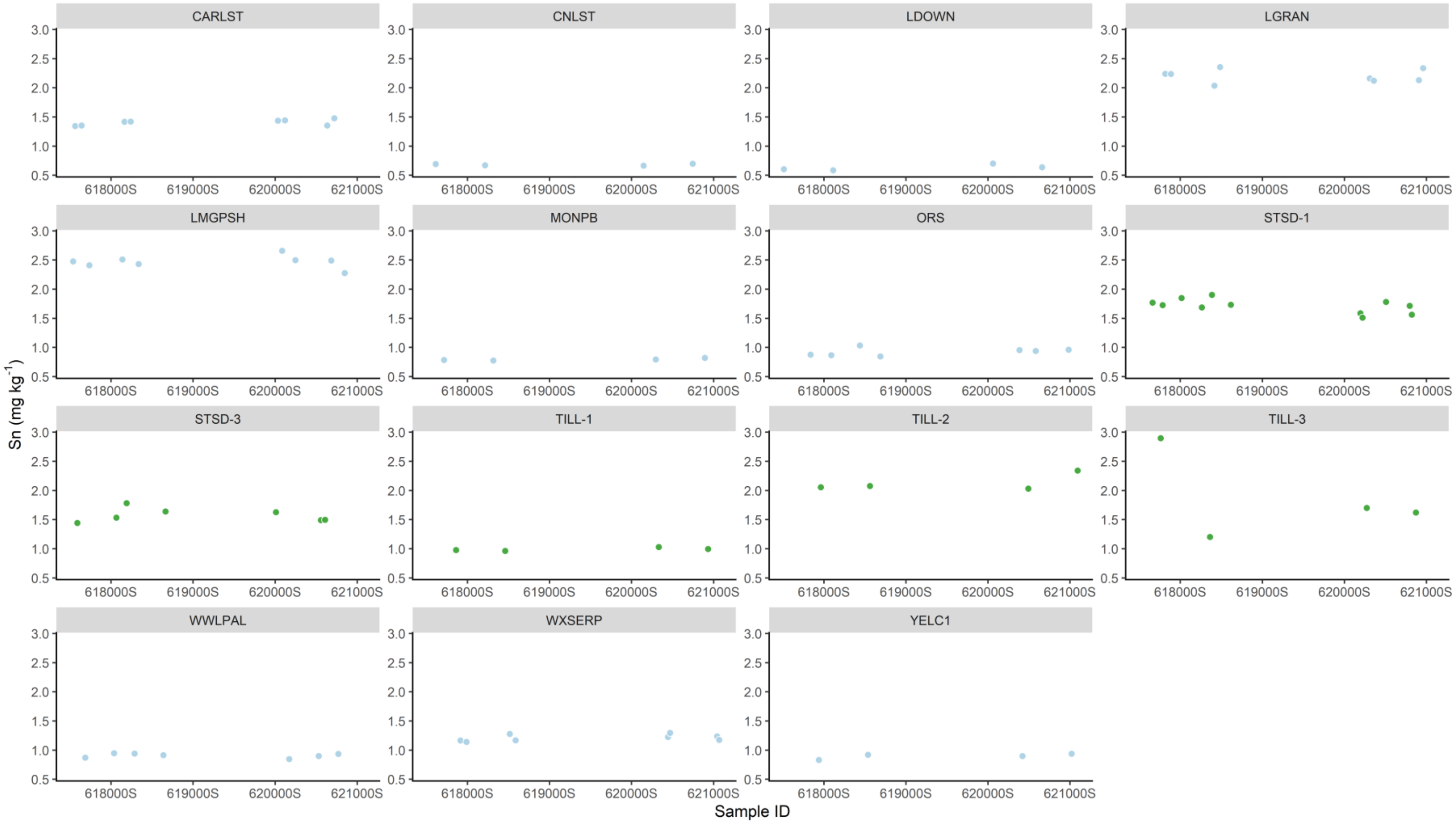
Scandium (Sc) sample data IQR: 3.30–4.11 mg kg^{-1}

Selenium (Se) MS41L-BLD



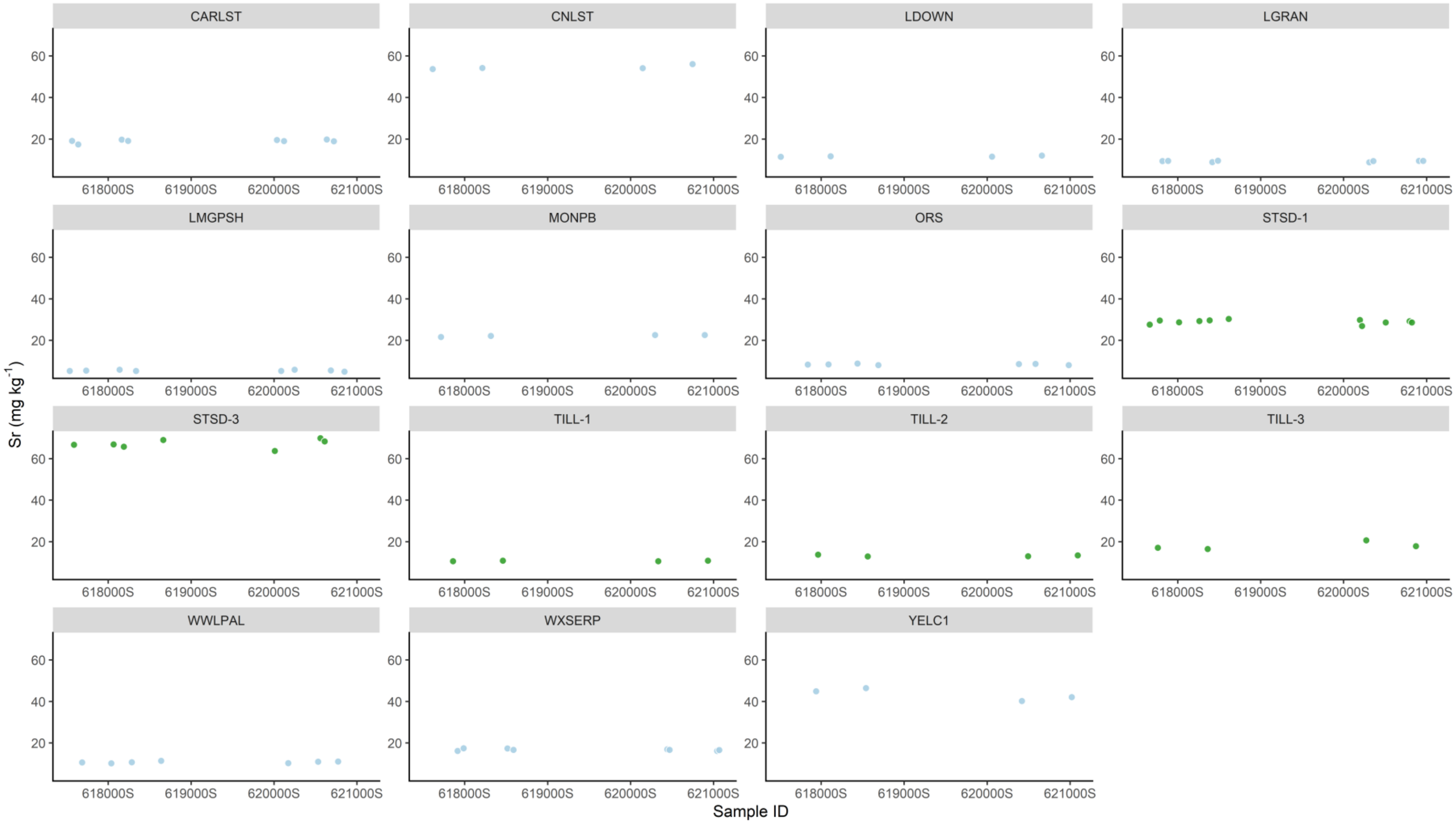
Selenium (Se) sample data IQR: 0.799–1.14 mg kg^{-1}

Tin (Sn) MS41L-BLD

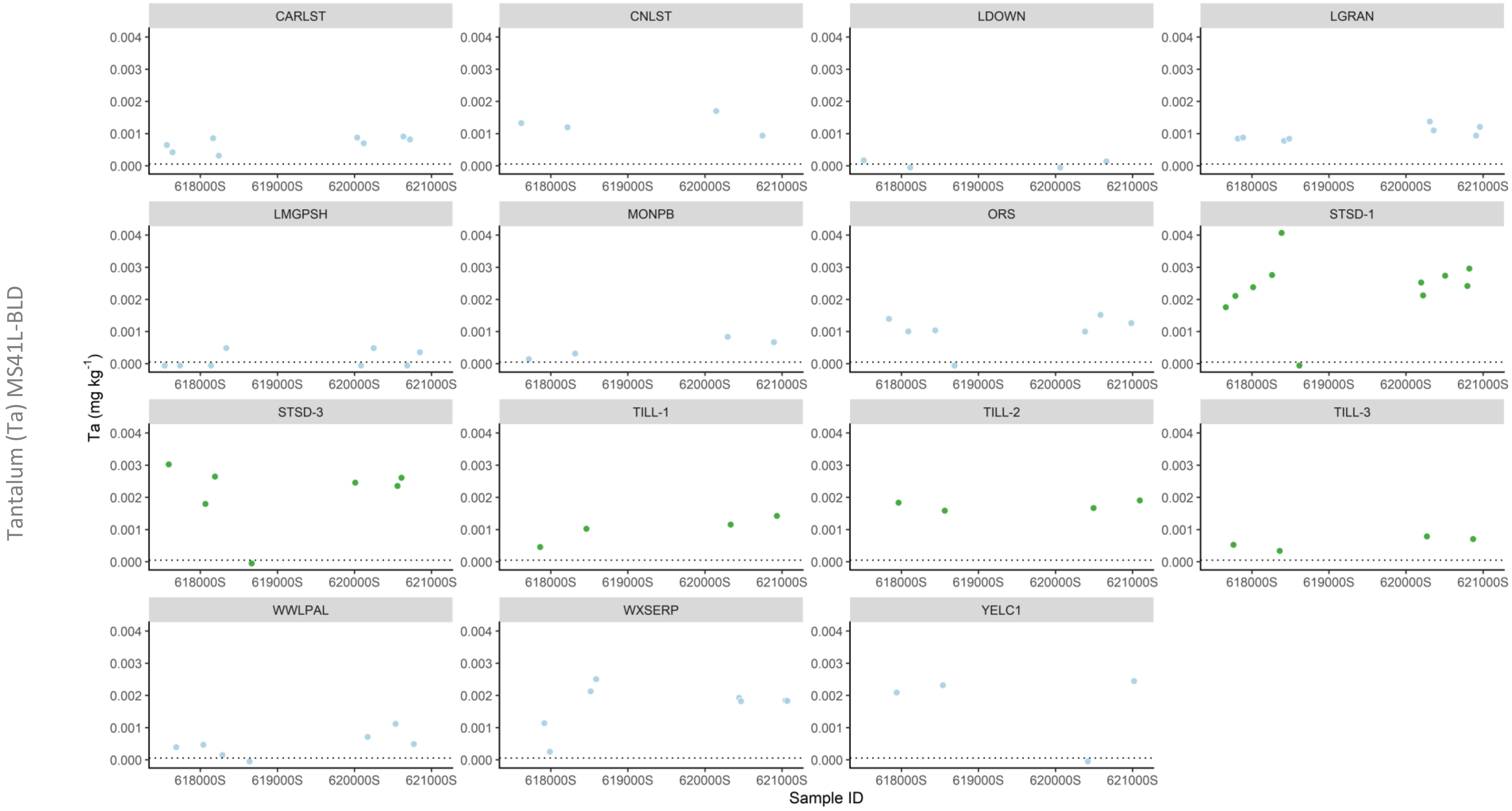


Tin (Sn) sample data IQR: 2.33–9.20 mg kg^{-1}

Strontium (Sr) MS41L-BLD

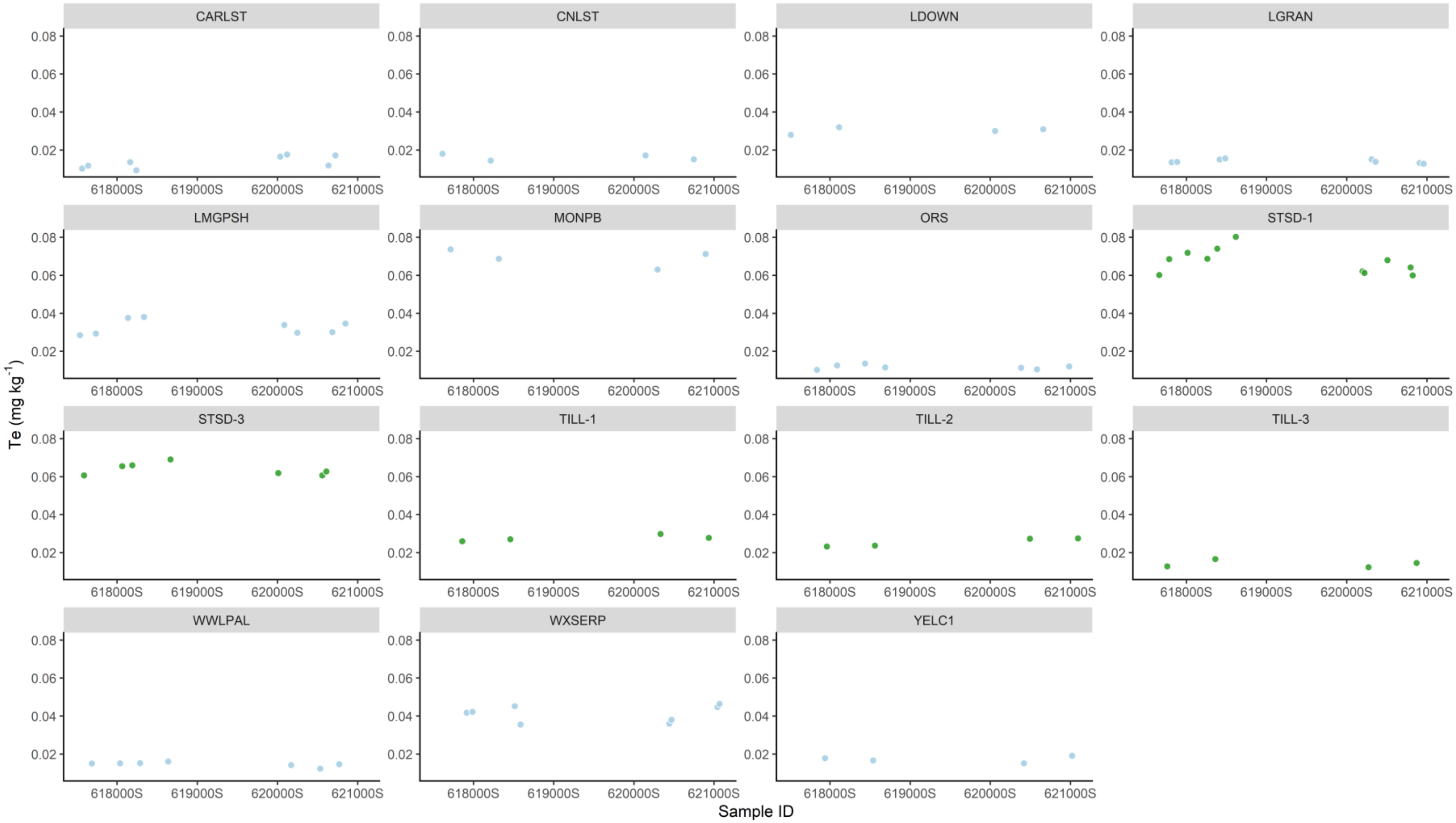


Strontium (Sr) sample data IQR: 59.8–153 mg kg^{-1}

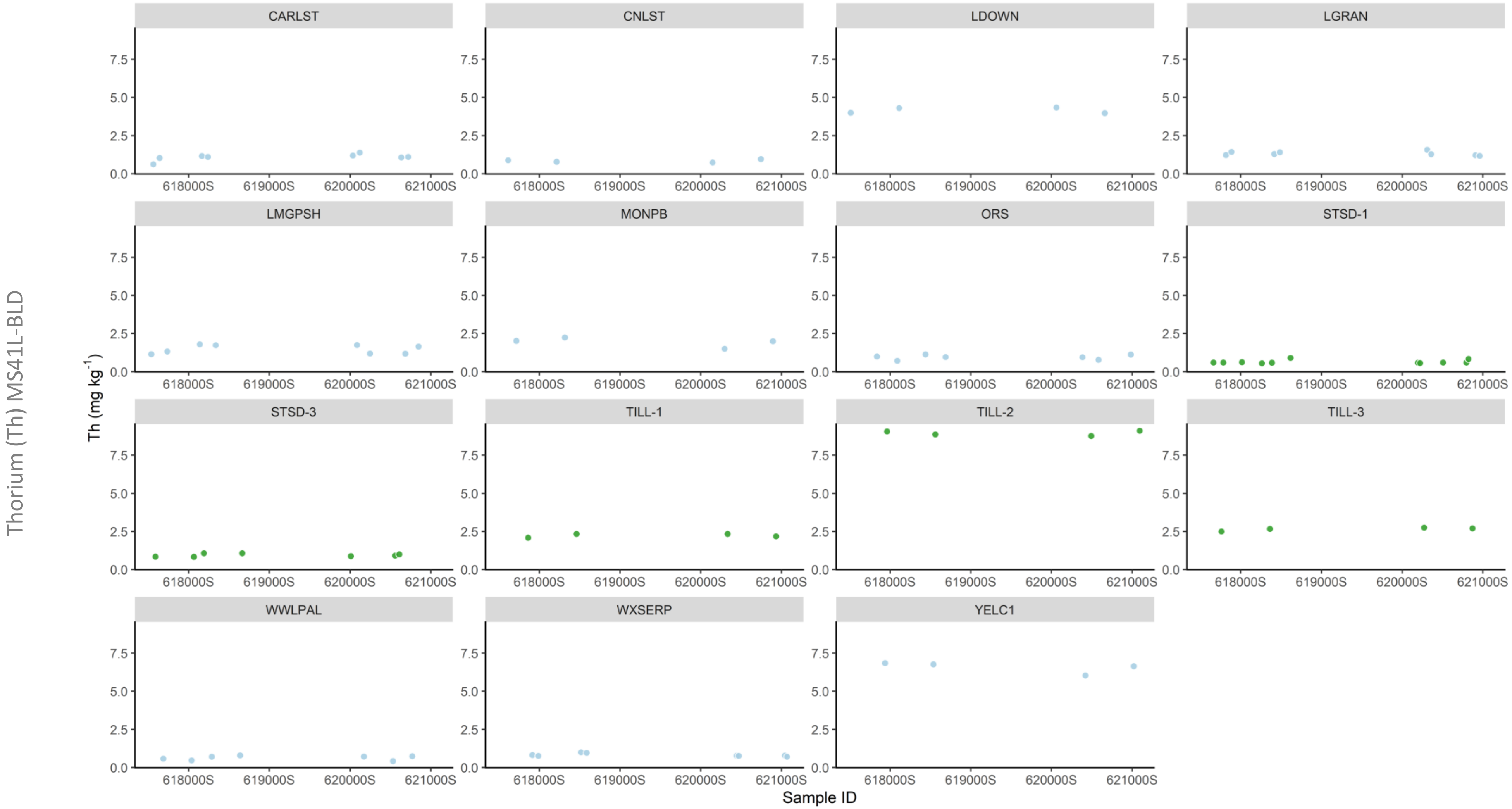


Tantalum (Ta) sample data IQR: 0.00036-0.00092 mg kg^{-1}

Tellurium (Te) MS41L-BLD

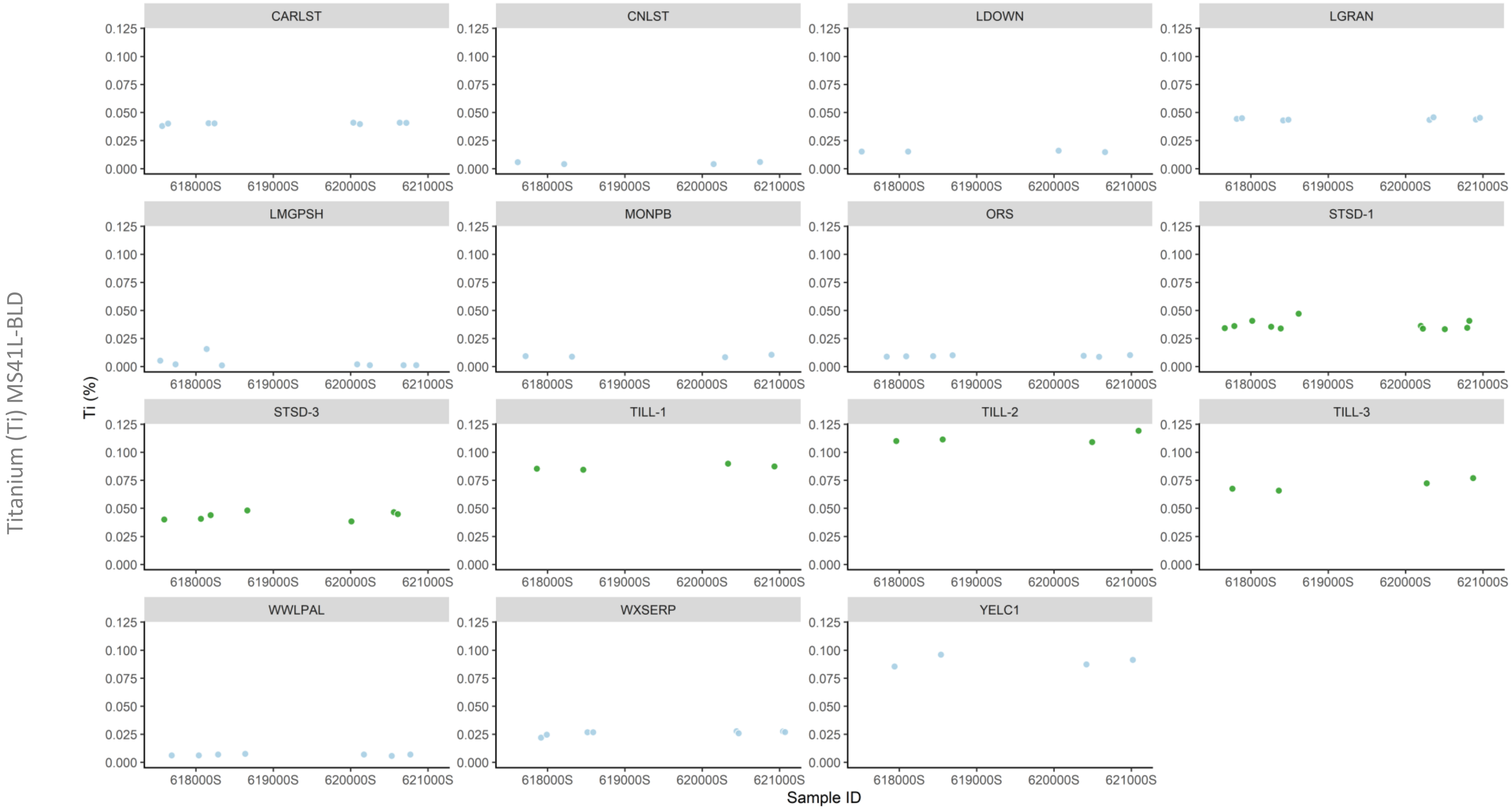


Tellurium (Te) sample data IQR: 0.0263-0.0364 mg kg^{-1}

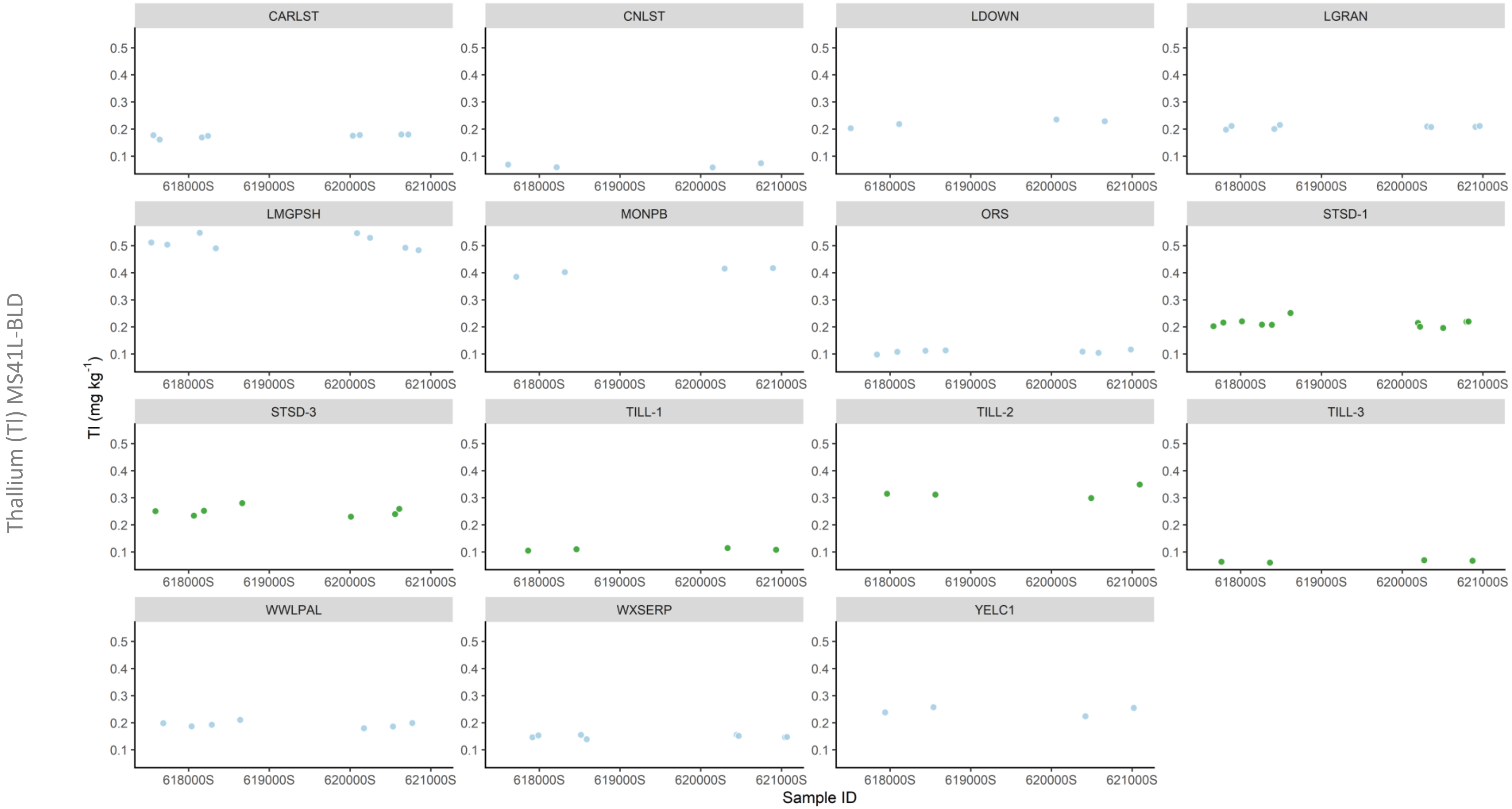


Thorium (Th) sample data IQR: 1.24–1.63 mg kg^{-1}

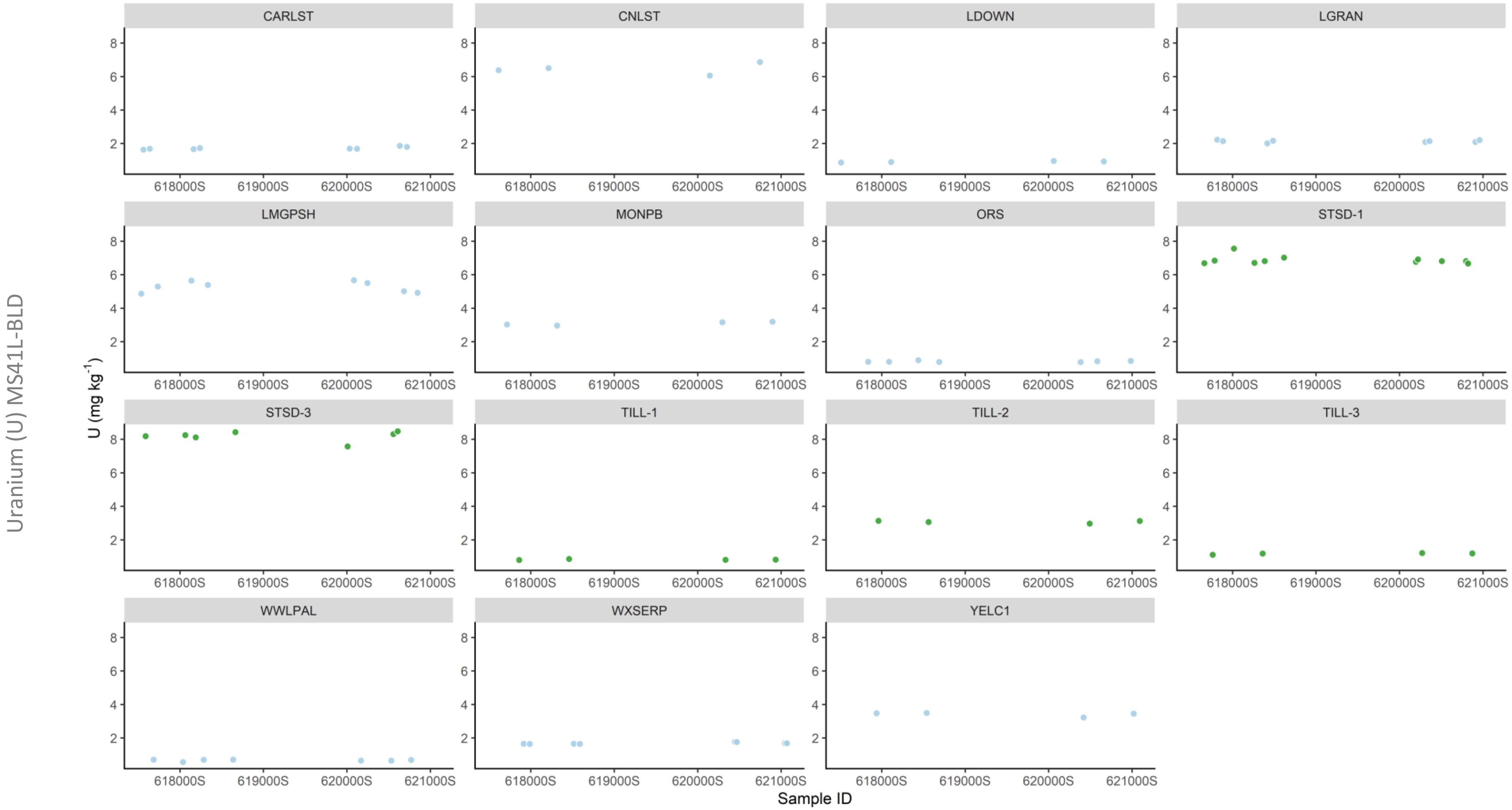
AURUM GLOBAL EXPLORATION



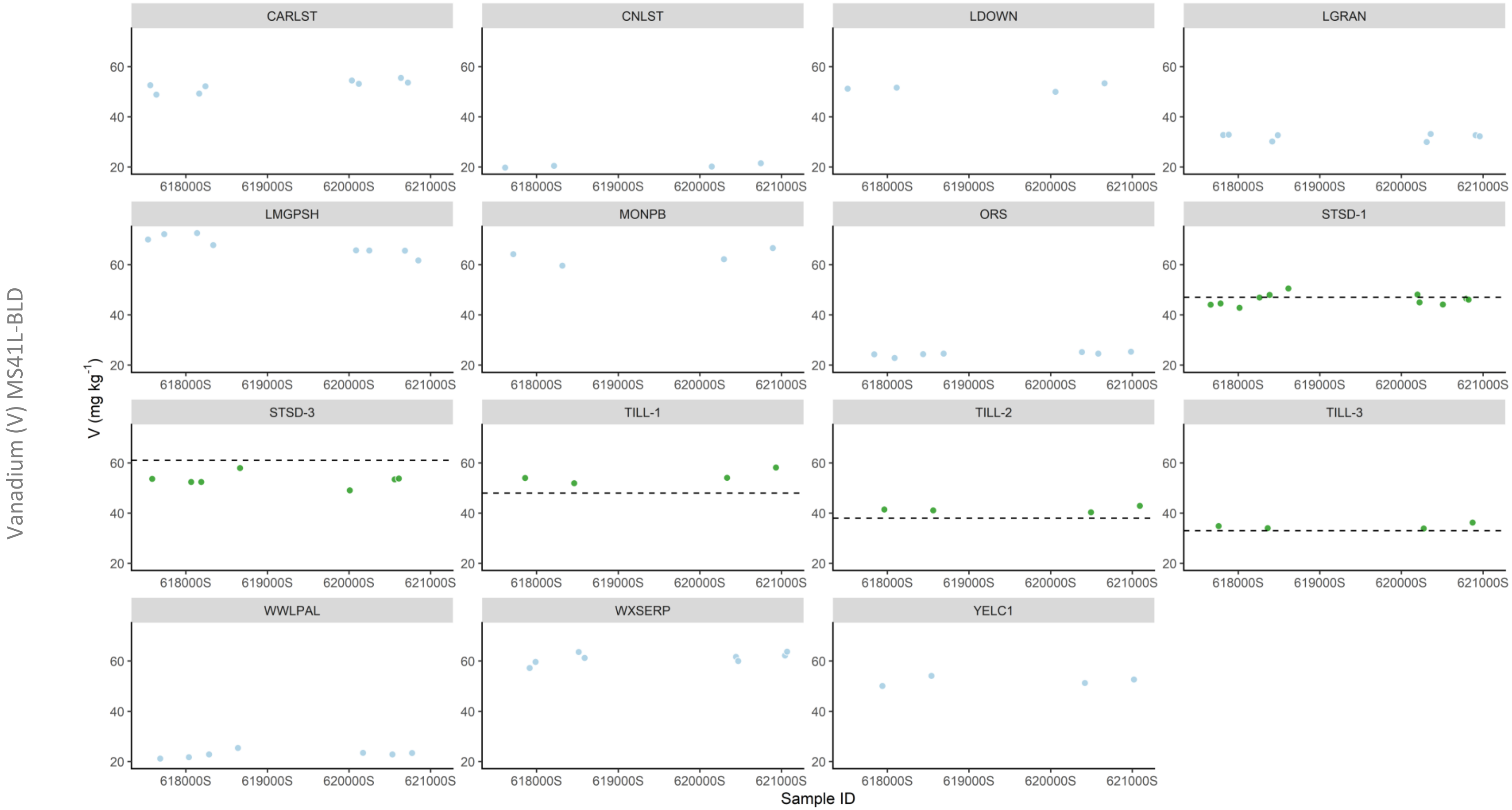
Titanium (Ti) sample data IQR: 0.00408-0.00712 %



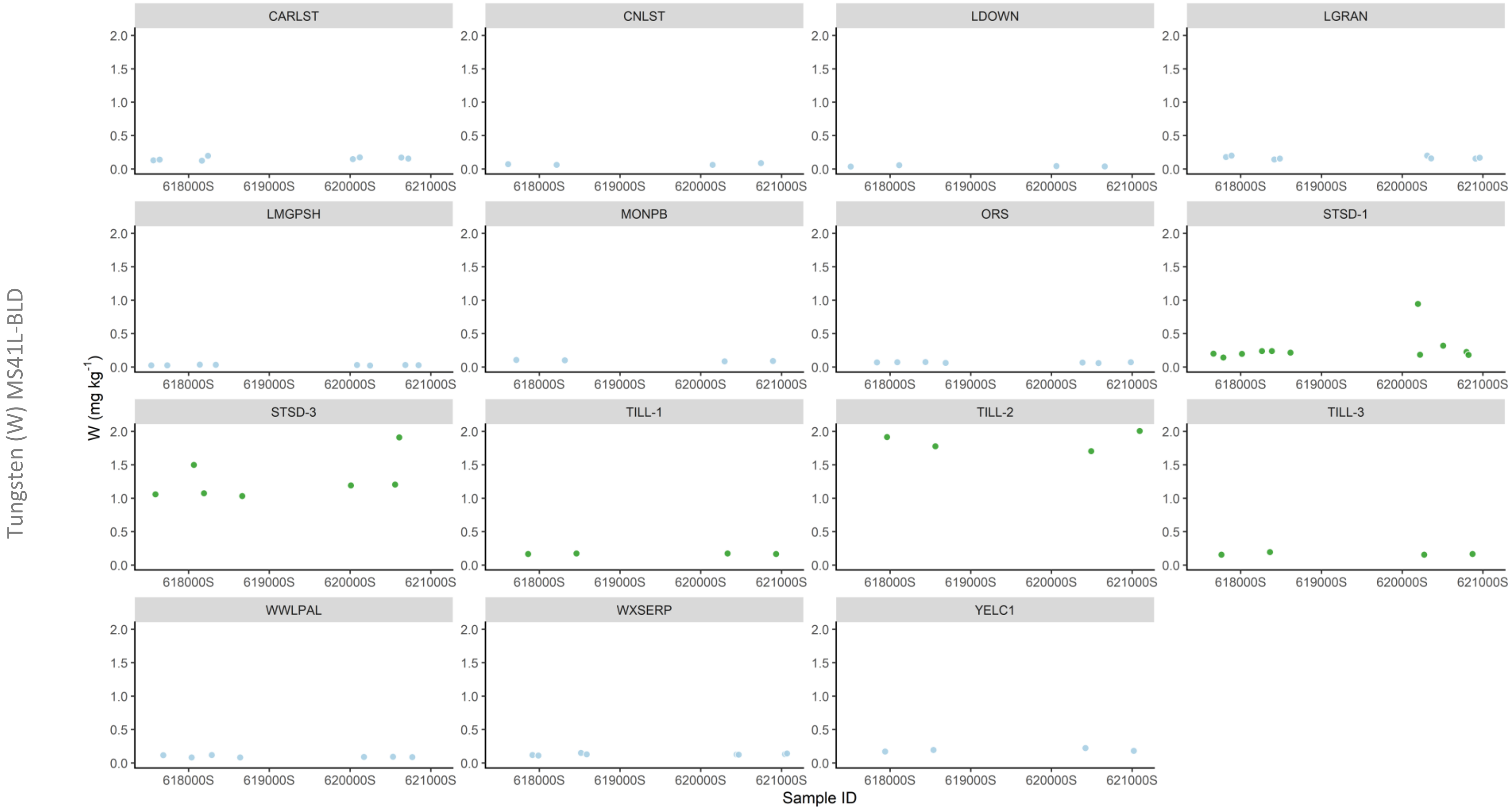
Thallium (Tl) sample data IQR: 0.203–0.251 mg kg^{-1}



Uranium (U) sample data IQR: 0.825–1.05 mg kg^{-1}

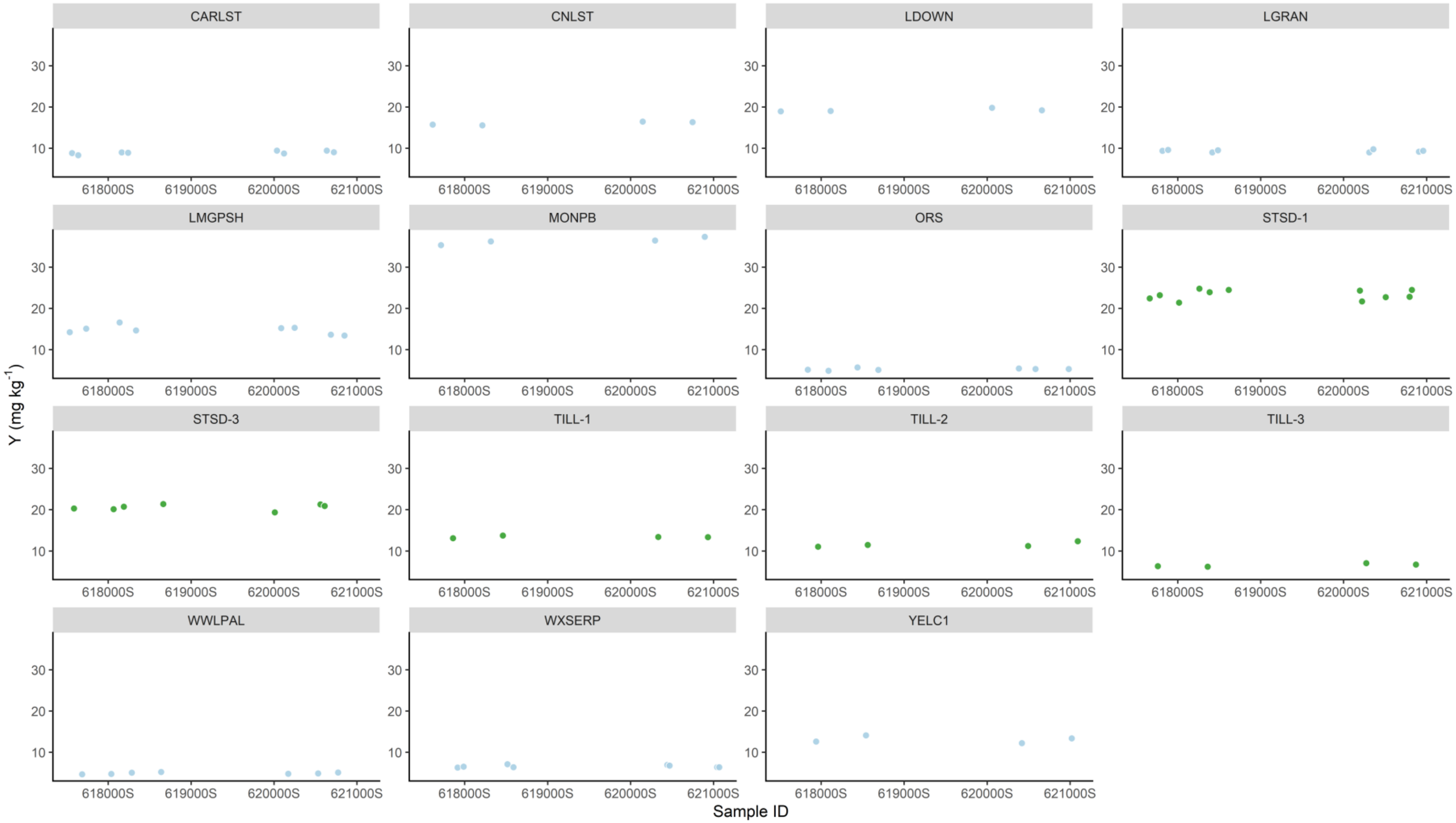


Vanadium (V) sample data IQR: 34.6–42.2 mg kg^{-1}



Tungsten (W) sample data IQR: 0.0875-0.159 mg kg^{-1}

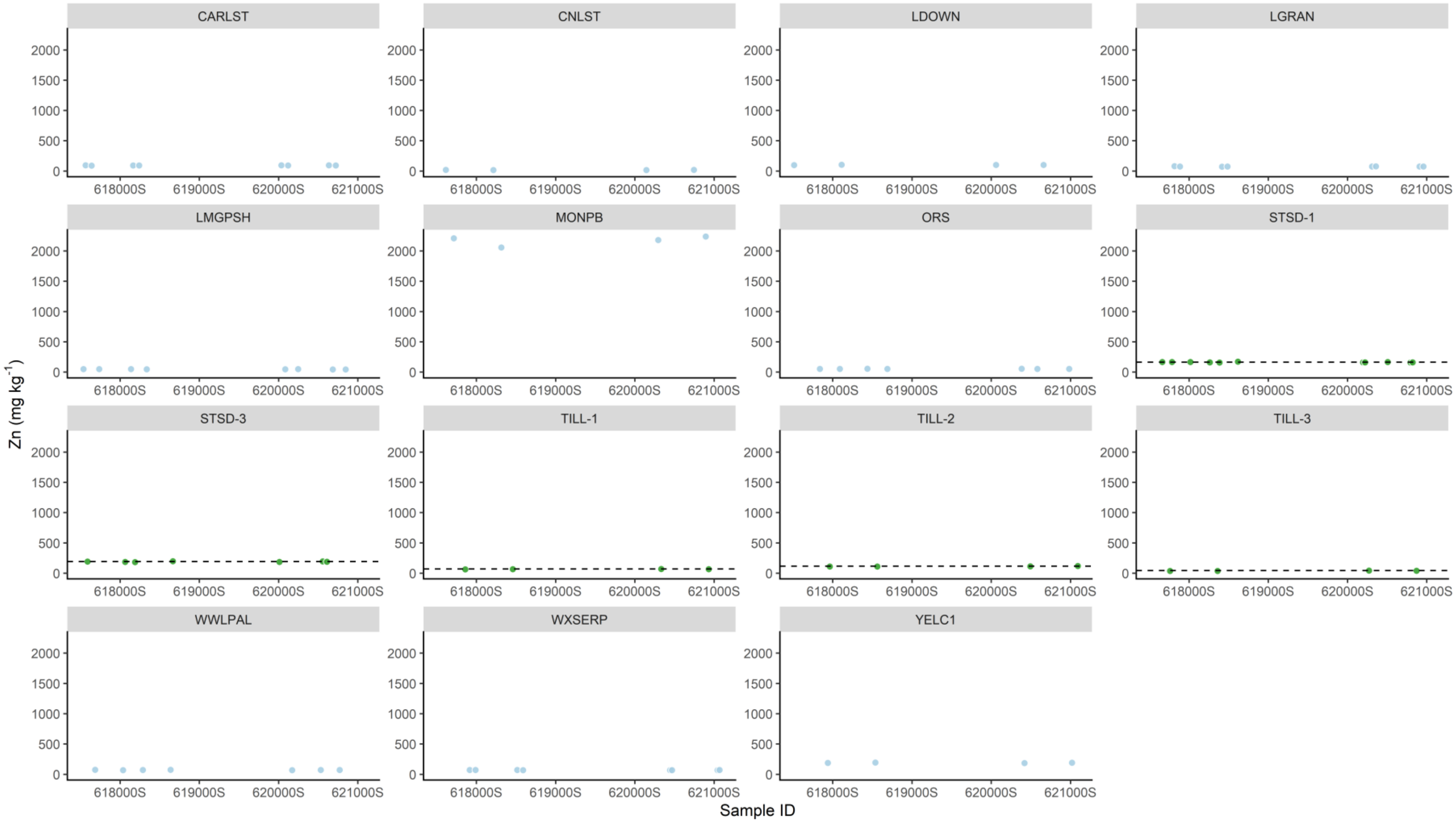
Yttrium (Y) MS41L-BLD



Yttrium (Y) sample data IQR: 14.5–18.0 mg kg^{-1}

AURUM GLOBAL EXPLORATION

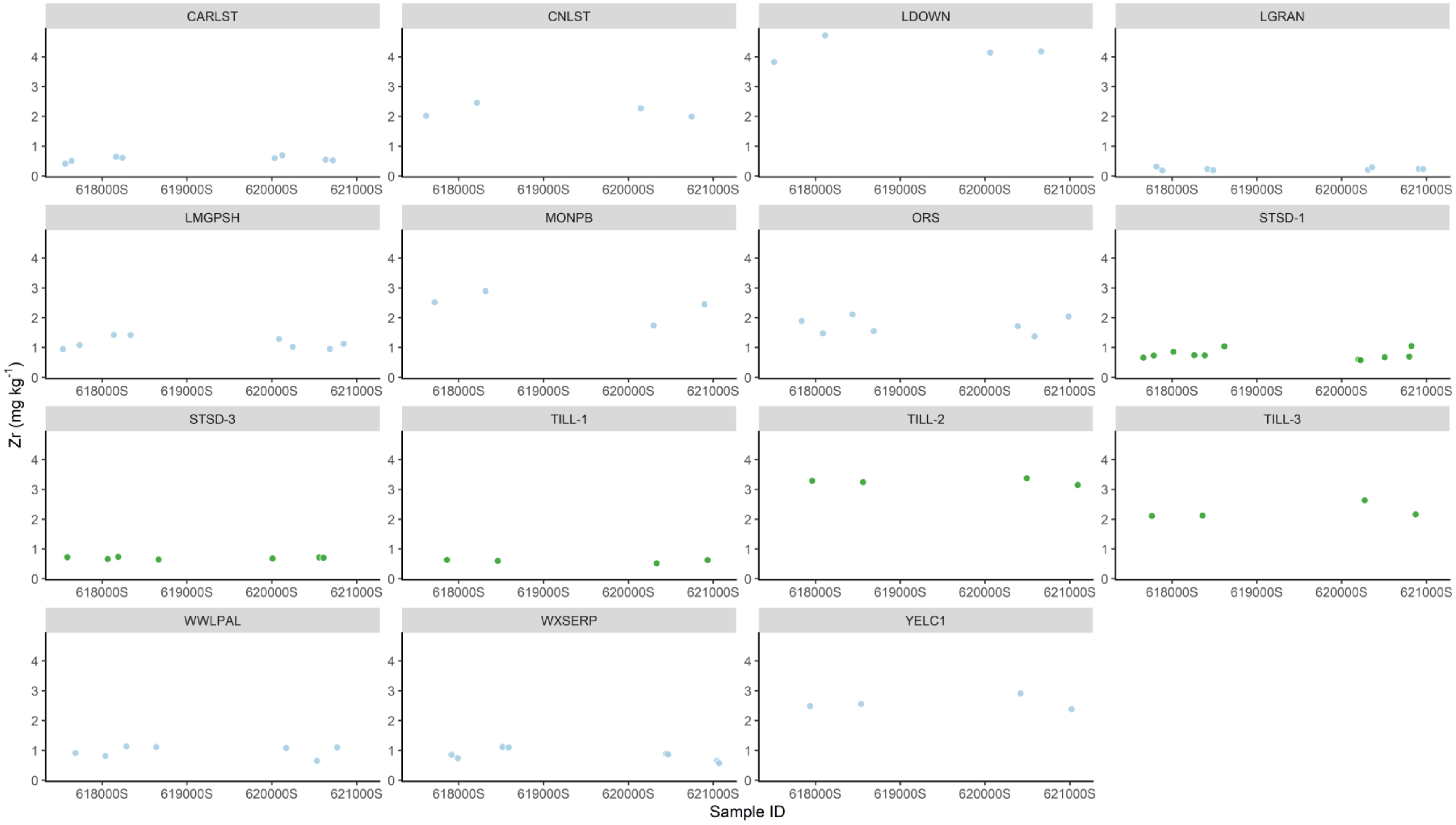
Zinc (Zn) MS41L-BLD



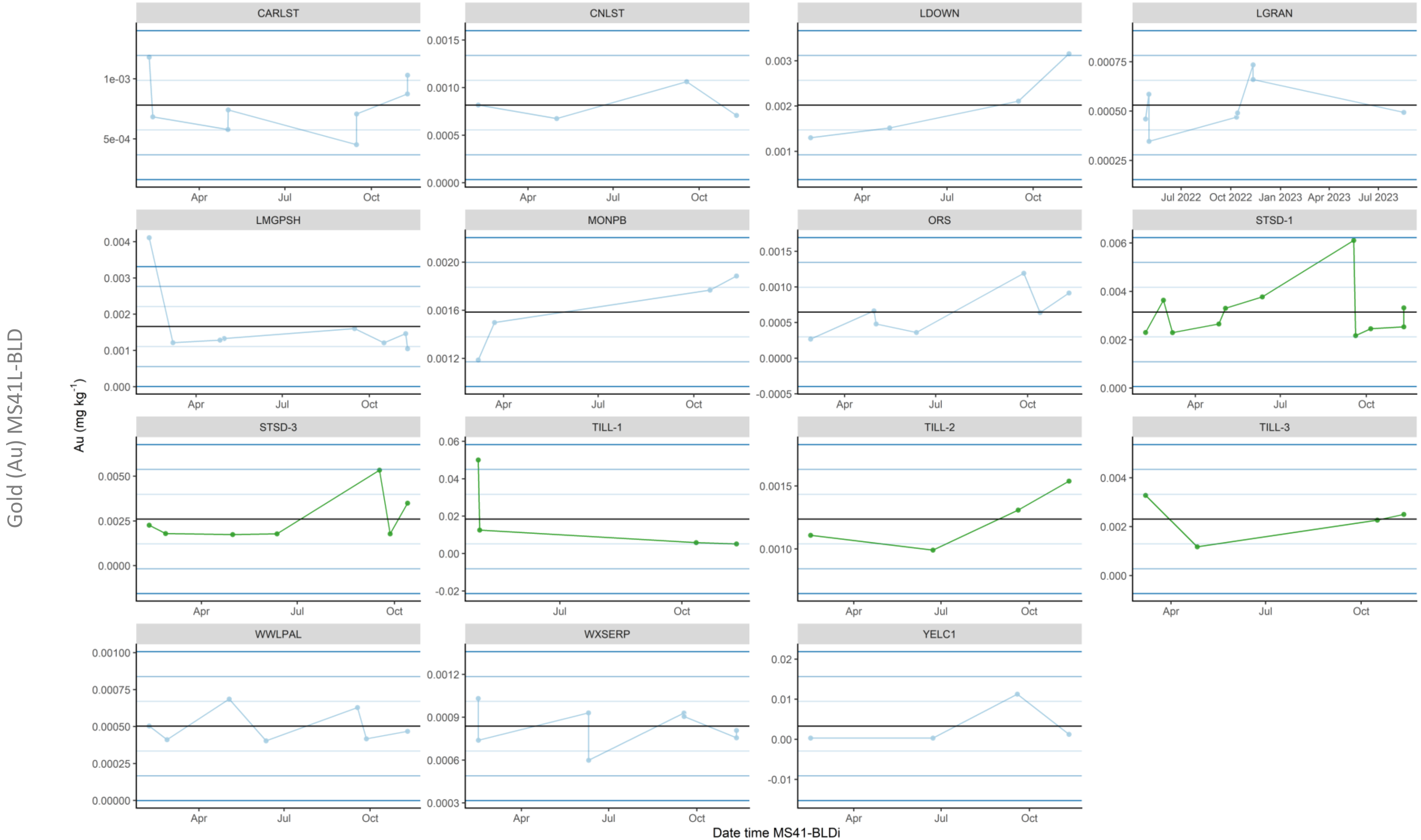
Zinc (Zn) sample data IQR: 119–181 mg kg^{-1}

AURUM GLOBAL EXPLORATION

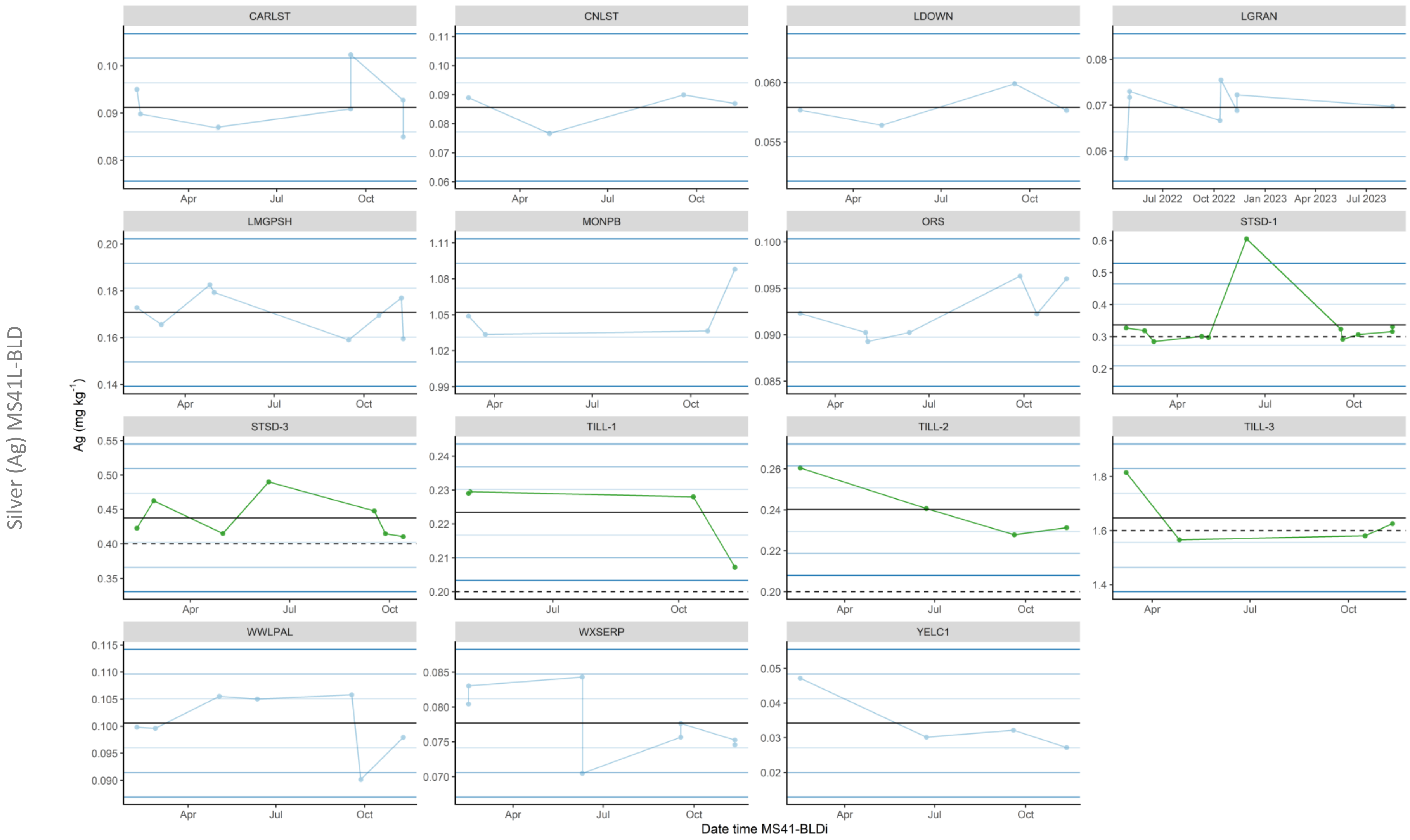
Zirconium (Zr) MS41L-BLD



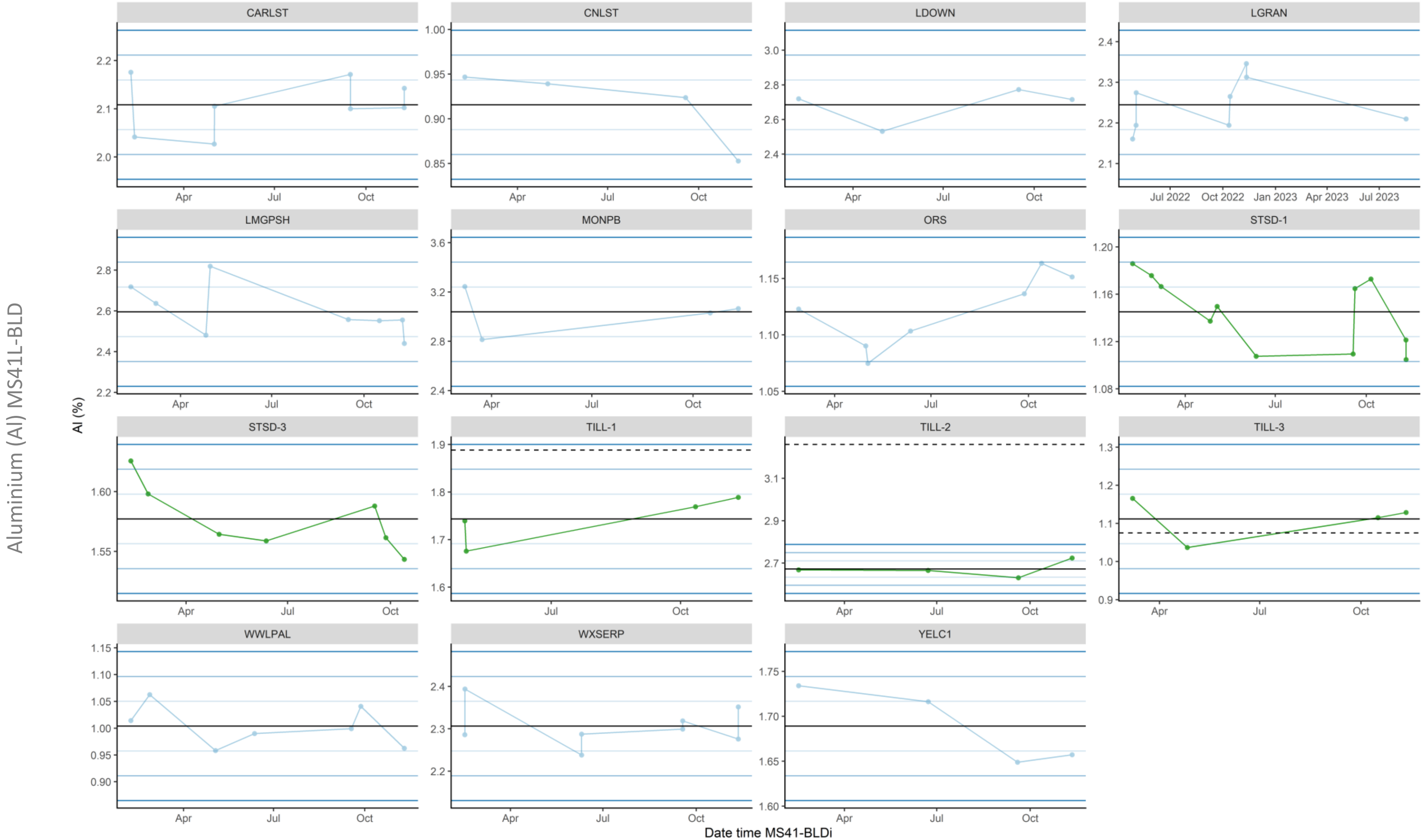
Zirconium (Zr) sample data IQR: 2.67–3.59 mg kg^{-1}



Gold (Au) sample data IQR: 0.00222–0.00455 mg kg^{-1}

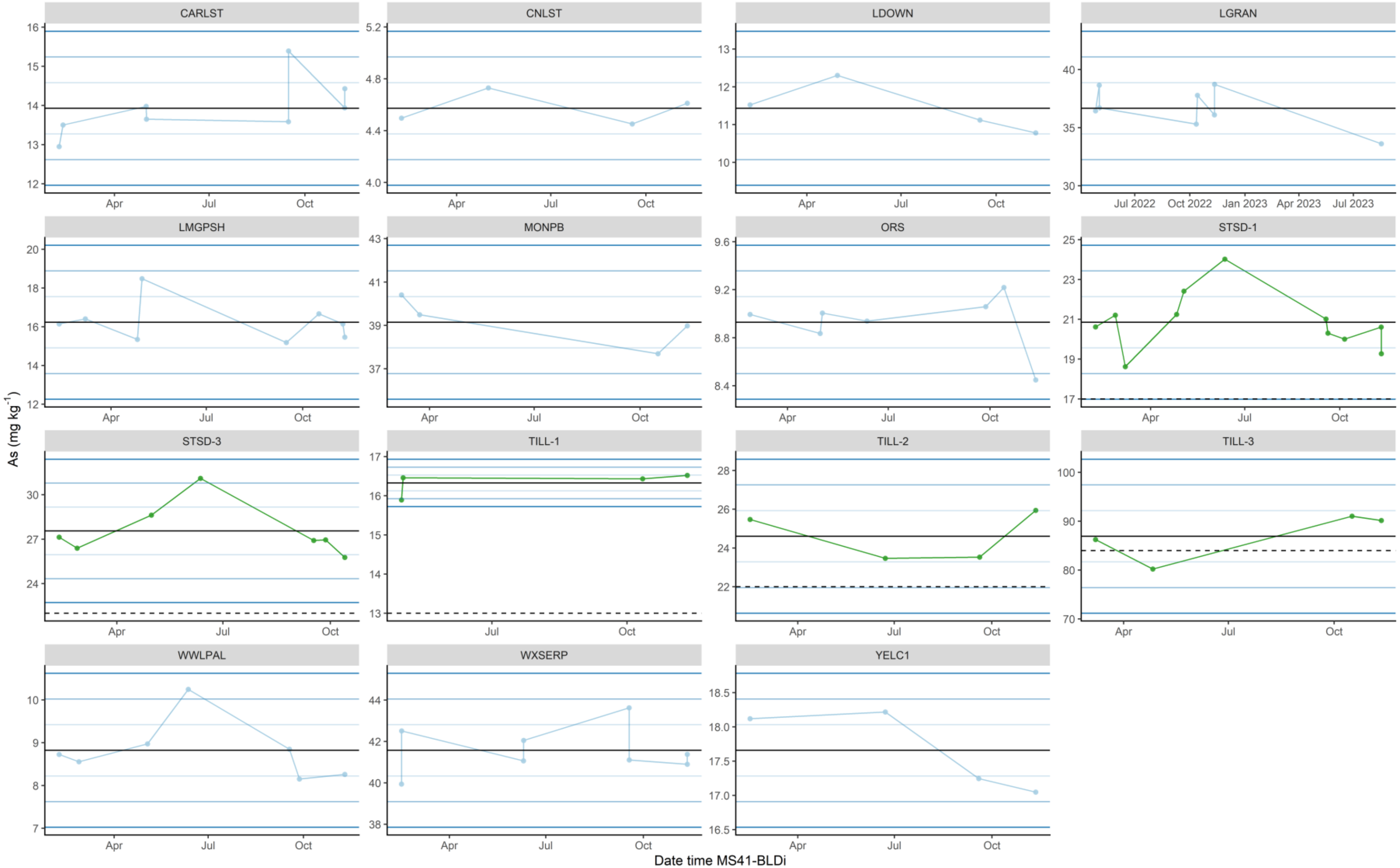


Silver (Ag) sample data IQR: 0.183–0.386 mg kg^{-1}

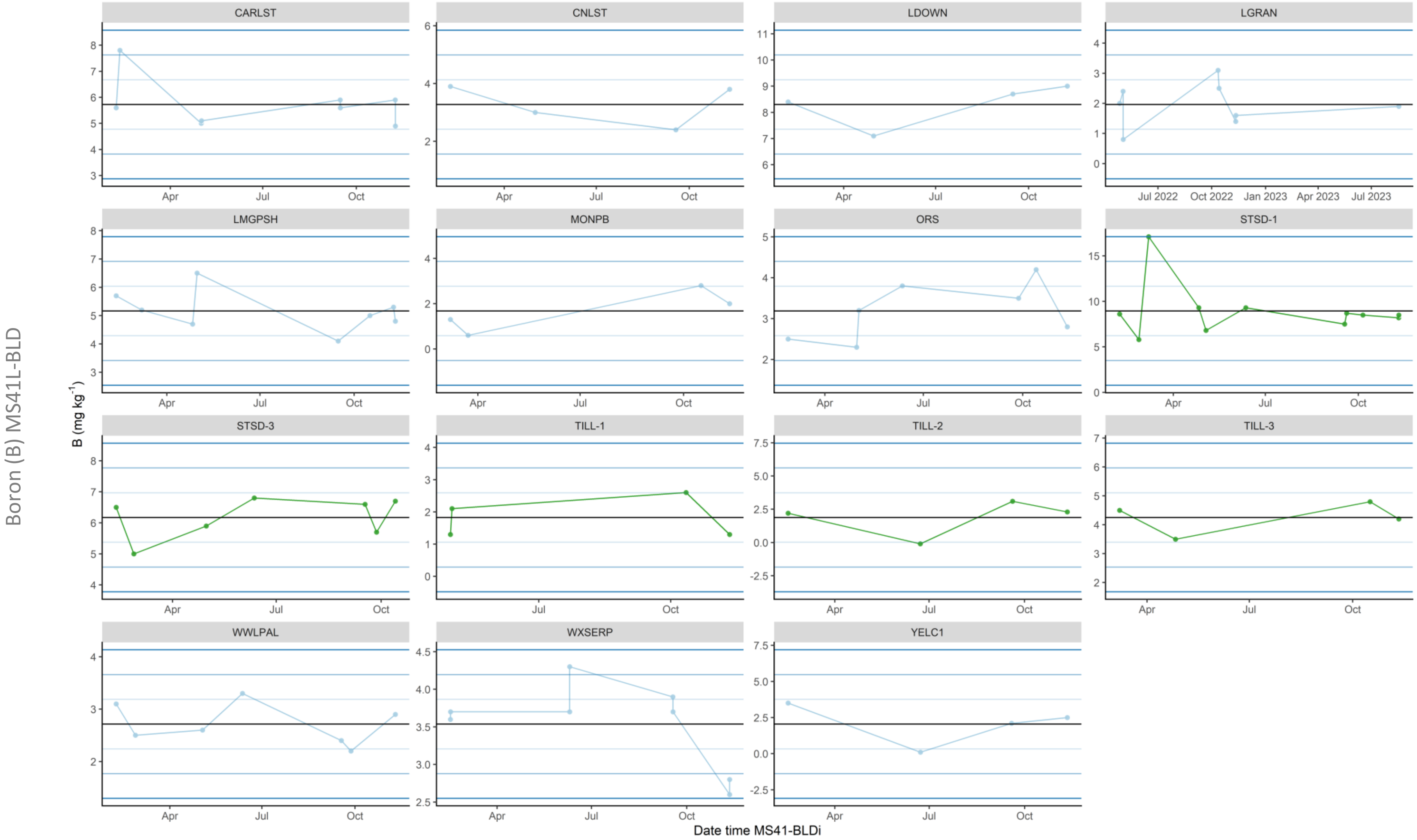


Aluminium (Al) sample data IQR: 0.972–1.16 %

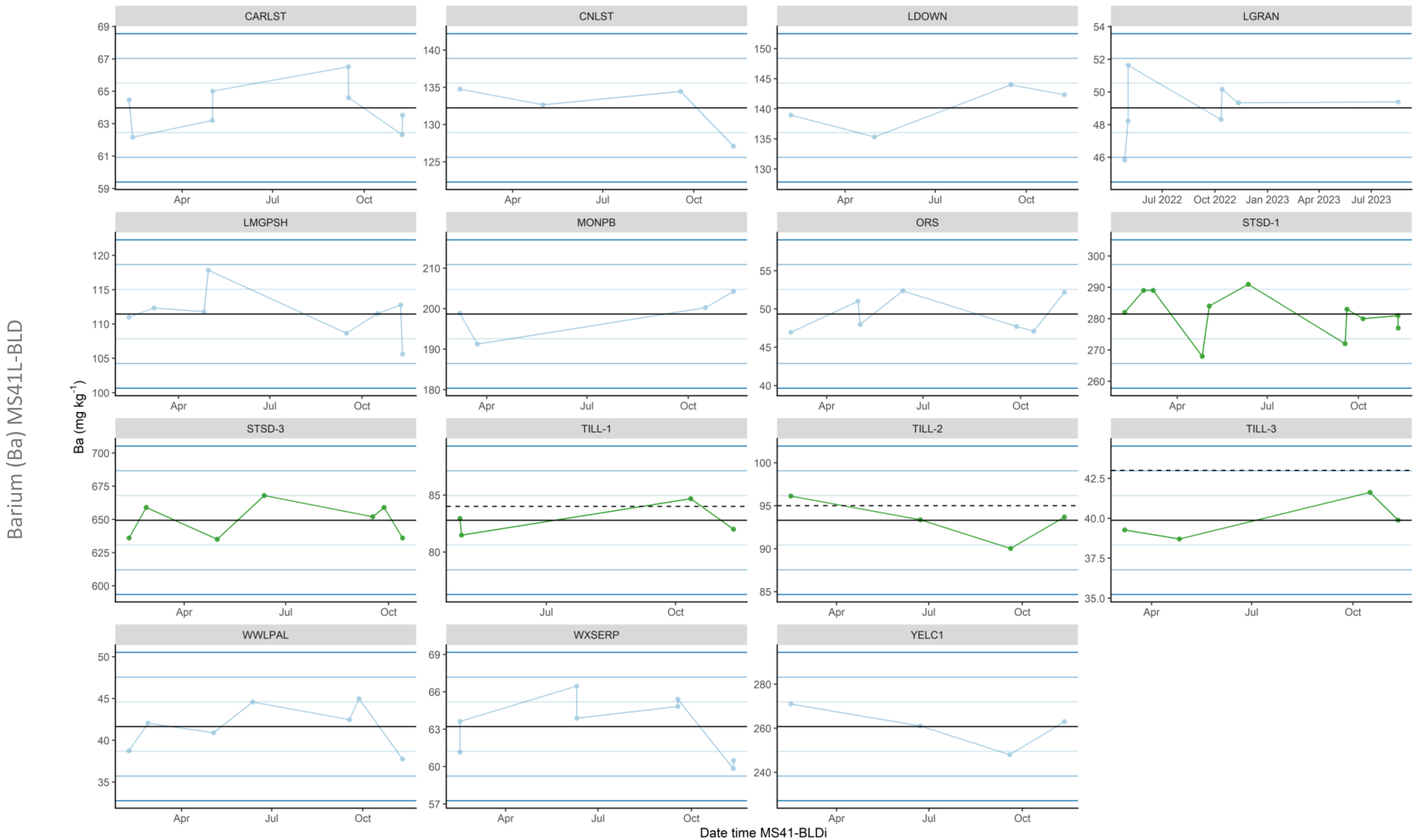
Arsenic (As) MS41L-BLD



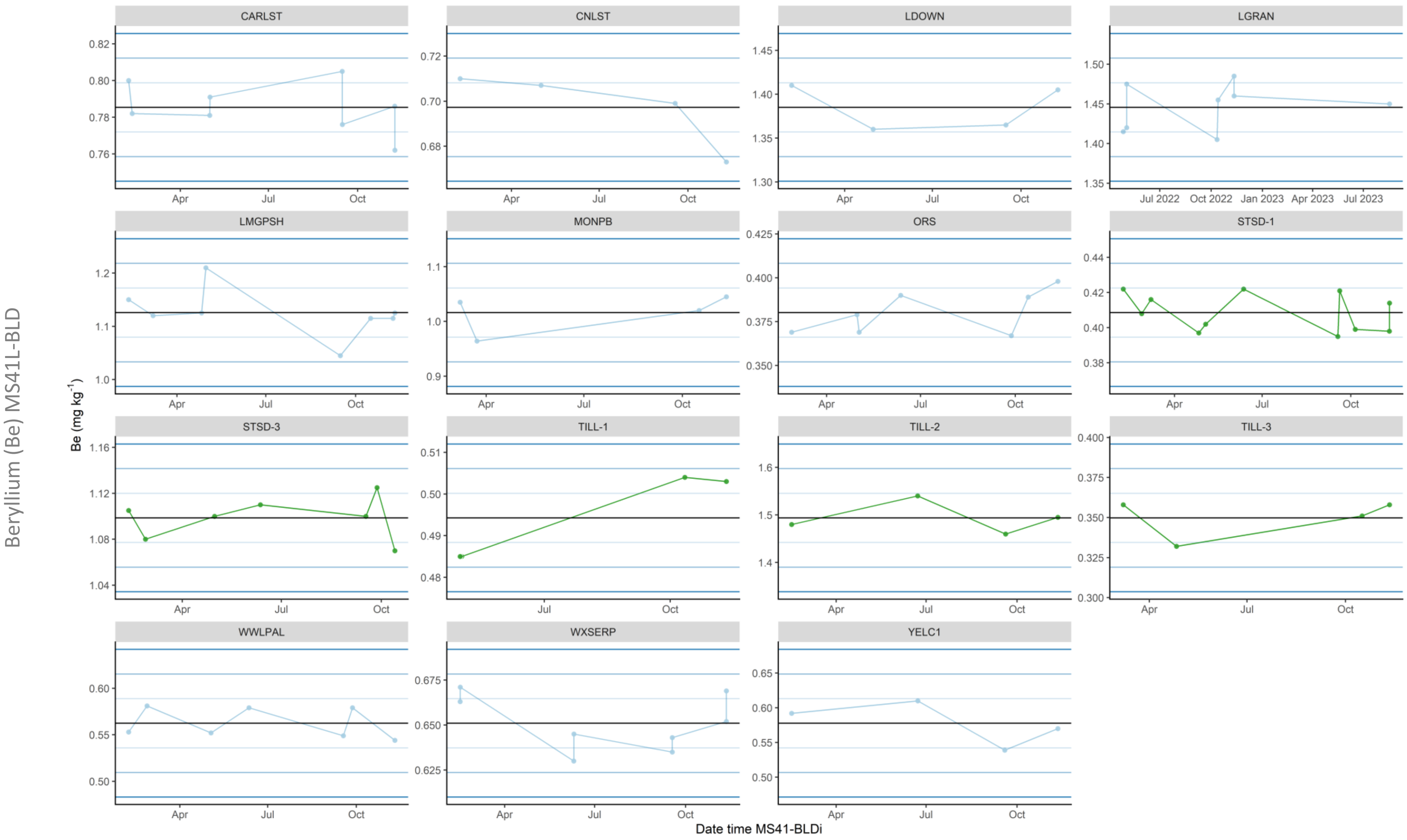
Arsenic (As) sample data IQR: 16.3–23.0 mg kg^{-1}



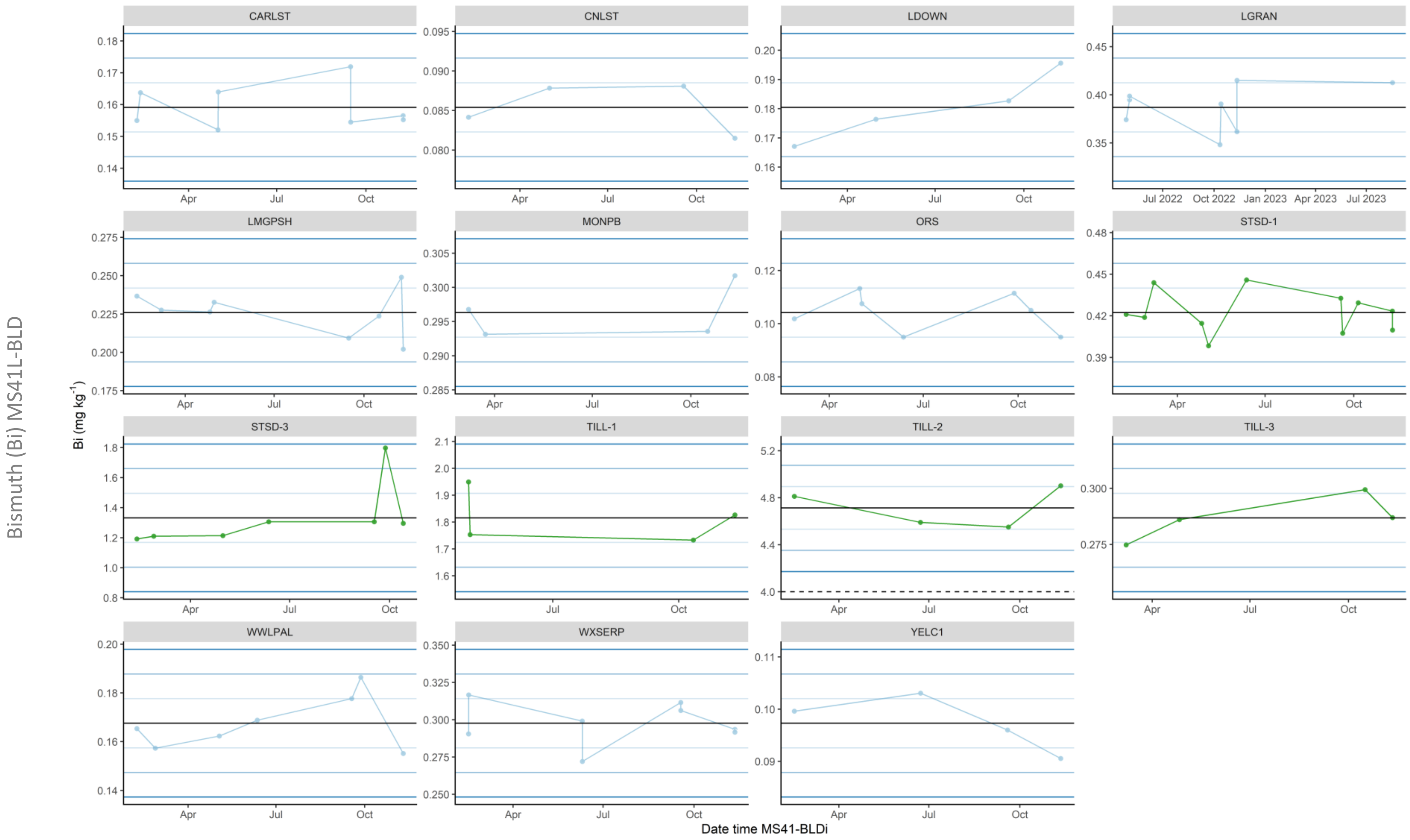
Boron (B) sample data IQR: 5.5 -8.1 mg kg^{-1}



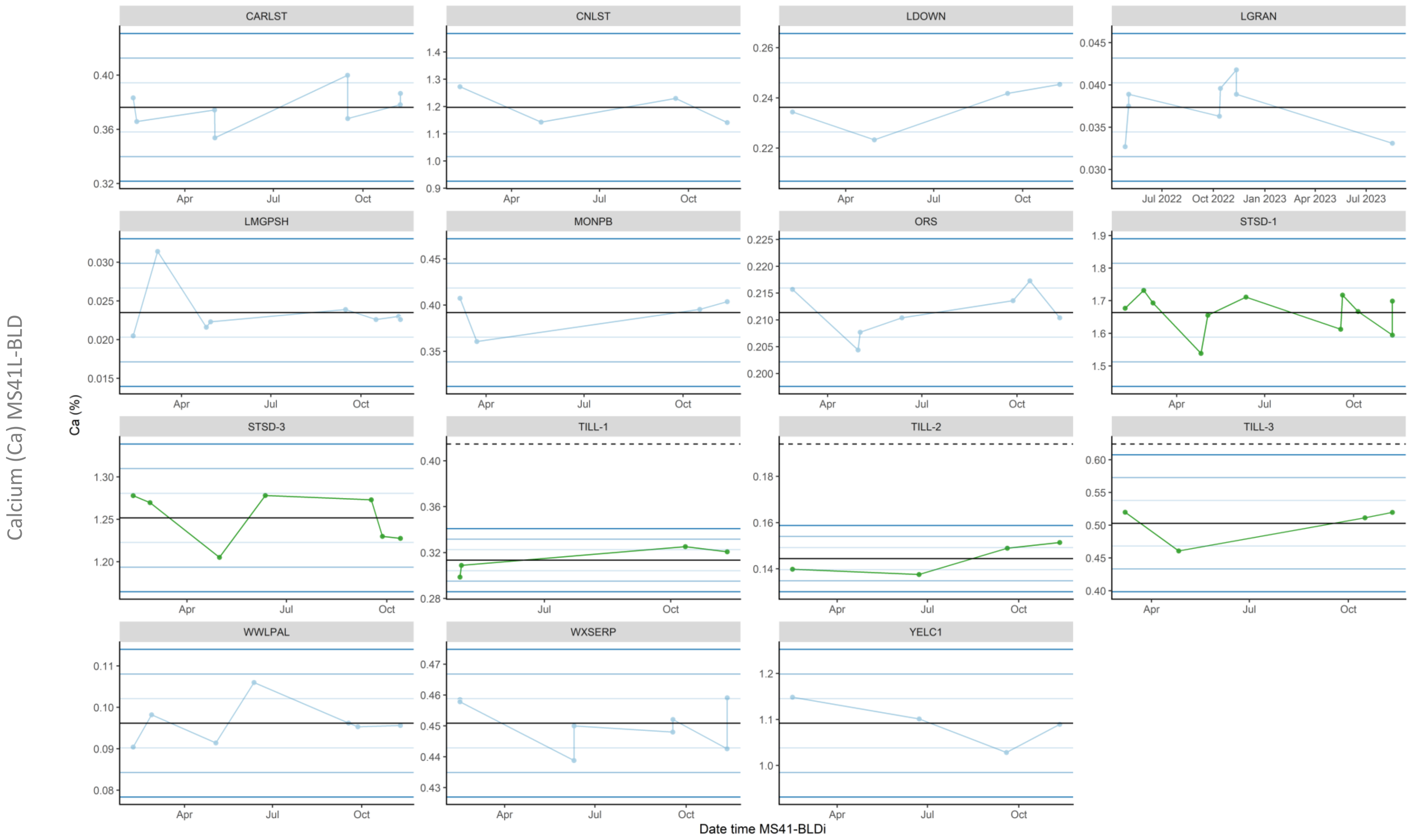
Barium (Ba) sample data IQR: 93.9–139 mg kg-1



Beryllium (Be) sample data IQR: 1.04–1.34 mg kg^{-1}

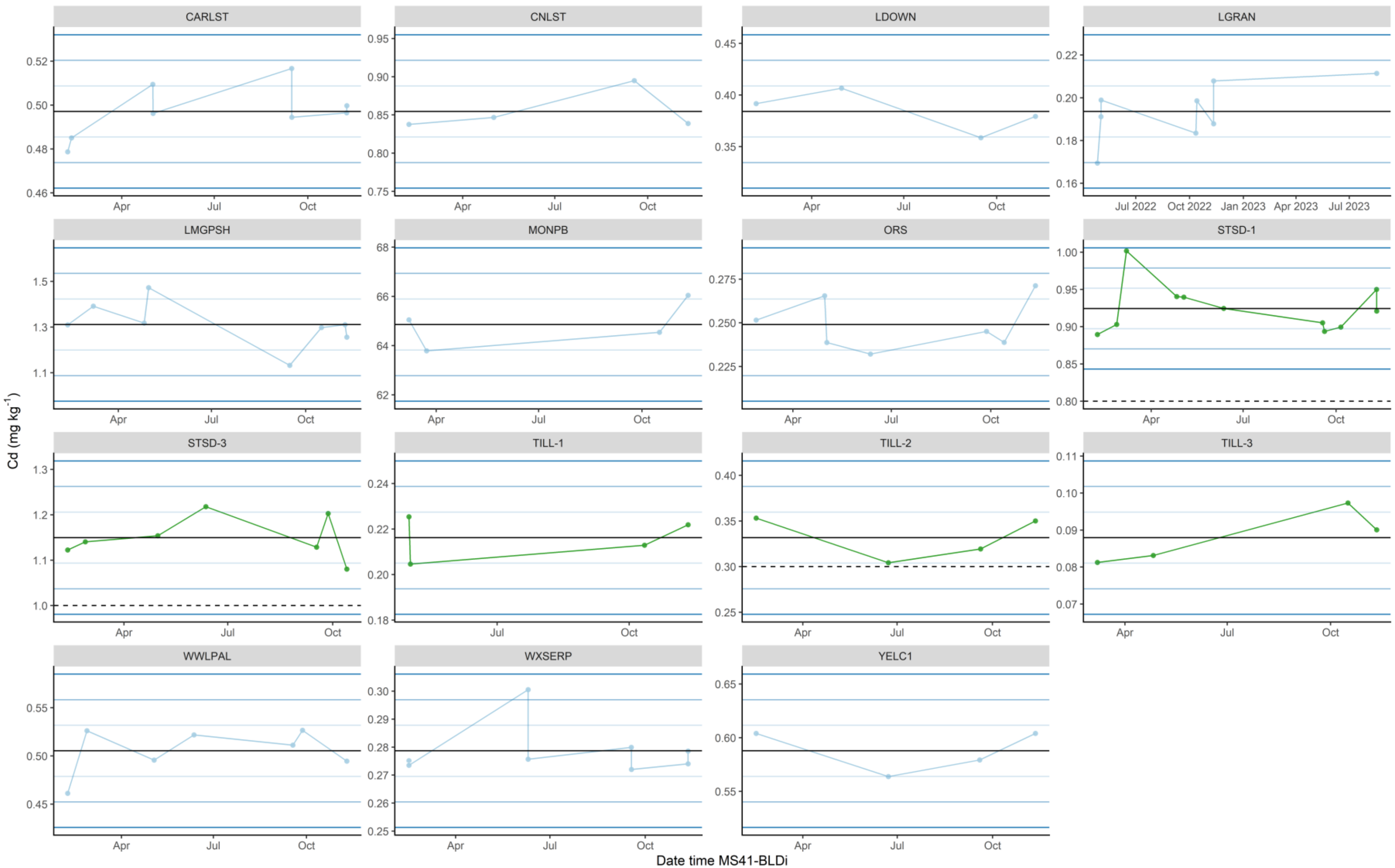


Bismuth (Bi) sample data IQR: 0.181–0.286 mg kg^{-1}



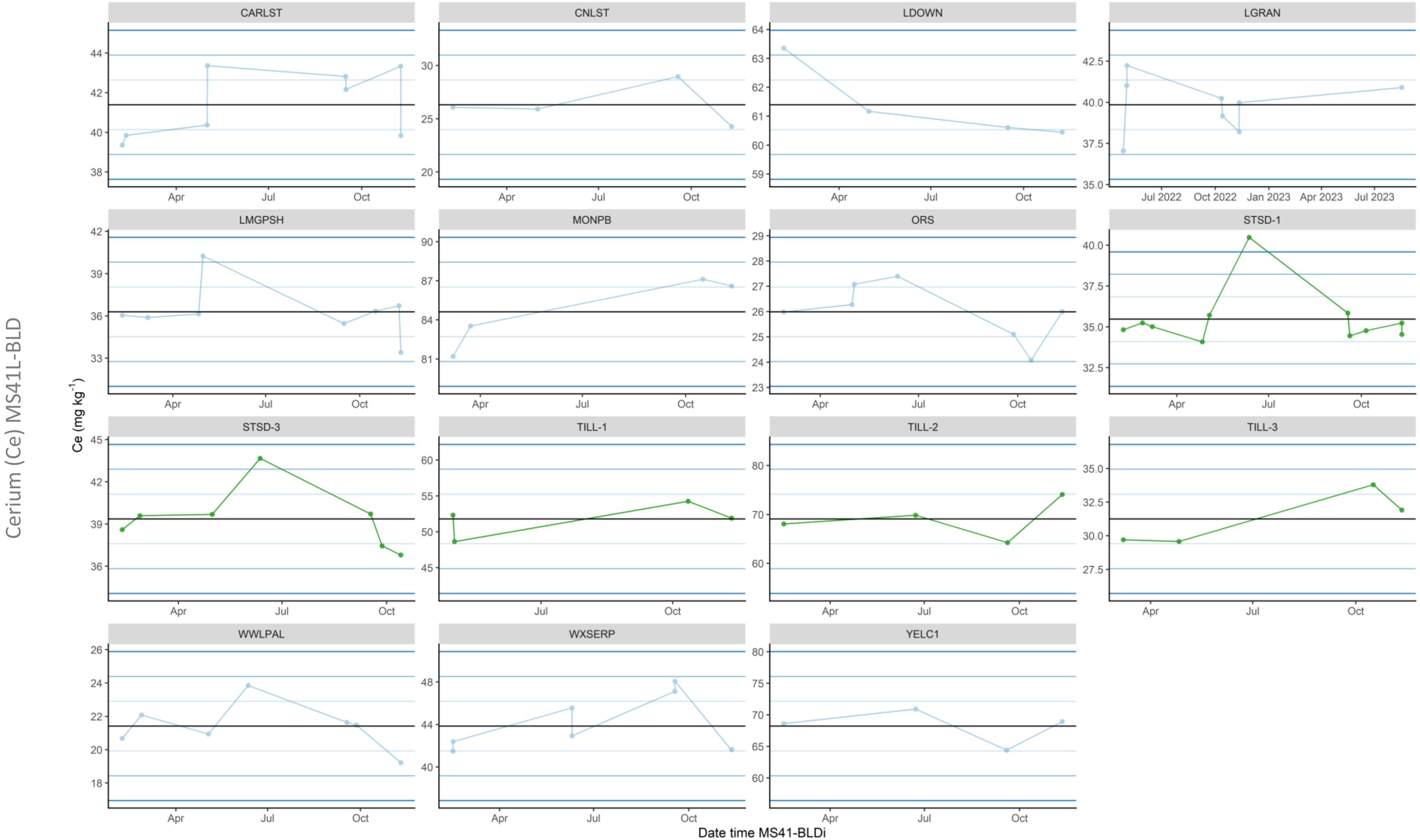
Calcium (Ca) sample data IQR: 1.78–5.19 %

Cadmium (Cd) MS41L-BLD

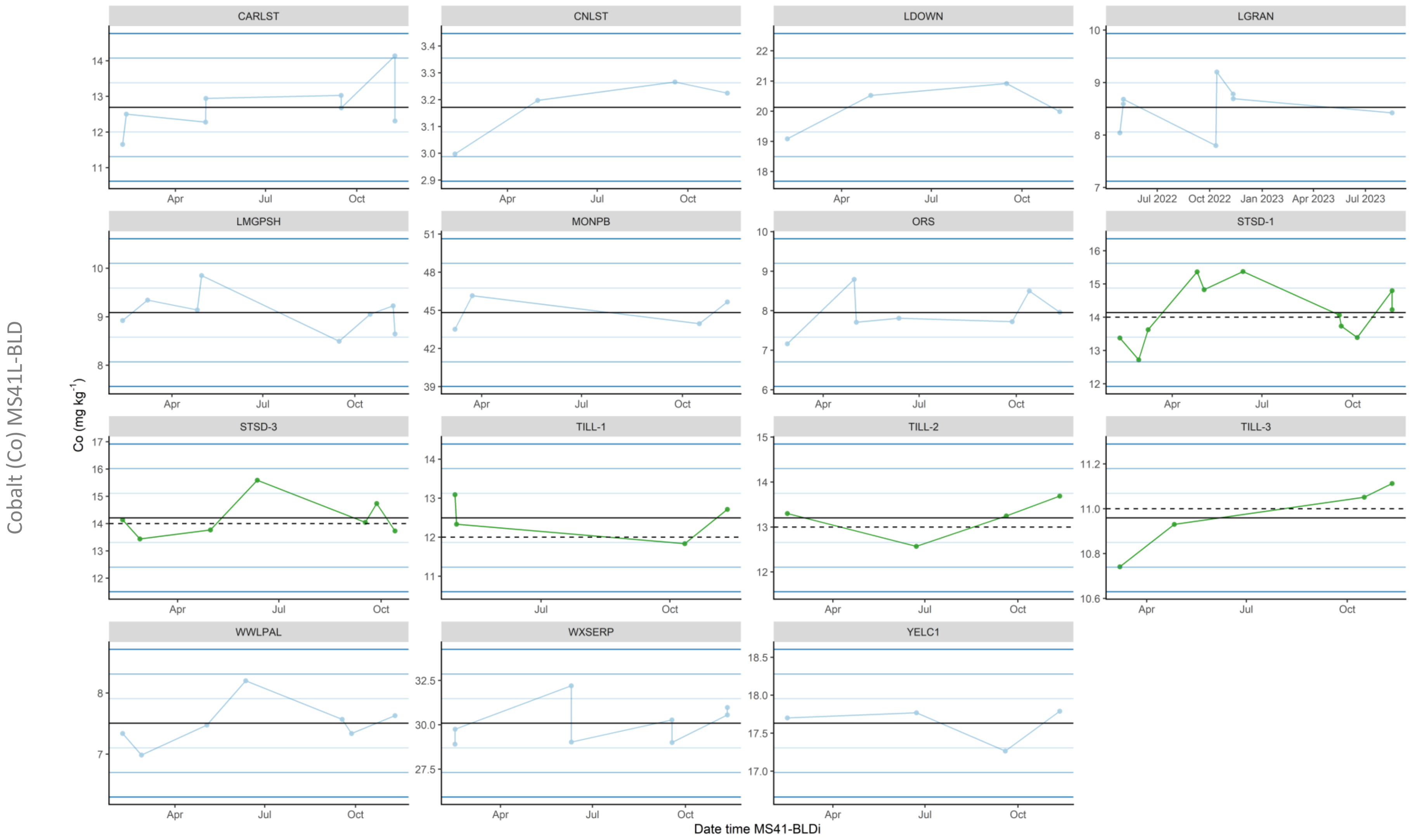


Cadmium (Cd) sample data IQR: 1.60–2.28 mg kg^{-1}

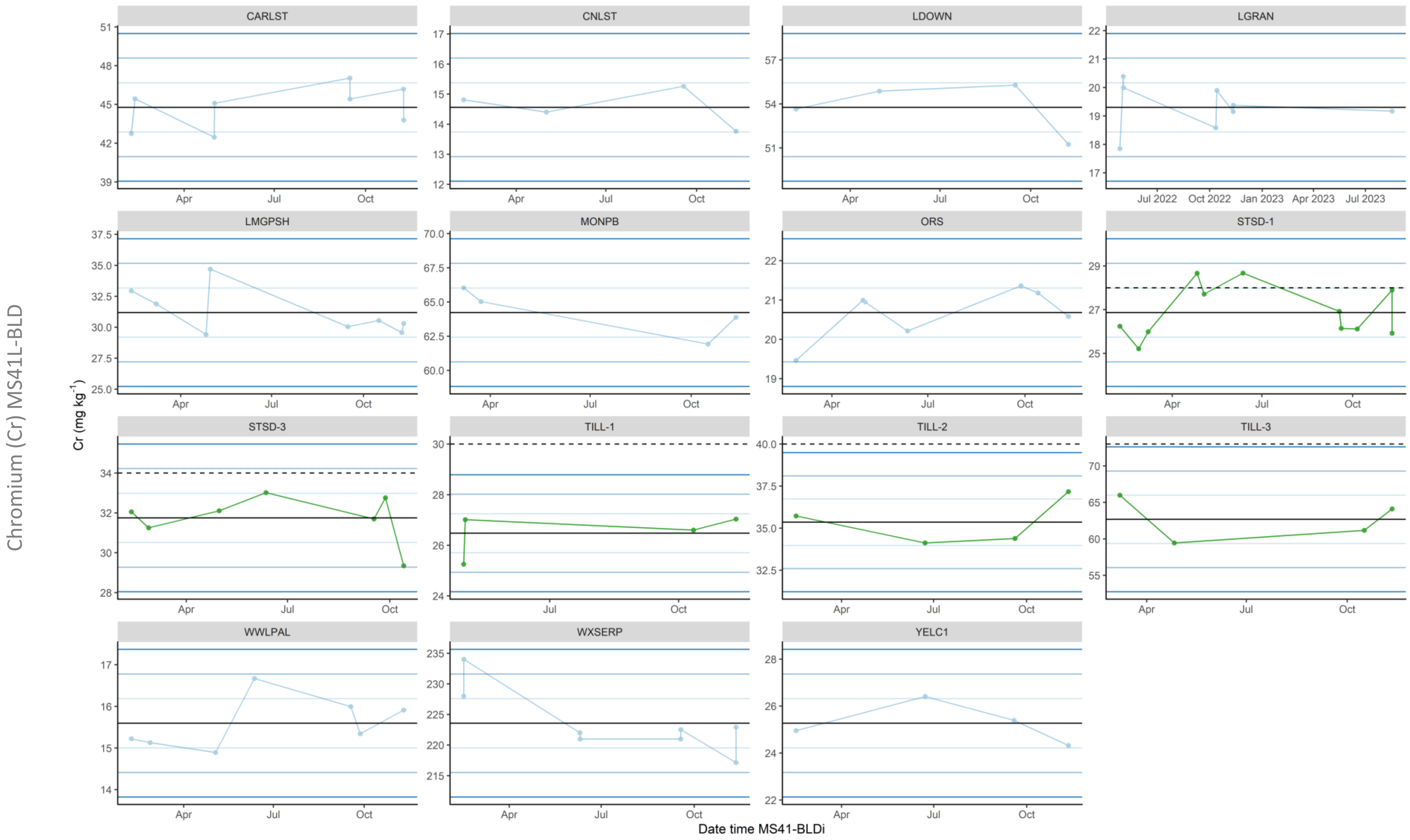
AURUM GLOBAL EXPLORATION



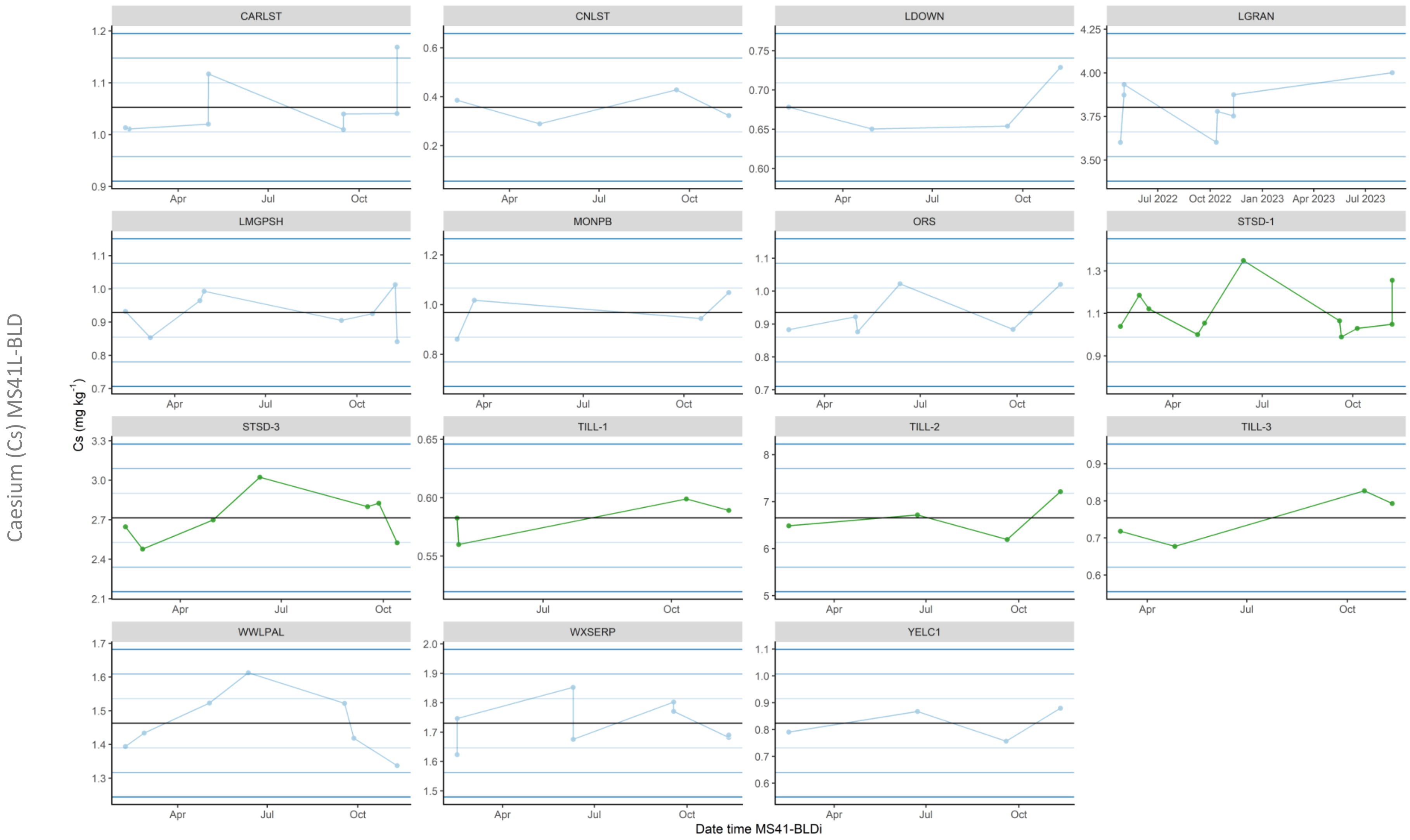
Cerium (Ce) sample data IQR: 23.6–28.2 mg kg^{-1}



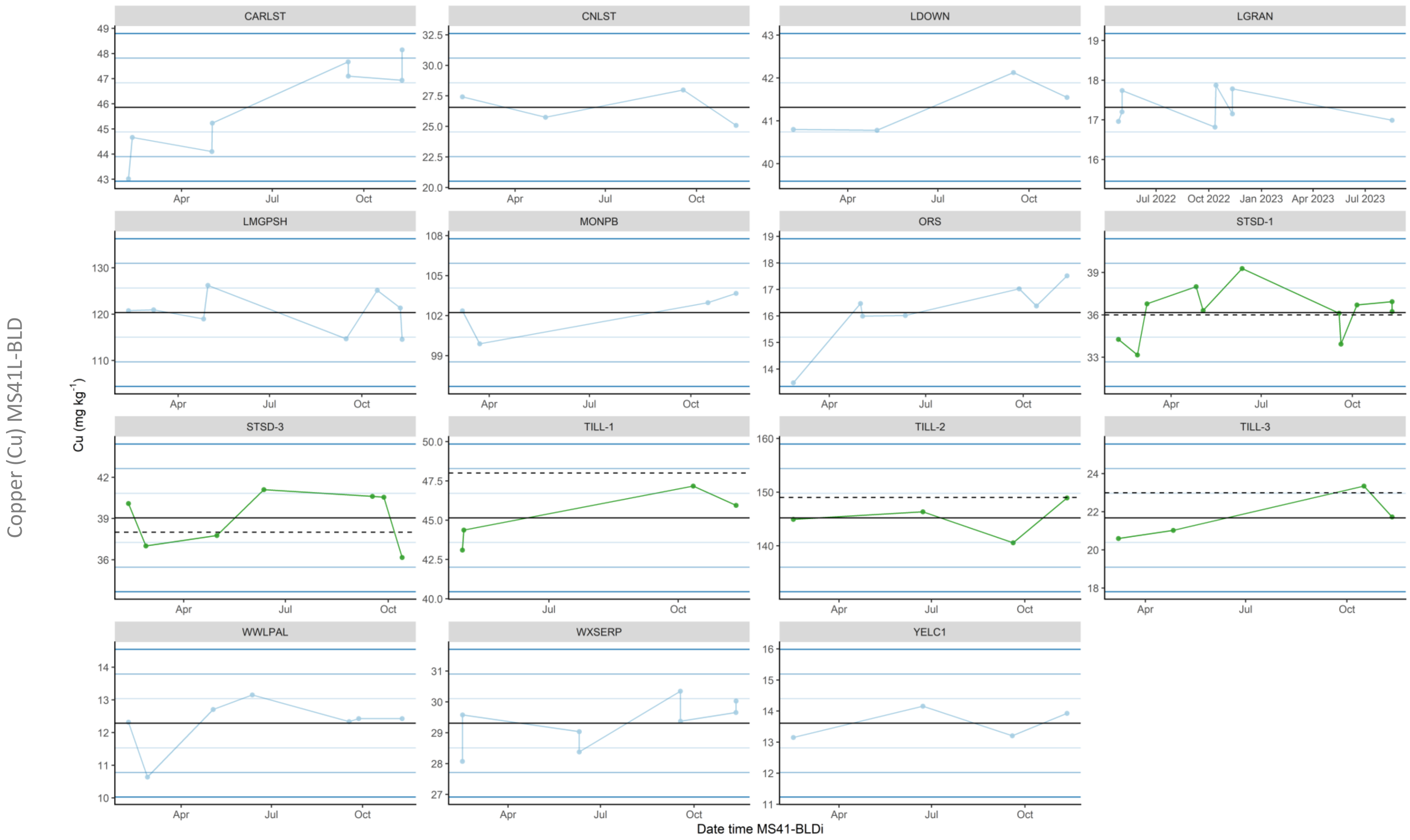
Cobalt (Co) sample data IQR: 10.4–13.2 mg kg^{-1}



Chromium (Cr) sample data IQR: 20.2–23.7 mg kg^{-1}

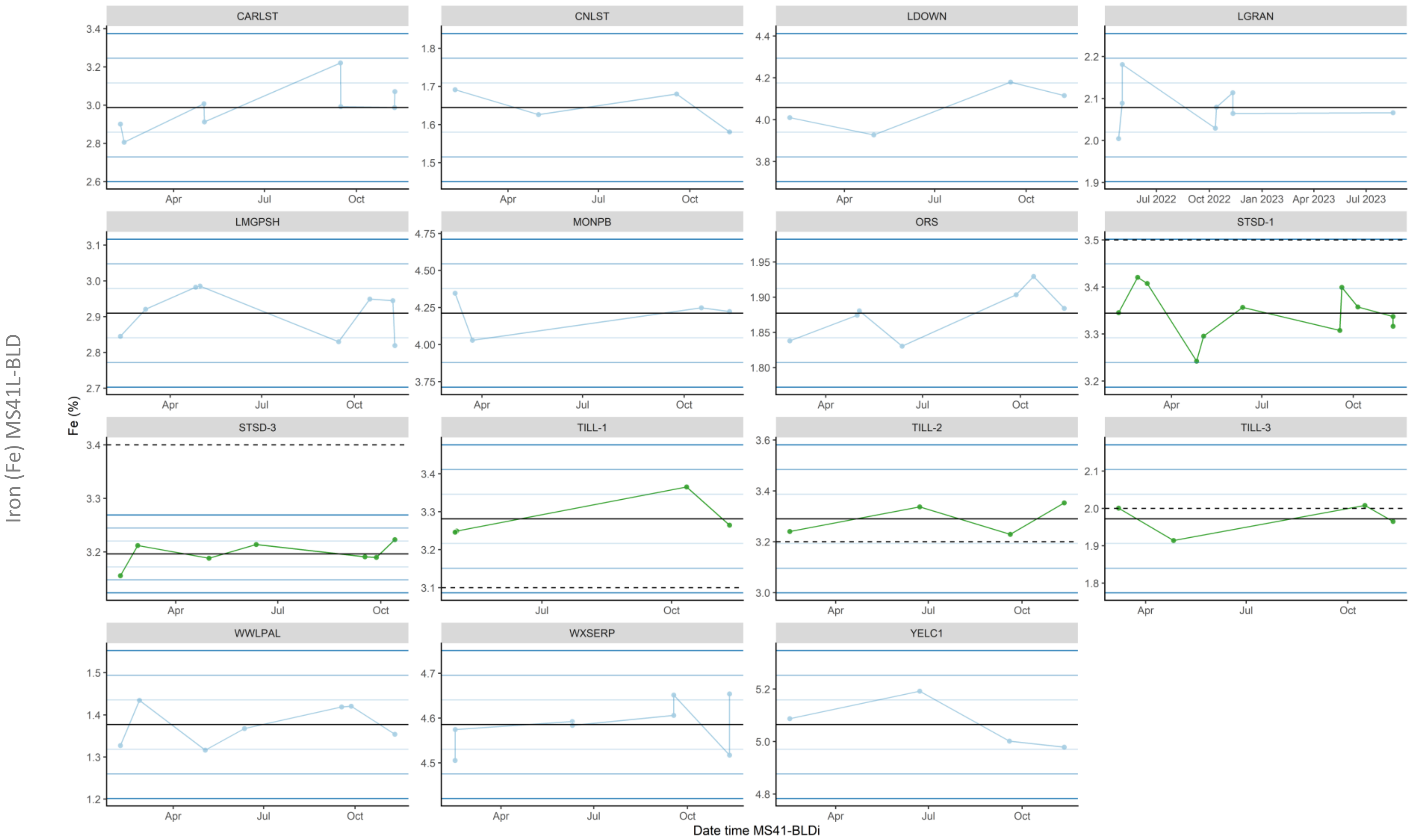


Caesium (Cs) sample data IQR: 0.448–0.663 mg kg^{-1}



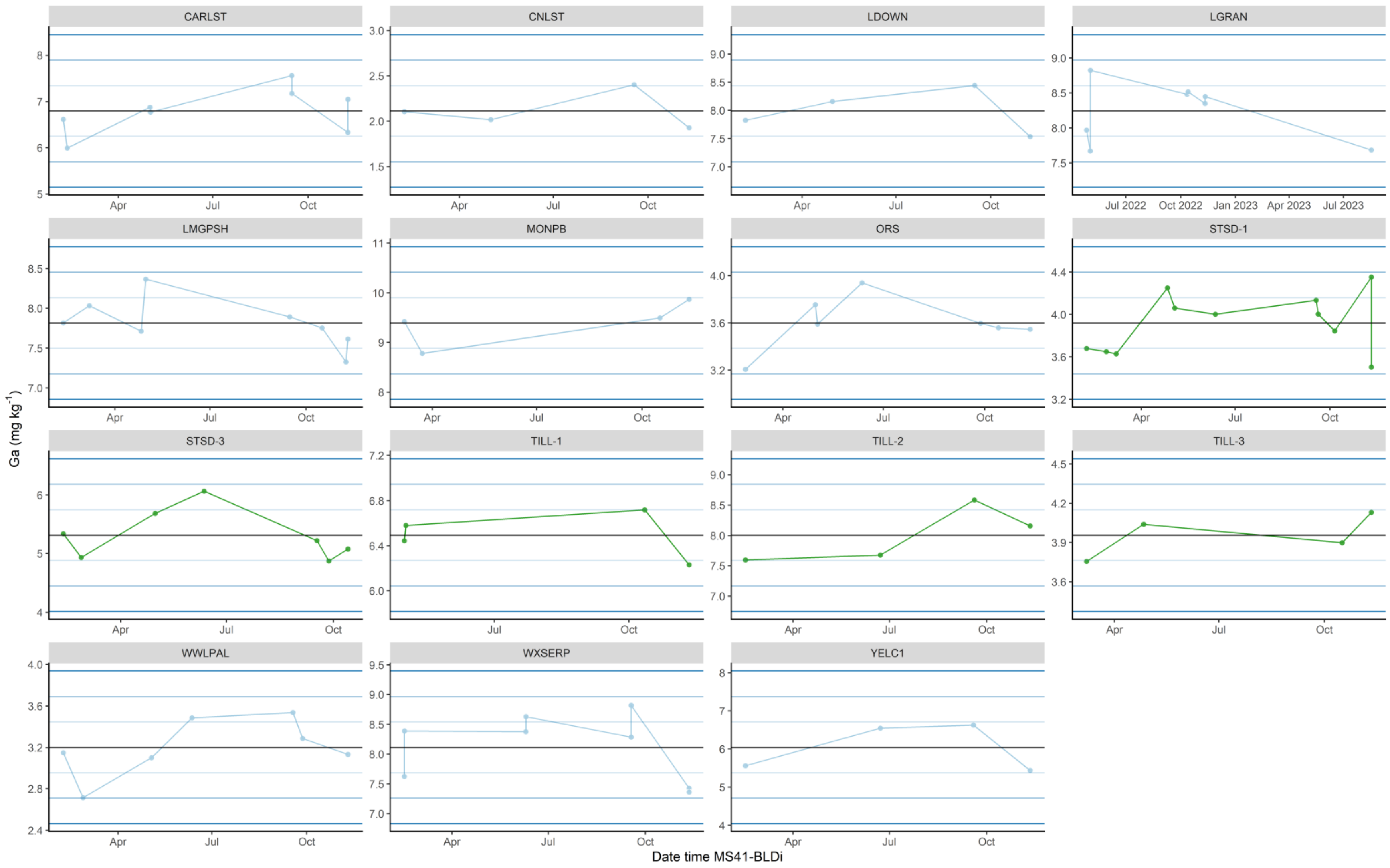
Copper (Cu) sample data IQR: 35.7–62.0 mg kg^{-1}

AURUM GLOBAL EXPLORATION



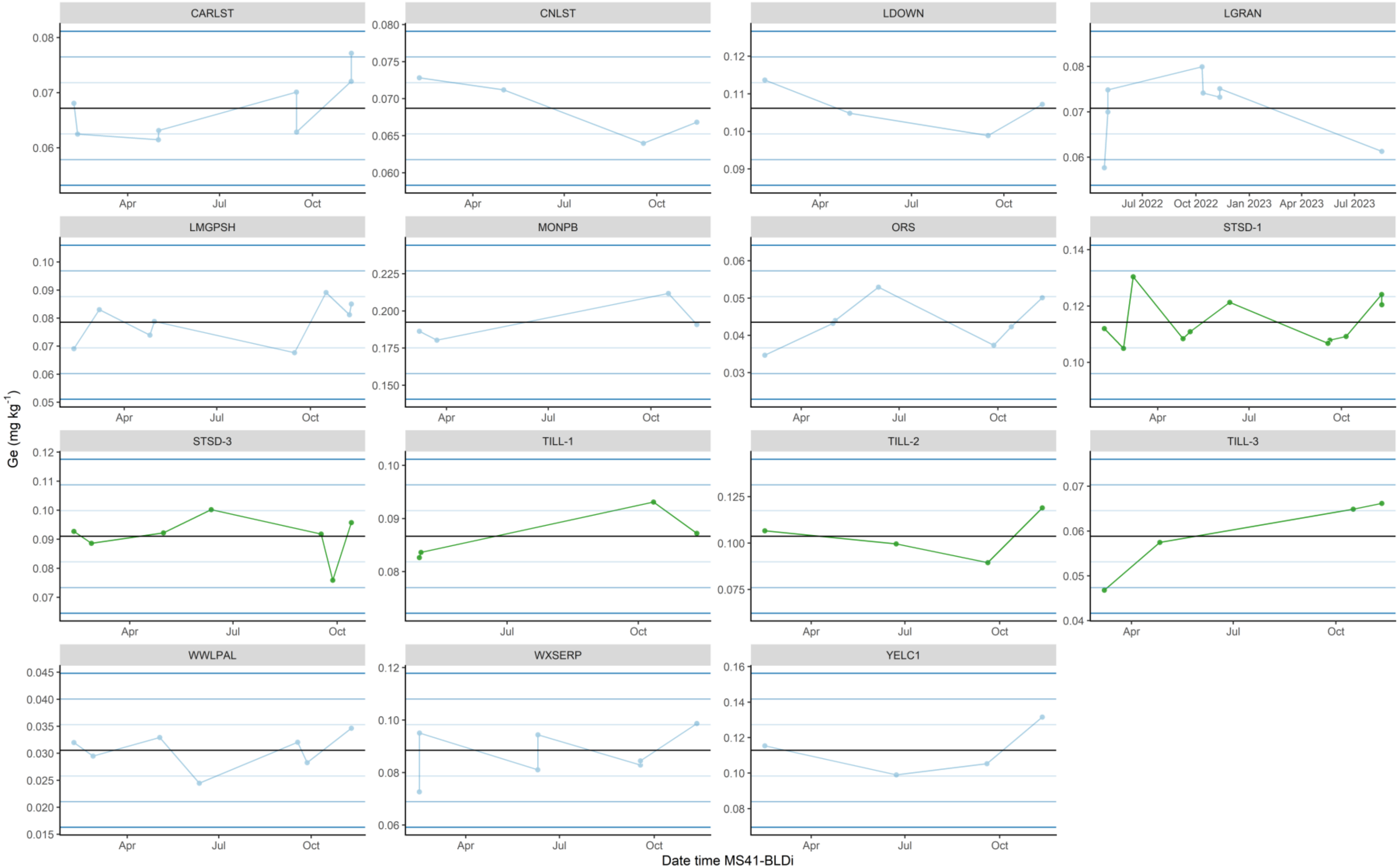
Iron (Fe) sample data IQR: 2.20–2.59 %

Gallium (Ga) MS41L-BLD

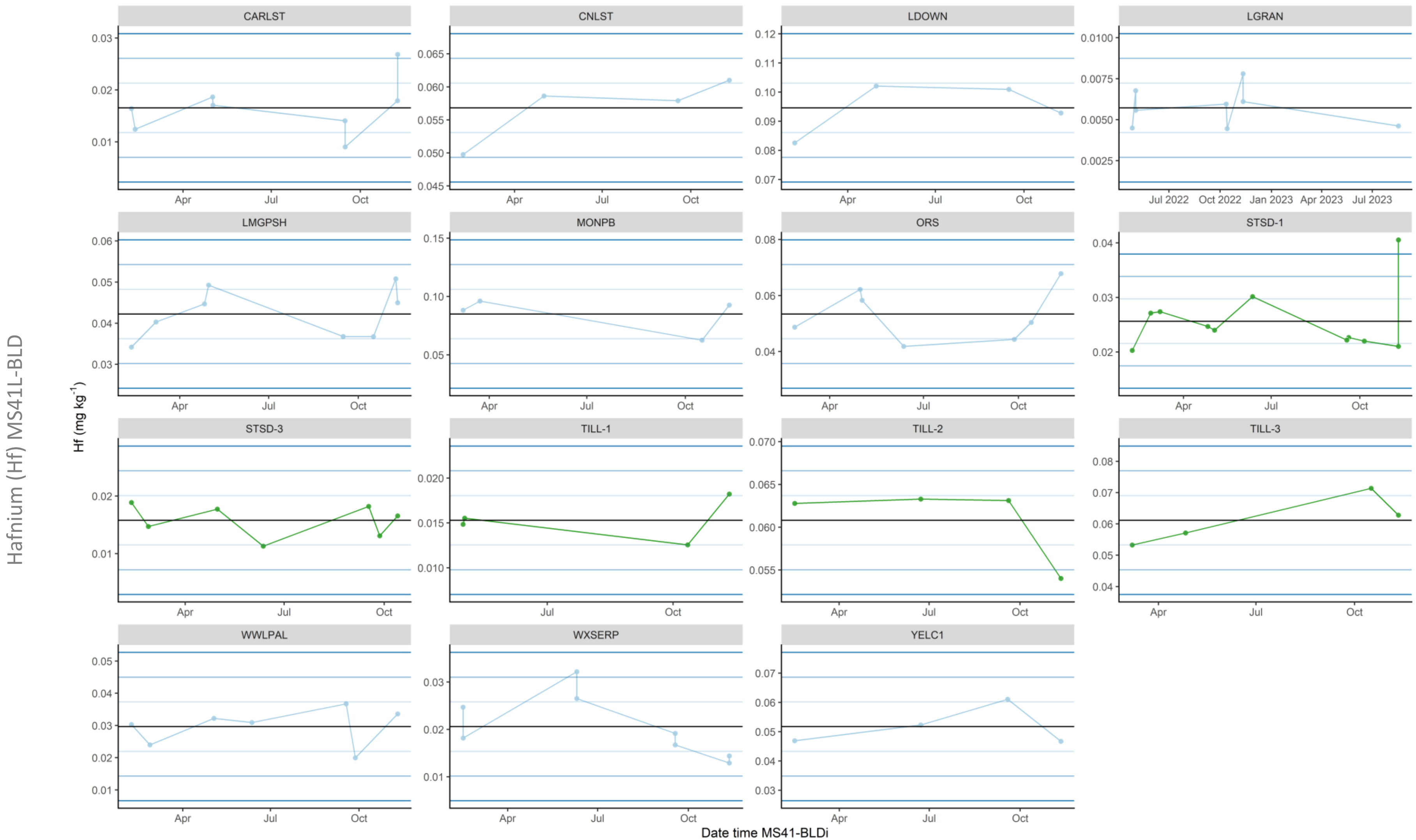


Gallium (Ga) sample data IQR: 2.86–3.68 mg kg^{-1}

Germanium (Ge) MS41L-BLD

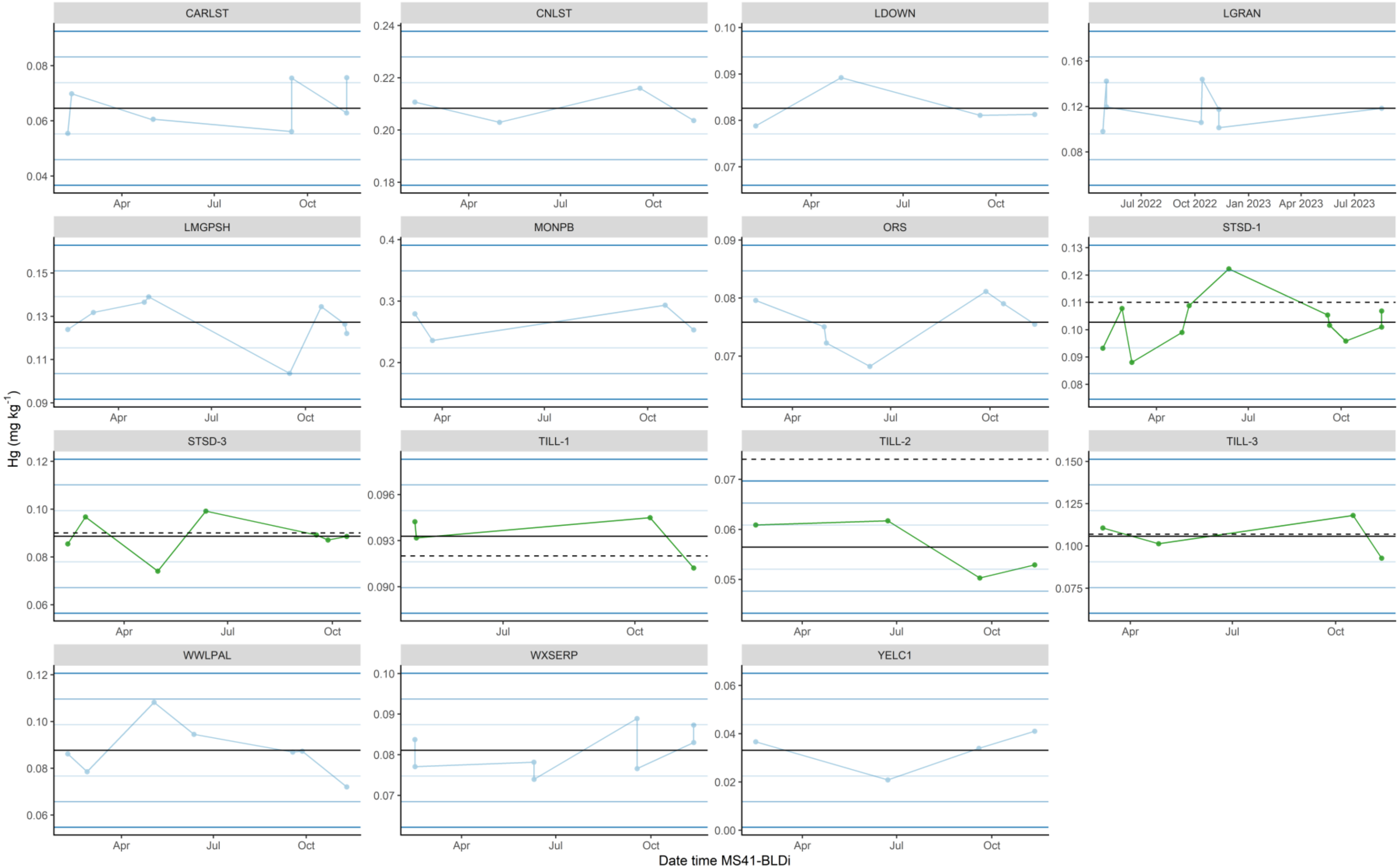


Germanium (Ge) sample data IQR: 0.0537-0.0695 mg kg^{-1}



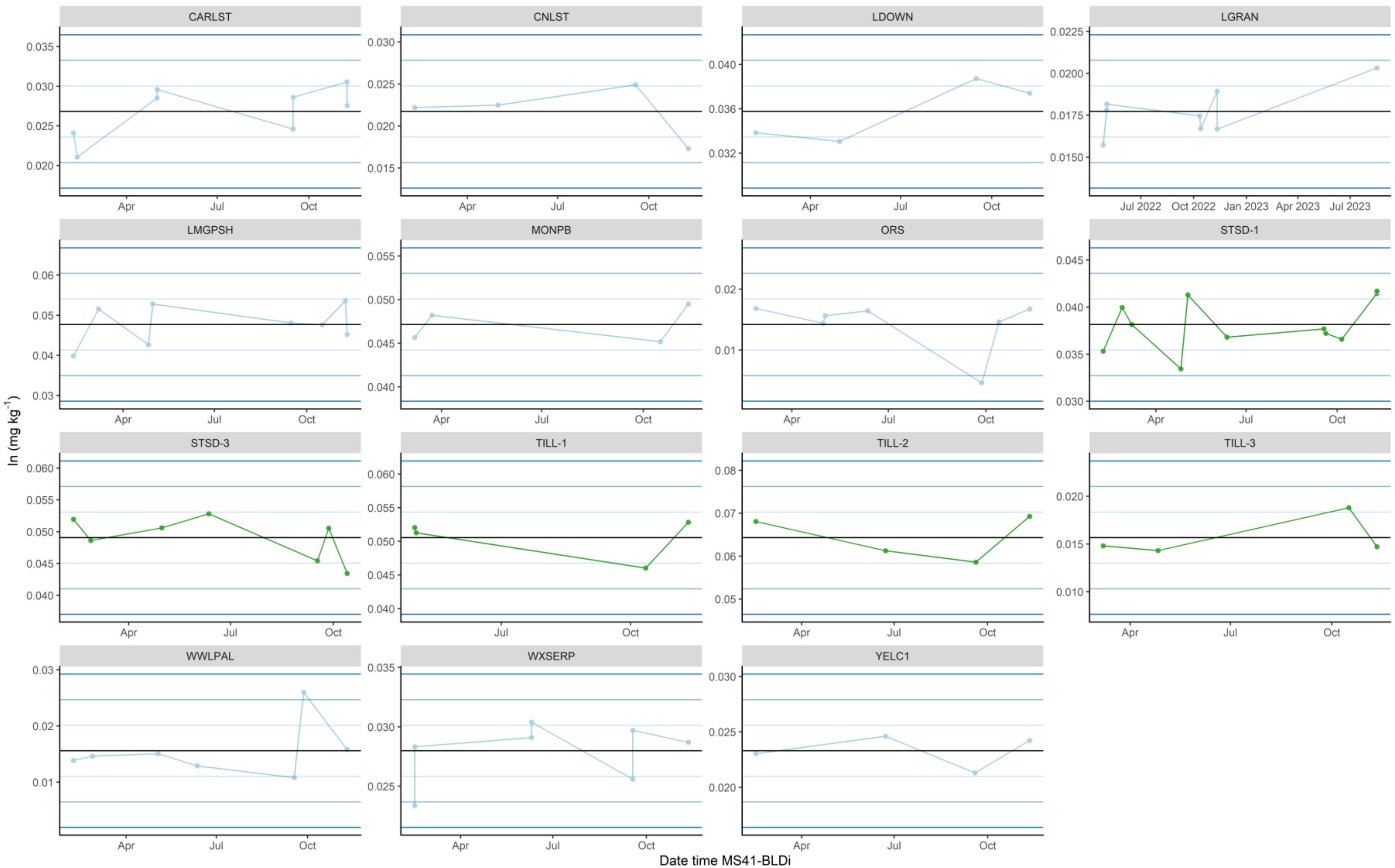
Hafnium (Hf) sample data IQR: 0.0781–0.107 mg kg^{-1}

Mercury (Hg) MS41L-BLD

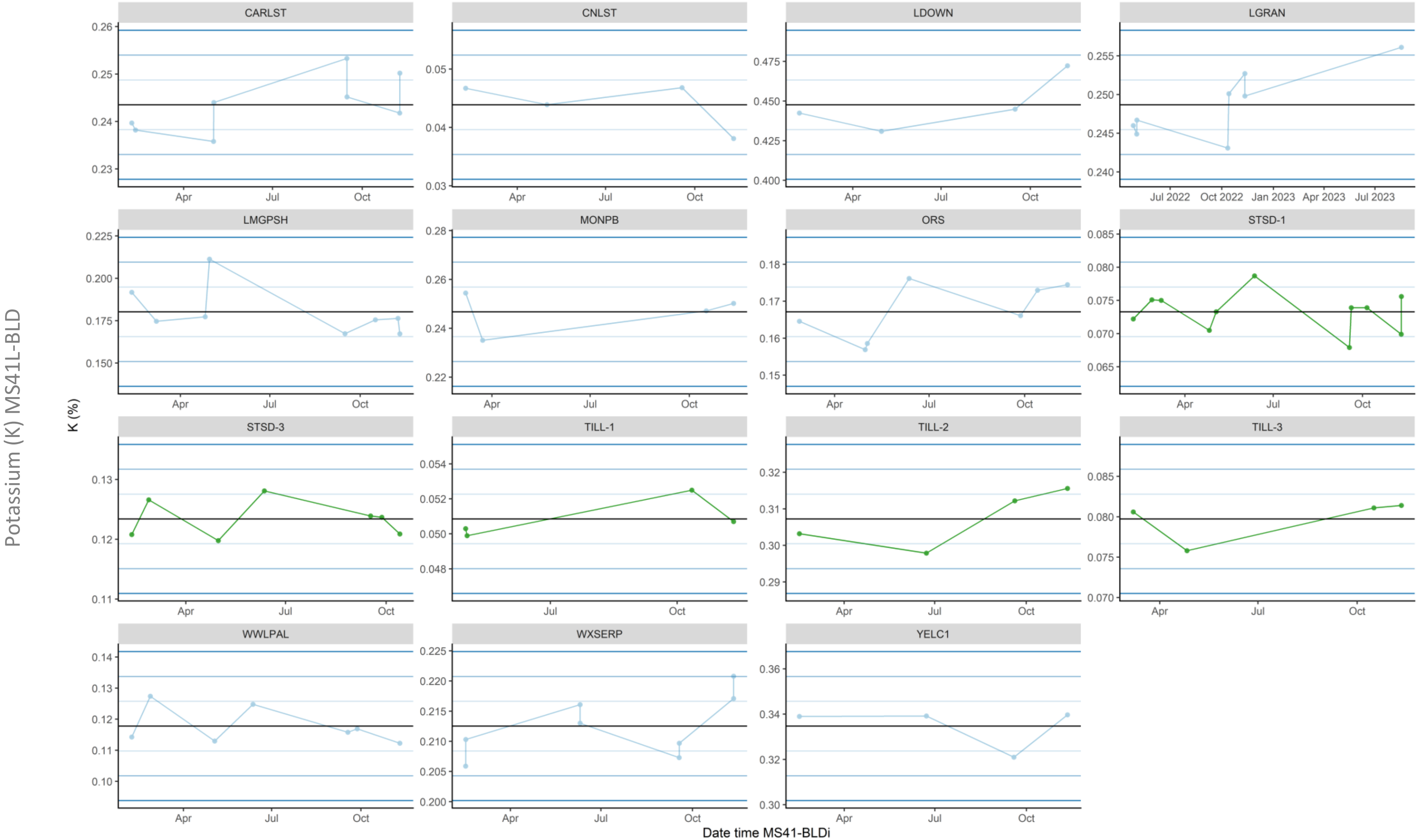


Mercury (Hg) sample data IQR: 0.155–0.458 mg kg^{-1}

Indium (In) MS41L-BLD

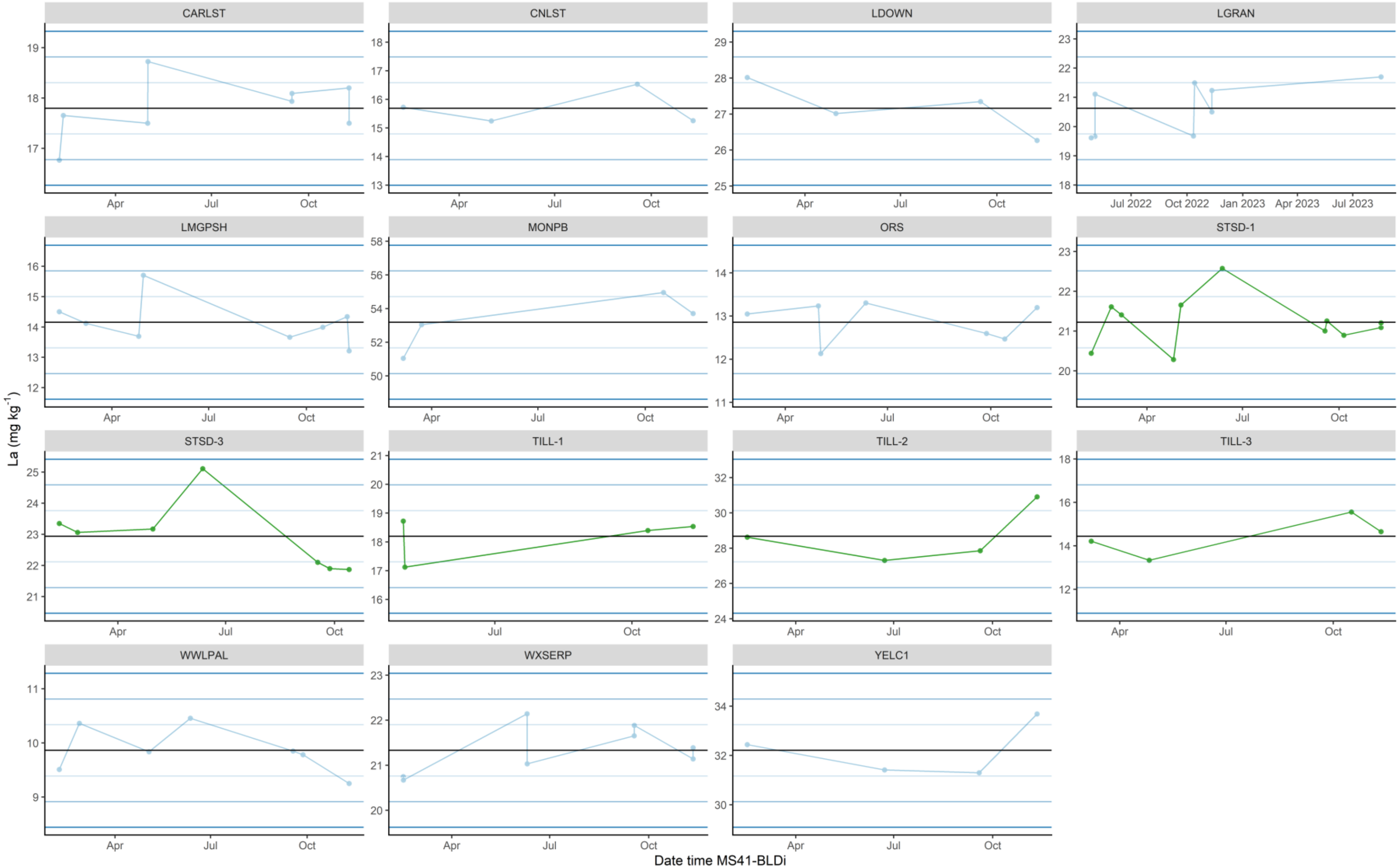


Indium (In) sample data IQR: 0.0210–0.0278 mg kg^{-1}

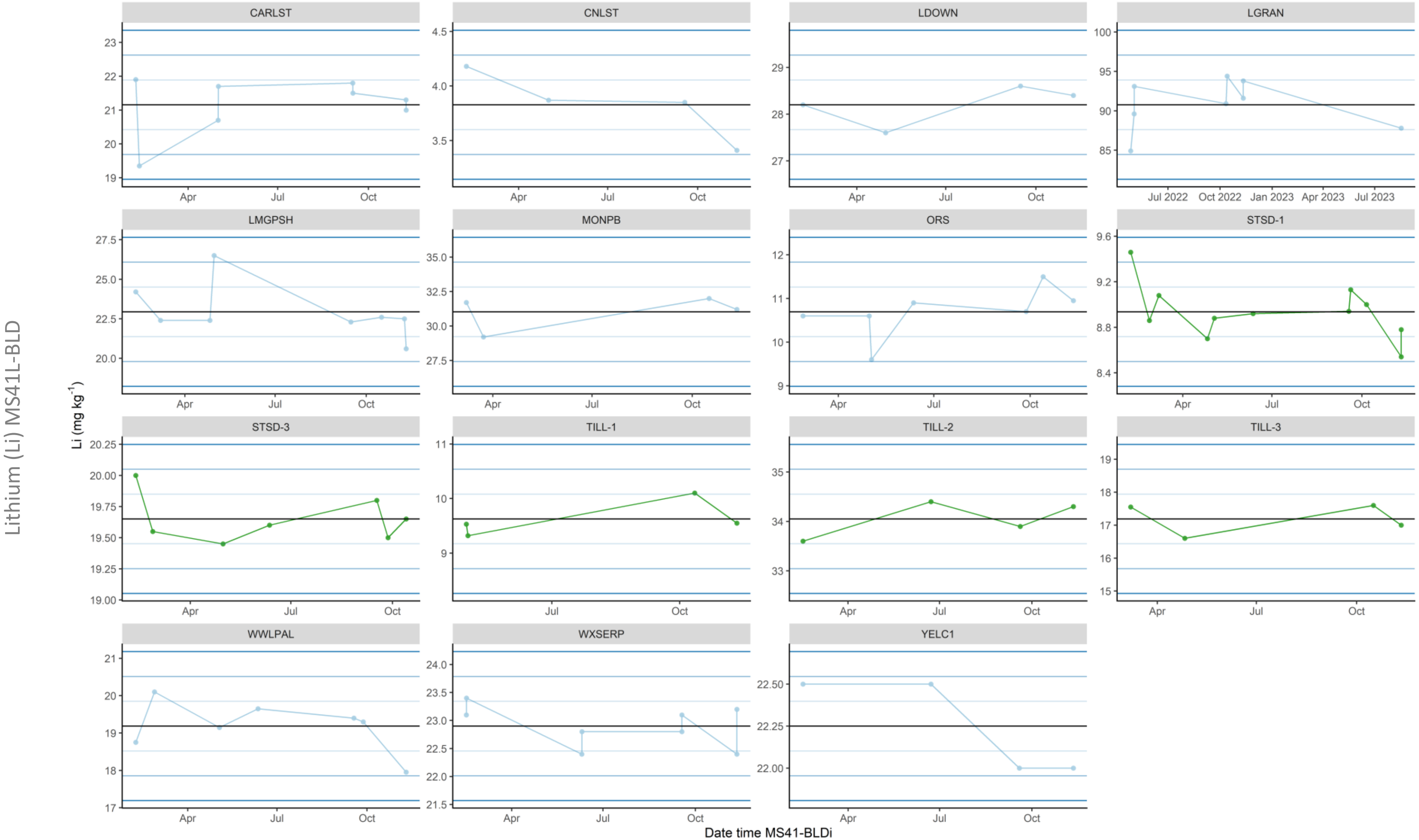


Potassium (K) sample data IQR: 0.118–0.145 %

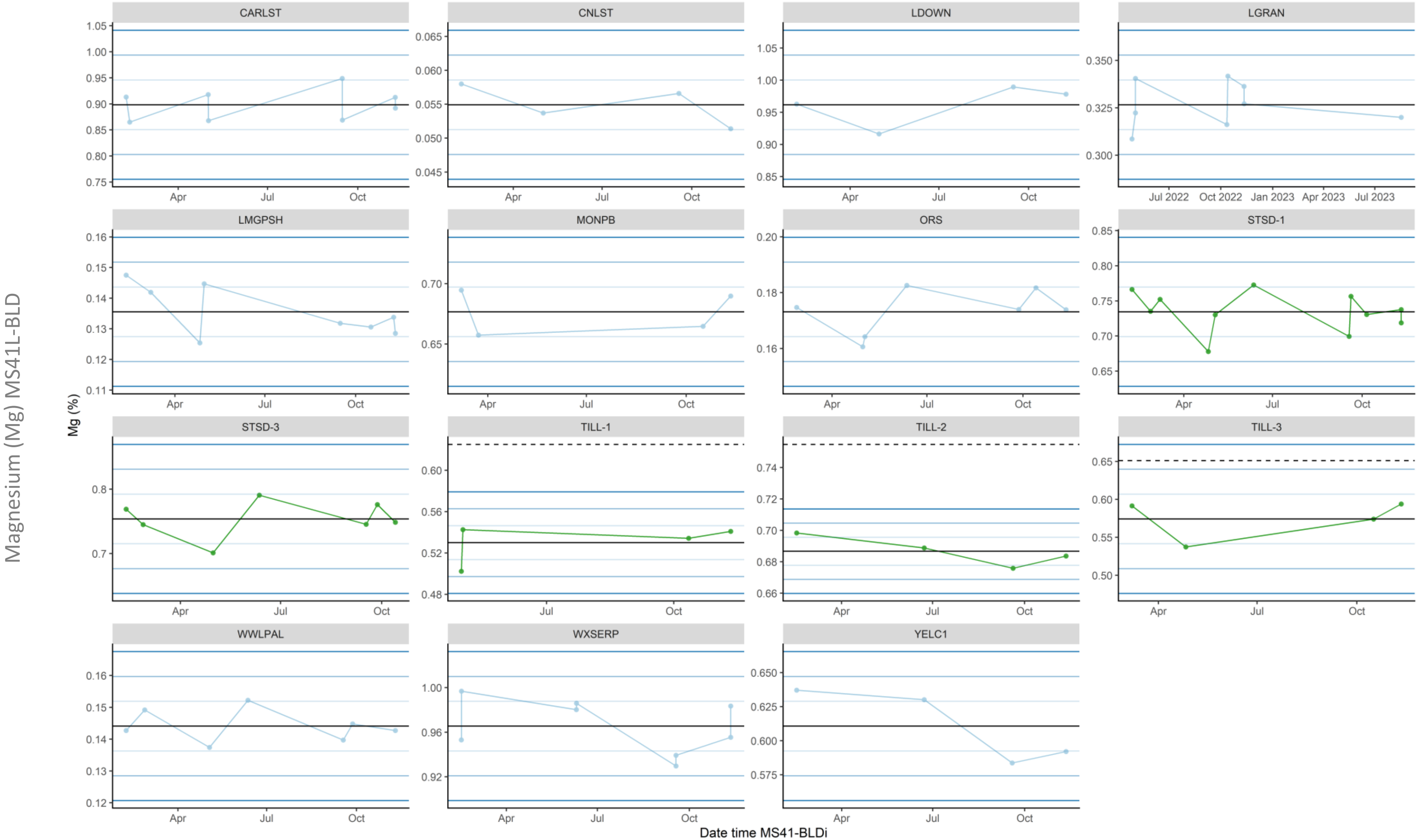
Lanthanum (La) MS41L-BLD



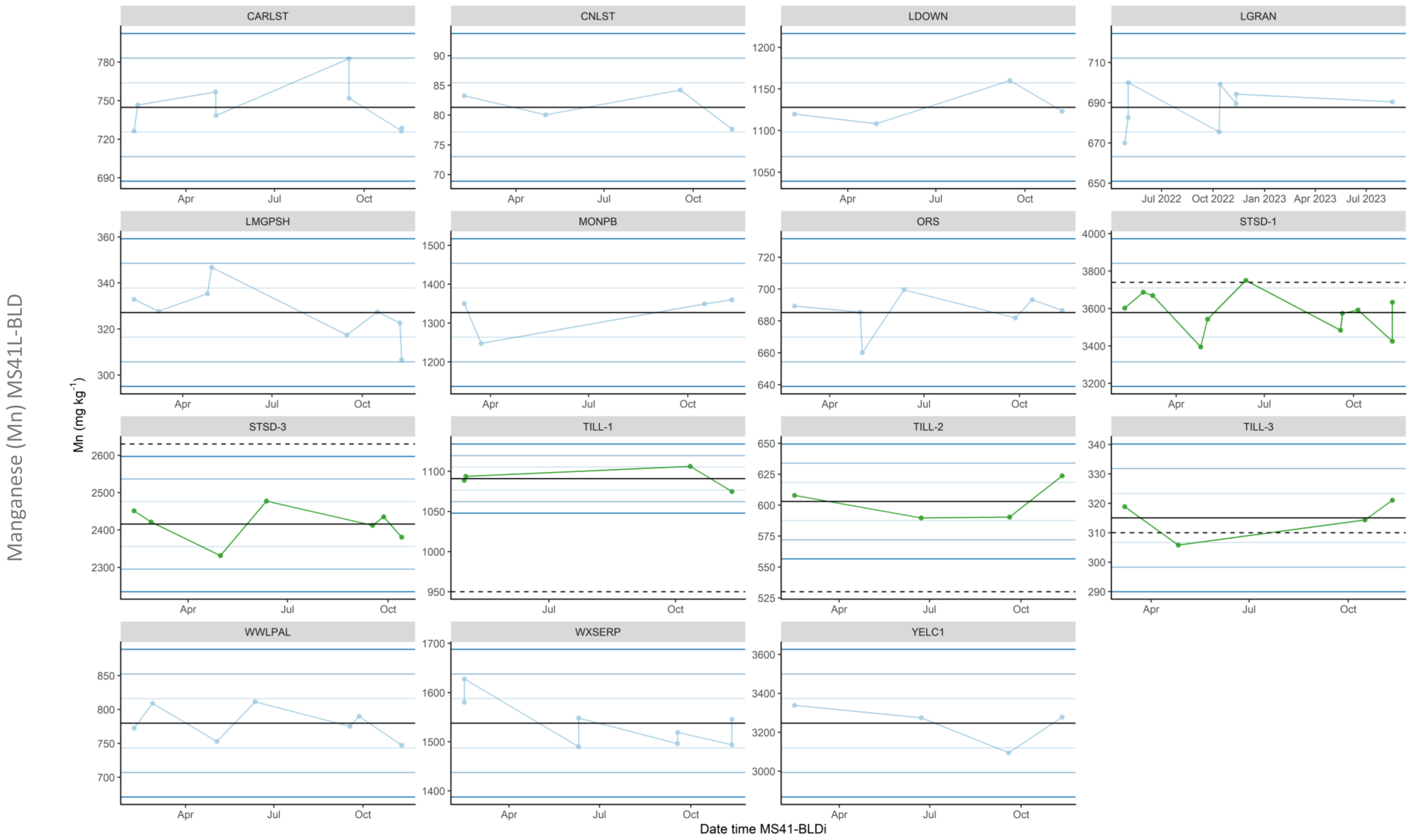
Lanthanum (La) sample data IQR: 12.0–14.1 mg kg^{-1}



Lithium (Li) sample data IQR: 11.4–17.5 mg kg^{-1}

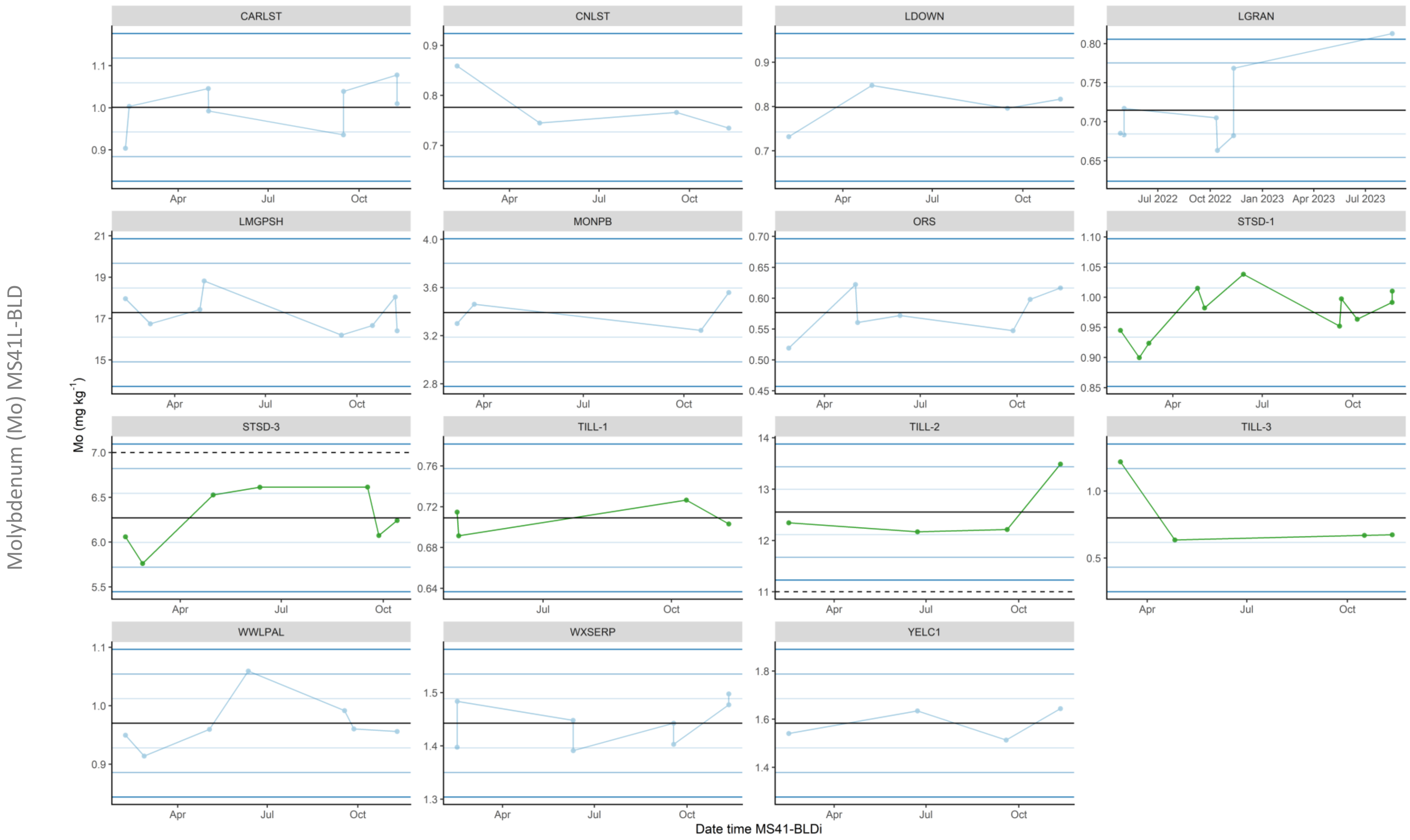


Magnesium (Mg) sample data IQR: 0.214–0.302 %

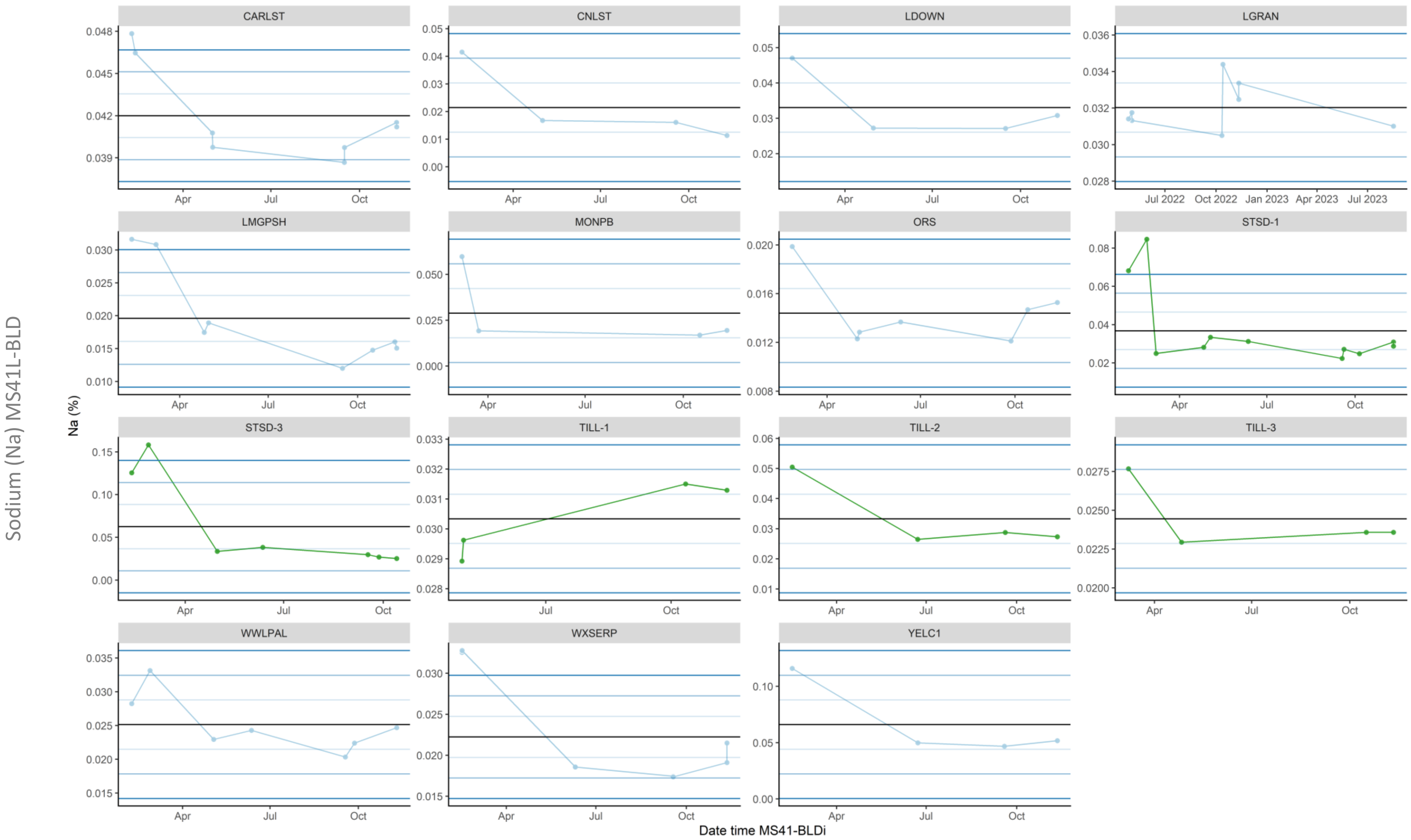


Manganese (Mn) sample data IQR: 916–1450 mg kg^{-1}

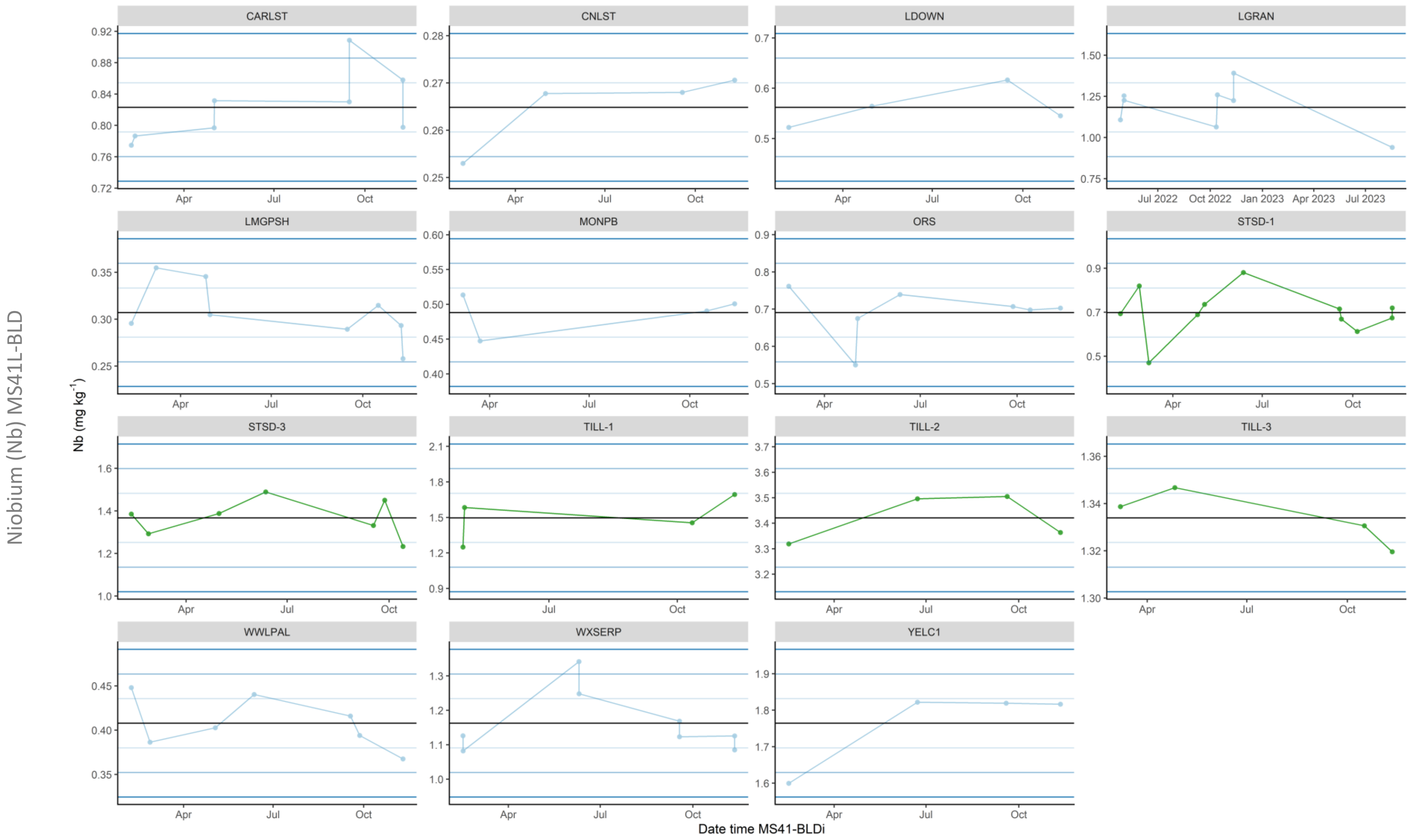
AURUM GLOBAL EXPLORATION



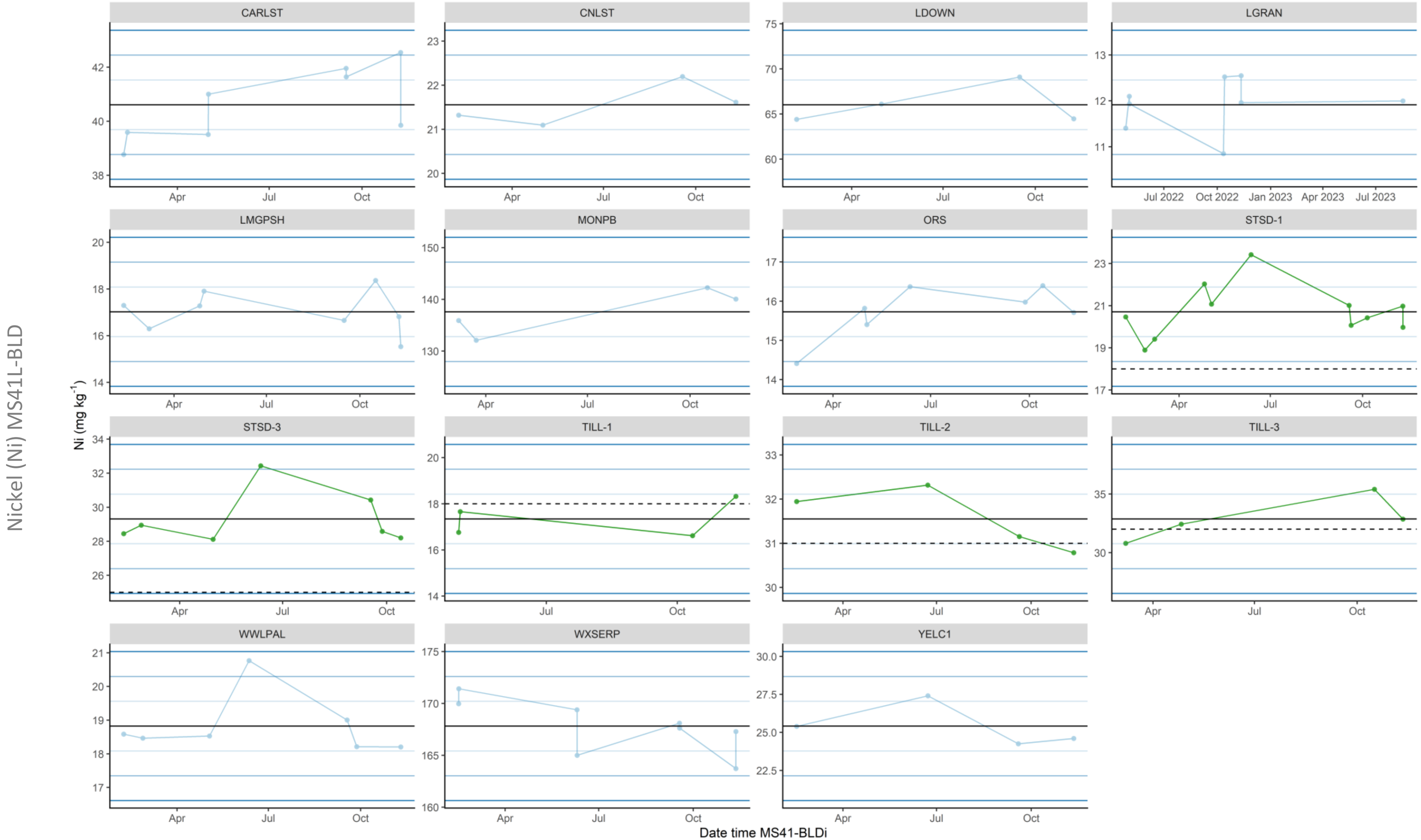
Molybdenum (Mo) sample data IQR: 2.57–3.79 mg kg^{-1}



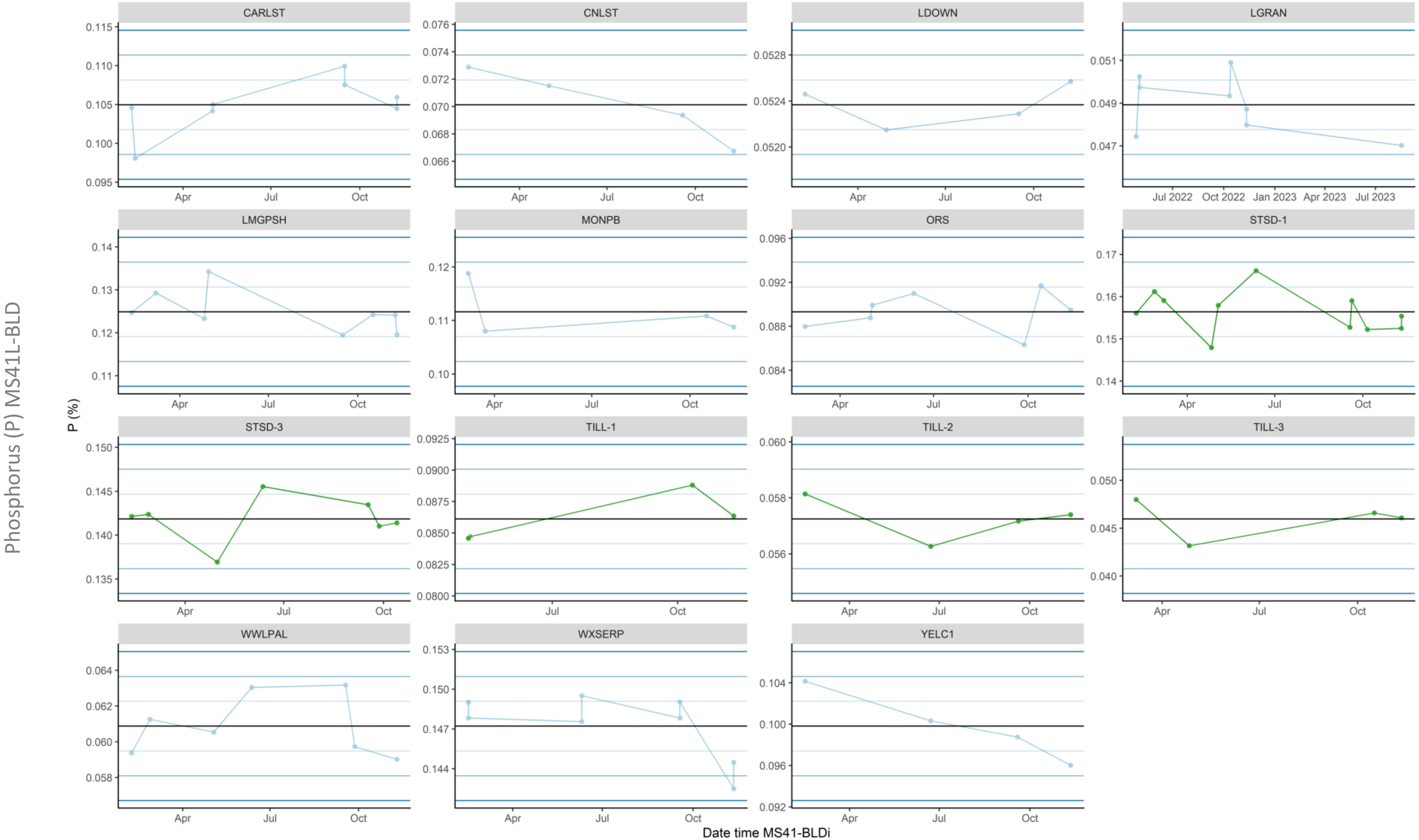
Sodium (Na) sample data IQR: 0.0154–0.0210 %



Niobium (Nb) sample data IQR: 0.291–0.404 mg kg^{-1}

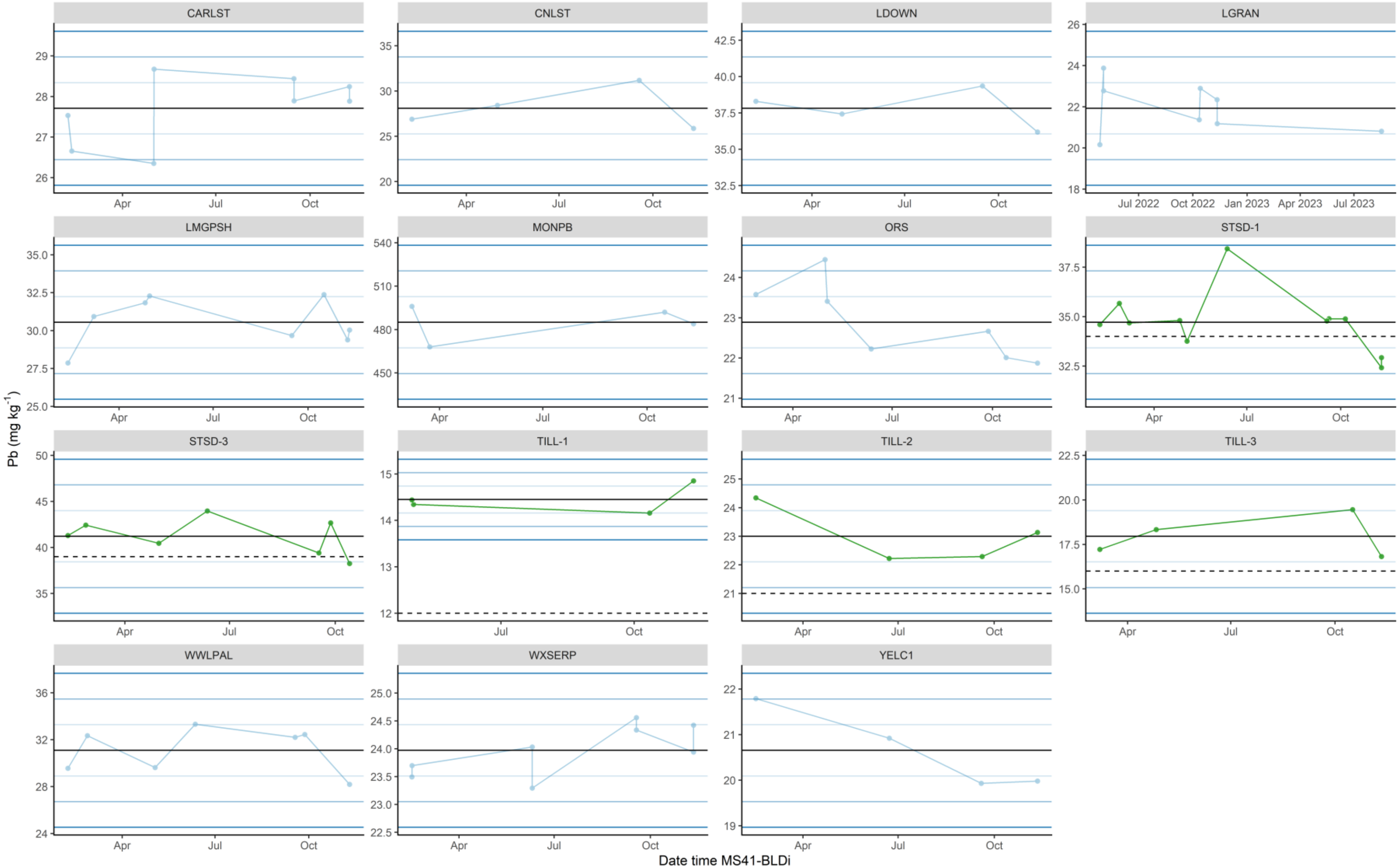


Nickel (Ni) sample data IQR: 38.9–51.9 mg kg^{-1}



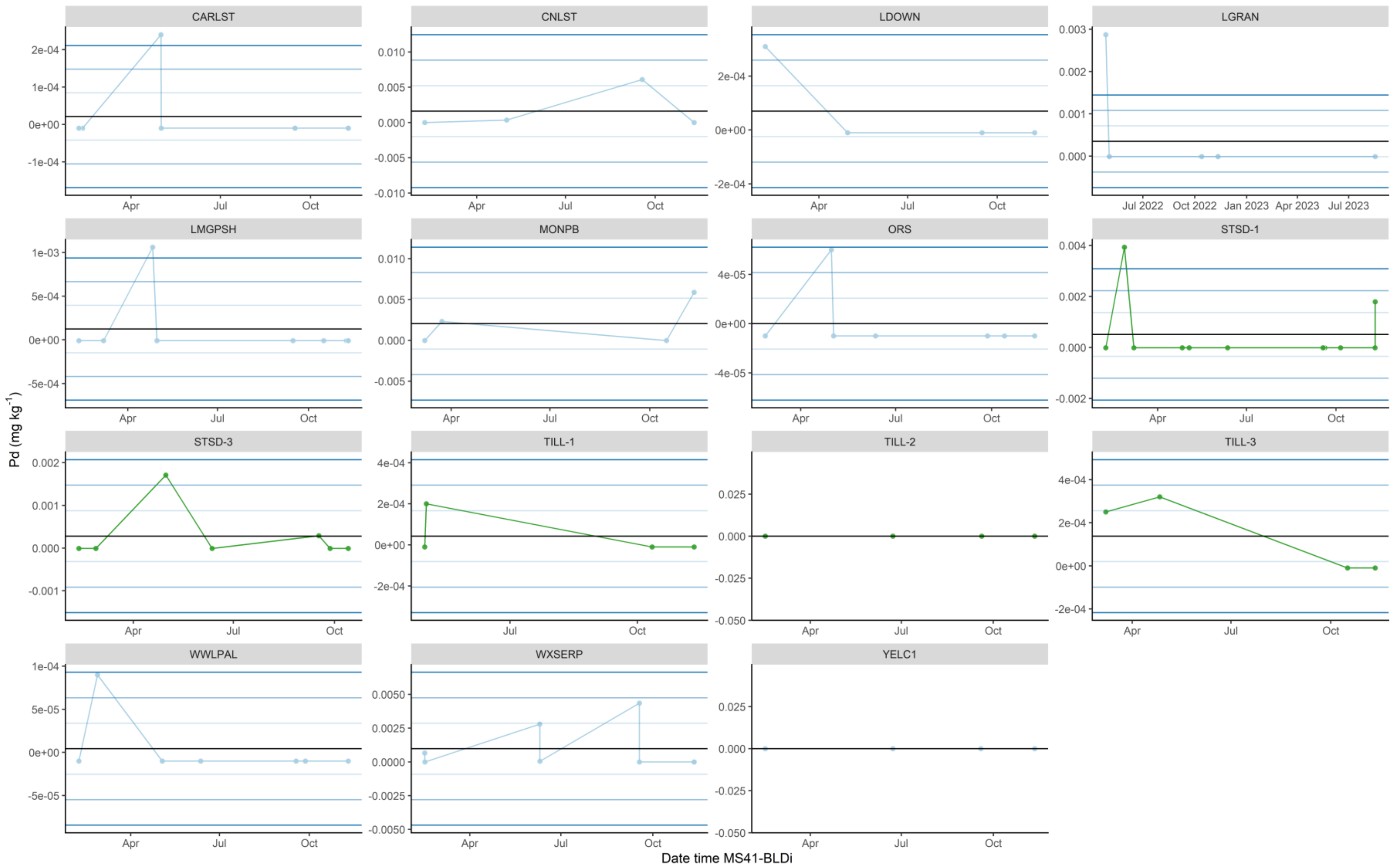
Phosphorus (P) sample data IQR: 694–1090 mg kg^{-1}

Lead (Pb) MS41L-BLD



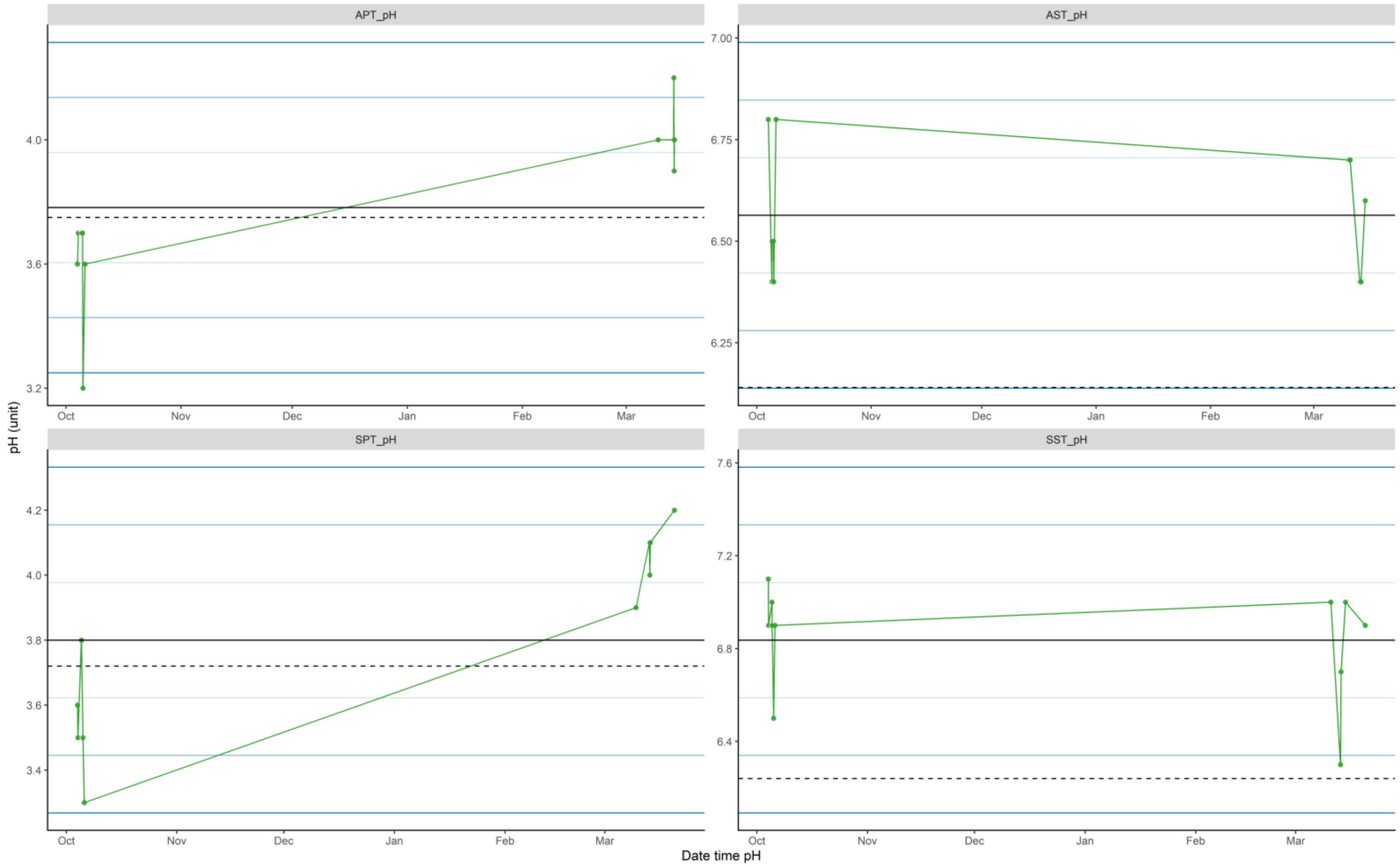
Lead (Pb) sample data IQR: 59.8–161 mg kg^{-1}

Palladium (Pd) MS41L-BLD



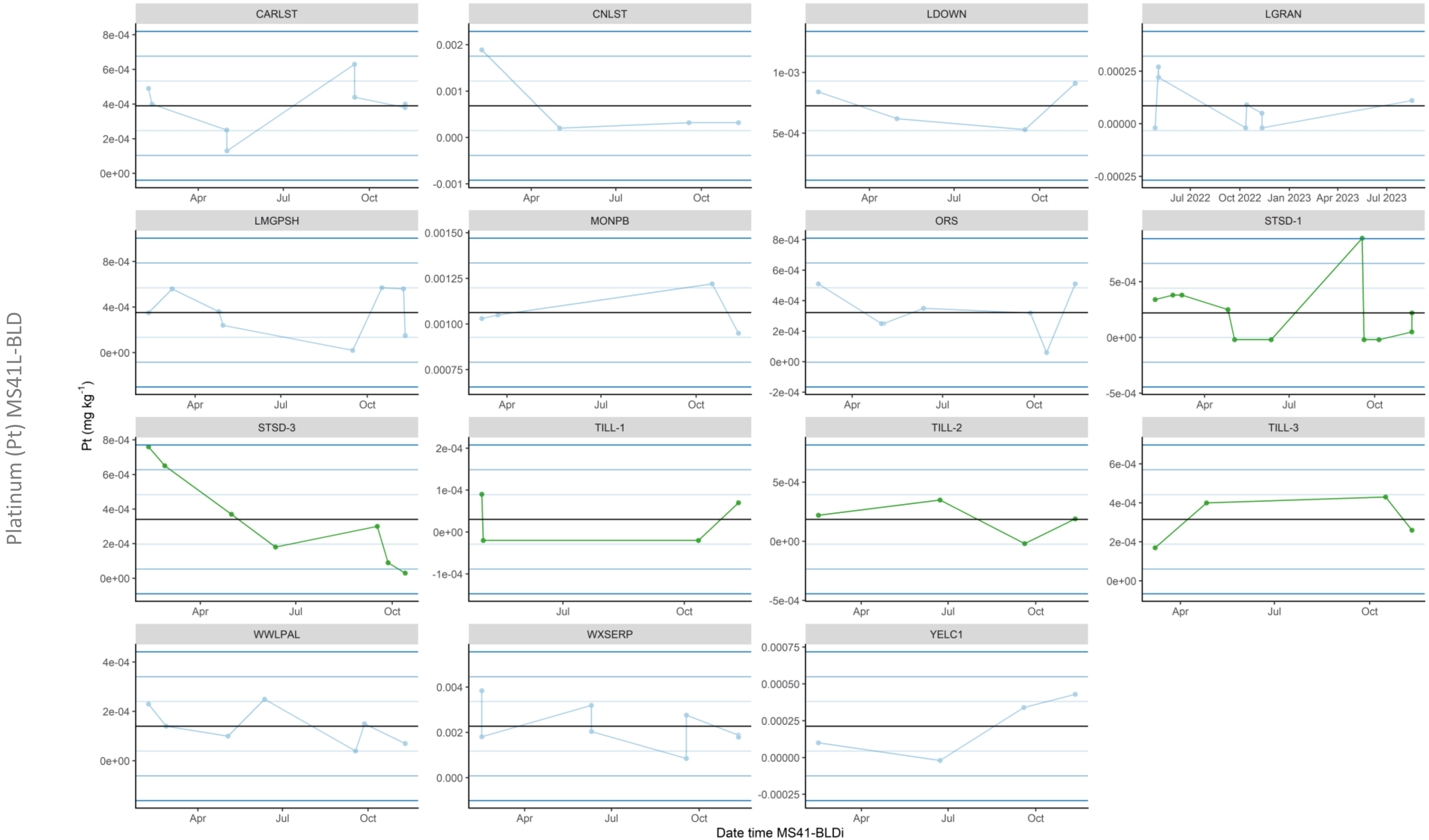
Palladium (Pd) sample data IQR: 0.00000612–0.000162 mg kg^{-1}

pH CaCl$_2$

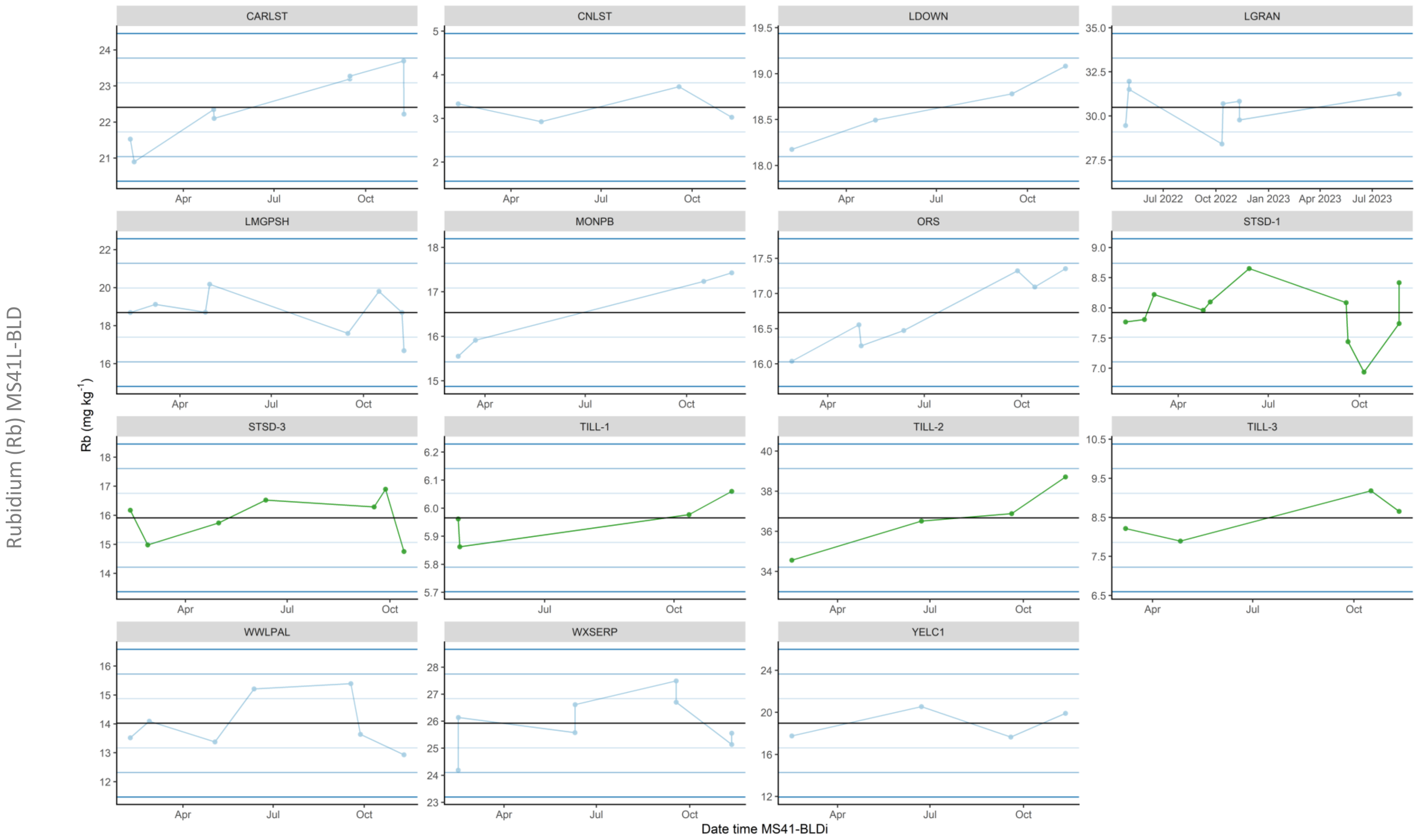


pH sample data IQR: 6.5–7.0

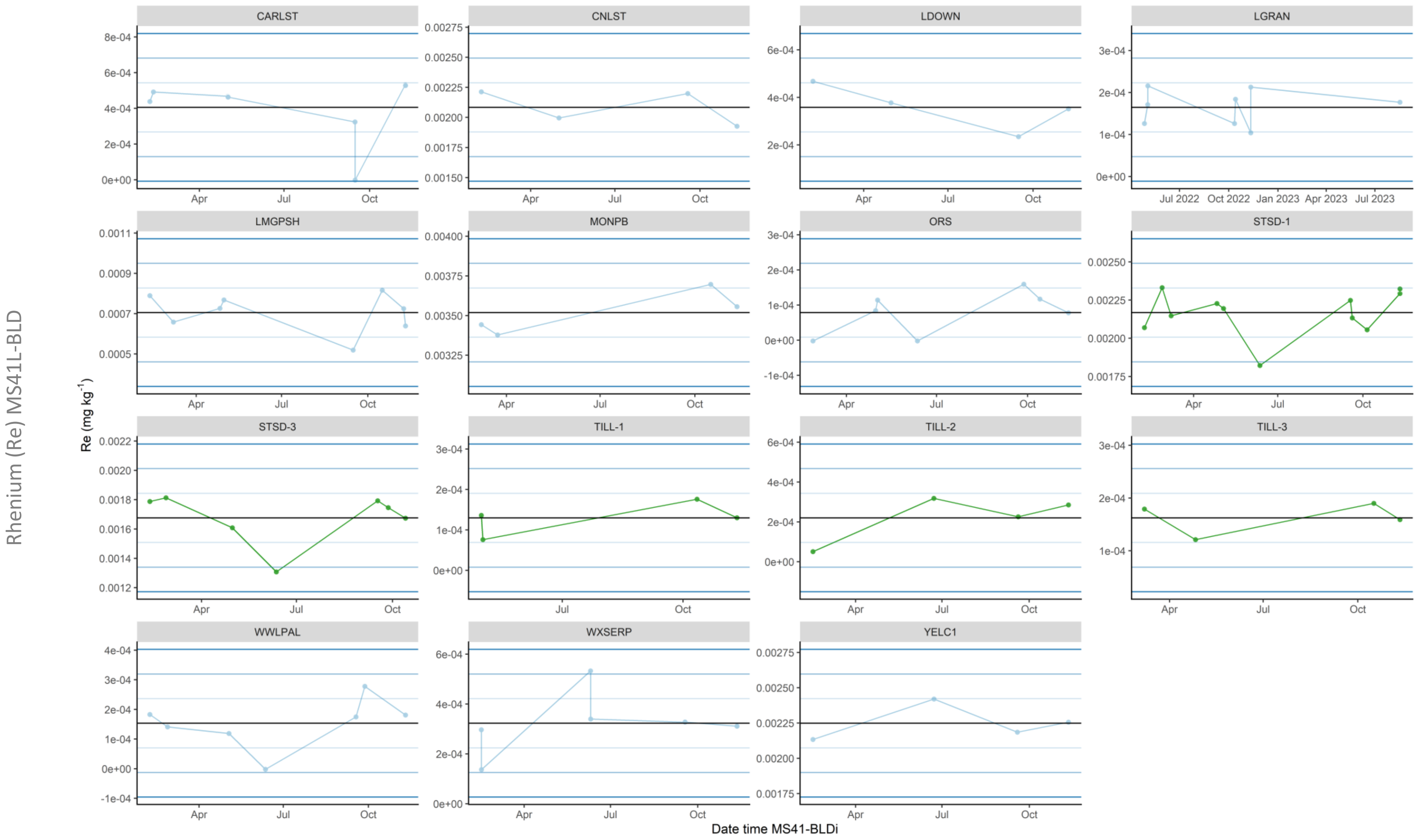
AURUM GLOBAL EXPLORATION



Platinum (Pt) sample data IQR: 0.00047–0.00096 mg kg^{-1}

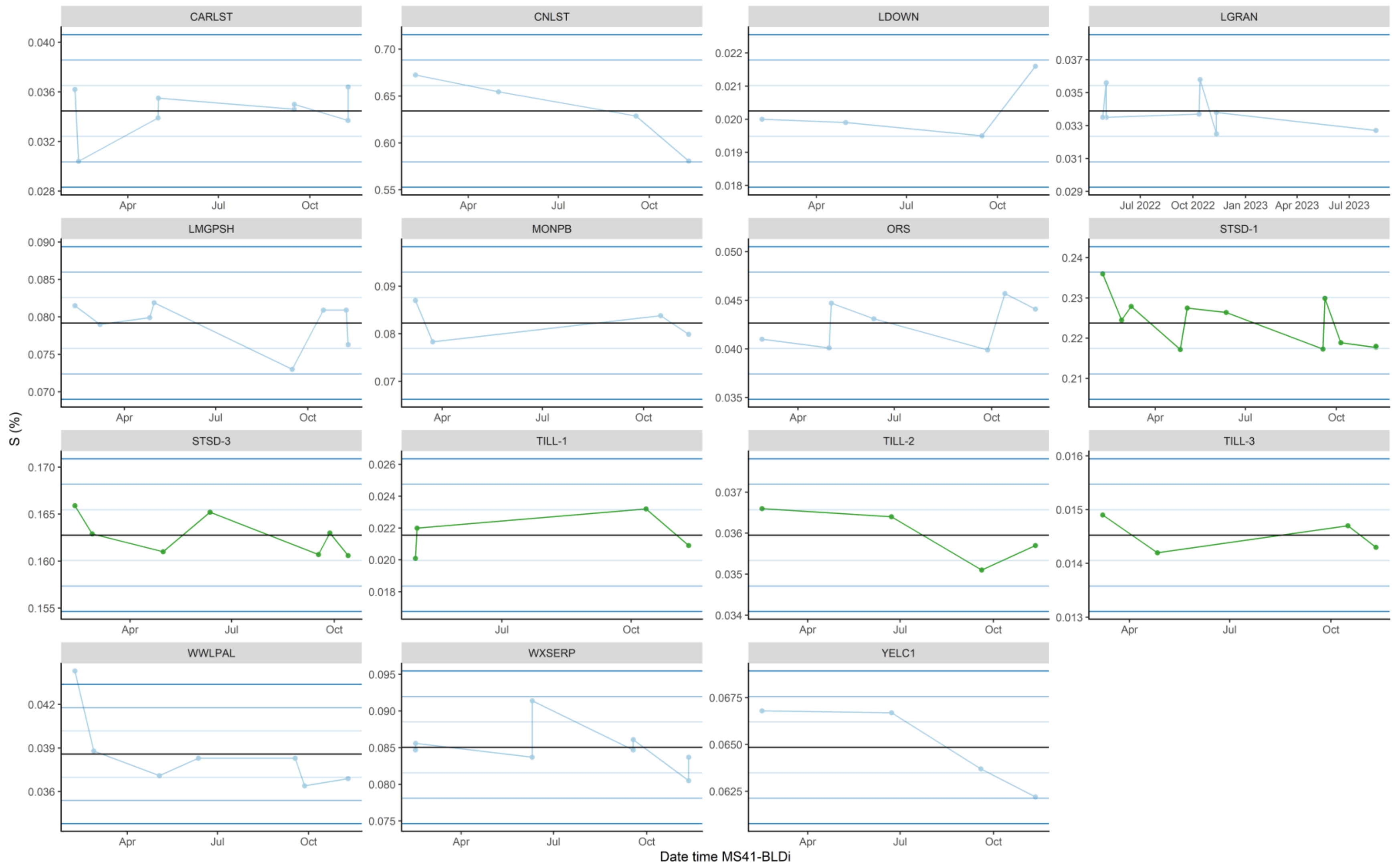


Rubidium (Rb) sample data IQR: 8.37–10.7 mg kg^{-1}

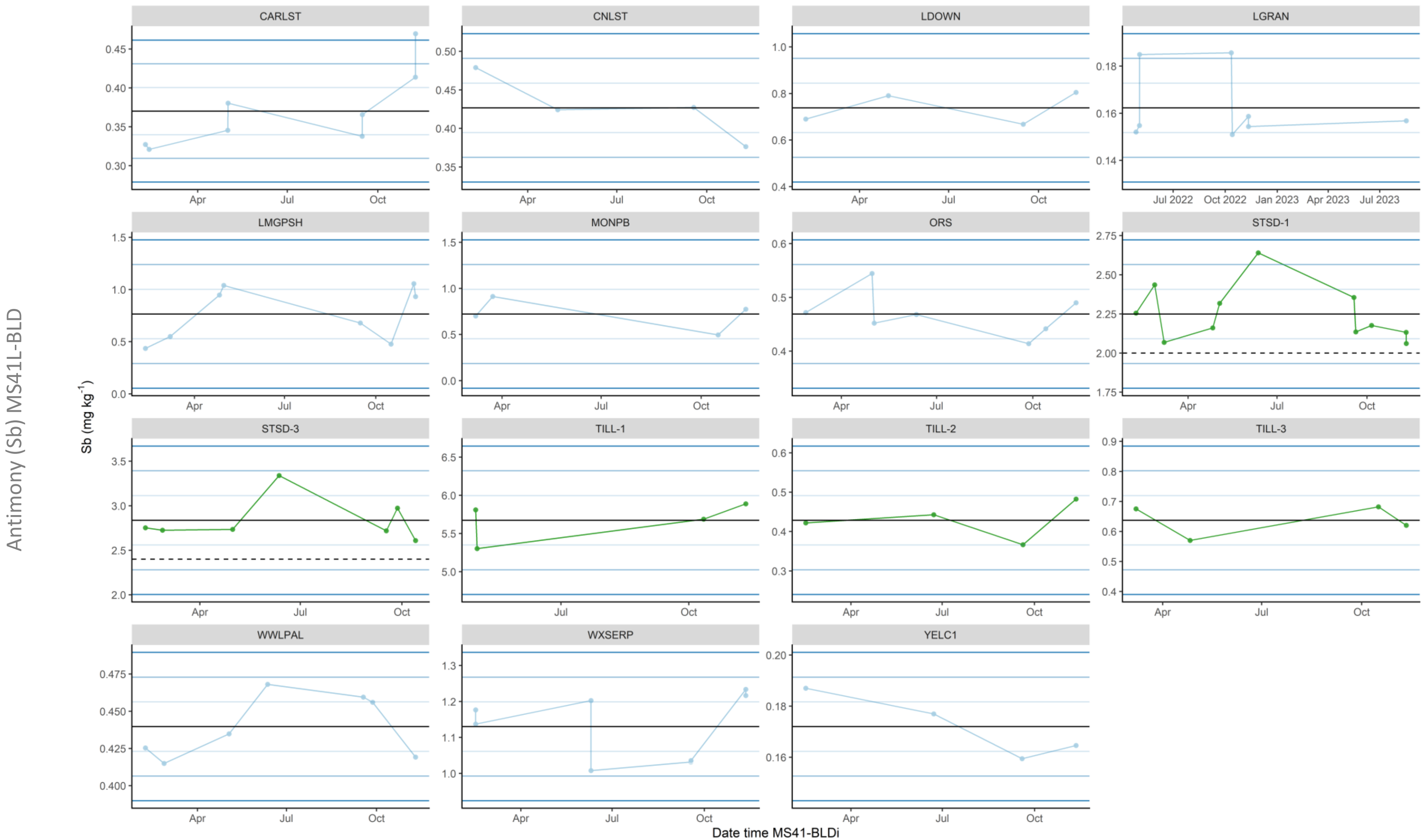


Rhenium (Re) sample data IQR: 0.000878–0.00179 mg kg^{-1}

Sulphur (S) MS41L-BLD

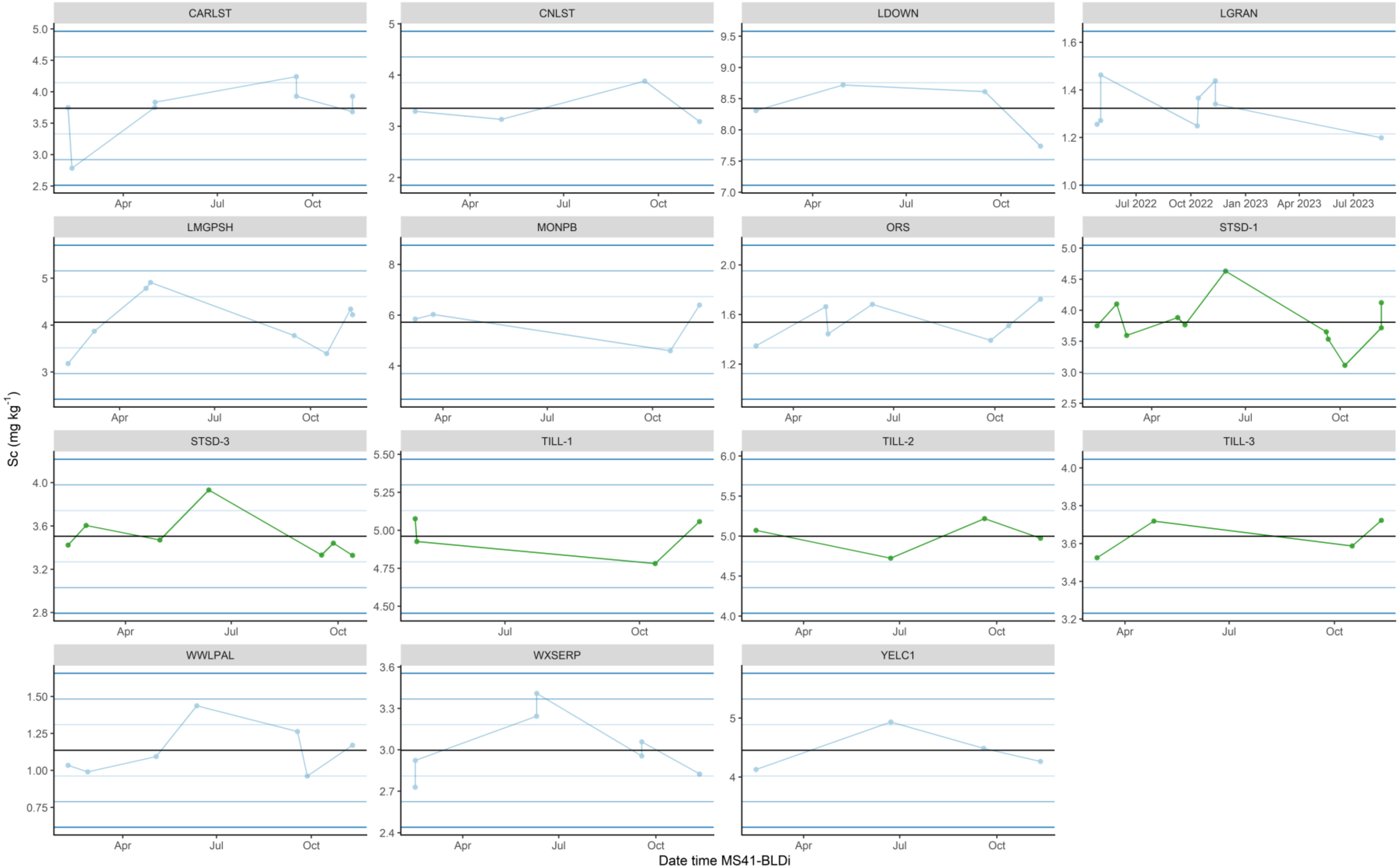


Sulphur (S) sample data IQR: 0.0452–0.071 %



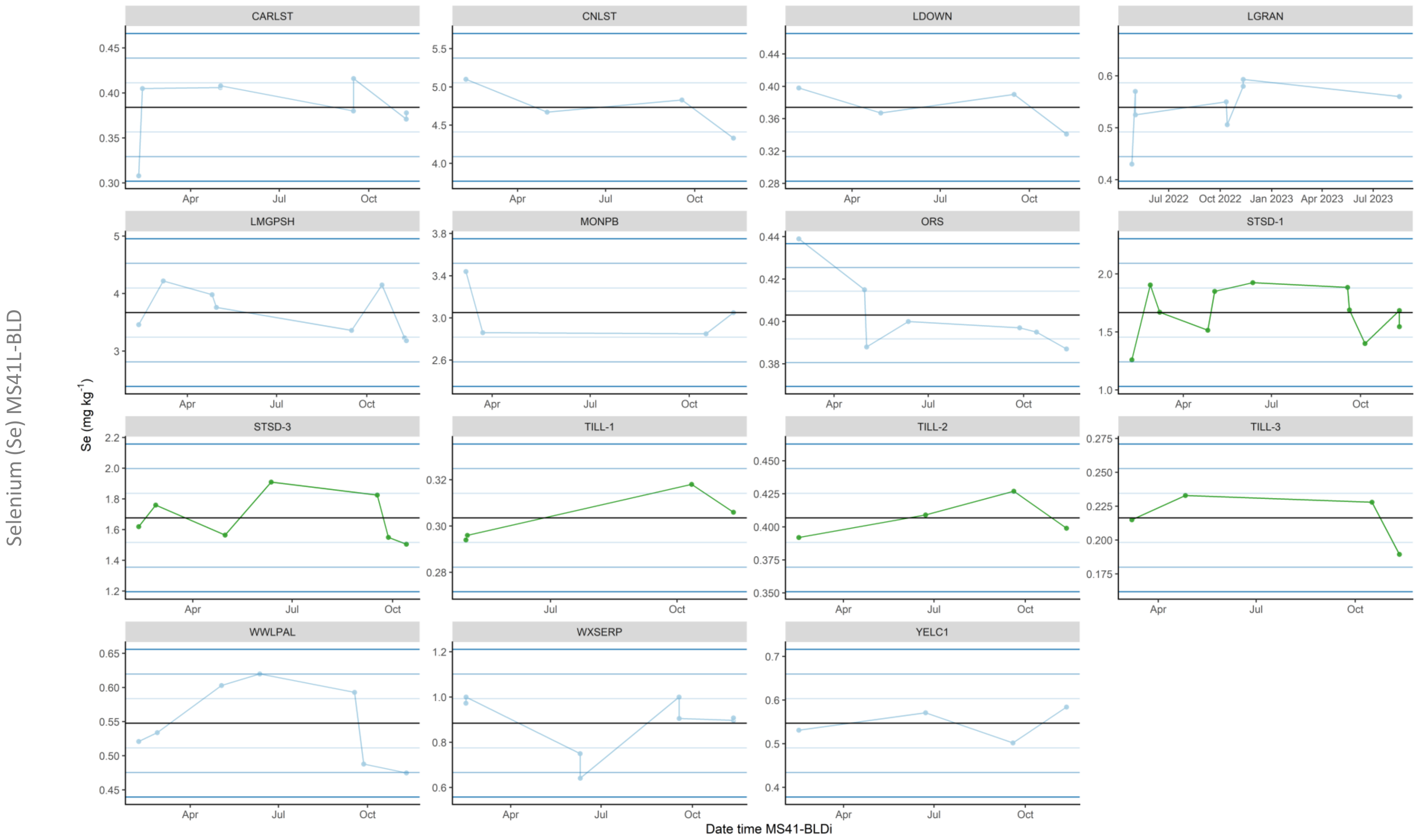
Antimony (Sb) sample data IQR: 1.10–2.05 mg kg^{-1}

Scandium (Sc) MS41L-BLD



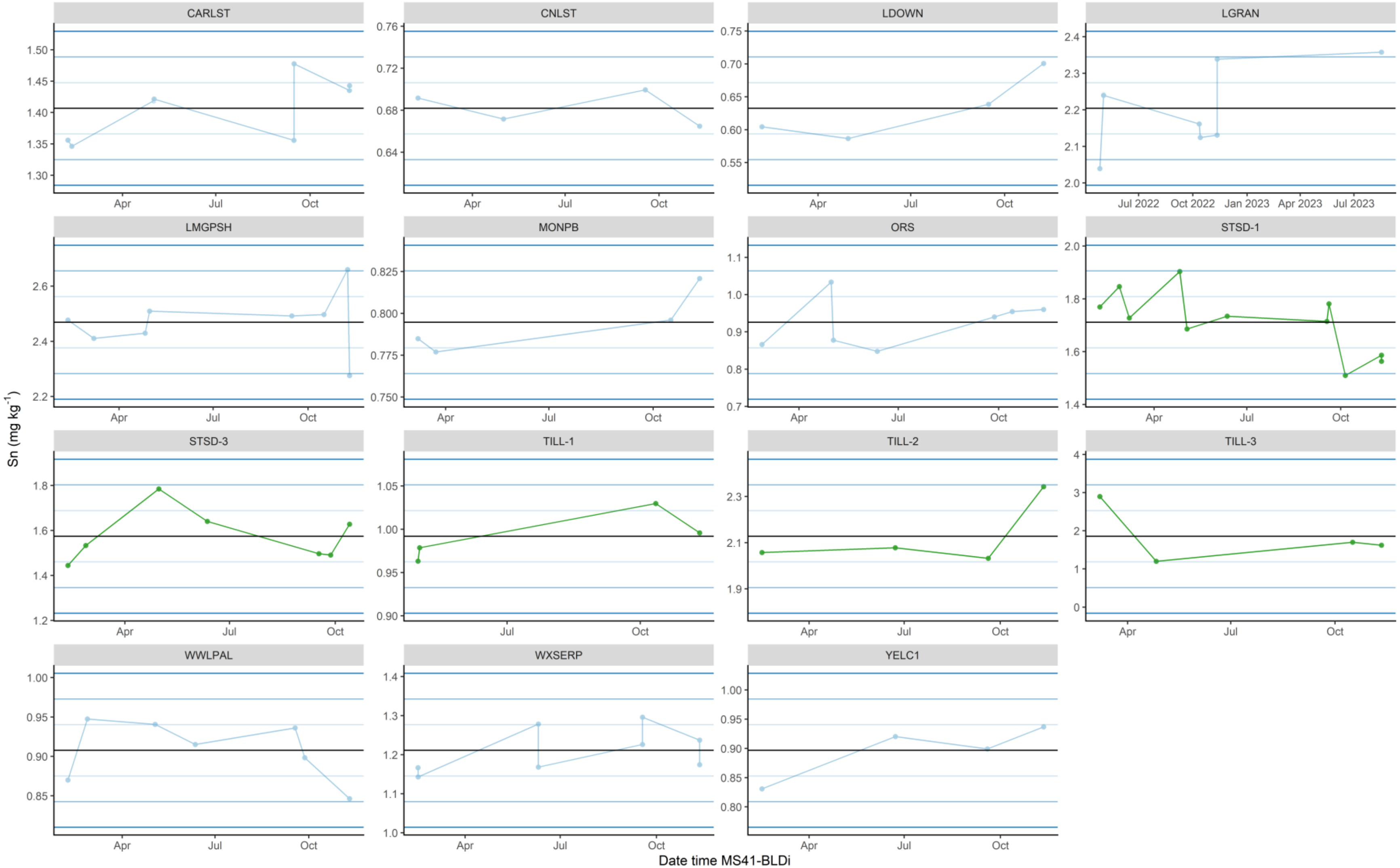
Scandium (Sc) sample data IQR: 3.30–4.11 $mg\ kg^{-1}$

AURUM GLOBAL EXPLORATION



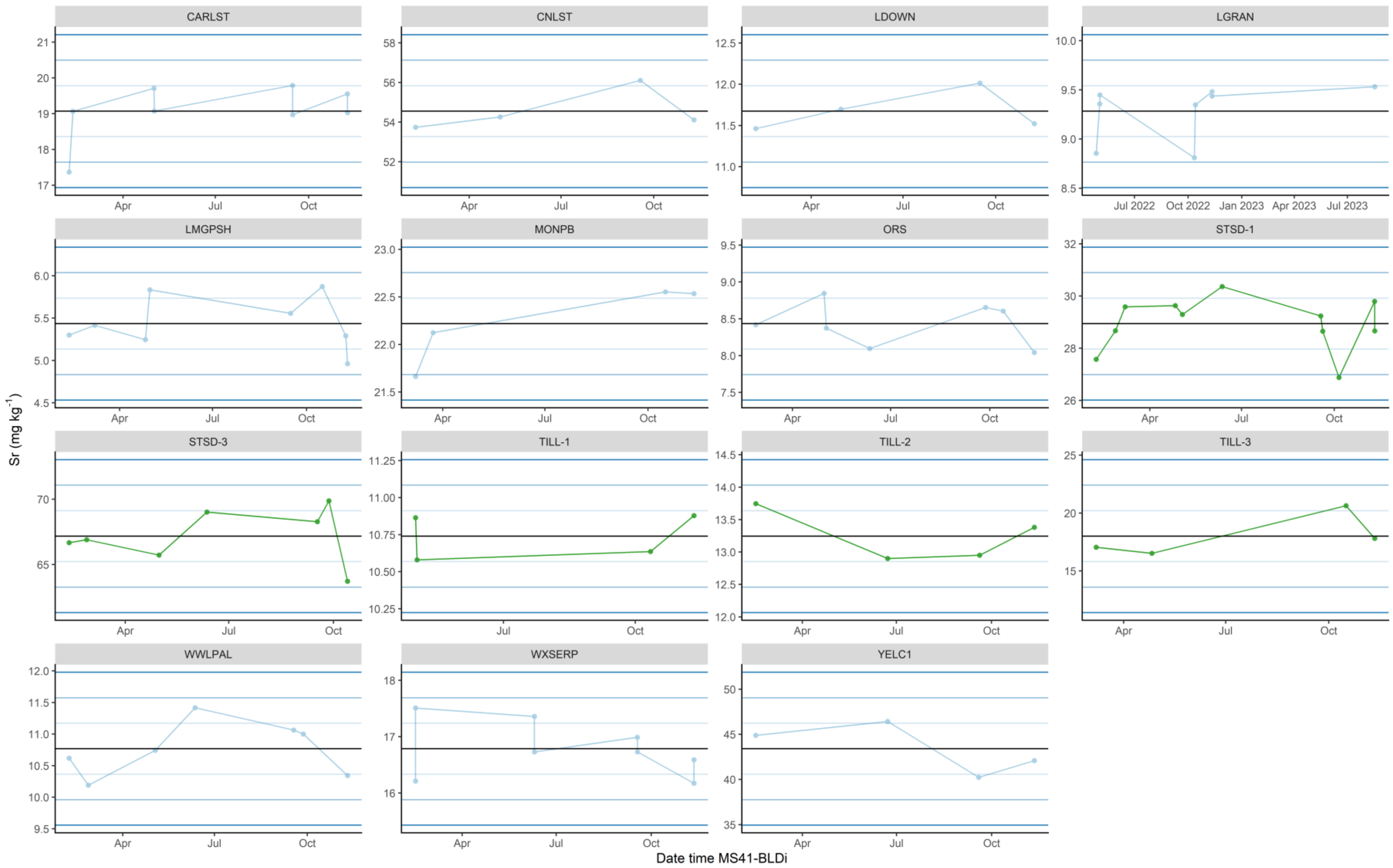
Selenium (Se) sample data IQR: 0.799–1.14 mg kg^{-1}

Tin (Sn) MS41L-BLD

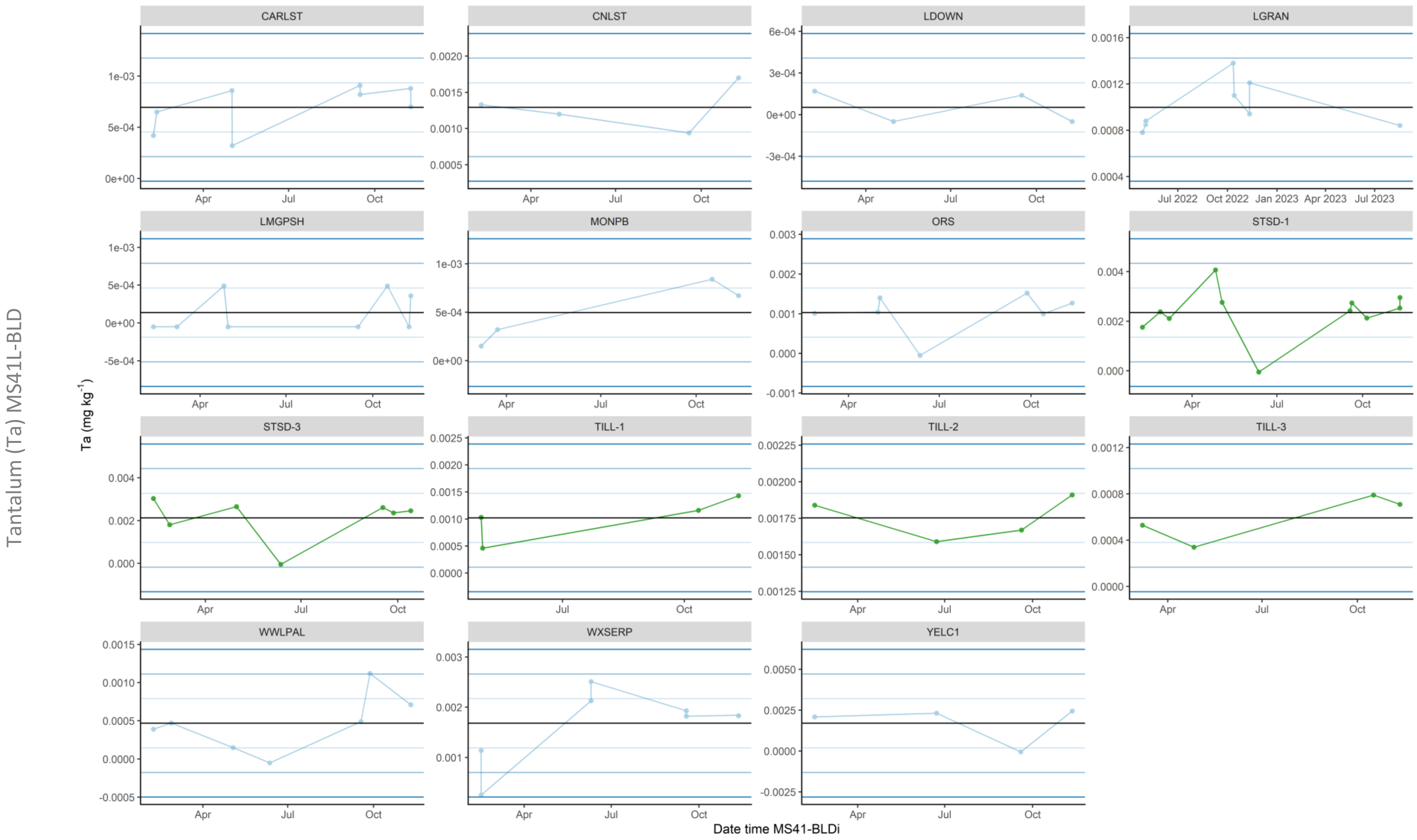


Tin (Sn) sample data IQR: 2.33–9.20 mg kg^{-1}

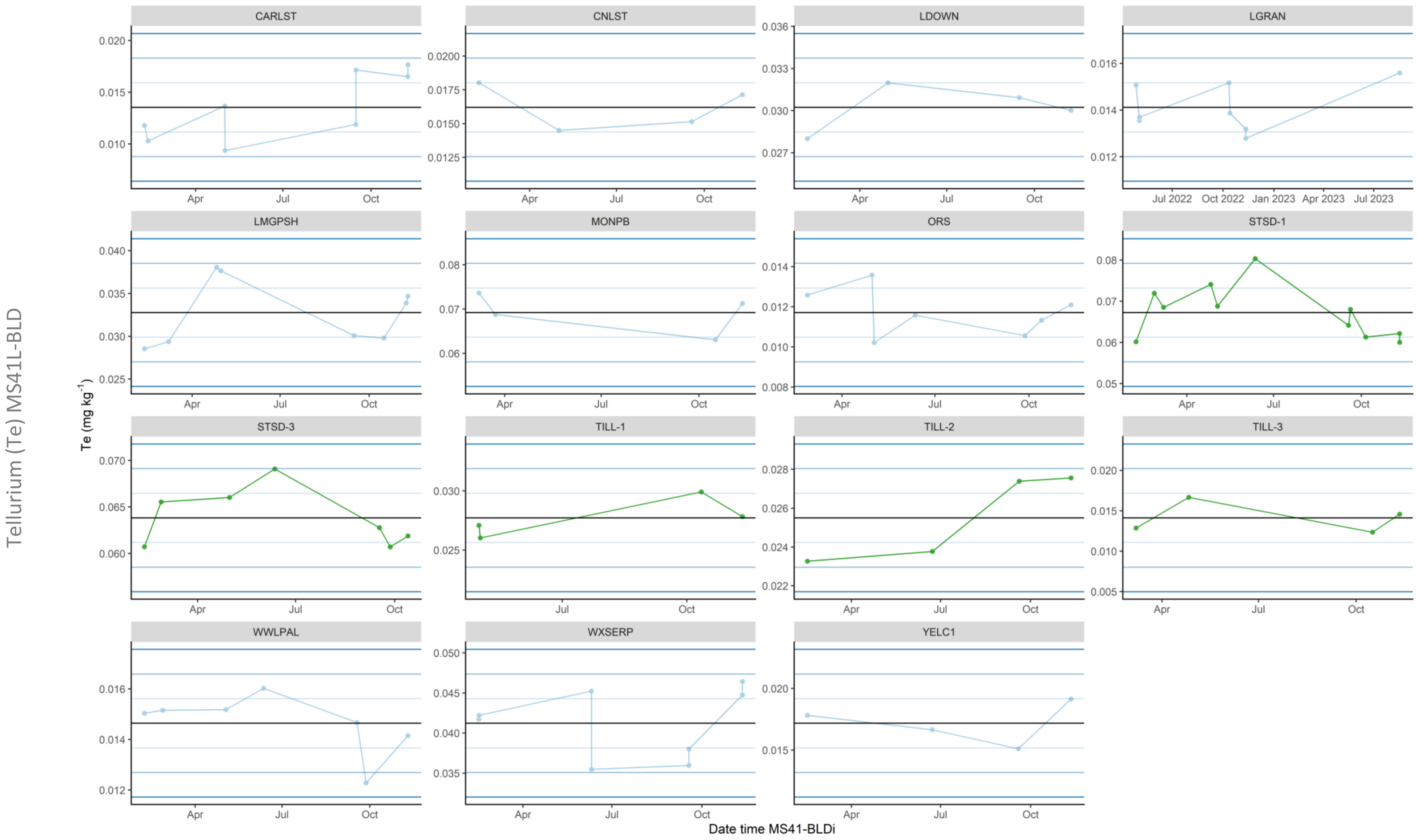
Strontium (Sr) MS41L-BLD



Strontium (Sr) sample data IQR: 59.8–153 mg kg^{-1}

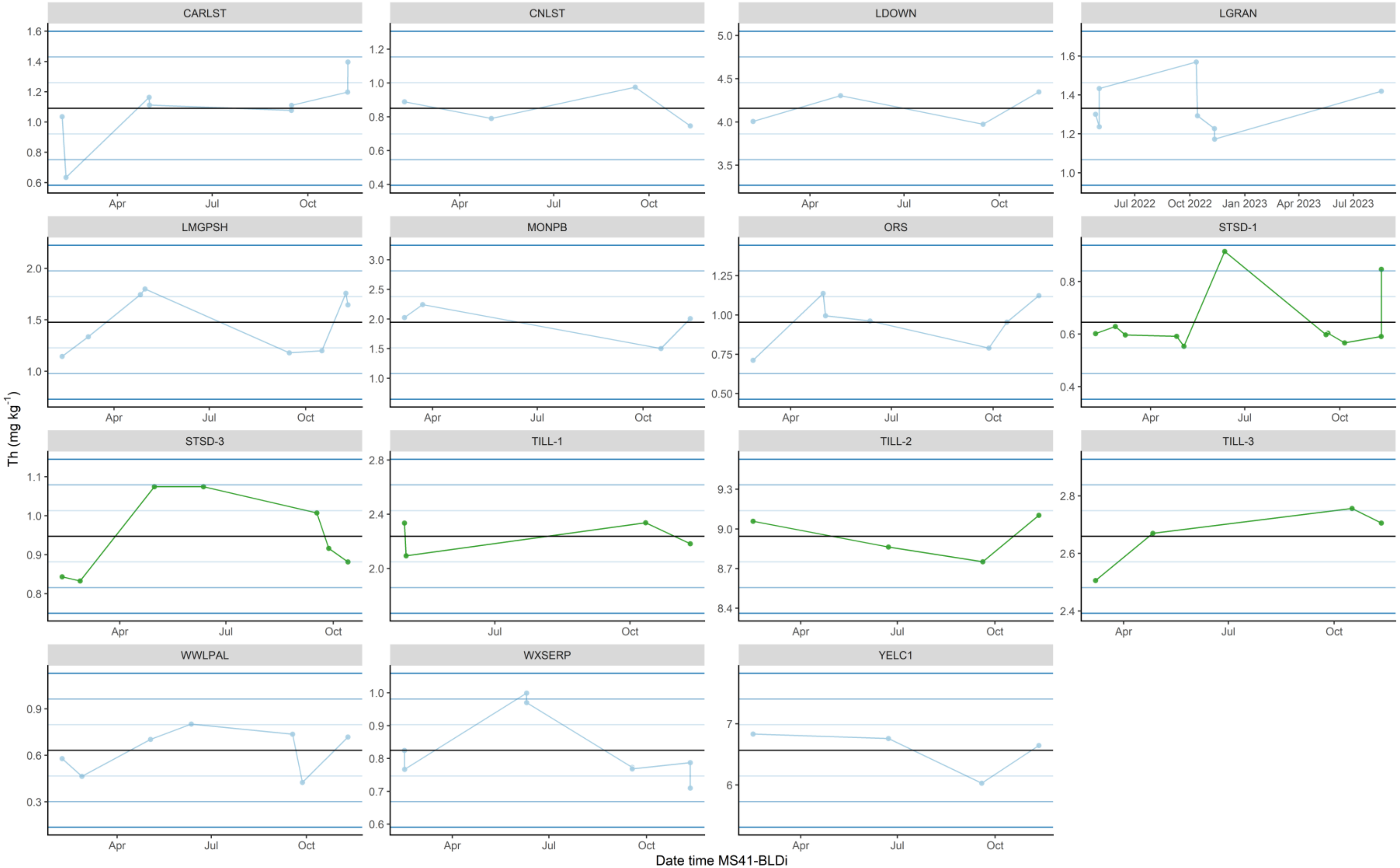


Tantalum (Ta) sample data IQR: 0.00036-0.00092 mg kg^{-1}

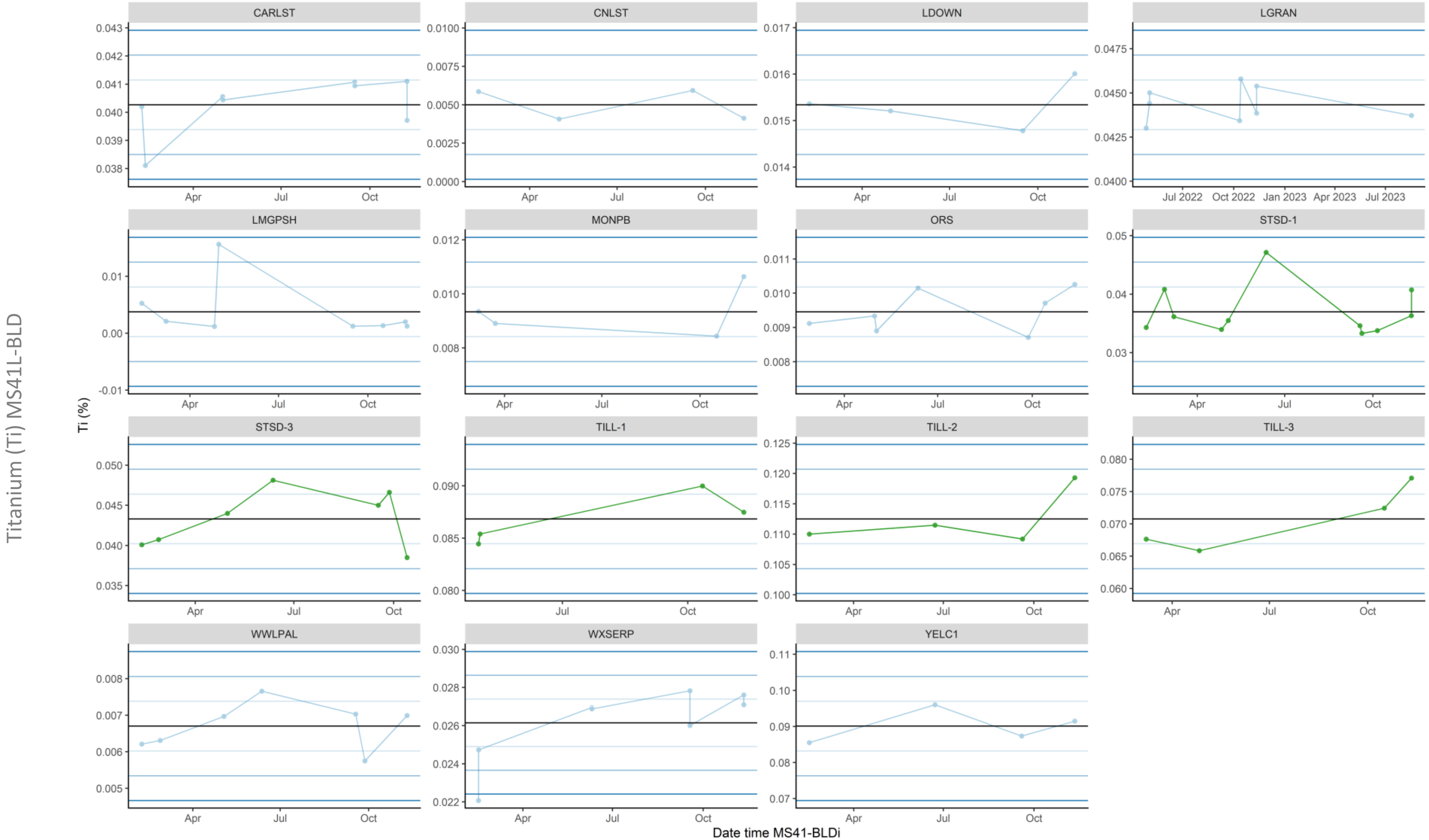


Tellurium (Te) sample data IQR: 0.0263-0.0364 mg kg^{-1}

Thorium (Th) MS41L-BLD

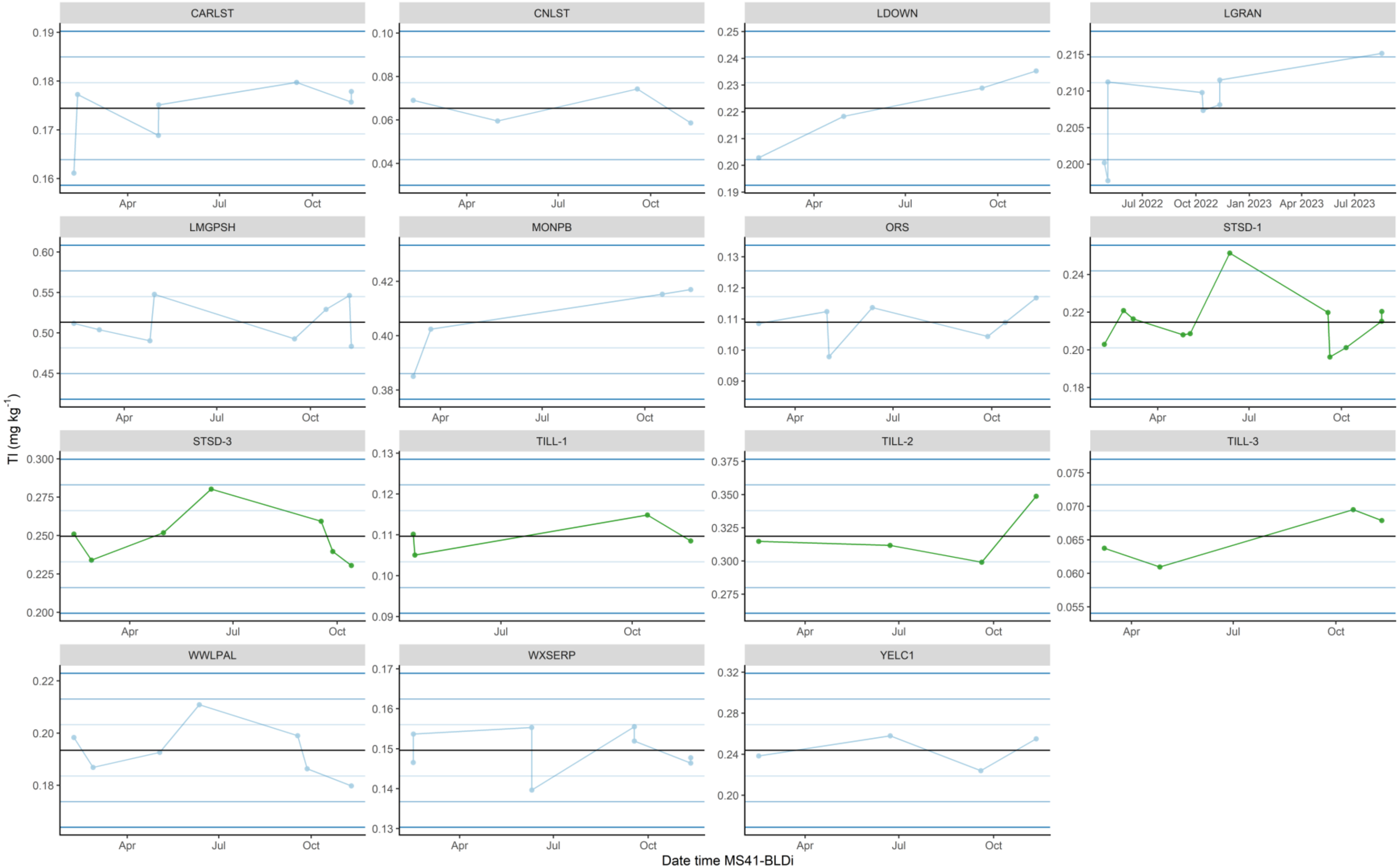


Thorium (Th) sample data IQR: 1.24–1.63 mg kg^{-1}

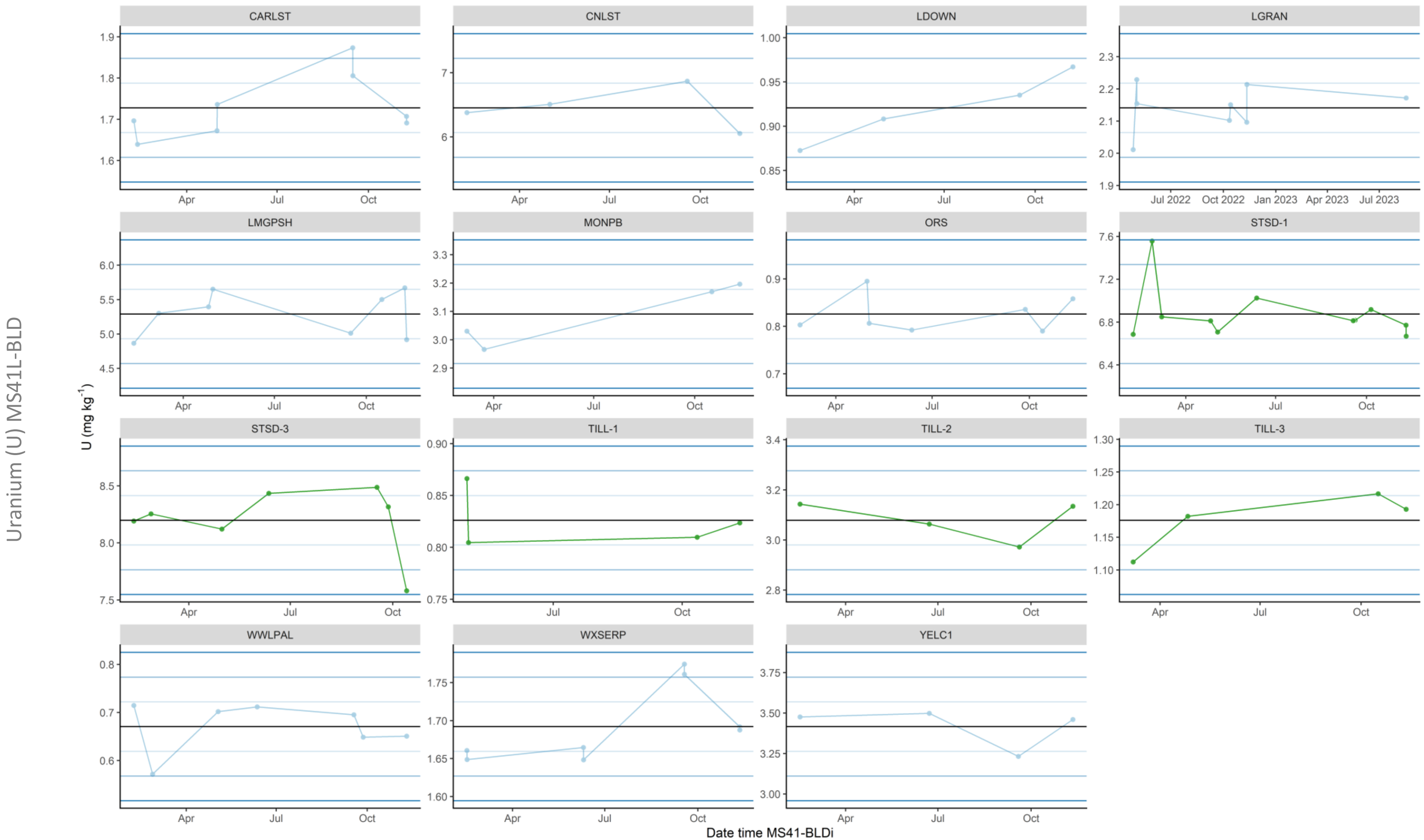


Titanium (Ti) sample data IQR: 0.00408-0.00712 %

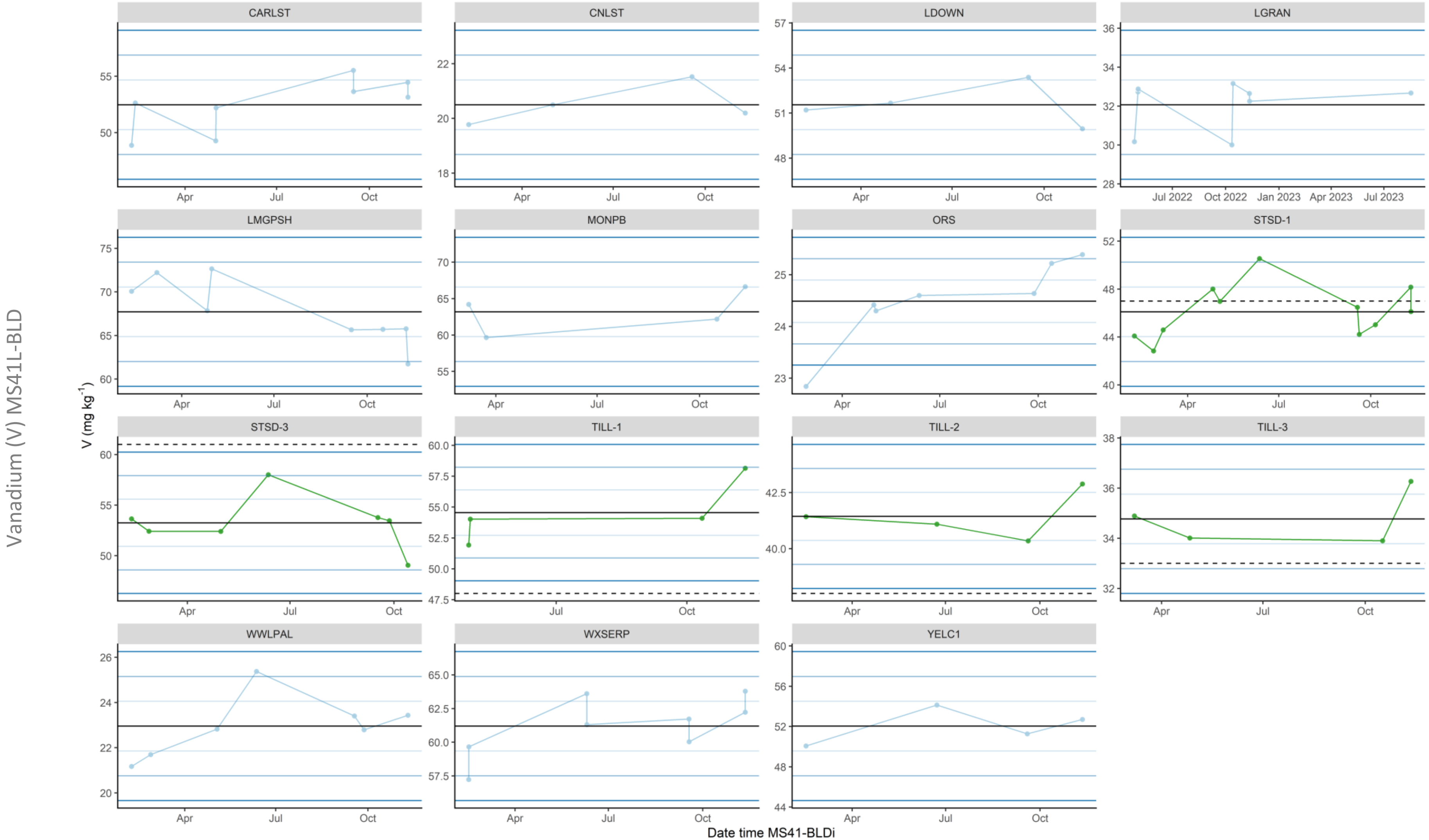
Thallium (Tl) MS41L-BLD



Thallium (Tl) sample data IQR: 0.203–0.251 mg kg^{-1}

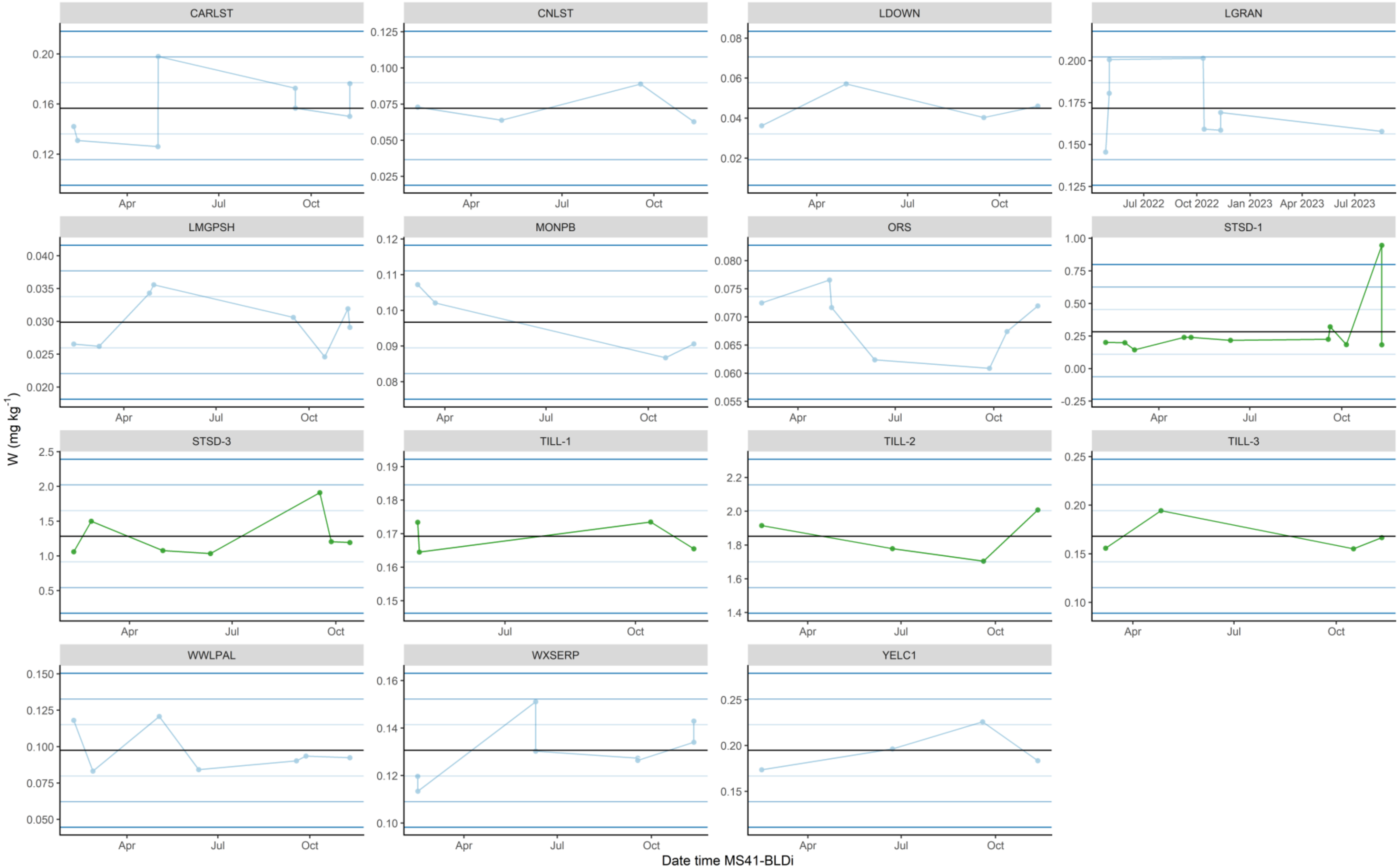


Uranium (U) sample data IQR: 0.825–1.05 mg kg^{-1}



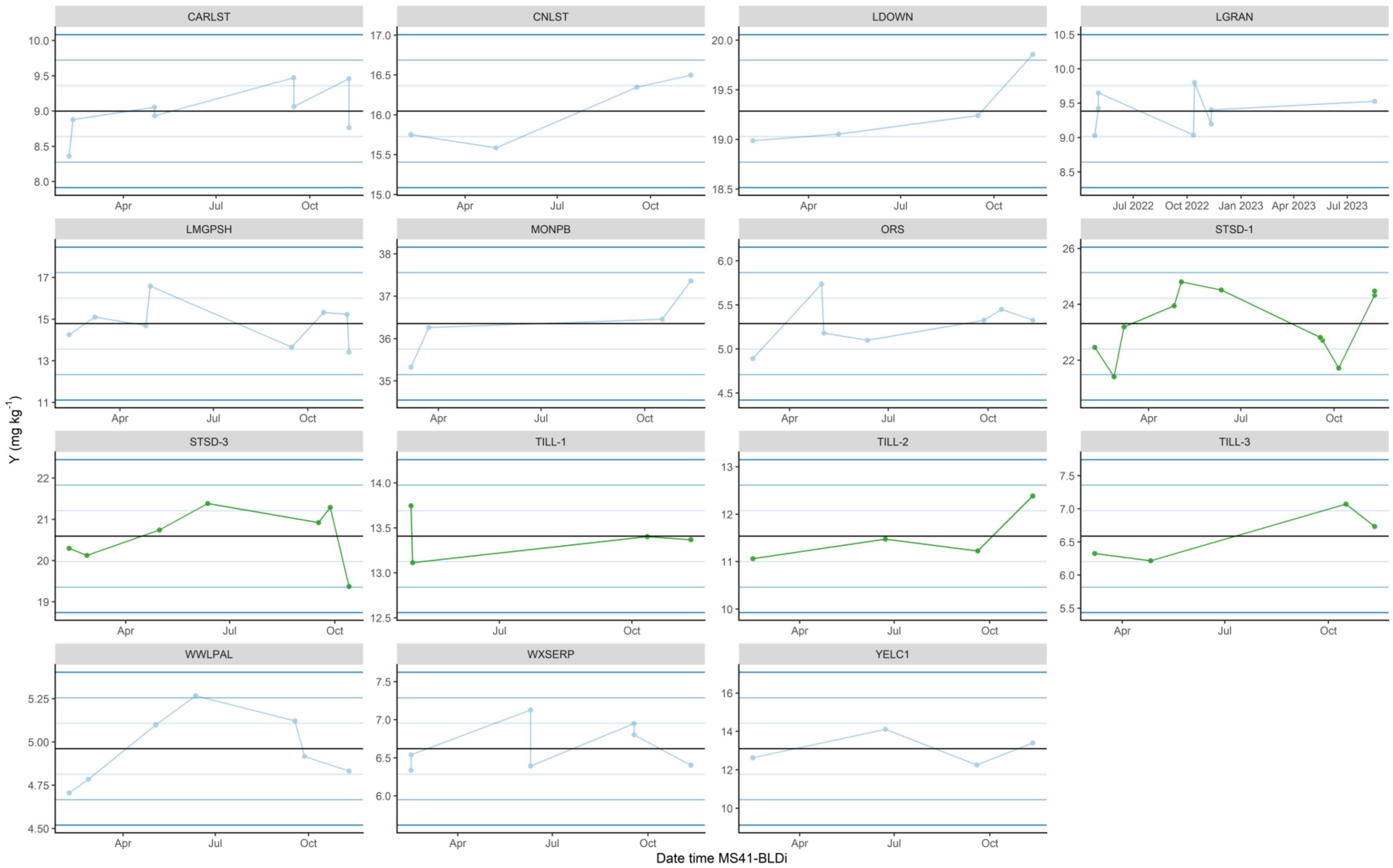
Vanadium (V) sample data IQR: 34.6–42.2 mg kg^{-1}

Tungsten (W) MS41L-BLD



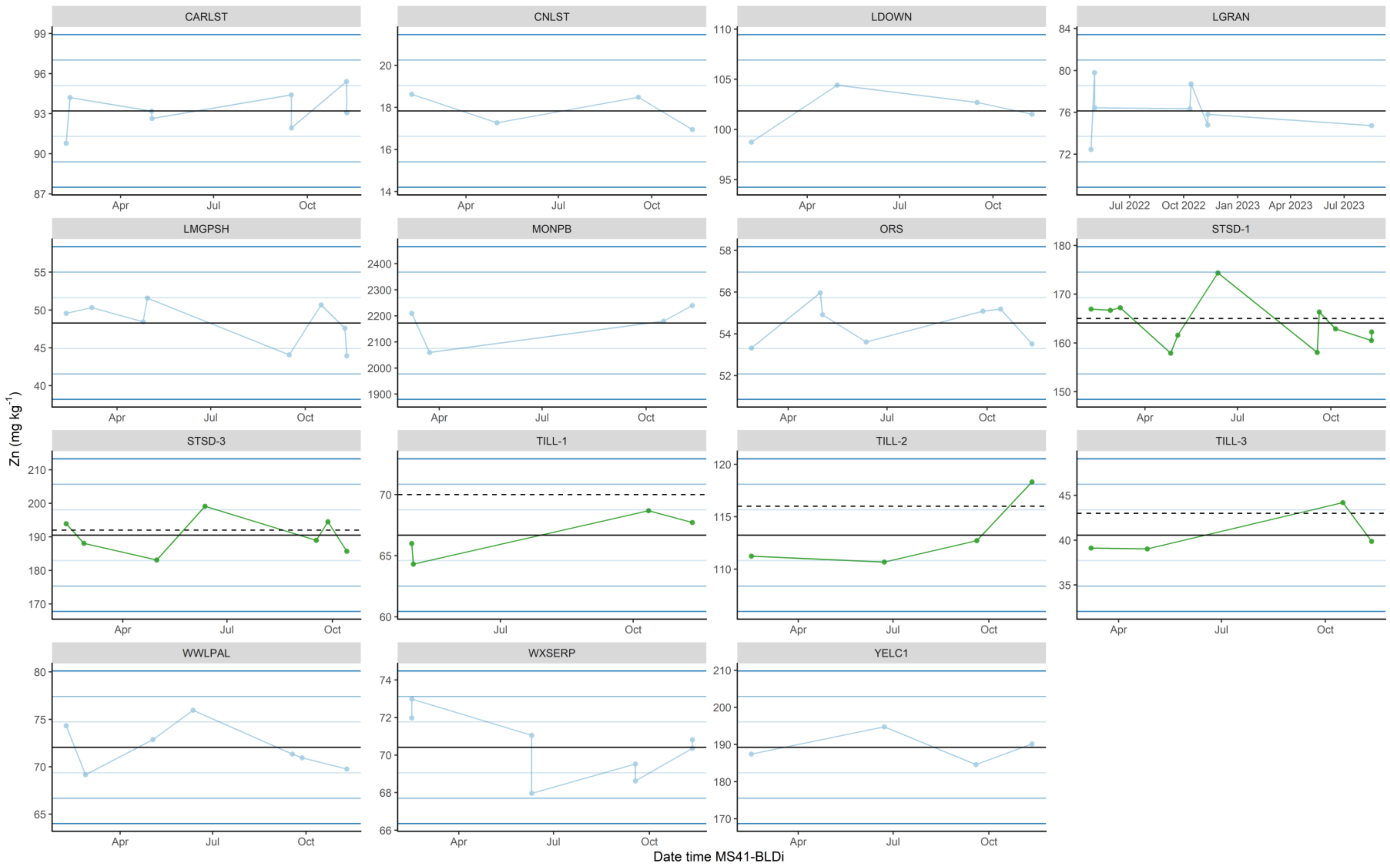
Tungsten (W) sample data IQR: 0.0875-0.159 mg kg^{-1}

Yttrium (Y) MS41L-BLD

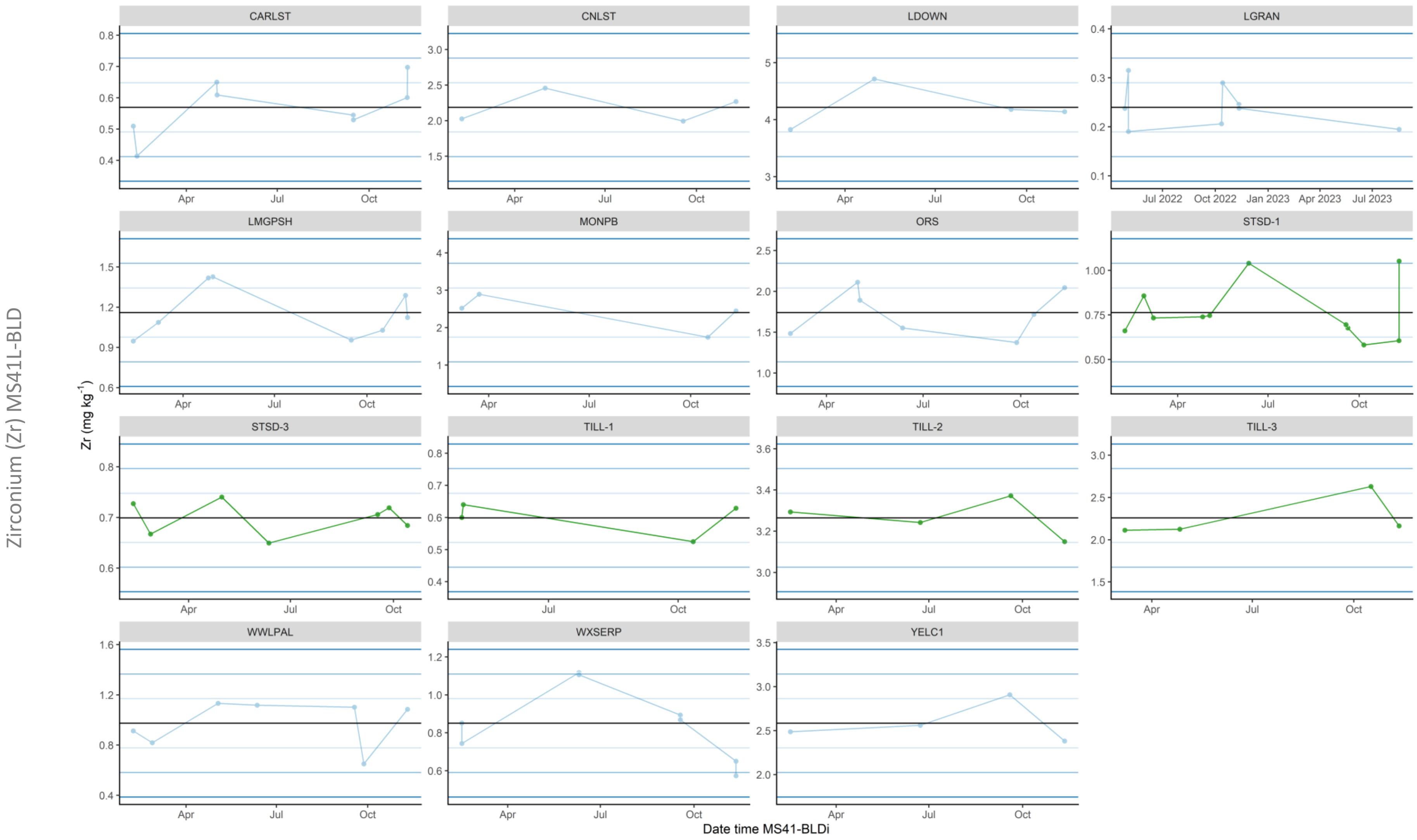


Yttrium (Y) sample data IQR: 14.5–18.0 mg kg^{-1}

Zinc (Zn) MS41L-BLD



Zinc (Zn) sample data IQR: 119–181 mg kg^{-1}



Zirconium (Zr) sample data IQR: 2.67–3.59 mg kg^{-1}

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

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

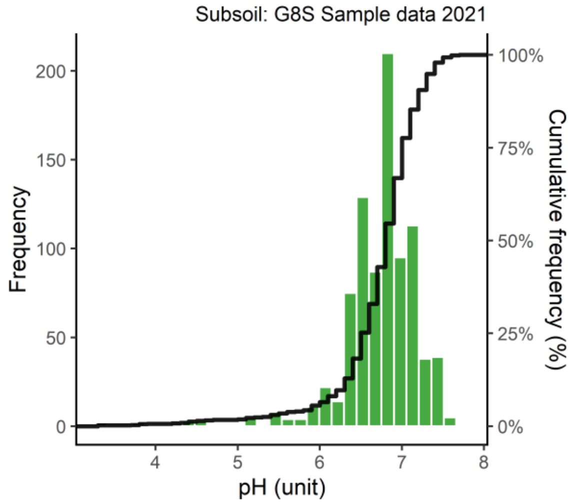
- The first chart (left) is the combined cumulative frequency and histogram. The histogram frequency (y axis left) and the cumulative frequency % (y axis right) are plotted against the analyte concentration (x axis).
- The second chart (right) is the same but data are log_{10} transformed (an exception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

These data are censored: all “<LLD” values have been replaced with 0.5*”LLD”. ICPar data are from the MS41-BLD dataset. Concentration units are shown in parentheses.

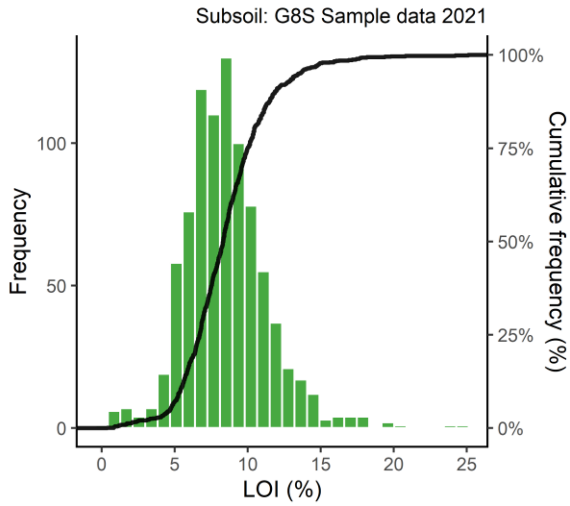
Typically a log transformation results in a less skewed distribution, and geochemical data are broadly log-normal. Censored data will sometimes display as an isolated histogram bar away from the normal data population above the LLD.

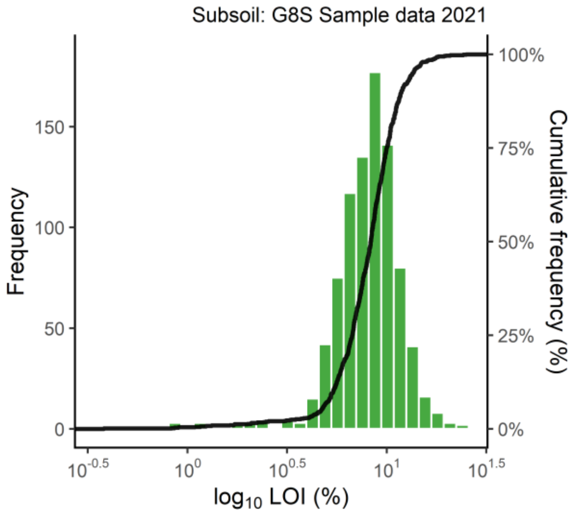
pH and LOI sample site data

Soil pH ($CaCl_2$)



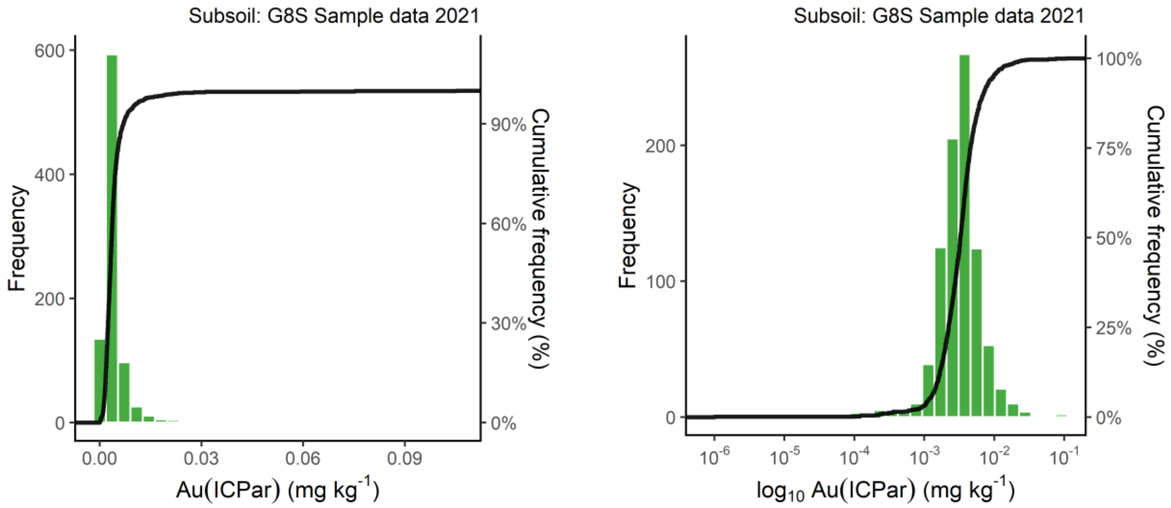
Soil loss-on-ignition (at 450C) %



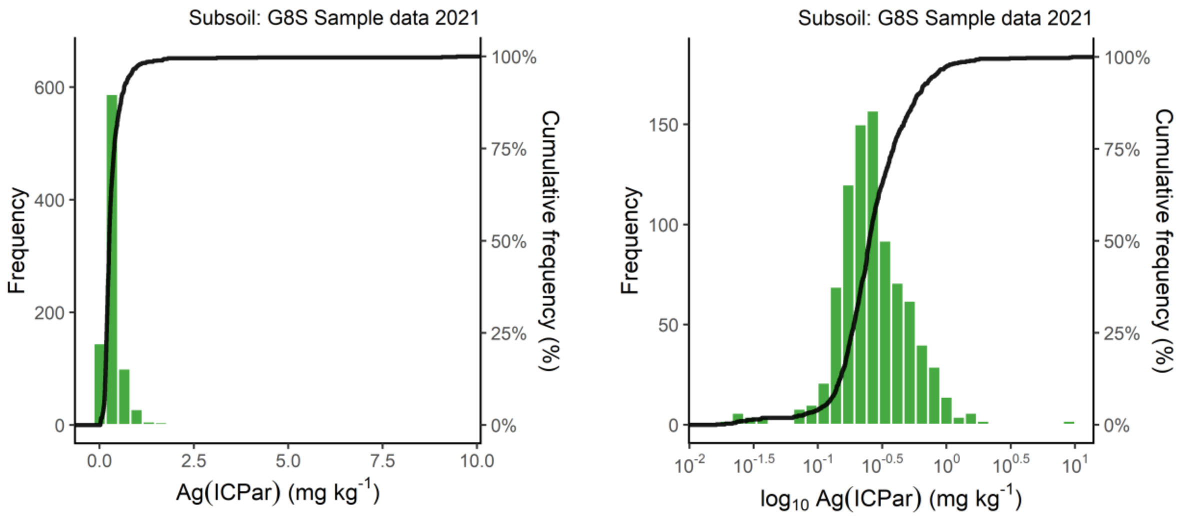


ICP$_{ar}$ sample site data

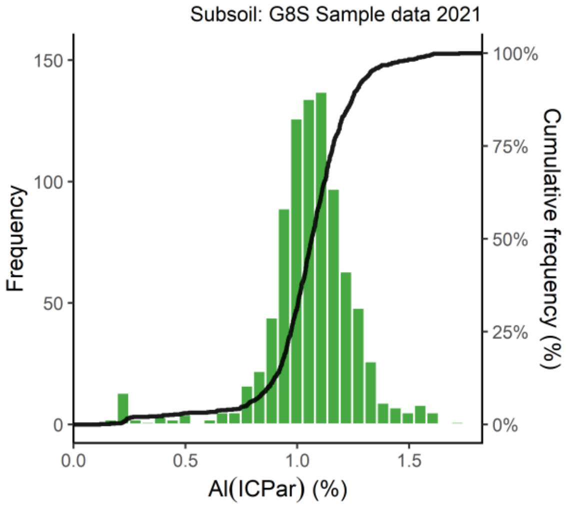
Gold (Au) ICP$_{ar}$

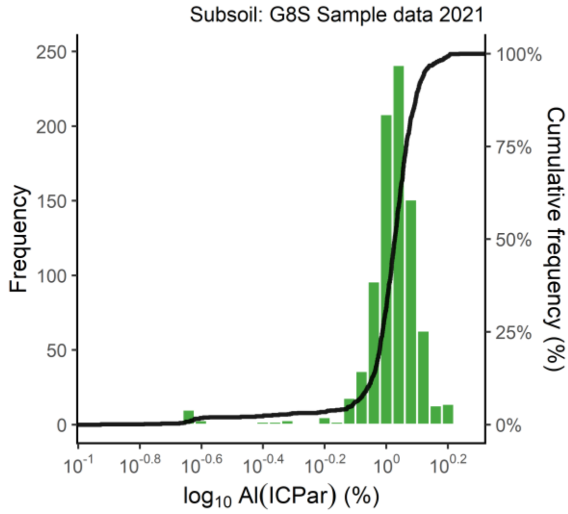


Silver (Ag) ICP$_{ar}$

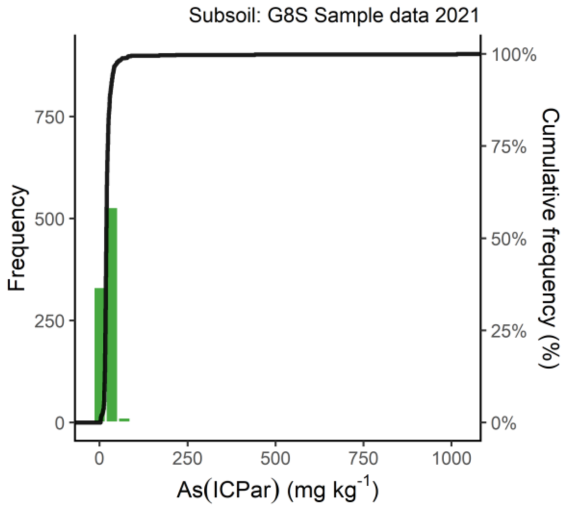


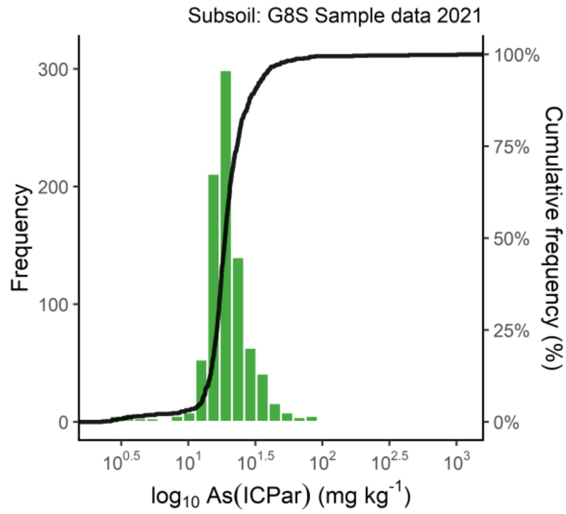
Aluminium (Al) ICP_{ar}



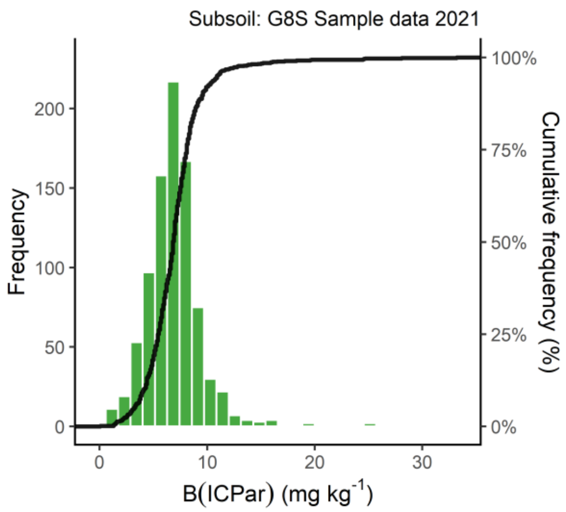


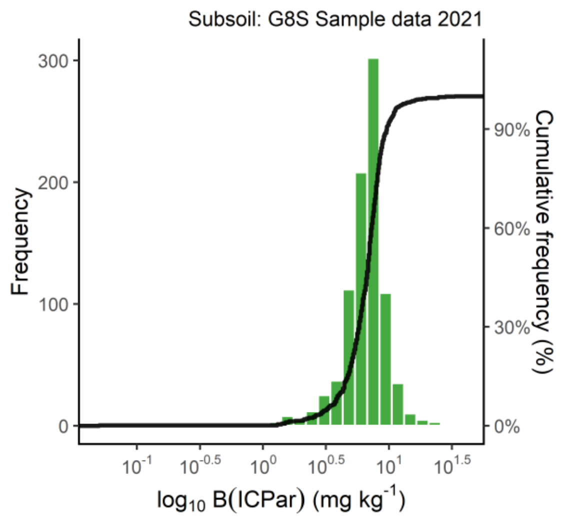
Arsenic (As) ICP_{ar}



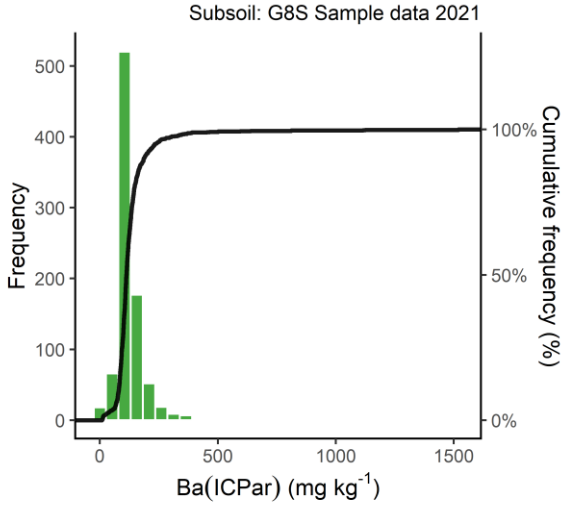


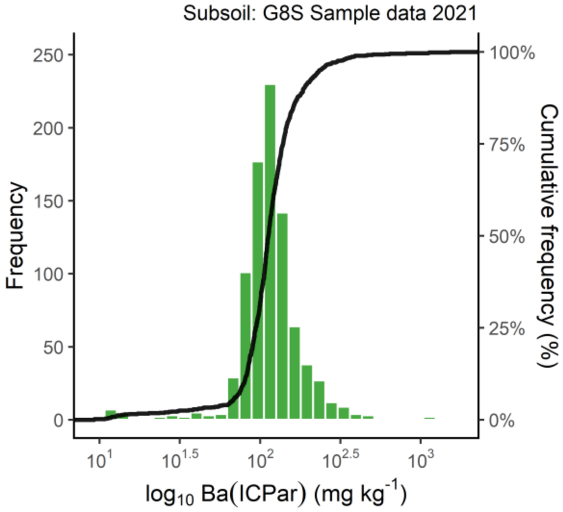
Boron (B) ICP_{ar}



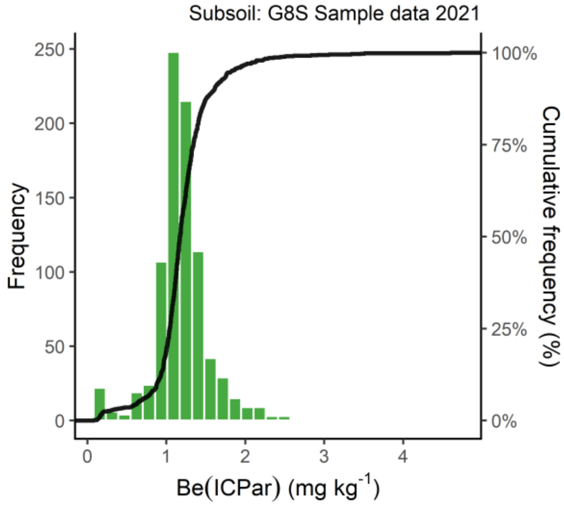


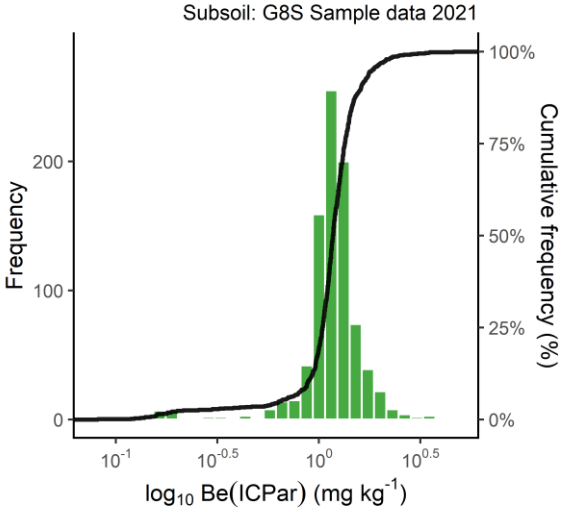
Barium (Ba) ICP_{ar}



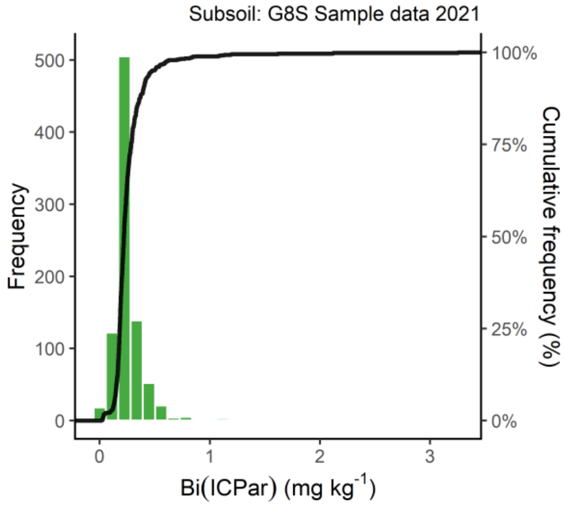


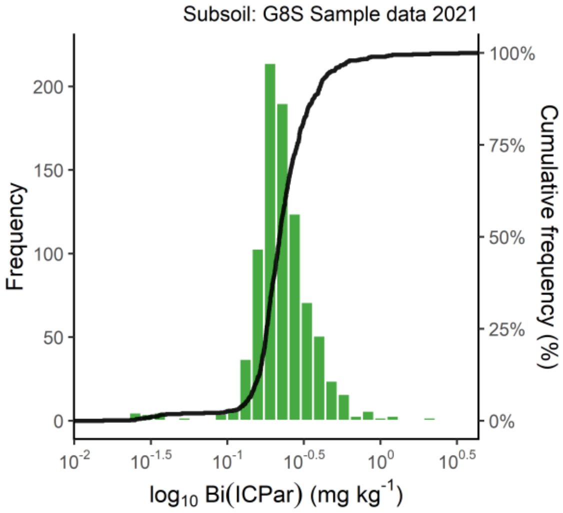
Beryllium (Be) ICP_{ar}



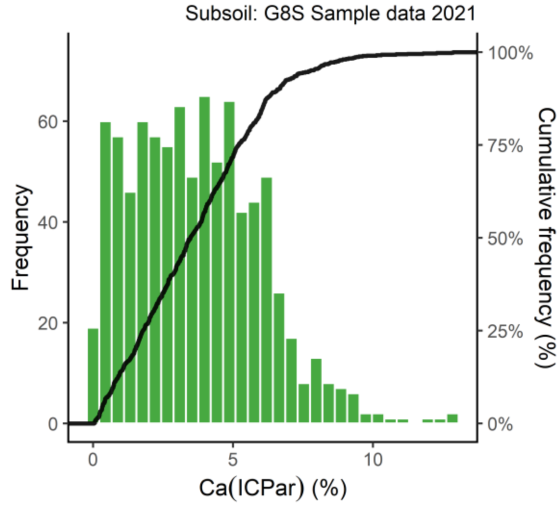


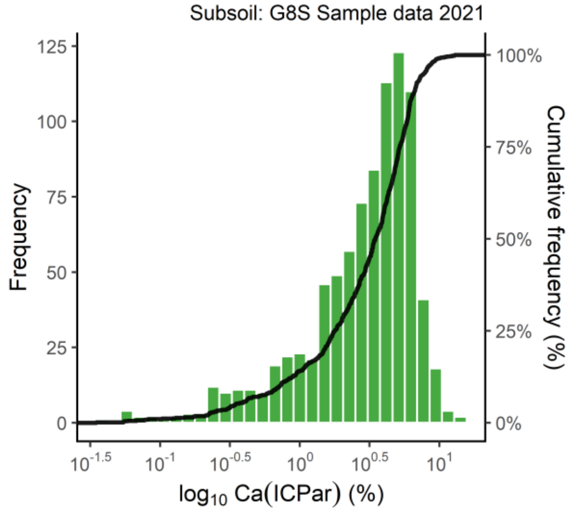
Bismuth (Bi) ICP_{ar}



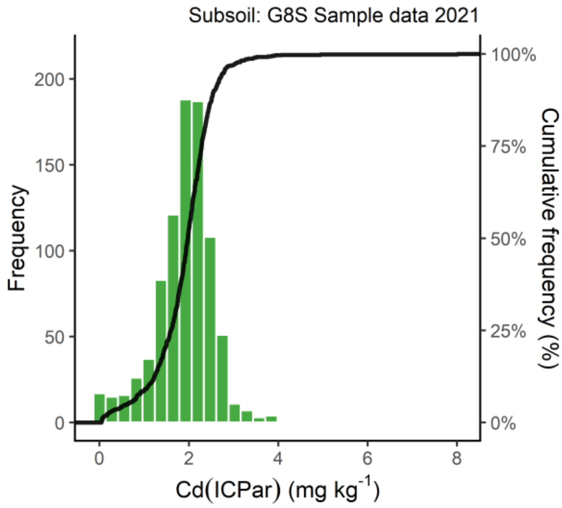


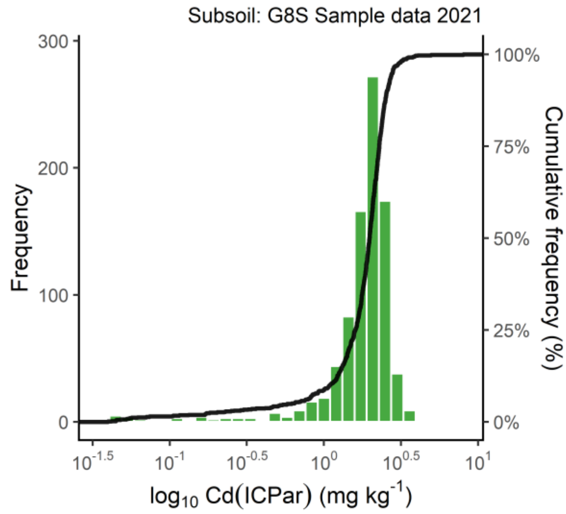
Calcium (Ca) ICPar



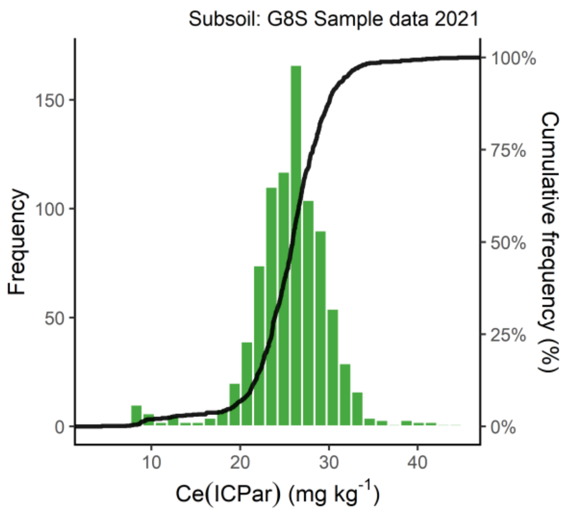


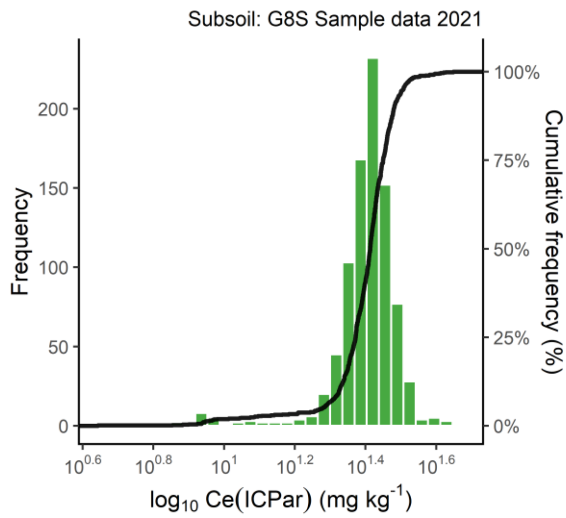
Cadmium (Cd) ICPar



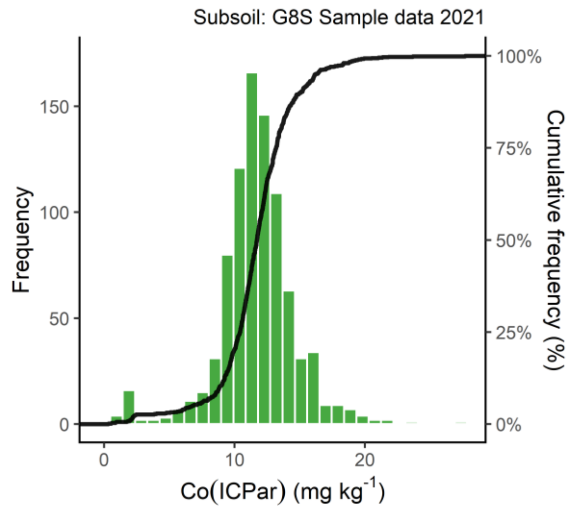


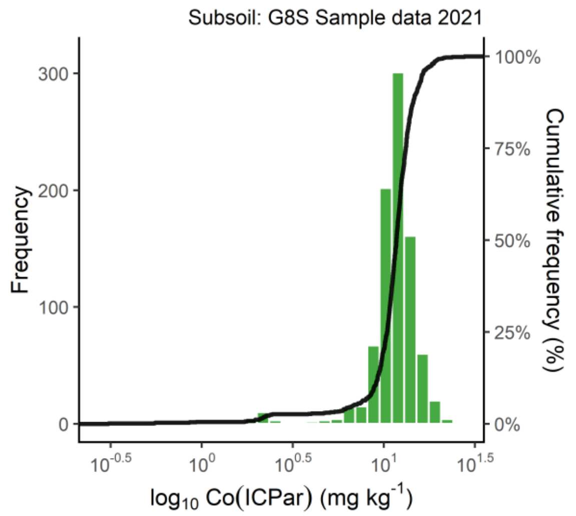
Cerium (Ce) ICPar



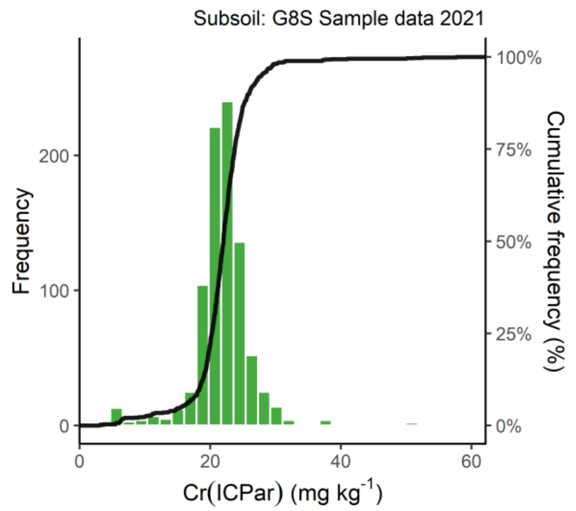


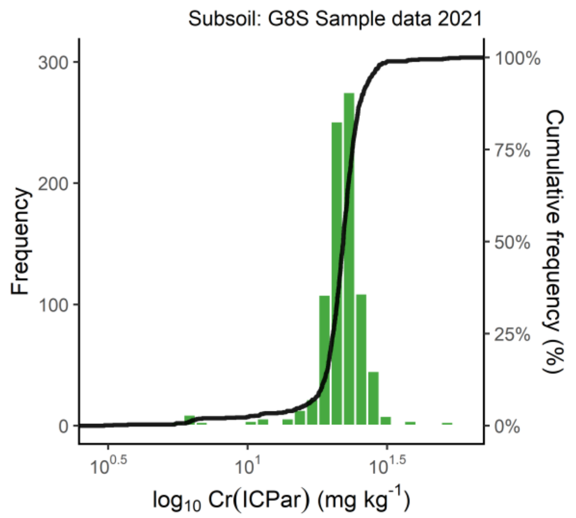
Cobalt (Co) ICP_{ar}



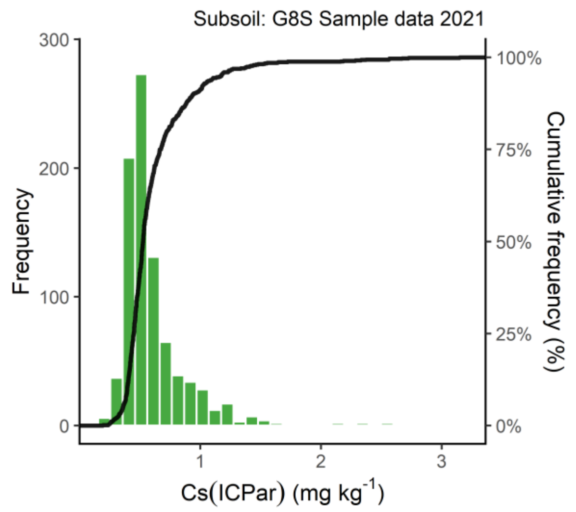


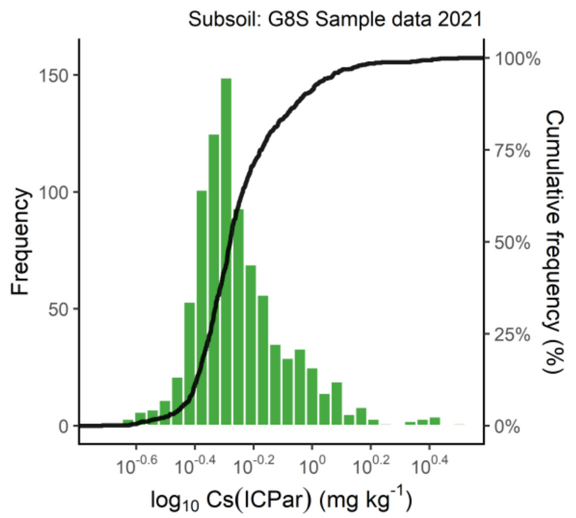
Chromium (Cr) ICP_{ar}



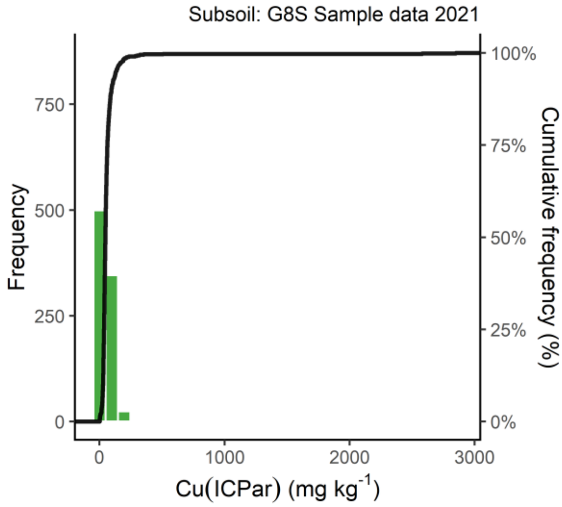


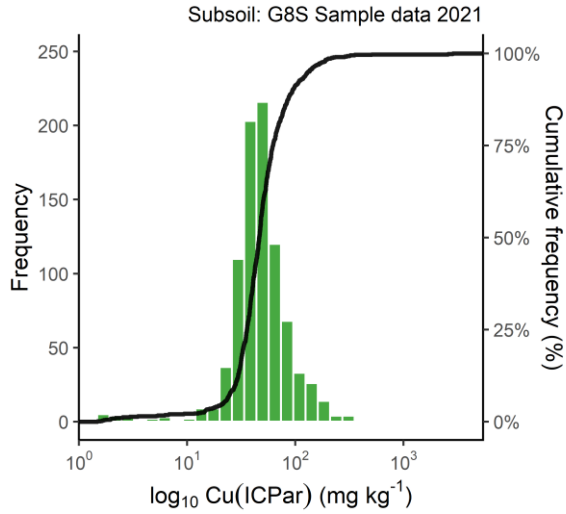
Caesium (Cs) ICP_{ar}



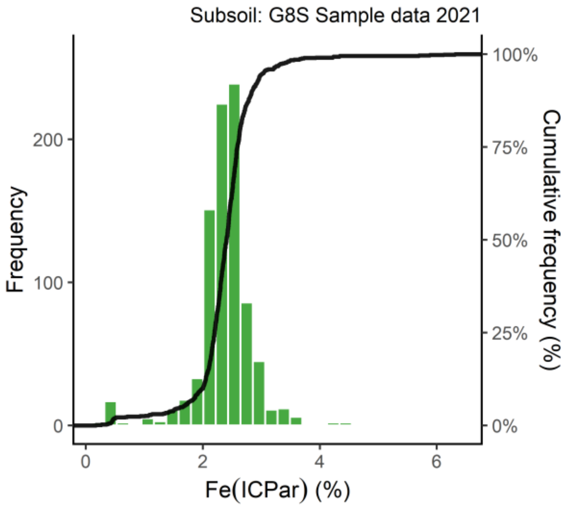


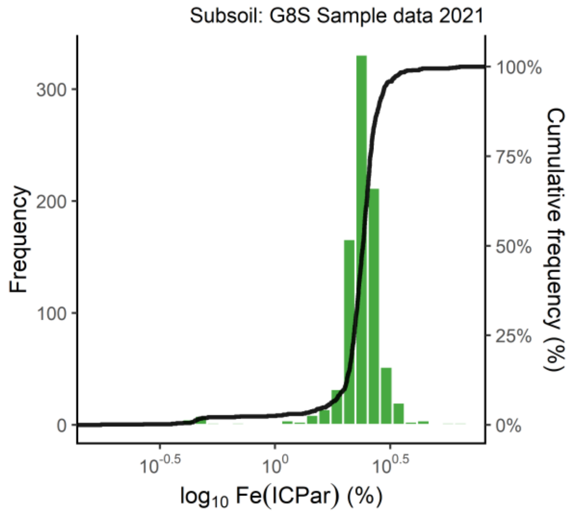
Copper (Cu) ICP$_{ar}$



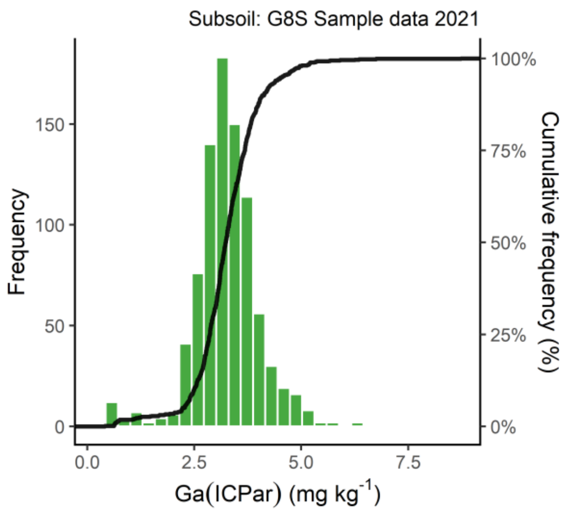


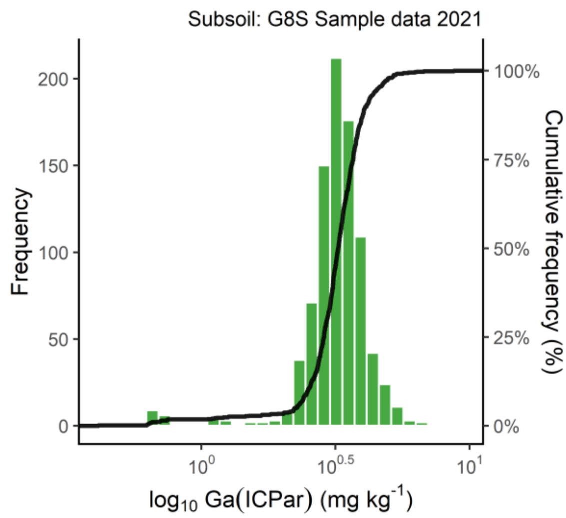
Iron (Fe) ICP$_{ar}$



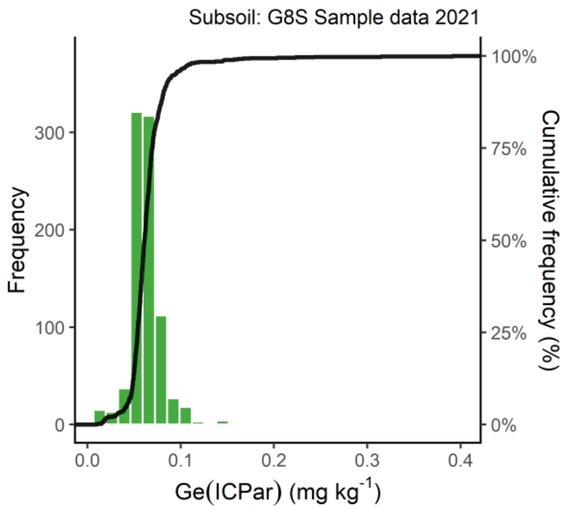


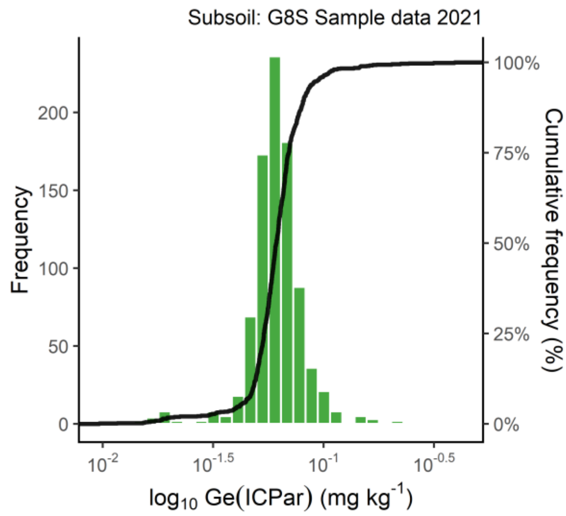
Gallium (Ga) ICP$_{ar}$



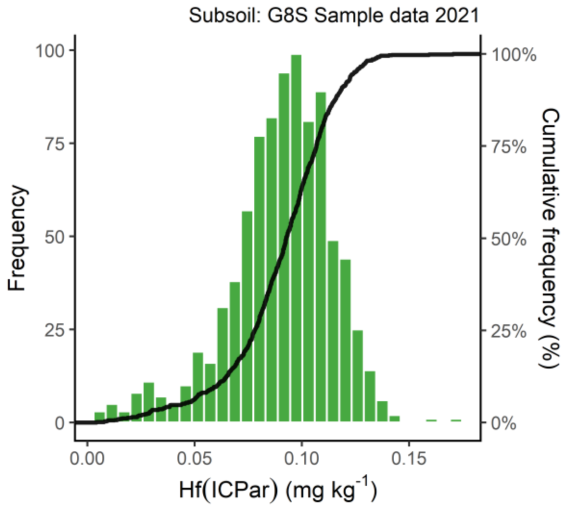


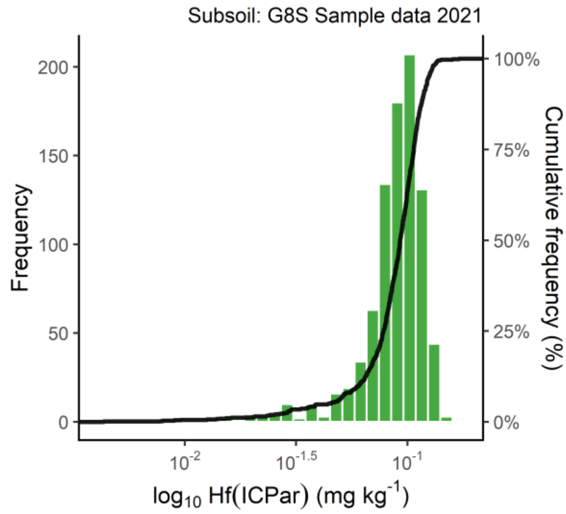
Germanium (Ge) ICP$_{ar}$



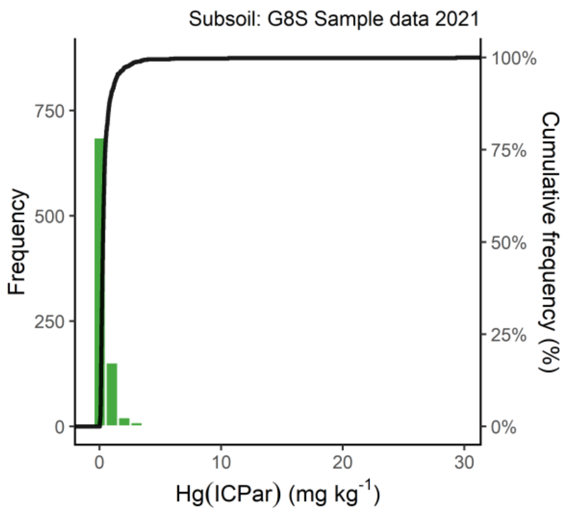


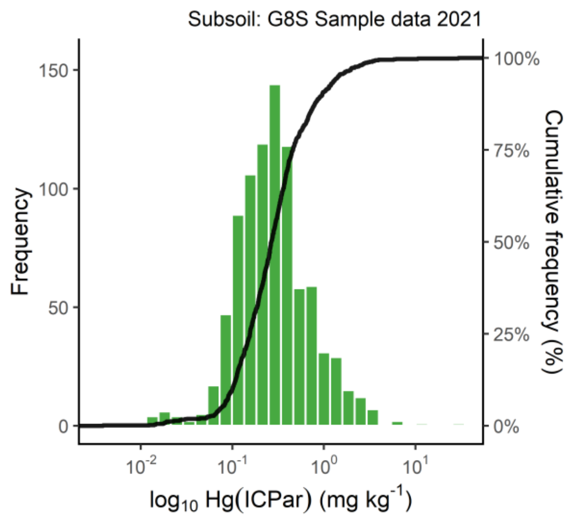
Hafnium (Hf) ICP$_{ar}$



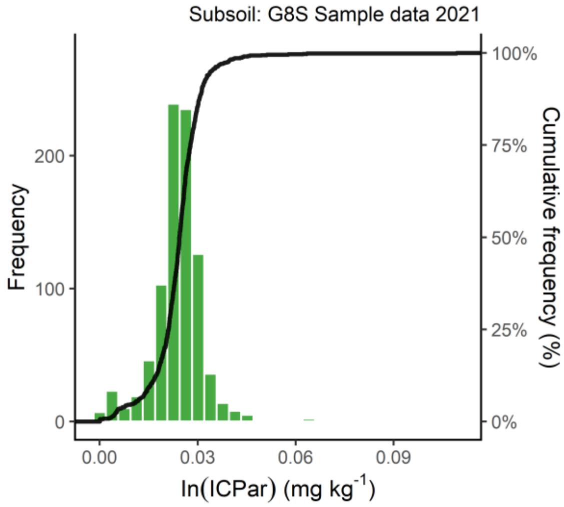


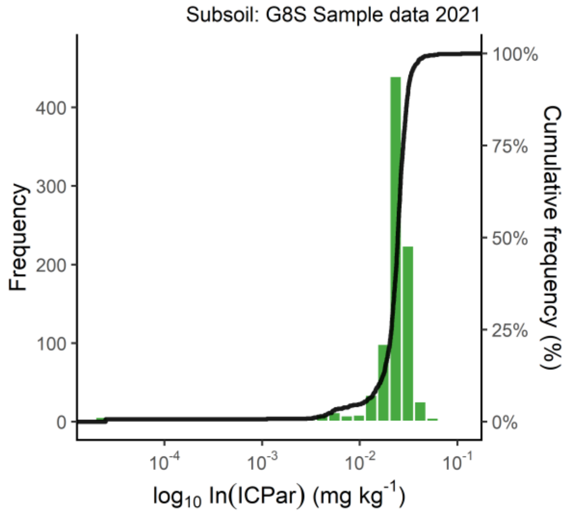
Mercury (Hg) ICP$_{ar}$



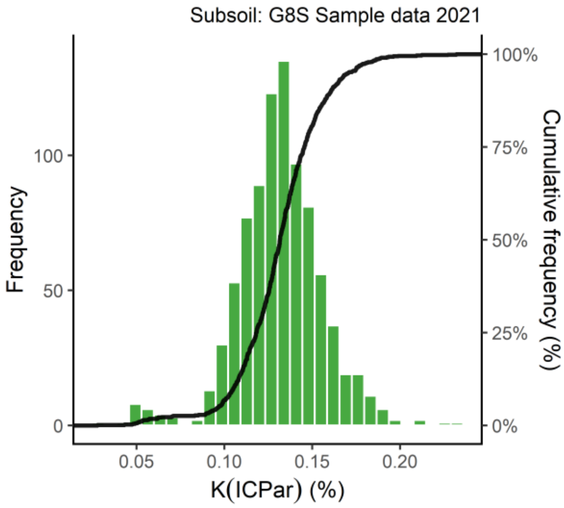


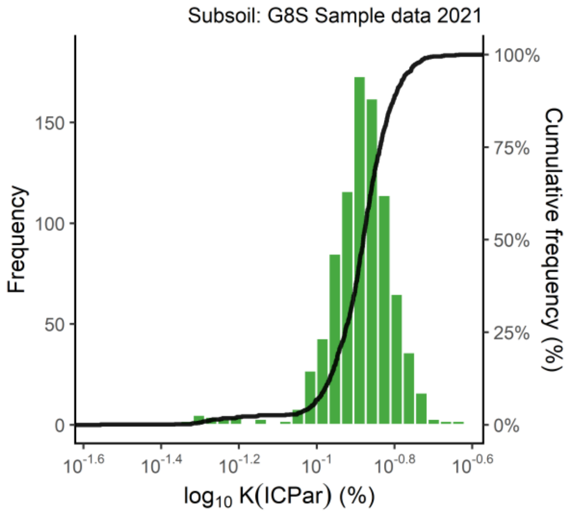
Indium (In) ICP_{ar}



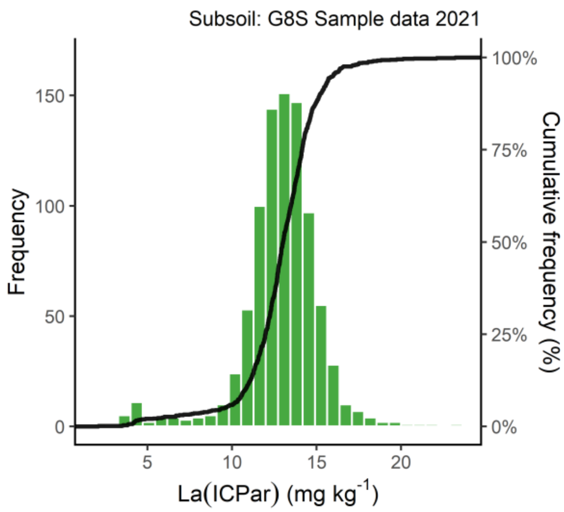


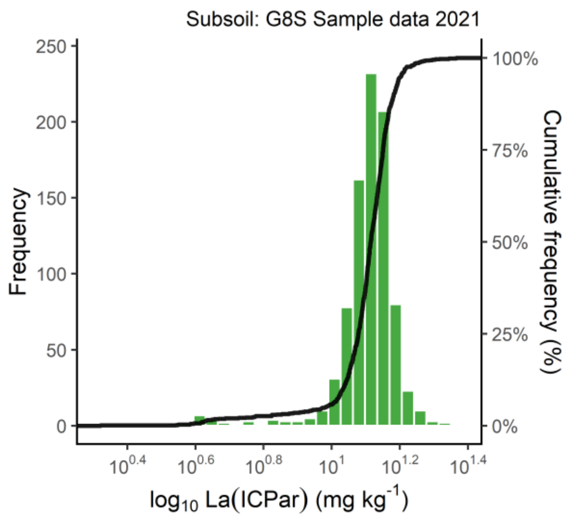
Potassium (K) ICP_{ar}



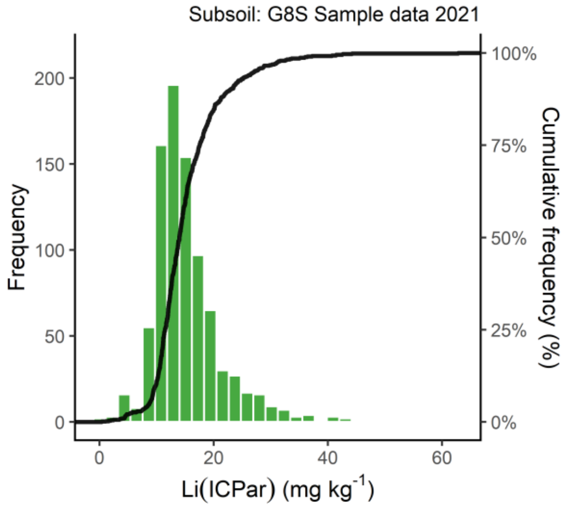


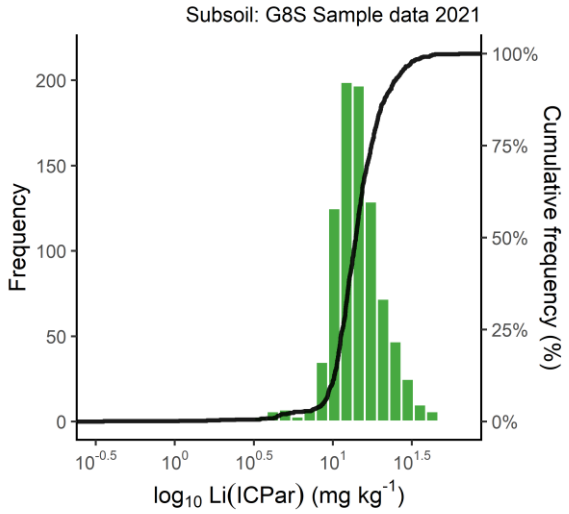
Lanthanum (La) ICP_{ar}



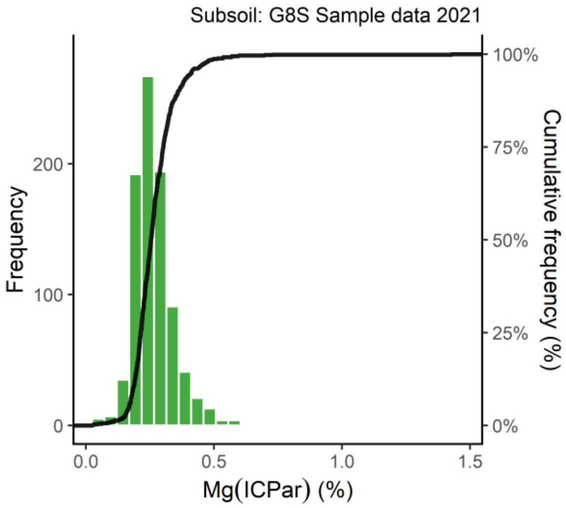


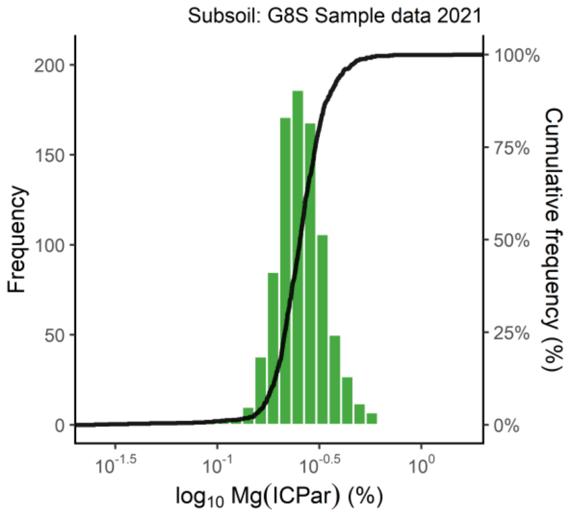
Lithium (Li) ICP_{ar}



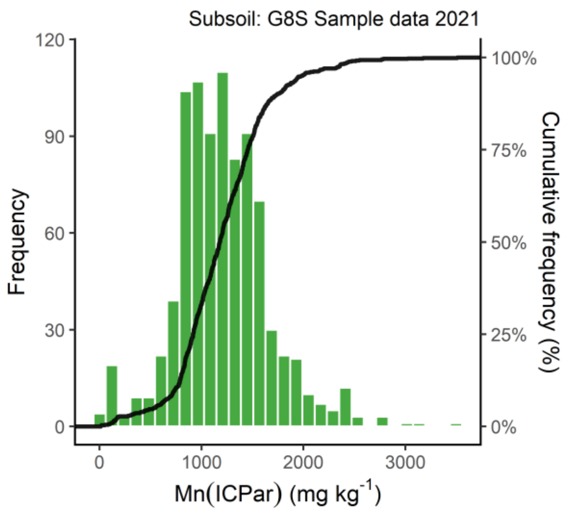


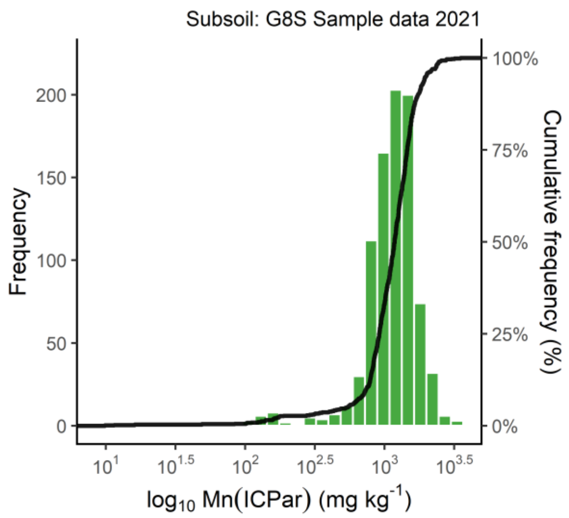
Magnesium (Mg) ICP_{ar}



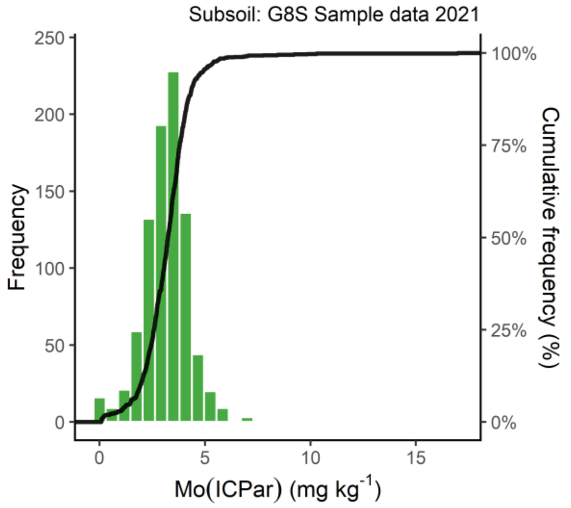


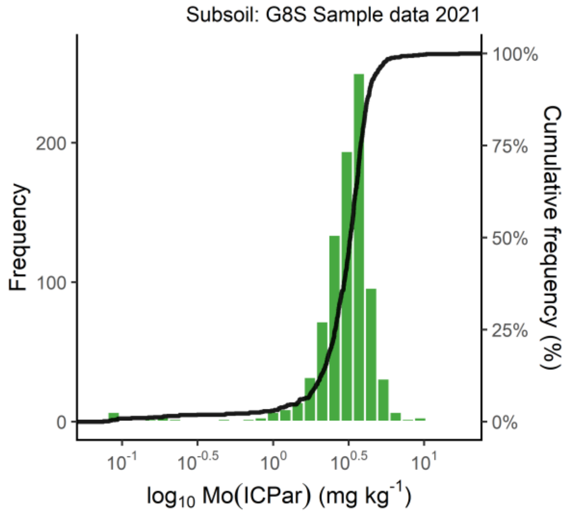
Manganese (Mn) ICP_{ar}



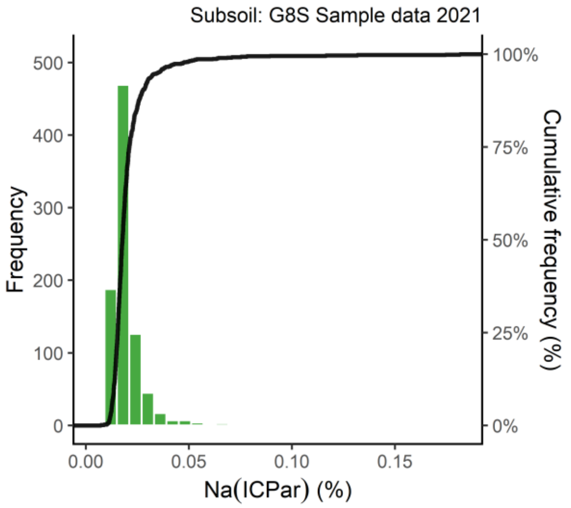


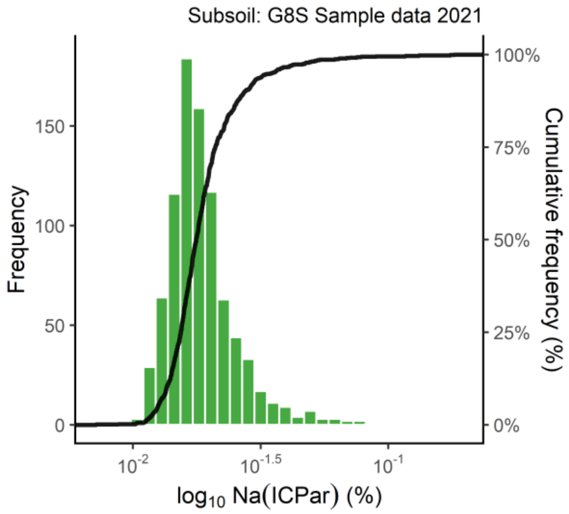
Molybdenum (Mo) ICPar



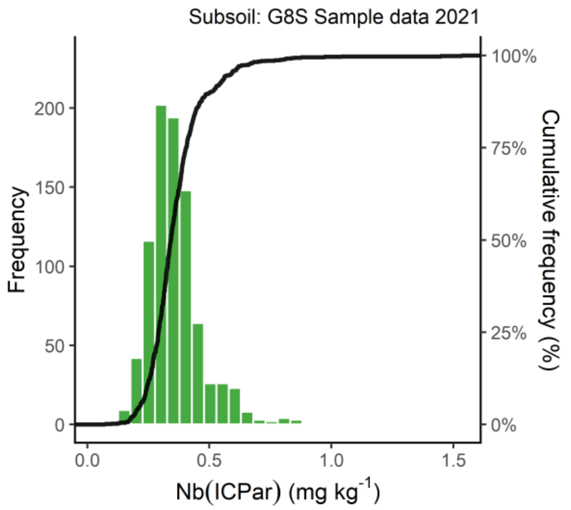


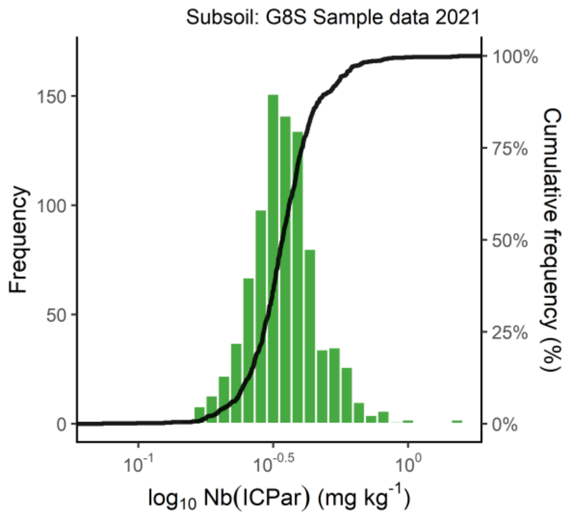
Sodium (Na) ICPar



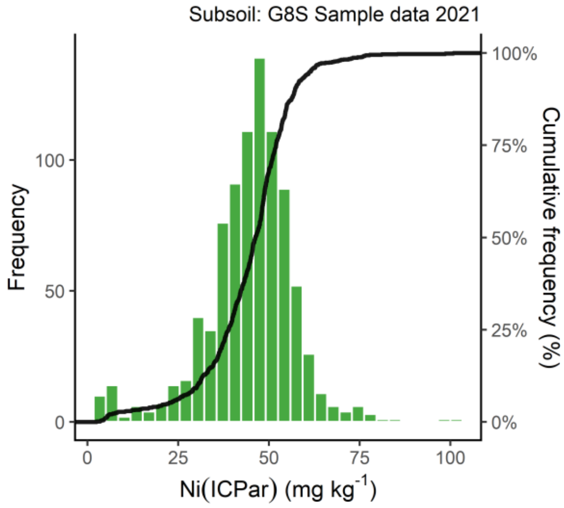


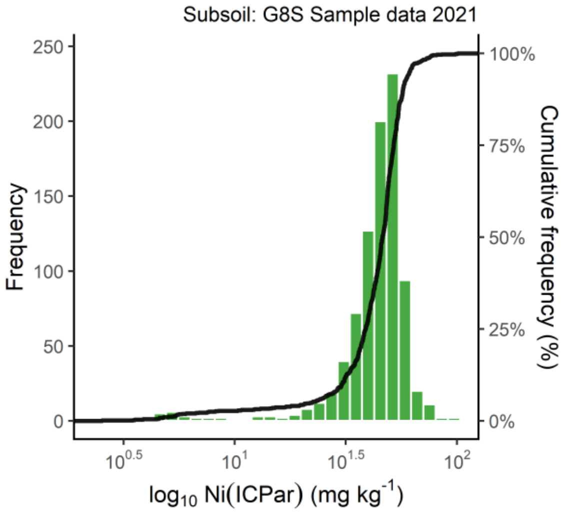
Niobium (Nb) ICPar



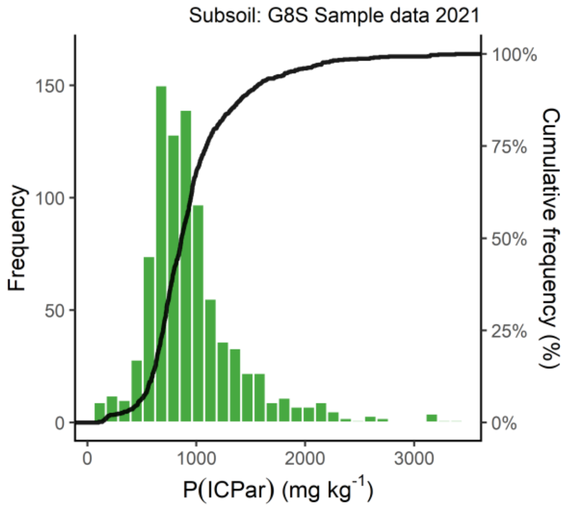


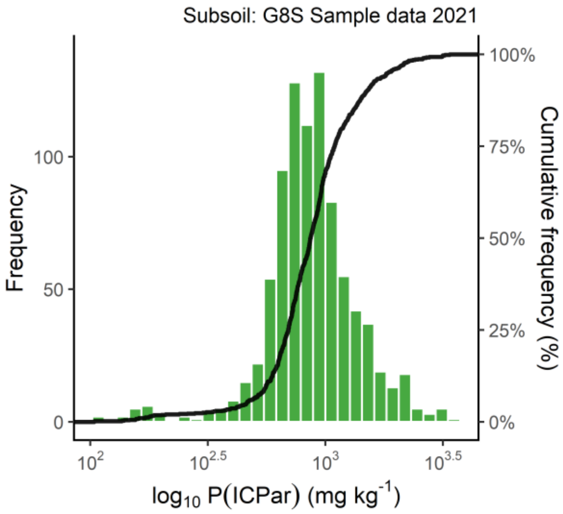
Nickel (Ni) ICP_{ar}



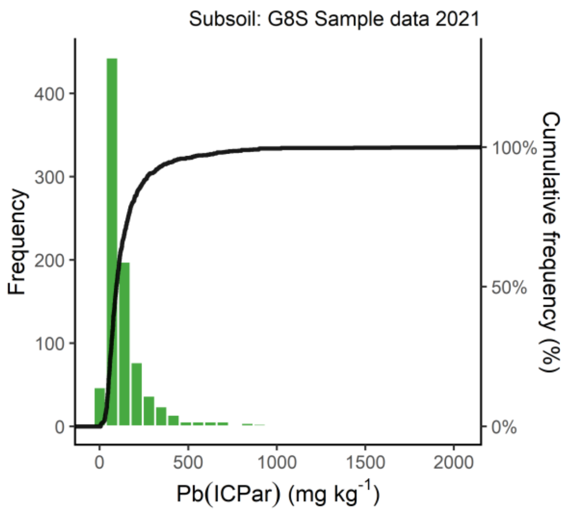


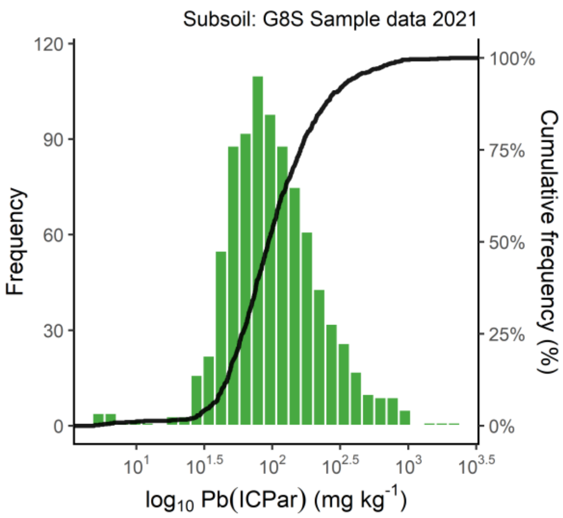
Phosphorus (P) ICP_{ar}



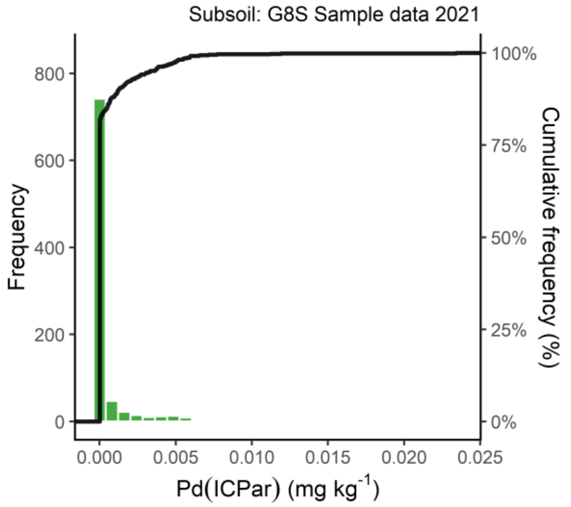


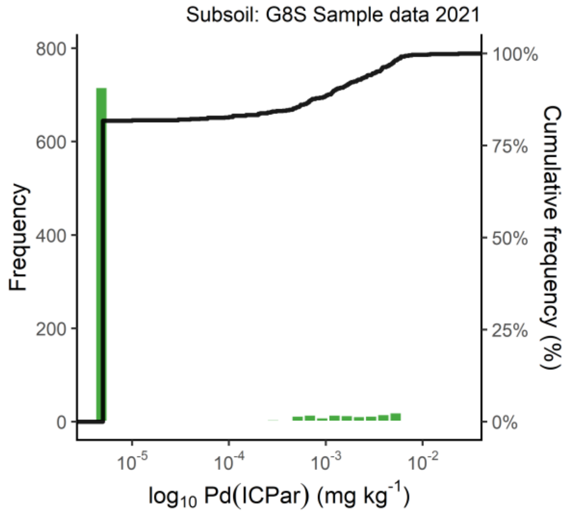
Lead (Pb) ICP_{ar}



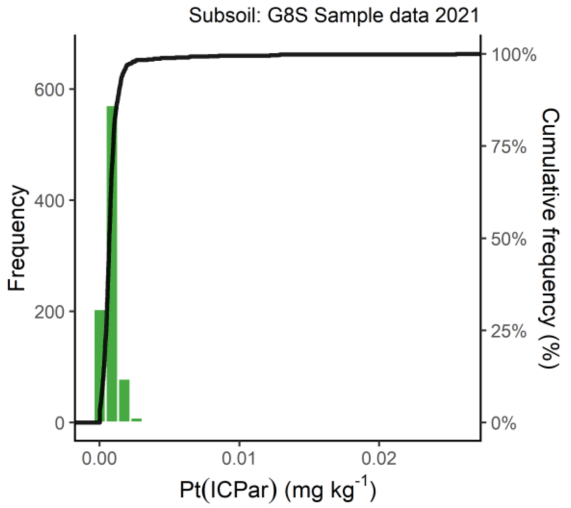


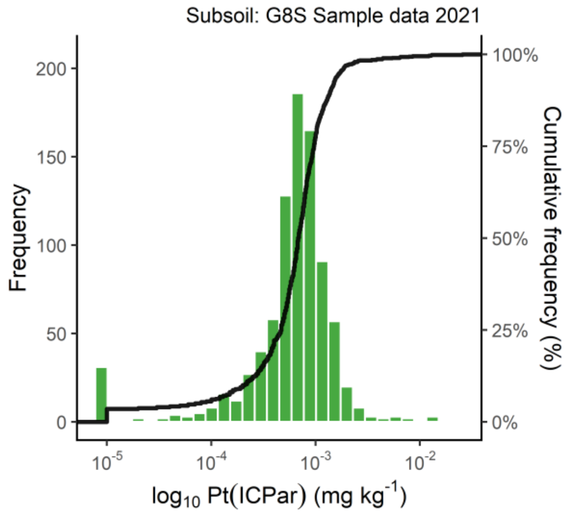
Palladium (Pd) ICP_{ar}



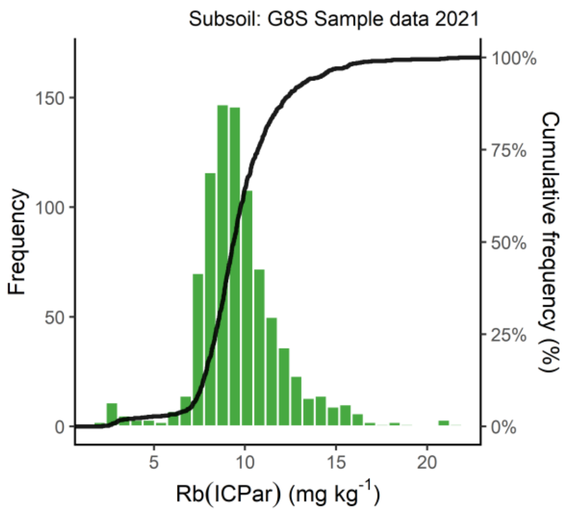


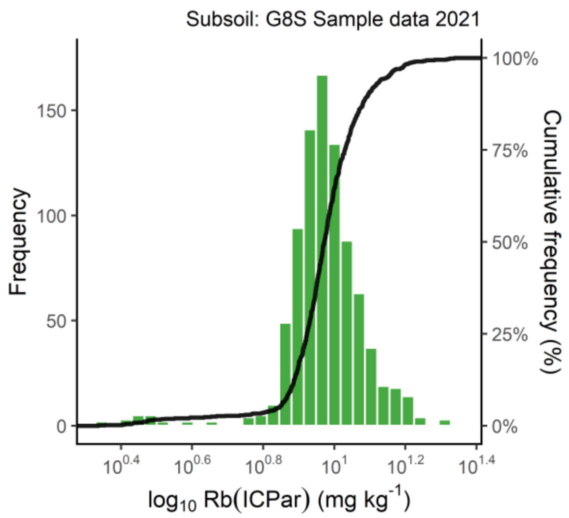
Platinum (Pt) ICP_{ar}



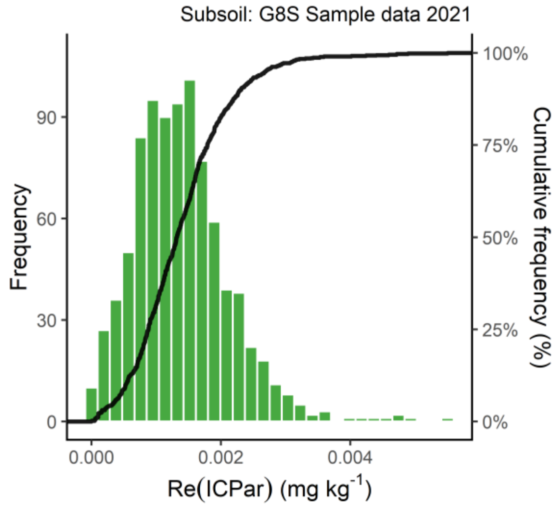


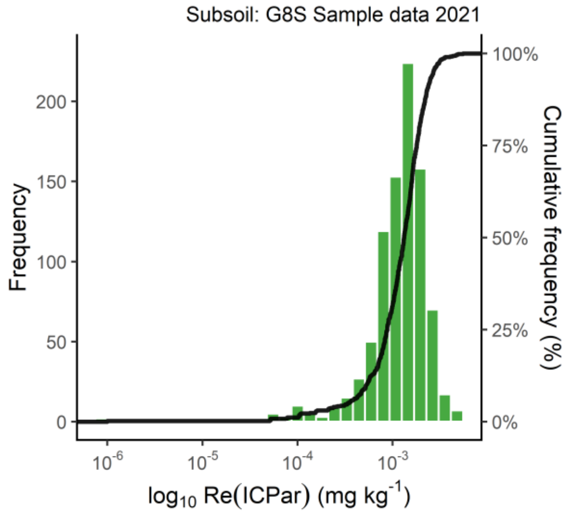
Rubidium (Rb) ICP_{ar}



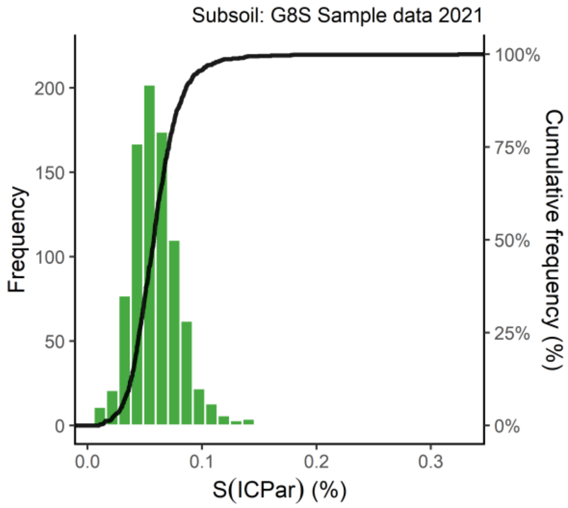


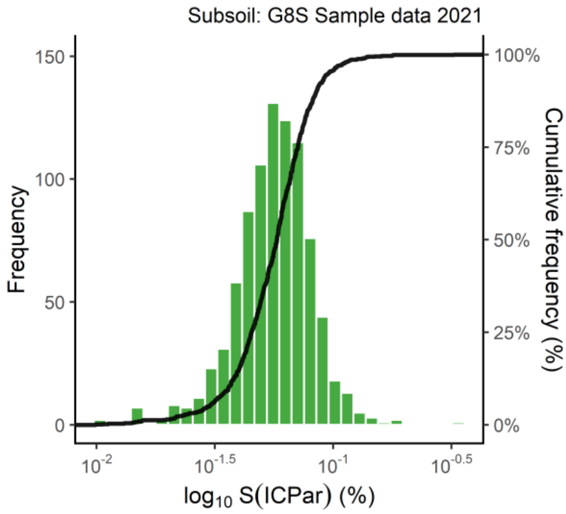
Rhenium (Re) ICP_{ar}



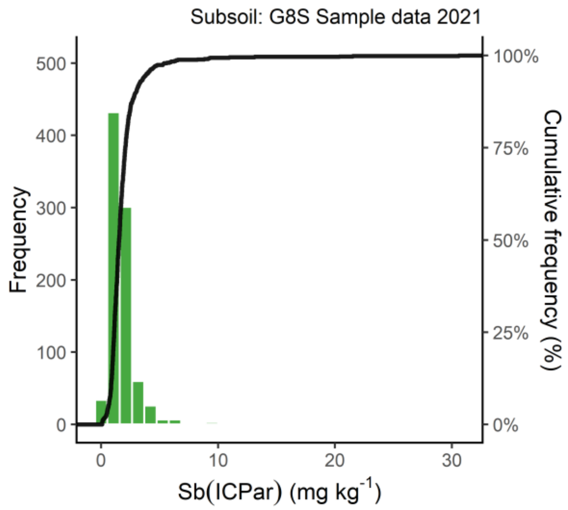


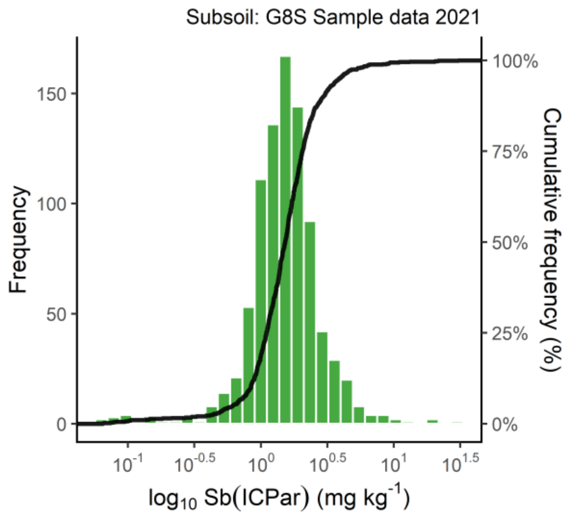
Sulphur (S) ICP_{ar}



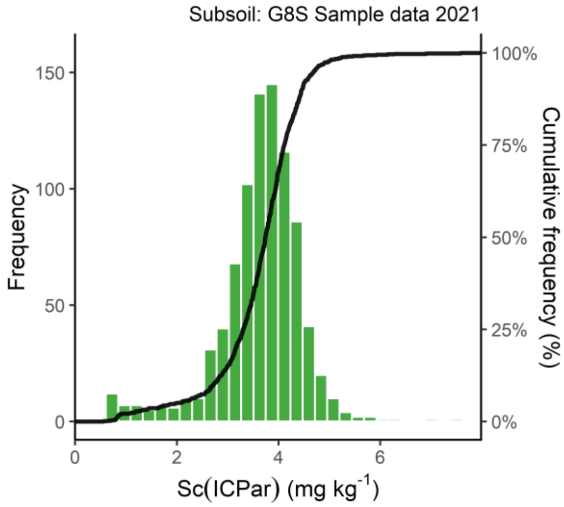


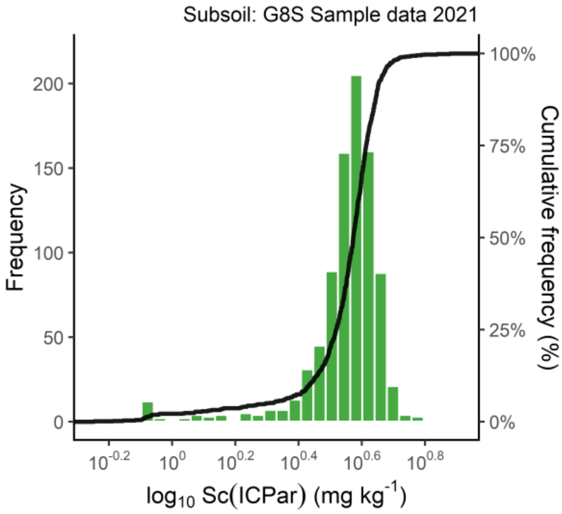
Antimony (Sb) ICP_{ar}



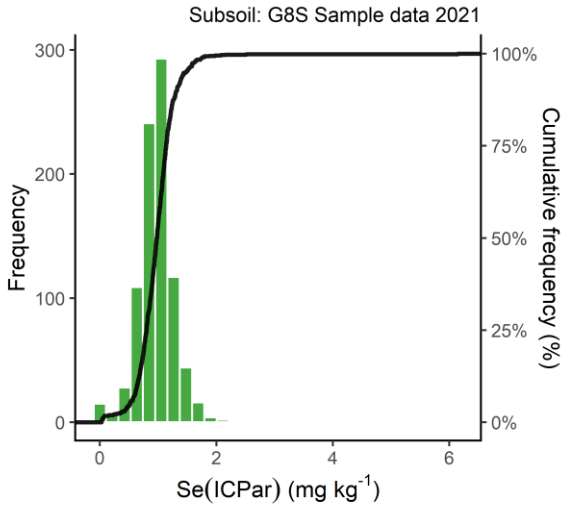


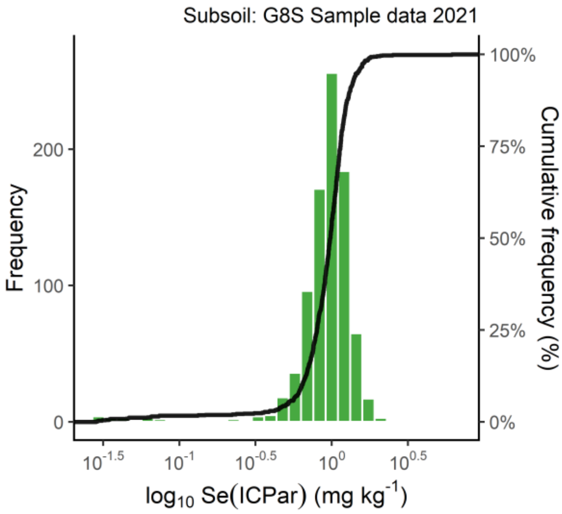
Scandium (Sc) ICP_{ar}



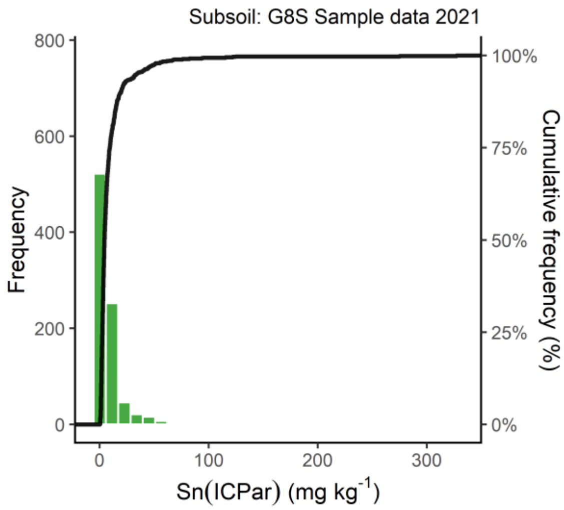


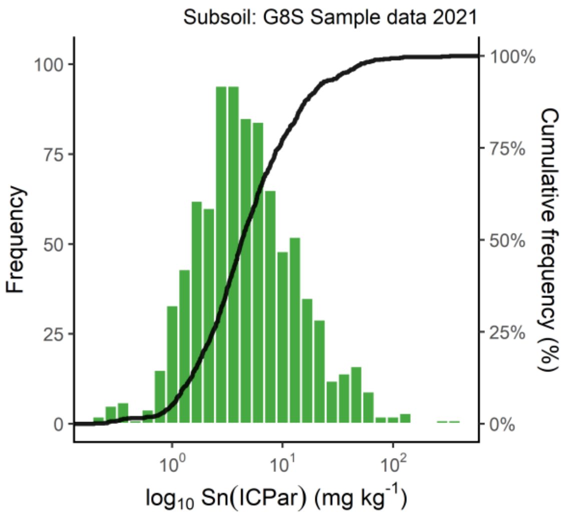
Selenium (Se) ICP_{ar}



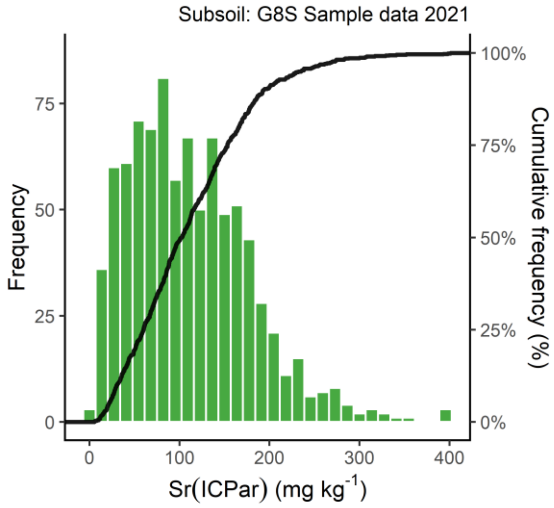


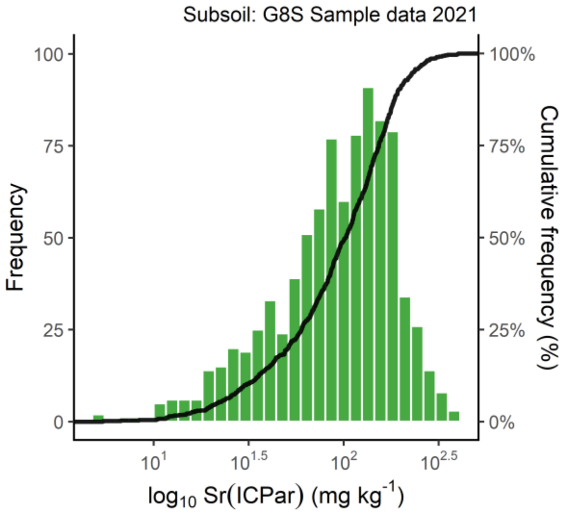
Tin (Sn) ICP_{ar}



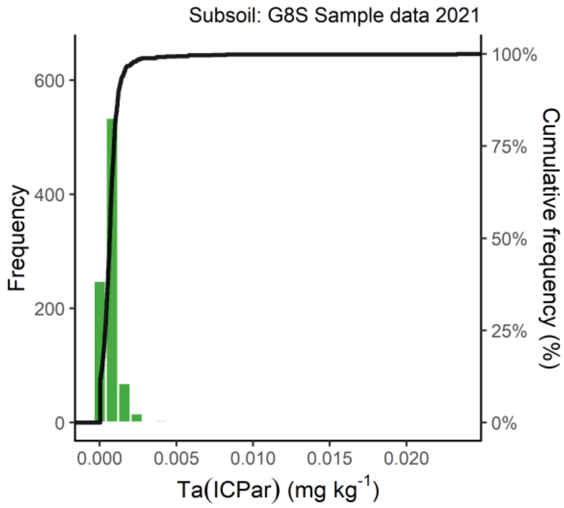


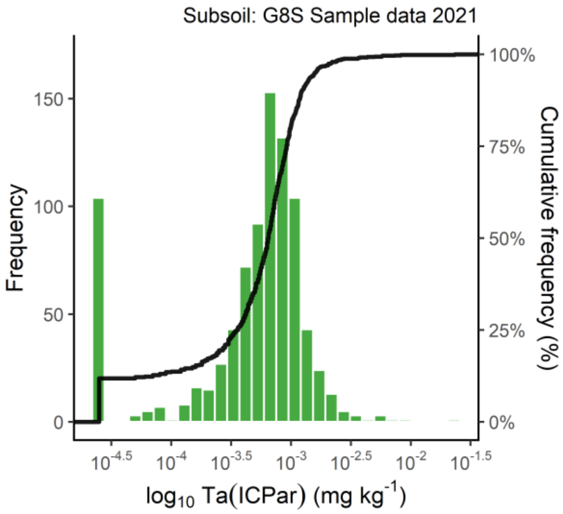
Strontium (Sr) ICP_{ar}



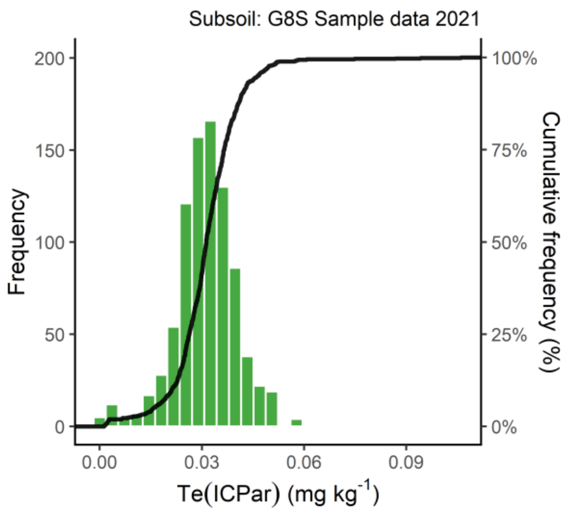


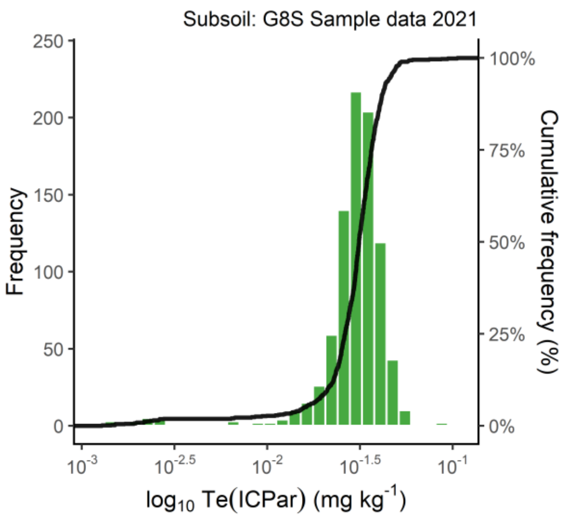
Tantalum (Ta) ICP_{ar}



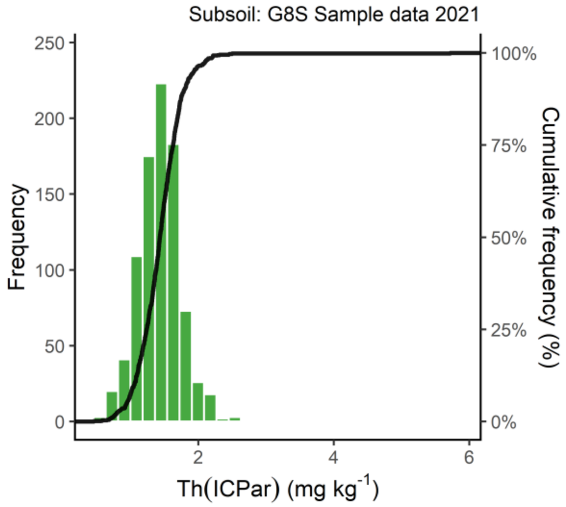


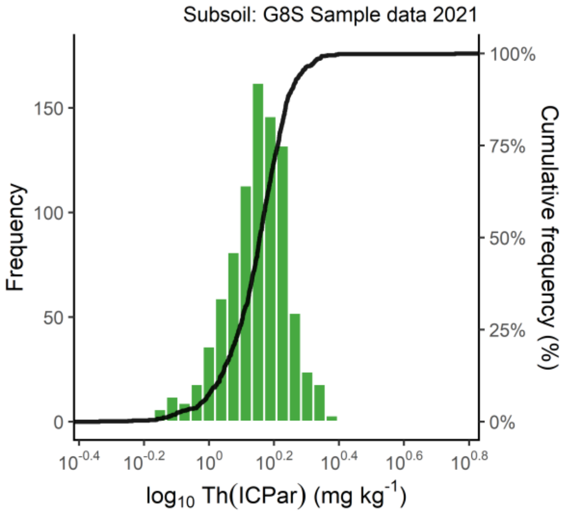
Tellurium (Te) ICP_{ar}



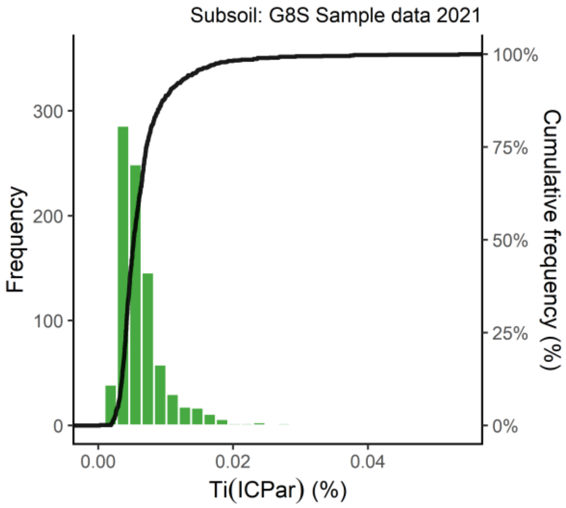


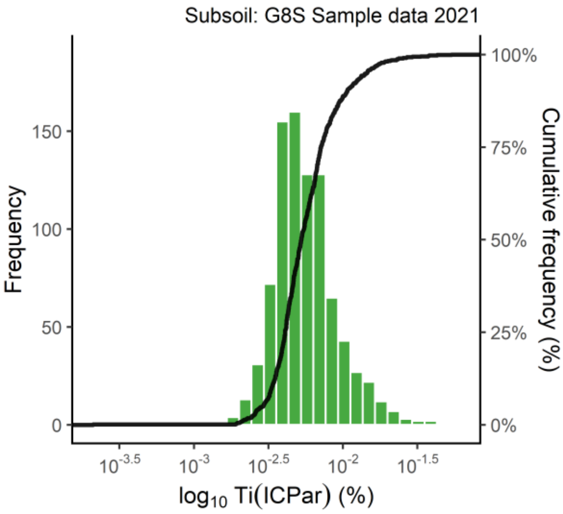
Thorium (Th) ICP_{ar}



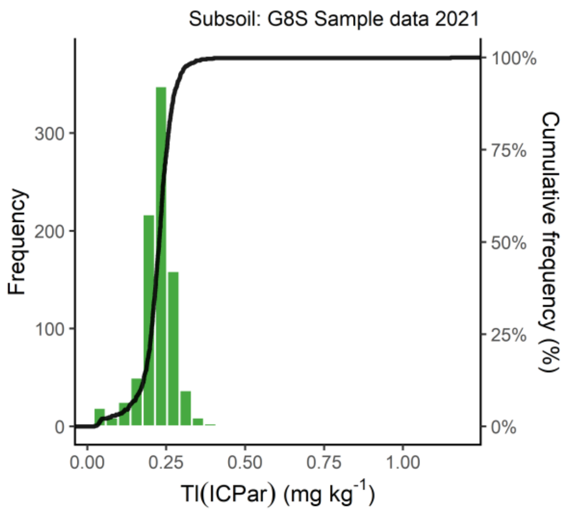


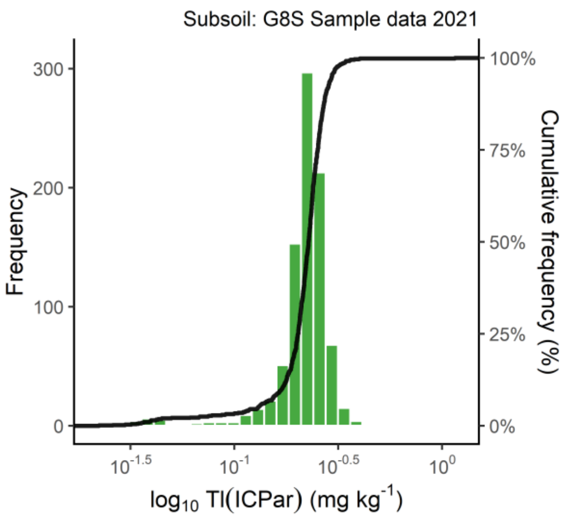
Titanium (Ti) ICP_{ar}



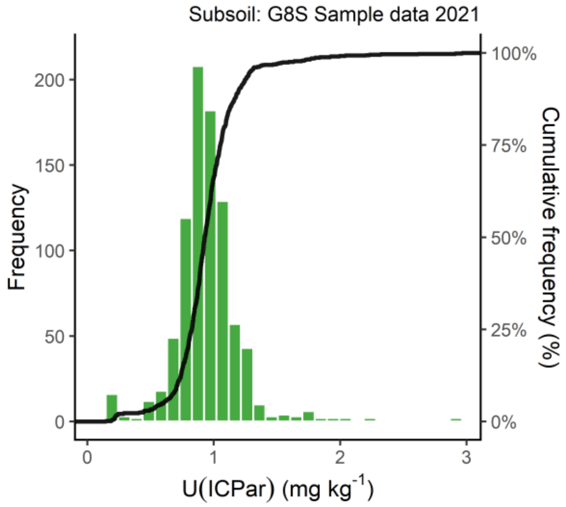


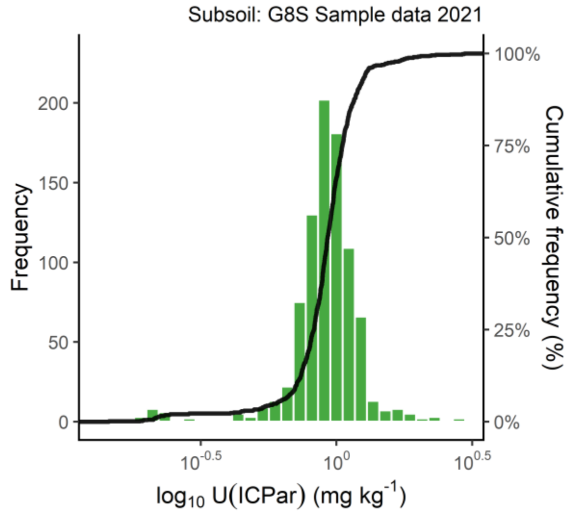
Thallium (Tl) ICP_{ar}



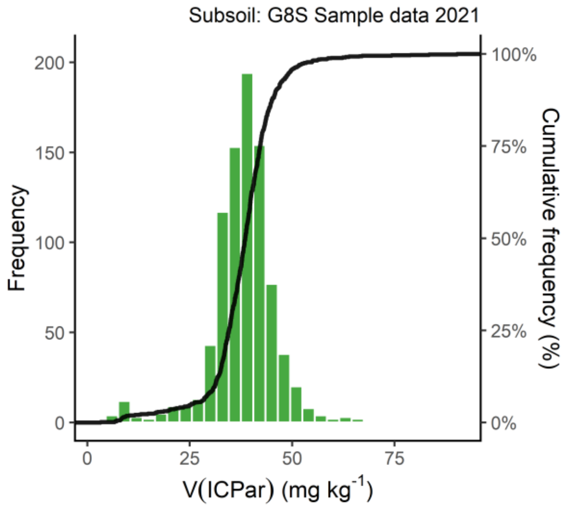


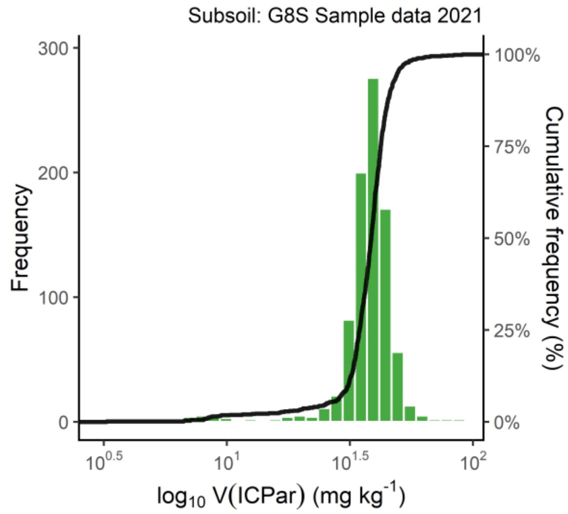
Uranium (U) ICP_{ar}



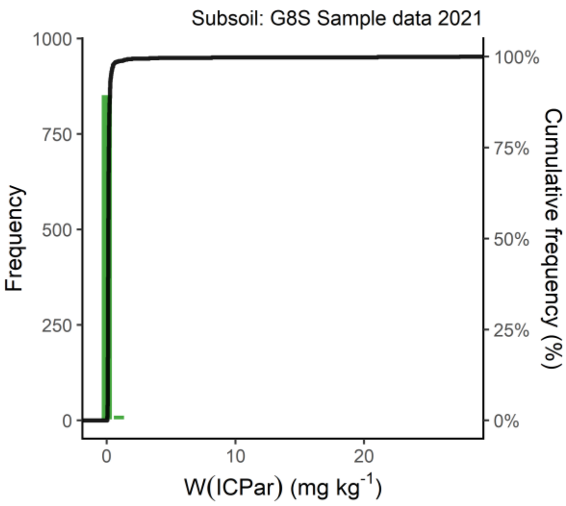


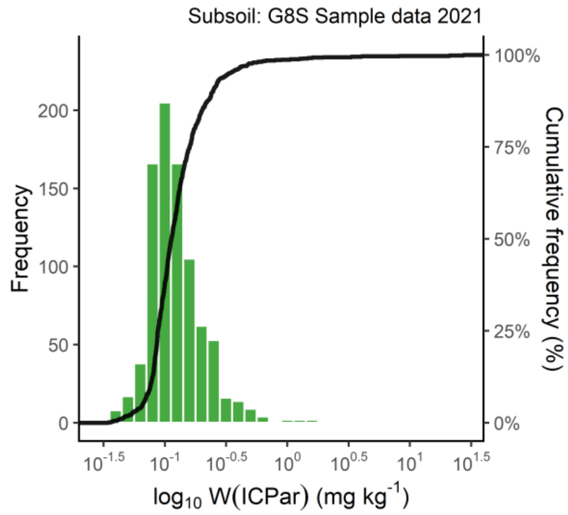
Vanadium (V) ICP_{ar}



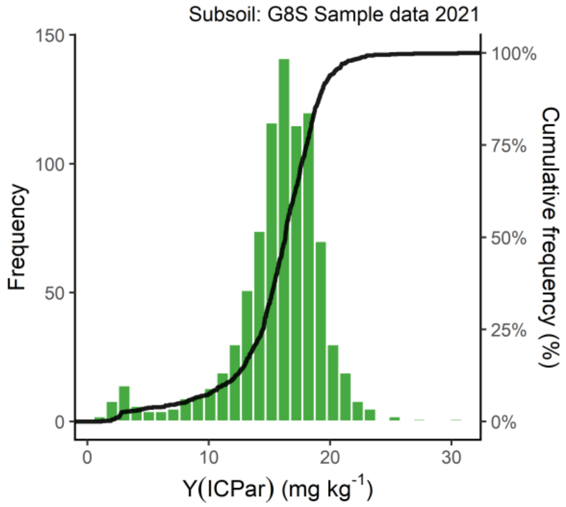


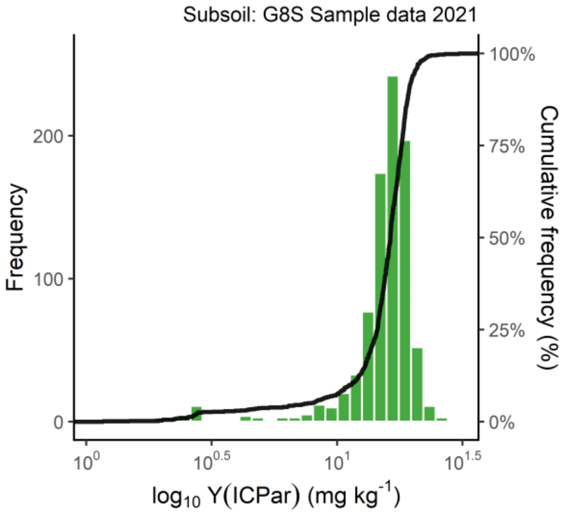
Tungsten (W) ICP_{ar}



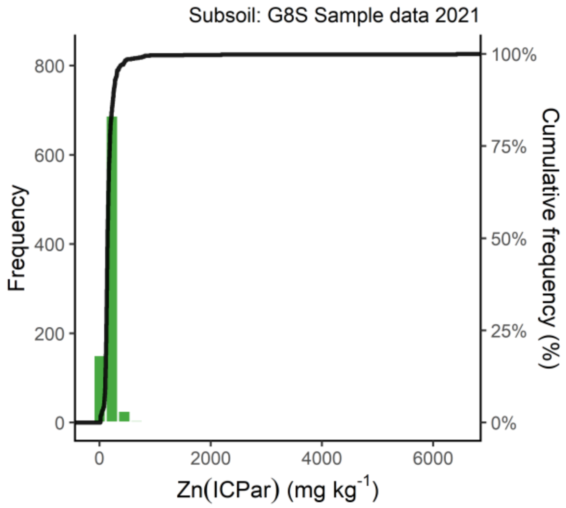


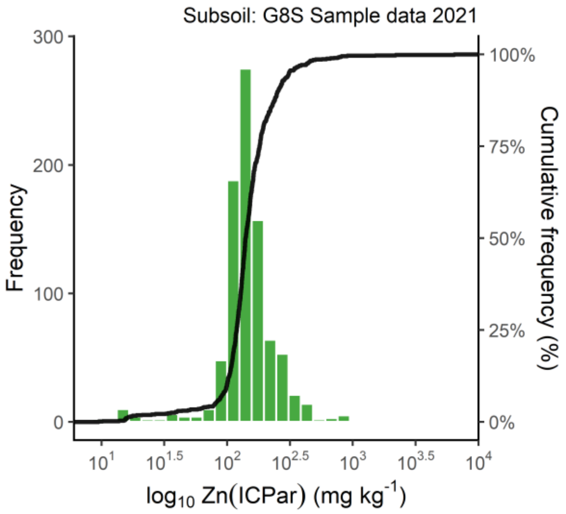
Yttrium (Y) ICPar



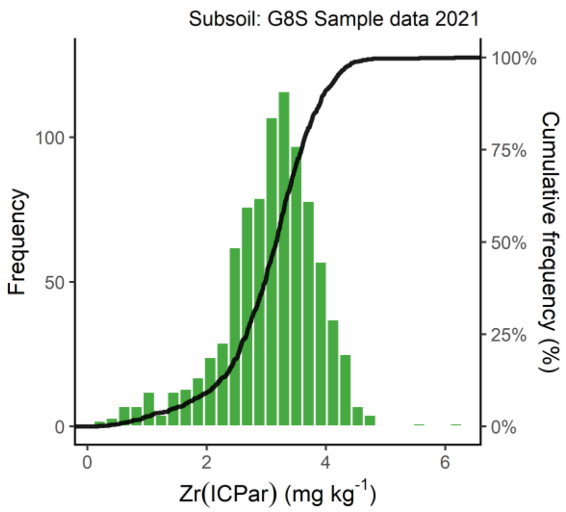


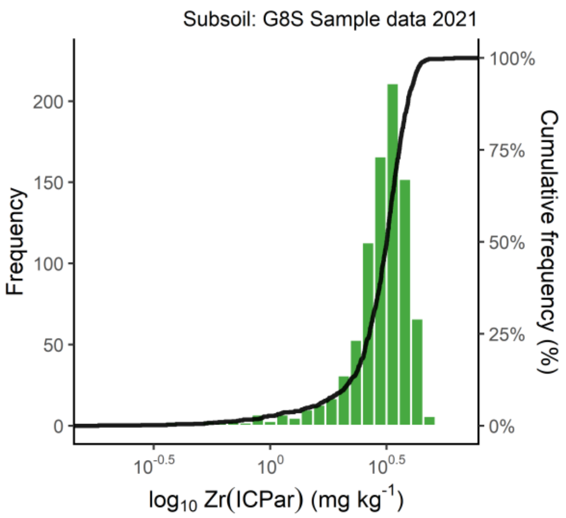
Zinc (Zn) ICPar





Zirconium (Zr) ICPar





C. Method summaries

In this appendix are method summaries from the contracted laboratories.

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

Principles of Method – ME-MS41L

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

Sample Decomposition:

Aqua Regia (GEO-AR01)

Analytical Method:

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

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

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

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

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

> *NOTE 1: Reactive samples may require slow acid addition and/or reduction of the nominal sample weight by half.*
>
> *NOTE 2: An aqua regia leach is an ideal medium for the dissolution of sulphide minerals and for the release of elements adsorbed on clay particles or trapped in manganese and iron oxides and oxyhydroxides. However, it represents only the leachable portion of the particular analyte and will not dissolve significant quantities of the silicate and alumino-silicate minerals. Major refractory minerals such as chromite, columbite, tantalite, cassiterite, rutile, scheelite, wolfram and zircon are only slightly soluble. The solubility of certain elements such as Ba and Sr will depend on the mineralisation in which they occur. The sulphates of these elements (barite and celestite) are basically insoluble, whereas the carbonates are readily soluble.*
>
> *Coarse and malleable minerals such as native gold and silver, platinum and palladium are not representatively characterized by the small sample size.*

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

List of Reportable Analytes for ME-MS41L:

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

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

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 previous 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

OA-GRA05f

Loss on Ignition (L.O.I.) is to measure the amount of moisture (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.

Sample Decomposition:

None

Analytical Method:

For TELLUS (GSI) project a pulverised sample is pre-weighed into a disposable glass vial and placed in a drying oven set at 105° C for a minimum of 1 hour.

The dried sample is then placed in a desiccator and cooled to room temperature.

Using a 4 decimal place electronic balance, 0.5g of this pre-dried sample is then weighed into a ceramic crucible. The crucible with sample is placed in a muffle furnace set at 450° C for four hours.

After ignition the samples are cooled and then weighed again. The percent loss on ignition is calculated from the difference in weight.

% L.O.I. Calculation

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

$$\% \text{LOI} = \frac{\text{Difference in Sample Weight}}{\text{Sample Weight}} \times 100$$

OA-ELE07 – Soil pH

Sample Decomposition:

None

Analytical Method:

Potentiometric

5g +/-10% of dried soil sample, sieved to <2mm is well mixed 12.5 ml of 0.01M $CaCl_2$ solution in a 50ml disposable plastic vial and homogenised on a shaker for 5 minutes.

The suspension is then left to settle for 1 hour and the pH is measured using 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.

List of Reportable Analytes:

Method Code	Reporting Analyte	Sample Weight (g)	Volume (mL)	Leach Time (min)	Lower Limit	Upper Limit
OA-ELE07	pH	5	12.5	60	0.1	14