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on behalf of Geological Survey Ireland

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

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Executive Summary

This report accompanies the publication of data and maps that present the inorganic geochemical data for shallow 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 shallow topsoil samples, denoted sample type 'A', 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.

Shallow topsoil samples

Sampling and sample summary

Survey design and sample locations

Maps displaying the survey extent and sample site locations of shallow topsoil samples are shown below (Map 1 and Map 2). The survey design is a systematic one based on a predefined fishnet of 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

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

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:

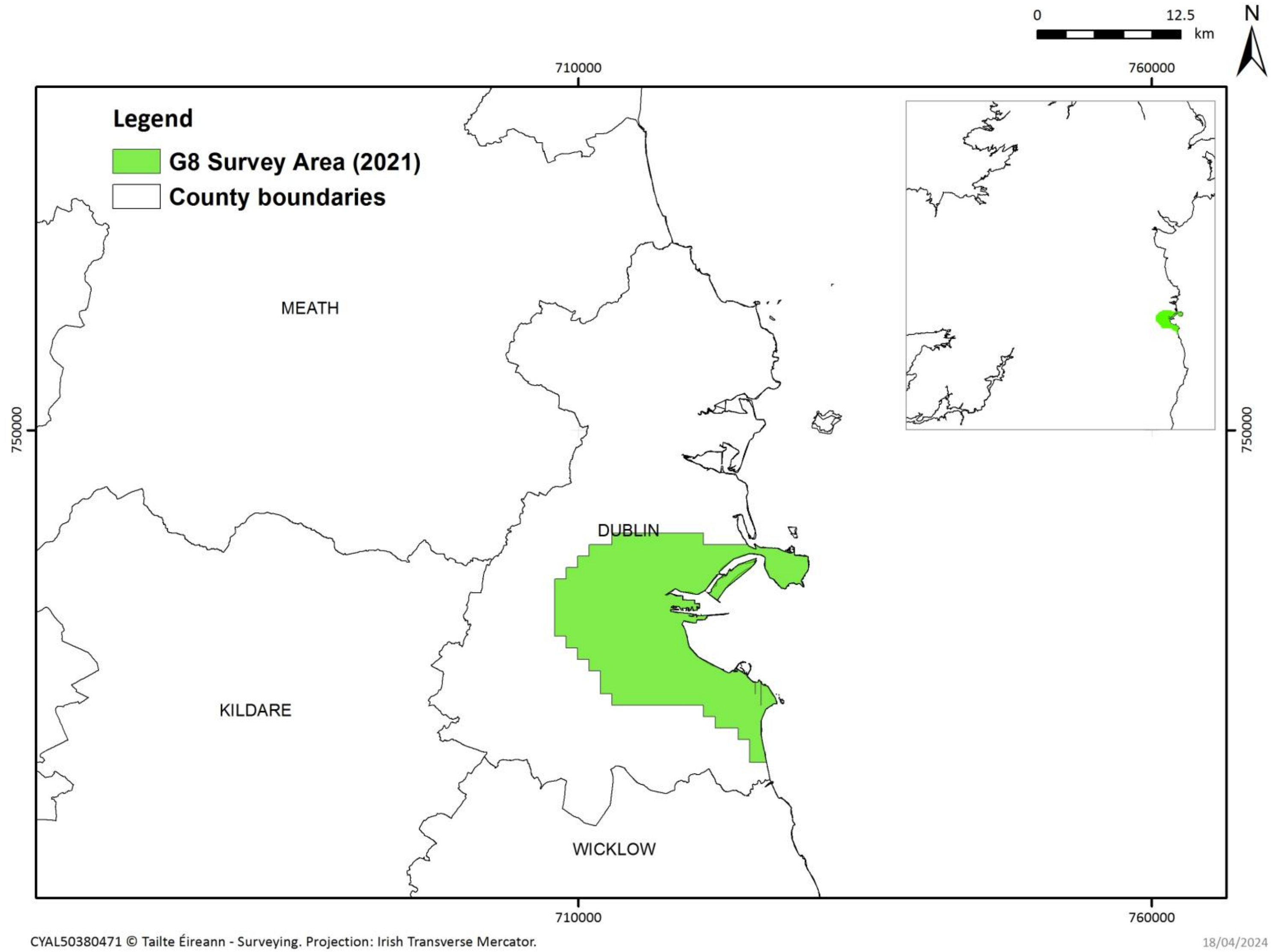
- Four sets of field duplicates (DUP) were collected in each batch, denoted duplicate pairs A-B, C-D, E-F and G-H, with each pair collected from a single site. DUPA, DUPC, DUPE and DUPG are treated as true samples for the purpose of the survey.
- Each duplicate site number has a corresponding replicate 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.

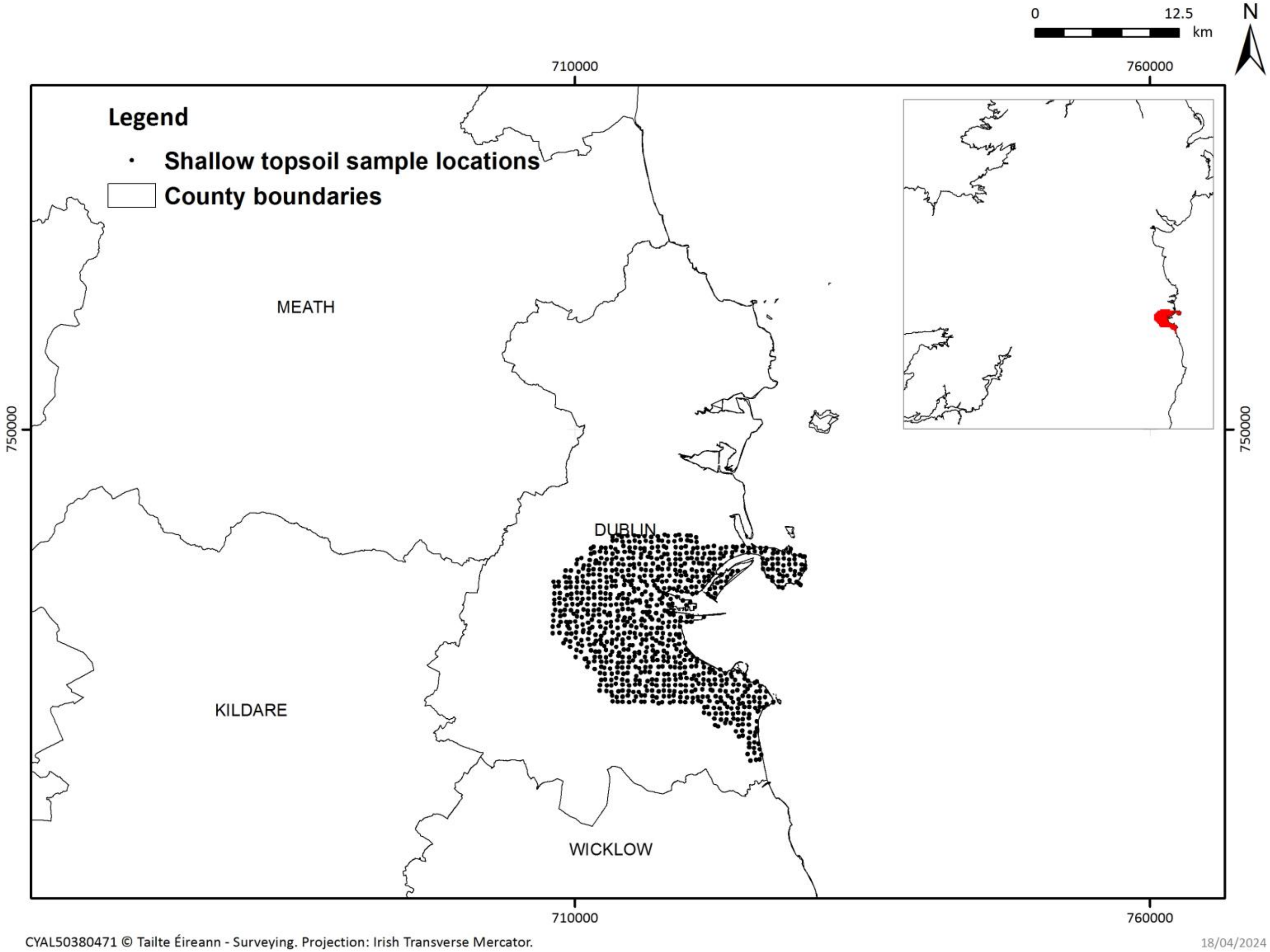
Table 1 Summary of QCS by field hundred batches.

(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	670001A	670100A	08/06/2021	05/07/2021	100	84	1	3	16
2	6701xx	670101A	670200A	14/06/2021	22/06/2021	100	84	1	3	16
3	6702xx	670201A	670300A	14/06/2021	07/07/2021	100	84	2	2	16
4	6703xx	670301A	670400A	21/06/2021	06/07/2021	100	84	1	3	16
5	6704xx	670401A	670500A	21/06/2021	19/07/2021	100	84	1	3	16
6	6705xx	670501A	670600A	29/06/2021	12/07/2021	100	84	2	2	16
1	6706xx	670601A	670700A	07/07/2021	28/07/2021	100	84	1	3	16
2	6707xx	670701A	670800A	05/07/2021	02/09/2021	100	84	1	3	16
3	6708xx	670801A	670900A	14/07/2021	03/09/2021	100	84	2	2	16
4	6709xx	670901A	671000A	21/07/2021	14/09/2021	100	84	1	3	16
5	6710xx	671001A	671099A	19/07/2021	16/09/2021	53	37	1	3	16



Map 1 Survey campaign area G8.



Map 2 Shallow 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 20 mm Ø 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 has an advantage of not having artefacts of rounding which can lead to step changes in the data distribution. This practice greatly facilitates the QC procedures and is particularly relevant where an analyte's natural abundance is low in relation to the detection limit. The reported uncensored concentration values are maintained throughout the QC process and uploaded in this format to the database.

Soil loss-on-ignition at 450°C

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

Method code OA-GRA05f is used for soil loss-on-ignition (LOI) analyses of prepared (milled/pulped) soil samples. A weighed 1 g sample is combusted in a tared, pre-ignited crucible in a temperature-controlled Vecstar benchtop muffle furnace at 450^{o}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 21/04/2023. Data for 1053 sample IDs by pH were reported to GSI by 12/05/2023. Data for 1053 sample IDs by ICPar were reported to GSI by 11/06/2024.

Table 2 Laboratory work orders for soil analyses

Analysis	ALS Work Order	Reporting date	Sample ID	
			From	To
ICPar	LR22288968	11/06/2024	670001A	670200A
ICPar	LR22307651	10/01/2023	670201A	670400A
ICPar	LR23008685	20/03/2023	670401A	670600A
ICPar	LR23002999	23/02/2023	670601A	670800A
ICPar	LR22324665	06/04/2023	670801A	671099A
LOI	LR22289250	08/11/2022	670001A	670200A
LOI	LR22307665	14/02/2023	670201A	670400A
LOI	LR23008674	15/03/2023	670401A	670600A
LOI	LR23003069	30/03/2023	670601A	670800A
LOI	LR22324714	21/04/2023	670801A	671099A
pH	LR22289177	12/05/2023	670001A	670200A
pH	LR22307658	12/05/2023	670201A	670400A
pH	LR23008649	12/05/2023	670401A	670600A
pH	LR23003083	12/05/2023	670601A	670800A
pH	LR22324675	12/05/2023	670801A	671099A

Table 3 Shallow 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 Shallow 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

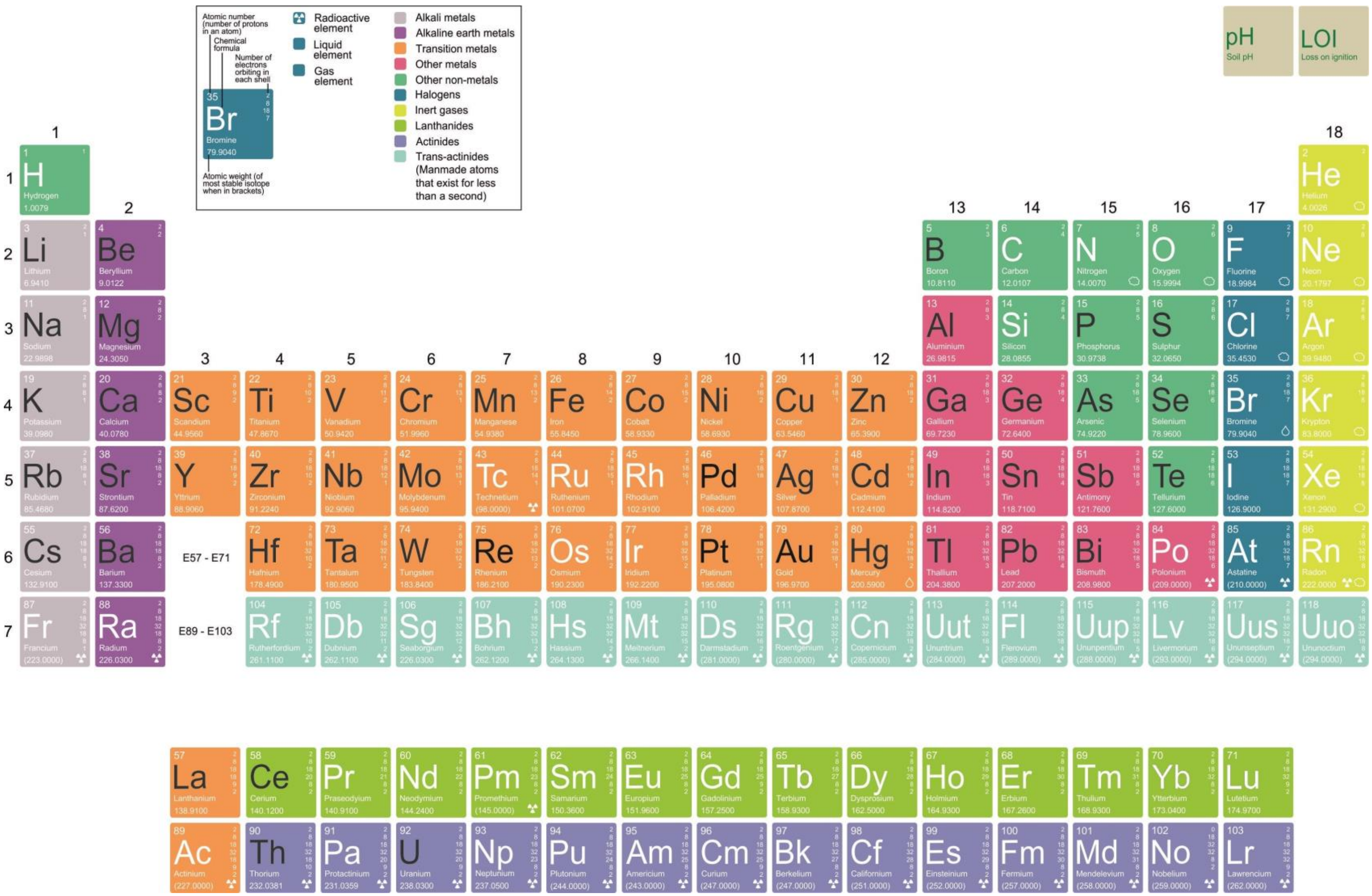


Figure 1 Graphic of the periodic table, with ICPar element analytes for shallow topsoil samples shown in black text, Soil pH ($CaCl_2$) and LOI (at 450°C) in green text. Adapted after http://www.sciencegeek.net/tables/PToE_basic.pdf

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 G8A samples, initial checks using QCS identified two incidences of sample switches, involving five samples altogether, that occurred at the preparation stage – these were corrected prior to analysis.

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.

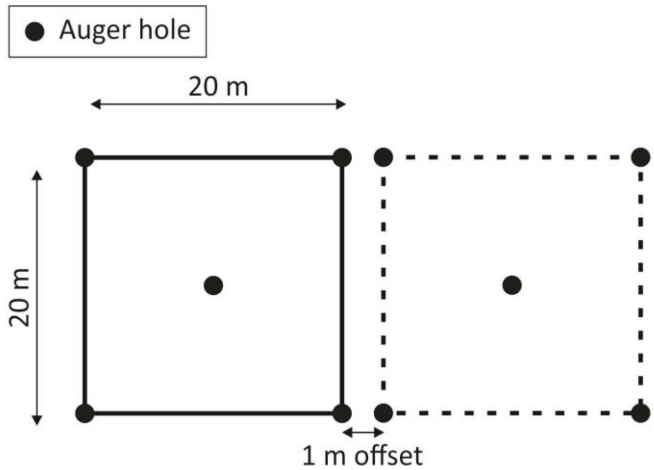


Figure 2 Diagrammatic plan for collection of a five-auger-hole composite soil sample and a field duplicate sample (indicated by dashed line pictogram).

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.

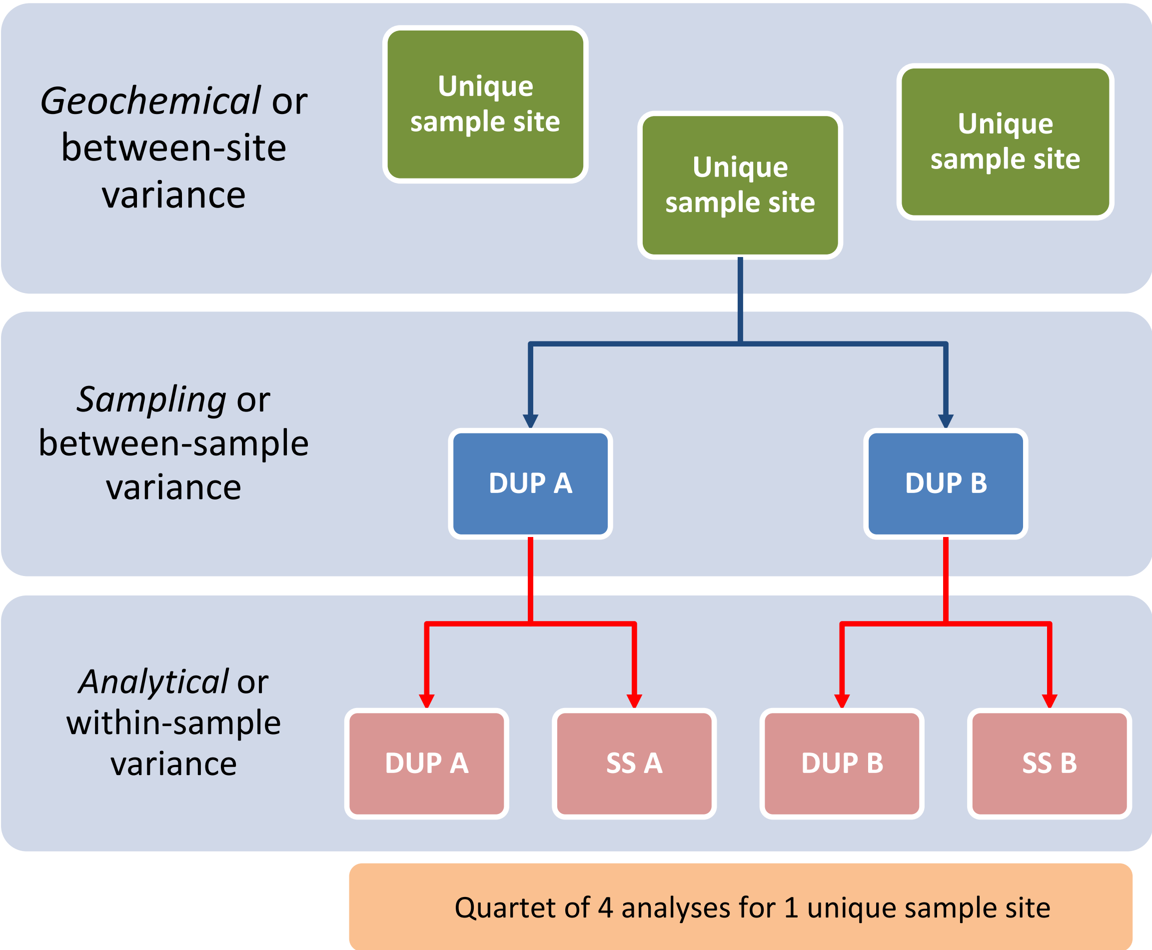


Figure 3 Diagram to show the relationship between field duplicates ("DUP") and replicate ("SS") samples, used to apportion data variance.

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. However, inspection of conditionally formatted data for each of the 44 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 G8A reveal consistently large positive and negative values for some elements, for many or even most of the pairs: Au, Ag, Hg, In, Na, Pd, Pt, Re, Sn, Ta, Ti 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, Ti 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, Ag, 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, B, Ba, Bi, Ca, Cd, Cu, Hg, In, K, Mn, Mo, Na, Nb, P, Pb, Pd, Pt, Re, S, Sb, Sn, Sr, Ta, Ti, W, Zn, Zr. 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 XY 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 Re (data available for 43 quartets), Ta (41 quartets) and Pt (37 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: gold (Au), boron (B), chromium (Cr), germanium (Ge), hafnium (Hf), indium (In), potassium (K), platinum (Pt), rubidium (Rb), rhenium (Re), tin (Sn), tantalum (Ta), tellurium (Te), titanium (Ti), tungsten (W) and pH. Elements for which the between-site (geochemical) variance falls below 80 % include gold (Au), boron (B), potassium (K), platinum (Pt), indium (In), tungsten (W), 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 seven 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 one element (K). The within-sample variance, as measured by the difference between duplicate and corresponding replicate samples, is above 4 % for 16 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* (Hf, Sn, Ti) or are otherwise are prone to significant analytical variability owing to their generally very low concentrations (Pt, Re).

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

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

Variable	Method	Variance component (100% sum)			*n* quartets
		Between site (%)	Between sample (%)	Within sample (%)	
Li	ICPar	97.8	1.77	0.47	44
As	ICPar	97.7	1.40	0.92	44
Mg	ICPar	96.9	2.64	0.47	44
Ni	ICPar	96.8	2.29	0.90	44
Be	ICPar	96.2	3.09	0.75	44
Ca	ICPar	96.1	3.80	0.08	44
Sr	ICPar	96.1	3.75	0.18	44
Cs	ICPar	96.0	2.32	1.64	44
Co	ICPar	95.6	3.15	1.27	44
Na	ICPar	95.0	2.99	2.02	44
Fe	ICPar	94.9	3.82	1.26	44
P	ICPar	94.7	4.62	0.64	44
U	ICPar	94.7	4.29	0.99	44
Cd	ICPar	94.7	3.35	1.96	44
Zr	ICPar	94.7	3.66	1.68	44
Mo	ICPar	94.5	4.13	1.36	44
Pb	ICPar	94.4	4.55	1.02	44
Mn	ICPar	94.3	4.81	0.87	44
Bi	ICPar	94.1	3.22	2.71	44
Sb	ICPar	93.9	4.34	1.71	44
Hg	ICPar	93.9	5.42	0.69	44
Se	ICPar	93.7	3.99	2.32	44
V	ICPar	93.7	4.37	1.93	44
Y	ICPar	93.3	4.75	1.95	44
Sc	ICPar	93.0	4.24	2.76	44
Nb	ICPar	92.5	4.50	2.99	44
S	ICPar	92.2	6.24	1.59	44
Ba	ICPar	91.9	5.18	2.93	44
Zn	ICPar	91.5	7.71	0.76	44
Th	ICPar	91.4	5.98	2.61	44

Variable	Method	Variance component (100% sum)			*n* quartets
		Between site (%)	Between sample (%)	Within sample (%)	
Cu	ICPar	91.0	6.73	2.26	44
Ti	ICPar	91.0	4.65	4.36	44
LOI	LOI at 450˚C	90.9	7.58	1.53	44
Sn	ICPar	90.4	4.94	4.66	44
Ga	ICPar	90.0	7.01	2.96	44
Hf	ICPar	89.8	5.99	4.18	44
Ag	ICPar	89.8	8.62	1.61	44
pH	pH $CaCl_2$	89.2	4.71	6.10	44
Te	ICPar	88.8	5.89	5.26	44
La	ICPar	88.6	7.58	3.85	44
Tl	ICPar	88.4	8.34	3.31	44
Rb	ICPar	87.1	8.38	4.56	44
Ce	ICPar	86.1	10.3	3.61	44
Cr	ICPar	85.2	9.13	5.67	44
Al	ICPar	85.1	11.2	3.68	44
Ge	ICPar	84.9	9.81	5.28	44
Re	ICPar	84.7	10.6	4.72	43
Au	ICPar	76.6	11.8	11.6	44
B	ICPar	74.9	12.2	12.9	44
K	ICPar	73.9	21.8	4.23	44
Pt	ICPar	62.4	14.0	23.6	37
In	ICPar	60.2	14.7	25.1	44
W	ICPar	57.4	15.6	27.0	44
Ta	ICPar	57.3	11.6	31.1	41

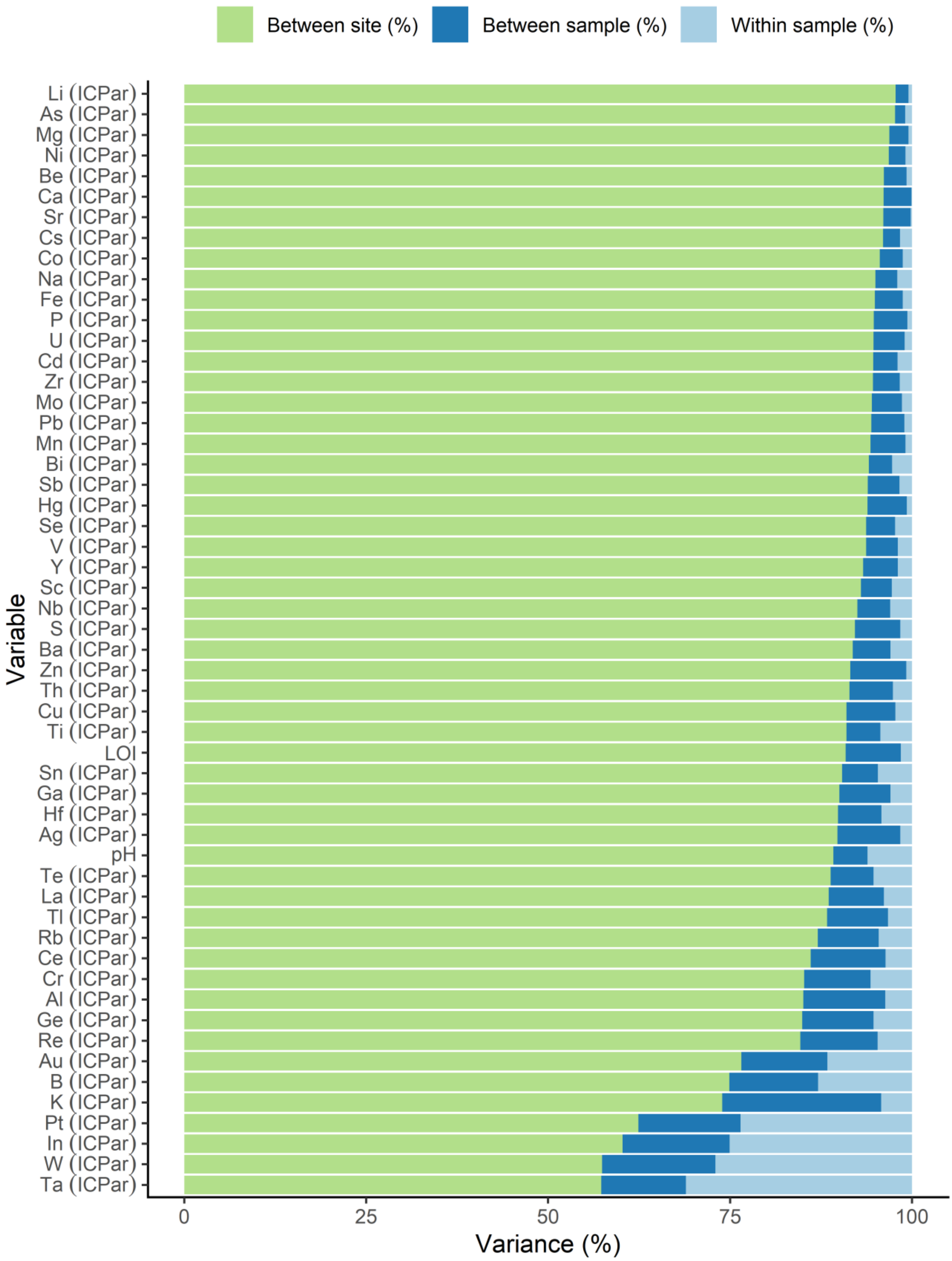


Chart 1 Stacked bar chart to display ANOVA results for all duplicate site shallow topsoil data.

Reference materials data

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

RMs comprise primary or certified reference materials (CRMs), purchased from suppliers with an accompanying certificate of elemental analyses, and secondary reference materials (SRMs) produced and used by the geochemical mapping programme. All are submitted blindly to the laboratory in order to assess the results without bias. In addition to these control samples, the laboratory has used its own "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.
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	
LGRAN	697129E 695189N	Topsoil	Pasture (BAB0) and agricultural grassland (BA00)		Sandy soil derived from granite till, overlying quartz diorite	

SRM name	Location co-ordinates (ITM)	Material type	Primary land uses	Stream order	Description	Stream drainage type
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 (AEBB) to the west of site and deciduous woodland – established	Yellow River. 2nd 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
			(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. 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 four in-house CRMs were carried out by the laboratory as part of each analytical batch, giving a total of 149 analyses of in-house CRMs. For pH analyses, 44 SRM analyses, eleven each of four individual SRMs, were completed for G8A.

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 observed violations are classed as single analyte failures and/or warnings and are interpreted as random errors and deemed inconsequential for the quality of the data. Multiple analyte failures were further investigated in detail to rule out a true analysis failure. 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 most cases the recorded failures were observed for analytes displaying very tight trends and narrow control limits (Ag, Pd, W) or where the concentration of the analytes is generally low (Re, Ta), in many cases close to method LLD, and where greater variability is therefore to be expected. Most of the events are type 1_{3S} violations and only one case of 2_{2S} violations was recorded. 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 13/06/2022 and 14/06/2022 four consecutive, multiple element failures and warnings occurred. Barium (Ba) and cadmium (Cd) failed in more than one instance. Affected batches: LR22136803 and LR22147409, both involving G7A samples. Possible cause: poor analytical performance.
- Between 26/02/2023 and 28/02/2023, two consecutive analyses of hafnium (Hf) and zirconium (Zr) breached the upper warning limit. Element failures were also recorded for Pd and Sb and there were multiple-element warnings for barium (Ba), bismuth (Bi), boron (B), caesium (Cs), germanium (Ge), gold (Au), lithium (Li), mercury (Hg), molybdenum (Mo), niobium (Nb), rhenium (Re), rubidium (Rb), selenium (Se), strontium (Sr), sulphur (S), Tellurium (Te), thorium (Th), tin (Sn), titanium (Ti) and yttrium (Y). Affected batches: LR23008685 and LR22324665, both involving G8A samples. Possible cause: poor analytical performance.

Blind RMs: pH analyses

The rationale for combining G7A and G8A 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 G8A 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. Control charts for the four pH SRMs (Appendix A) display only one failure (type 1_{3S} violation for SST) and one warning (APT) (Table 10). Neither of these, in themselves, raise concerns about the pH data.

A plot of Tellus pH SRM data collected to date (Figure 4), for both A and S samples, 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 G8A 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 conditioning. 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.

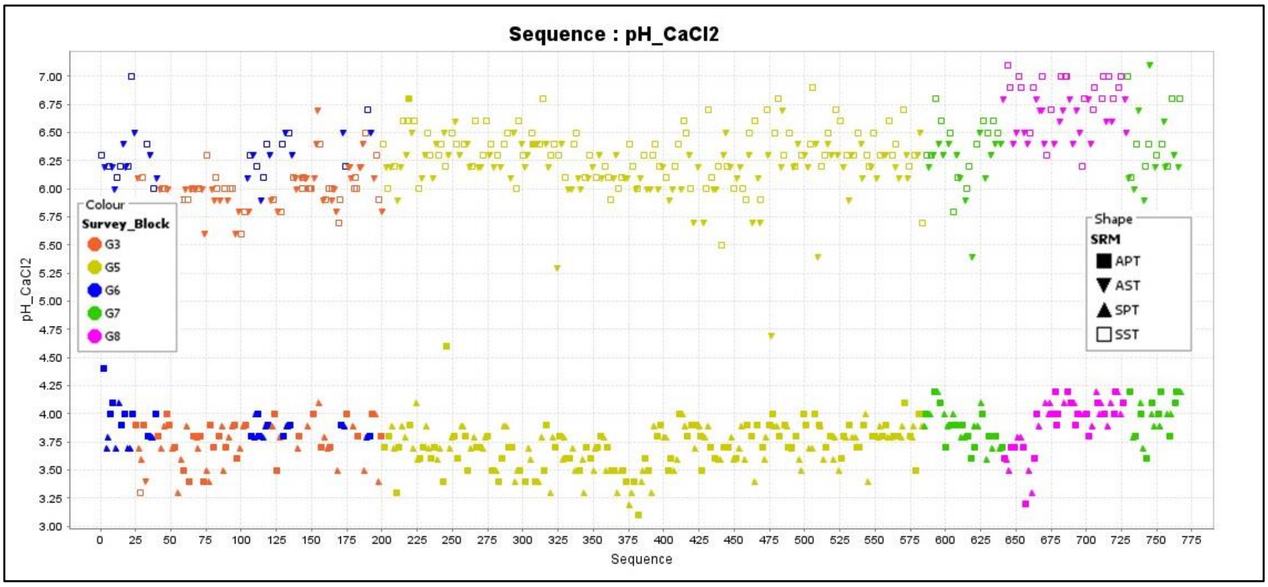


Figure 4 Tellus SRM pH data for survey blocks G3 to G8, plotted in order of analysis (oldest analyses on left).

In-house RMs: ICPar analyses

Four 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 09/06/2022 and 11/06/2022 six consecutive, multiple element failures and warnings occurred. Gold (Au) failed in more than one instance. Affected batches: LR22104615 and LR22136803, both involving G7A samples. Possible cause: poor analytical performance. Note that batch LR22136803 has also been cited in respect of blind RMs.
- Between 13/06/2022 and 14/06/2022 nine consecutive, multiple element failures and warnings occurred. Ce failed in two instances. Two consecutive analyses of sodium (Na), niobium (Nb), rhenium (Re), tin (Sn), thallium (Tl), tungsten (W) and uranium (U) breached the upper control and/or warning limit. Individual element breaches of the control limit were also recorded for gold (Au), tantalum (Ta), tellurium (Te), barium (Ba), lanthanum (La) and silver (Ag). Affected batch: LR22147409 (G7A samples). Possible cause: poor analytical performance.
- Between 13/09/2022 and 16/09/2022 seven consecutive, multiple element failures and warnings occurred. Three consecutive analyses of sodium (Na), potassium (K) and sulphur (S) breached the control and/or warning limit. Two consecutive analyses of niobium (Nb) (twice), sodium (Na), and iron (Fe) breached the control and/or warning limit. Individual element breaches of the control limit were also recorded for palladium (Pd) (twice), antimony (Sb), Indium (In), arsenic (As), mercury (Hg), sodium (Na), selenium (Se), tungsten (W) (twice), magnesium (Mg) (twice), calcium (Ca), copper (Cu), manganese (Mn), phosphorus (P), lead (Pb), tantalum (Ta) and zinc (Zn). Affected batches: LR22231925 and LR22242928 (G7A samples). Possible cause: poor analytical performance.

- Between 26/02/2023 and 28/02/2023 five consecutive, multiple element failures and warnings occurred. Two consecutive analyses of hafnium (Hf), tellurium (Te), zirconium (Zr), niobium (Nb) and lithium (Li) breached the control and/or warning limit. Individual element breaches of the control limit were also recorded for boron (B) (thrice), titanium (Ti), cadmium (Cd) (twice), gold (Au), silver (Ag), mercury (Hg), manganese (Mn) and lead (Pb). Affected batches: LR23008685 and LR22324665, both involving G8A samples. Possible cause: poor analytical performance. Note that both of these batches have also been cited in respect of blind RMs.

Table 10. Summary of data quality issues observed by control charts for ICPar analyses of Tellus CRMs (G7A and G8A) and pH analyses of SRMs (G8A).

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
LMGPSH	617735A	LR22104615	ICP-MS	23/05/2022 15:38	Multiple analyte failure (Re, Ta)	Outwith lower/upper control limits
STSD-1	617784A	LR22104615	ICP-MS	23/05/2022 17:19	Single analyte failure (Na) and single analyte warning (U)	Outwith upper control and warning limits
LGRAN	617815A	LR22104615	ICP-MS	24/05/2022 21:49	Multiple analyte warnings: Ag, As, Ba, Cd, Ce, La, Th	Outwith upper/lower warning limits
LGRAN	617884A	LR22104615	ICP-MS	25/05/2022 02:03	Multiple analyte warnings: K, W	Outwith lower warning limits
STSD-3	617588A	LR22136803	ICP-MS	11/06/2022 15:45	Single analyte failure (Au) and multiple analyte warnings (Ag, Cr, Ga, Na, W)	Outwith upper/lower control and warning limits
WWLPAL	617685A	LR22136803	ICP-MS	13/06/2022 13:12	Single analyte failure (Ag) and single analyte warning (Fe)	Outwith upper control and warning limits
YELC1	617938A	LR22147409	ICP-MS	13/06/2022 16:22	Multiple analyte warnings: Al, Fe, V	Outwith lower warning limits
LMGPSH	617537A	LR22136803	ICP-MS	13/06/2022 22:42	Multiple analyte warnings: Ba, Cd, Co, Cr, Mo, Ni, Rb, Sr, U, V, Y, Zn	Outwith upper warning limits
CARLST	617563A	LR22136803	ICP-MS	13/06/2022 23:39	Multiple analyte warnings: Ba, Cd, Cu, Pb, Re	Outwith upper warning limits
WXSERP	617987A	LR22147409	ICP-MS	14/06/2022 00:57	Multiple analyte failure (Re, W) and multiple analyte warnings (Cs, Ta, Th)	Outwith lower control and warning limits
STSD-3	618064A	LR22147409	ICP-MS	14/06/2022 04:21	Multiple analyte warnings: Hg, Na, U	Outwith upper/lower warning limits
CNLST	617613A	LR22136803	ICP-MS	17/06/2022 21:39	Multiple analyte warnings: Ba, Cs, Hf, Rb, Tl	Outwith upper warning limits
STSD-1	617661A	LR22136803	ICP-MS	17/06/2022 23:49	Multiple analyte failure (Ag, Ta) and multiple analyte warnings (Bi, Te, Zr)	Outwith upper/lower control and upper warning limits
WXSERP	617914A	LR22147409	ICP-MS	29/06/2022 04:58	Multiple analyte warnings: Cd, Co, Ga	Outwith lower warning limits
LMGPSH	618335A	LR22161430	ICP-MS	14/07/2022 15:55	Multiple analyte warnings: Ce, La, Pt	Outwith upper warning limits

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
STSD-1	618384A	LR22161430	ICP-MS	14/07/2022 19:46	Single analyte failure (Pt) and multiple analyte warnings (Cd, Ge, Ta, U, W)	Outwith upper control and upper/lower warning limits
ORS	618437A	LR22161430	ICP-MS	15/07/2022 12:47	Multiple analyte warnings: Ge, Pt	Outwith upper/lower warning limits
WXSERP	618514A	LR22231925	ICP-MS	13/09/2022 13:01	Multiple analyte warnings: Pb, Pd, Te	Outwith upper/lower warning limits
STSD-1	618615A	LR22231925	ICP-MS	13/09/2022 16:26	Single analyte failure (Zn) and multiple analyte warnings (Cr, K, Ni, Th)	Outwith lower control and upper/lower warning limits
WWLPAL	618637A	LR22231925	ICP-MS	13/09/2022 20:16	Multiple analyte warnings: Bi, Cd, Pt	Outwith upper/lower warning limits
LMGPSH	618137A	LR22242928	ICP-MS	13/09/2022 22:39	Single analyte failure (Pd) and multiple analyte warnings (Hg, Sb)	Outwith upper control and warning limits
CARLST	618163A	LR22242928	ICP-MS	14/09/2022 00:16	Single analyte failure (Pd) and multiple analyte warnings (V, W)	Outwith upper control and upper/lower warning limits
STSD-3	618188A	LR22242928	ICP-MS	16/09/2022 16:06	Multiple analyte warnings: In, Pd	Outwith upper warning limits
STSD-1	670195A	LR22288968	ICP-MS	16/11/2022 09:45	Multiple analyte warnings: Al, Mn, Pb	Outwith lower warning limits
WWLPAL	670170A	LR22288968	ICP-MS	16/11/2022 12:02	Multiple analyte warnings: K, Ti	Outwith upper warning limits
STSD-1	670221A	LR22307651	ICP-MS	07/12/2022 16:57	Multiple analyte warnings: Ge, Pd	Outwith upper warning limits
LMGPSH	670247A	LR22307651	ICP-MS	07/12/2022 18:17	Single analyte failure: Au	Outwith lower control limit
LGRAN	670308A	LR22307651	ICP-MS	07/12/2022 21:03	Multiple analyte warnings: B, Fe, S	Outwith upper warning limits
ORS	670383A	LR22307651	ICP-MS	09/12/2022 12:21	Multiple analyte warnings: Hf, Mo, W, Zr	Outwith upper warning limits
TILL-3	670871A	LR22324665	ICP-MS	13/12/2022 03:07	Single analyte failure (Au) and multiple analyte warnings (B, In, Pd)	Outwith lower control and upper warning limits
MONPB	670894A	LR22324665	ICP-MS	13/12/2022 04:17	Multiple analyte warnings: Pd, Ta	Outwith upper warning limits
TILL-1	670932A	LR22324665	ICP-MS	13/12/2022 07:06	Multiple analyte warnings: Ca, Ga, Mg	Outwith lower warning limits

CRM	Sample ID	Laboratory batch number/LIMS code	Analyses application	Date	Description	Failure/warning
ORS	670983A	LR22324665	ICP-MS	15/12/2022 10:10	Multiple analyte warnings: B, W	Outwith upper/lower warning limits
WXSERP	671042A	LR22324665	ICP-MS	05/01/2023 22:55	Multiple analyte warnings: Ge, Hf	Outwith upper/lower warning limits
STSD-1	618015A	LR22147409	ICP-MS	11/01/2023 11:28	Single analyte failure (B) and single analyte warning (Y)	Outwith upper control and lower warning limits
CARLST	670720A	LR23002999	ICP-MS	16/01/2023 23:17	Single analyte failure: Au	Outwith lower control limit
WWLPAL	670770A	LR23002999	ICP-MS	17/01/2023 14:50	Multiple analyte warnings: Nb, Re, Ta	Outwith upper/lower warning limits
STSD-1	670795A	LR23002999	ICP-MS	17/01/2023 16:13	Multiple analyte warnings: Be, Sb	Outwith upper warning limits
WXSERP	670442A	LR23008685	ICP-MS	26/02/2023 09:49	Multiple analyte warnings: B, Hf, Ti, Zr	Outwith upper warning limits
WXSERP	670468A	LR23008685	ICP-MS	26/02/2023 10:28	Multiple analyte warnings: Hf, Zr	Outwith upper warning limits
TILL-2	670492A	LR23008685	ICP-MS	26/02/2023 11:55	Multiple analyte warnings: Ge, Hf, Te	Outwith upper/lower warning limits
STSD-1	670506A	LR23008685	ICP-MS	26/02/2023 12:16	Multiple analyte failures (Pd, Sb) and multiple analyte warnings (B, Ge, Li, Mo, Re, Sr, Y)	Outwith upper control and upper/lower warning limits
WWLPAL	670531A	LR23008685	ICP-MS	27/02/2023 03:45	Multiple analyte warnings: S, Th	Outwith upper/lower warning limits
ORS	670582A	LR23008685	ICP-MS	27/02/2023 06:22	Multiple analyte warnings: Au, Nb, Se	Outwith upper/lower warning limits
WXSERP	671068A	LR22324665	ICP-MS	28/02/2023 02:47	Multiple analyte warnings: Ba, Bi, Cs, Hf, Hg, Li, Rb, Sn, Y, Zr	Outwith upper warning limits
APT_pH	671019A	LR22324675	pH CaCl2	17/03/2023 07:39		Outwith lower warning
SST_pH	670894A	LR22324675	pH CaCl2	16/03/2023 21:47		Outwith lower failure

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	LR22104615	RR22871393-009	ICP-MS	23/05/2022 13:55	Multiple analyte warnings (Ba, La, Nb, Sr, Zr)	Outwith lower warning limit
MRGeo08	LR22104615	RR22871393-040	ICP-MS	23/05/2022 15:18	Single analyte warning (Se)	Outwith lower warning limit
OREAS-45f	LR22104615	RR22871394-028	ICP-MS	23/05/2022 16:14	Single analyte warning (Ga)	Outwith upper warning limit
OREAS 920	LR22104615	RR22871394-040	ICP-MS	23/05/2022 16:34	Multiple analyte warnings (Bi, La, Pb, V)	Outwith upper warning limit
OREAS 46	LR22104615	RR22871395-007	ICP-MS	23/05/2022 16:58	Multiple analyte warnings (Bi, V)	Outwith upper / lower warning limits
MRGeo08	LR22104615	RR22871395-040	ICP-MS	23/05/2022 17:49	Single analyte failure (Re) and multiple analyte warnings (Ag, As, Bi, Cr, Se, Te, Th, Zr)	Outwith lower control and warning limits
OREAS-45f	LR22104615	RR22871396-005	ICP-MS	24/05/2022 21:29	Single analyte failure (Tl) and multiple analyte warnings (Bi, Cs, Hf, Pb, Sb, Th, Ti, U)	Outwith upper control limit and upper / lower warning limits
OREAS 920	LR22104615	RR22871396-040	ICP-MS	24/05/2022 22:37	Multiple analyte failures (La, Re) and warnings (Cd, Ce, Hg, Ni, P, Sr, Tl, U, Y)	Outwith upper control limit and upper / lower warning limits
OREAS 46	LR22104615	RR22871397-035	ICP-MS	25/05/2022 00:19	Single analyte failure (P) and multiple analyte warnings (Co, Cu, Rb, Sr)	Outwith lower control limit and upper / lower warning limits
MRGeo08	LR22104615	RR22871397-040	ICP-MS	25/05/2022 00:28	Multiple analyte warnings (Ba, Nb)	Outwith lower warning limit
OREAS-45f	LR22104615	RR22871398-025	ICP-MS	25/05/2022 02:15	Single analyte warning (Hf)	Outwith upper warning limit
OREAS 920	LR22104615	RR22871398-036	ICP-MS	25/05/2022 02:33	Multiple analyte warnings (Al, P)	Outwith lower warning limit
OREAS 46	LR22104615	RR23047075-016	ICP-MS	09/06/2022 22:48	Multiple analyte failures (Pt, Te) and warnings (Cs, Y, Zr)	Outwith upper control and upper warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
MRGeo08	LR22104615	RR23047075-040	ICP-MS	09/06/2022 23:46	Multiple analyte warnings (Ag, Cs, Re, Sn, Y, Zr)	Outwith upper warning limit
OREAS 46	LR22136803	RR23047079-018	ICP-MS	11/06/2022 12:08	Single analyte warning (La)	Outwith lower warning limit
MRGeo08	LR22136803	RR23047079-040	ICP-MS	11/06/2022 13:09	Multiple analyte failures (Au, Nb) and warnings (Ag, Bi, Ce, Cs, La, Mo, Pb, Pd, Re, Sn, Tl, W, Y, Zr)	Outwith upper control limit and upper / lower warning limits
OREAS 46	LR22136803	RR23047081-027	ICP-MS	11/06/2022 15:42	Multiple analyte warnings (Bi, Cd)	Outwith lower warning limit
MRGeo08	LR22136803	RR23047081-040	ICP-MS	11/06/2022 16:04	Single analyte failure (Au) and multiple analyte warnings (Cr, Cu, Ta)	Outwith upper control limit and upper / lower warning limits
OREAS 46	LR22136803	RR23048317-014	ICP-MS	13/06/2022 12:56	Multiple analyte warnings (As, Cs, Pb, Te)	Outwith upper warning limit
MRGeo08	LR22136803	RR23048317-040	ICP-MS	13/06/2022 13:47	Multiple analyte warnings (Bi, Co, Cs)	Outwith lower warning limit
OREAS 46	LR22147409	RR23056657-007	ICP-MS	13/06/2022 14:15	Single analyte warning (Sb)	Outwith lower warning limit
MRGeo08	LR22147409	RR23056657-040	ICP-MS	13/06/2022 15:22	Single analyte failure (Nb) and multiple analyte warnings (Cd, Mo, Ta)	Outwith lower warning limit
OREAS-45f	LR22147409	RR23056658-003	ICP-MS	13/06/2022 15:45	Multiple analyte failures (Au, Ta) and warnings (Bi, Hf, In, Sc, Sn, Tl)	Outwith upper / lower control limits and lower warning limits
MRGeo08	LR22136803	RR23048315-040	ICP-MS	13/06/2022 23:43	Single analyte failure (Te) and single analyte warning (Nb)	Outwith lower control and warning limits
OREAS 46	LR22147409	RR23056659-016	ICP-MS	14/06/2022 00:29	Multiple analyte failures (Ba, Ce, La) and warnings (Cd, Cs, Ge, Tl, U)	Outwith upper control and upper / lower warning limits
MRGeo08	LR22147409	RR23056659-040	ICP-MS	14/06/2022 01:29	Multiple analyte warnings (Be, Fe, Sb, Ta, Tl, W)	Outwith upper / lower warning limits
OREAS 46	LR22147409	RR23056661-018	ICP-MS	14/06/2022 03:56	Multiple analyte failures (Ag, U) and warnings (Ce, K)	Outwith upper control and upper warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
MRGeo08	LR22147409	RR23056661-040	ICP-MS	14/06/2022 04:34	Single analyte failure (Fe) and multiple analyte warnings (Bi, Ce, La, Rb, Re, Th, Tl, U, W, Zr)	Outwith upper control and upper warning limits
MRGeo08	LR22147409	RR23056660-040	ICP-MS	14/06/2022 11:18	Single analyte failure (Na) and multiple analyte warnings (Ce, Cs, Re, Sn)	Outwith upper control and upper warning limits
OREAS-45f	LR22147409	RR23056662-010	ICP-MS	14/06/2022 12:17	Multiple analyte warnings (Sb, Th)	Outwith upper / lower warning limits
MRGeo08	LR22147409	RR23056662-036	ICP-MS	14/06/2022 12:58	Multiple analyte failures (Ti, Zn) and warnings (Al, Ba, Ce, Hf, Mn, Na, Sn, W, Zr)	Outwith upper control and upper warning limits
MRGeo08	LR22136803	RR23093501-040	ICP-MS	17/06/2022 22:13	Single analyte failure (Te) and multiple analyte warnings (B, Cd, Cr, Cu, Ga, Ge, In, Na, Sr, Ti, U, V, Y)	Outwith upper control and upper / lower warning limits
OREAS 46	LR22136803	RR23093502-032	ICP-MS	17/06/2022 23:46	Single analyte warning (Cd)	Outwith lower warning limit
MRGeo08	LR22136803	RR23093502-040	ICP-MS	18/06/2022 00:17	Single analyte failure (Te) and multiple analyte warnings (Ba, Be, Na)	Outwith upper control and lower warning limits
OREAS 46	LR22136803	RR23165593-003	ICP-MS	29/06/2022 04:28	Multiple analyte warnings (Fe, Ga, Mn)	Outwith upper / lower warning limits
MRGeo08	LR22136803	RR23165593-008	ICP-MS	29/06/2022 04:37	Multiple analyte warnings (Cu, Mn)	Outwith lower warning limit
OREAS-45f	LR22147409	RR23169800-006	ICP-MS	29/06/2022 05:01	Single analyte failure (Hf) and single analyte warning (Co)	Outwith lower control and warning limits
OREAS 920	LR22147409	RR23169800-024	ICP-MS	29/06/2022 06:25	Multiple analyte failures (Cs, Nb, Ta) and warnings (Au, Ba, Ca, Hf, La, Rb, Sb, Se, Ti, Zr)	Outwith upper control and warning limits
MRGeo08	LR22147409	RR23181426-009	ICP-MS	30/06/2022 18:20	Multiple analyte warnings (B, Mo, Re, Sb, Y)	Outwith upper / lower warning limits
OREAS 46	LR22147409	RR23181426-003	ICP-MS	30/06/2022 18:30	Multiple analyte failures (Ga, Sc) and single analyte warning (Pb)	Outwith upper / lower control and lower warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS 46	LR22161430	RR23225534-024	ICP-MS	14/07/2022 16:26	Multiple analyte failures (Mo, W) and warnings (Co, Cu, Ni, Zn, Zr)	Outwith upper / lower control and lower warning limits
MRGeo08	LR22161430	RR23225534-040	ICP-MS	14/07/2022 17:11	Multiple analyte failures (Ge, Re) and warnings (Bi, Pt, Sc)	Outwith lower control and warning limits
OREAS-45f	LR22161430	RR23225531-006	ICP-MS	14/07/2022 17:36	Multiple analyte failures (Bi, La, Sn) and warnings (Ce, Cs, K, Mg, Pb, Tl, U, Y)	Outwith lower control and upper / lower warning limits
MRGeo08	LR22161430	RR23225531-040	ICP-MS	14/07/2022 18:46	Multiple analyte warnings (Ca, Ce, Ga, Zn)	Outwith upper / lower warning limits
MRGeo08	LR22161430	RR23225535-040	ICP-MS	14/07/2022 20:19	Multiple analyte warnings (Cd, Cr, La, Mo, Th, Tl, U, V)	Outwith upper / lower warning limits
OREAS 46	LR22161430	RR23225538-022	ICP-MS	15/07/2022 11:42	Multiple analyte warnings (Ni, Th)	Outwith upper warning limit
OREAS-45f	LR22161430	RR23225537-025	ICP-MS	15/07/2022 13:21	Single analyte warning (Al)	Outwith upper warning limit
MRGeo08	LR22161430	RR23225537-040	ICP-MS	15/07/2022 14:56	Multiple analyte warnings (La, Pt)	Outwith upper / lower warning limits
OREAS 46	LR22161430	RR23225536-028	ICP-MS	15/07/2022 16:12	Multiple analyte warnings (Hg, P, Te)	Outwith upper / lower warning limits
MRGeo08	LR22161430	RR23225536-040	ICP-MS	15/07/2022 16:35	Single analyte failure (V) and single analyte warning (Cr)	Outwith lower control and warning limits
OREAS 46	LR22161430	RR23281762-006	ICP-MS	19/07/2022 21:12	Multiple analyte failures (Pt, Ta) and warnings (Au, Fe, Li, Sb, Se)	Outwith upper control and upper / lower warning limits
MRGeo08	LR22161430	RR23281762-010	ICP-MS	19/07/2022 21:20	Multiple analyte failures (Fe, Ta) and single analyte warning (Ti)	Outwith upper / lower control and lower warning limits
OREAS-45f	LR22161430	RR23332701-003	ICP-MS	29/07/2022 02:16	Multiple analyte failures (Rb, Sr) and warnings (Ca, Cs, Y,)	Outwith lower control and warning limits
OREAS 920	LR22161430	RR23332701-008	ICP-MS	29/07/2022 02:25	Multiple analyte warnings (Be, Li, Mg, V)	Outwith upper / lower warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS 46	LR22231925	RR23650685-011	ICP-MS	13/09/2022 12:50	Multiple analyte failures (K, Na, Nb) and single analyte warning (Be)	Outwith upper control and warning limits
MRGeo08	LR22231925	RR23650685-040	ICP-MS	13/09/2022 13:43	Multiple analyte failures (Na, Pd) and warnings (Be, Ge, Se, Ta)	Outwith upper control and upper / lower warning limits
OREAS-45f	LR22231925	RR23650686-010	ICP-MS	13/09/2022 14:14	Multiple analyte failures (Nb, Sb) and warnings (Hf, Zr)	Outwith upper control and warning limits
MRGeo08	LR22231925	RR23650686-040	ICP-MS	13/09/2022 15:07	Multiple analyte warnings (As, Cr, Na)	Outwith upper / lower warning limits
OREAS 46	LR22231925	RR23650687-014	ICP-MS	13/09/2022 15:51	Multiple analyte failures (In, Nb, Pd) and warnings (K, Na, Zn)	Outwith upper control and upper / lower warning limits
MRGeo08	LR22231925	RR23650687-040	ICP-MS	13/09/2022 16:30	Multiple analyte warnings (Ga, K, Ti, Y)	Outwith upper / lower warning limits
OREAS-45f	LR22242928	RR23650688-016	ICP-MS	13/09/2022 20:25	Multiple analyte failures (As, Hg, Na, Nb, Se, W) and warnings (Ba, Cu, Ni, Sn, Te)	Outwith upper / lower control and warning limits
MRGeo08	LR22242928	RR23650688-040	ICP-MS	13/09/2022 21:14	Single analyte failure (S) and single analyte warning (Nb)	Outwith lower control and upper warning limits
OREAS 46	LR22242928	RR23650689-023	ICP-MS	13/09/2022 22:18	Multiple analyte warnings (K, Na)	Outwith upper / lower warning limits
MRGeo08	LR22242928	RR23650689-040	ICP-MS	13/09/2022 22:47	Multiple analyte warnings (S, Sb)	Outwith upper / lower warning limits
OREAS-45f	LR22242928	RR23650690-021	ICP-MS	14/09/2022 00:07	Single analyte failure (Mg) and multiple analyte warnings (Be, K)	Outwith lower control and warning limits
MRGeo08	LR22242928	RR23650690-040	ICP-MS	14/09/2022 00:37	Multiple analyte failures (Ca, Cu, Fe, Mg, Mn, P, Pb, S, Ta, Zn) and warnings (Li, Ni)	Outwith upper / lower control and lower warning limits
MRGeo08	LR22242928	RR23654870-040	ICP-MS	15/09/2022 02:12	Multiple analyte warnings (As, Fe)	Outwith lower warning limits
OREAS 46	LR22242928	RR23650691-012	ICP-MS	16/09/2022 16:00	Single analyte failure (W) and single analyte warning (Pd)	Outwith upper control and warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
MRGeo08	LR22242928	RR23650691-040	ICP-MS	16/09/2022 16:50	Multiple analyte warnings (Pd, Sb)	Outwith upper / lower warning limits
OREAS-45f	LR22242928	RR23650692-022	ICP-MS	16/09/2022 17:39	Multiple analyte warnings (Mo, Te, Ti)	Outwith lower warning limits
MRGeo08	LR22242928	RR23650692-040	ICP-MS	16/09/2022 18:14	Multiple analyte warnings (Pd, Se)	Outwith upper warning limit
OREAS-45f	LR22242928	RR23654878-007	ICP-MS	16/09/2022 18:40	Single analyte warning (Ti)	Outwith lower warning limit
MRGeo08	LR22242928	RR23654878-040	ICP-MS	16/09/2022 19:40	Multiple analyte warnings (Fe, W)	Outwith upper / lower warning limits
OREAS-45f	LR22288968	RR24022806-004	ICP-MS	11/11/2022 09:32	Single analyte warning (Ge)	Outwith upper warning limit
MRGeo08	LR22288968	RR24022807-040	ICP-MS	11/11/2022 16:31	Single analyte warning (Nb)	Outwith upper warning limit
OREAS 46	LR22288968	RR24022809-022	ICP-MS	11/11/2022 19:19	Single analyte failure (W) and multiple analyte warnings (Fe, Pb)	Outwith upper control and lower warning limits
MRGeo08	LR22288968	RR24022809-040	ICP-MS	11/11/2022 19:48	Single analyte failure (B)	Outwith lower control limit
OREAS 46	LR22288968	RR24022834-025	ICP-MS	16/11/2022 09:51	Single analyte warning (Mn)	Outwith lower warning limit
MRGeo08	LR22288968	RR24022834-030	ICP-MS	16/11/2022 10:00	Single analyte failure (Mn) and multiple analyte warnings (Al, Au, Ba, Be, Ca, Pb)	Outwith lower control and warning limits
OREAS-45f	LR22288968	RR24022810-002	ICP-MS	16/11/2022 11:12	Multiple analyte failures (Cr, P) and warnings (Fe, Li, Mn, Ni, V)	Outwith lower control and warning limits
OREAS 920	LR22288968	RR24022810-040	ICP-MS	16/11/2022 12:37	Multiple analyte warnings (In, P)	Outwith lower warning limit
OREAS 46	LR22288968	RR24123603-002	ICP-MS	24/11/2022 22:01	Single analyte failure (Au) and multiple analyte warnings (Na, S)	Outwith upper control and warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
MRGeo08	LR22288968	RR24123603-040	ICP-MS	24/11/2022 23:29	Single analyte failure (K)	Outwith lower control limit
MRGeo08	LR22307651	RR24166957-040	ICP-MS	07/12/2022 17:39	Single analyte warning (Li)	Outwith lower warning limit
OREAS-45f	LR22307651	RR24166958-005	ICP-MS	07/12/2022 18:03	Multiple analyte warnings (Co, Fe, In, Na)	Outwith upper warning limit
OREAS 920	LR22307651	RR24166958-040	ICP-MS	07/12/2022 19:09	Multiple analyte warnings (Cr, Hg, Li, Mo, Ni)	Outwith upper / lower warning limits
OREAS 46	LR22307651	RR24166959-003	ICP-MS	07/12/2022 19:30	Single analyte failure (S) and multiple analyte warnings (Ca, Cr, Ti)	Outwith upper control and warning limits
MRGeo08	LR22307651	RR24166959-040	ICP-MS	07/12/2022 21:06	Multiple analyte warnings (Ga, Li)	Outwith lower warning limit
OREAS-45f	LR22307651	RR24166960-022	ICP-MS	08/12/2022 18:15	Single analyte warning (Pb)	Outwith upper warning limit
OREAS 920	LR22307651	RR24166960-040	ICP-MS	08/12/2022 19:06	Single analyte failure (Li)	Outwith lower control limit
OREAS 46	LR22307651	RR24166961-022	ICP-MS	09/12/2022 11:05	Single analyte warning (Co)	Outwith lower warning limit
MRGeo08	LR22307651	RR24166961-040	ICP-MS	09/12/2022 11:58	Multiple analyte warnings (Ce, Cs, Ni, Th, Tl, U)	Outwith upper warning limit
OREAS-45f	LR22307651	RR24166962-024	ICP-MS	09/12/2022 12:53	Multiple analyte warnings (Bi, Ce, Cr, Cu, Fe, Pt, Sn, Th, U)	Outwith upper warning limit
OREAS 920	LR22307651	RR24166962-040	ICP-MS	09/12/2022 13:47	Multiple analyte warnings (Ce, V)	Outwith upper / lower warning limits
OREAS 46	LR22324665	RR24166963-018	ICP-MS	09/12/2022 14:55	Single analyte failure (Tl) and single analyte warning (Ga)	Outwith lower control and warning limits
MRGeo08	LR22324665	RR24166963-040	ICP-MS	09/12/2022 15:30	Multiple analyte failures (Cu, Fe, Ni, P, Pb) and warnings (Li, Mn, S)	Outwith upper control and warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS-45f	LR22324665	RR24166964-002	ICP-MS	13/12/2022 02:35	Multiple analyte failures (B, Re) and single analyte warning (Pt)	Outwith upper control and warning limits
OREAS 920	LR22324665	RR24166964-040	ICP-MS	13/12/2022 03:50	Multiple analyte warnings (Ga, Cs)	Outwith upper / lower warning limits
OREAS 46	LR22324665	RR24231108-003	ICP-MS	15/12/2022 09:35	Multiple analyte warnings (Ge, Mo)	Outwith upper warning limit
MRGeo08	LR22324665	RR24231108-040	ICP-MS	15/12/2022 10:49	Single analyte failure (La) and multiple analyte warnings (Co, Cs, Rb, Th, Tl)	Outwith lower control and warning limits
OREAS 46	LR22324665	RR24375494-025	ICP-MS	05/01/2023 22:52	Single analyte failure (Be) and multiple analyte warnings (Al, Ca, In, Na, P, Sn, Ti, Zr)	Outwith upper control and upper / lower warning limits
MRGeo08	LR22324665	RR24375494-040	ICP-MS	05/01/2023 23:18	Single analyte failure (Be) and multiple analyte warnings (In, Mo, Pt, Sn, Zr)	Outwith upper control and lower warning limits
OREAS 46	LR22147409	RR24391142-007	ICP-MS	11/01/2023 11:02	Multiple analyte failures (B, Mg) and single analyte warning (Ca)	Outwith upper control and warning limits
MRGeo08	LR22147409	RR24391142-036	ICP-MS	11/01/2023 12:22	Single analyte failure (B) and single analyte warning (Cr)	Outwith upper control and warning limits
MRGeo08	LR23002999	RR24418378-040	ICP-MS	13/01/2023 02:53	Multiple analyte failures (Fe, Ni, Pb, Ta) and warnings (Al, Ba, Ca, Cr, Cu, K, Li, Mn, Ti, V, Zn)	Outwith upper control and warning limits
OREAS-45f	LR23002999	RR24418379-027	ICP-MS	13/01/2023 04:33	Single analyte failure (Cd)	Outwith upper control limit
OREAS 920	LR23002999	RR24418379-040	ICP-MS	13/01/2023 04:54	Single analyte warning (La)	Outwith lower warning limit
MRGeo08	LR23002999	RR24418380-040	ICP-MS	16/01/2023 22:15	Multiple analyte warnings (Ag, Cu, Fe, Ni)	Outwith upper / lower warning limits
OREAS 920	LR23002999	RR24418381-040	ICP-MS	17/01/2023 00:05	Multiple analyte failures (Na, Pd) and warnings (Ag, Au, K, Mg, Sb, Sn, Tl)	Outwith upper control and upper / lower warning limits
OREAS 46	LR23002999	RR24418382-015	ICP-MS	17/01/2023 14:28	Multiple analyte warnings (Ca, Co, Cu, Fe, Se)	Outwith upper / lower warning limits

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
MRGeo08	LR23002999	RR24418382-040	ICP-MS	17/01/2023 15:21	Single analyte failure (B) and single analyte warning (Au)	Outwith lower control and upper warning limits
OREAS-45f	LR23002999	RR24418406-003	ICP-MS	17/01/2023 15:43	Single analyte failure (Cd) and multiple analyte warnings (B, Be, Ge, Mg)	Outwith upper control and upper / lower warning limits
OREAS 920	LR23002999	RR24418406-024	ICP-MS	17/01/2023 16:24	Multiple analyte warnings (Be, Mg, Sc)	Outwith upper / lower warning limits
OREAS-45f	LR22324665	RR24481853-016	ICP-MS	27/01/2023 15:38	Multiple analyte failures (Cd, Zn) and warnings (B, K)	Outwith upper / lower control and warning limits
OREAS 920	LR22324665	RR24481853-022	ICP-MS	27/01/2023 15:48	Single analyte failure (In)	Outwith upper control limit
OREAS 46	LR23002999	RR24564358-027	ICP-MS	08/02/2023 23:24	Single analyte failure (Li)	Outwith upper control limit
MRGeo08	LR23002999	RR24564358-040	ICP-MS	08/02/2023 23:59	Multiple analyte failures (Li, Ni) and warnings (B, Cu, Ge, P, Pb)	Outwith upper control and upper / lower warning limits
OREAS-45f	LR22324665	RR24585878-010	ICP-MS	13/02/2023 14:00	Multiple analyte failures (Ag, Ni) and warnings (B, Cd, Cu, Te)	Outwith upper / lower control and warning limits
OREAS 920	LR22324665	RR24585878-032	ICP-MS	13/02/2023 14:35	Multiple analyte warnings (Ag, In, P)	Outwith upper warning limit
OREAS 46	LR23008685	RR24651749-002	ICP-MS	26/02/2023 09:35	Multiple analyte failures (B, Ti) and warnings (Co, V)	Outwith upper control and warning limits
MRGeo08	LR23008685	RR24651749-040	ICP-MS	26/02/2023 10:46	Multiple analyte warnings (Mo, Ni, Pb, Pd)	Outwith upper / lower warning limits
OREAS-45f	LR23008685	RR24651750-009	ICP-MS	26/02/2023 11:18	Multiple analyte failures (Cd, Te) and warnings (B, Na, Nb, Pb)	Outwith upper / lower control and warning limits
OREAS 920	LR23008685	RR24651750-040	ICP-MS	26/02/2023 12:19	Multiple analyte failures (Hf, Zr) and single analyte warning (Te)	Outwith lower control and warning limits
OREAS 46	LR23008685	RR24651751-026	ICP-MS	27/02/2023 03:42	Multiple analyte warnings (Li, Pb, Zr)	Outwith upper warning limit

CRM	Batch number	LIMS code	Analysis	Date / Time	Description	Failure / warning
OREAS-45f	LR23008685	RR24651752-018	ICP-MS	27/02/2023 04:56	Single analyte failure (B) and multiple analyte warnings (As, Cd, Cr, Ge, Li, Nb, Sb, Te, W)	Outwith upper control and upper / lower warning limits
OREAS 920	LR23008685	RR24651752-040	ICP-MS	27/02/2023 05:43	Multiple analyte failures (Hf, Te, Zr) and warnings (Li, Sc)	Outwith upper / lower control and upper warning limits
OREAS 46	LR23008685	RR24651753-015	ICP-MS	27/02/2023 06:38	Multiple analyte failures (Ag, Au)	Outwith upper / lower control limit
MRGeo08	LR23008685	RR24651753-026	ICP-MS	27/02/2023 06:56	Single analyte warning (Pb)	Outwith upper warning limit
OREAS-45f	LR22324665	RR24672134-009	ICP-MS	28/02/2023 02:41	Multiple analyte failures (B, Cd, Hg) and warnings (Ba, Cu, Ni)	Outwith upper / lower control and upper warning limits
OREAS 920	LR22324665	RR24672134-019	ICP-MS	28/02/2023 03:03	Single analyte failure (Li) and multiple analyte warnings (Al, La, Mn, P, S)	Outwith upper control and upper / lower warning limits
OREAS 922	LR22324665	RR24672134-020	ICP-MS	28/02/2023 03:05	Single analyte warning (Cs)	Outwith lower warning limit
OREAS 46	LR22324665	RR24672133-033	ICP-MS	28/02/2023 04:27	Single analyte failure (Mn) and single analyte warning (Li)	Outwith upper control and warning limits
MRGeo08	LR22324665	RR24672133-040	ICP-MS	28/02/2023 04:40	Single analyte failure (Pb) and multiple analyte warnings (Cs, Li, Mn, Ni, S)	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 G7A and G8A surveys are combined, data for the LOI and pH SRMs are derived solely from the G8A 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 G8A data are generally higher than those for adjacent survey blocks. Consequently, the G8A data require conditioning, or levelling, if they are to be mapped together with data for other blocks. The linear regression relationship between the G8A 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.

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R squared
Ag (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	0.0556	0.897	0.999
Al (%)	TILL-1, TILL-2, TILL-3	partial	0.351	0.713	0.997
As (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	3.59	0.966	0.998
Au (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-0.000631	0.733	0.59

Analyte	CRMs	Digestion	Linear regression relationships		
			Intercept	Slope	R squared
B (mg kg^{-1})	STSD-1, STSD-3	total	-10.2	0.201	1
Ba (mg kg^{-1})	TILL-1, TILL-2, TILL-3	partial	-4.99	1.01	0.998
Be (mg kg^{-1})	TILL-1, TILL-2, TILL-3	partial	-0.401	8.68	0.992
Bi (mg kg^{-1})					
Ca (%)	TILL-1, TILL-2, TILL-3	partial	0.0757	0.657	0.978
Cd (mg kg^{-1})	TILL-1, TILL-2, TILL-3	partial	-0.00343	1.13	0.995
Ce (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-3.08	0.732	0.95
Co (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	-0.773	1.05	0.974
Cr (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	5.52	0.736	0.991
Cs (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-0.00145	0.545	0.998
Cu (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	0.972	0.955	0.998
Fe (%)	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	0.22	0.918	0.95
Ga (mg kg^{-1})					
Ge (mg kg^{-1})					
Hf (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	0.0176	0.00196	0.0949
Hg (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	-0.0285	1.22	0.993
In (mg kg^{-1})					
K (%)	TILL-1, TILL-2, TILL-3	partial	-0.0294	0.777	0.993
La (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-	total	2.46	0.576	0.847
Li (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-	total	0.957	0.725	0.977
Mg (%)	TILL-1, TILL-2, TILL-3	partial	-0.116	1.05	0.985
Mn (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	92.4	0.918	0.997
Mo (mg kg^{-1})	TILL-1, TILL-2, TILL-3	partial	-1.65	1.22	0.983
Na (%)	TILL-1, TILL-2, TILL-3	partial	0.0142	0.273	0.898
Nb (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-0.239	0.173	0.92
Ni (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	4.56	0.864	0.892
P (%)	TILL-1, TILL-2, TILL-3	partial	0.0123	0.674	0.631
Pb (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	2.09	0.955	0.998
Pd (mg kg^{-1})					
Pt (mg kg^{-1})					
Rb (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-2.55	0.267	0.94
Re (mg kg^{-1})					
S (%)	STSD-1, STSD-3	total	-0.03	1.37	1
Sb (mg kg^{-1})	STSD-1, STSD-3	partial	-0.435	1.35	1
Sc (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	3.49	0.0358	0.00638
Se (mg kg^{-1})					
Sn (mg kg^{-1})					

Analyte	CRMs	Digestion	Linear regression relationships		
			Intercept	Slope	R squared
Sr (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	34.9	-0.0178	0.00258
Ta (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2	total	0.00269	-8.00E-04	0.531
Te (mg kg^{-1})					
Th (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-1.31	0.5	0.797
Ti (%)	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	0.0453	0.0125	0.585
Tl (mg kg^{-1})					
U (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-1.11	0.912	0.972
V (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	16.6	0.611	0.746
W (mg kg^{-1})					
Y (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	-4	0.587	0.546
Zn (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	partial	-4.62	1	0.999
Zr (mg kg^{-1})	STSD-1, STSD-3, TILL-1, TILL-2, TILL-3	total	0.628	0.00239	0.0757

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

Analyte	Linear regression relationships		
	Intercept	Slope	R squared
LOI at 450°C (%)	0.424	0.998	1
pH $CaCl_2$	-0.0616	1.1	0.999

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

Analyte	CRMs	Digestion	Linear regression relationships		
			Intercept	Slope	R^2
Ag (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00332	0.981	1
Al (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0343	1.01	0.999
As (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0359	1.03	1
Au (mg kg^{-1})	OREAS45f, MRGeo08	partial	2.79E-04	0.935	1
B (mg kg^{-1})		n/a			
Ba (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-4.08	1.01	1
Be (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.00293	0.96	0.996
Bi (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00411	0.972	0.998
Ca (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.0052	0.992	1
Cd (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00515	1.02	1
Ce (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.696	0.995	1
Co (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00452	0.995	1
Cr (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.234	1	1
Cs (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0503	1	1
Cu (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.965	1.01	1

Analyte	CRMs	Digestion	Linear regression relationships Intercept	Slope	R^2
Fe (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0872	1.03	1
Ga (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.445	1.04	0.999
Ge (mg kg^{-1})	OREAS45f, OREAS46, MRGeo08	partial	0.0253	0.856	0.858
Hf (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00307	0.965	0.99
Hg (mg kg^{-1})	OREAS45f, OREAS46, MRGeo08	partial	8.06E-04	1.01	0.997
In (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0018	0.991	1
K (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0129	1.03	0.999
La (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.486	1.01	0.996
Li (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.115	1.01	1
Mg (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0345	1.05	0.999
Mn (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-4.38	1	0.999
Mo (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0687	1.01	1
Na (%)	OREAS45f, OREAS46, MRGeo08	partial	4.78E-04	1.02	1
Nb (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	-0.21	1.16	0.995
Ni (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-2.42	1.03	1
P (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	2.97E-04	1.01	0.999
Pb (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.15	1.01	1
Pd (mg kg^{-1})	OREAS45f, MRGeo08	partial	-0.0045	1.07	1
Pt (mg kg^{-1})	OREAS45f, MRGeo08	partial	-7.75E-04	0.999	1
Rb (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.465	1	1
Re (mg kg^{-1})		n/a			
S (%)	OREAS45f, OREAS920, MRGeo08	partial	7.08E-04	0.978	1
Sb (mg kg^{-1})	OREAS46, OREAS920, MRGeo08	partial	0.0127	0.932	1
Sc (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.265	1.04	1
Se (mg kg^{-1})	OREAS920, MRGeo08	partial	-0.653	1.01	1
Sn (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0535	1.01	0.999
Sr (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-1.16	1.01	1
Ta (mg kg^{-1})		n/a			
Te (mg kg^{-1})	OREAS46, MRGeo08	partial	-0.00829	1.43	1
Th (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0822	0.986	1
Ti (%)	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.00386	0.972	1
Tl (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.00807	1	1
U (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.0402	1.01	1
V (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.595	0.99	0.999
W (mg kg^{-1})	OREAS46, MRGeo08	partial	0.00232	0.95	1
Y (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	0.338	0.945	0.995
Zn (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.285	1.01	1

			Linear regression relationships		
Analyte	CRMs	Digestion	Intercept	Slope	R^2
Zr (mg kg^{-1})	OREAS45f, OREAS46, OREAS920, MRGeo08	partial	-0.376	0.99	0.993

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.

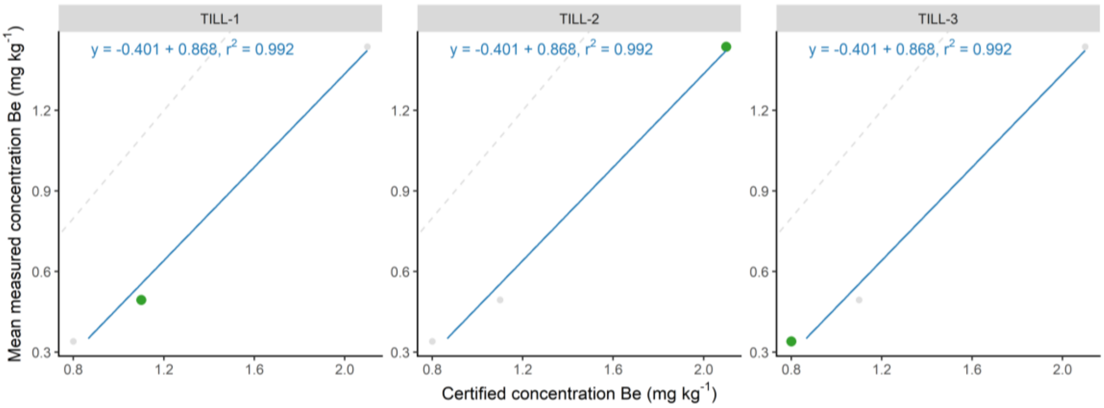


Chart 2 Beryllium (Be) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is not visible but lies to the right of the chart area.

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.

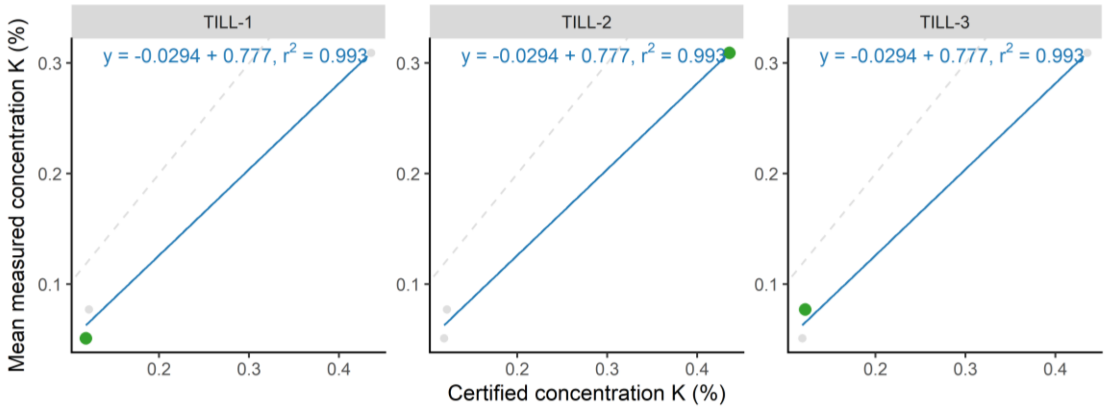


Chart 3 Potassium (K) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

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.

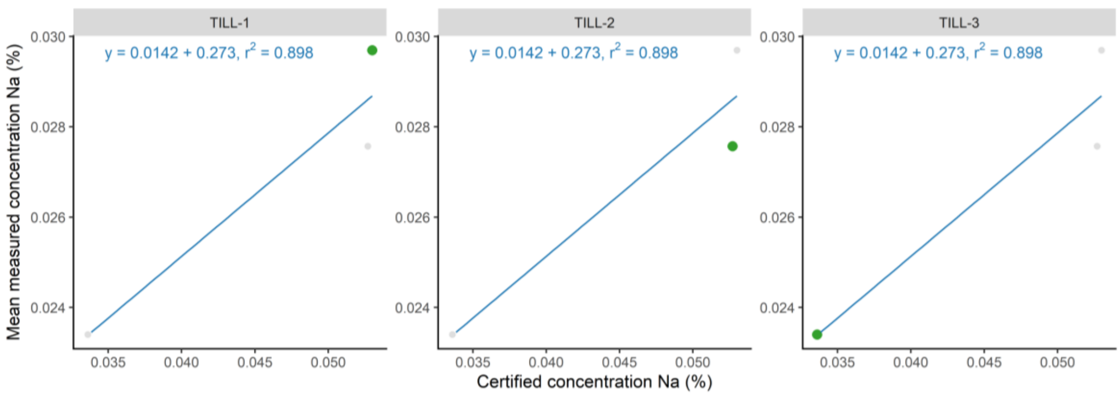


Chart 4 Sodium (Na) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is not visible but lies to the left of the chart area.

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.

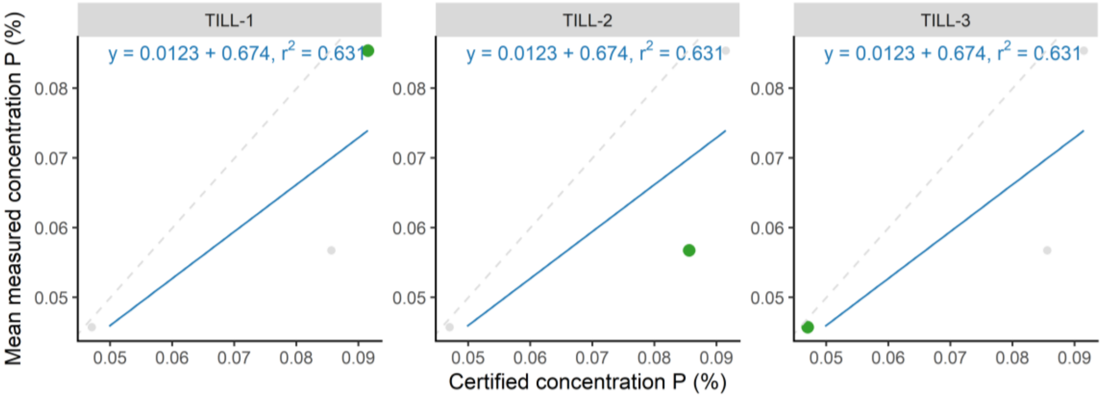


Chart 5 Phosphorus (P) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

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.

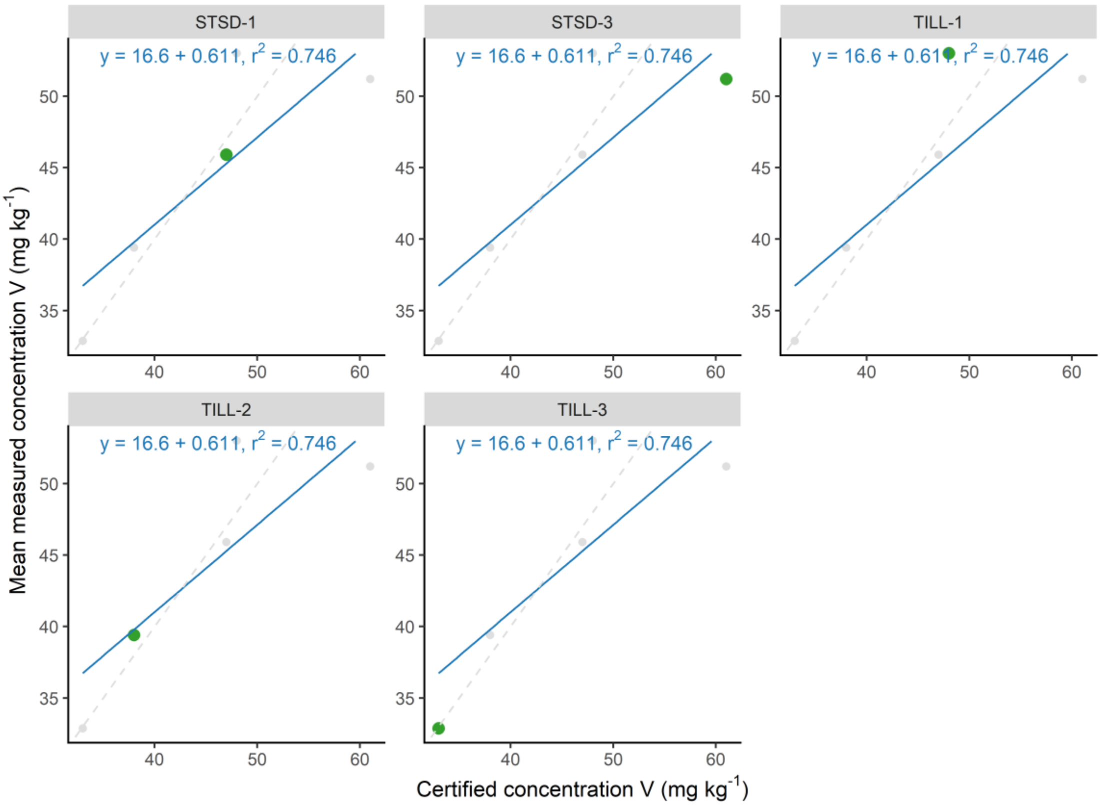


Chart 6 Vanadium (V) (MS41L-BLD) determined by ICP-MS in blind CRMs, faceted by CRM name. The 1:1 equality line is shown as a feint dashed grey line.

pH $CaCl_2$

Reported pH values for SRMs for G8A 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).

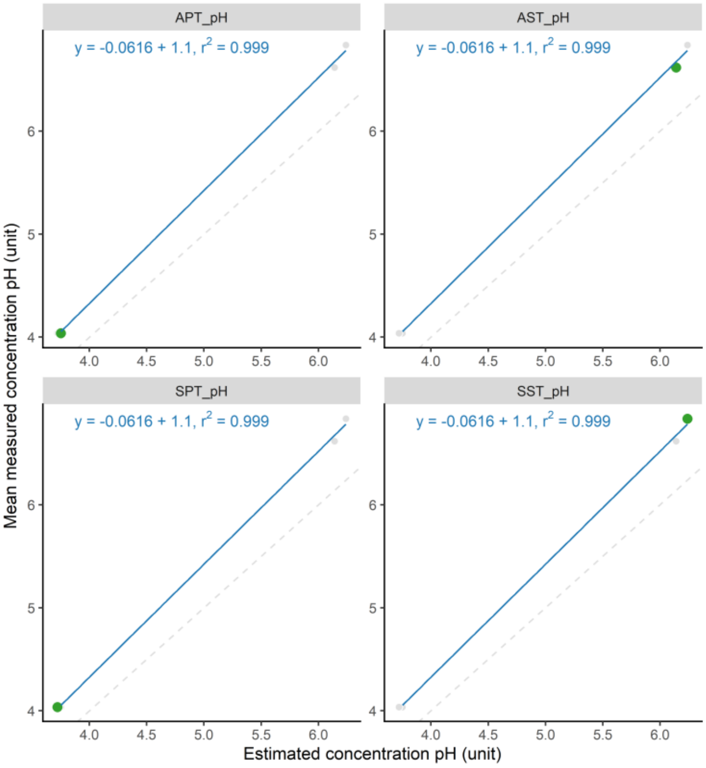


Chart 7 pH CaCl2 in blind SRMs, faceted by SRM name. The 1:1 equality line is shown as a feint dashed grey line.

AURUM GLOBAL EXPLORATION

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 %	-8.75%	8.64%	-76.53%	19.71%	-92.85%	-55.60%	-74.89%	N/A	-36.69%	14.98%	-30.48%	-0.10%
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 %	-3.67%	-40.65%	1.64%	-3.09%	N/A	N/A	-99.55%	-2.81%	N/A	-92.88%	-30.12%	-19.92%
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 %	-45.26%	-4.81%	-49.23%	-97.93%	-85.72%	14.87%	-11.74%	0.45%	N/A	N/A	-74.10%	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%	90.9%	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 %	20.20%	13.18%	-73.29%	N/A	-58.98%	-82.86%	-101.25%	N/A	-82.23%	-92.11%	N/A	-16.97%
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%	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 %	-2.30%	N/A	-43.20%	-1.79%	-99.63%							
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 %	-63.06%	5.21%	-72.77%	16.69%	-87.80%	-55.71%	-57.69%	N/A	-46.58%	10.43%	-39.50%	-0.36%
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 %	-9.33%	-47.31%	0.34%	-4.16%	N/A	N/A	-99.64%	-9.05%	N/A	-91.68%	-42.42%	-15.34%
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 %	-44.34%	-8.26%	-12.33%	-97.38%	-88.30%	13.31%	-16.95%	1.87%	N/A	N/A	-77.41%	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%	85.7%	100%	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 %	17.35%	16.73%	-72.65%	N/A	-62.50%	-71.93%	-100.56%	N/A	-88.46%	-90.26%	N/A	-21.82%
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%	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 %	-16.02%	N/A	-45.08%	-2.27%	-99.62%							
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 %	-37.31%	6.00%	-7.85%	22.21%	N/A	-7.11%	350.00%	N/A	-23.40%	N/A	-30.74%	1.35%
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 %	-13.25%	-42.63%	-7.92%	4.76%	N/A	N/A	-99.88%	-9.51%	N/A	-57.91%	-38.26%	-36.67%
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 %	-14.80%	13.42%	N/A	-94.39%	-84.16%	-6.88%	-6.83%	11.88%	N/A	N/A	-87.17%	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%	100%	100%	0.0%	75.0%

	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	-31.73%	-61.75%	N/A	N/A	-96.66%	-100.71%	N/A	-65.51%	-85.68%	N/A	-65.57%
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 %	10.47%	N/A	-68.29%	-8.96%	-99.87%
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 %	-23.75%	22.88%	-18.48%	3.18%	N/A	-3.42%	585.71%	16.75%	-25.26%	6.83%	-27.27%	-3.94%
Cert	Total	Partial	Partial	Partial	N/A	Partial	Partial	Partial	Partial	Partial	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 %	-17.06%	-45.06%	-3.78%	3.36%	N/A	N/A	-99.41%	-15.88%	N/A	-28.82%	-31.19%	-27.39%
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 %	-10.23%	15.61%	14.20%	-94.83%	-82.29%	-2.50%	-33.70%	9.05%	N/A	N/A	-74.11%	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%	100%	0.0%	50.0%
	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	-48.88%	-60.13%	N/A	N/A	-90.80%	-100.26%	N/A	-51.88%	-97.91%	N/A	-45.31%
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 %	3.68%	-62.40%	-70.28%	-4.74%	-99.14%							
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 %	-73.75%	-6.95%	1.40%	0.92%	N/A	-10.23%	325.00%	N/A	-19.47%	N/A	-28.04%	-2.84%
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%	75.0%	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 %	-18.18%	-55.41%	-9.89%	-0.56%	N/A	N/A	-99.28%	-7.01%	N/A	-34.43%	-31.73%	-20.60%
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 %	-10.91%	-0.89%	N/A	-93.01%	-84.12%	-1.95%	-3.19%	7.42%	N/A	N/A	-84.93%	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%	100%	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	-32.56%	-66.73%	N/A	N/A	-94.30%	N/A	N/A	-40.65%	-75.77%	N/A	-46.01%
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%	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 %	-0.38%	N/A	-61.85%	-6.05%	-99.08%							
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 37 blank analyses for the G8 A 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 seven elements contained exceedances of the LLD concentrations: Ag (two exceedances of the LLD across two laboratory analytical batches), Cd (two exceedances across two batches), Co (two exceedances across two batches), Hg (two exceedances in one batch), Na (two exceedances across two batches), Tl (four exceedances across four batches) and W (four exceedances across two batches). These exceedances are not systematic, indicating random deviations. The LLD for all these elements, except Hg, is 0.001 mg/kg and in most cases the exceedances reported were either 0.002 or 0.003 mg/kg. For Ag, Cd, Co, 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 five elements do not have material significance for the sample dataset. For Hg, the two blank exceedances in batch LR22324665 were reported as 0.005 and 0.012 mg/kg – four samples in the sample dataset have reported concentrations between the

LLD (0.004 mg/kg) and ≤ 0.012 mg/kg so some caution is required when considering Hg data in this range. For Na, the two observed exceedances of the LLD for blank samples were each reported as 0.002 mg/kg. This concentration overlaps measured concentrations reported for three samples and user caution is thus advised when interpreting data at the lower end of the concentration spectrum for Na.

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	37	37	37	37	37	37	37	37	37	37
Count > LLD	0	2	0	0	0	0	0	0	0	2
% > LLD	0.0%	5.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	5.4%
	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	37	37	37	37	37	37	37	37	37	37
Count > LLD	0	2	0	0	1	0	0	0	1	2
% > LLD	0.0%	5.4%	0.0%	0.0%	2.7%	0.0%	0.0%	0.0%	2.7%	5.4%
	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	37	37	37	37	37	37	37	37	37	37
Count > LLD	0	0	0	0	0	0	0	2	0	0
% > LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	5.4%	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	37	37	37	37	37	37	37	37	37	37
Count > LLD	0	0	0	0	0	0	0	1	1	1
% > LLD	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	2.7%	2.7%	2.7%
	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	37	37	37	37	37	37	37	37	37	37
Count > LLD	0	1	0	0	0	0	4	0	0	4
% > LLD	0.0%	2.7%	0.0%	0.0%	0.0%	0.0%	10.8%	0.0%	0.0%	10.8%
	Y mg kg^{-1}	Zn mg kg^{-1}	Zn mg kg^{-1}							
Count	37	37	37							
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	37	37	37	37	37	37	37	37	37	37
Count > LLD	7	28	14	19	10	9	15	25	21	29
% > LLD	18.9%	75.7%	37.8%	51.4%	27.0%	24.3%	40.5%	67.6%	56.8%	78.4%

	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	37	37	37	37	37	37	37	37	37	37
Count > LLD	18	20	26	15	27	10	26	30	14	27
% > LLD	48.6%	54.1%	70.3%	40.5%	73.0%	27.0%	70.3%	81.1%	37.8%	73.0%

	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	37	37	37	37	37	37	37	37	37	37
Count > LLD	16	13	24	12	3	19	24	22	19	22
% > LLD	43.2%	35.1%	64.9%	32.4%	8.1%	51.4%	64.9%	59.5%	51.4%	59.5%

	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	37	37	37	37	37	37	37	37	37	37
Count > LLD	23	17	15	4	18	17	25	28	21	19
% > method LLD	62.2%	45.9%	40.5%	10.8%	48.6%	45.9%	67.6%	75.7%	56.8%	51.4%

	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	37	37	37	37	37	37	37	37	37	37
Count > LLD	25	26	30	17	15	1	21	11	23	30
% > LLD	67.6%	70.3%	81.1%	45.9%	40.5%	2.7%	56.8%	29.7%	62.2%	81.1%

	Y mg kg^{-1}	Zn mg kg^{-1}	Zn mg kg^{-1}
Count	37	37	37
Count > LLD	18	20	24
% > LLD	48.6%	54.1%	64.9%

Analytical interferences

In analytical chemistry there is always potential for interferences between analytes. This can be due to the chemical properties of a measurand, spectral interferences (where a signal overlaps or masks another) or physical matrix effects whereby the chemical behaviour in a given matrix needs to be specifically accounted for by calibration. Typically, these are addressed by the laboratory through adaptation of the method and/or instrument (*e.g.* sample dilution), or 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 shallow 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	3.2	5.5	6.1	6.4	6.6	6.9	7.1	7.1	7.2	7.3	7.4	7.5	7.6	7.7
LOI (450°C)	0.01	%	877	0	0	1.29	7.18	8.32	8.95	9.77	11.5	13	13.4	13.8	15.3	16.8	18.9	22.9	50.6

Table 23 Univariate summary statistics for shallow 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	0.0208	0.115	0.146	0.166	0.194	0.263	0.352	0.385	0.449	0.598	0.832	0.987	1.38	3.39
Al	0.0001	%	877	0	0	0.128	0.661	0.837	0.885	0.949	1.04	1.1	1.12	1.14	1.2	1.3	1.39	1.5	1.76
As	0.0001	mg kg^{-1}	877	0	0	2.28	11.4	13.3	14.4	15.6	17.9	20.8	21.9	23.7	28.9	35.6	42.4	67.7	1000
B	0.1	mg kg^{-1}	877	7	0.80	0.4	2.48	3.3	4.2	5.3	6.9	8.3	8.7	9	10.5	11.8	13.5	16.3	38.5
Ba	0.005	mg kg^{-1}	877	0	0	8.43	56.4	70.4	75.8	86.3	107	125	133	145	181	234	316	426	954
Be	0.0001	mg kg^{-1}	877	0	0	0.0812	0.573	0.824	0.921	1	1.14	1.26	1.31	1.36	1.54	1.76	1.96	2.2	4.21
Bi	0.000005	mg kg^{-1}	877	0	0	0.026	0.139	0.161	0.173	0.189	0.226	0.276	0.292	0.315	0.402	0.511	0.625	1.01	3.71
Ca	0.0001	%	877	0	0	0.0303	0.353	0.573	0.772	1.27	2.63	3.99	4.28	4.72	5.55	6.17	7.61	8.82	13.2
Cd	0.00001	mg kg^{-1}	877	0	0	0.046	0.53	0.98	1.19	1.45	1.82	2.06	2.12	2.19	2.38	2.56	2.74	2.96	6.79
Ce	0.00003	mg kg^{-1}	877	0	0	6.41	17.3	19.9	21.1	22.6	24.7	26.5	26.9	27.3	28.6	29.8	31.6	33.1	39
Co	0.00001	mg kg^{-1}	877	0	0	0.461	6	7.87	8.56	9.5	10.9	12	12.3	12.8	14.1	15.6	16.8	19	26.8
Cr	0.0001	mg kg^{-1}	877	0	0	3	14.1	17.8	18.9	19.9	21.5	22.9	23.4	23.9	25.5	27.2	29.1	31.8	57
Cs	0.00005	mg kg^{-1}	877	0	0	0.196	0.32	0.346	0.367	0.392	0.469	0.571	0.614	0.673	0.864	1.06	1.38	1.82	3.26
Cu	0.0001	mg kg^{-1}	877	0	0	1.61	20.8	27.2	31	36	46.5	57.2	60.9	67.4	91.2	109	139	188	582
Fe	0.00001	%	877	0	0	0.348	1.48	1.81	1.97	2.09	2.28	2.44	2.49	2.59	2.76	2.92	3.14	3.43	6.01

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	0.598	1.99	2.44	2.57	2.77	3.1	3.37	3.47	3.58	3.88	4.17	4.54	4.79	7.2
Ge	0.00005	mg kg^{-1}	877	0	0	0.00658	0.0375	0.046	0.0502	0.0546	0.0615	0.0672	0.0693	0.0721	0.0782	0.0864	0.0965	0.126	0.247
Hf	0.00002	mg kg^{-1}	877	0	0	0.00522	0.0449	0.0622	0.0704	0.0818	0.0979	0.107	0.109	0.112	0.119	0.125	0.131	0.137	0.158
Hg	0.00004	mg kg^{-1}	877	1	0.11	0.00572	0.0772	0.102	0.122	0.163	0.27	0.416	0.48	0.565	0.927	1.28	1.96	2.86	17
In	0.00005	mg kg^{-1}	877	7	0.80	0.00102	0.0114	0.0162	0.0182	0.0205	0.0241	0.0265	0.0273	0.0285	0.0306	0.0332	0.0357	0.043	0.287
K	0.0001	%	877	0	0	0.0427	0.0966	0.108	0.114	0.124	0.138	0.15	0.154	0.159	0.171	0.181	0.193	0.211	0.258
La	0.00002	mg kg^{-1}	877	0	0	3.06	8.4	10.1	10.8	11.6	12.6	13.4	13.6	13.8	14.5	15.1	15.9	16.6	21.3
Li	0.001	mg kg^{-1}	877	0	0	0.012	8.05	9.4	9.97	10.9	13.2	15.8	16.6	17.5	21.6	26.3	29.9	34.4	65.7
Mg	0.0001	%	877	0	0	0.0258	0.159	0.176	0.187	0.204	0.241	0.276	0.289	0.3	0.344	0.387	0.442	0.495	0.846
Mn	0.001	mg kg^{-1}	877	0	0	8.44	449	602	686	799	1020	1250	1300	1370	1540	1790	1990	2190	3470
Mo	0.0001	mg kg^{-1}	877	0	0	0.085	1.29	1.92	2.21	2.57	3.17	3.58	3.7	3.82	4.28	4.66	5.13	5.64	30.3
Na	0.00001	%	877	0	0	0.00752	0.0125	0.0135	0.0142	0.0154	0.0182	0.0211	0.0218	0.0227	0.027	0.0318	0.0413	0.0631	0.218
Nb	0.00002	mg kg^{-1}	877	0	0	0.0542	0.228	0.257	0.274	0.298	0.344	0.407	0.429	0.452	0.519	0.597	0.635	0.769	1.19
Ni	0.0004	mg kg^{-1}	877	0	0	3.23	19.6	27.2	31.3	36.6	43.1	47.8	49.1	50.3	53.7	57.3	60.9	65.1	98.1
P	0.00001	mg kg^{-1}	877	0	0	117	606	715	773	869	1020	1190	1260	1370	1650	1960	2220	2560	3570
Pb	0.00005	mg kg^{-1}	877	0	0	4.45	38.2	46.6	52.4	64.6	98.1	149	172	203	292	401	523	829	1580
Rb	0.00005	mg kg^{-1}	877	0	0	2.32	6.44	7.24	7.56	7.99	8.96	9.94	10.3	10.7	12.3	13.7	15.8	17.2	21.7
Re	0.000002	mg kg^{-1}	877	4	0.46	0.00006	0.00028	0.00043	0.000539	0.00072	0.00113	0.00145	0.00155	0.0017	0.00202	0.00239	0.00273	0.00303	0.00389
S	0.0001	%	877	0	0	0.0152	0.0472	0.0546	0.0589	0.0658	0.0785	0.0902	0.0931	0.0967	0.107	0.116	0.127	0.139	0.275
Sb	0.00005	mg kg^{-1}	877	0	0	0.0711	0.699	0.854	1	1.18	1.63	1.99	2.16	2.38	3.29	4.29	5.76	8.47	21.9
Sc	0.00005	mg kg^{-1}	877	0	0	0.511	1.76	2.45	2.7	3.05	3.42	3.67	3.74	3.81	4.05	4.19	4.38	4.53	5.97
Se	0.00003	mg kg^{-1}	877	0	0	0.0234	0.497	0.641	0.718	0.817	0.978	1.09	1.14	1.2	1.35	1.5	1.67	2.02	6.87
Sn	0.0001	mg kg^{-1}	877	0	0	0.248	1.24	1.48	1.83	2.55	4.56	7.52	8.78	10.8	19.3	28.7	44.7	67.3	293
Sr	0.0001	mg kg^{-1}	877	0	0	5.64	20	25.1	32.2	45.1	78.7	114	124	136	163	191	222	258	424

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	36	4.11	0.0001	0.00021	0.00031	0.00041	0.00052	0.00074	0.00096	0.00101	0.0011	0.00139	0.00174	0.00213	0.00318	0.0167
Te	0.00003	mg kg^{-1}	877	1	0.11	0.0006	0.0145	0.0197	0.0219	0.0255	0.0303	0.0341	0.0354	0.0364	0.0404	0.0438	0.0468	0.0545	0.0887
Th	0.00002	mg kg^{-1}	877	0	0	0.239	0.802	0.935	1.02	1.12	1.26	1.37	1.41	1.43	1.54	1.62	1.73	1.83	2.2
Ti	0.00001	%	877	0	0	0.00193	0.00296	0.00335	0.00367	0.00414	0.00529	0.0067	0.00703	0.00772	0.00969	0.0124	0.0156	0.0193	0.0296
Tl	0.00001	mg kg^{-1}	877	1	0.11	0.0207	0.107	0.16	0.174	0.193	0.216	0.234	0.239	0.246	0.263	0.275	0.297	0.313	1.13
U	0.00005	mg kg^{-1}	877	0	0	0.119	0.552	0.677	0.719	0.782	0.882	0.973	0.998	1.03	1.13	1.21	1.4	1.79	2.56
V	0.001	mg kg^{-1}	877	0	0	5.91	23.5	29.3	31.6	33.5	37.3	40.4	41.4	42.1	45	48.8	52.2	58.6	82.2
W	0.00001	mg kg^{-1}	877	0	0	0.0398	0.0807	0.0916	0.0986	0.112	0.144	0.193	0.211	0.232	0.311	0.46	0.611	1.13	20.8
Y	0.00003	mg kg^{-1}	877	0	0	1	7.28	10.8	12.5	14.2	16	17	17.3	17.8	18.8	19.4	19.9	21.1	23.7
Zn	0.001	mg kg^{-1}	877	0	0	12	75.8	102	111	125	151	189	201	220	284	379	505	706	2280
Zr	0.0001	mg kg^{-1}	877	0	0	0.166	1.47	2.07	2.35	2.76	3.26	3.6	3.7	3.77	3.99	4.15	4.29	4.48	5.25
Au	0.000002	mg kg^{-1}	877	0	0	0.000068	0.00128	0.0016	0.00192	0.00253	0.00383	0.00508	0.0058	0.00638	0.00883	0.0124	0.0181	0.0305	0.117
Pd	0.00001	mg kg^{-1}	877	736	83.9	1.86E-08	5.96E-07	0.00000143	0.0000026	0.00000627	0.0000318	0.000112	0.000157	0.00023	0.00116	0.0024	0.00385	0.00602	0.0283
Pt	0.00002	mg kg^{-1}	877	49	5.59	0.00003	0.000121	0.00019	0.0003	0.00043	0.00067	0.000912	0.001	0.00113	0.00155	0.00217	0.00309	0.00597	0.142

Table 24 Univariate summary statistics for shallow 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	0.021	0.115	0.146	0.166	0.194	0.263	0.352	0.385	0.449	0.598	0.833	0.987	1.38	3.39
Al	0.01	%	877	0	0	0.13	0.658	0.84	0.884	0.95	1.04	1.1	1.12	1.15	1.2	1.3	1.39	1.5	1.76
As	0.01	mg kg^{-1}	877	0	0	2.28	11.4	13.3	14.4	15.6	17.9	20.8	21.9	23.7	28.9	35.5	42.4	67.7	1000
B	10	mg kg^{-1}	877	863	98.4	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	10.3	12.9	15.6	20	40
Ba	0.5	mg kg^{-1}	877	0	0	8.4	56.4	70.4	75.8	86.3	108	126	133	145	181	234	316	426	954
Be	0.01	mg kg^{-1}	877	0	0	0.08	0.576	0.826	0.92	1.01	1.15	1.26	1.31	1.37	1.54	1.77	1.96	2.2	4.21
Bi	0.0005	mg kg^{-1}	877	0	0	0.026	0.139	0.161	0.173	0.189	0.226	0.276	0.292	0.315	0.403	0.511	0.624	1.01	3.71
Ca	0.01	%	877	0	0	0.03	0.35	0.57	0.774	1.27	2.63	3.99	4.28	4.72	5.55	6.17	7.61	8.81	13.2
Cd	0.001	mg kg^{-1}	877	0	0	0.046	0.531	0.979	1.18	1.46	1.82	2.05	2.12	2.19	2.38	2.56	2.74	2.96	6.79
Ce	0.003	mg kg^{-1}	877	0	0	6.41	17.3	19.9	21.1	22.6	24.7	26.5	26.9	27.3	28.6	29.8	31.6	33.1	39
Co	0.001	mg kg^{-1}	877	0	0	0.461	6	7.87	8.56	9.5	10.8	12	12.3	12.8	14.2	15.6	16.9	19	26.8
Cr	0.01	mg kg^{-1}	877	0	0	3	14.1	17.8	18.9	19.9	21.5	22.9	23.4	23.9	25.4	27.2	29.1	31.8	57
Cs	0.005	mg kg^{-1}	877	0	0	0.196	0.32	0.346	0.367	0.392	0.469	0.571	0.614	0.673	0.865	1.06	1.38	1.82	3.26
Cu	0.01	mg kg^{-1}	877	0	0	1.61	20.8	27.2	31	36	46.5	57.2	60.9	67.4	91.2	109	139	188	582
Fe	0.001	%	877	0	0	0.348	1.48	1.8	1.97	2.09	2.28	2.44	2.49	2.59	2.76	2.92	3.14	3.42	6.01
Ga	0.004	mg kg^{-1}	877	0	0	0.598	1.99	2.44	2.57	2.77	3.1	3.37	3.47	3.58	3.87	4.16	4.54	4.79	7.2
Ge	0.005	mg kg^{-1}	877	0	0	0.007	0.038	0.046	0.05	0.055	0.061	0.067	0.069	0.072	0.078	0.0862	0.0961	0.126	0.247
Hf	0.002	mg kg^{-1}	877	0	0	0.005	0.0446	0.062	0.07	0.082	0.098	0.107	0.109	0.112	0.119	0.125	0.131	0.137	0.158
Hg	0.004	mg kg^{-1}	877	1	0.11	0.006	0.077	0.102	0.122	0.163	0.27	0.416	0.48	0.565	0.927	1.28	1.96	2.86	17.1
In	0.005	mg kg^{-1}	877	17	1.94	0.006	0.012	0.016	0.018	0.021	0.024	0.027	0.027	0.028	0.031	0.033	0.036	0.0432	0.287
K	0.01	%	877	0	0	0.04	0.098	0.11	0.11	0.12	0.14	0.15	0.15	0.16	0.17	0.18	0.19	0.212	0.26
La	0.002	mg kg^{-1}	877	0	0	3.06	8.4	10.1	10.8	11.6	12.6	13.4	13.6	13.8	14.5	15.1	15.9	16.6	21.3
Li	0.1	mg kg^{-1}	877	1	0.11	0.3	8.08	9.4	10	11	13.3	15.8	16.6	17.5	21.6	26.3	29.9	34.4	65.7
Mg	0.01	%	877	0	0	0.03	0.16	0.18	0.19	0.2	0.24	0.28	0.29	0.3	0.344	0.39	0.441	0.5	0.85

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	8.4	449	602	686	799	1020	1250	1300	1370	1540	1790	1990	2190	3470
Mo	0.01	mg kg^{-1}	877	0	0	0.09	1.29	1.93	2.21	2.57	3.17	3.58	3.7	3.82	4.28	4.66	5.12	5.64	30.3
Na	0.001	%	877	0	0	0.008	0.012	0.0136	0.014	0.015	0.018	0.021	0.022	0.023	0.027	0.032	0.041	0.0652	0.218
Nb	0.002	mg kg^{-1}	877	0	0	0.054	0.228	0.257	0.274	0.298	0.344	0.407	0.429	0.452	0.52	0.597	0.635	0.769	1.19
Ni	0.04	mg kg^{-1}	877	0	0	3.23	19.6	27.2	31.3	36.6	43.1	47.8	49.1	50.3	53.6	57.3	60.8	65.1	98.1
P	0.001	mg kg^{-1}	877	0	0	120	608	716	770	870	1020	1190	1260	1370	1650	1960	2220	2560	3570
Pb	0.005	mg kg^{-1}	877	0	0	4.45	38.2	46.6	52.4	64.6	98.1	149	172	203	292	401	523	829	1580
Rb	0.005	mg kg^{-1}	877	0	0	2.32	6.43	7.24	7.56	7.99	8.96	9.94	10.3	10.7	12.2	13.7	15.8	17.2	21.7
Re	0.0002	mg kg^{-1}	877	42	4.79	<LLD	0.00037	0.0004	0.0005	0.0007	0.0011	0.0015	0.0015	0.0017	0.002	0.0024	0.0027	0.003	0.0039
S	0.01	%	877	0	0	0.02	0.05	0.05	0.06	0.07	0.08	0.09	0.09	0.1	0.11	0.12	0.13	0.14	0.27
Sb	0.005	mg kg^{-1}	877	0	0	0.071	0.699	0.854	1	1.18	1.64	1.99	2.16	2.38	3.29	4.3	5.76	8.47	21.9
Sc	0.005	mg kg^{-1}	877	0	0	0.511	1.76	2.45	2.7	3.05	3.42	3.67	3.74	3.82	4.05	4.19	4.38	4.53	5.97
Se	0.003	mg kg^{-1}	877	0	0	0.023	0.497	0.641	0.718	0.817	0.978	1.09	1.14	1.2	1.35	1.5	1.67	2.02	6.87
Sn	0.01	mg kg^{-1}	877	0	0	0.25	1.24	1.49	1.83	2.55	4.56	7.51	8.78	10.8	19.3	28.8	44.7	67.3	293
Sr	0.01	mg kg^{-1}	877	0	0	5.64	20	25.1	32.1	45.1	78.7	114	124	136	163	191	222	258	424
Ta	0.005	mg kg^{-1}	877	874	99.7	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.017
Te	0.003	mg kg^{-1}	877	9	1.03	0.004	0.0148	0.02	0.022	0.025	0.03	0.034	0.035	0.036	0.04	0.044	0.047	0.0542	0.089
Th	0.002	mg kg^{-1}	877	0	0	0.239	0.802	0.936	1.02	1.11	1.26	1.37	1.4	1.43	1.54	1.62	1.73	1.83	2.2
Ti	0.001	%	877	0	0	0.002	0.003	0.003	0.004	0.004	0.005	0.007	0.007	0.008	0.01	0.012	0.016	0.0192	0.03
Tl	0.001	mg kg^{-1}	877	1	0.11	0.021	0.107	0.159	0.174	0.193	0.216	0.234	0.239	0.246	0.263	0.275	0.297	0.313	1.13
U	0.005	mg kg^{-1}	877	0	0	0.119	0.551	0.677	0.719	0.782	0.882	0.972	0.998	1.03	1.12	1.21	1.4	1.79	2.56
V	0.1	mg kg^{-1}	877	0	0	5.9	23.5	29.3	31.6	33.5	37.3	40.4	41.4	42.1	44.9	48.8	52.2	58.6	82.2
W	0.001	mg kg^{-1}	877	0	0	0.04	0.0808	0.092	0.099	0.112	0.144	0.193	0.211	0.232	0.311	0.46	0.611	1.13	20.8
Y	0.003	mg kg^{-1}	877	0	0	1	7.29	10.8	12.5	14.2	16.1	17	17.4	17.8	18.8	19.4	19.9	21.1	23.7
Zn	0.1	mg kg^{-1}	877	0	0	12	75.8	102	111	125	151	188	201	220	284	379	505	706	2280

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
Zr	0.01	mg kg^{-1}	877	0	0	0.17	1.47	2.07	2.35	2.76	3.26	3.6	3.7	3.77	3.98	4.15	4.29	4.48	5.25
Au	0.0002	mg kg^{-1}	877	4	0.46	0.0003	0.0013	0.0016	0.0019	0.0025	0.0038	0.0051	0.0058	0.0064	0.0088	0.0124	0.0181	0.0305	0.117
Pd	0.001	mg kg^{-1}	877	808	92.1	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.0014	0.002	0.004	0.006	0.028
Pt	0.002	mg kg^{-1}	877	842	96.0	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	0.003	0.006	0.142

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	6.77	6.73	0.445	5.85	7.35	6.9	6.9	6.73	6.77	6.77	6.77	0.601	0.601	0.69
LOI	0.01	%	877	0	0	11.8	11.3	2.67	4.25	15.3	11.5	11.5	11.3	11.8	11.8	11.9	3.53	3.53	3.74

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	0.34	0.276	0.126	-0.0939	0.481	0.263	0.263	0.276	0.34	0.34	0.337	0.273	0.273	0.238
Al	0.0001	%	877	0	0	1.02	0.99	0.131	0.686	1.21	1.04	1.04	0.99	1.02	1.02	1.03	0.202	0.202	0.292
As	0.0001	mg kg^{-1}	877	0	0	21.8	18.6	4.3	6.21	25.1	17.9	17.9	18.6	21.8	21.8	20.6	38	38	9.76
B	0.1	mg kg^{-1}	877	7	0.80	7.13	6.44	2.52	0.2	10.4	6.9	6.9	6.22	7.08	7.09	7.54	3.18	3.16	5.18
Ba	0.005	mg kg^{-1}	877	0	0	122	107	34.4	16.4	156	107	107	107	122	122	122	73.2	73.2	66.9
Be	0.0001	mg kg^{-1}	877	0	0	1.16	1.09	0.224	0.547	1.46	1.14	1.14	1.09	1.16	1.16	1.19	0.358	0.358	0.503
Bi	0.000005	mg kg^{-1}	877	0	0	0.269	0.238	0.0694	0.0342	0.344	0.226	0.226	0.238	0.269	0.269	0.265	0.198	0.198	0.13

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	2.92	2.11	2.23	-3.25	5.78	2.63	2.63	2.11	2.92	2.92	3.25	2.02	2.02	3.82
Cd	0.00001	mg kg^{-1}	877	0	0	1.75	1.58	0.485	0.458	2.45	1.82	1.82	1.58	1.75	1.75	1.86	0.623	0.623	1.15
Ce	0.00003	mg kg^{-1}	877	0	0	24.3	23.9	3.25	16.1	29.1	24.7	24.7	23.9	24.3	24.3	24.4	4.26	4.26	5.38
Co	0.00001	mg kg^{-1}	877	0	0	10.9	10.3	2.08	5.24	13.8	10.9	10.9	10.3	10.9	10.9	11.1	2.97	2.97	4.43
Cr	0.0001	mg kg^{-1}	877	0	0	21.5	20.9	2.55	14.7	25.1	21.5	21.5	20.9	21.5	21.5	21.6	4.5	4.5	5.59
Cs	0.00005	mg kg^{-1}	877	0	0	0.559	0.511	0.138	0.0586	0.725	0.469	0.469	0.511	0.559	0.559	0.551	0.303	0.303	0.222
Cu	0.0001	mg kg^{-1}	877	0	0	55	46.6	17.8	-1.4	73.3	46.5	46.5	46.6	55	55	55.7	40.9	40.9	36.4
Fe	0.00001	%	877	0	0	2.27	2.19	0.297	1.49	2.69	2.28	2.28	2.19	2.27	2.27	2.3	0.509	0.509	0.707
Ga	0.00004	mg kg^{-1}	877	0	0	3.1	3	0.521	1.72	3.82	3.1	3.1	3	3.1	3.1	3.12	0.694	0.694	0.892
Ge	0.00005	mg kg^{-1}	877	0	0	0.0627	0.0604	0.0108	0.0324	0.0767	0.0615	0.0615	0.0604	0.0627	0.0627	0.0629	0.0179	0.0179	0.0182
Hf	0.00002	mg kg^{-1}	877	0	0	0.0934	0.0884	0.0199	0.0406	0.123	0.0979	0.0979	0.0884	0.0934	0.0934	0.0954	0.0244	0.0244	0.0388
Hg	0.00004	mg kg^{-1}	877	1	0.11	0.47	0.287	0.196	-0.313	0.639	0.27	0.27	0.284	0.47	0.47	0.452	0.898	0.898	0.56
In	0.00005	mg kg^{-1}	877	7	0.80	0.0242	0.0228	0.00499	0.0106	0.0307	0.0241	0.0241	0.0217	0.024	0.0241	0.0271	0.0114	0.0113	0.0203
K	0.0001	%	877	0	0	0.139	0.136	0.0224	0.0789	0.169	0.138	0.138	0.136	0.139	0.139	0.139	0.0276	0.0276	0.031
La	0.00002	mg kg^{-1}	877	0	0	12.4	12.1	1.47	8.63	14.6	12.6	12.6	12.1	12.4	12.4	12.4	2.19	2.19	2.88
Li	0.001	mg kg^{-1}	877	0	0	14.6	13.4	3.93	2.55	19.4	13.2	13.2	13.4	14.6	14.6	15	6.01	6.01	7.55
Mg	0.0001	%	877	0	0	0.253	0.242	0.0597	0.0768	0.332	0.241	0.241	0.242	0.253	0.253	0.253	0.0778	0.0778	0.0796
Mn	0.001	mg kg^{-1}	877	0	0	1060	961	372	45.7	1550	1020	1020	961	1060	1060	1110	415	415	643
Mo	0.0001	mg kg^{-1}	877	0	0	3.15	2.88	0.823	0.89	4.26	3.17	3.17	2.88	3.15	3.15	3.28	1.37	1.37	1.77
Na	0.00001	%	877	0	0	0.0204	0.019	0.00461	0.0058	0.025	0.0182	0.0182	0.019	0.0204	0.0204	0.0201	0.0126	0.0126	0.00688
Nb	0.00002	mg kg^{-1}	877	0	0	0.371	0.355	0.0864	0.101	0.495	0.344	0.344	0.355	0.371	0.371	0.371	0.117	0.117	0.114
Ni	0.0004	mg kg^{-1}	877	0	0	41.8	39.3	9.02	17.9	55.4	43.1	43.1	39.3	41.8	41.8	42.7	11.5	11.5	18.2
P	0.00001	mg kg^{-1}	877	0	0	1110	1040	273	282	1460	1020	1020	1040	1110	1110	1120	432	432	450
Pb	0.00005	mg kg^{-1}	877	0	0	147	107	63.5	-96.1	225	98.1	98.1	107	147	147	144	151	151	127
Rb	0.00005	mg kg^{-1}	877	0	0	9.34	9.03	1.64	4.48	11.5	8.96	8.96	9.03	9.34	9.34	9.37	2.41	2.41	2.57

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	4	0.46	0.0012	0.00101	0.000611	-0.000514	0.00197	0.00113	0.00113	0.000983	0.0012	0.0012	0.00133	0.000643	0.000642	0.00121
S	0.0001	%	877	0	0	0.0801	0.0769	0.0205	0.0248	0.107	0.0785	0.0785	0.0769	0.0801	0.0801	0.0804	0.0227	0.0227	0.0245
Sb	0.00005	mg kg^{-1}	877	0	0	1.99	1.63	0.71	-0.289	2.65	1.63	1.63	1.63	1.99	1.99	1.96	1.78	1.78	1.32
Sc	0.00005	mg kg^{-1}	877	0	0	3.3	3.17	0.505	2	4.09	3.42	3.42	3.17	3.3	3.3	3.33	0.737	0.737	1.08
Se	0.00003	mg kg^{-1}	877	0	0	0.995	0.919	0.24	0.325	1.31	0.978	0.978	0.919	0.995	0.995	1.03	0.38	0.38	0.515
Sn	0.0001	mg kg^{-1}	877	0	0	8.69	4.95	3.77	-6.79	11.9	4.56	4.56	4.95	8.69	8.69	7.99	15.4	15.4	10.1
Sr	0.0001	mg kg^{-1}	877	0	0	89.5	71.7	57	-73.2	163	78.7	78.7	71.7	89.5	89.5	92.3	56.7	56.7	74.8
Ta	0.00005	mg kg^{-1}	877	36	4.11	0.00089	0.000747	0.000341	-0.00012	0.00126	0.00074	0.00074	0.000662	0.000857	0.000861	0.000918	0.000793	0.00079	0.000881
Te	0.00003	mg kg^{-1}	877	1	0.11	0.0302	0.0282	0.00736	0.0107	0.0403	0.0303	0.0303	0.028	0.0301	0.0301	0.0316	0.00924	0.00922	0.0167
Th	0.00002	mg kg^{-1}	877	0	0	1.25	1.22	0.215	0.683	1.55	1.26	1.26	1.22	1.25	1.25	1.25	0.254	0.254	0.296
Ti	0.00001	%	877	0	0	0.00619	0.00557	0.00203	-0.000195	0.00847	0.00529	0.00529	0.00557	0.00619	0.00619	0.00613	0.00338	0.00338	0.00282
Tl	0.00001	mg kg^{-1}	877	1	0.11	0.212	0.203	0.0344	0.124	0.262	0.216	0.216	0.203	0.212	0.212	0.215	0.0579	0.0579	0.0753
U	0.00005	mg kg^{-1}	877	0	0	0.898	0.863	0.157	0.457	1.11	0.882	0.882	0.863	0.898	0.898	0.903	0.246	0.246	0.279
V	0.001	mg kg^{-1}	877	0	0	37.1	36	5.83	21.8	45.3	37.3	37.3	36	37.1	37.1	37.4	8.01	8.01	10.4
W	0.00001	mg kg^{-1}	877	0	0	0.229	0.161	0.0616	-0.0373	0.261	0.144	0.144	0.161	0.229	0.229	0.191	0.782	0.782	0.123
Y	0.00003	mg kg^{-1}	877	0	0	15.2	14.5	2.29	9.51	18.9	16	16	14.5	15.2	15.2	15.6	3.65	3.65	6.32
Zn	0.001	mg kg^{-1}	877	0	0	185	158	50.4	9.84	240	151	151	158	185	185	183	154	154	106
Zr	0.0001	mg kg-1	877	0	0	3.13	2.96	0.677	1.36	4.16	3.26	3.26	2.96	3.13	3.13	3.19	0.811	0.811	1.26
Au	0.000002	mg kg-1	877	0	0	0.0052	0.00377	0.00223	-0.00237	0.00743	0.00383	0.00383	0.00377	0.0052	0.0052	0.00507	0.00663	0.00663	0.00455
Pd	0.00001	mg kg-1	877	736	83.9	0.00239	0.00132	0.00142	-0.00256	0.00414	NA	0.0000318	5.11E-09	0.0004	0.000431	170000	0.00158	0.00157	5.69E+18
Pt	0.00002	mg kg-1	877	49	5.59	0.00113	0.000698	0.000393	-0.000326	0.0013	0.00067	0.00067	0.000561	0.00107	0.00108	0.00113	0.00501	0.00501	0.00198

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	0.34	0.276	0.126	-0.0925	0.48	0.263	0.263	0.276	0.34	0.34	0.337	0.273	0.273	0.238
Al	0.01	%	877	0	0	1.02	0.99	0.133	0.695	1.21	1.04	1.04	0.99	1.02	1.02	1.03	0.202	0.202	0.293
As	0.01	mg kg^{-1}	877	0	0	21.8	18.6	4.3	6.275	25	17.9	17.9	18.6	21.8	21.8	20.6	38	38	9.76
B	10	mg kg^{-1}	877	863	98.4	22.1	21.6	0	20	20	NA	4.71	0.147	20	5.69	1.03	0.783	3.84	7.12
Ba	0.5	mg kg^{-1}	877	0	0	122	107	34.2	16.25	156	108	108	107	122	122	122	73.2	73.2	66.9
Be	0.01	mg kg^{-1}	877	0	0	1.16	1.09	0.222	0.56	1.46	1.15	1.15	1.09	1.16	1.16	1.19	0.359	0.359	0.505
Bi	0.0005	mg kg^{-1}	877	0	0	0.269	0.238	0.0697	0.0345	0.343	0.226	0.226	0.238	0.269	0.269	0.265	0.198	0.198	0.13
Ca	0.01	%	877	0	0	2.92	2.11	2.22	-3.245	5.79	2.63	2.63	2.11	2.92	2.92	3.25	2.02	2.02	3.81
Cd	0.001	mg kg^{-1}	877	0	0	1.75	1.58	0.489	0.4575	2.45	1.82	1.82	1.58	1.75	1.75	1.86	0.623	0.623	1.15
Ce	0.003	mg kg^{-1}	877	0	0	24.3	23.9	3.26	16.15	29	24.7	24.7	23.9	24.3	24.3	24.4	4.26	4.26	5.38
Co	0.001	mg kg^{-1}	877	0	0	10.9	10.3	2.08	5.225	13.8	10.9	10.8	10.3	10.9	10.9	11.1	2.97	2.97	4.43
Cr	0.01	mg kg^{-1}	877	0	0	21.5	20.9	2.52	14.65	25.1	21.5	21.5	20.9	21.5	21.5	21.6	4.5	4.5	5.59
Cs	0.005	mg kg^{-1}	877	0	0	0.559	0.511	0.138	0.059	0.725	0.469	0.469	0.511	0.559	0.559	0.551	0.303	0.303	0.222
Cu	0.01	mg kg^{-1}	877	0	0	55	46.6	17.8	-1.35	73.3	46.5	46.5	46.6	55	55	55.7	40.8	40.8	36.4
Fe	0.001	%	877	0	0	2.27	2.19	0.297	1.49	2.69	2.28	2.28	2.19	2.27	2.27	2.3	0.509	0.509	0.707
Ga	0.004	mg kg^{-1}	877	0	0	3.1	3	0.519	1.72	3.82	3.1	3.1	3	3.1	3.1	3.12	0.694	0.694	0.892
Ge	0.005	mg kg^{-1}	877	0	0	0.0627	0.0604	0.0104	0.034	0.076	0.061	0.061	0.0604	0.0627	0.0627	0.0629	0.0179	0.0179	0.0182
Hf	0.002	mg kg^{-1}	877	0	0	0.0934	0.0884	0.0193	0.0415	0.122	0.098	0.098	0.0884	0.0934	0.0934	0.0954	0.0244	0.0244	0.0388
Hg	0.004	mg kg^{-1}	877	1	0.11	0.47	0.287	0.196	-0.31287	0.639	0.27	0.27	0.286	0.47	0.47	0.439	0.898	0.898	0.513
In	0.005	mg kg^{-1}	877	17	1.94	0.0245	0.0233	0.00445	0.012	0.03	0.024	0.024	0.0226	0.0241	0.0242	0.0243	0.0112	0.0111	0.00944
K	0.01	%	877	0	0	0.139	0.136	0.0148	0.075	0.165	0.14	0.14	0.136	0.139	0.139	0.139	0.0278	0.0278	0.0314
La	0.002	mg kg^{-1}	877	0	0	12.4	12.1	1.48	8.6	14.6	12.6	12.6	12.1	12.4	12.4	12.4	2.19	2.19	2.88
Li	0.1	mg kg^{-1}	877	1	0.11	14.6	13.5	4	2.6	19.4	13.3	13.3	13.5	14.6	14.6	14.8	6	5.99	6.9

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	0.253	0.242	0.0593	0.065	0.335	0.24	0.24	0.242	0.253	0.253	0.253	0.0781	0.0781	0.0793
Mn	0.1	mg kg^{-1}	877	0	0	1060	961	371	47.5	1550	1020	1020	961	1060	1060	1110	415	415	643
Mo	0.01	mg kg^{-1}	877	0	0	3.15	2.88	0.83	0.875	4.27	3.17	3.17	2.88	3.15	3.15	3.27	1.37	1.37	1.77
Na	0.001	%	877	0	0	0.0204	0.019	0.00445	0.0045	0.0255	0.018	0.018	0.019	0.0204	0.0204	0.0201	0.0126	0.0126	0.00687
Nb	0.002	mg kg^{-1}	877	0	0	0.371	0.355	0.086	0.1015	0.494	0.344	0.344	0.355	0.371	0.371	0.371	0.117	0.117	0.114
Ni	0.04	mg kg^{-1}	877	0	0	41.8	39.3	9.04	17.85	55.4	43.1	43.1	39.3	41.8	41.8	42.7	11.5	11.5	18.2
P	0.001	mg kg^{-1}	877	0	0	1110	1040	282	285	1460	1020	1020	1040	1110	1110	1120	432	432	449
Pb	0.005	mg kg^{-1}	877	0	0	147	107	63.5	-95.75	225	98.1	98.1	107	147	147	143	151	151	127
Rb	0.005	mg kg^{-1}	877	0	0	9.34	9.03	1.63	4.45	11.5	8.96	8.96	9.03	9.34	9.34	9.37	2.41	2.41	2.57
Re	0.0002	mg kg^{-1}	877	42	4.79	0.00125	0.0011	0.000593	-0.0004	0.002	0.0011	0.0011	0.00101	0.0012	0.00121	0.00125	0.000631	0.00063	0.000907
S	0.01	%	877	0	0	0.0801	0.0768	0.0148	0.04	0.1	0.08	0.08	0.0768	0.0801	0.0801	0.0803	0.0228	0.0228	0.0247
Sb	0.005	mg kg^{-1}	877	0	0	1.99	1.63	0.712	-0.29	2.65	1.64	1.64	1.63	1.99	1.99	1.96	1.78	1.78	1.32
Sc	0.005	mg kg^{-1}	877	0	0	3.3	3.17	0.504	2.015	4.09	3.42	3.42	3.17	3.3	3.3	3.33	0.737	0.737	1.08
Se	0.003	mg kg^{-1}	877	0	0	0.995	0.919	0.24	0.325	1.31	0.978	0.978	0.919	0.995	0.995	1.03	0.38	0.38	0.515
Sn	0.01	mg kg^{-1}	877	0	0	8.69	4.95	3.77	-6.795	11.9	4.56	4.56	4.95	8.69	8.69	7.99	15.4	15.4	10.1
Sr	0.01	mg kg^{-1}	877	0	0	89.5	71.7	56.8	-73.25	163	78.7	78.7	71.7	89.5	89.5	92.3	56.7	56.7	74.8
Ta	0.005	mg kg^{-1}	877	874	99.7	0.00967	0.00849	0	-0.00225	0.0142	NA	5.46E-07	0.0000461	0.00601	0.0000637	0.000207	0.000455	0.000661	0.000905
Te	0.003	mg kg^{-1}	877	9	1.03	0.0304	0.0289	0.00741	0.0125	0.0395	0.03	0.03	0.0282	0.0302	0.0302	0.0308	0.00916	0.00896	0.0135
Th	0.002	mg kg^{-1}	877	0	0	1.25	1.22	0.215	0.68	1.55	1.26	1.26	1.22	1.25	1.25	1.25	0.254	0.254	0.296
Ti	0.001	%	877	0	0	0.00619	0.00556	0.00148	-0.0005	0.0085	0.005	0.005	0.00556	0.00619	0.00619	0.00614	0.0034	0.0034	0.00288
Tl	0.001	mg kg^{-1}	877	1	0.11	0.212	0.203	0.0341	0.124	0.262	0.216	0.216	0.202	0.212	0.212	0.217	0.0582	0.058	0.0867
U	0.005	mg kg^{-1}	877	0	0	0.898	0.863	0.157	0.458	1.11	0.882	0.882	0.863	0.898	0.898	0.903	0.246	0.246	0.279
V	0.1	mg kg^{-1}	877	0	0	37.1	36	5.78	21.65	45.3	37.3	37.3	36	37.1	37.1	37.4	8.01	8.01	10.4
W	0.001	mg kg^{-1}	877	0	0	0.229	0.161	0.0623	-0.0365	0.261	0.144	0.144	0.161	0.229	0.229	0.191	0.784	0.784	0.123
Y	0.003	mg kg^{-1}	877	0	0	15.2	14.5	2.3	9.475	18.9	16.1	16.1	14.5	15.2	15.2	15.6	3.65	3.65	6.32

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	185	158	50.4	11	239	151	151	158	185	185	183	154	154	106
Zr	0.01	mg kg^{-1}	877	0	0	3.13	2.96	0.682	1.35	4.17	3.26	3.26	2.96	3.13	3.13	3.19	0.811	0.811	1.26
Au	0.0002	mg kg^{-1}	877	4	0.46	0.00522	0.00383	0.00222	-0.0022	0.0074	0.0038	0.0038	0.00378	0.0052	0.0052	0.00505	0.00663	0.00663	0.00446
Pd	0.001	mg kg^{-1}	877	808	92.1	0.00413	0.00334	0.00148	-0.001	0.005	NA	0.000206	0.0000334	0.00217	0.00062	0.000631	0.00125	0.00155	0.0119
Pt	0.002	mg kg^{-1}	877	842	96.0	0.0094	0.00488	0	-0.0015	0.0075	NA	0.0000389	0.000042	0.00326	0.000527	0.000478	0.00492	0.00504	0.00542

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 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 Shallow topsoil analytes where mapping of the certified ME-MS41L dataset is not recommended.

Variable	Method	Issue	Recommendation
B	ICP-MS (ME-MS41L)	98.4 % data <LLD.	Perhaps better presented as proportional colour/symbol point map.
Ta	ICP-MS (ME-MS41L)	99.7 % data <LLD.	Better presented as proportional colour/symbol point map.
Pd	ICP-MS (ME-MS41L)	92.1 % data <LLD.	Perhaps better presented as proportional colour/symbol point map.
Pt	ICP-MS (ME-MS41L)	96.0 % 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 25th and 75th 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

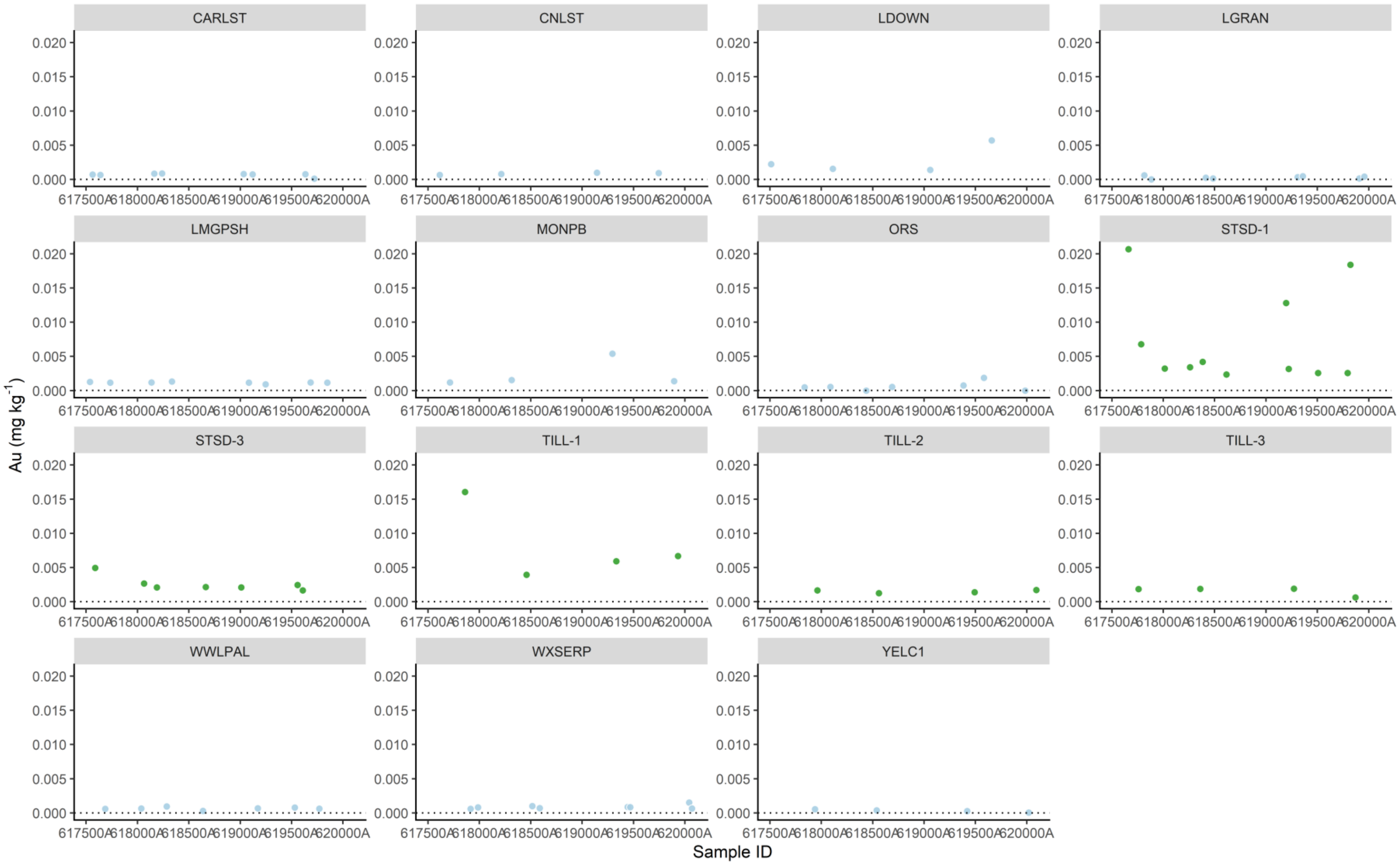
In this appendix all of the reference materials data are presented in two ways for each analyte (in the same order as data are reported by instrument and distributed):

- 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.

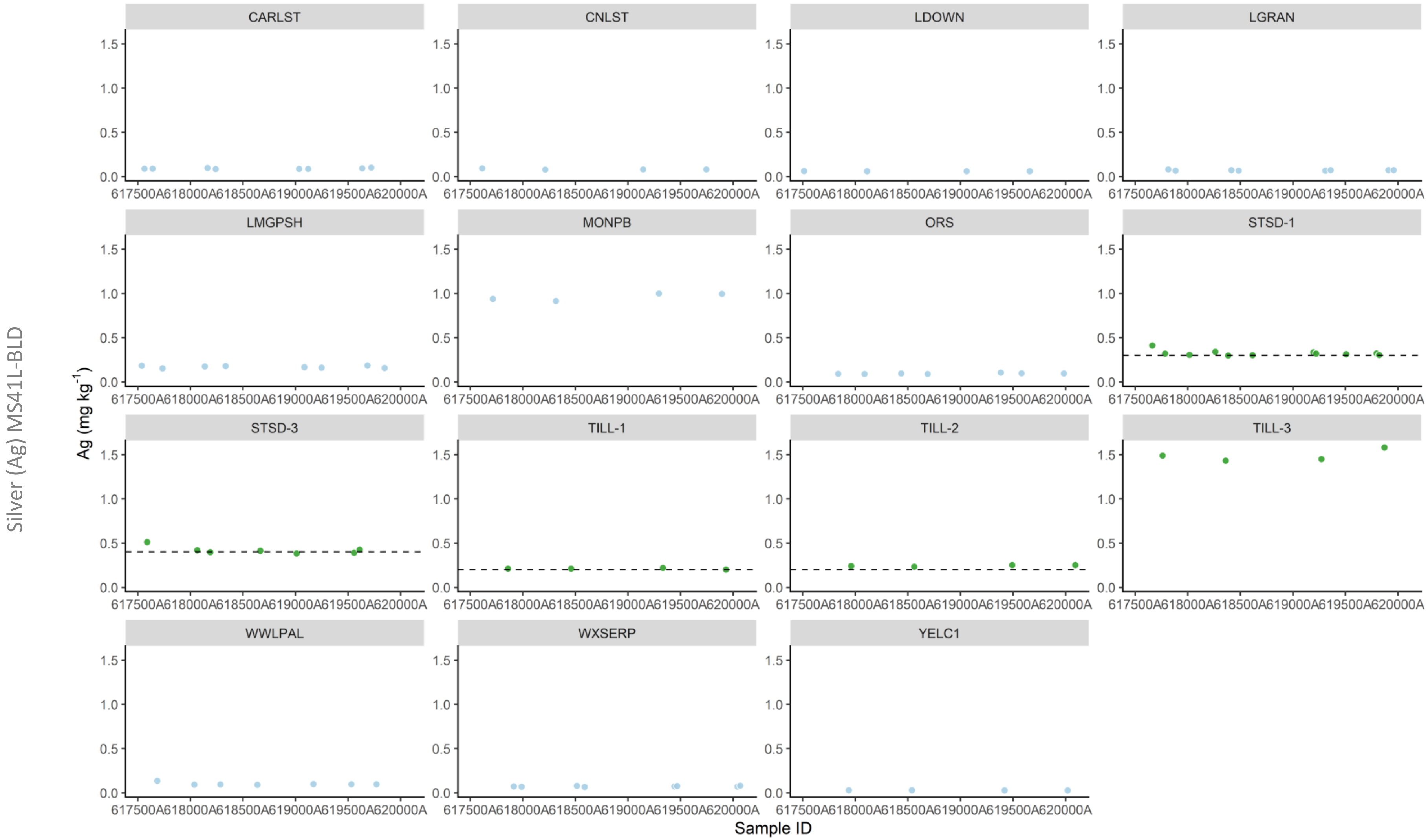
ICPar RMs data by ALS Minerals Ltd method code MS41L-BLD

Gold (Au) MS41L-BLD



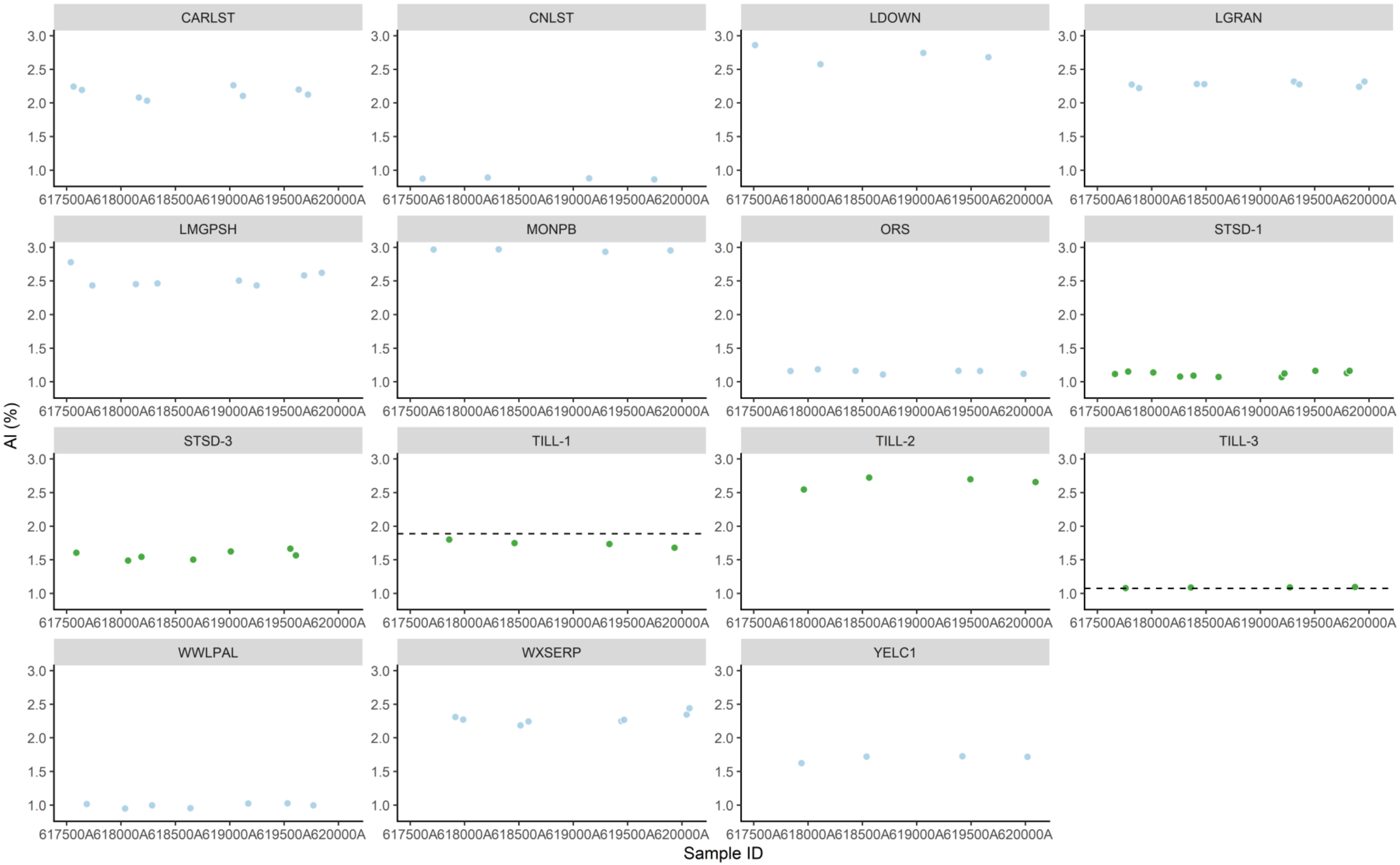
Gold (Au) sample data IQR: 0.00255–0.00583 mg kg^{-1}

AURUM GLOBAL EXPLORATION

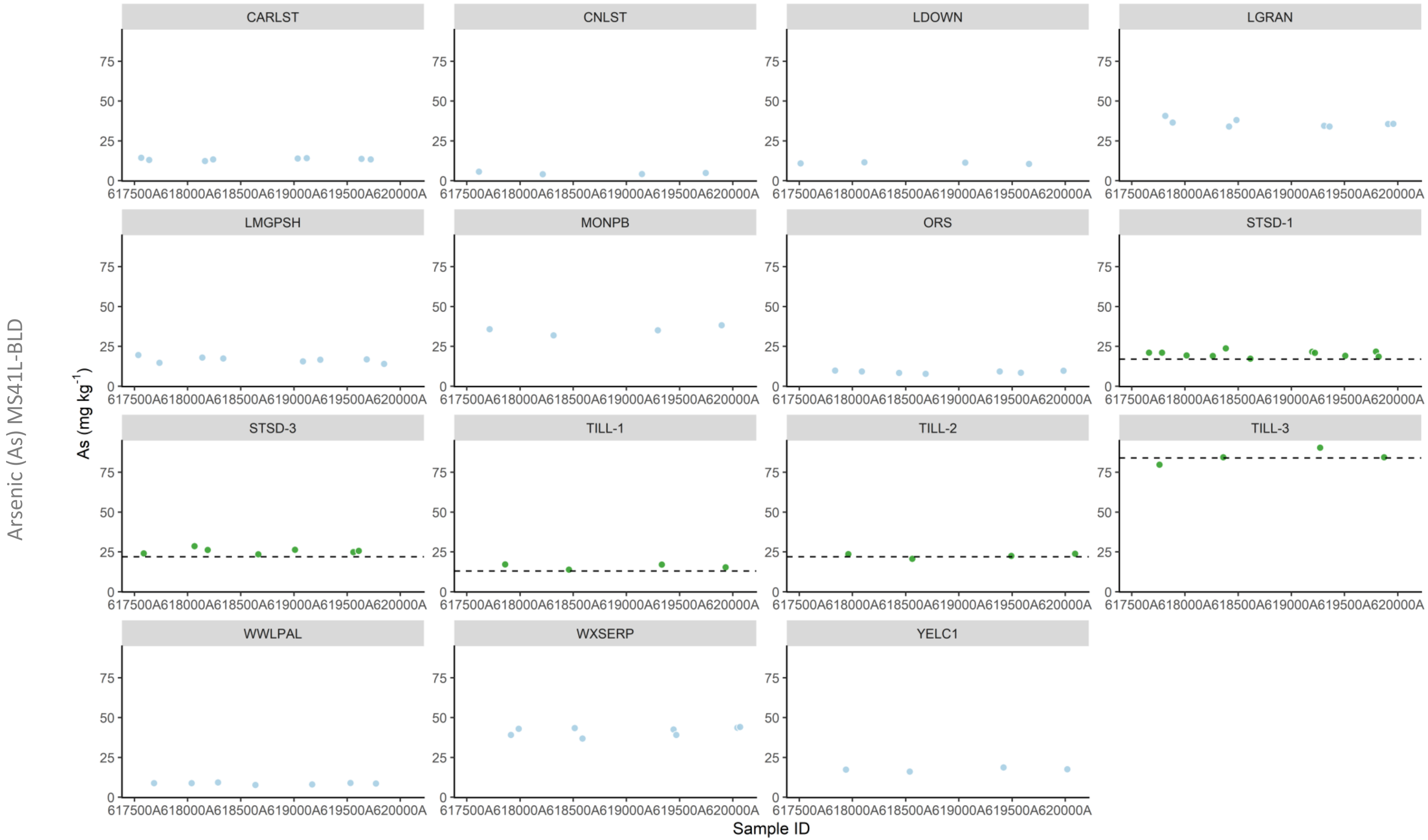


Silver (Ag) sample data IQR: 0.193–0.385 mg kg^{-1}

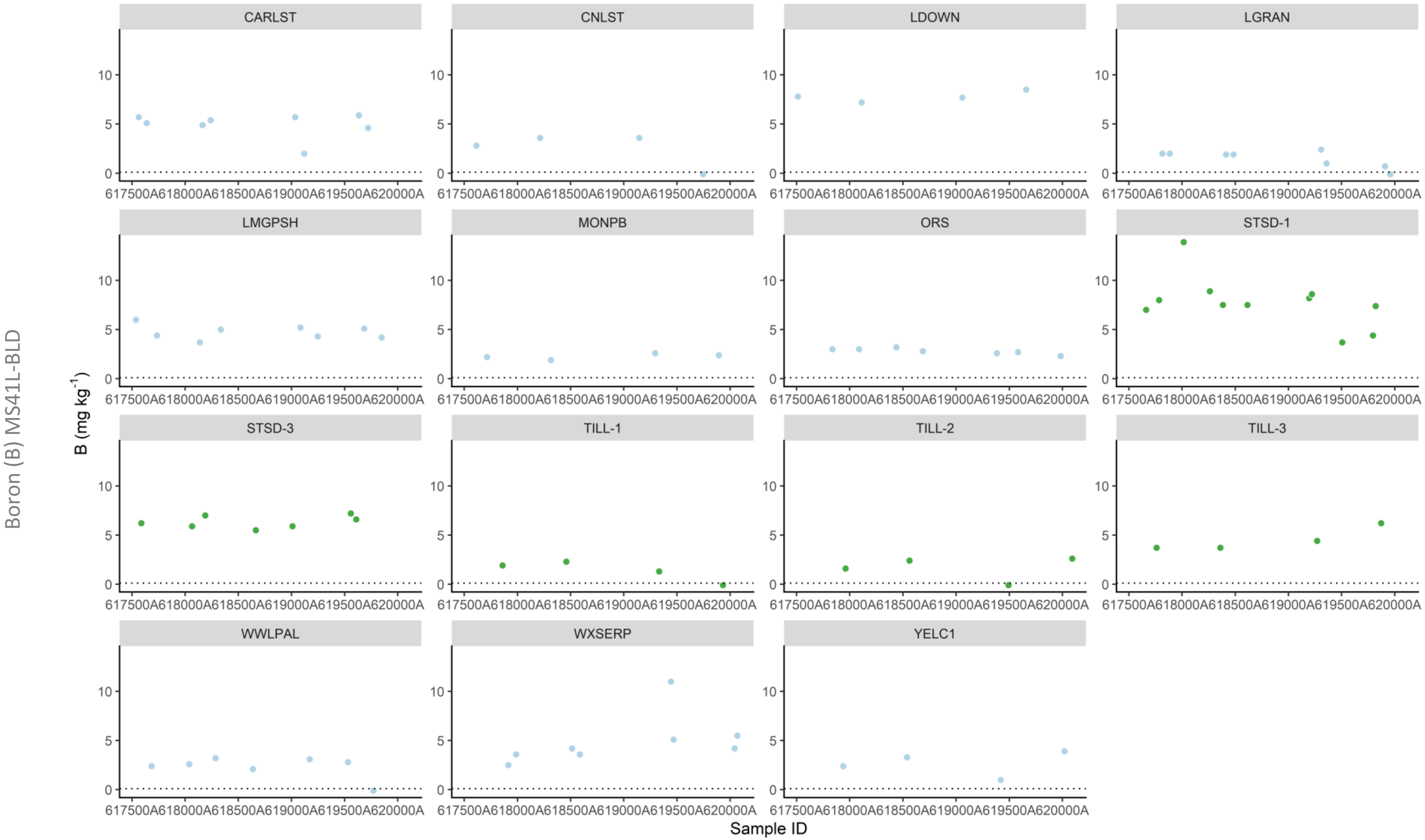
Aluminium (Al) MS41L-BLD



Aluminium (Al) sample data IQR: 0.949–1.12 %

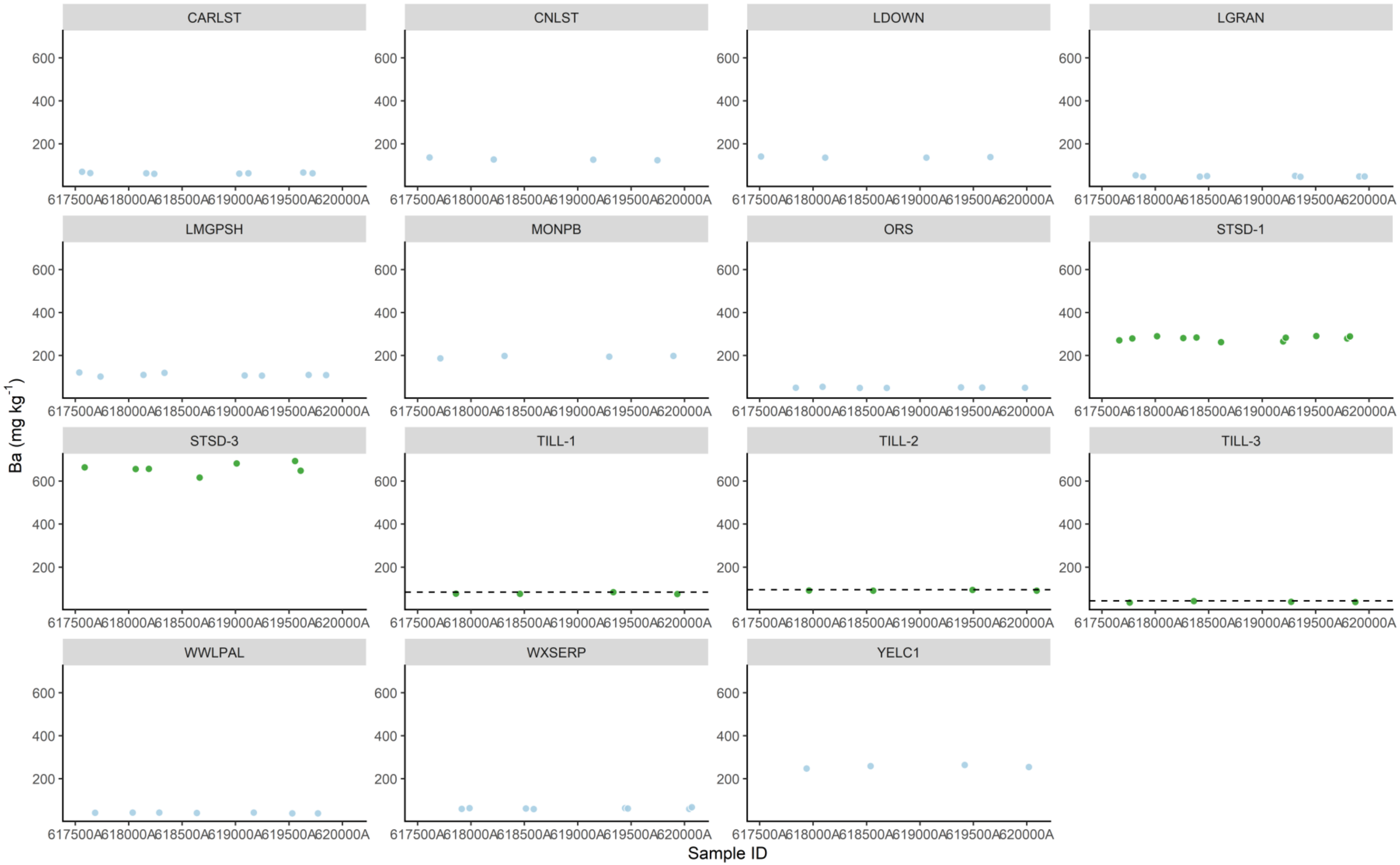


Arsenic (As) sample data IQR: 15.7–22.0 mg kg^{-1}



Boron (B) sample data IQR: 5.3 -8.7 mg kg^{-1}

Barium (Ba) MS41L-BLD



Barium (Ba) sample data IQR: 86.3–133 mg kg^{-1}

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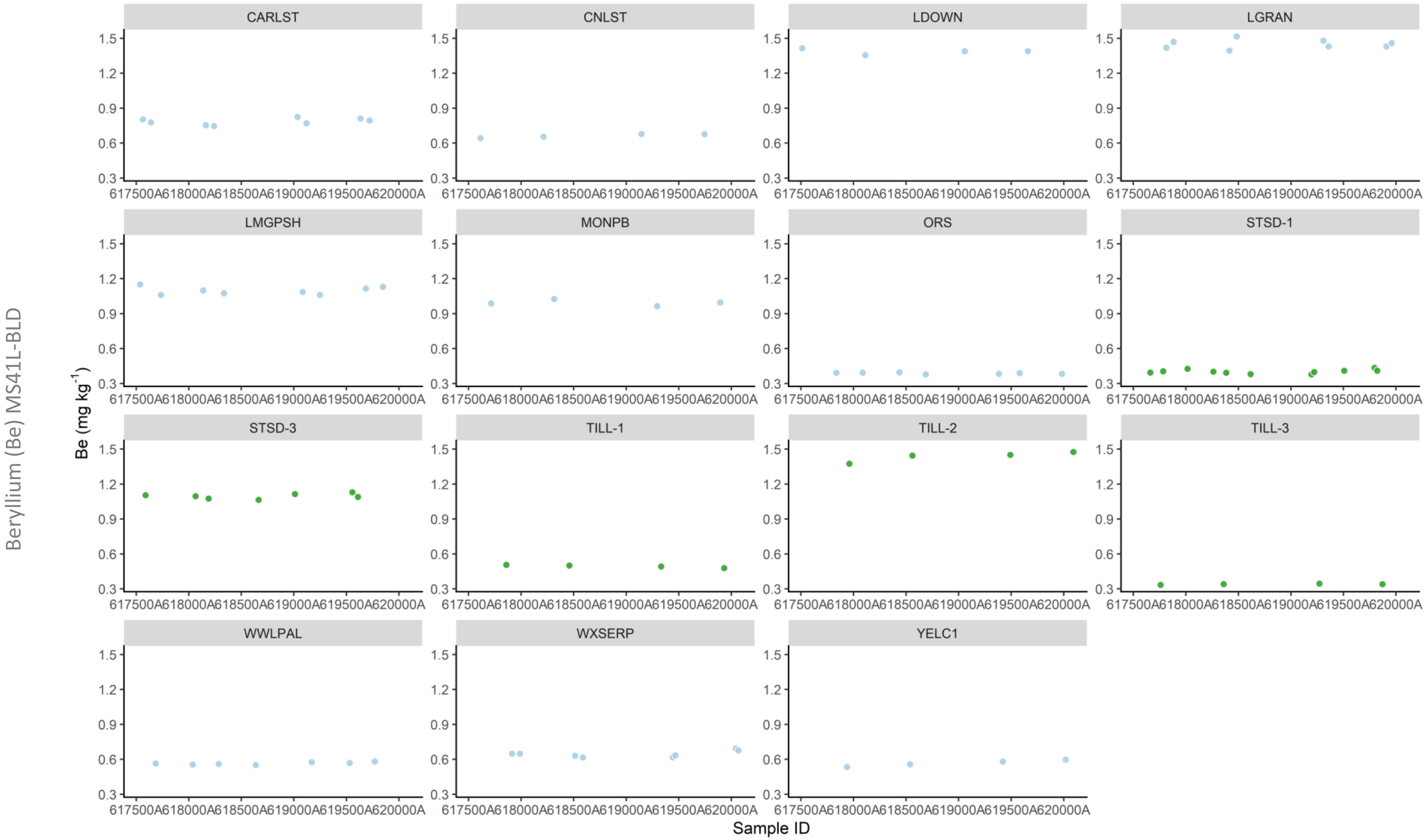
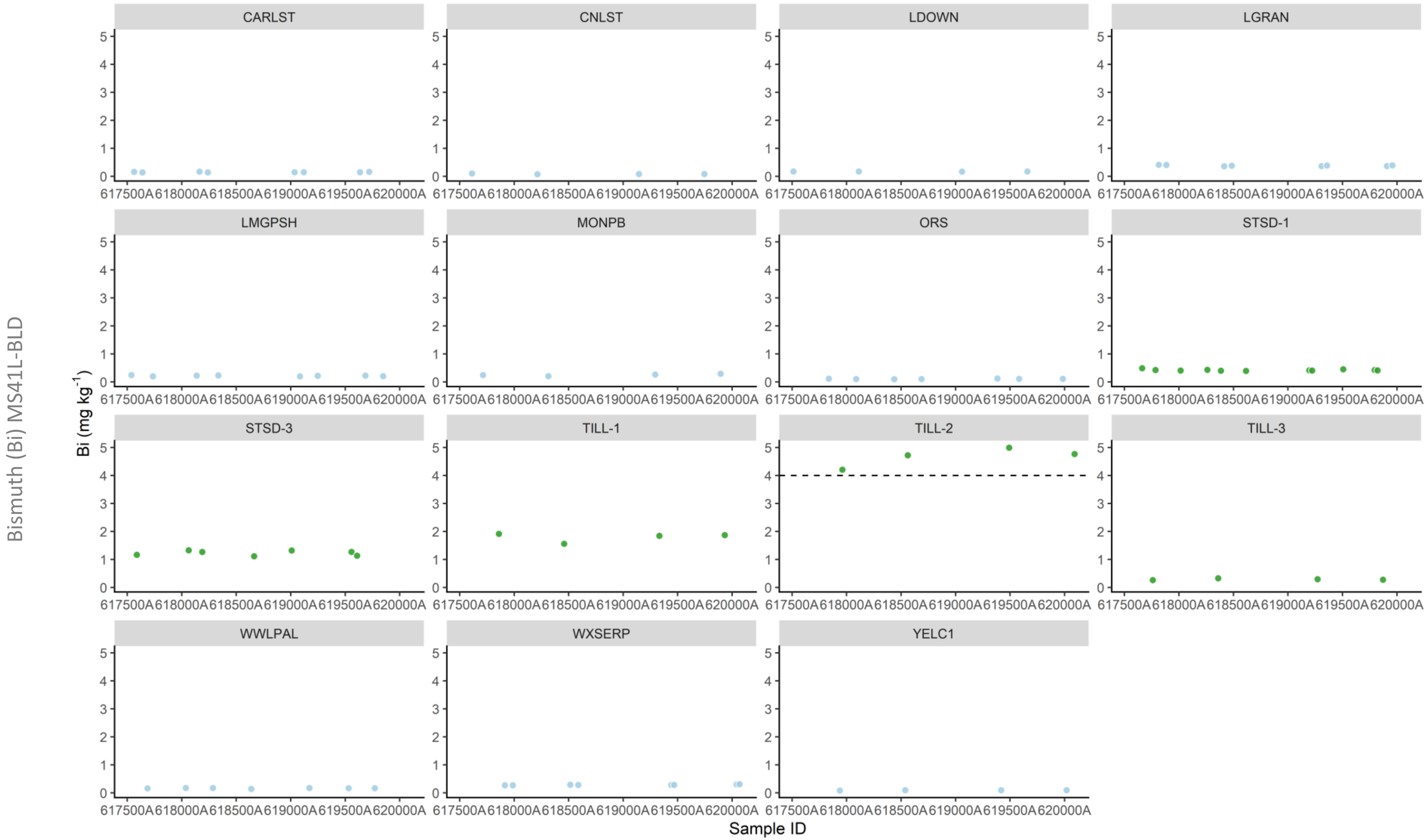
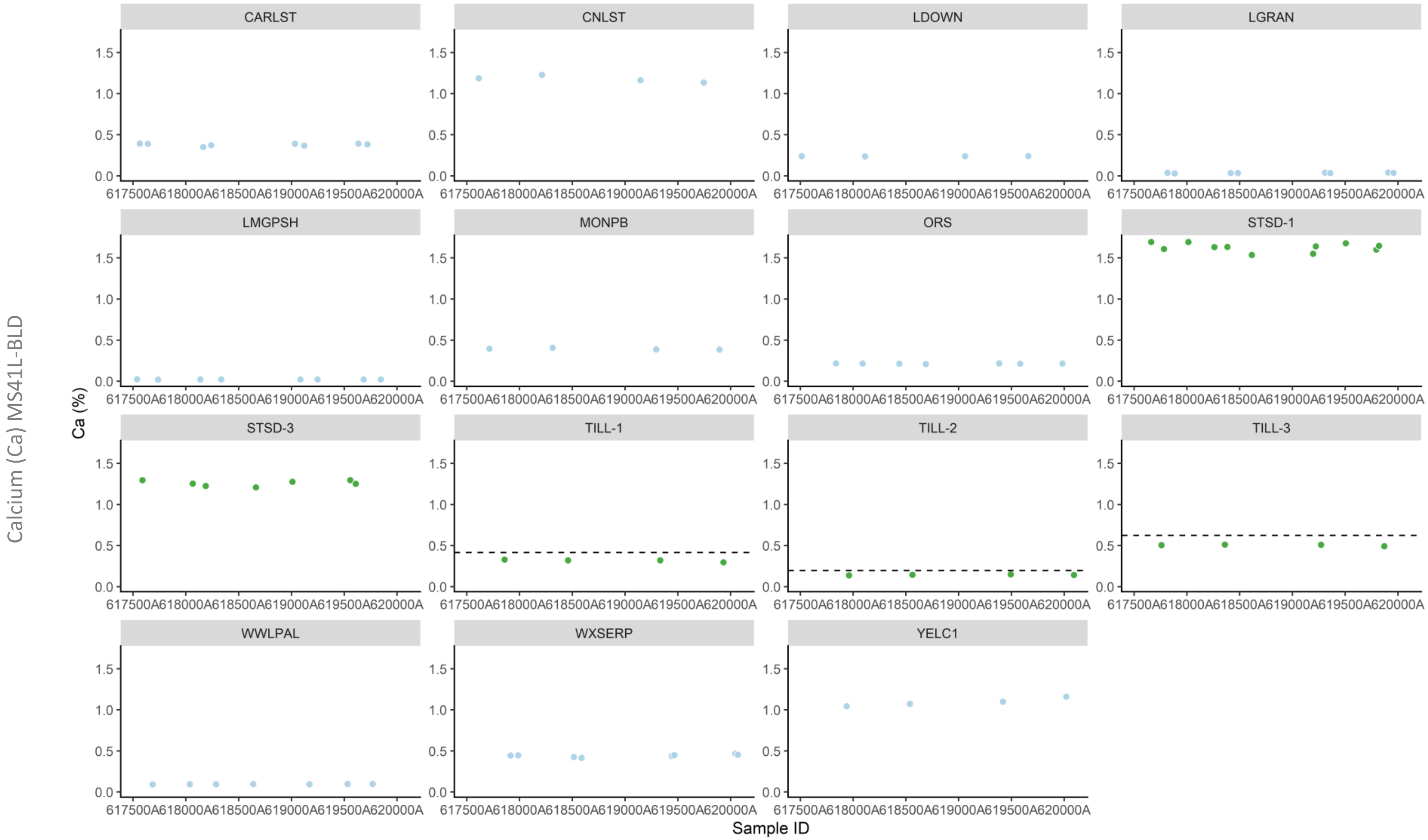


Beryllium (Be) sample data IQR: 1.00–1.31 mg kg^{-1}



Bismuth (Bi) sample data IQR: 0.19–0.293 mg kg^{-1}

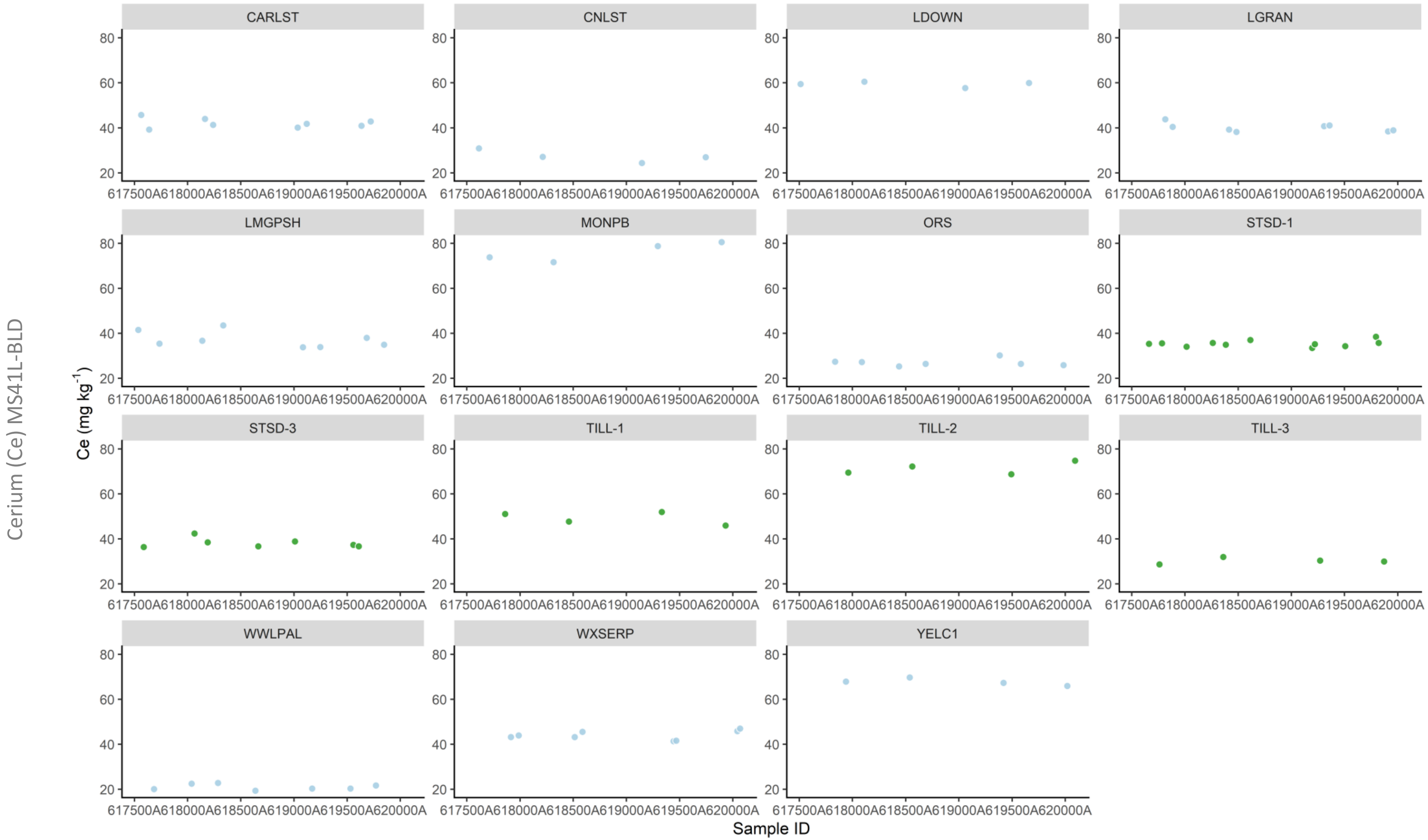


Calcium (Ca) sample data IQR: 1.27–4.30 %

Cadmium (Cd) MS41L-BLD

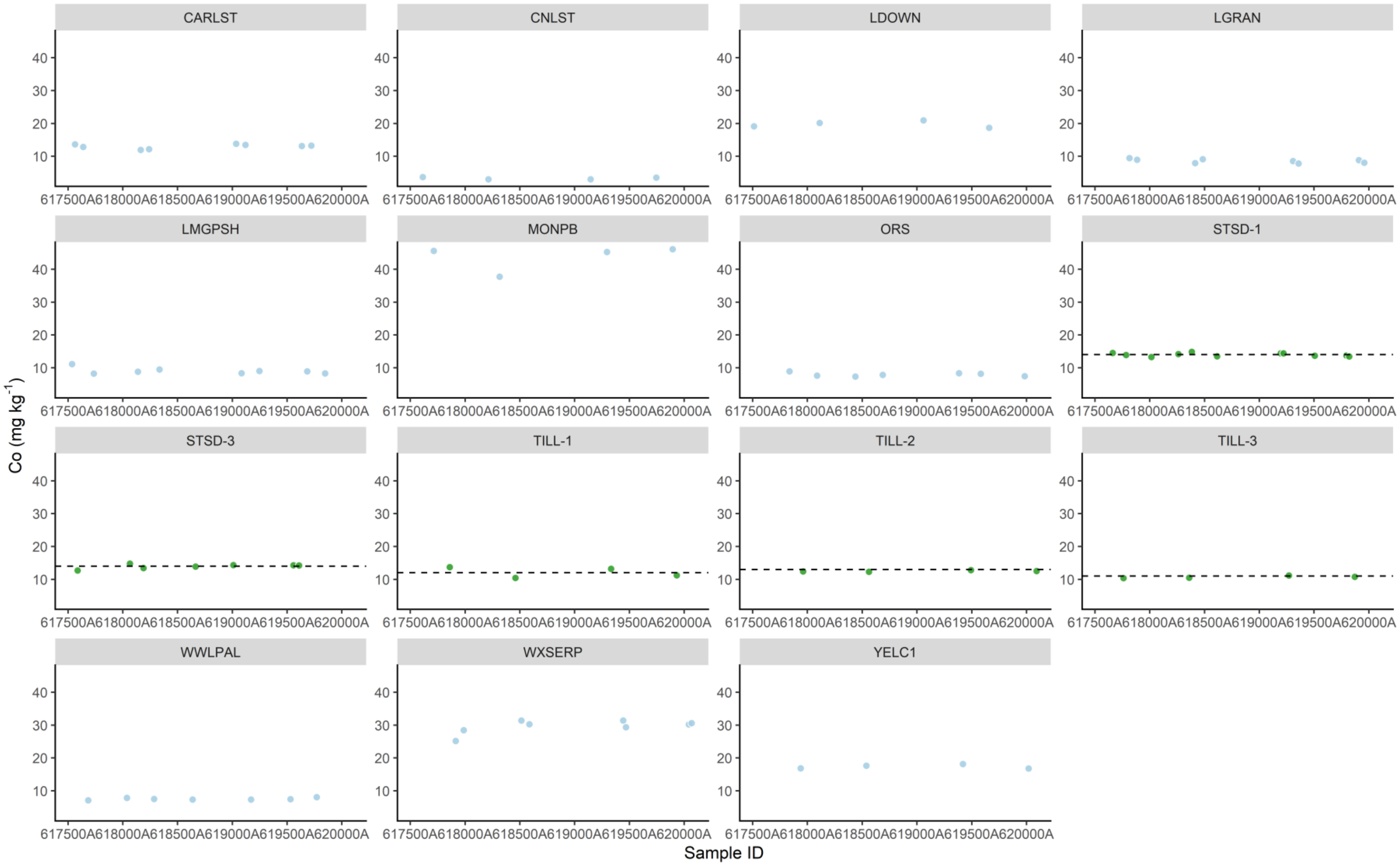
Cadmium (Cd) sample data IQR: 1.45–2.12 mg kg^{-1}

AURUM GLOBAL EXPLORATION



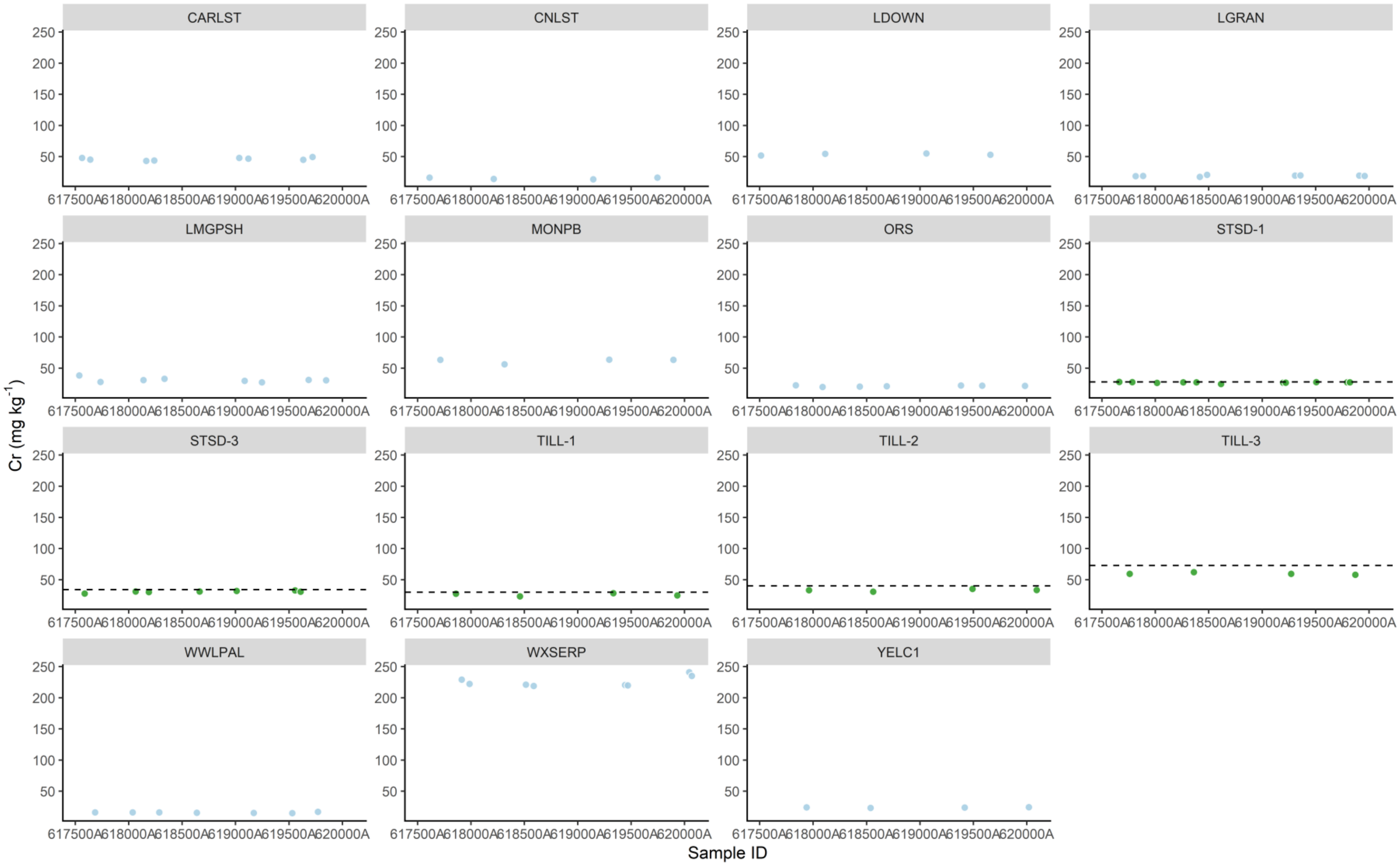
Cerium (Ce) sample data IQR: 22.6–26.9 mg kg^{-1}

Cobalt (Co) MS41L-BLD



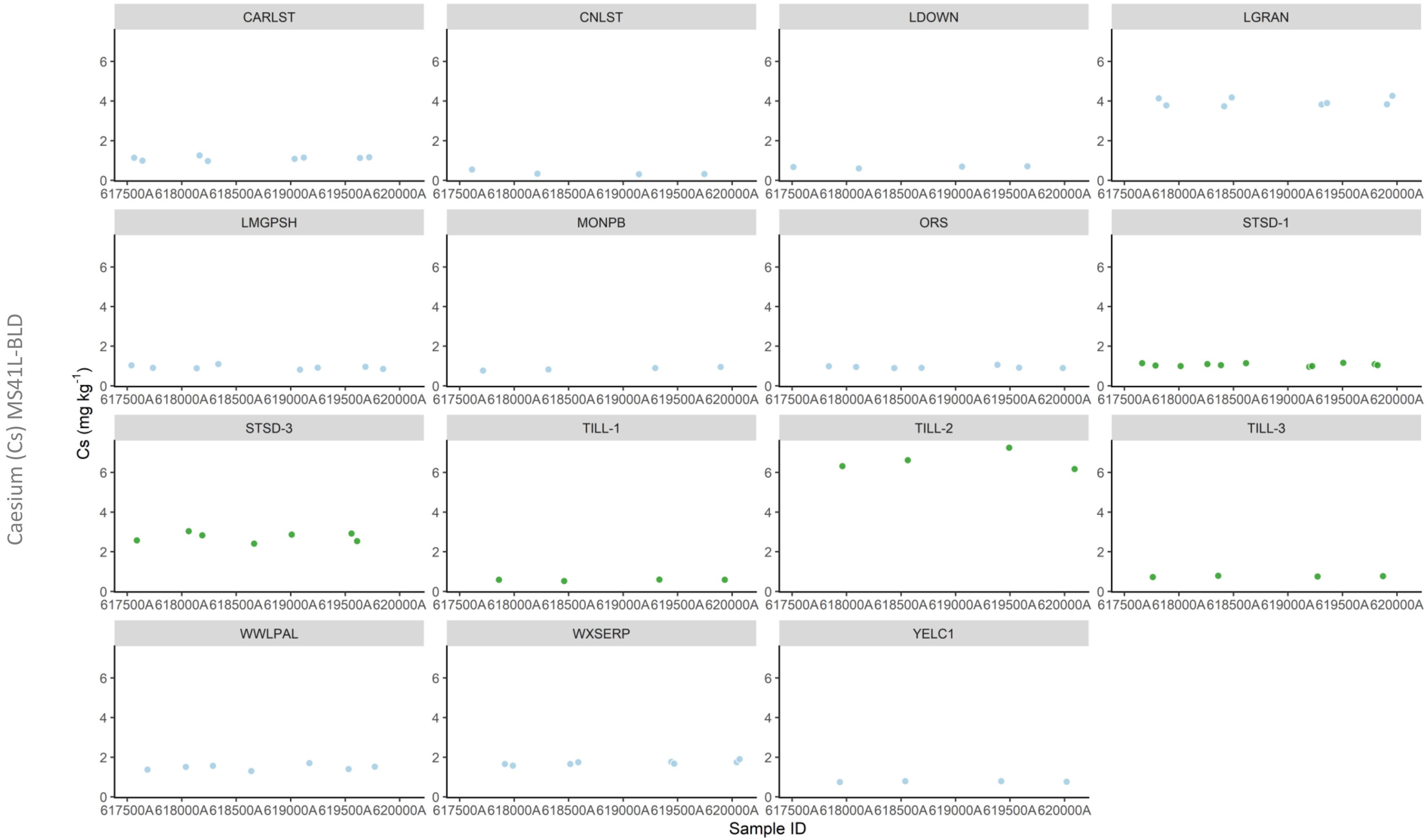
Cobalt (Co) sample data IQR: 9.51–12.3 mg kg^{-1}

Chromium (Cr) MS41L-BLD



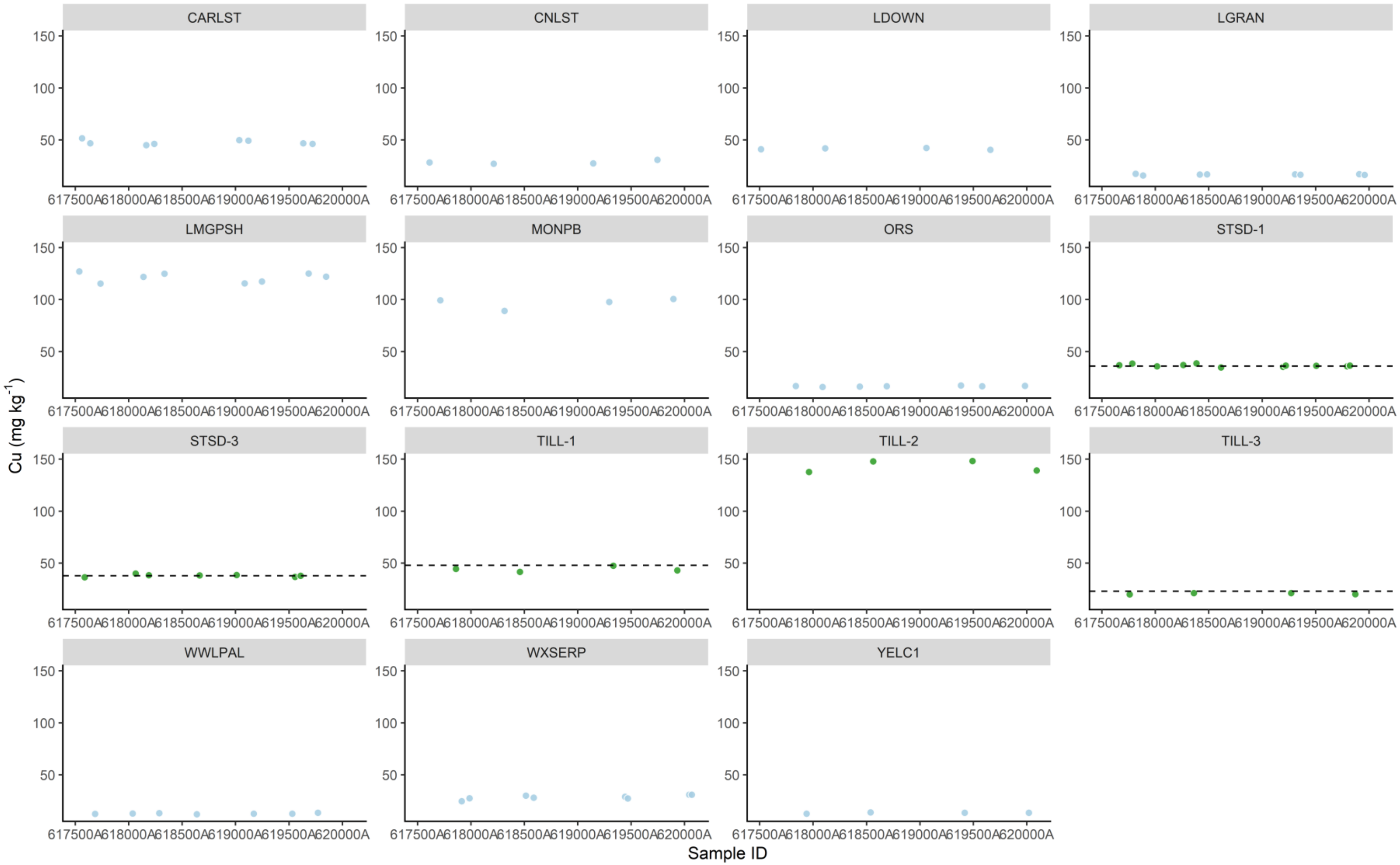
Chromium (Cr) sample data IQR: 19.9–23.4 mg kg^{-1}

AURUM GLOBAL EXPLORATION



Caesium (Cs) sample data IQR: 0.391–0.614 mg kg^{-1}

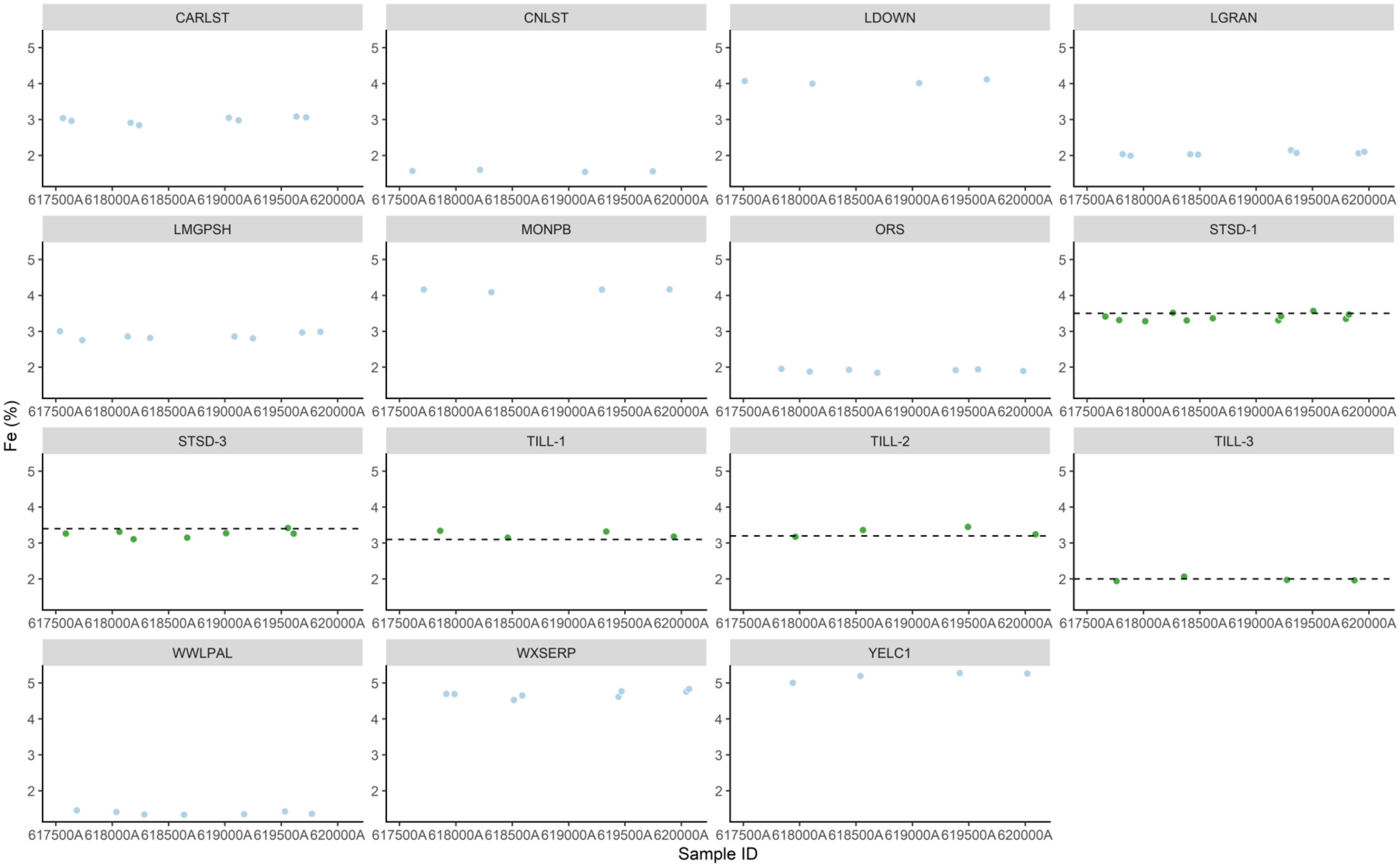
Copper (Cu) MS41L-BLD



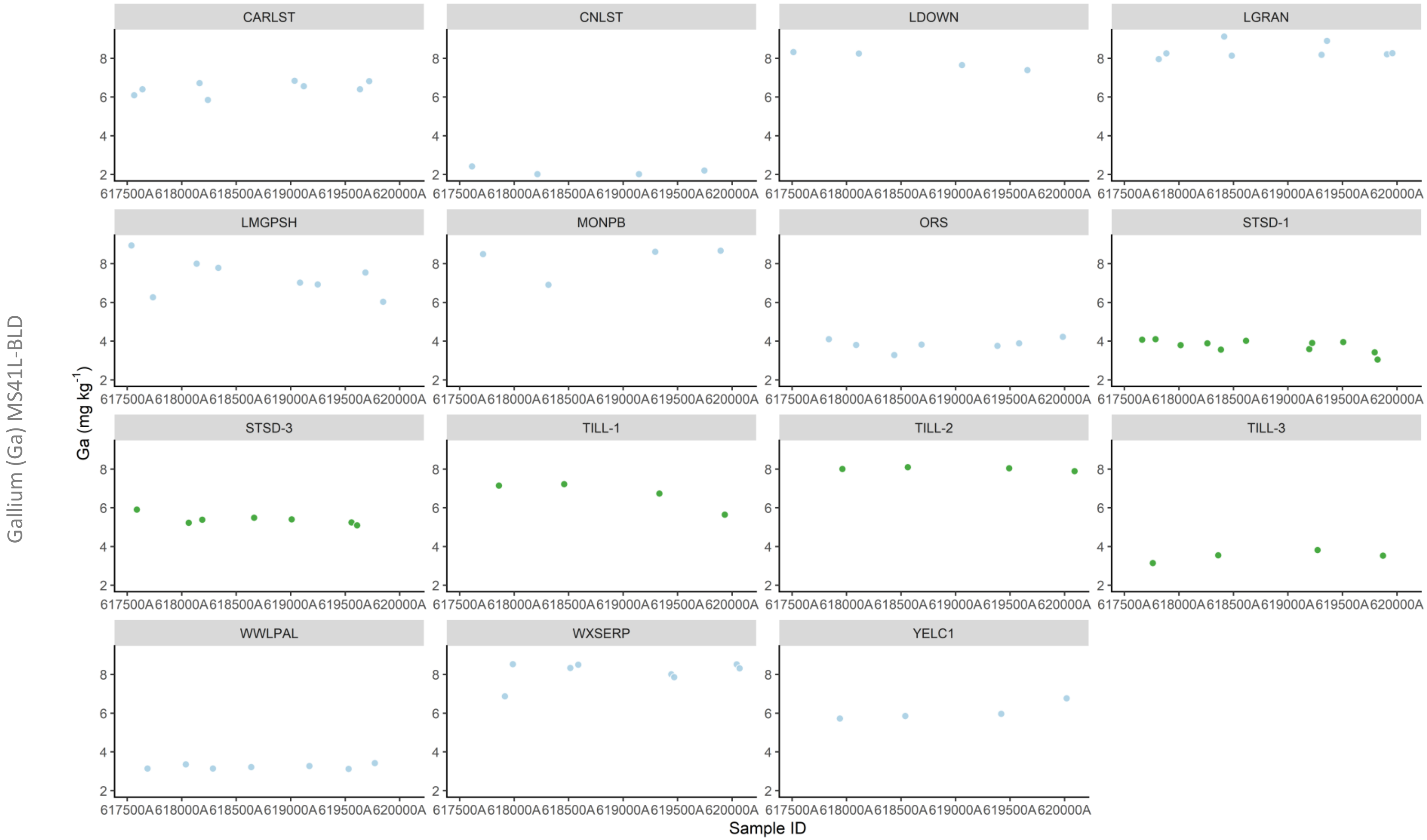
Copper (Cu) sample data IQR: 36.0–60.9 mg kg^{-1}

AURUM GLOBAL EXPLORATION

Iron (Fe) MS41L-BLD

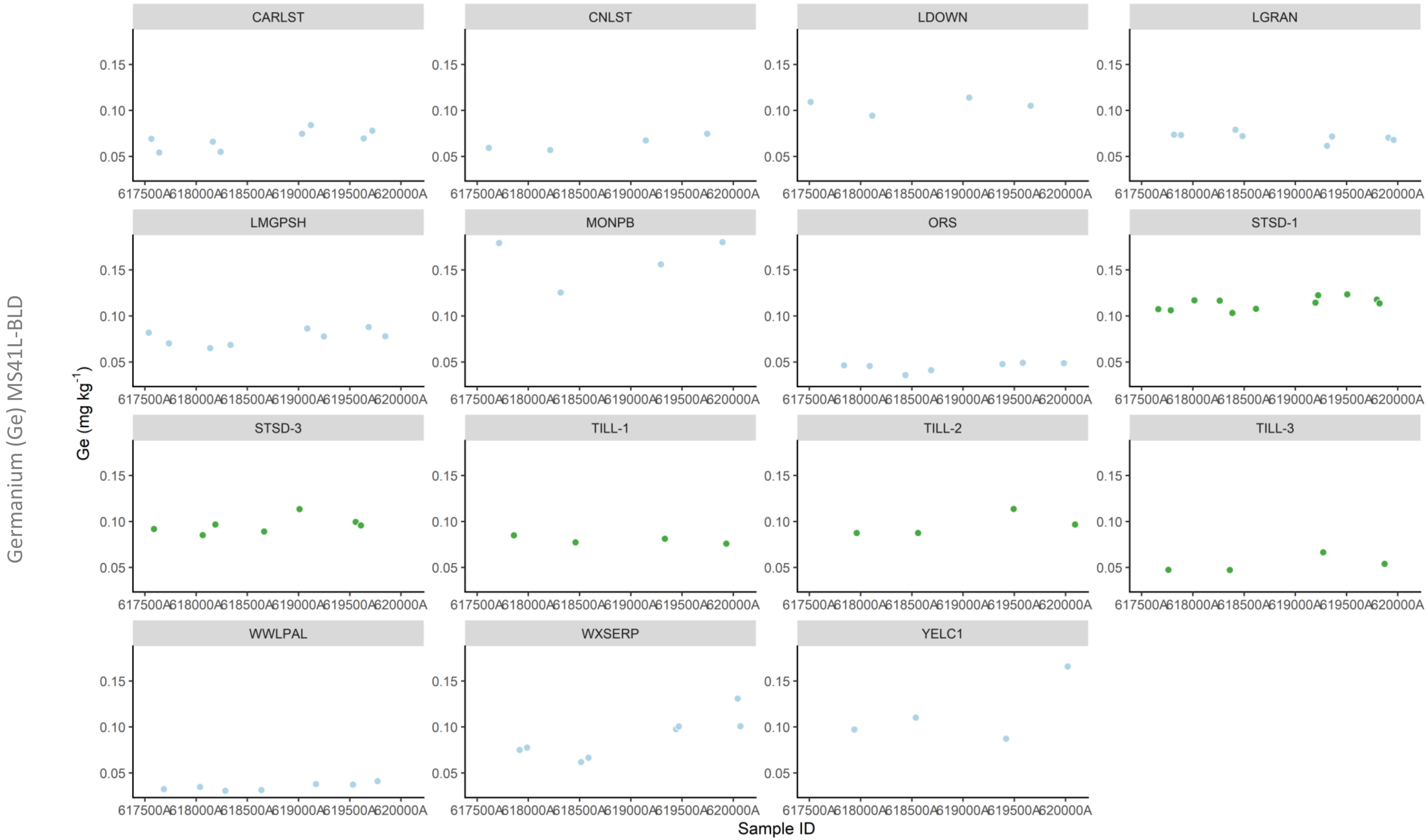


Iron (Fe) sample data IQR: 2.09–2.49 %

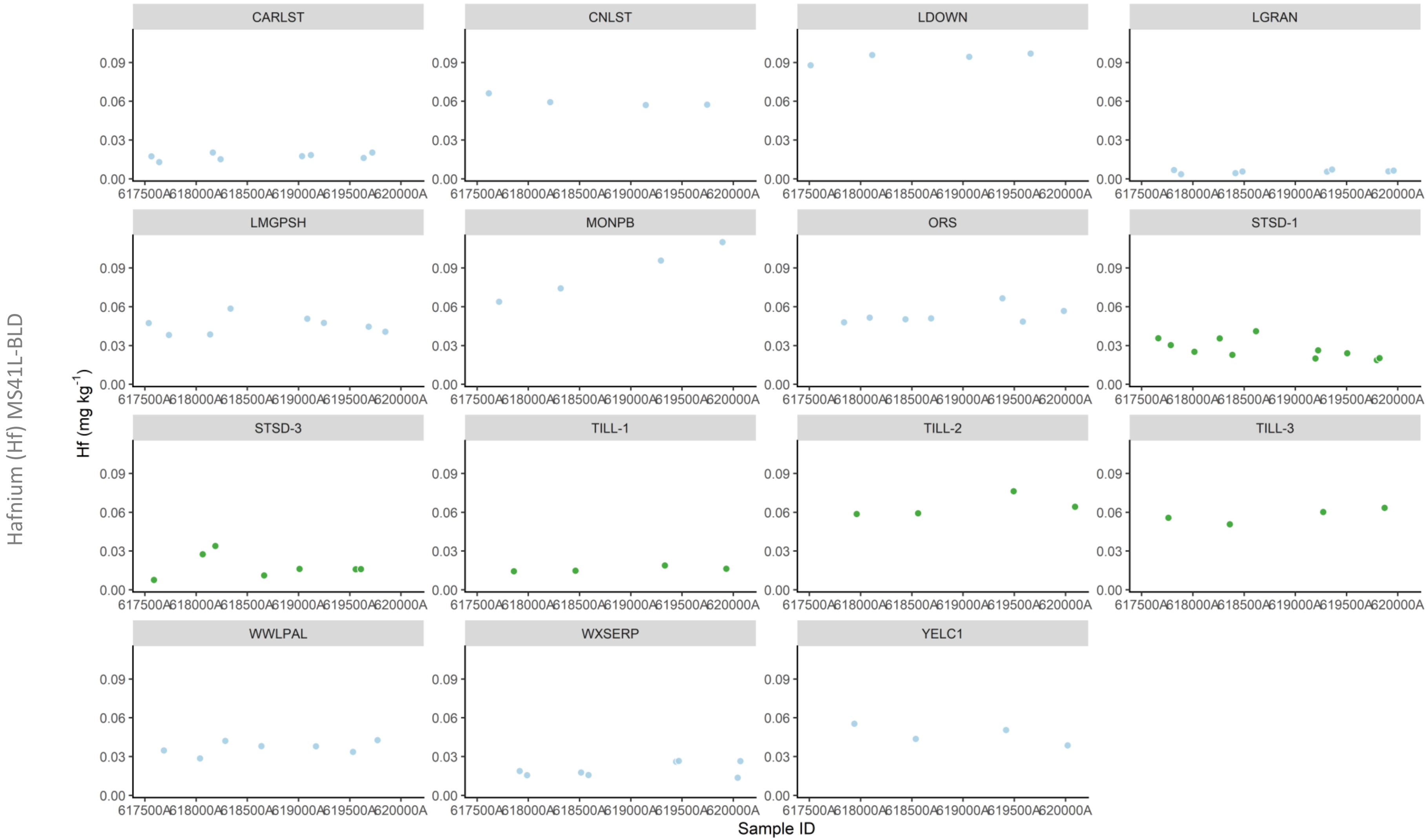


Gallium (Ga) sample data IQR: 2.77–3.47 mg kg^{-1}

AURUM GLOBAL EXPLORATION

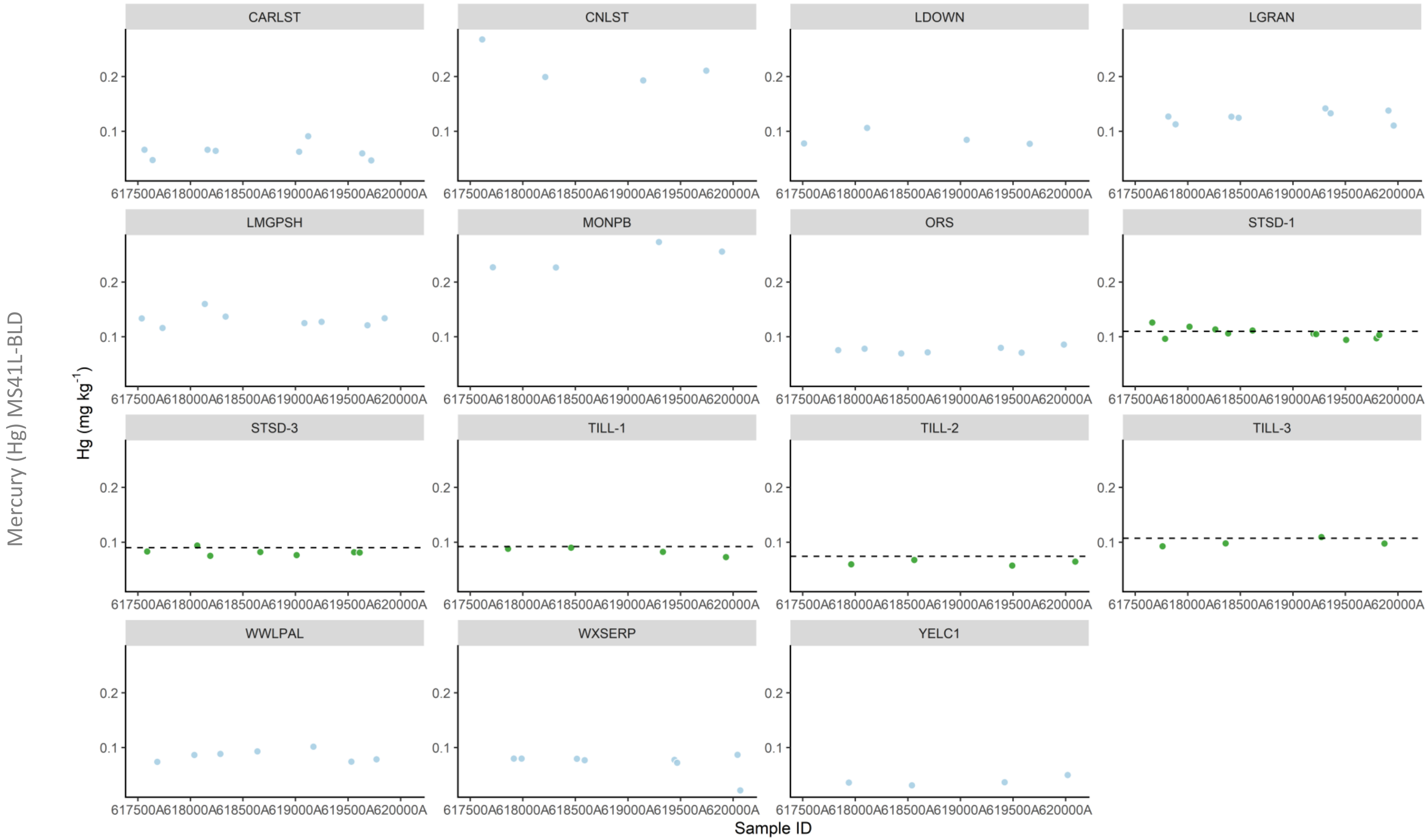


Germanium (Ge) sample data IQR: 0.0553-0.0696 mg kg^{-1}

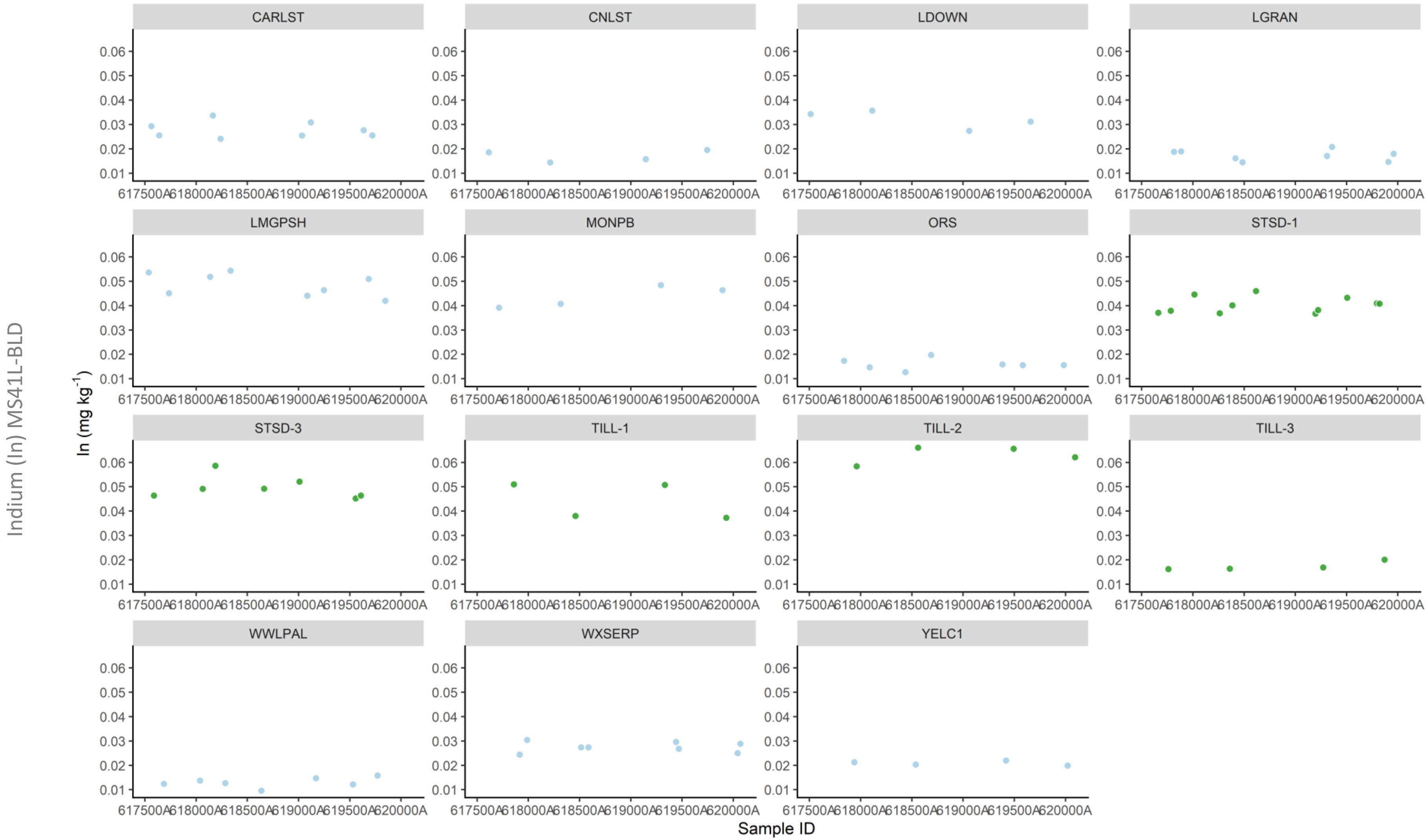


Hafnium (Hf) sample data IQR: 0.0818–0.109 mg kg^{-1}

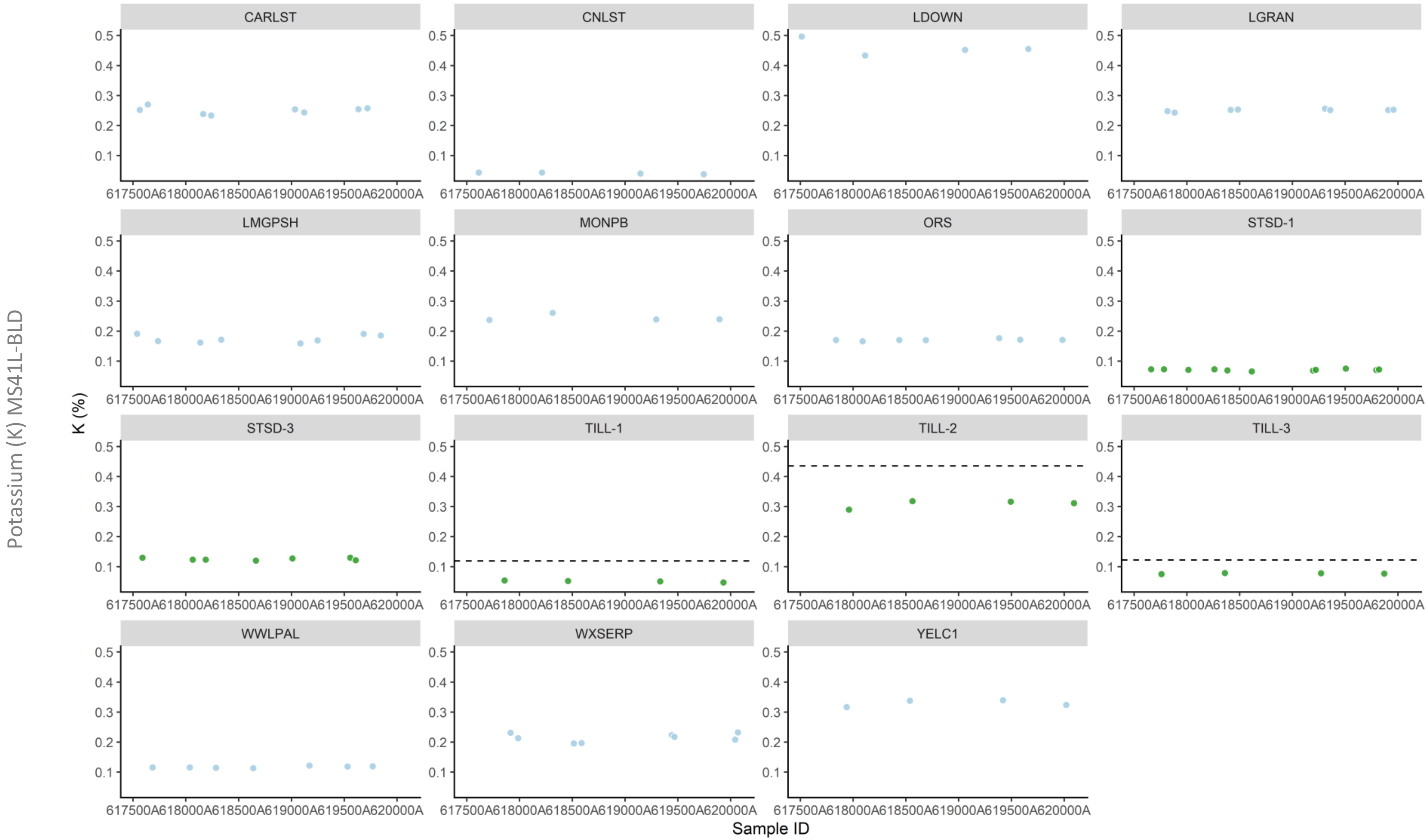
AURUM GLOBAL EXPLORATION



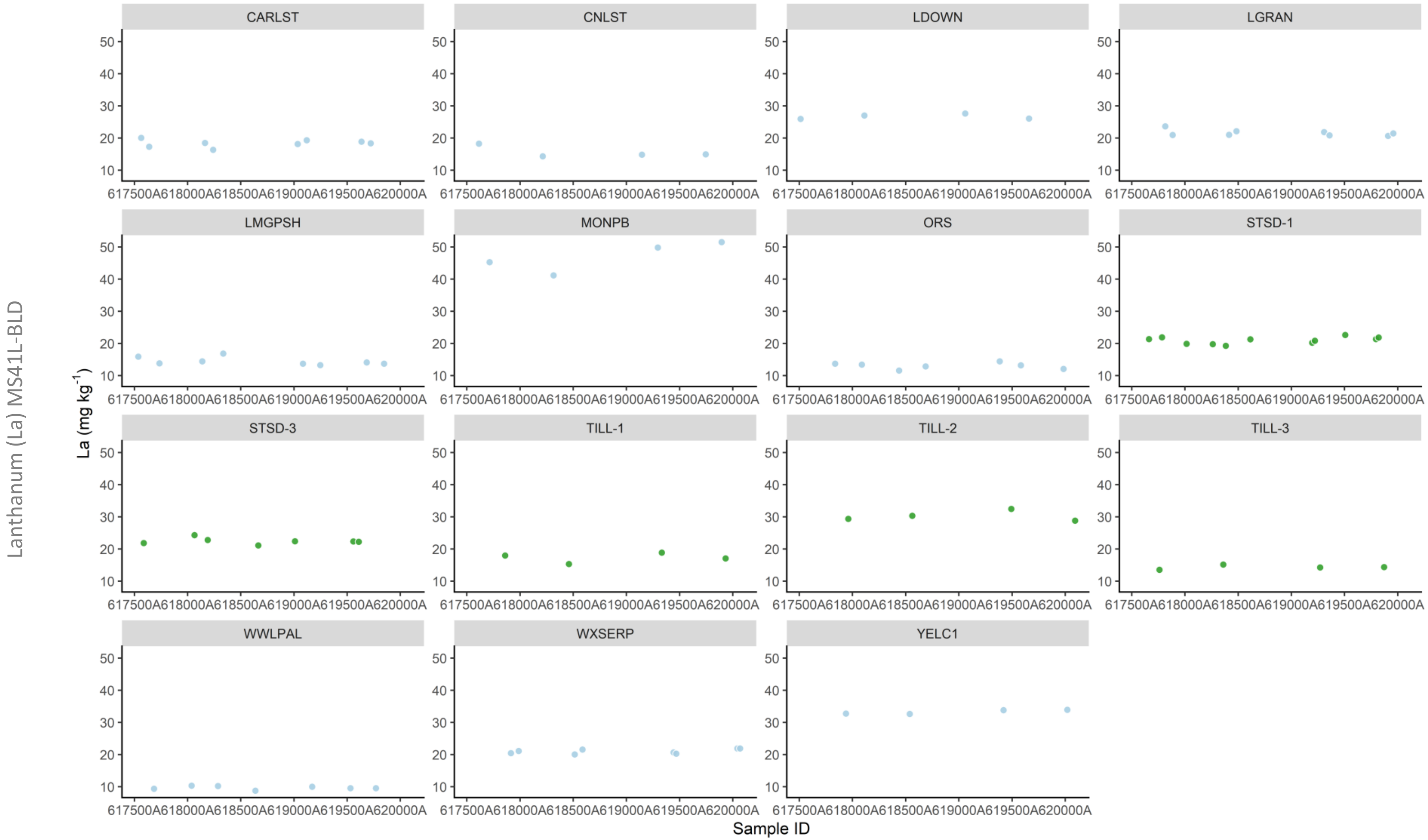
Mercury (Hg) sample data IQR: 0.163–0.481 mg kg^{-1}



Indium (In) sample data IQR: 0.0205–0.0272 mg kg^{-1}

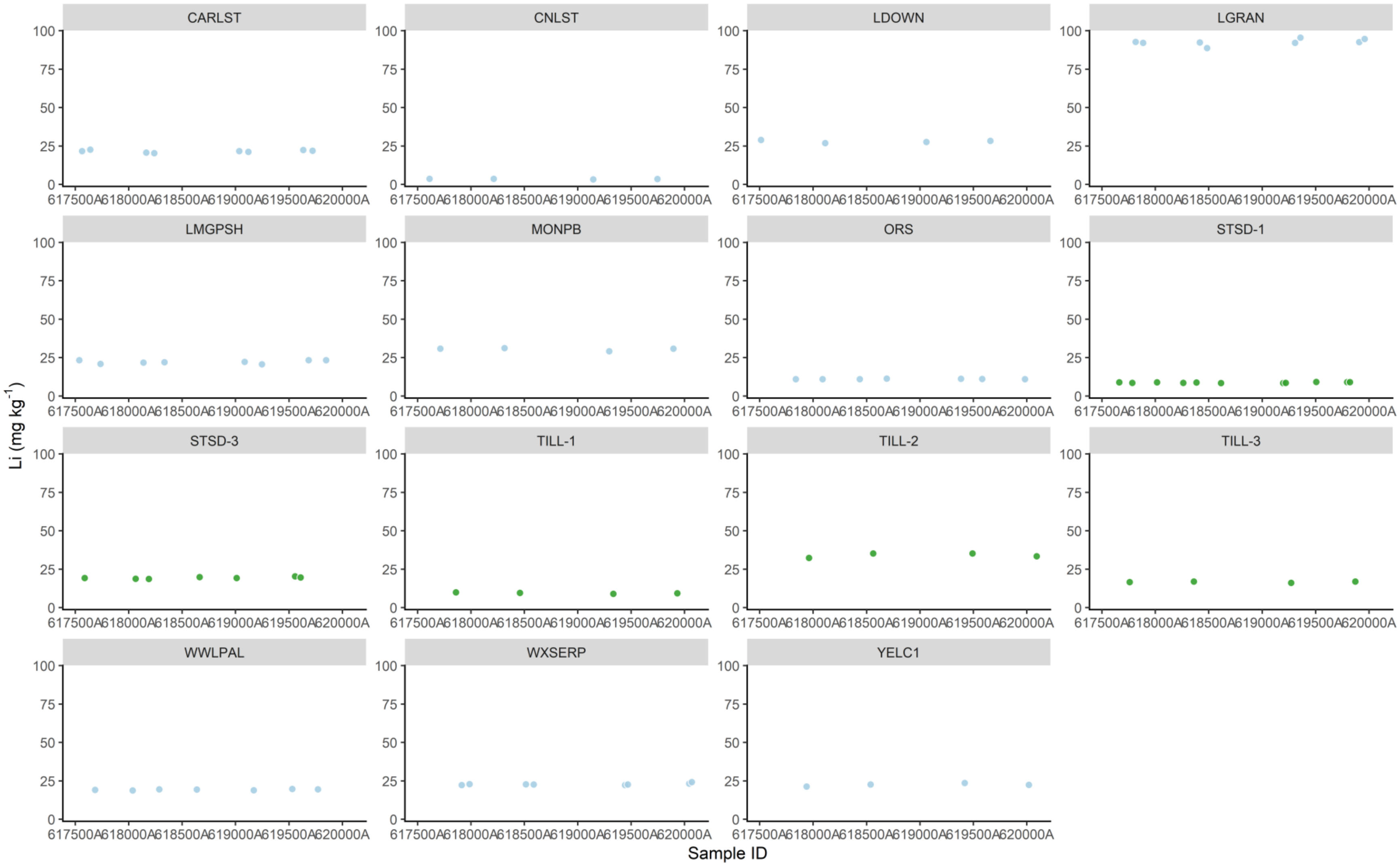


Potassium (K) sample data IQR: 0.124–0.154 %



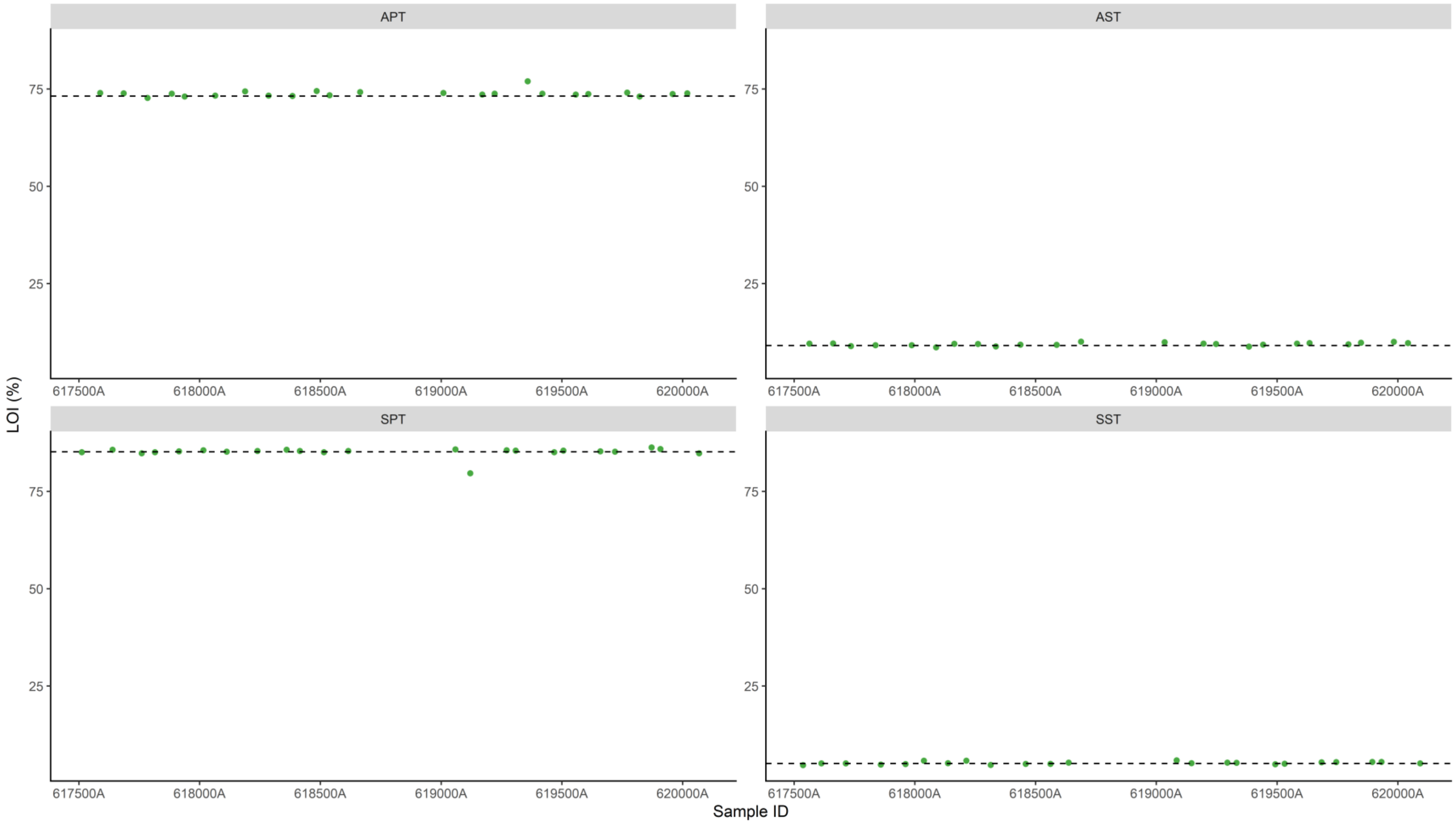
Lanthanum (La) sample data IQR: 11.6–13.6 mg kg^{-1}

Lithium (Li) MS41L-BLD

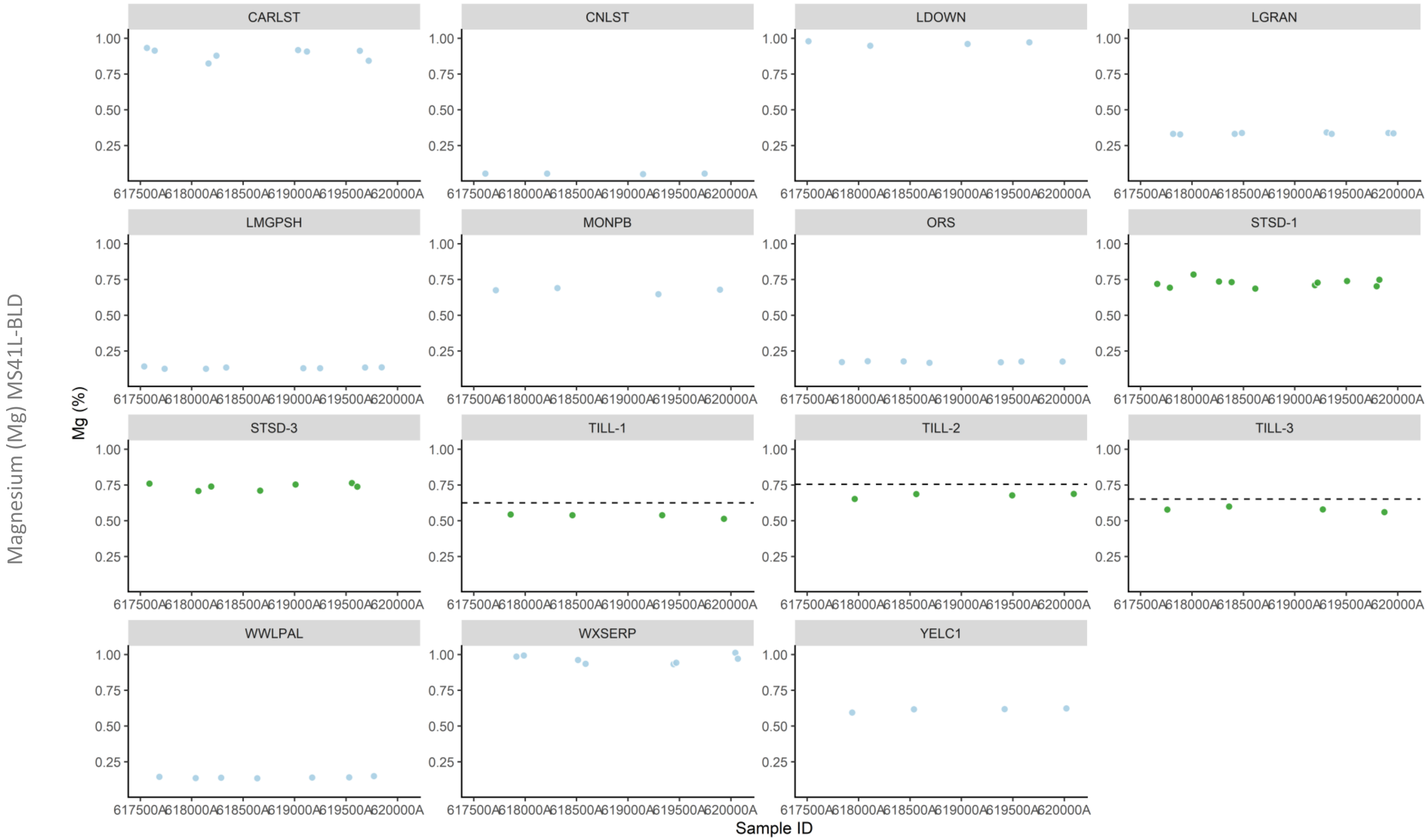


Lithium (Li) sample data IQR: 10.9–16.6 mg kg^{-1}

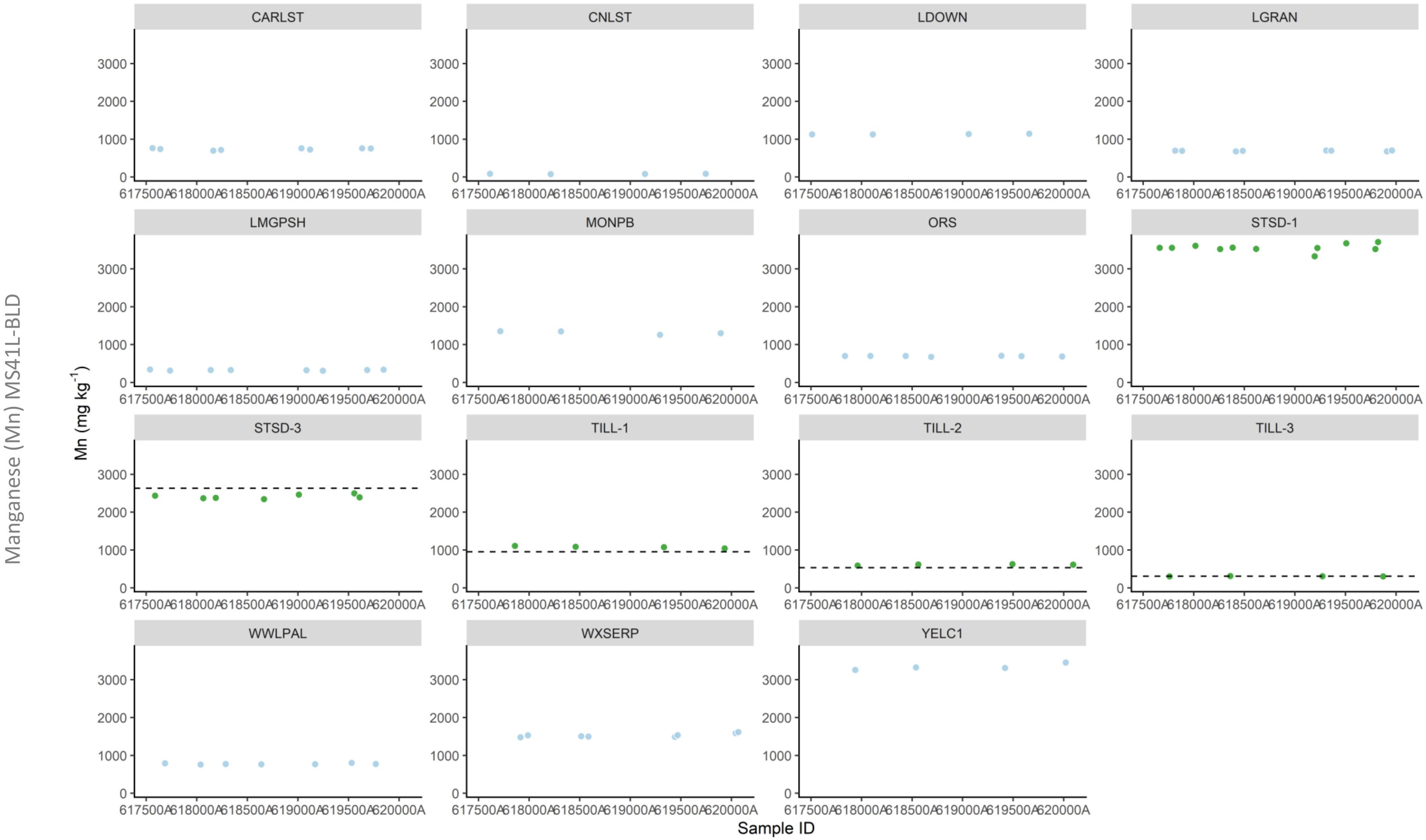
Loss-on-ignition



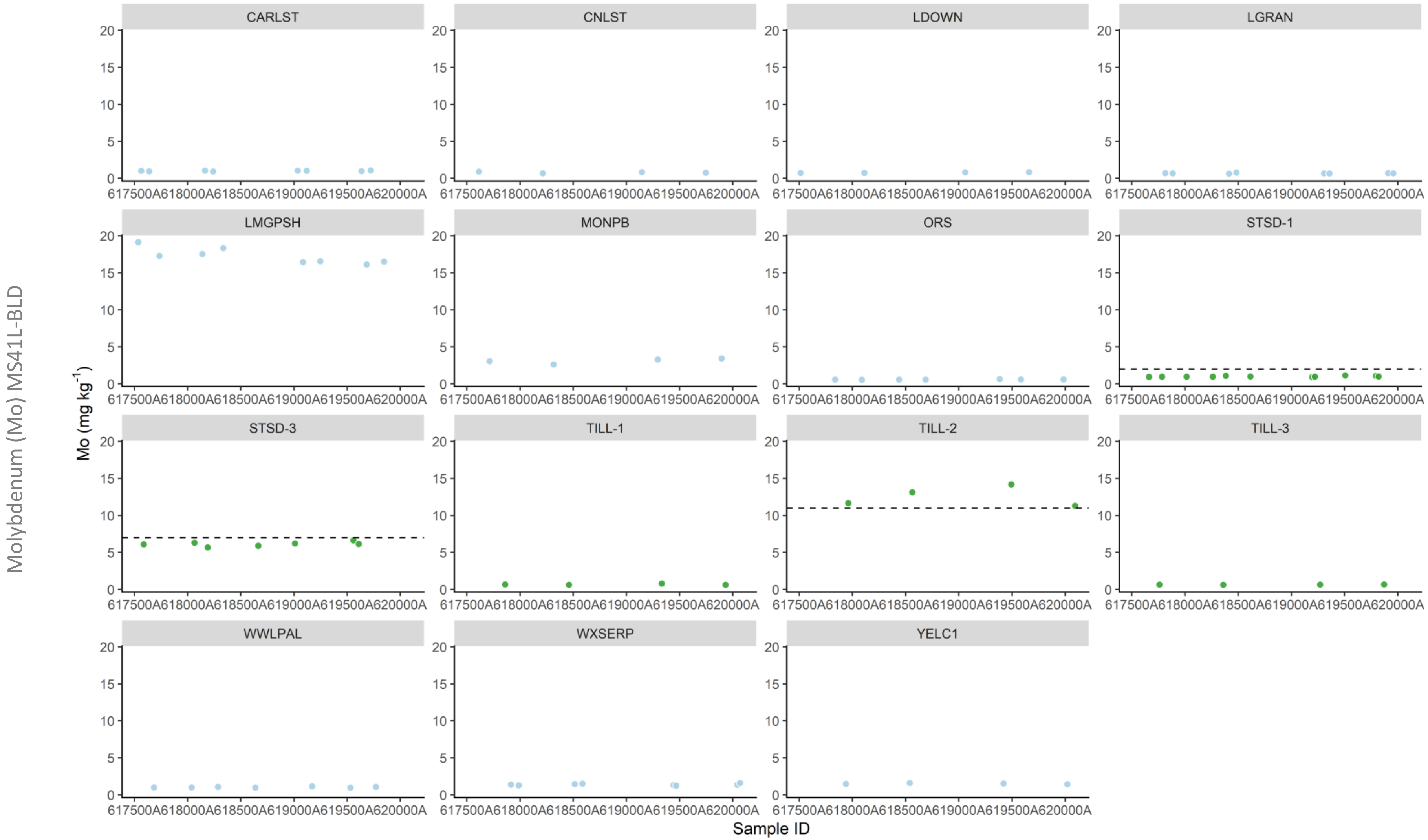
Loss on ignition (LOI) sample data IQR: 9.77–13.4 %



Magnesium (Mg) sample data IQR: 0.204–0.290 %

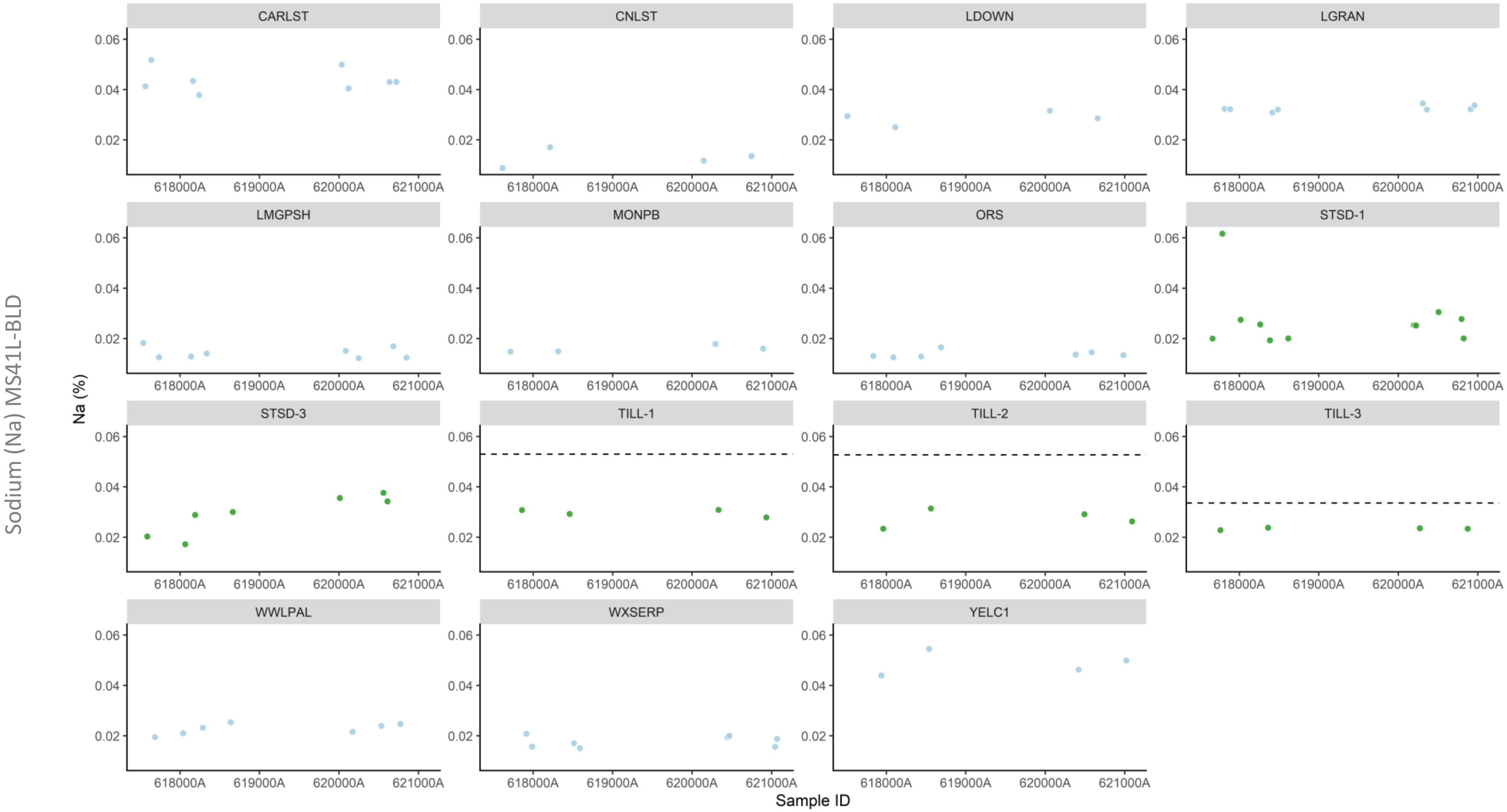


Manganese (Mn) sample data IQR: 802–1300 mg kg^{-1}



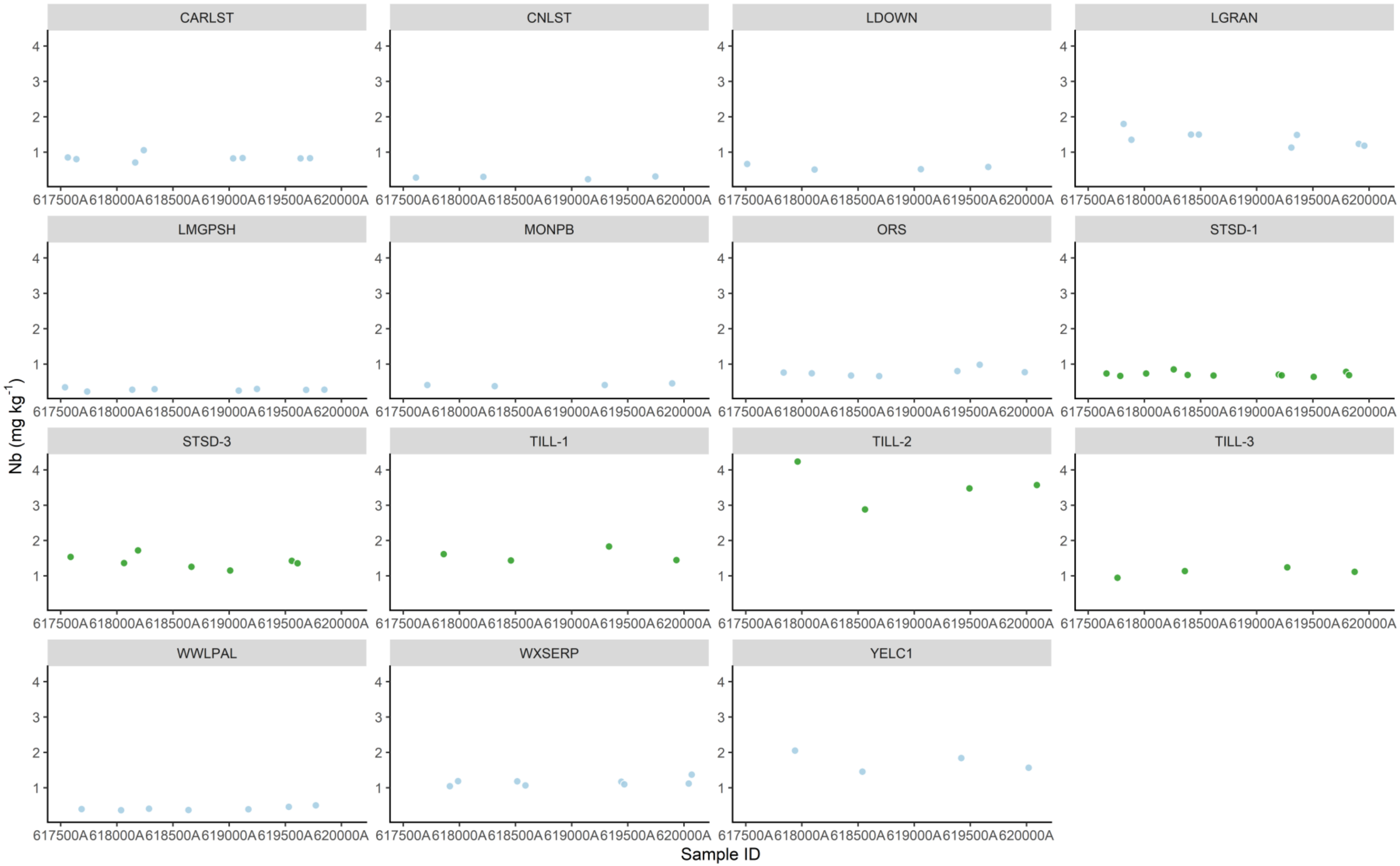
Molybdenum (Mo) sample data IQR: 2.57–3.70 mg kg^{-1}

AURUM GLOBAL EXPLORATION



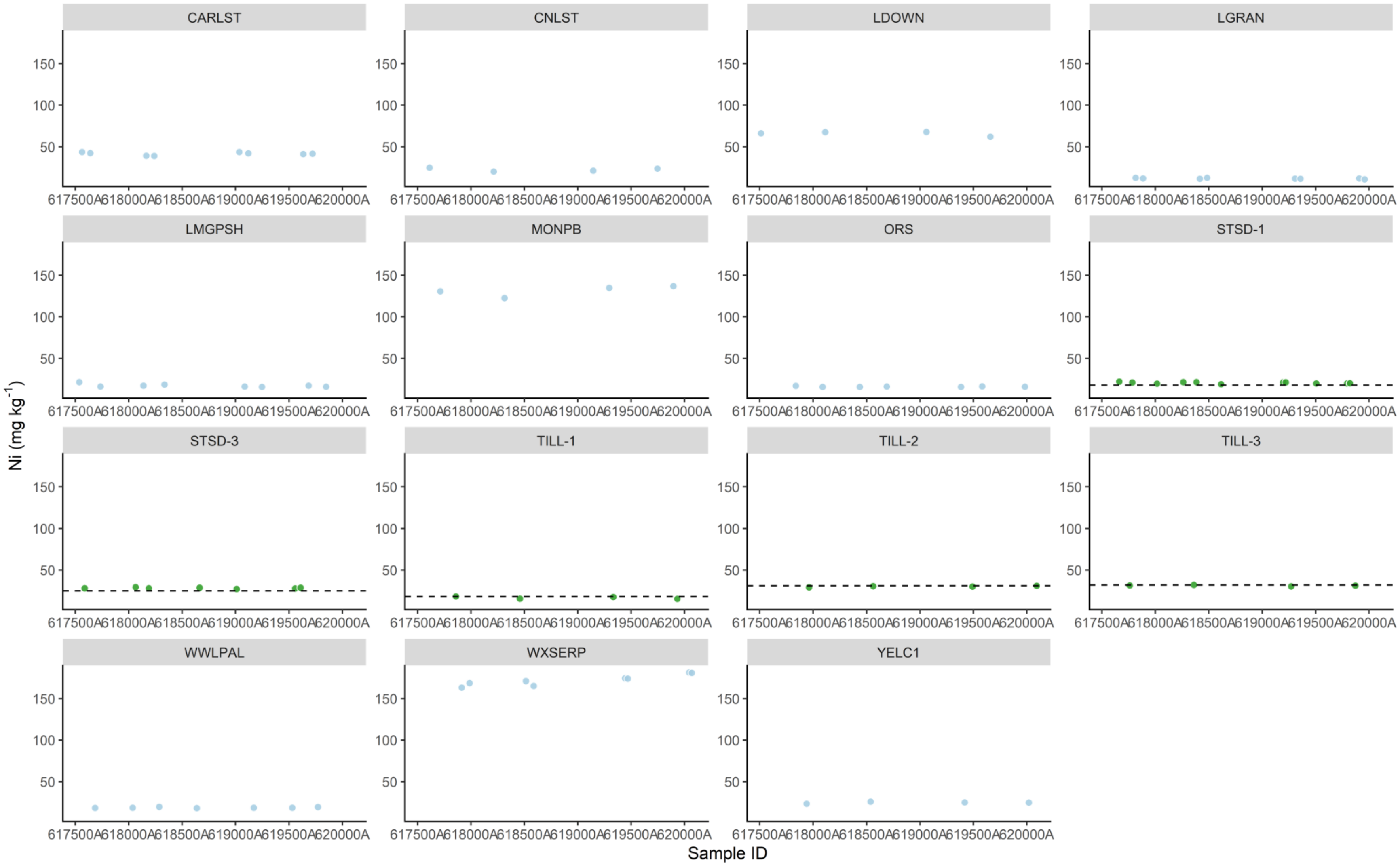
Sodium (Na) sample data IQR: 0.0154–0.0218 %

Niobium (Nb) MS41L-BLD

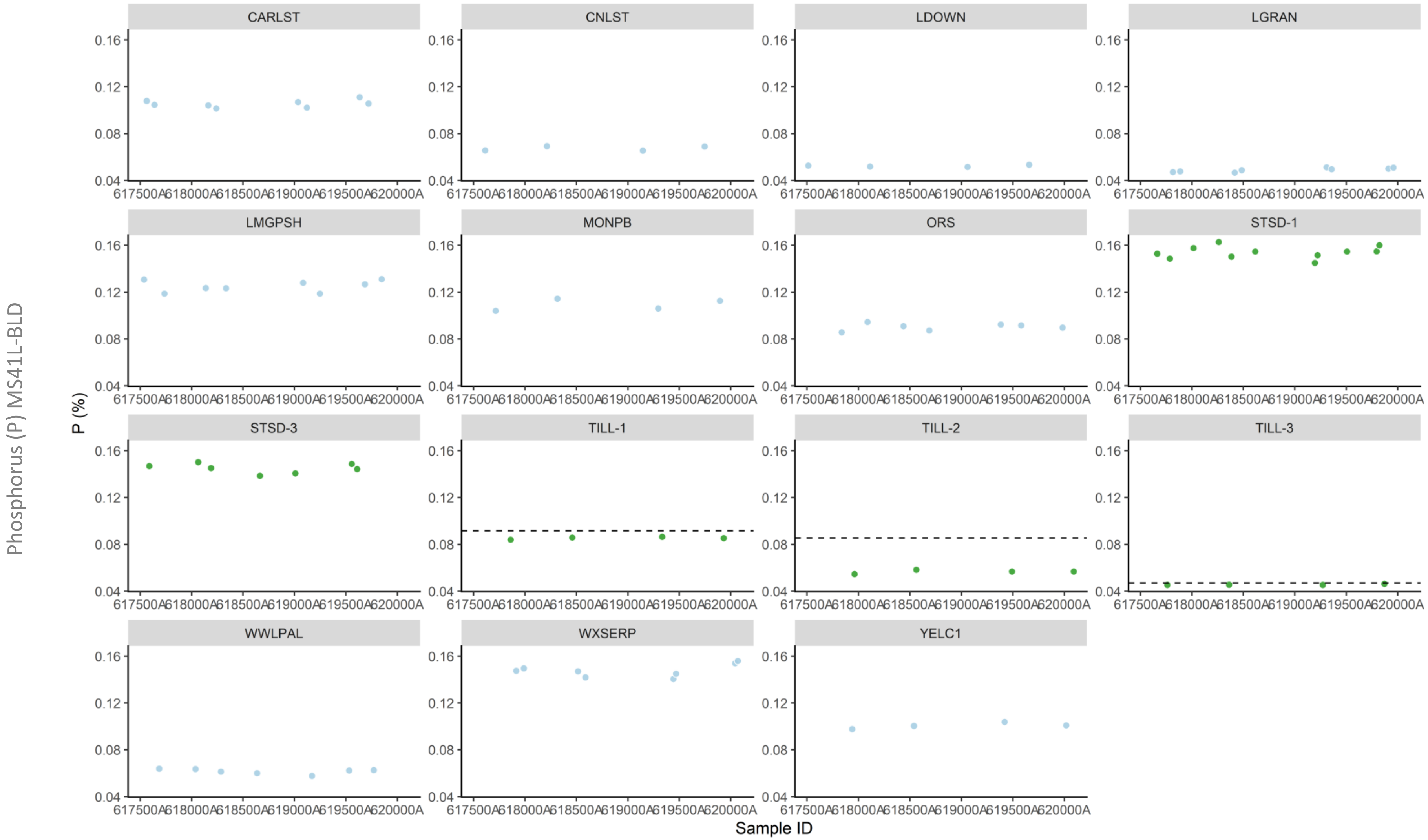


Niobium (Nb) sample data IQR: 0.297–0.429 mg kg^{-1}

Nickel (Ni) MS41L-BLD

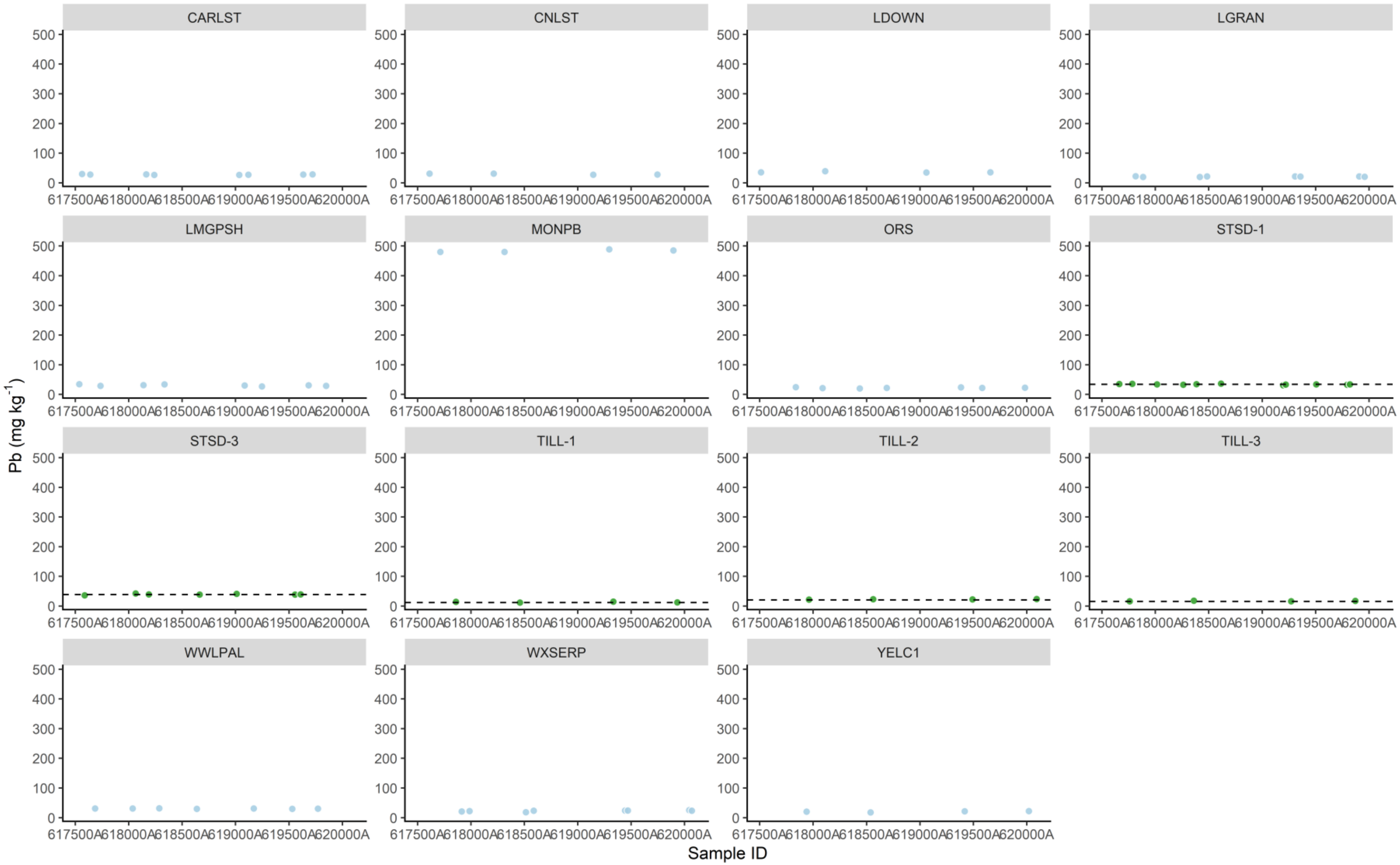


Nickel (Ni) sample data IQR: 36.6–49.1 mg kg^{-1}



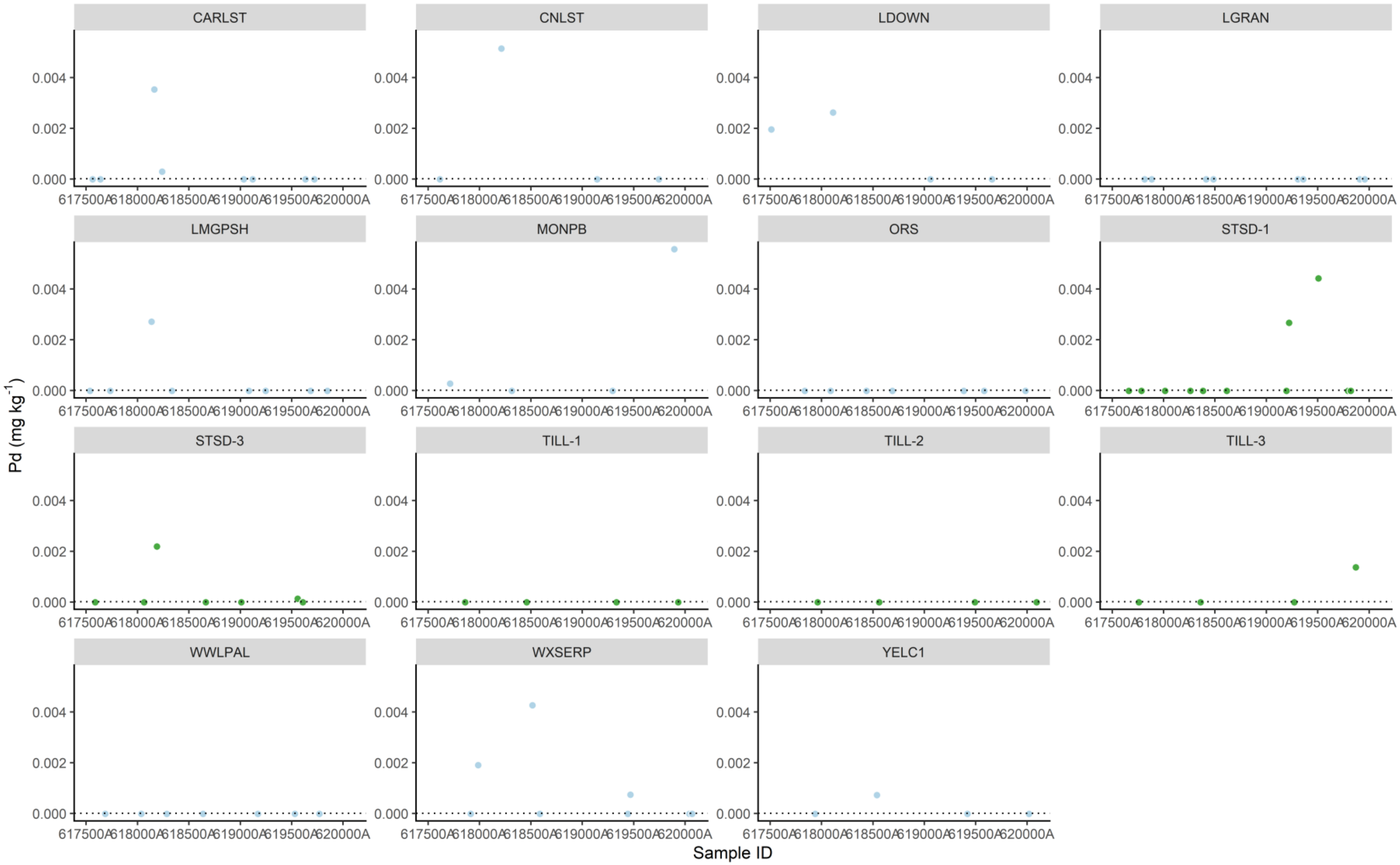
Phosphorus (P) sample data IQR: 869–1260 mg kg^{-1}

Lead (Pb) MS41L-BLD

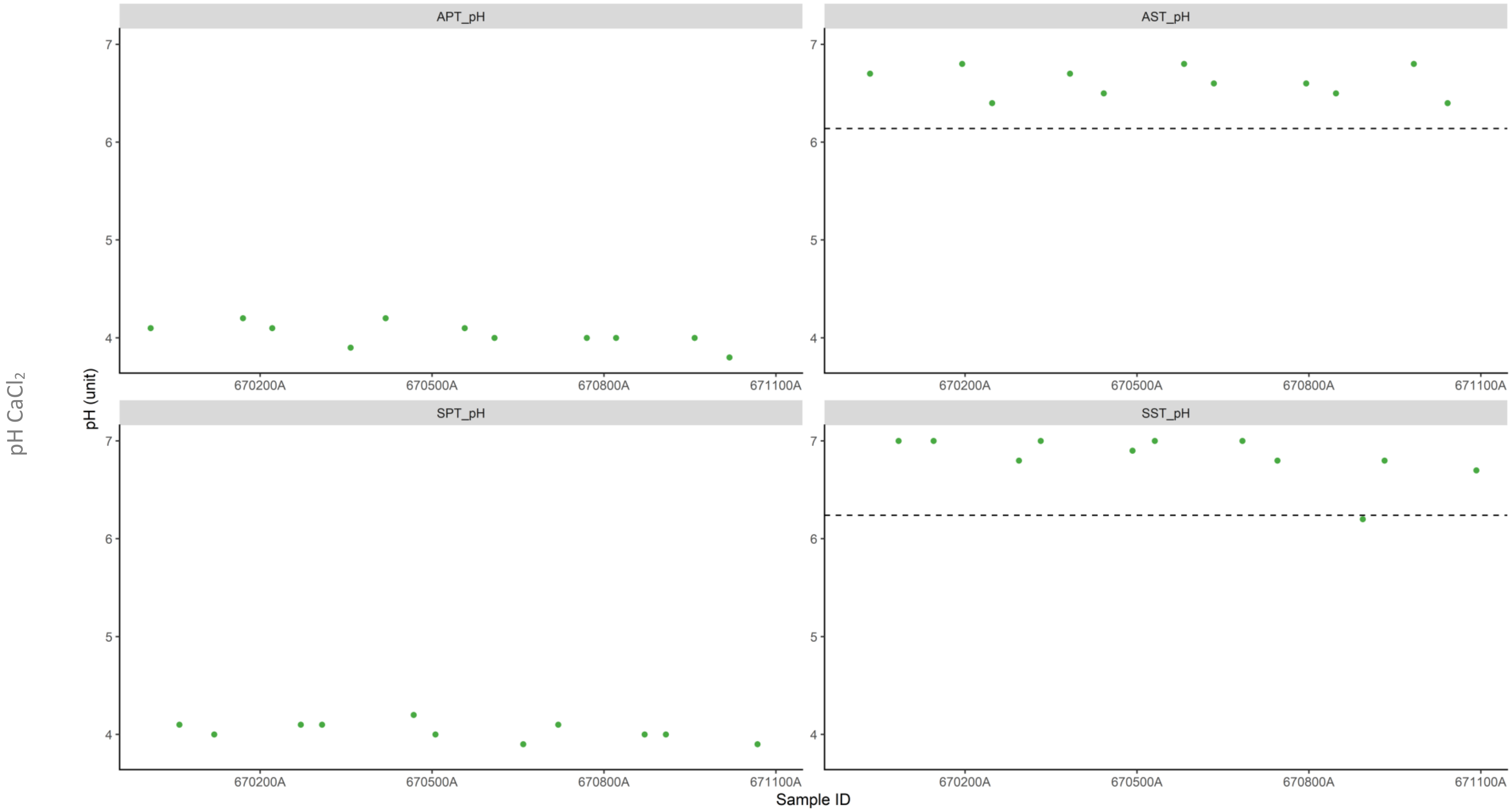


Lead (Pb) sample data IQR: 64.5–172 mg kg^{-1}

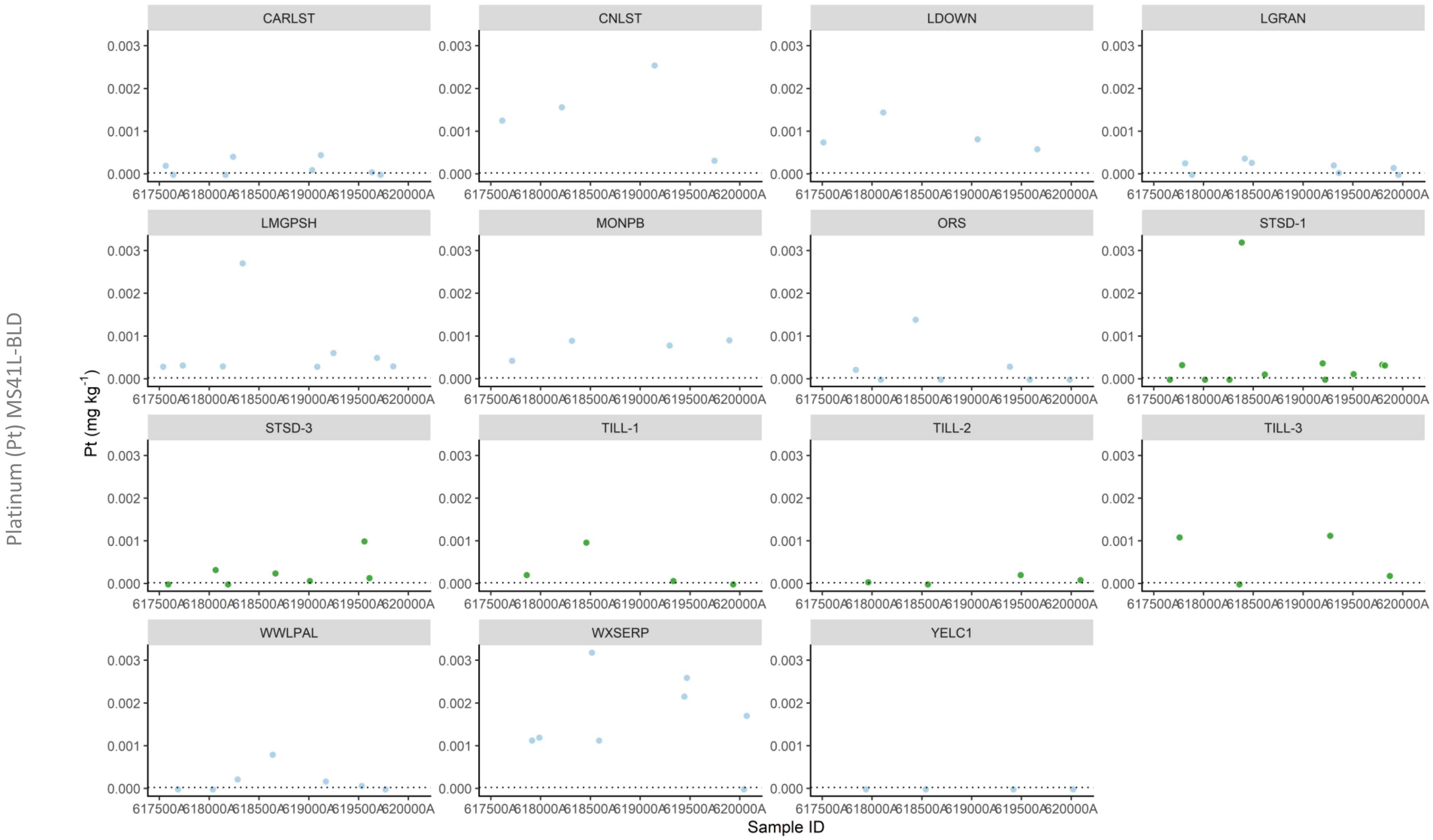
Palladium (Pd) MS41L-BLD



Palladium (Pd) sample data IQR: 0.0000065–0.000161 mg kg^{-1}



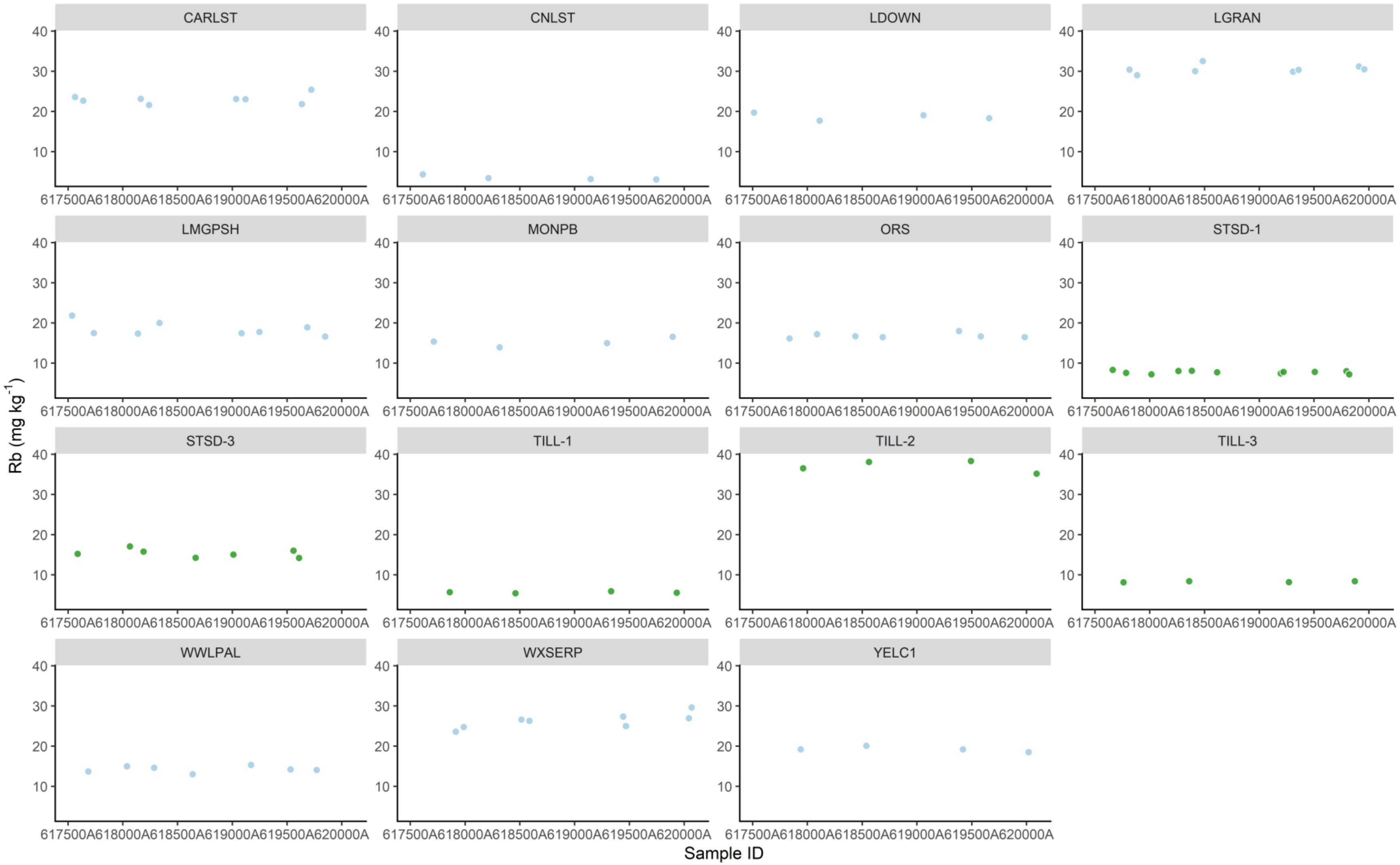
pH $CaCl_2$ sample data IQR: 6.6–7.1



Platinum (Pt) sample data IQR: 0.00044–0.001 mg kg^{-1}

AURUM GLOBAL EXPLORATION

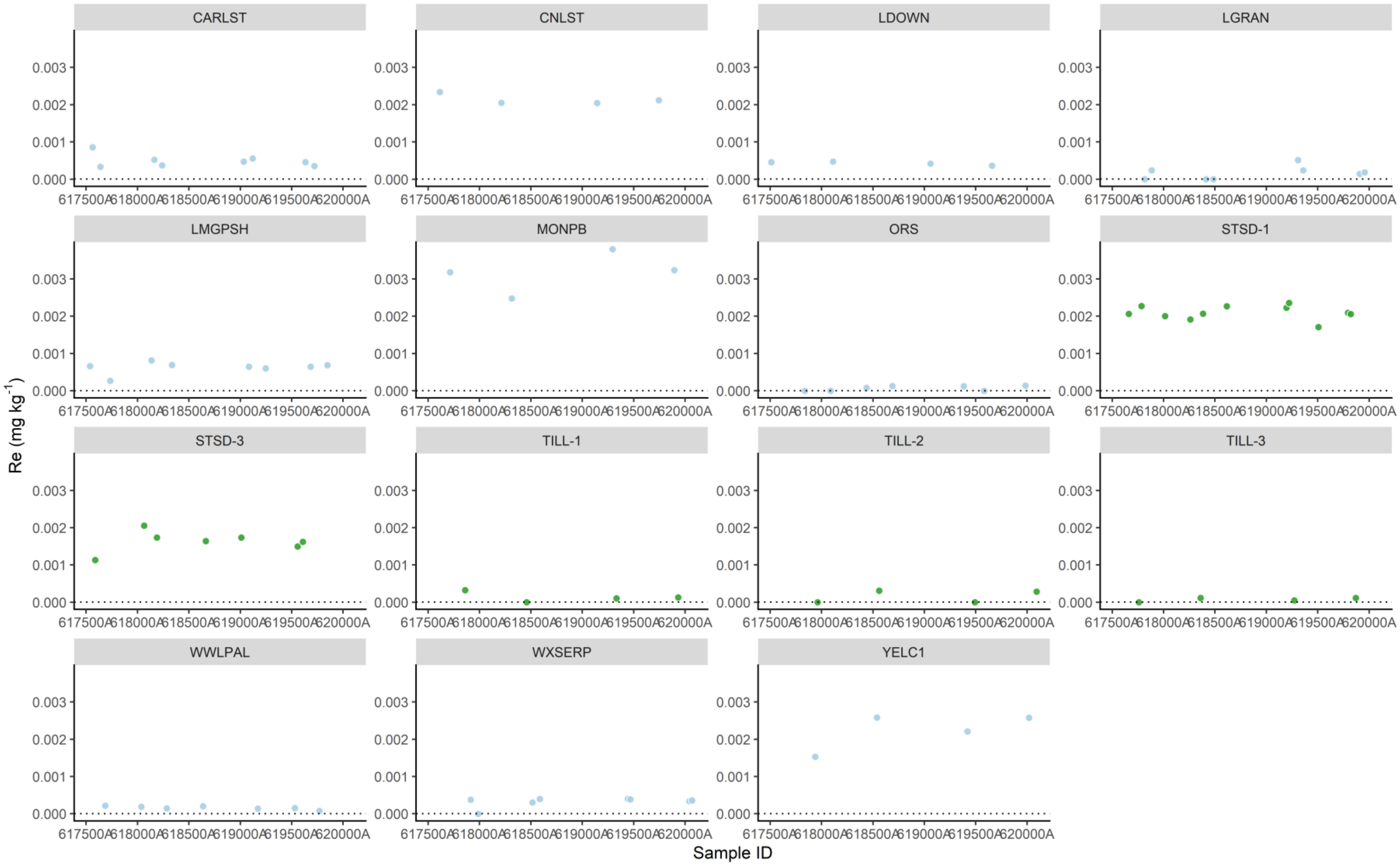
Rubidium (Rb) MS41L-BLD



Rubidium (Rb) sample data IQR: 8.01–10.3 mg kg^{-1}

AURUM GLOBAL EXPLORATION

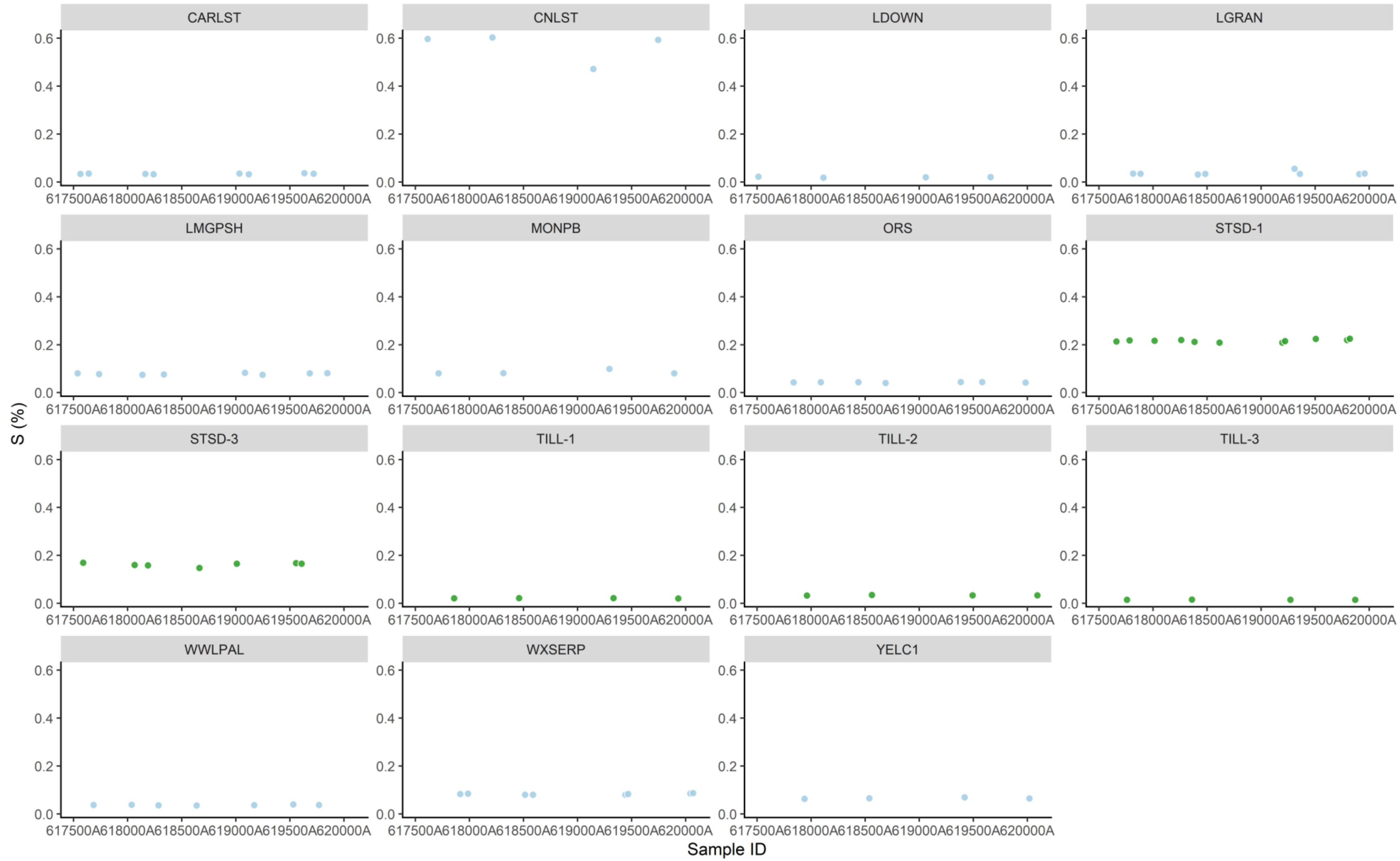
Rhenium (Re) MS41L-BLD



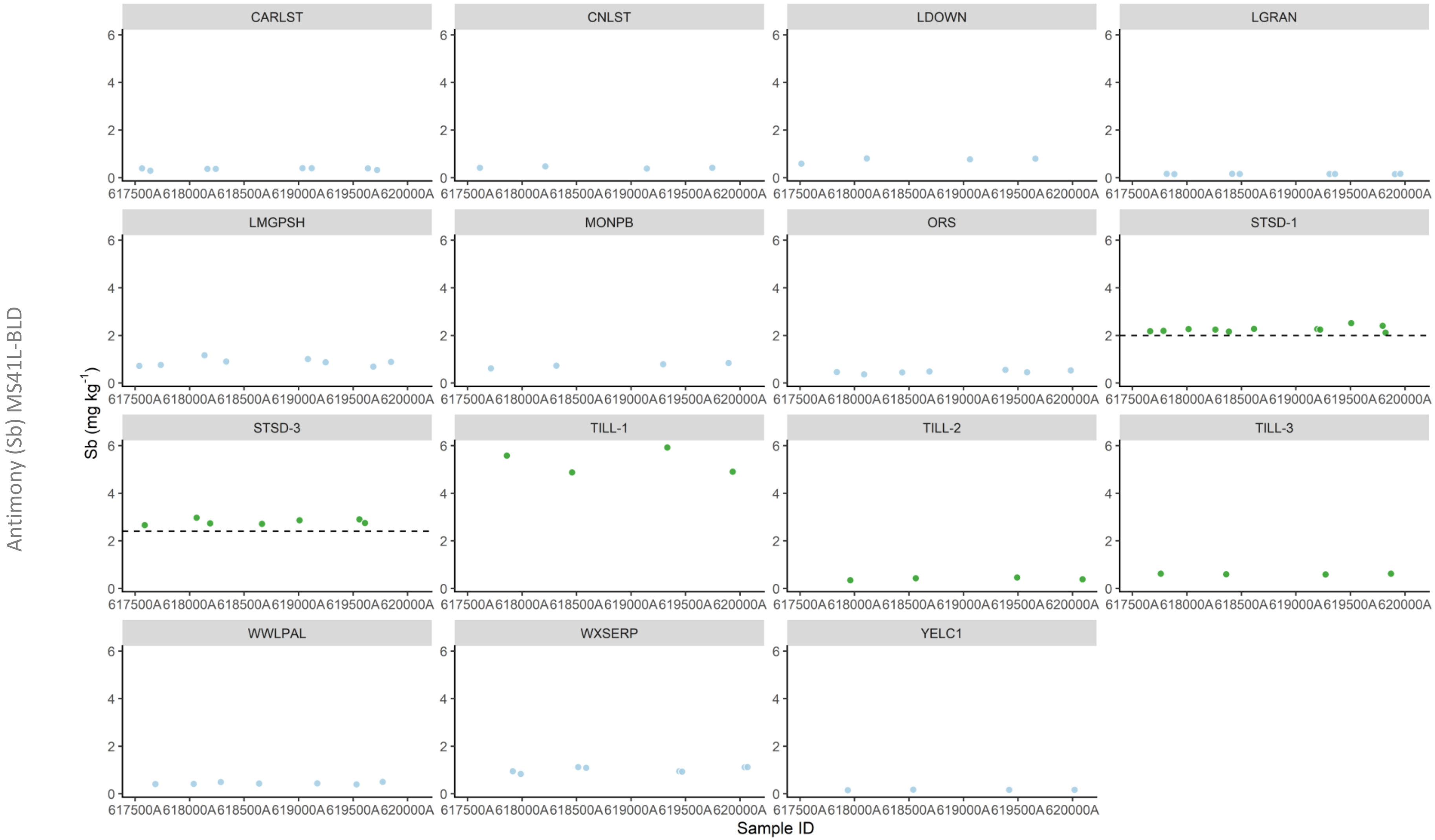
Rhenium (Re) sample data IQR: 0.000722–0.00158 mg kg^{-1}

AURUM GLOBAL EXPLORATION

Sulphur (S) MS41L-BLD

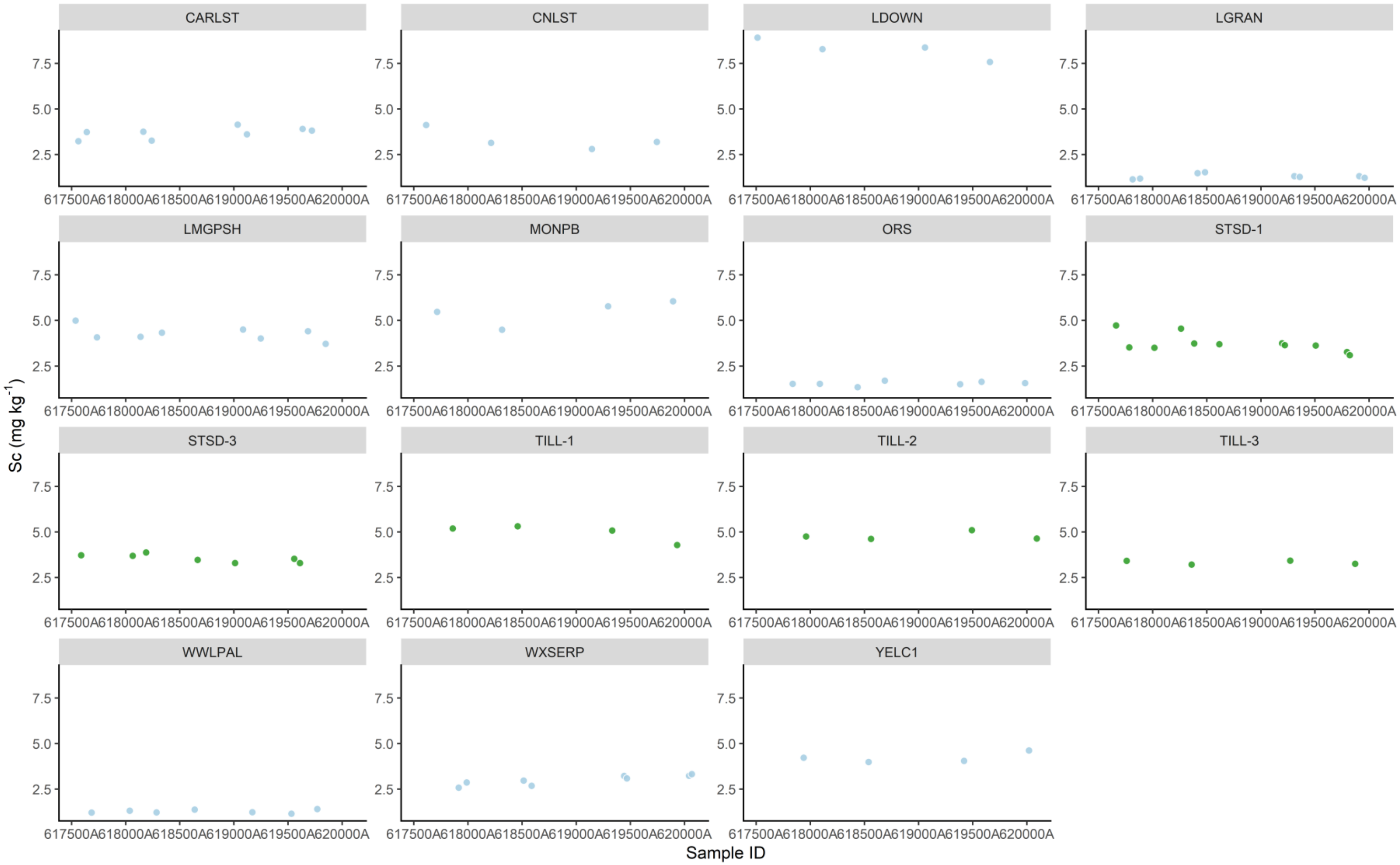


Sulphur (S) sample data IQR: 0.0658–0.093 %



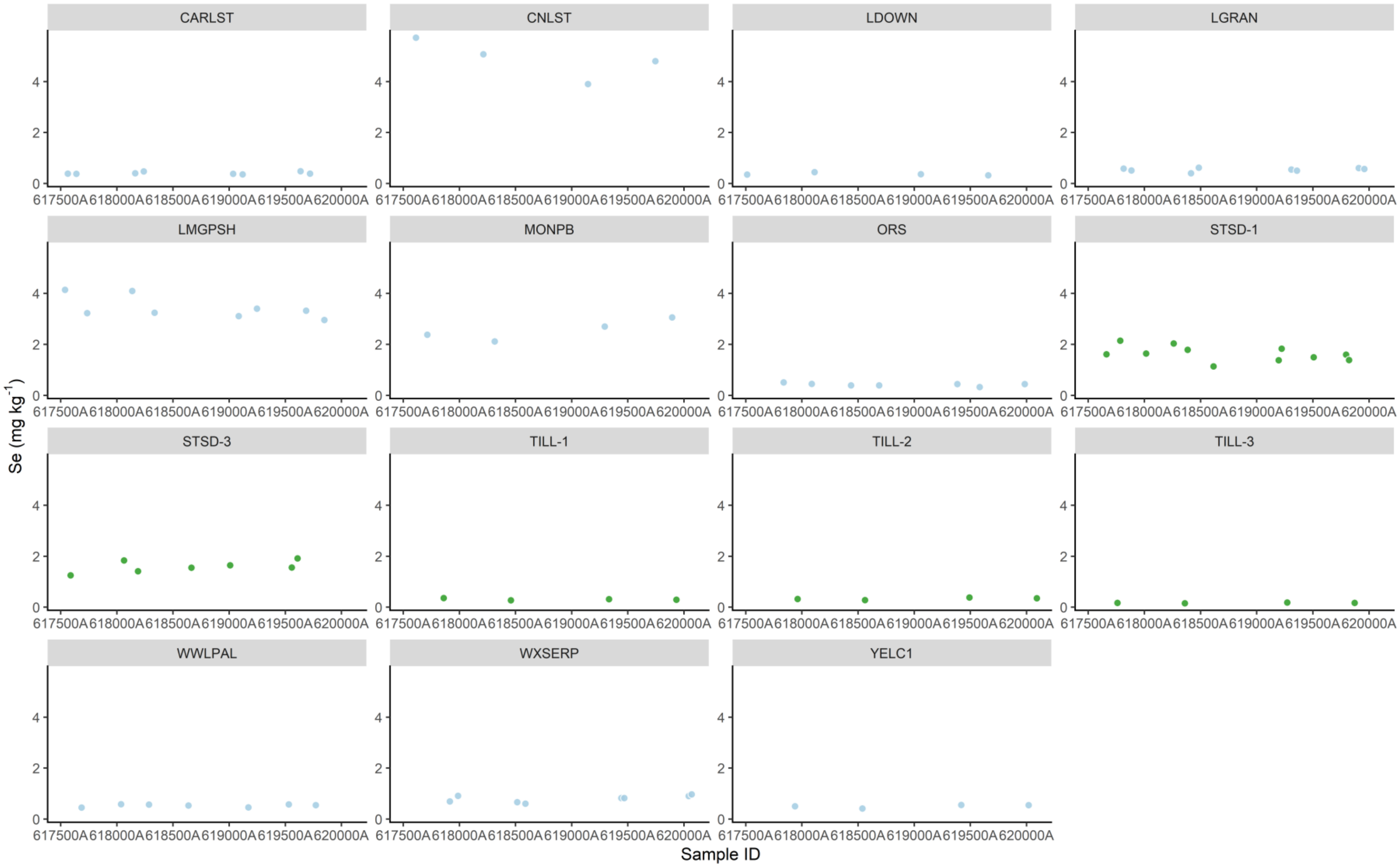
Antimony (Sb) sample data IQR: 1.18–2.16 mg kg^{-1}

Scandium (Sc) MS41L-BLD



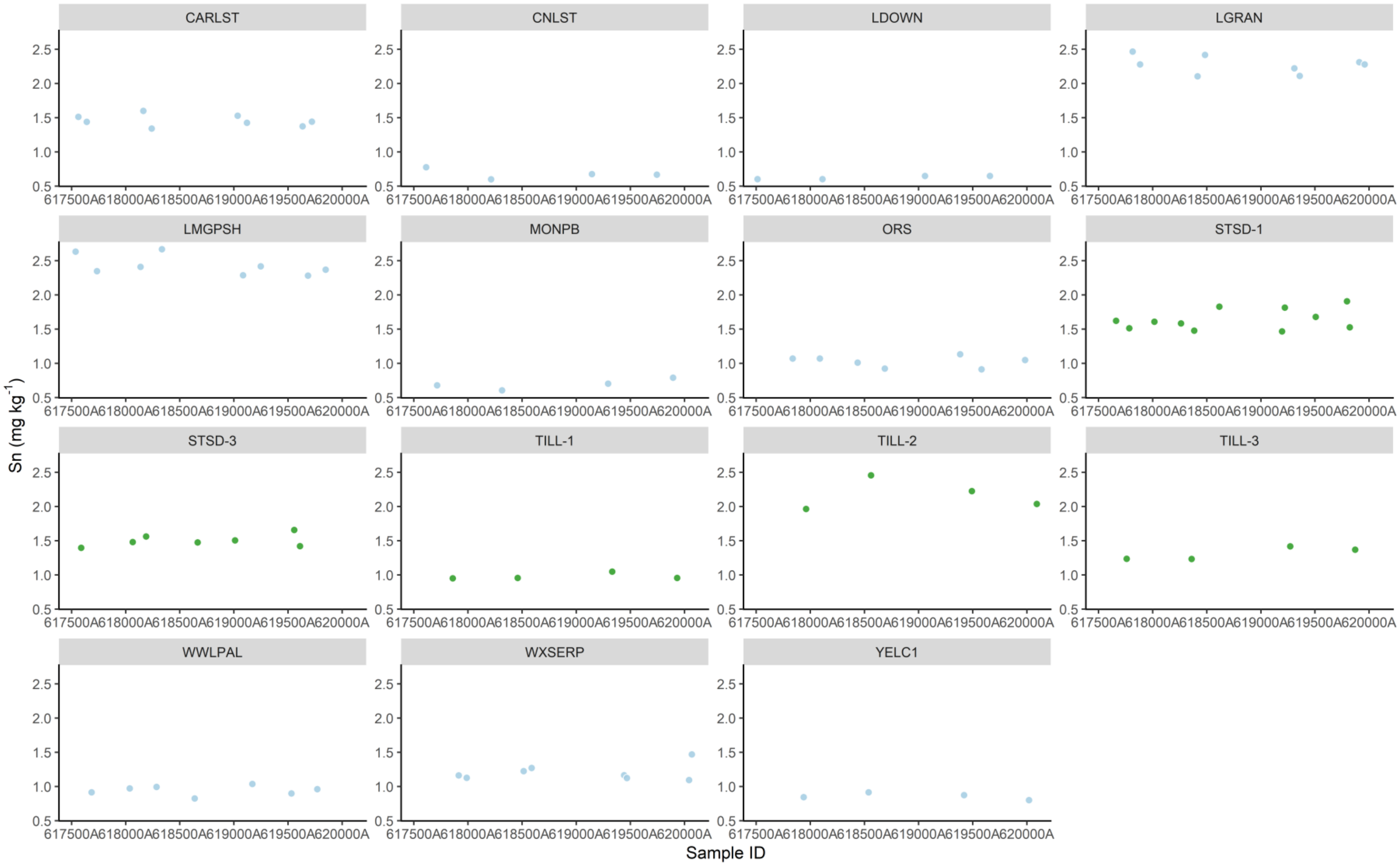
Scandium (Sc) sample data IQR: 3.05–3.75 mg kg^{-1}

Selenium (Se) MS41L-BLD

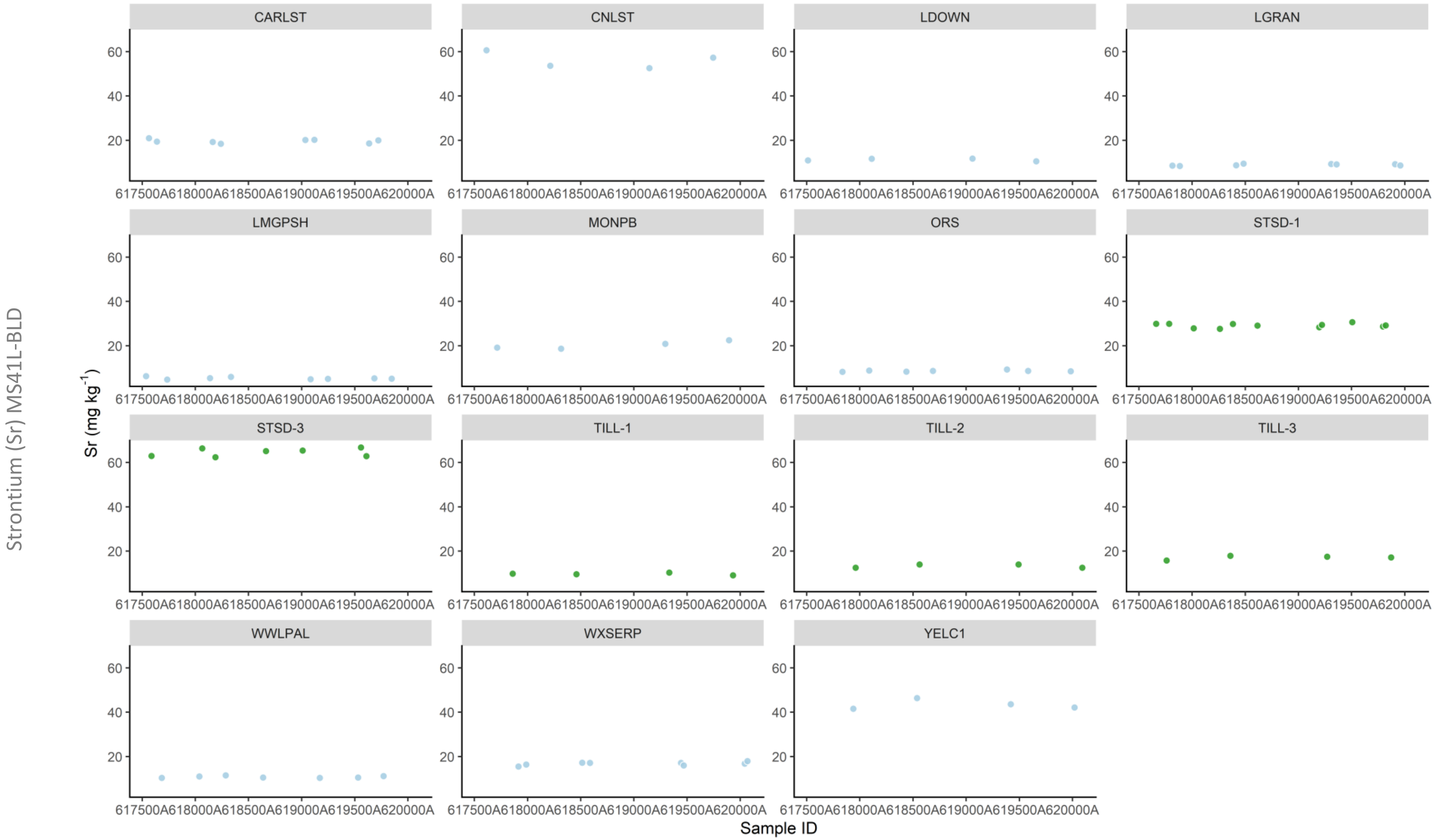


Selenium (Se) sample data IQR: 0.816–1.14 mg kg^{-1}

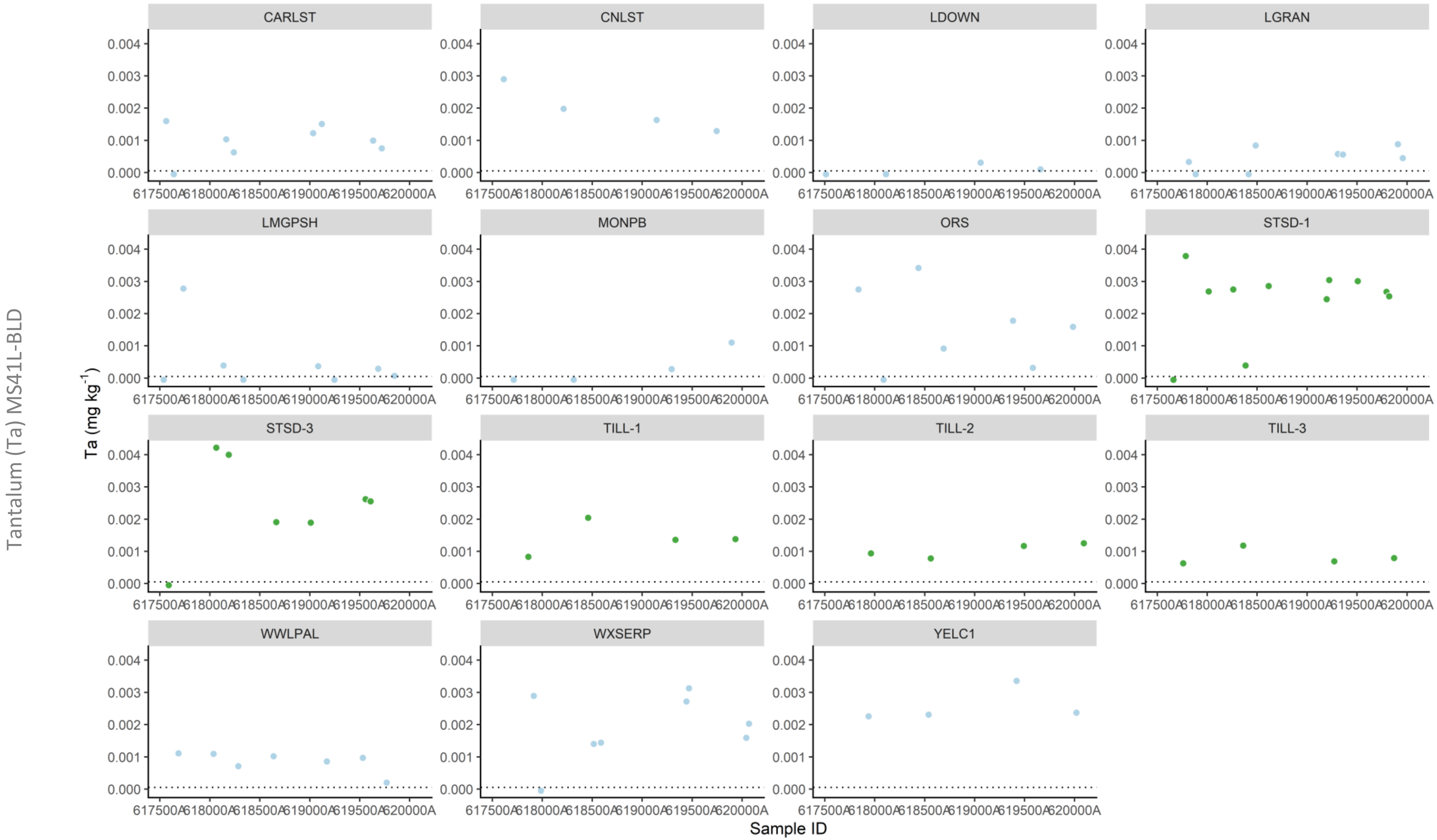
Tin (Sn) MS41L-BLD



Tin (Sn) sample data IQR: 2.55–8.78 mg kg^{-1}



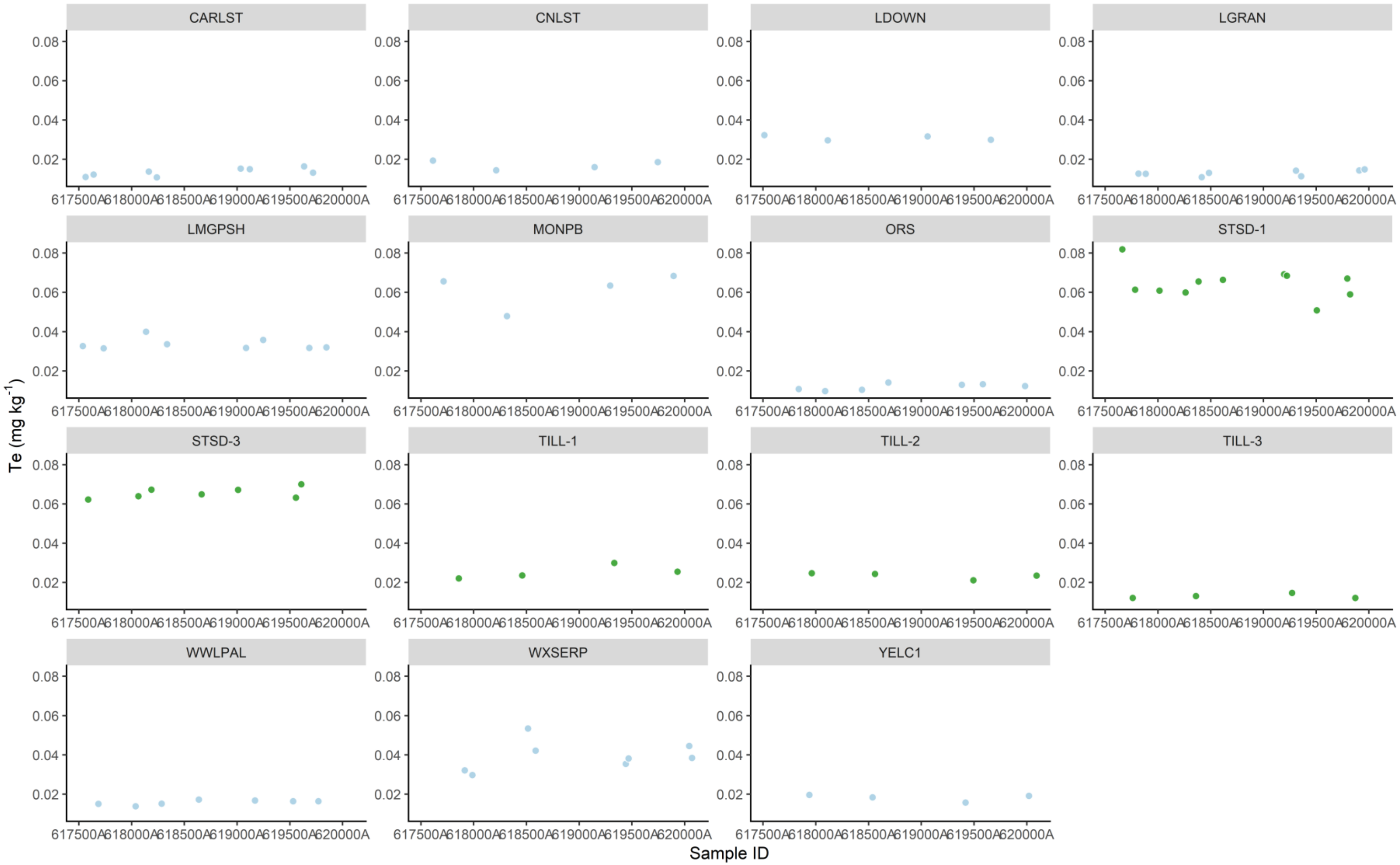
Strontium (Sr) sample data IQR: 45.1–124 mg kg^{-1}



Tantalum (Ta) sample data IQR: 0.00054-0.00101 mg kg^{-1}

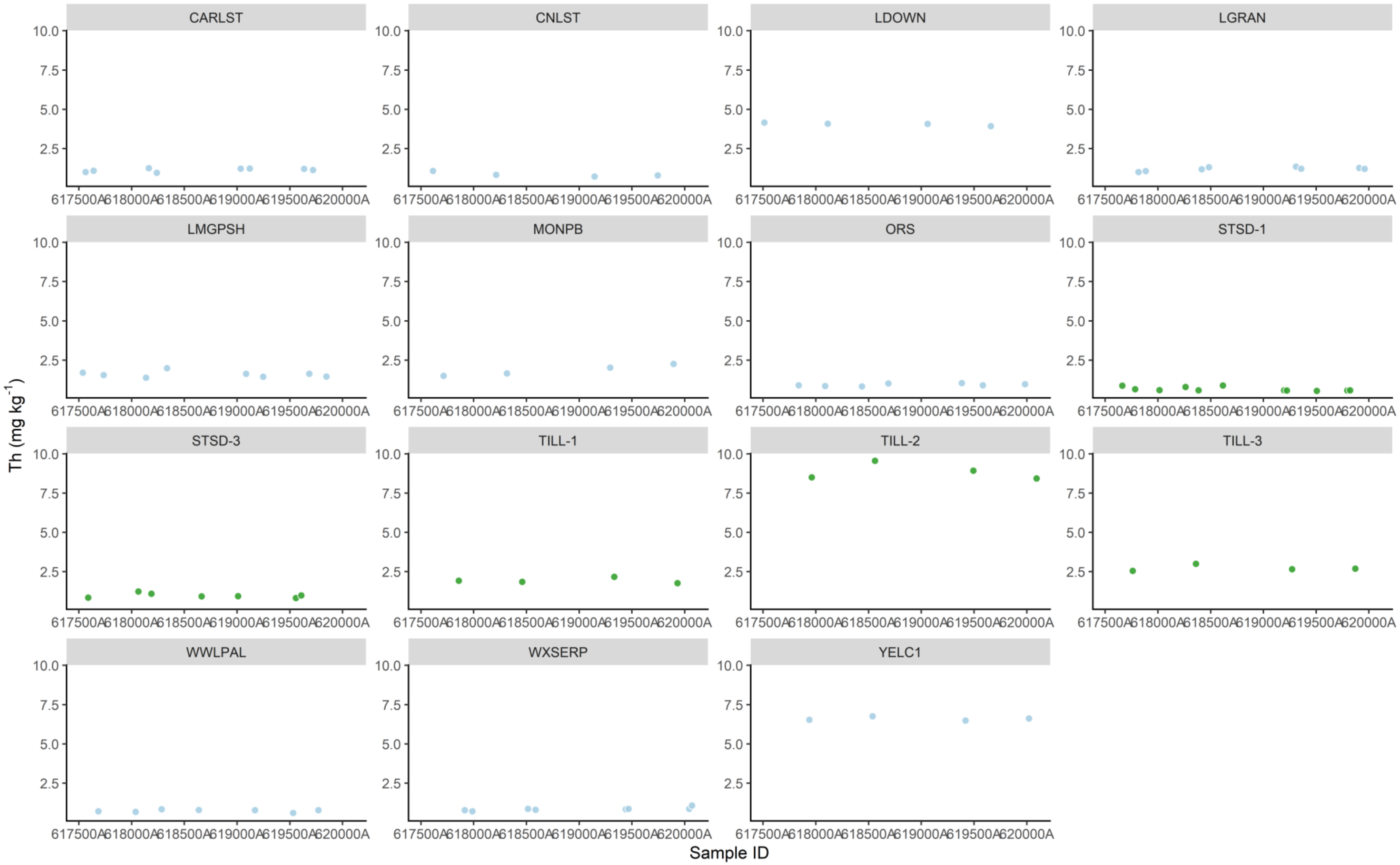
AURUM GLOBAL EXPLORATION

Tellurium (Te) MS41L-BLD

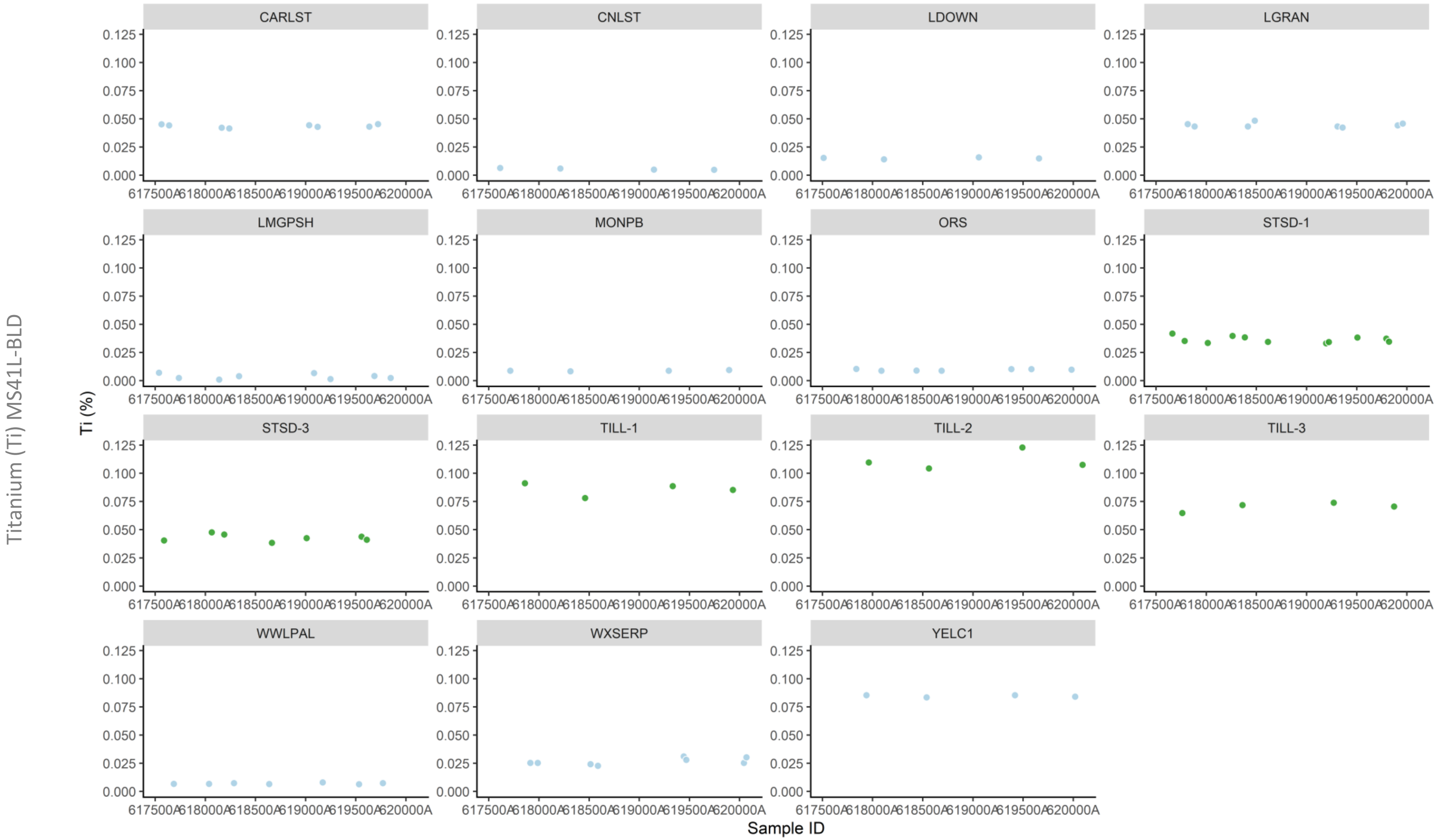


Tellurium (Te) sample data IQR: 0.0257-0.0355 mg kg^{-1}

Thorium (Th) MS41L-BLD

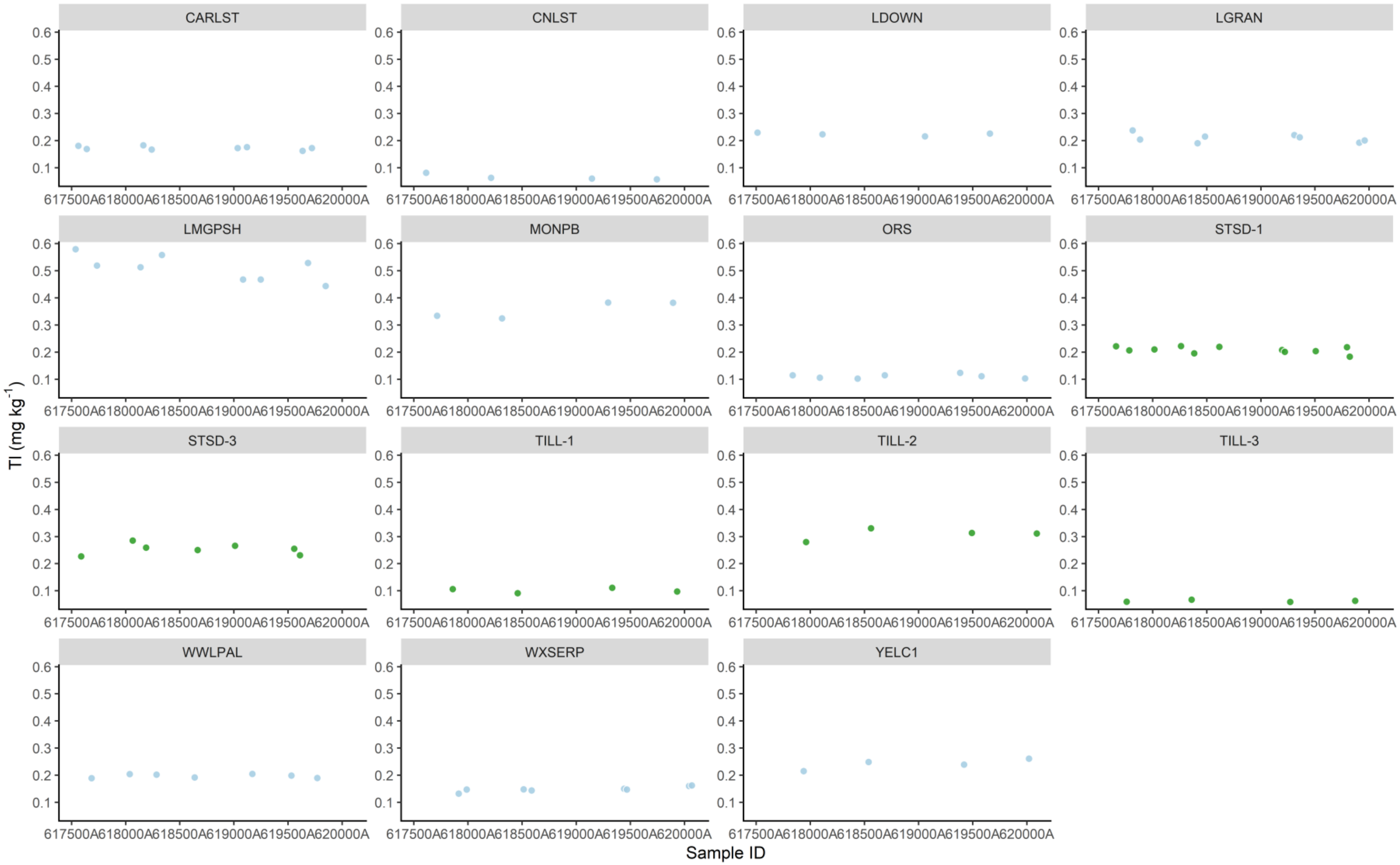


Thorium (Th) sample data IQR: 1.12–1.40 mg kg^{-1}

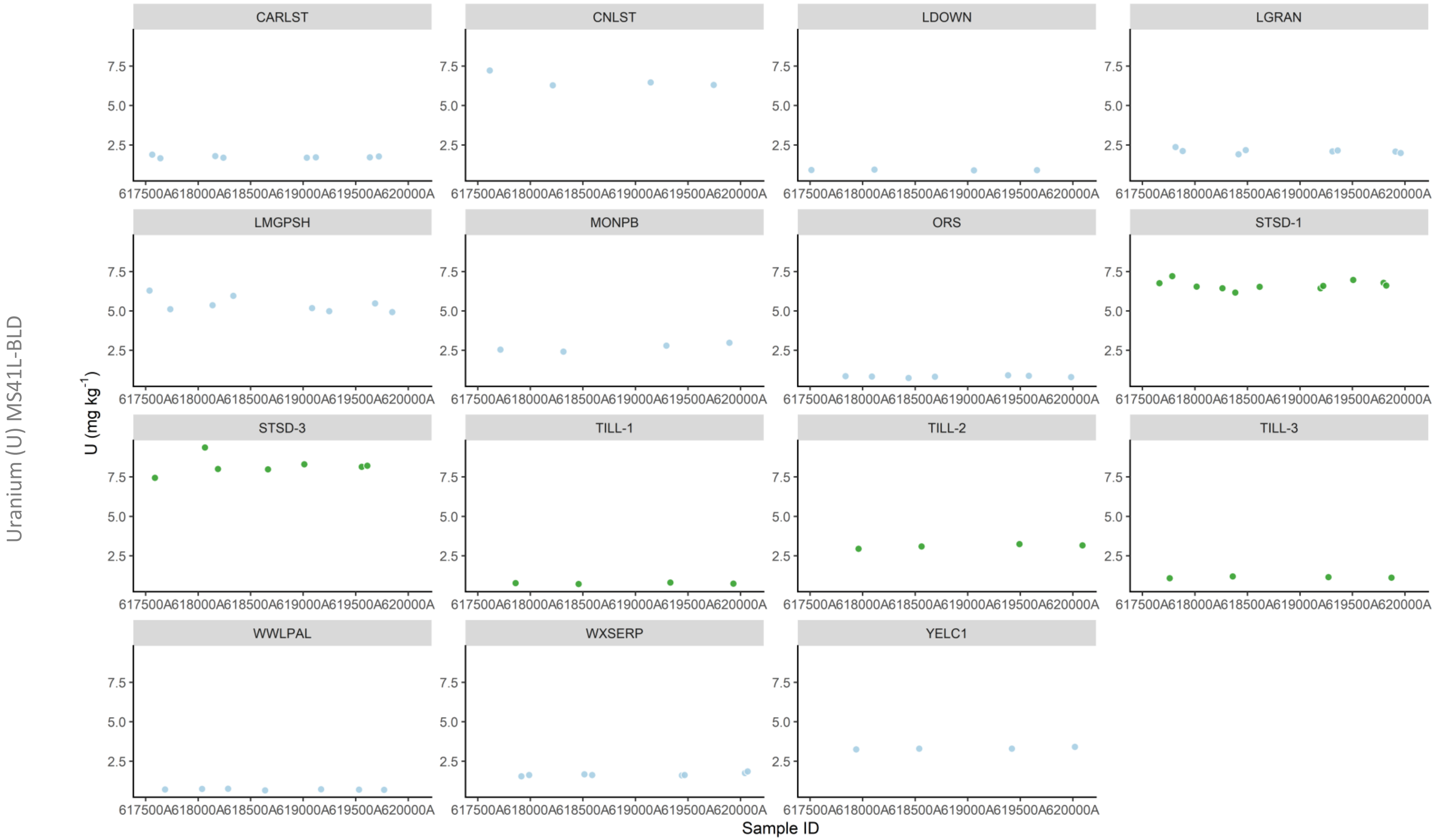


Titanium (Ti) sample data IQR: 0.0042-0.00709 %

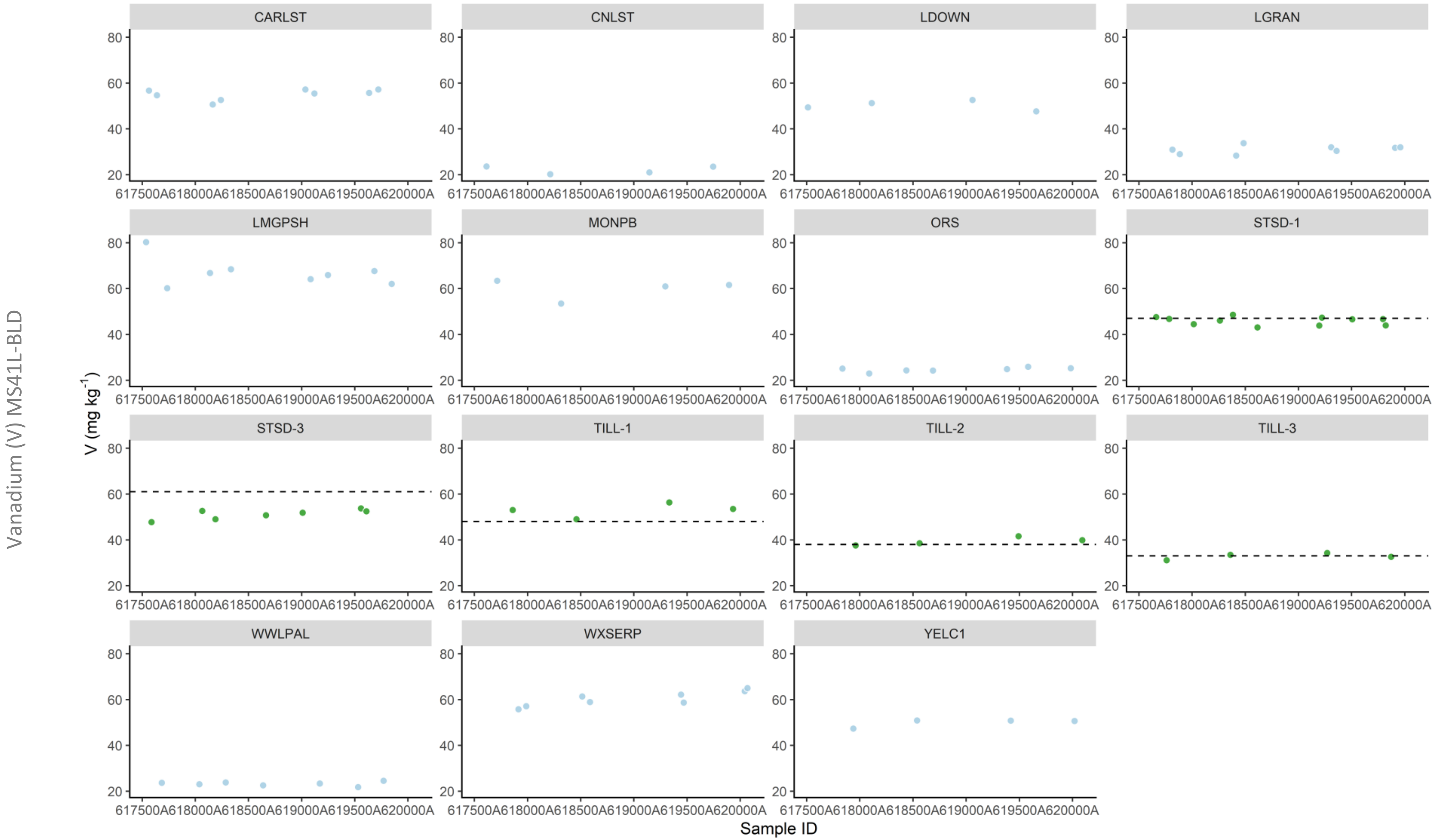
Thallium (Tl) MS41L-BLD



Thallium (Tl) sample data IQR: 0.193–0.239 mg kg^{-1}

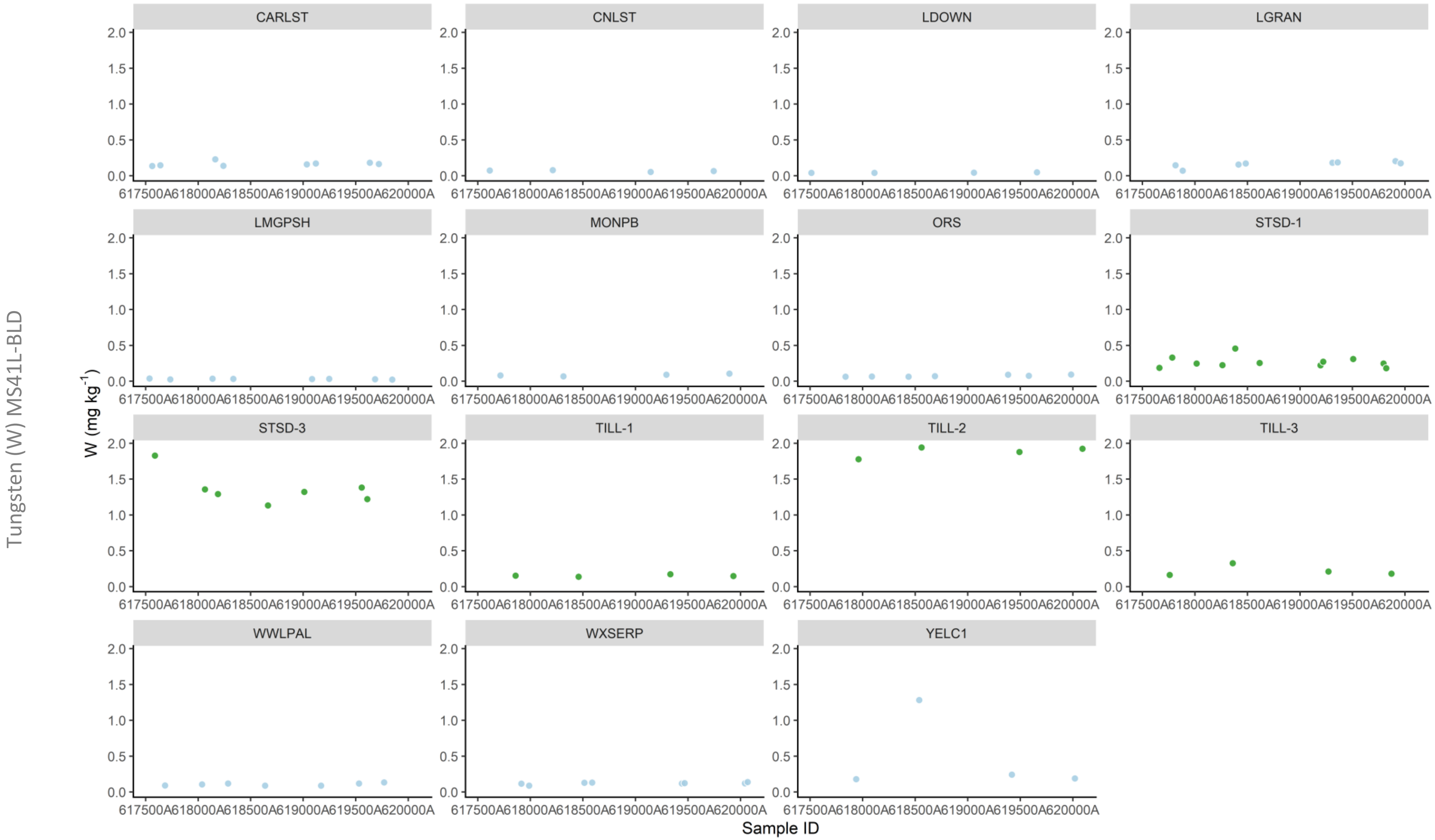


Uranium (U) sample data IQR: 0.781–0.997 mg kg^{-1}

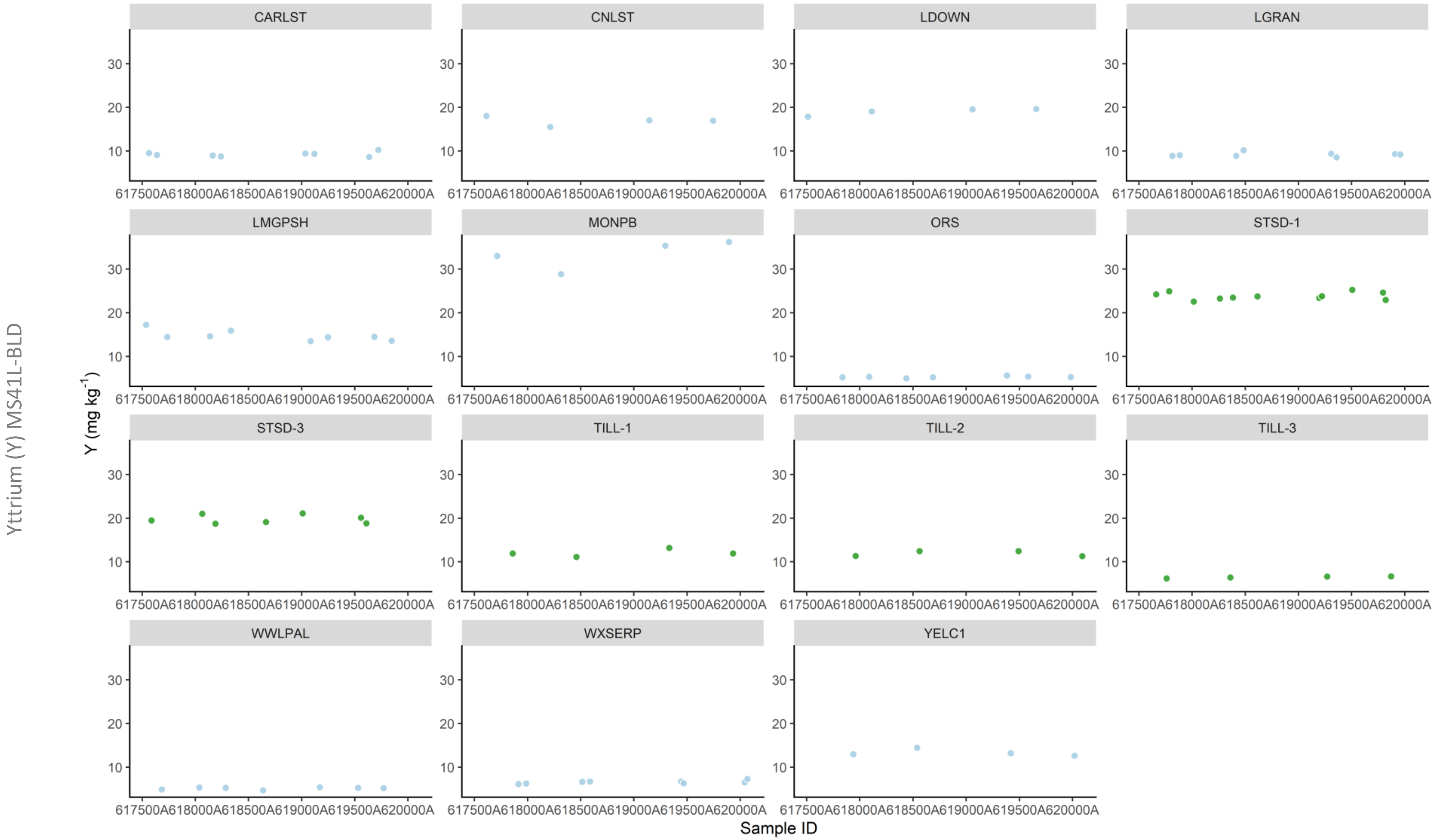


Vanadium (V) sample data IQR: 33.5–41.4 mg kg^{-1}

AURUM GLOBAL EXPLORATION

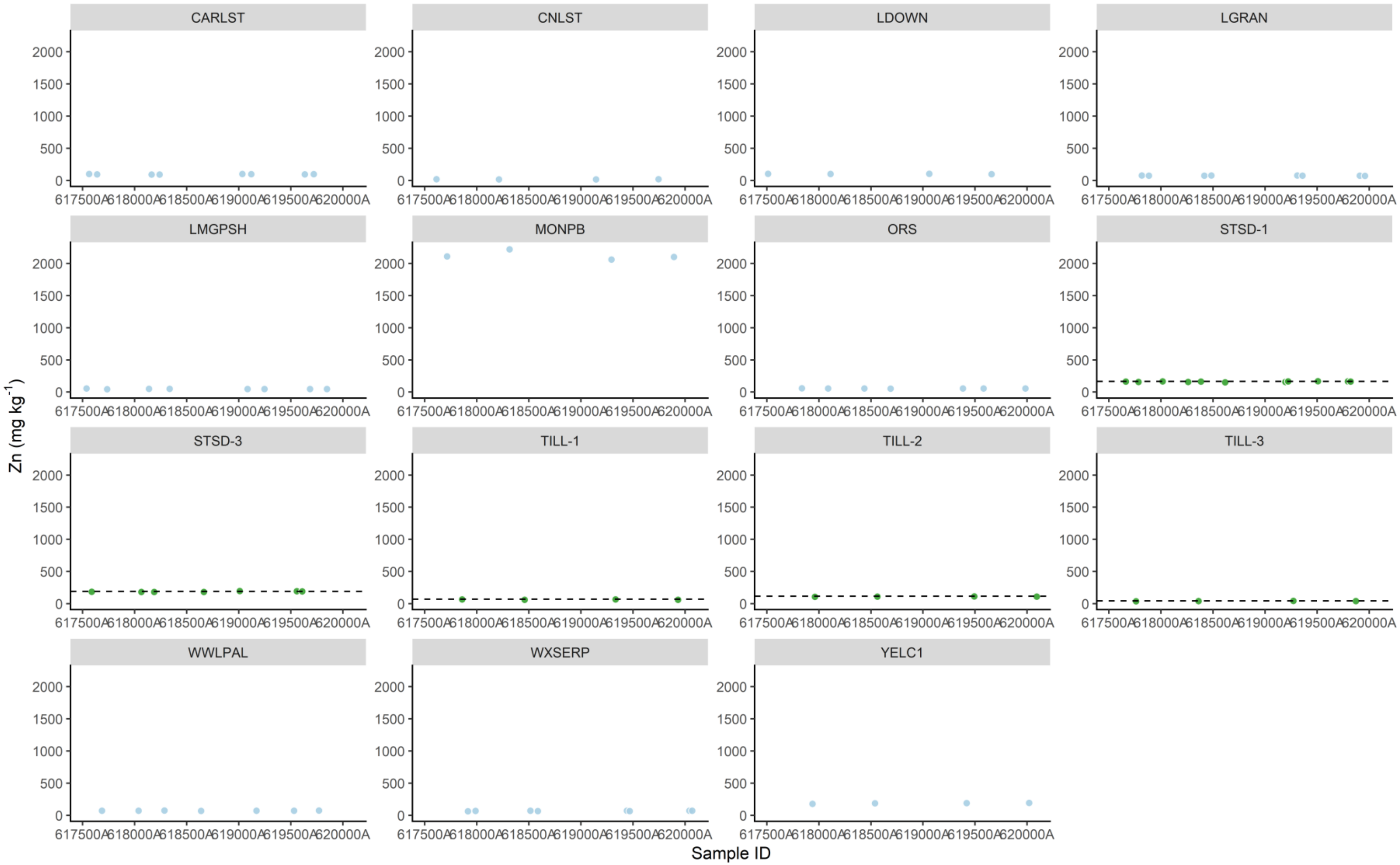


Tungsten (W) sample data IQR: 0.113-0.218 mg kg^{-1}



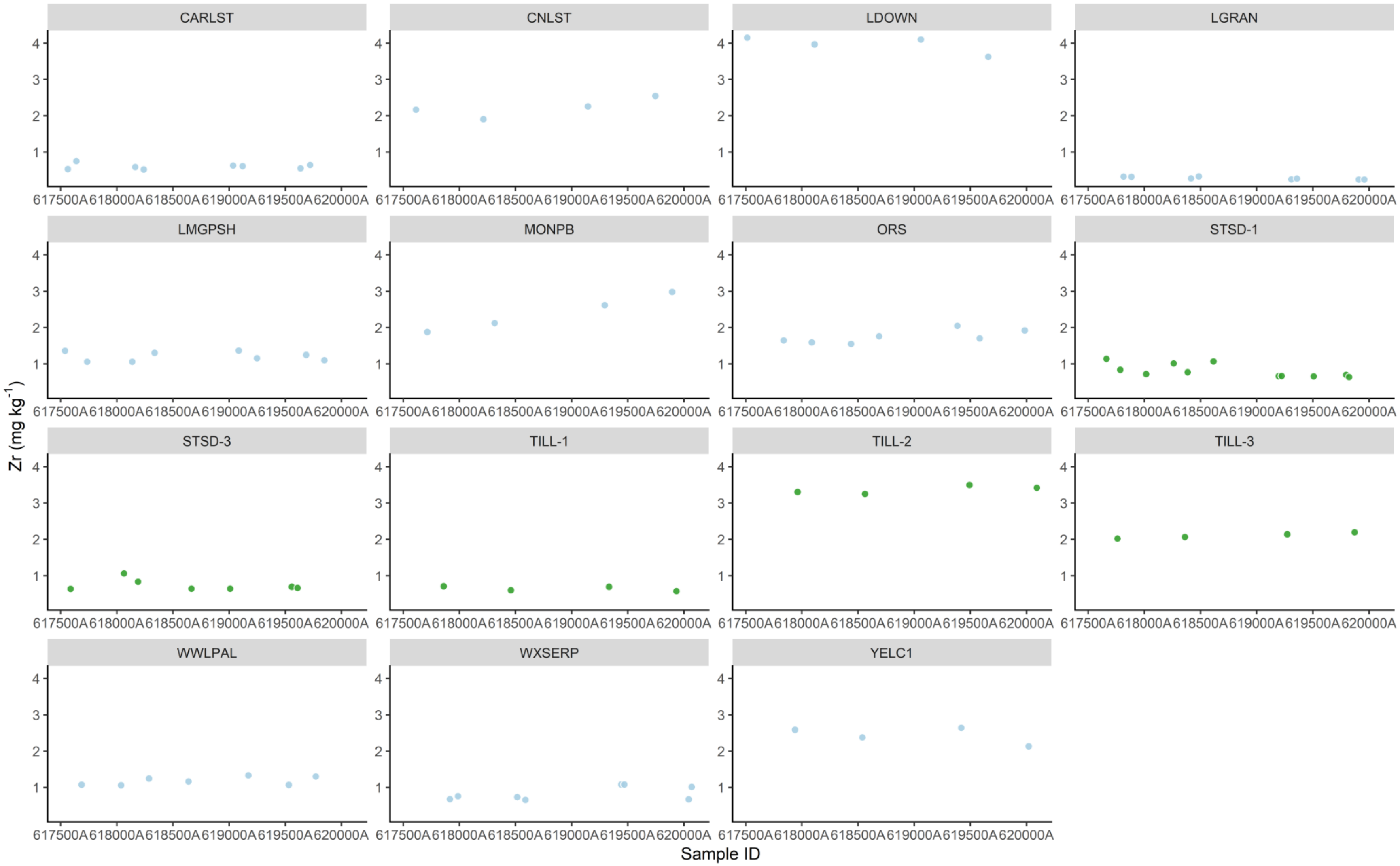
Yttrium (Y) sample data IQR: 14.2–17.3 mg kg^{-1}

Zinc (Zn) MS41L-BLD



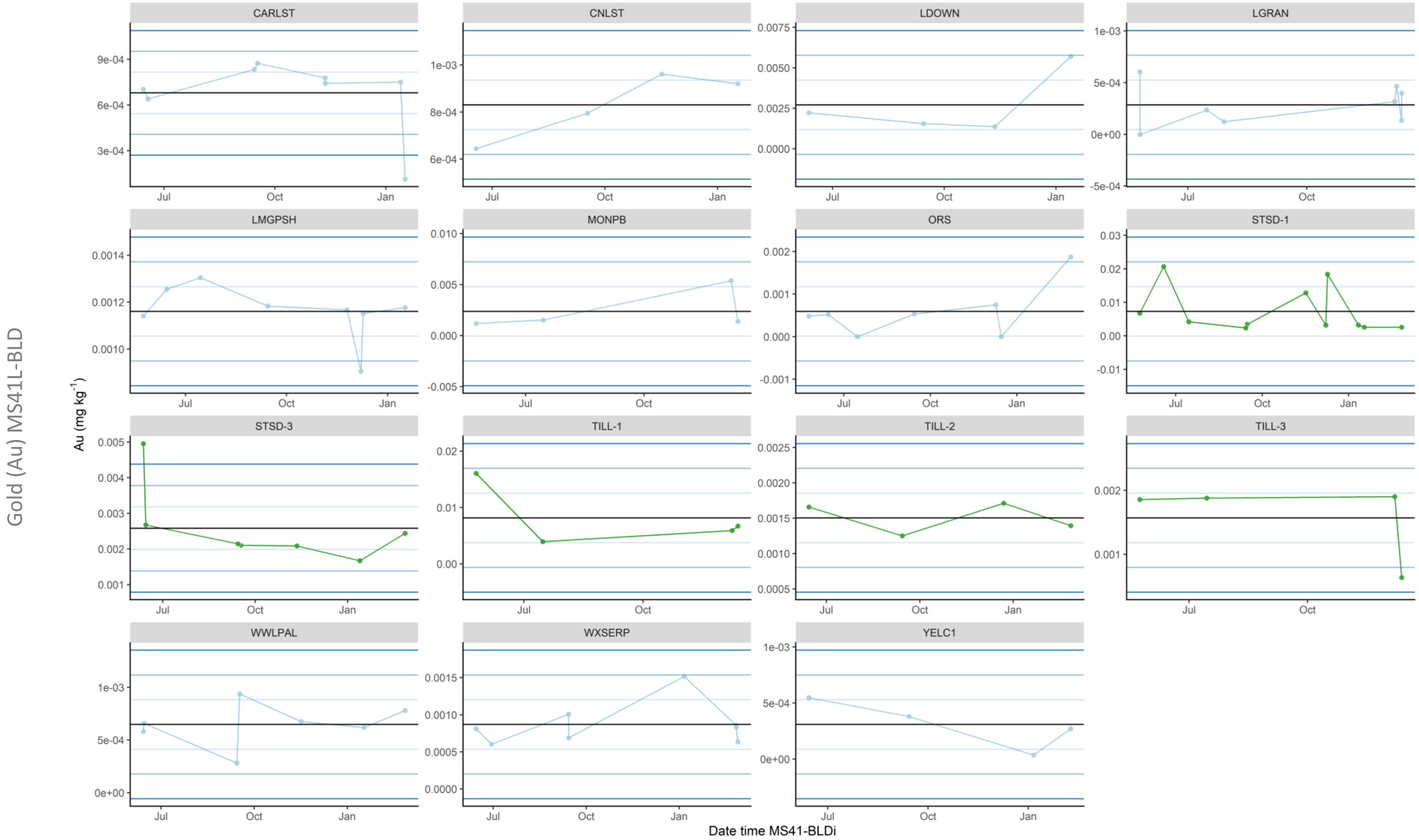
Zinc (Zn) sample data IQR: 125–203 mg kg^{-1}

Zirconium (Zr) MS41L-BLD

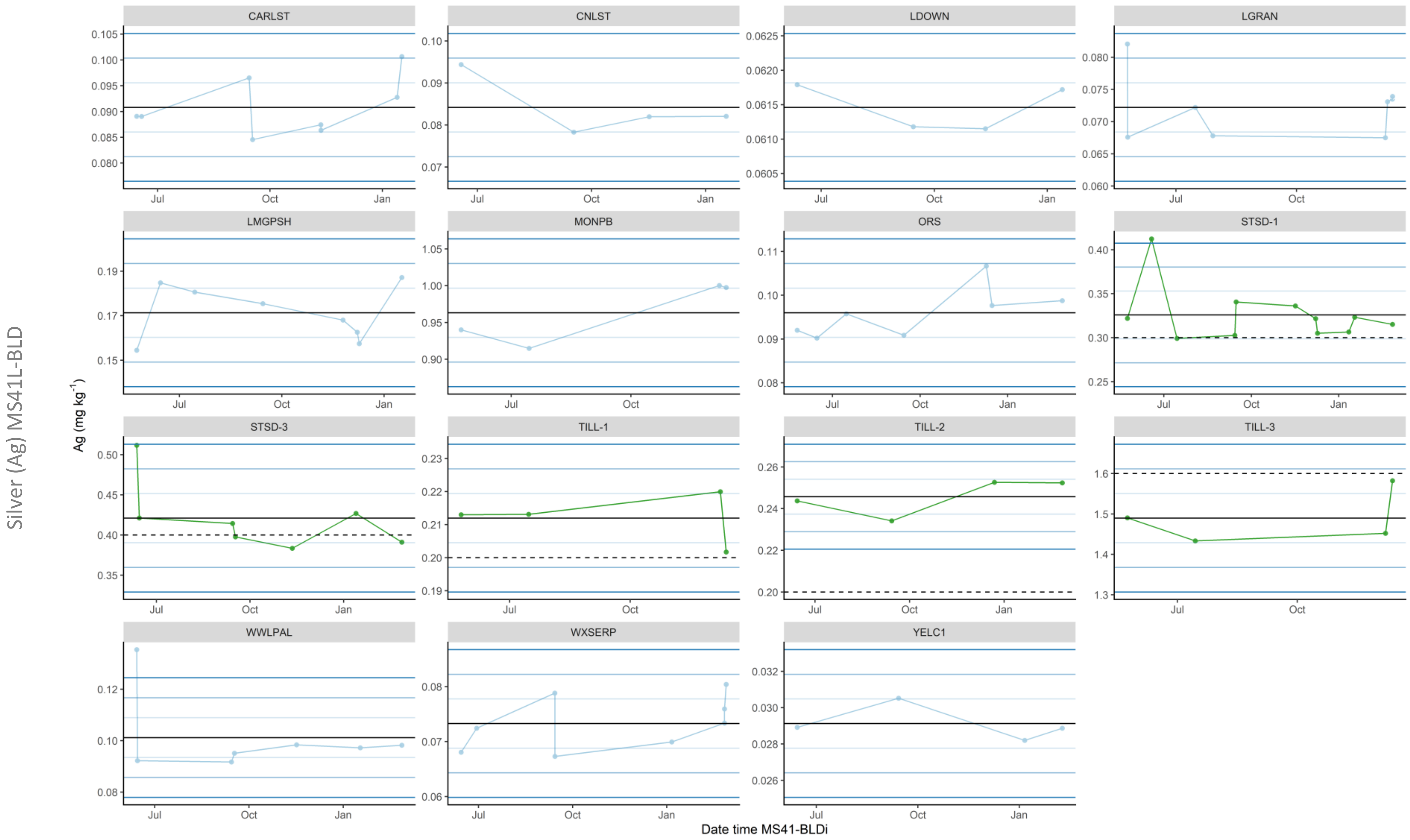


Zirconium (Zr) sample data IQR: 2.76–3.69 mg kg^{-1}

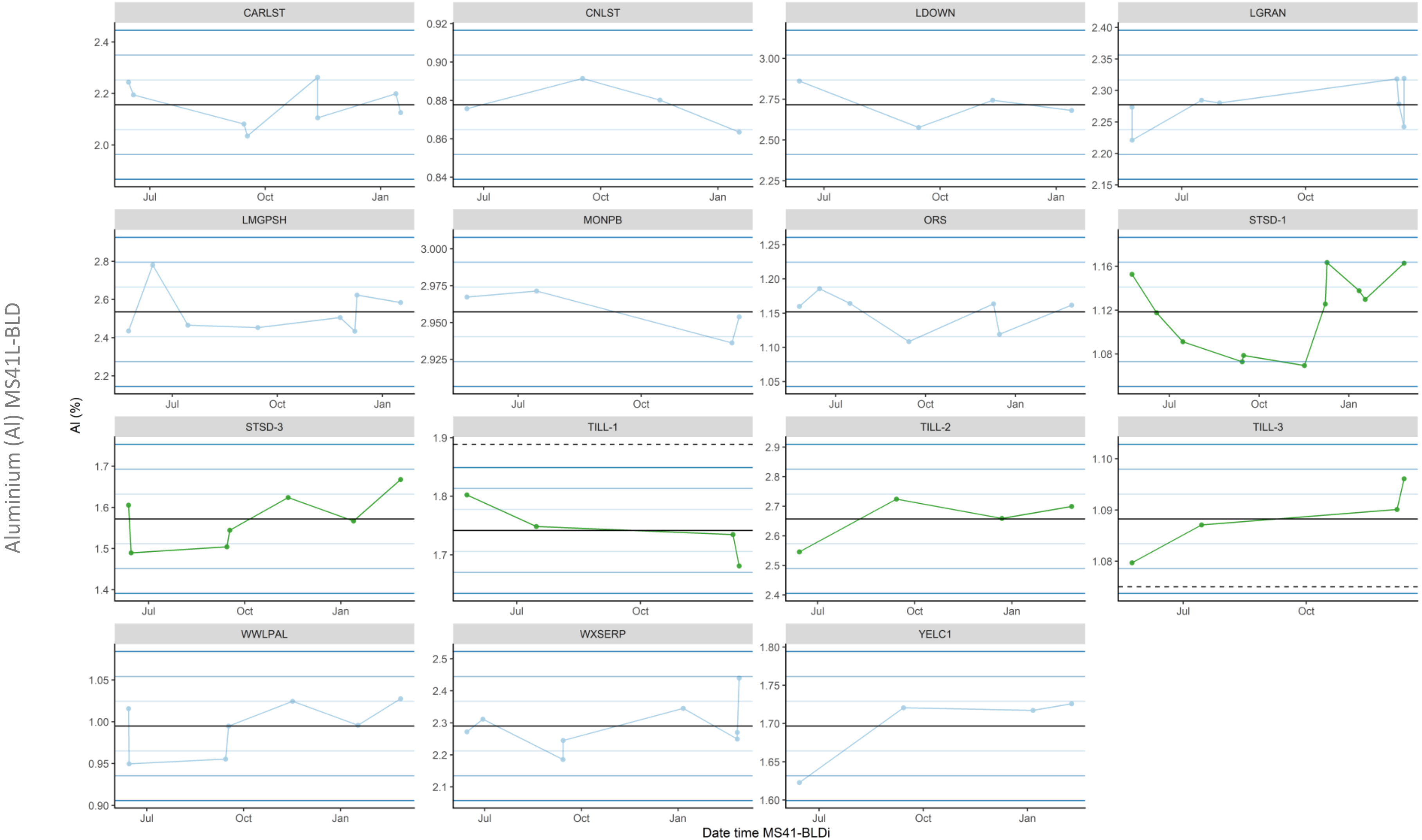
AURUM GLOBAL EXPLORATION



Gold (Au) sample data IQR: 0.00255–0.00583 mg kg^{-1}

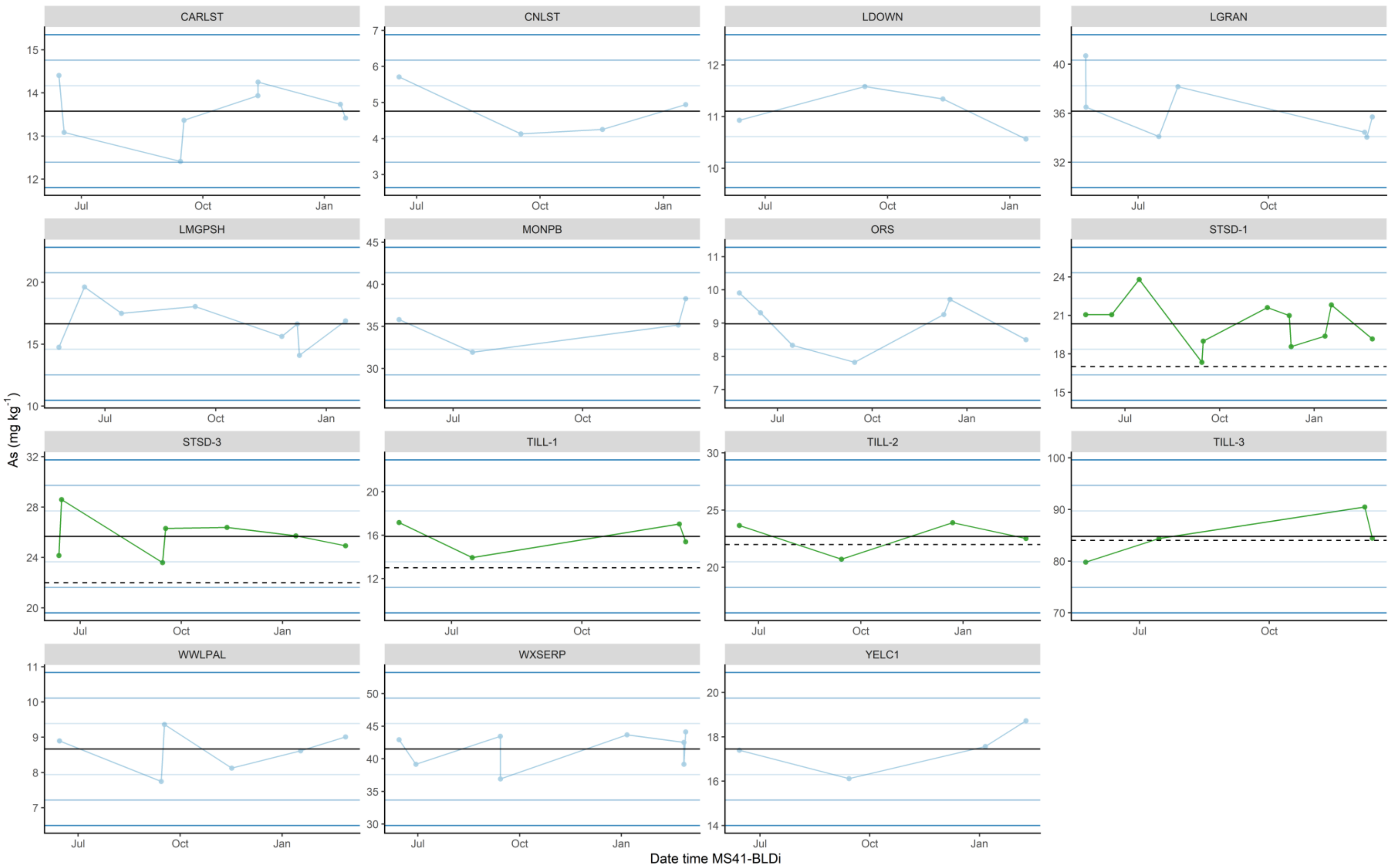


Silver (Ag) sample data IQR: 0.193–0.385 mg kg^{-1}

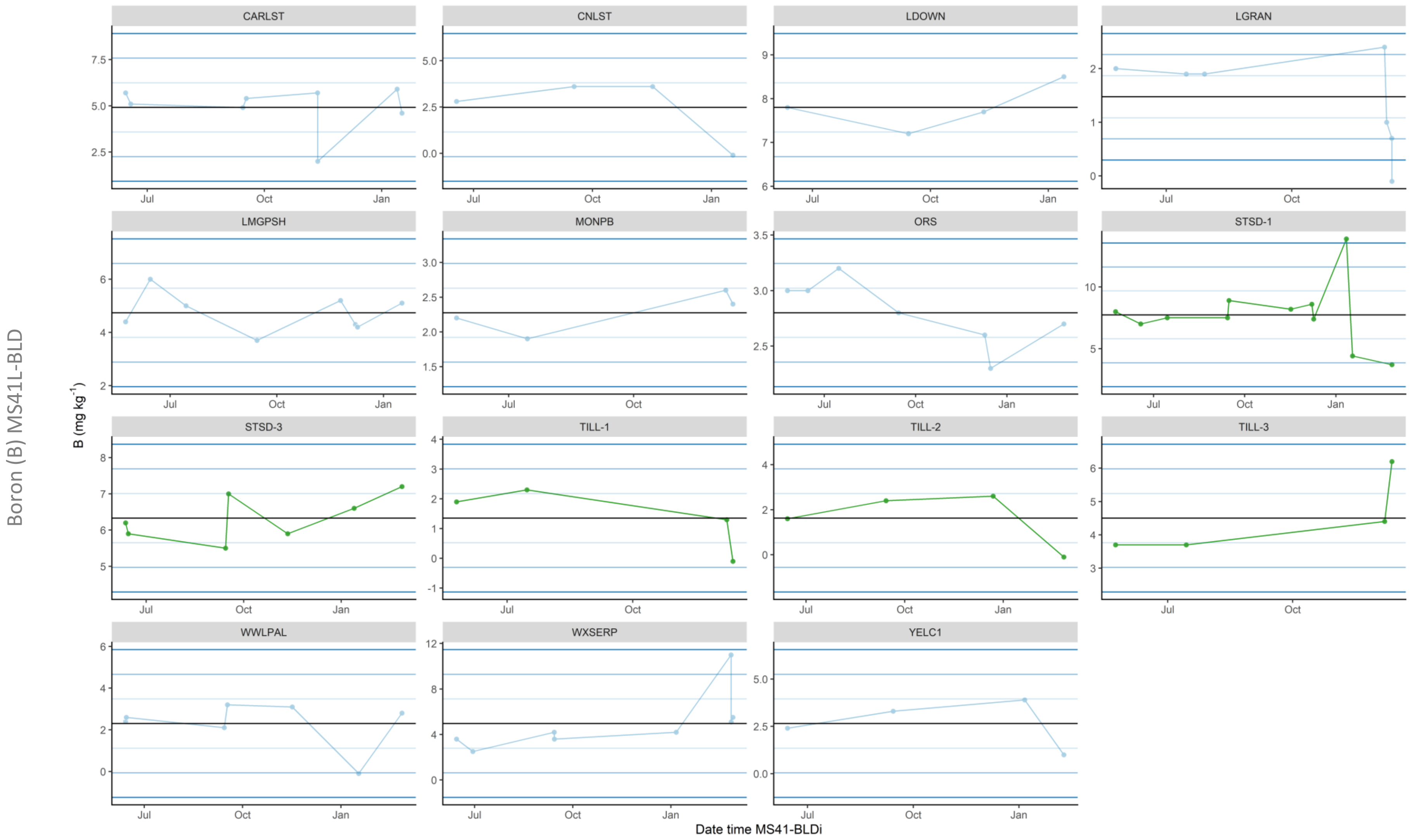


Aluminium (Al) sample data IQR: 0.949–1.12 %

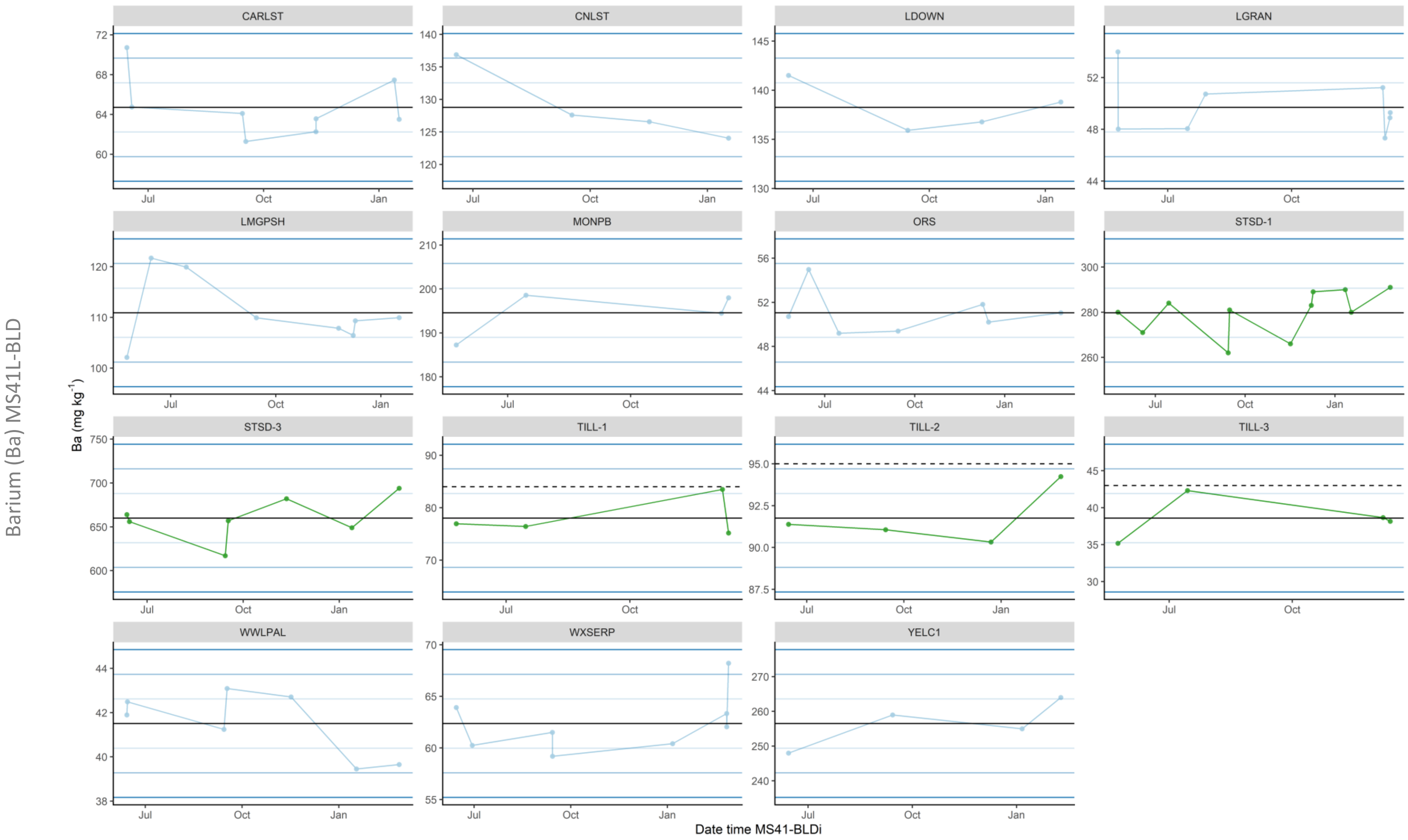
Arsenic (As) MS41L-BLD



Arsenic (As) sample data IQR: 15.7–22.0 mg kg^{-1}

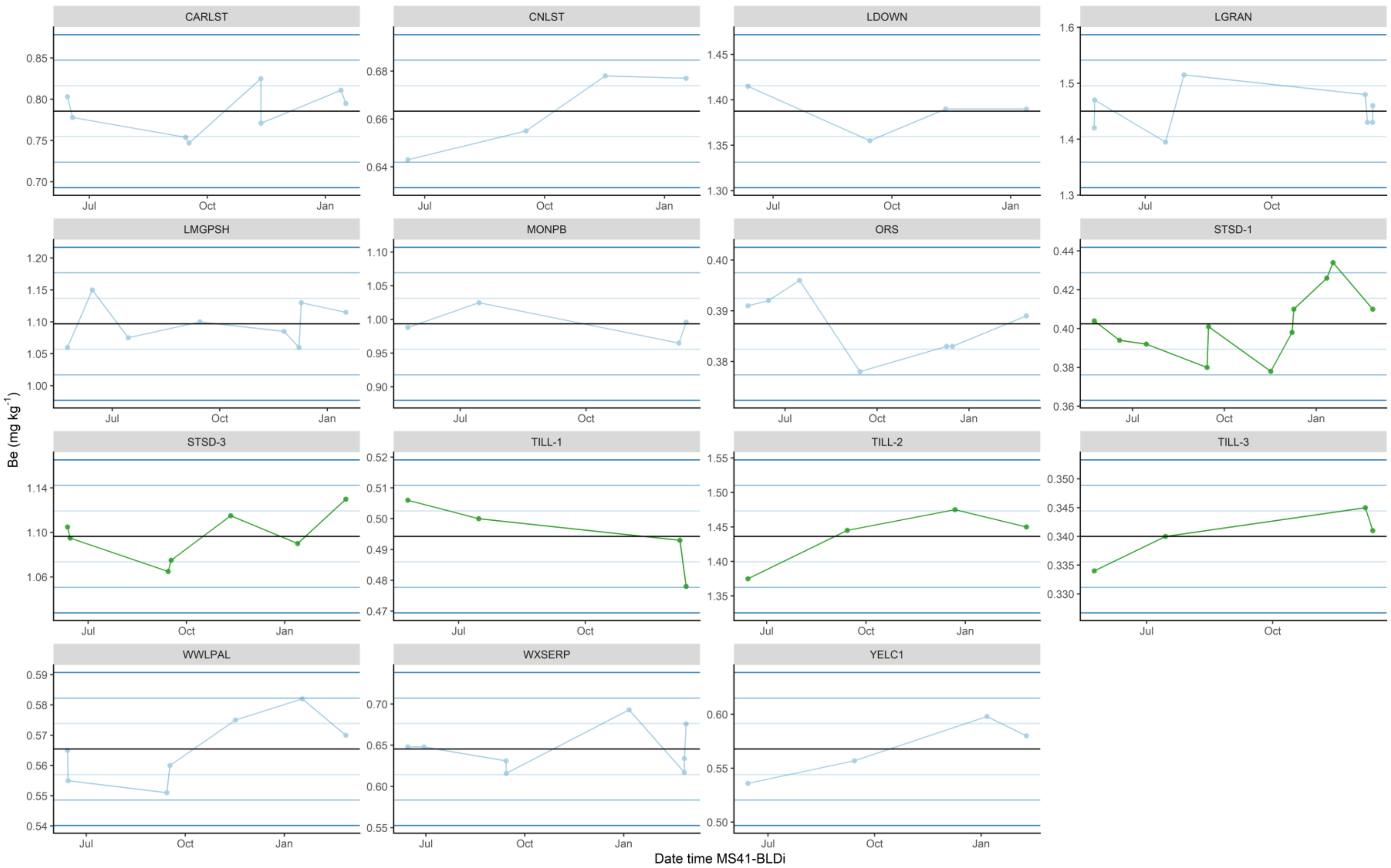


Boron (B) sample data IQR: 5.3 -8.7 mg kg^{-1}

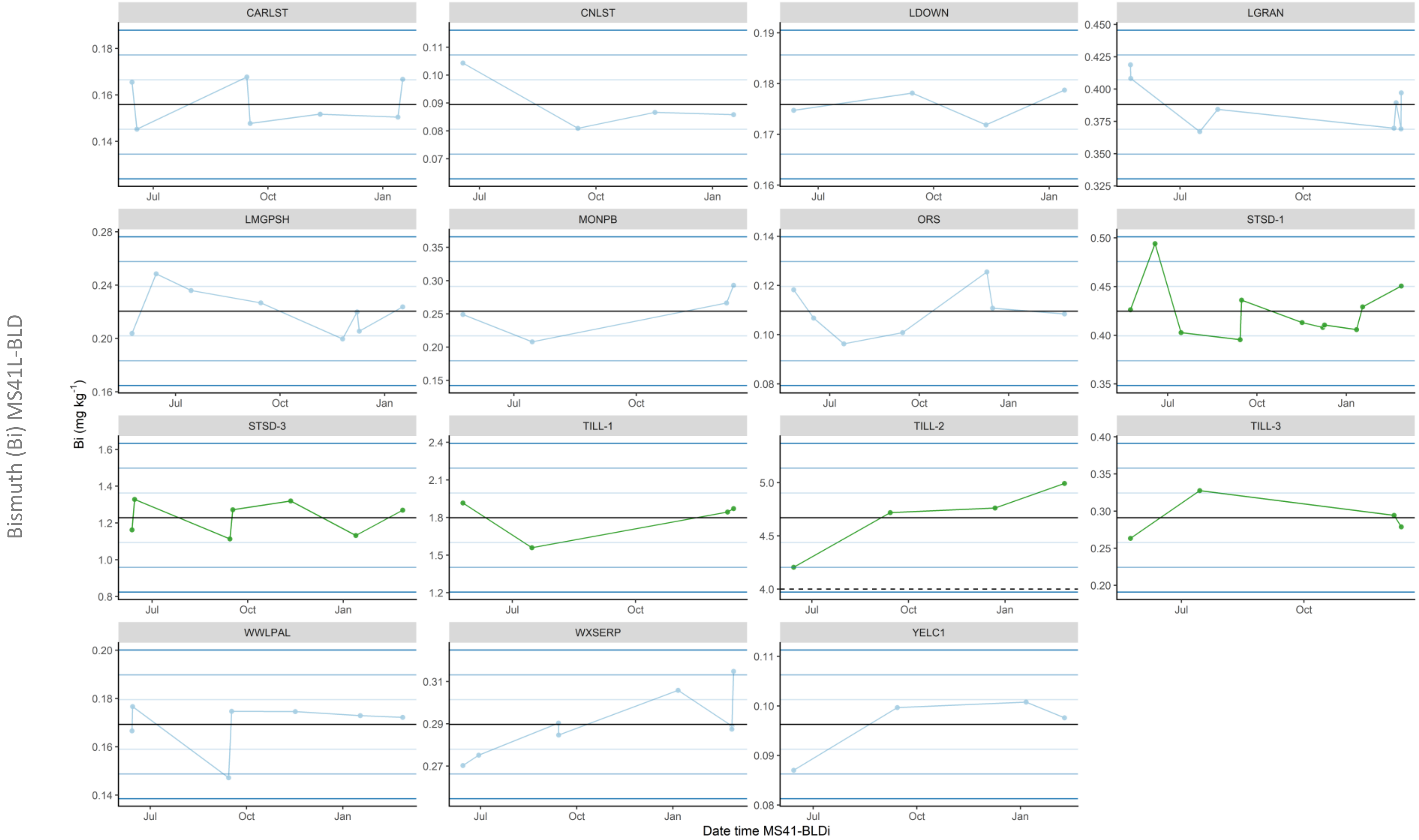


Barium (Ba) sample data IQR: 86.3–133 mg kg-1

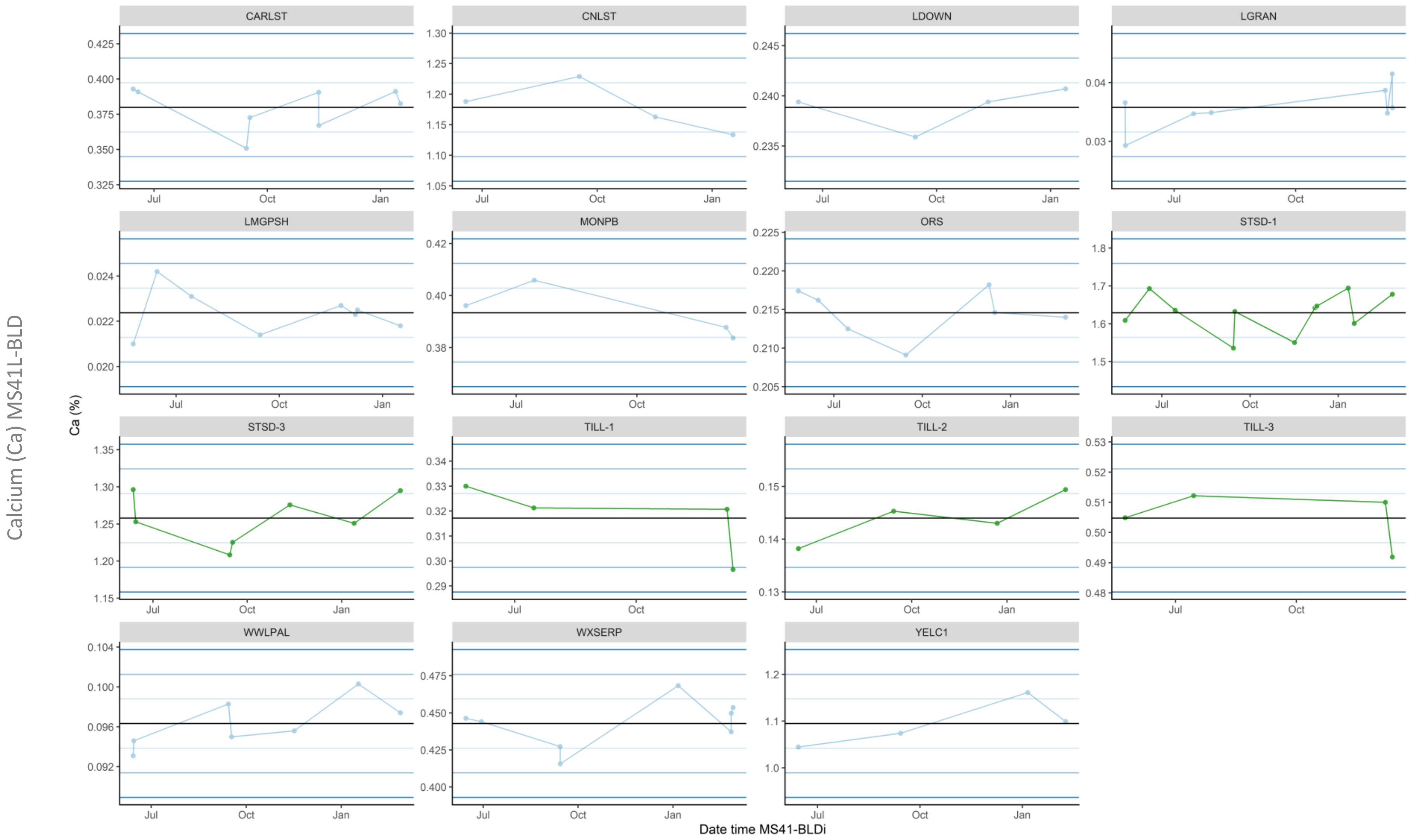
Beryllium (Be) MS41L-BLD



Beryllium (Be) sample data IQR: 1.00–1.31 mg kg^{-1}

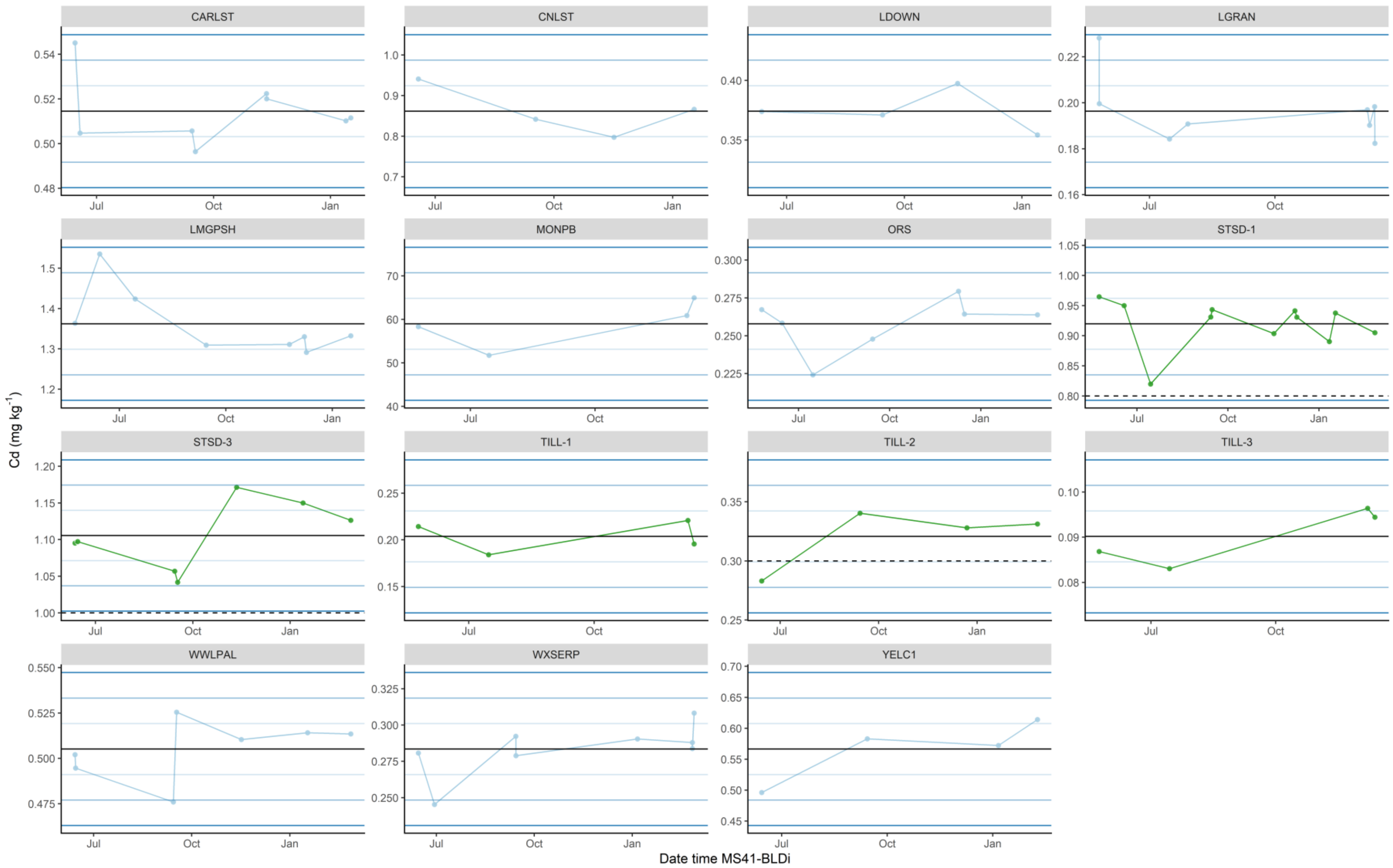


Bismuth (Bi) sample data IQR: 0.19–0.293 mg kg^{-1}



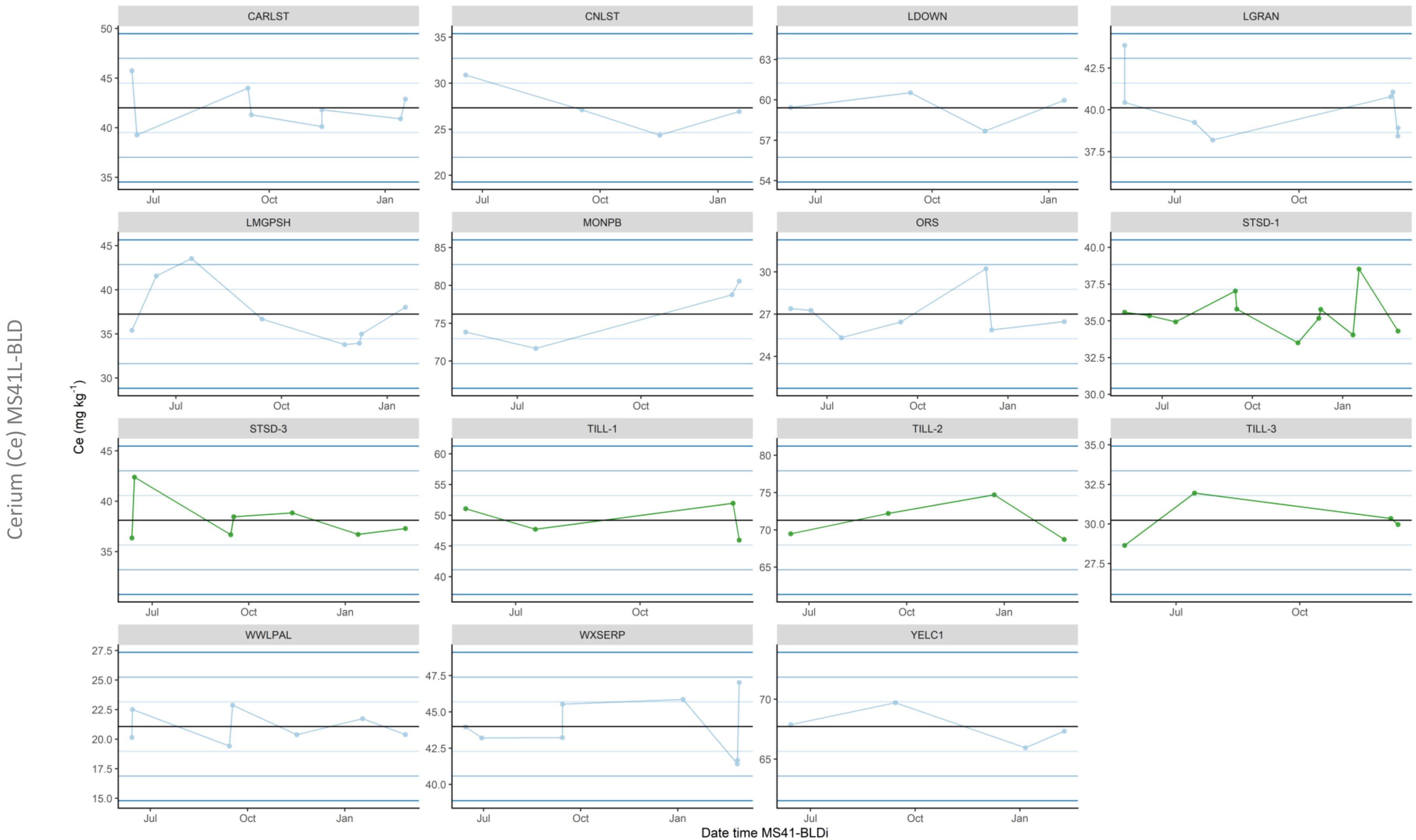
Calcium (Ca) sample data IQR: 1.27–4.3 %

Cadmium (Cd) MS41L-BLD

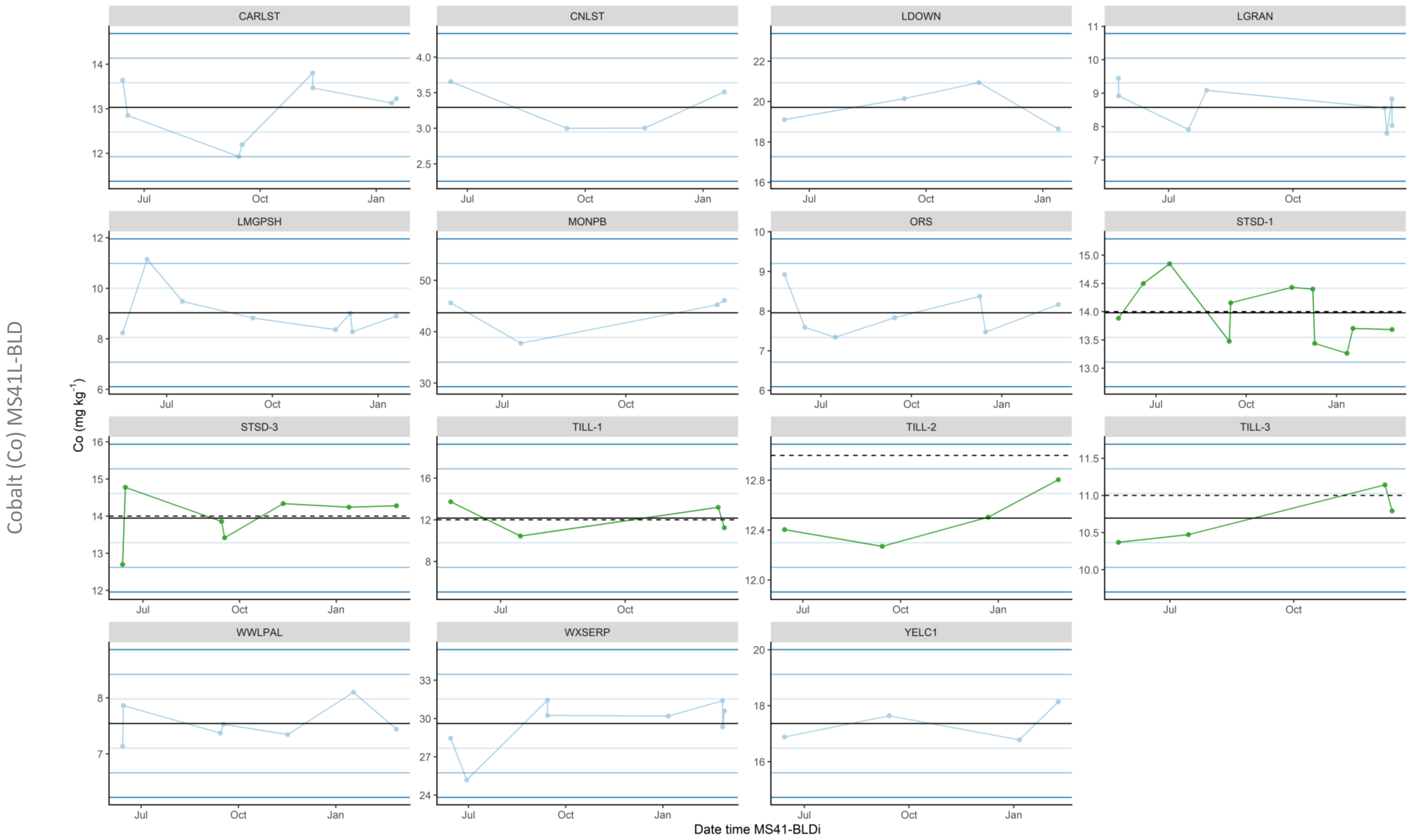


Cadmium (Cd) sample data IQR: 1.45–2.12 mg kg^{-1}

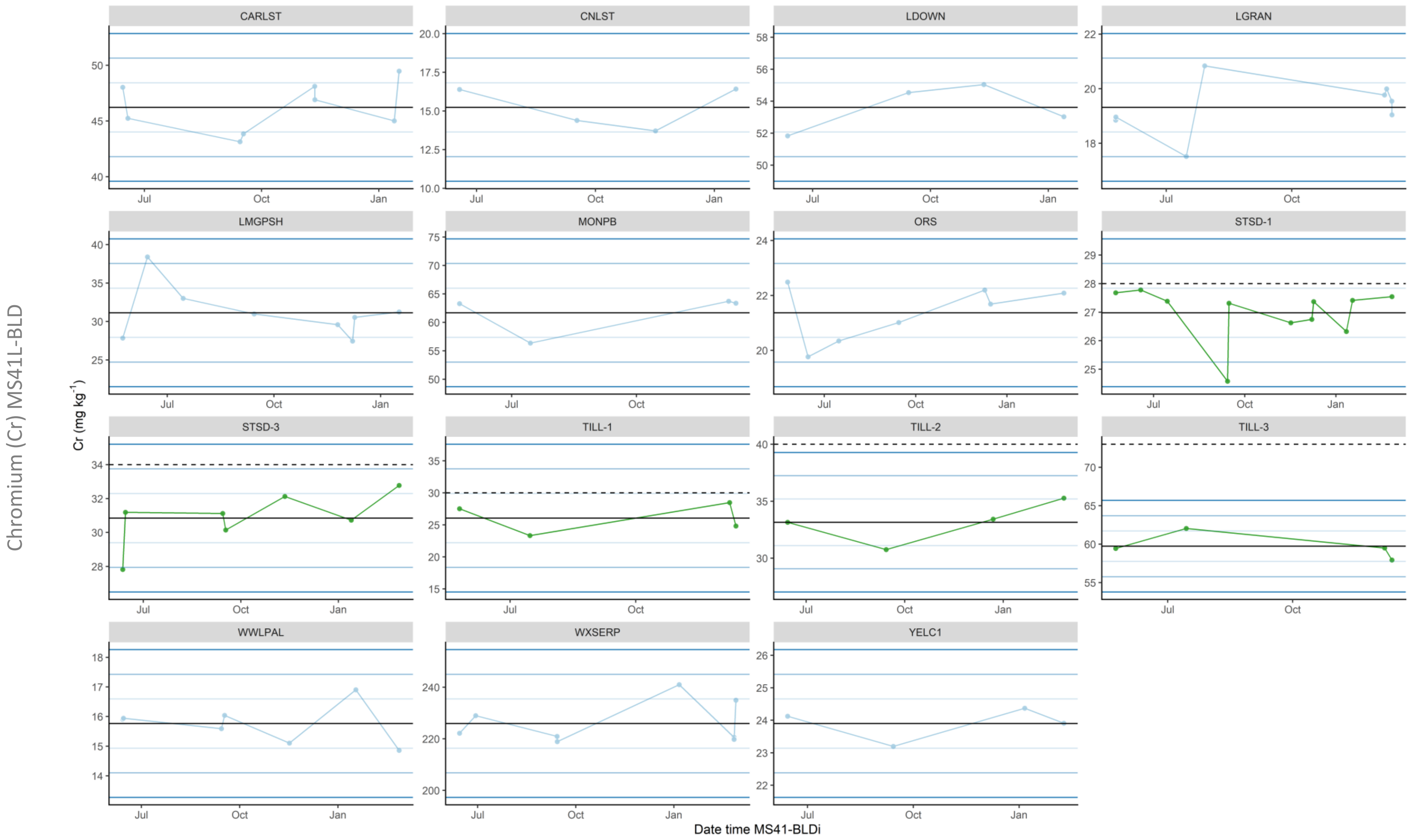
AURUM GLOBAL EXPLORATION



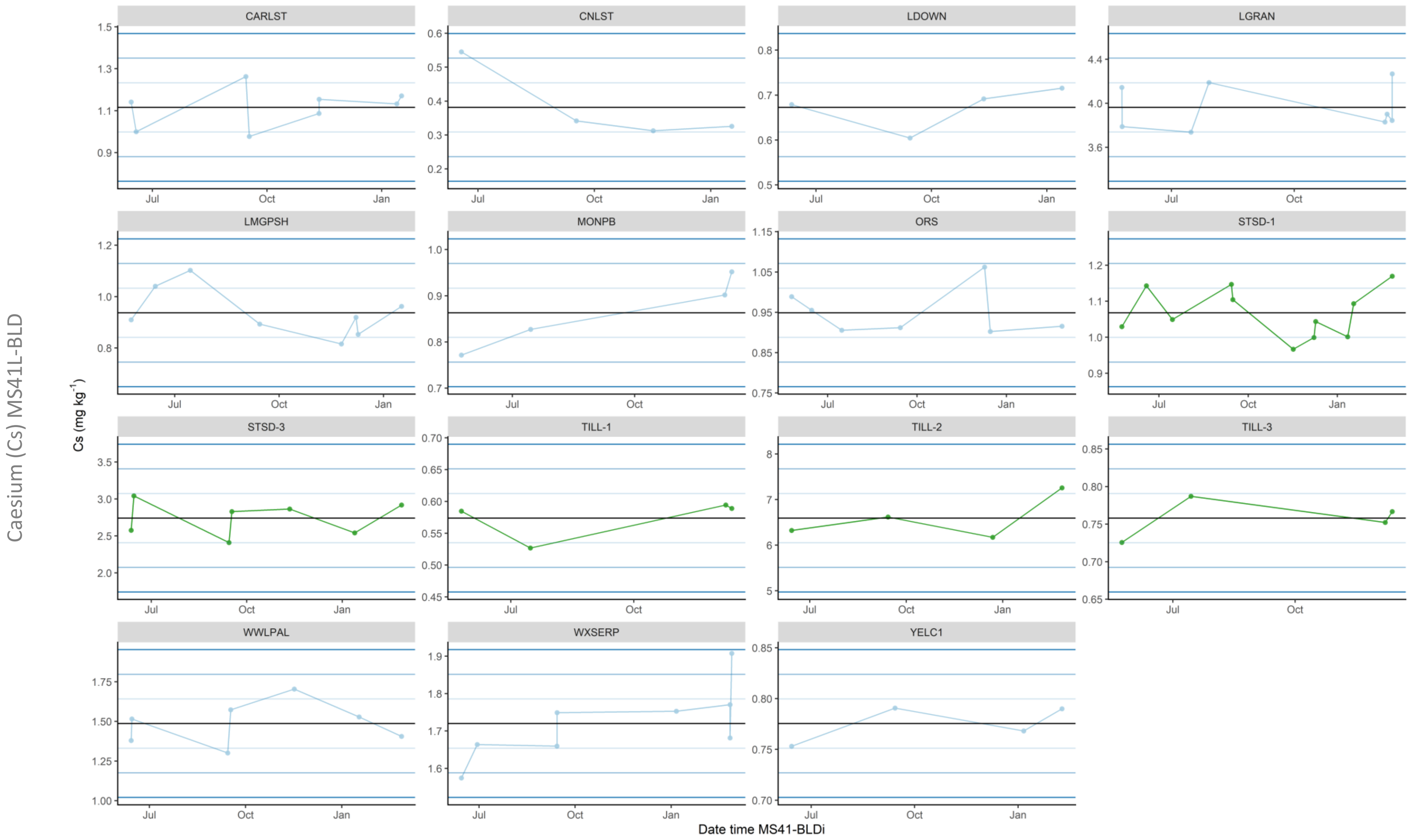
Cerium (Ce) sample data IQR: 22.6–26.9 mg kg^{-1}



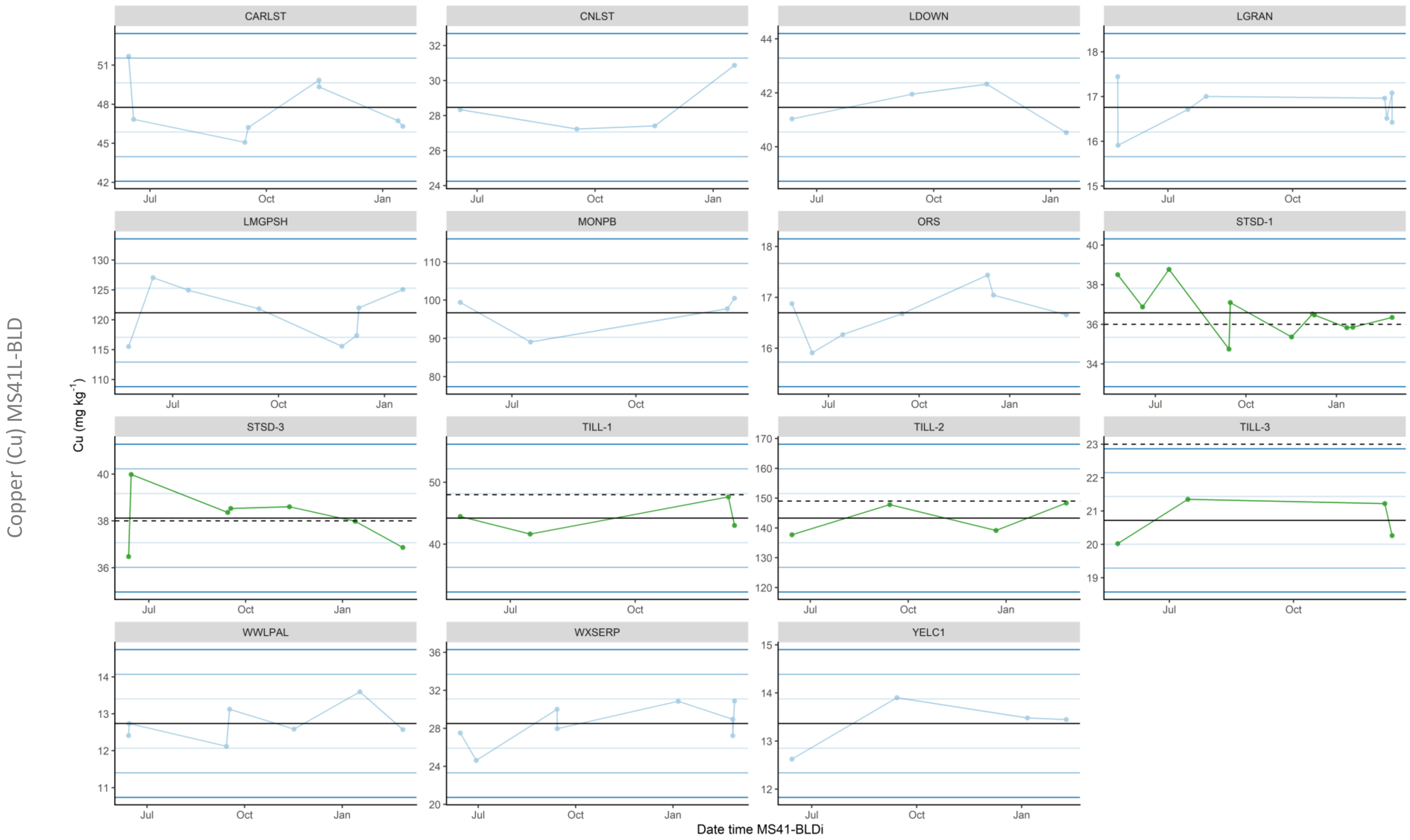
Cobalt (Co) sample data IQR: 9.51–12.3 mg kg^{-1}



Chromium (Cr) sample data IQR: 19.9–23.4 mg kg^{-1}



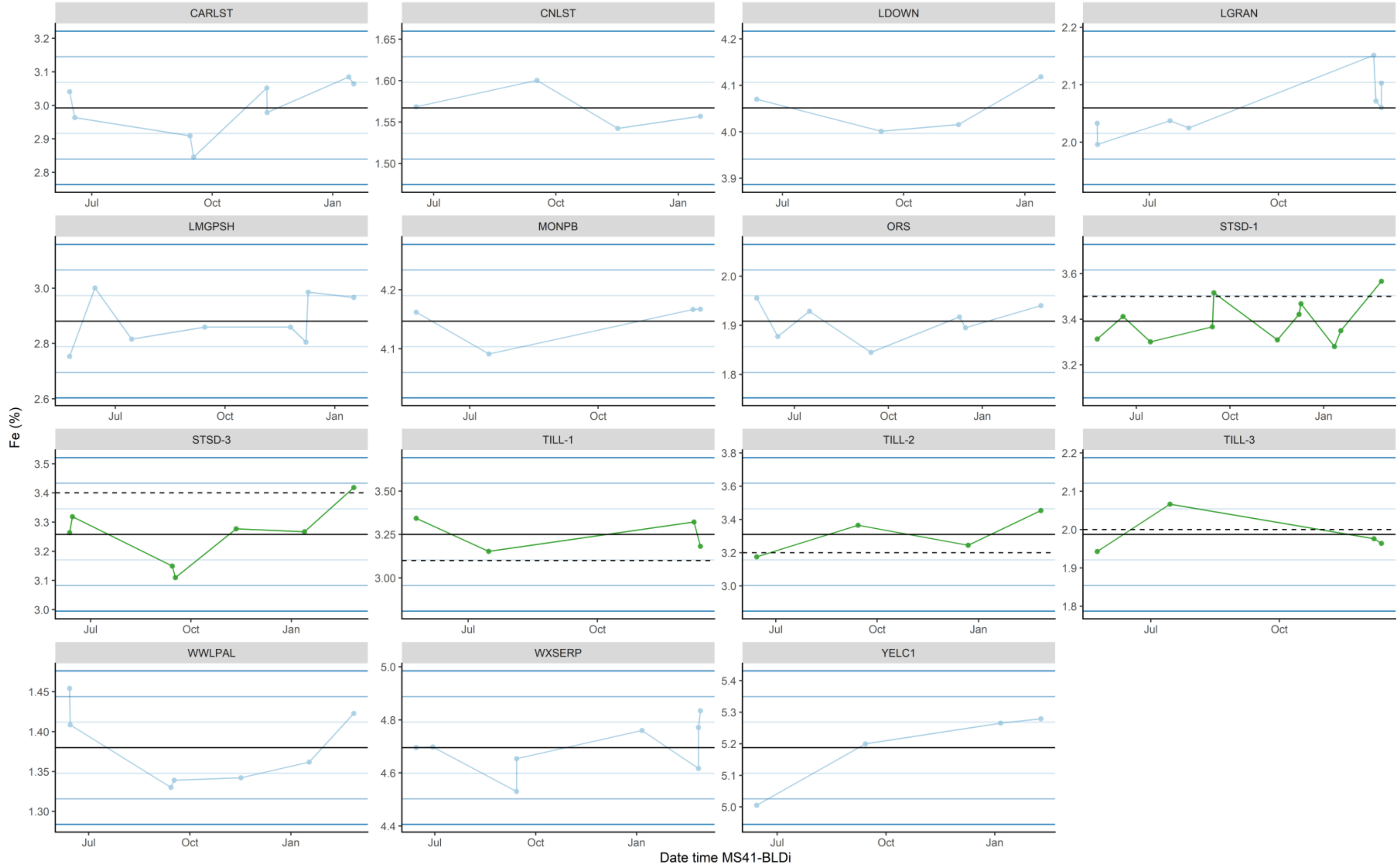
Caesium (Cs) sample data IQR: 0.391–0.614 mg kg^{-1}



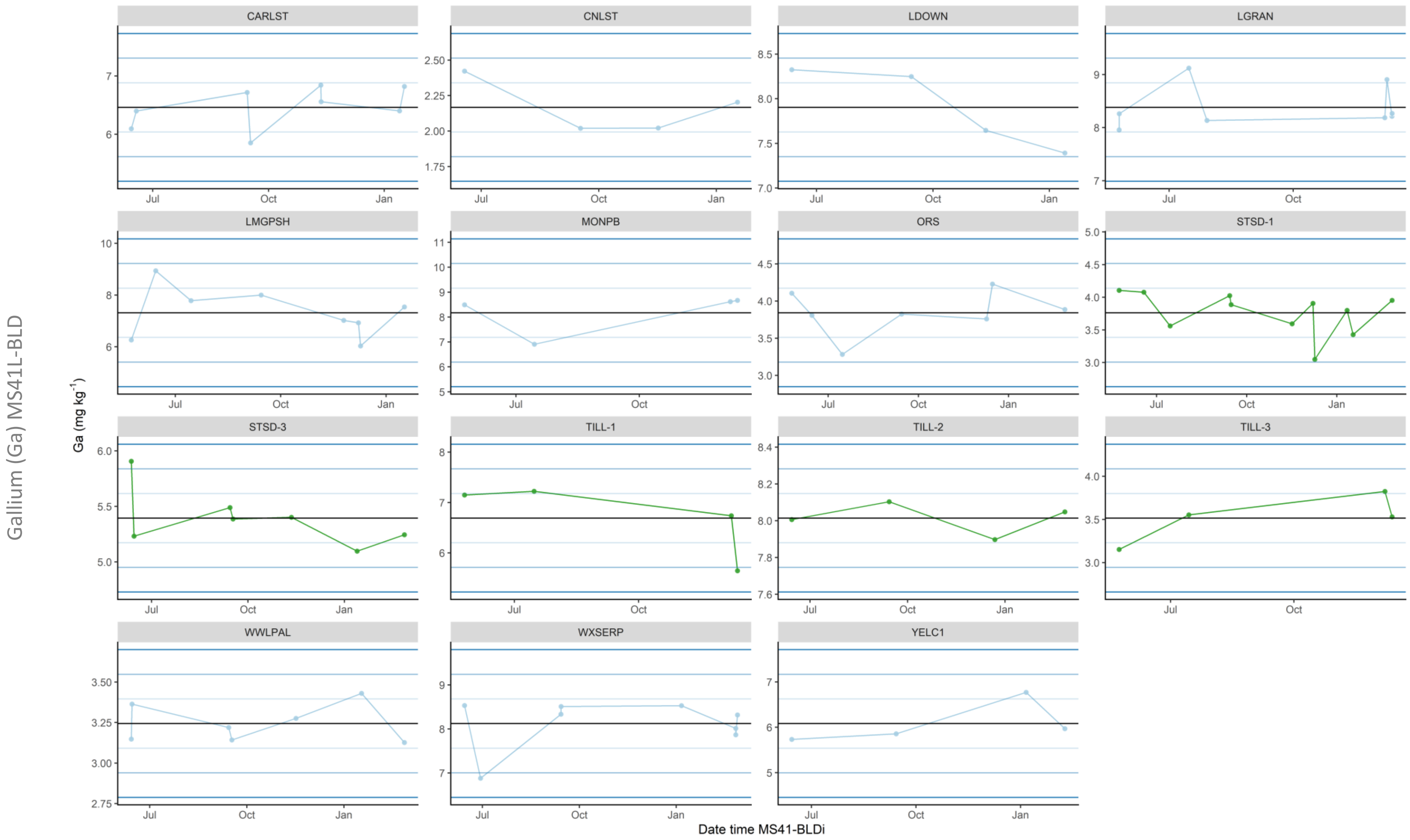
Copper (Cu) sample data IQR: 36.0–60.9 mg kg^{-1}

AURUM GLOBAL EXPLORATION

Iron (Fe) MS41L-BLD



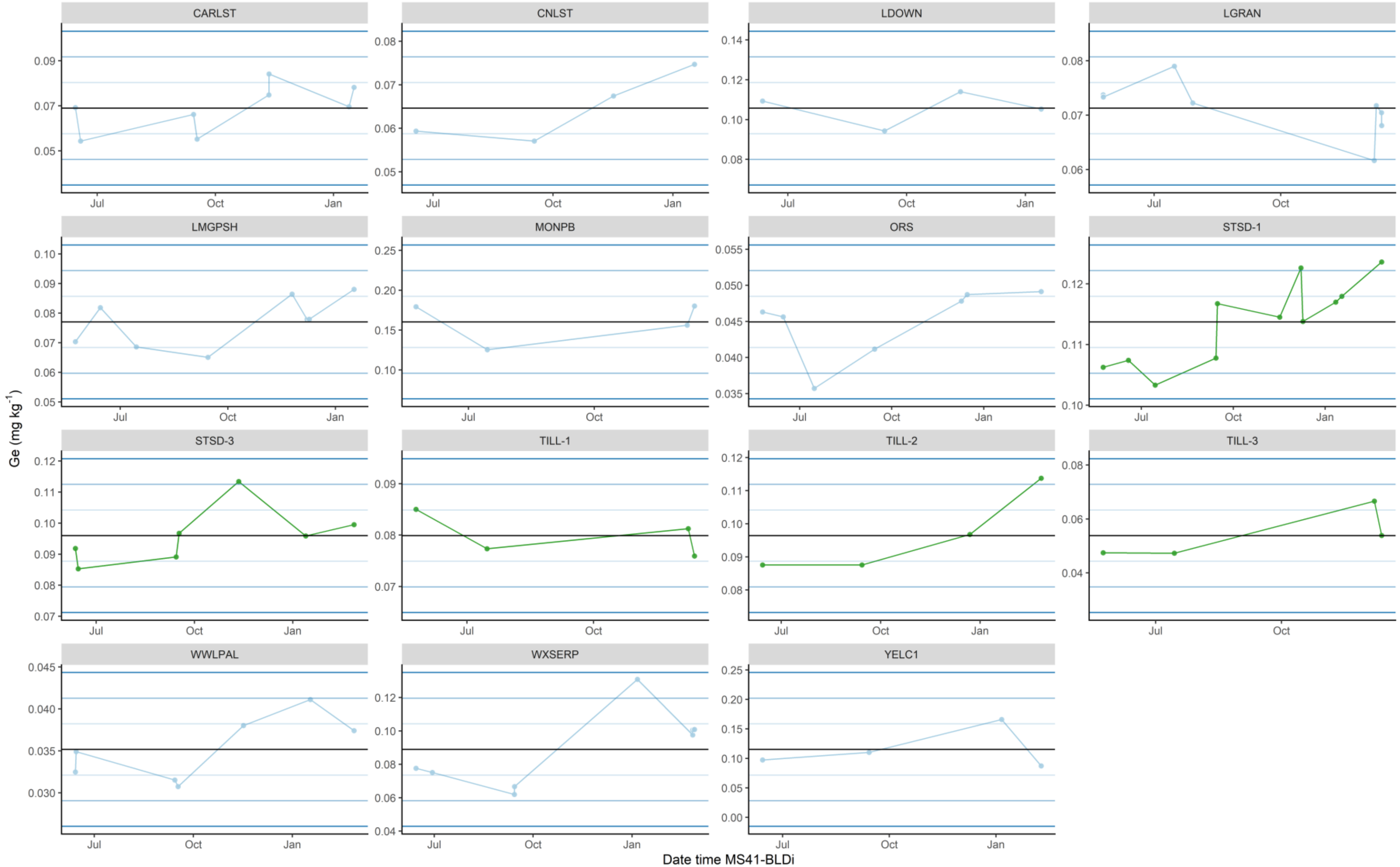
Iron (Fe) sample data IQR: 2.09–2.49 %



Gallium (Ga) sample data IQR: 2.77–3.47 mg kg^{-1}

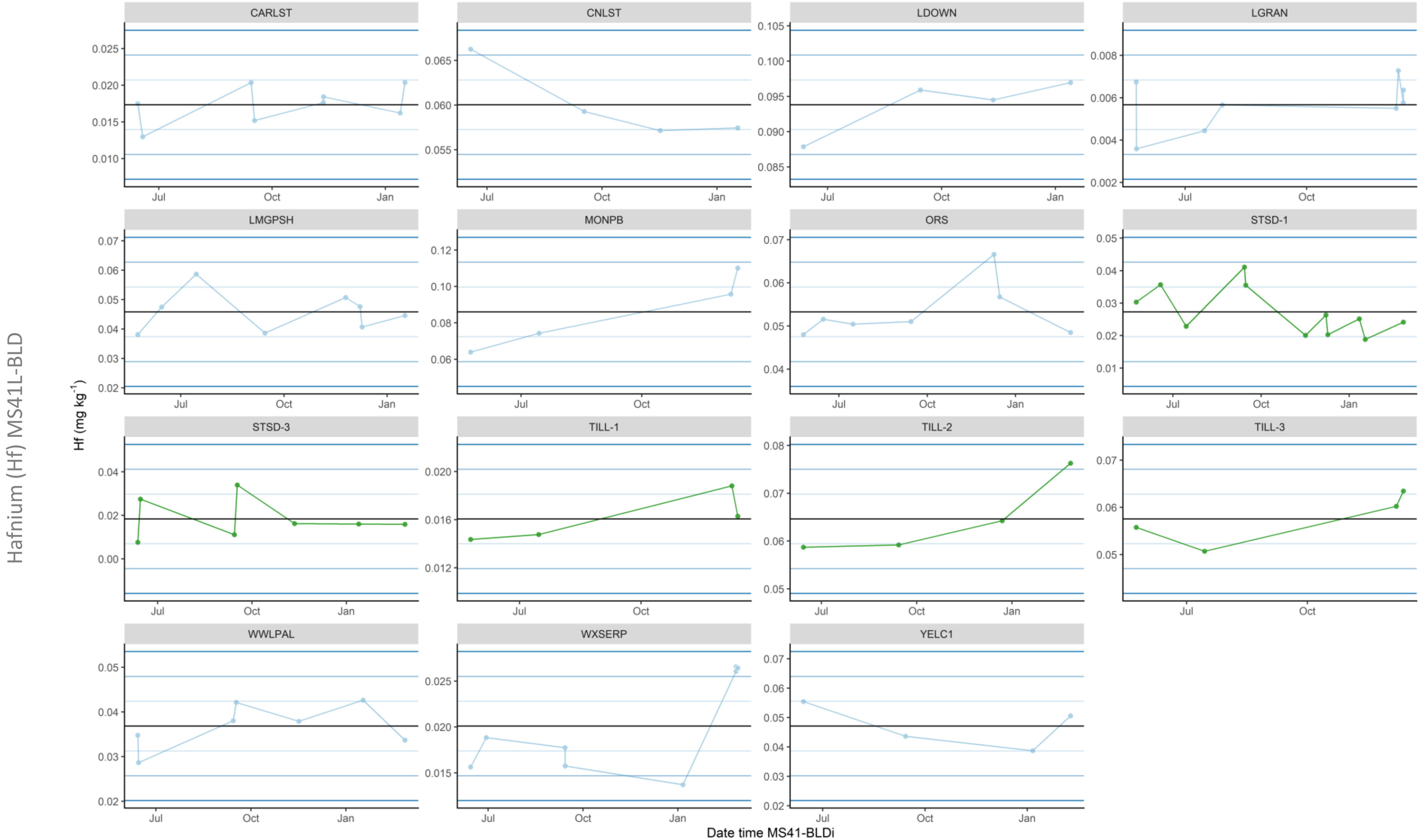
AURUM GLOBAL EXPLORATION

Germanium (Ge) MS41L-BLD

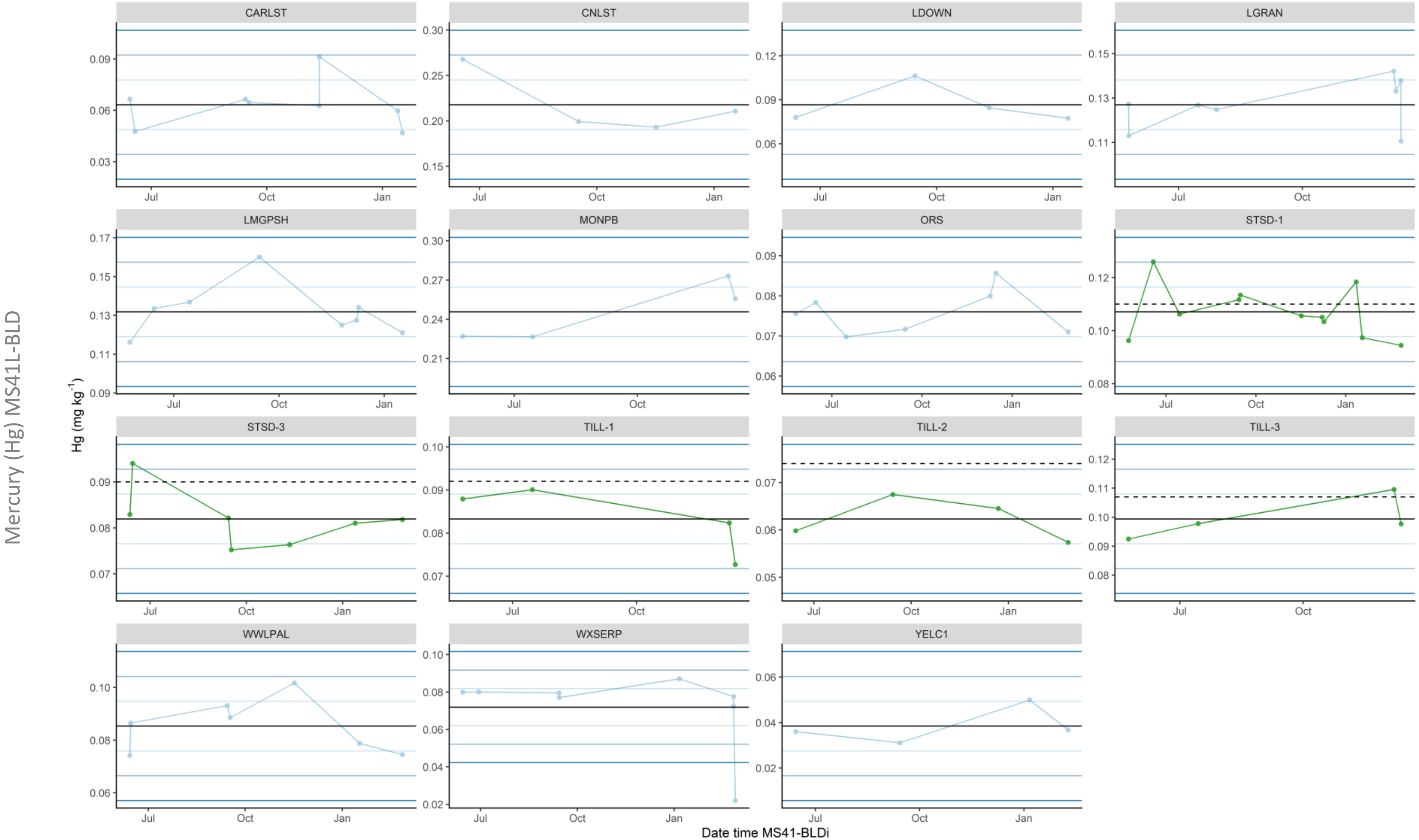


Germanium (Ge) sample data IQR: 0.0553-0.0696 mg kg^{-1}

AURUM GLOBAL EXPLORATION

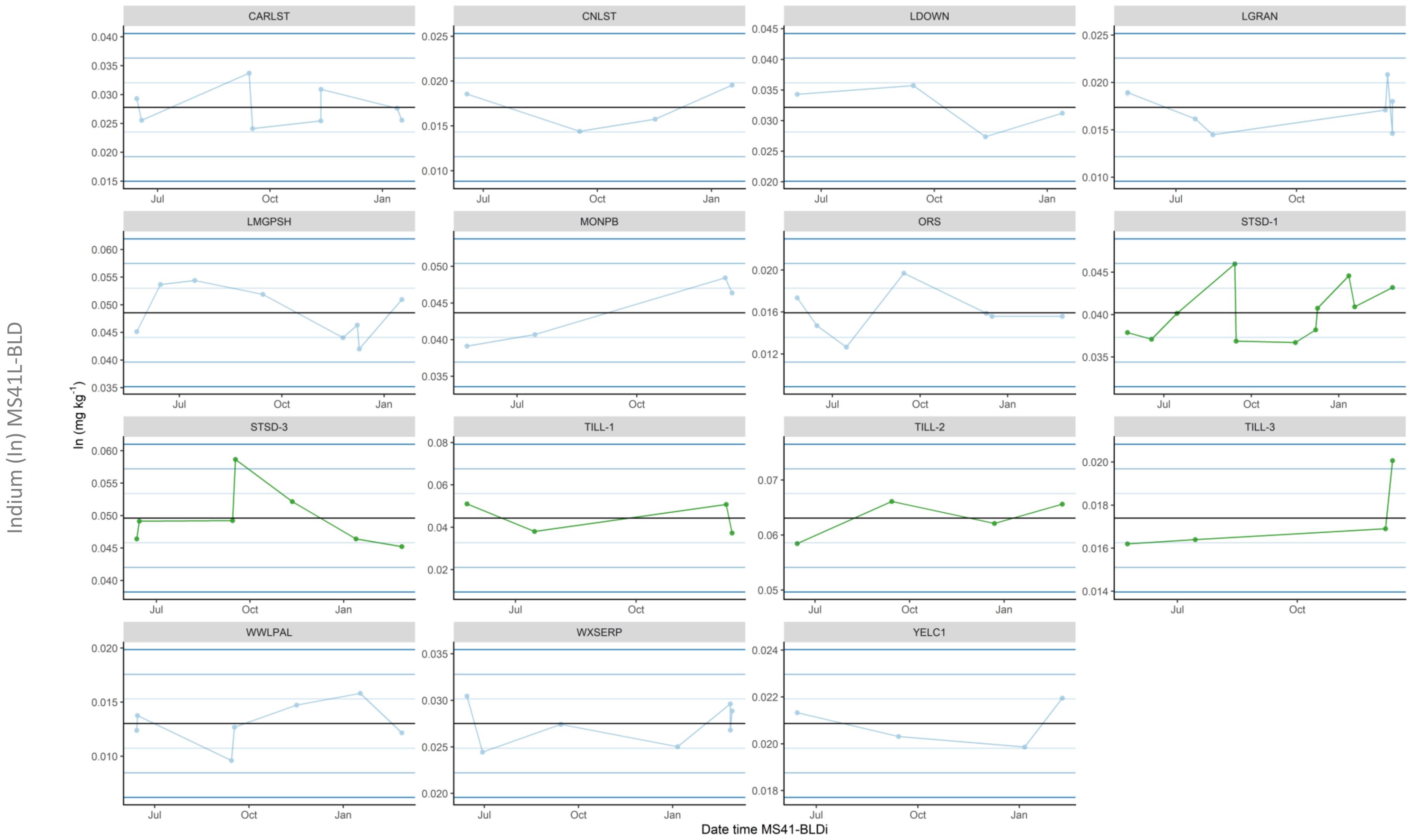


Hafnium (Hf) sample data IQR: 0.0818–0.109 mg kg^{-1}

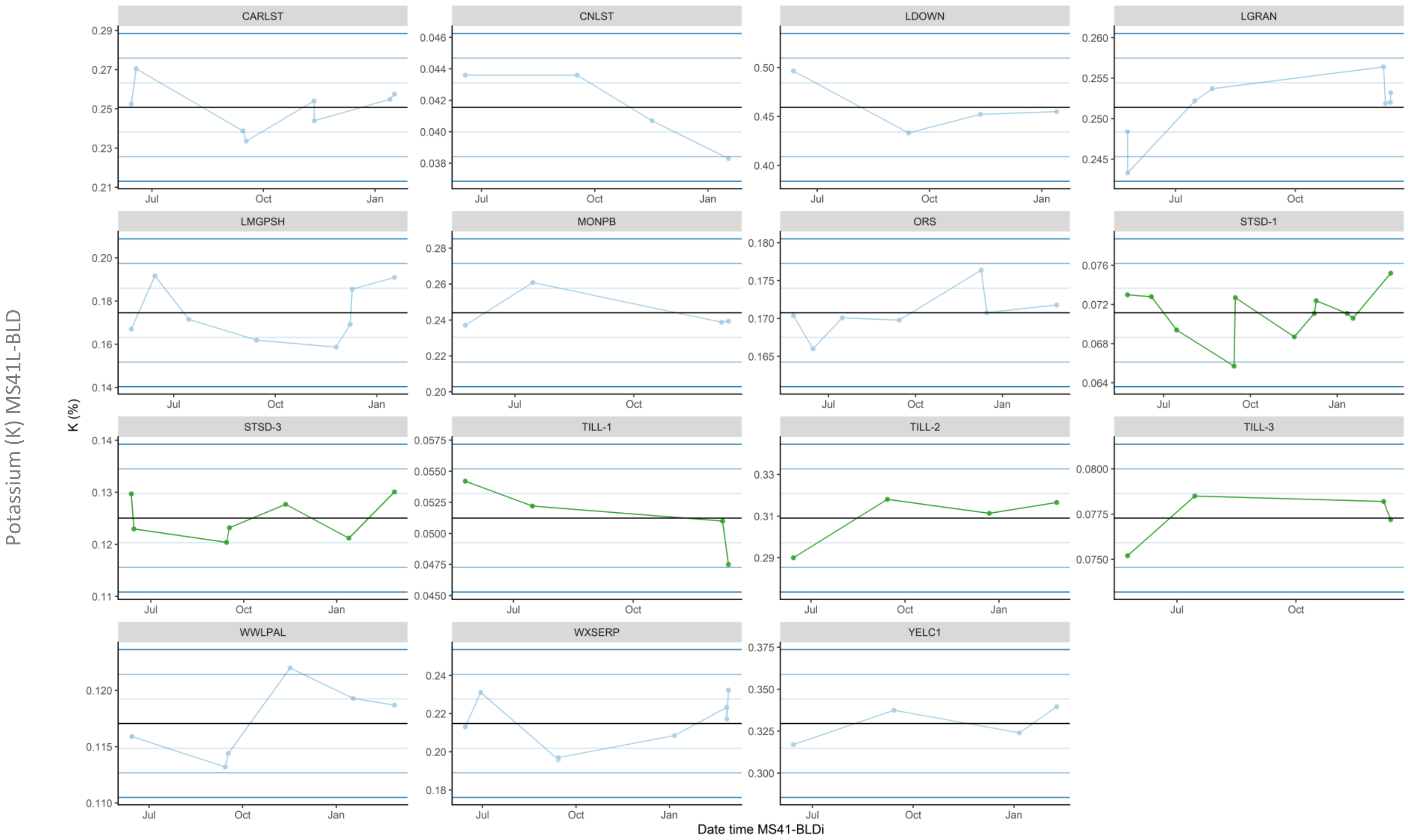


Mercury (Hg) sample data IQR: 0.163–0.481 mg kg^{-1}

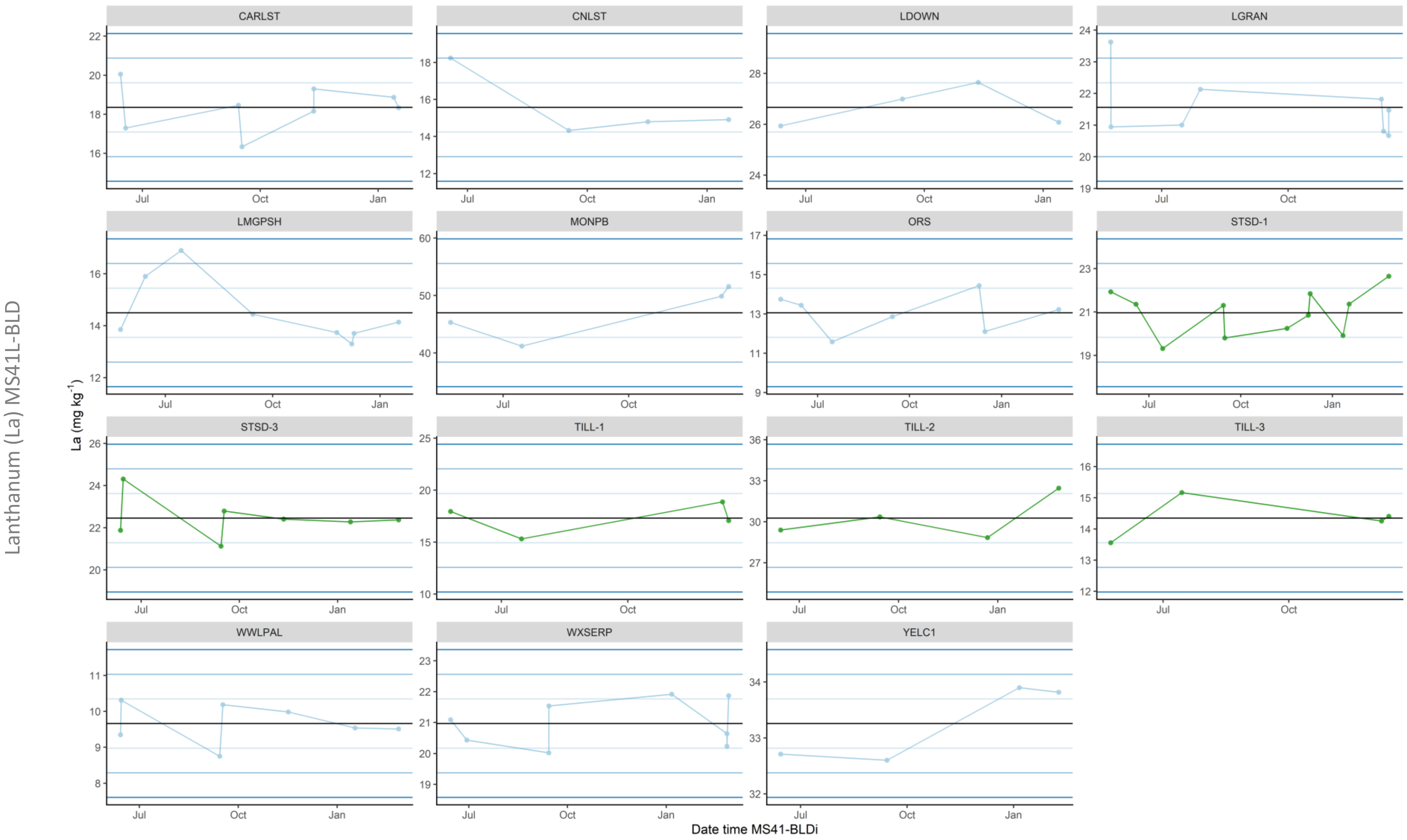
AURUM GLOBAL EXPLORATION



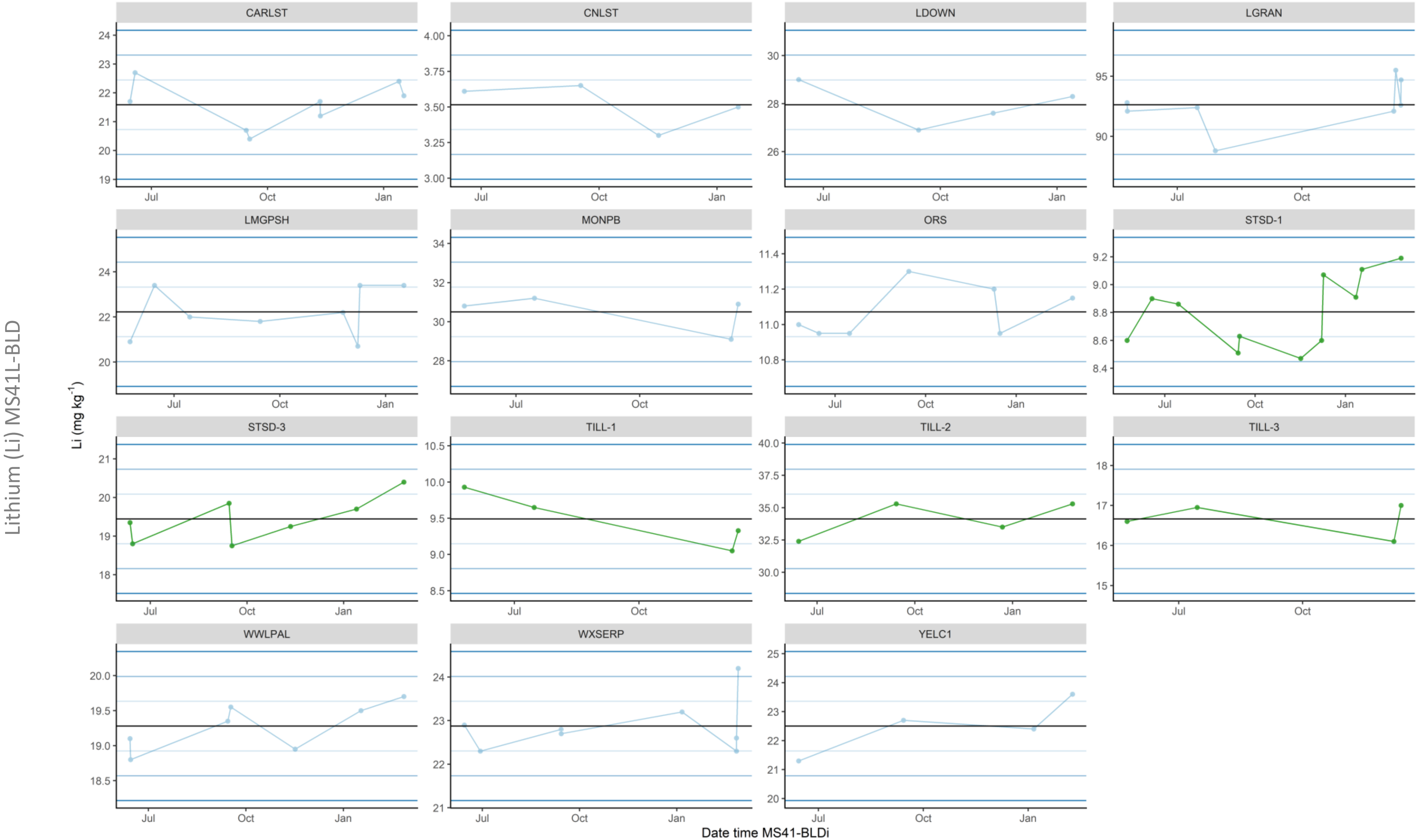
Indium (In) sample data IQR: 0.0205–0.0272 mg kg^{-1}



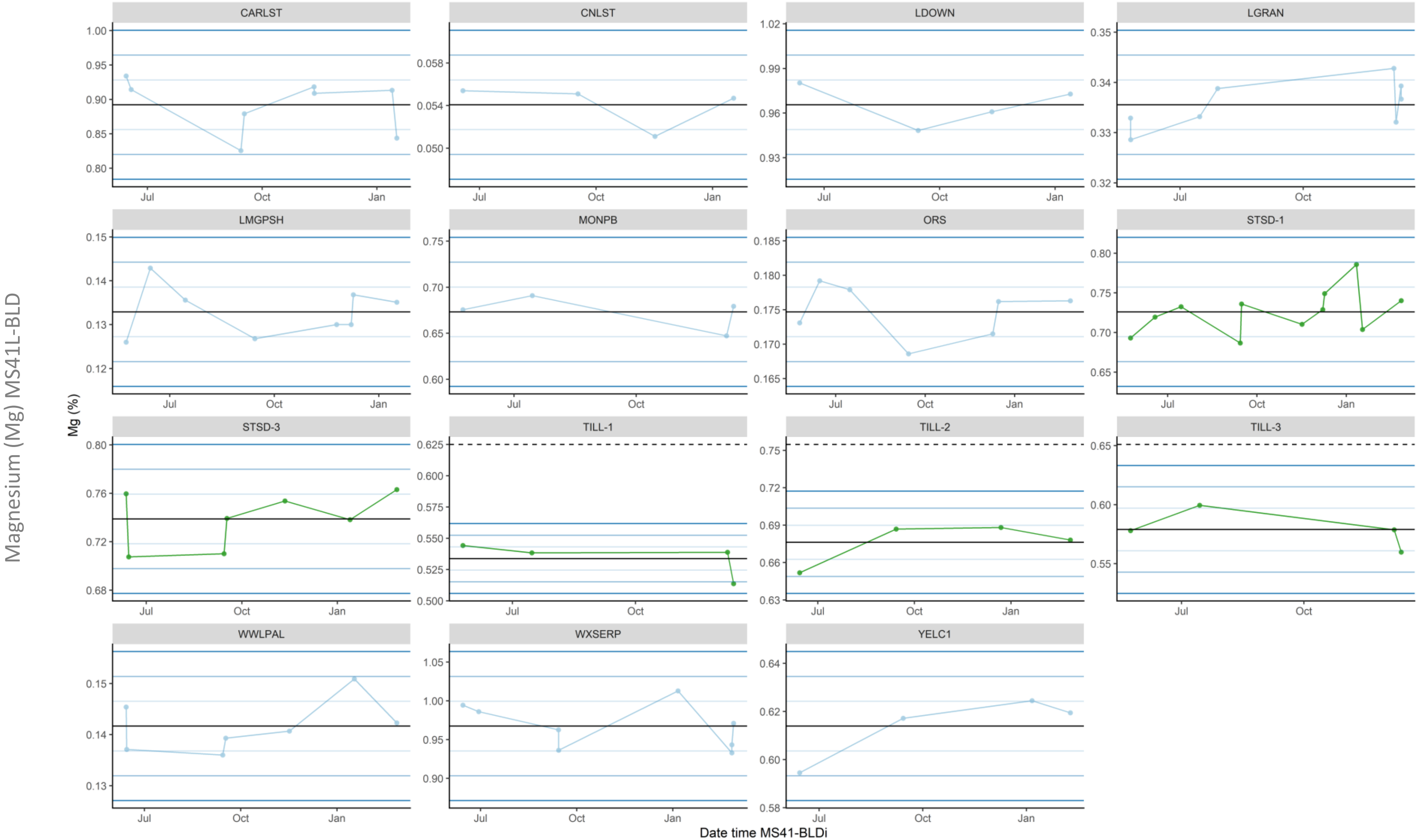
Potassium (K) sample data IQR: 0.124–0.154 %



Lanthanum (La) sample data IQR: 11.6–13.6 mg kg^{-1}

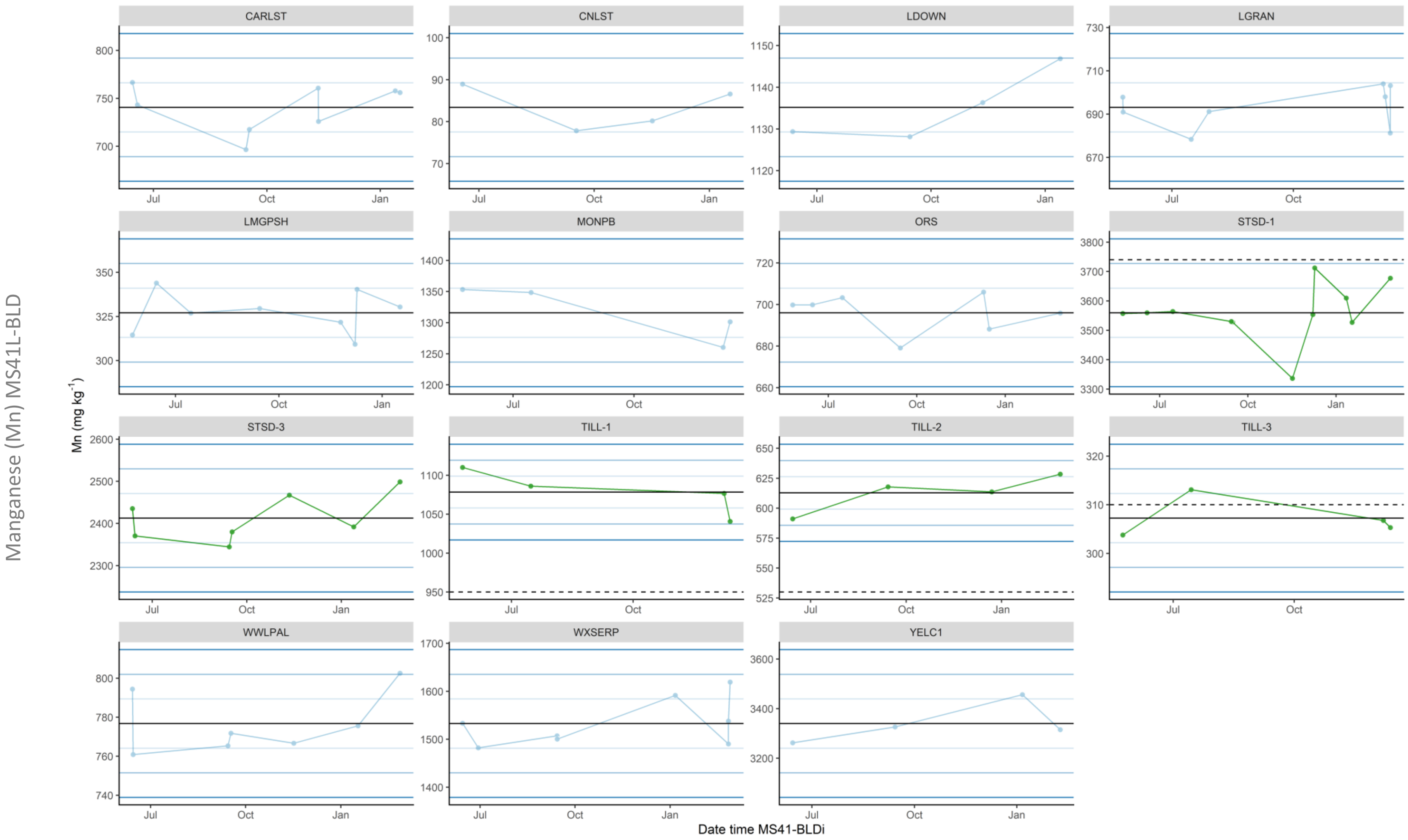


Lithium (Li) sample data IQR: 10.9–16.6 mg kg^{-1}

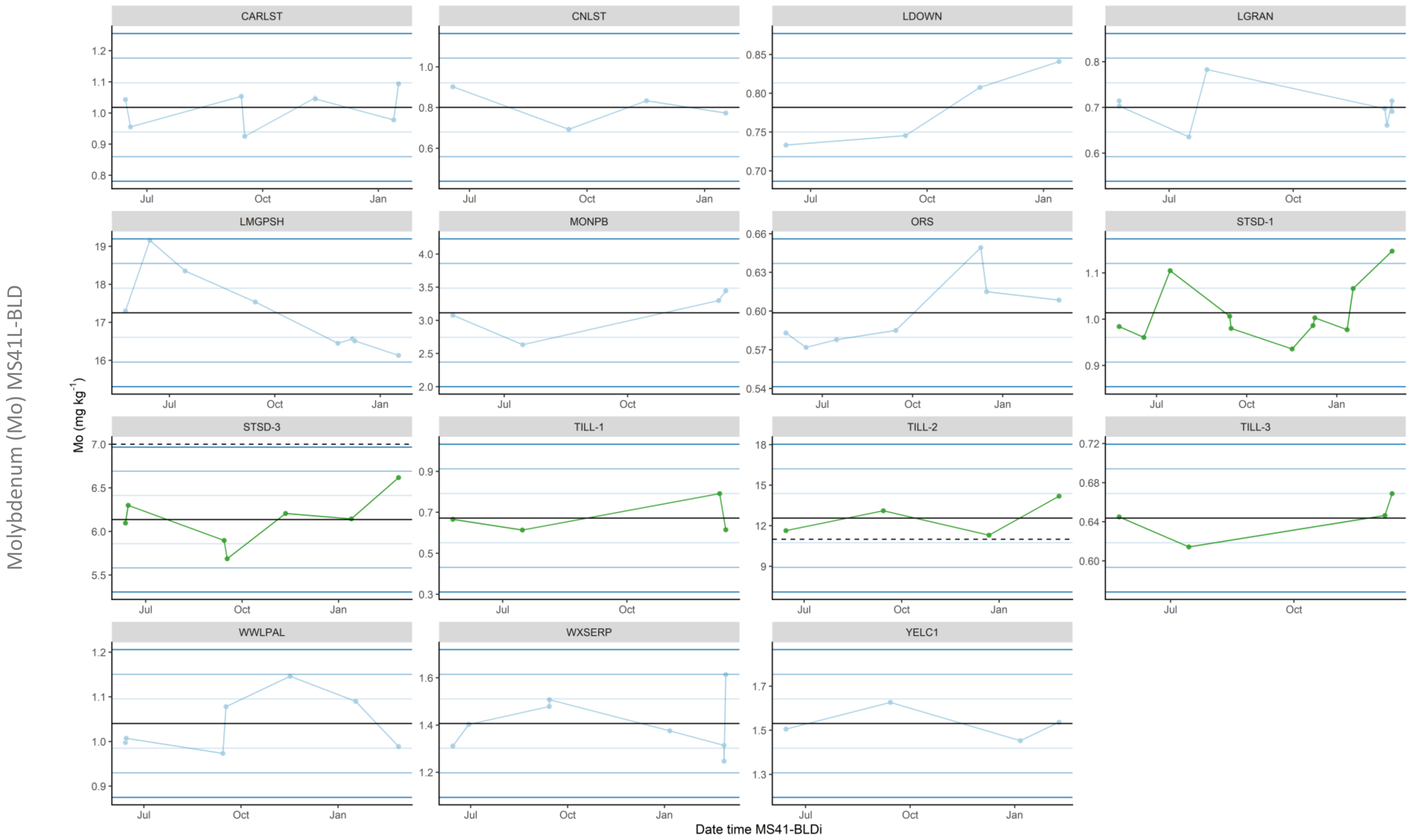


Magnesium (Mg) sample data IQR: 0.204–0.290 %

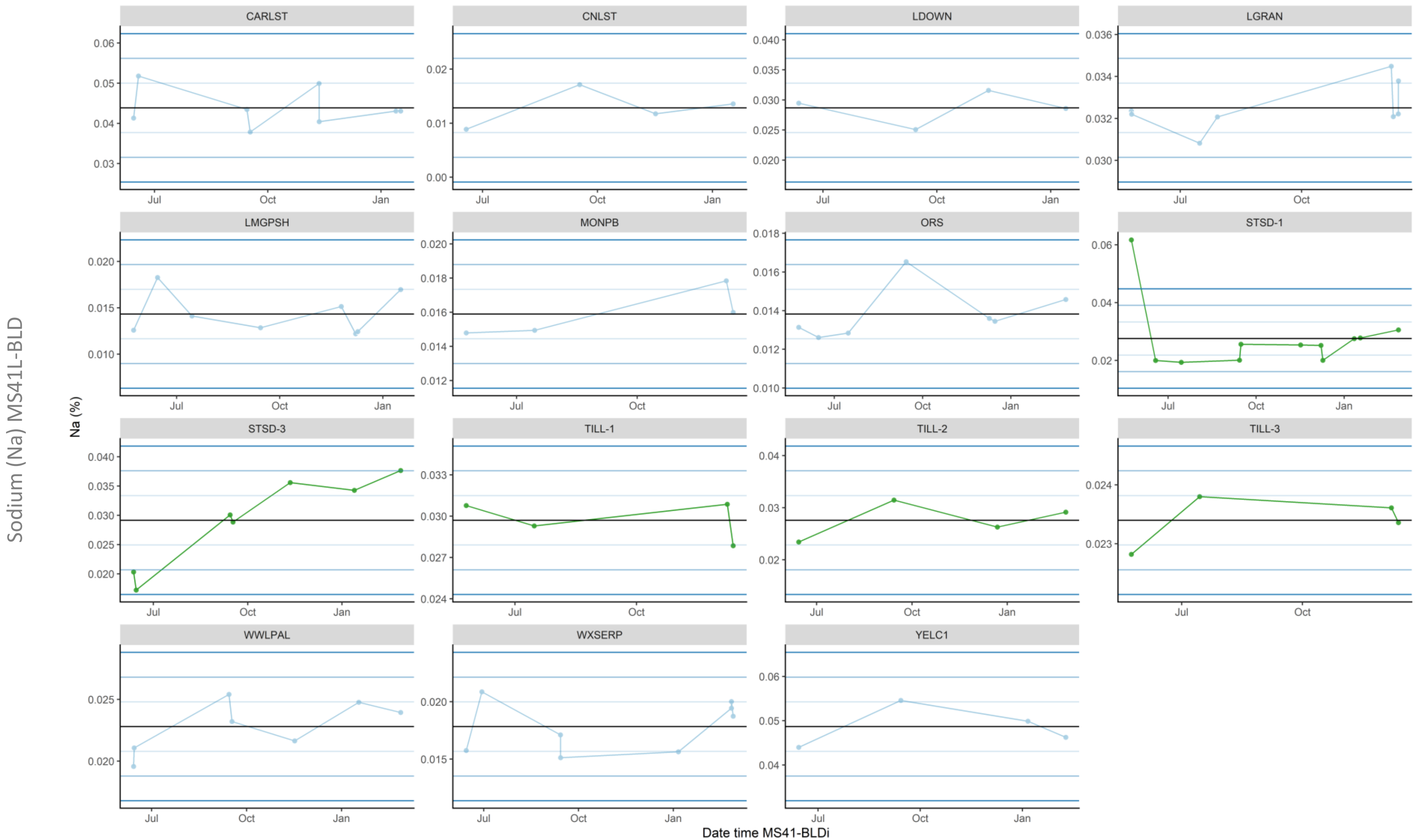
AURUM GLOBAL EXPLORATION



Manganese (Mn) sample data IQR: 802–1300 mg kg^{-1}

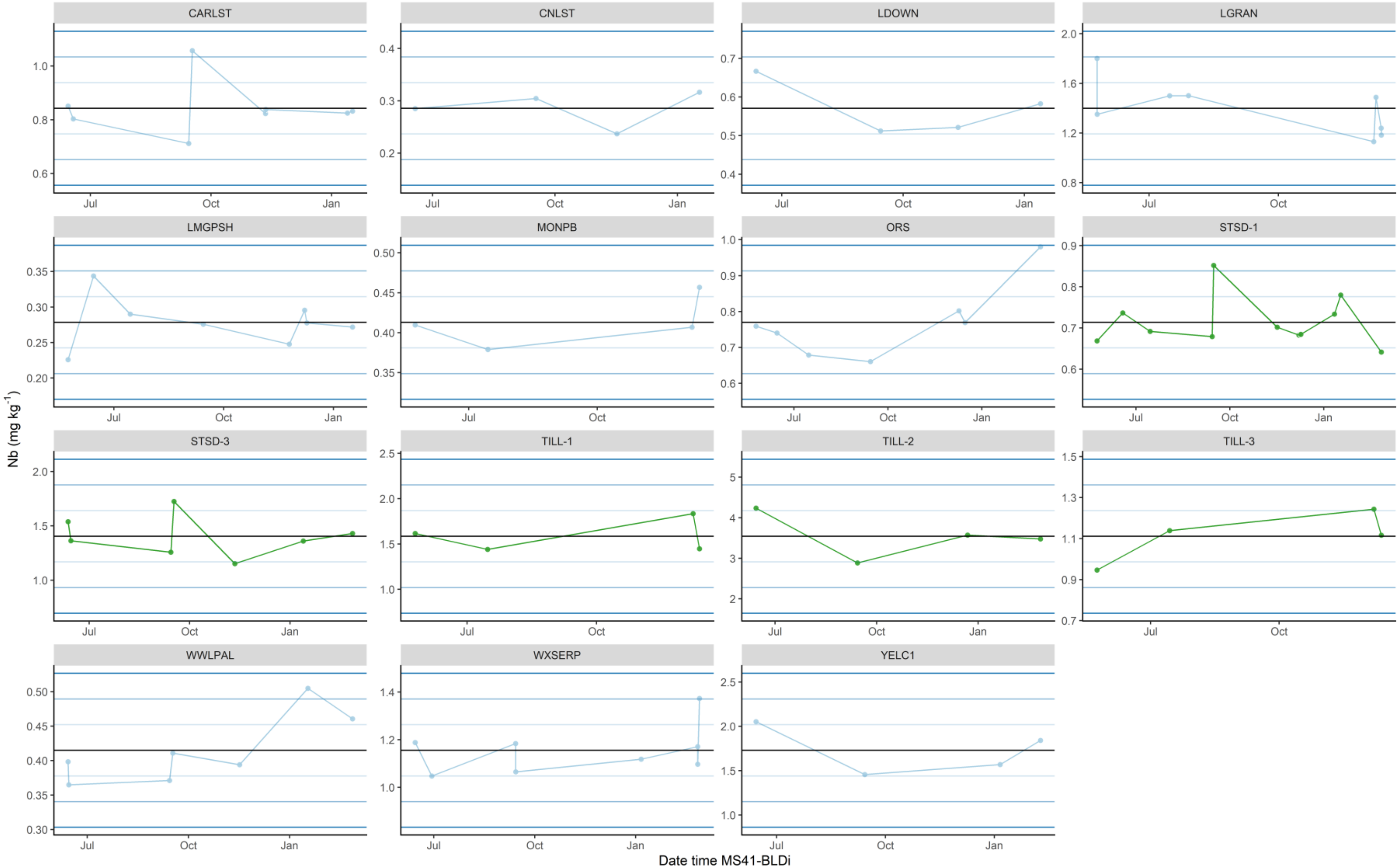


Molybdenum (Mo) sample data IQR: 2.57–3.70 mg kg^{-1}

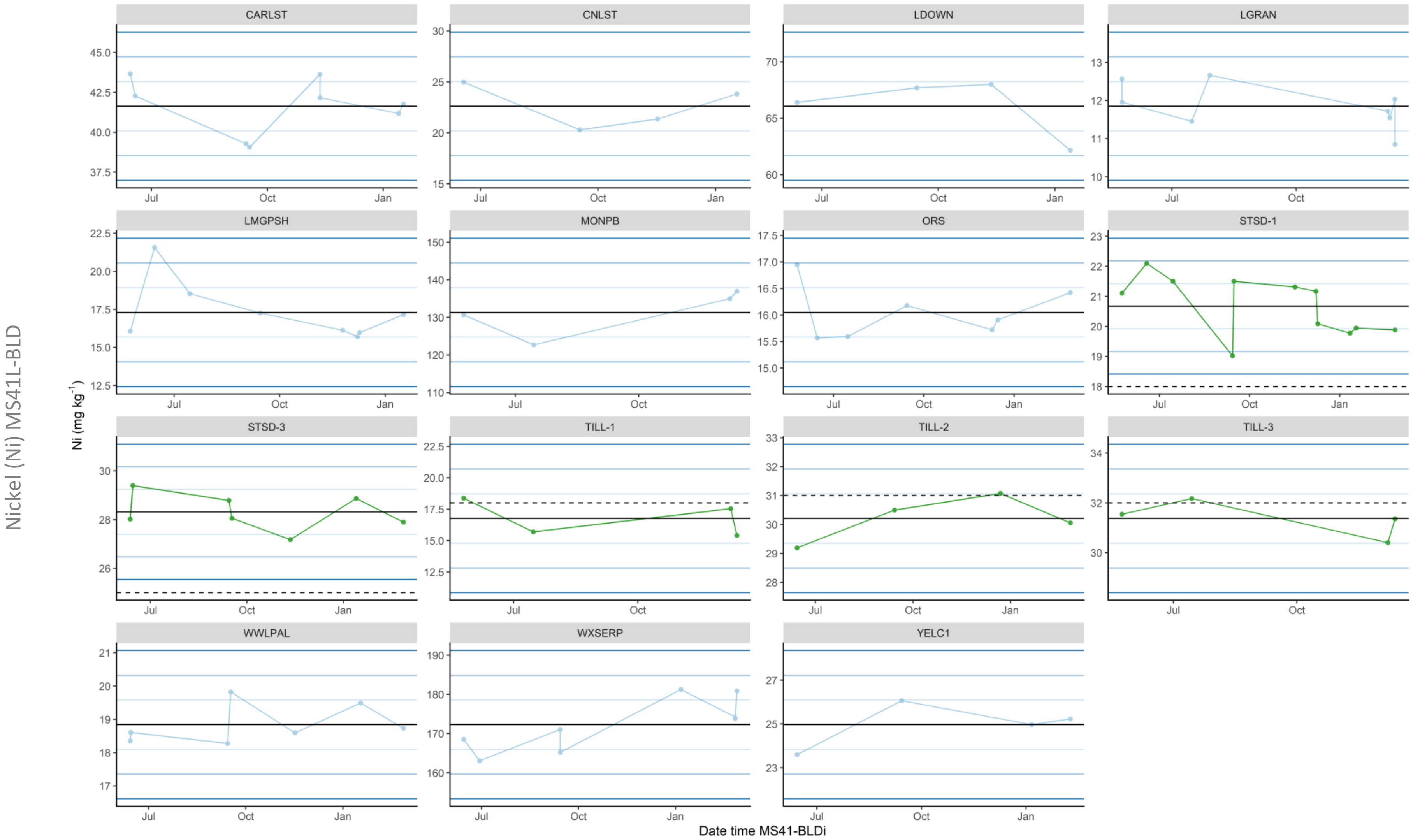


Sodium (Na) sample data IQR: 0.0154–0.0218 %

Niobium (Nb) MS41L-BLD

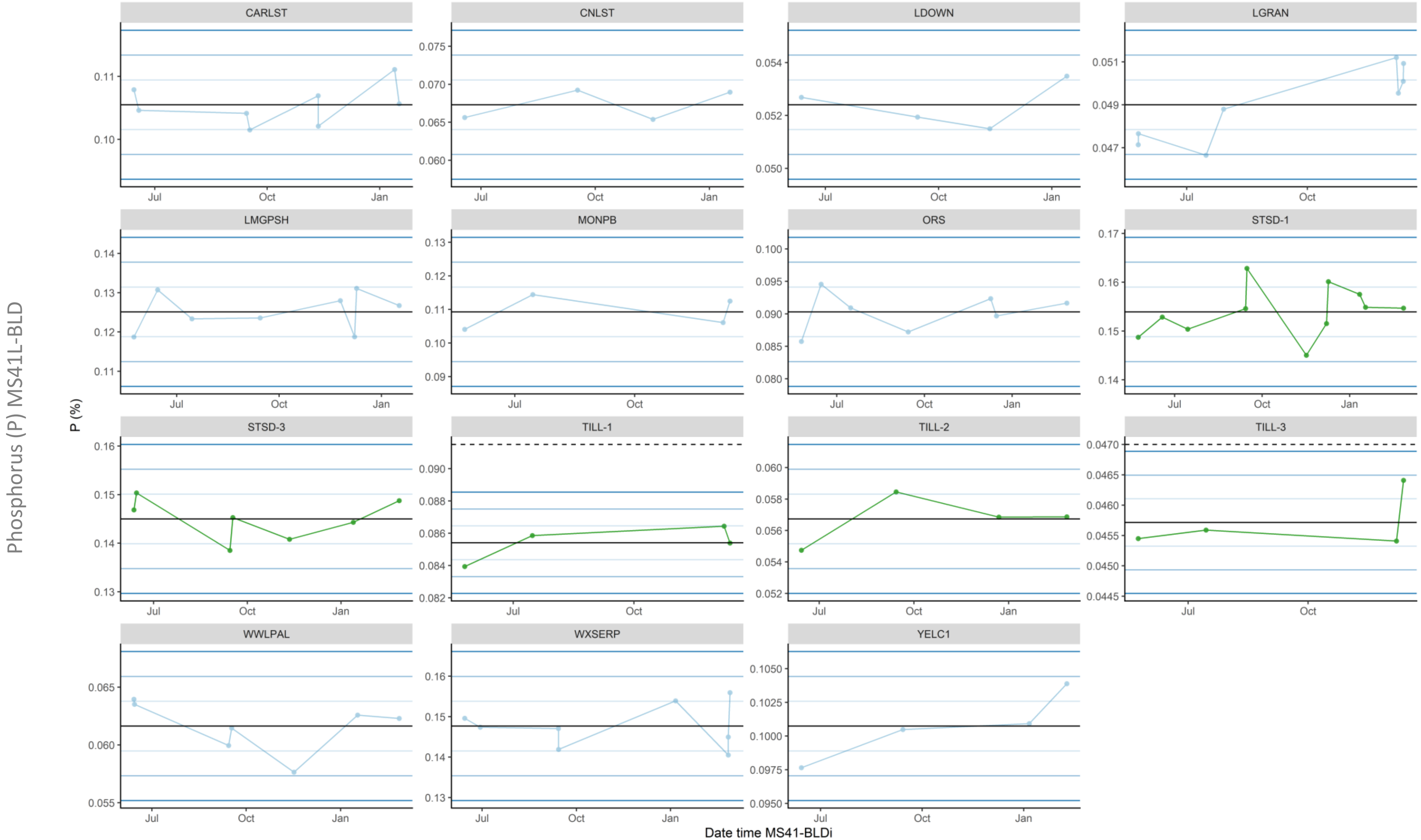


Niobium (Nb) sample data IQR: 0.297–0.429 mg kg^{-1}



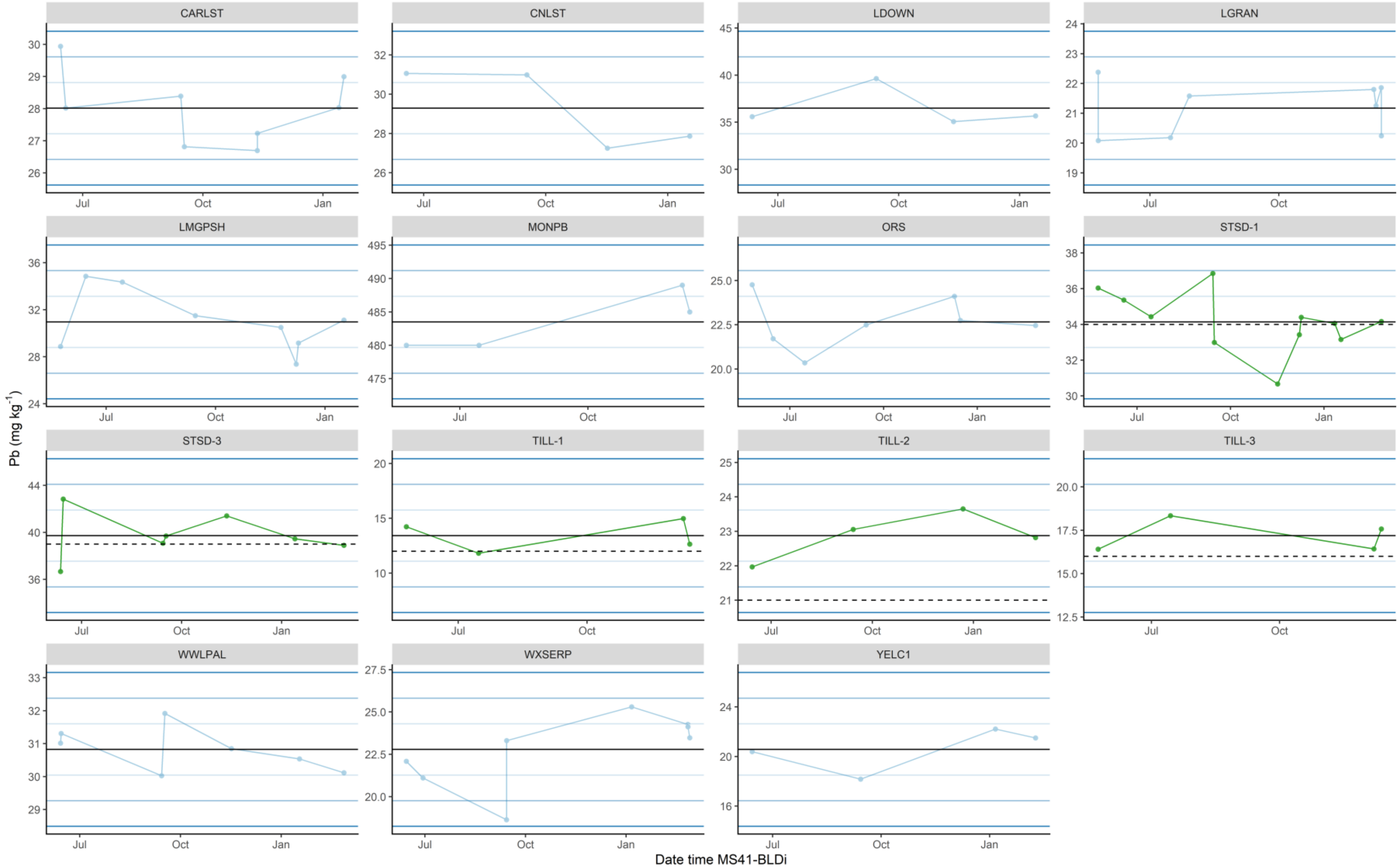
Nickel (Ni) sample data IQR: 36.6–49.1 mg kg^{-1}

AURUM GLOBAL EXPLORATION

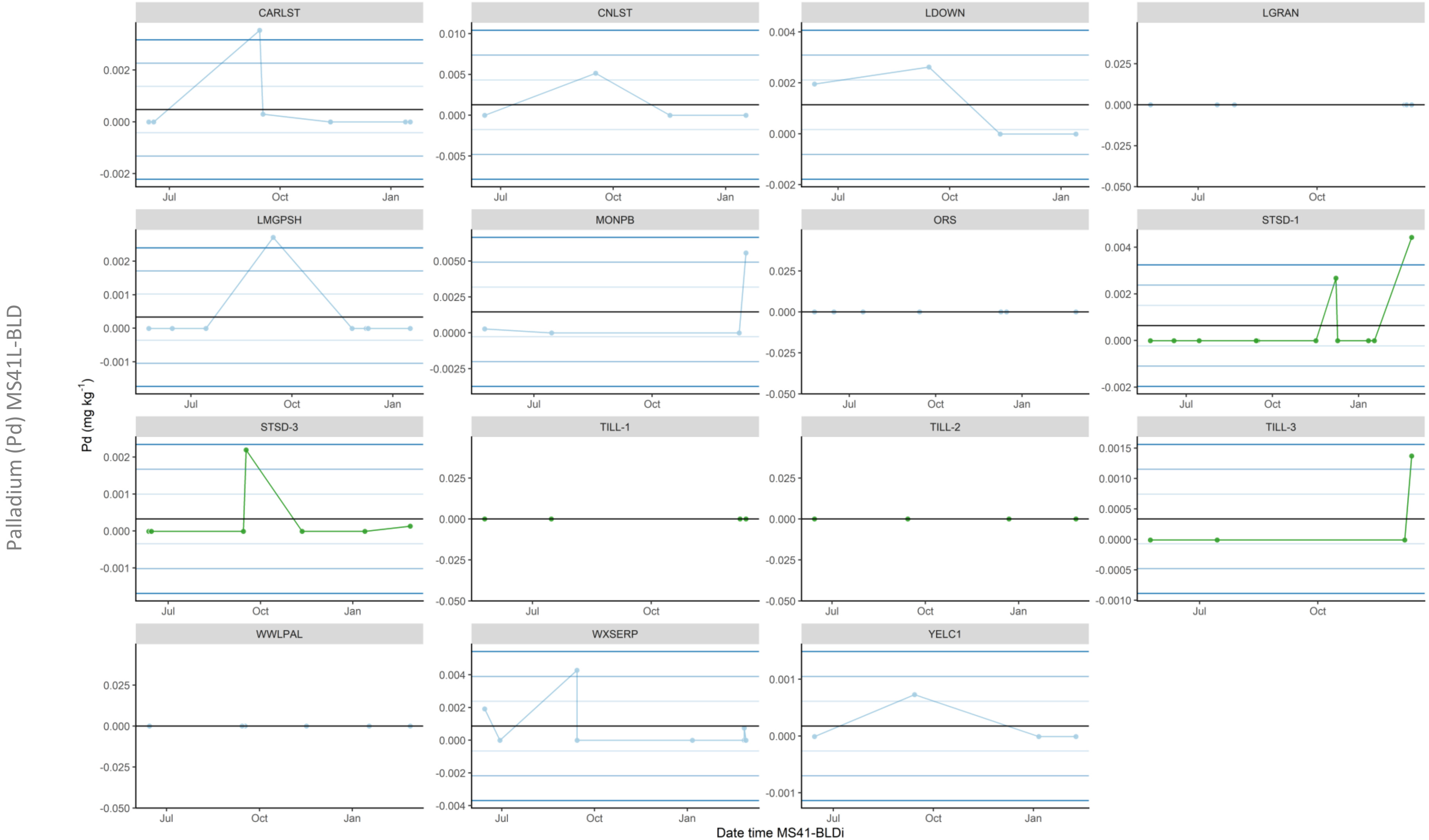


Phosphorus (P) sample data IQR: 869–1260 mg kg^{-1}

Lead (Pb) MS41L-BLD

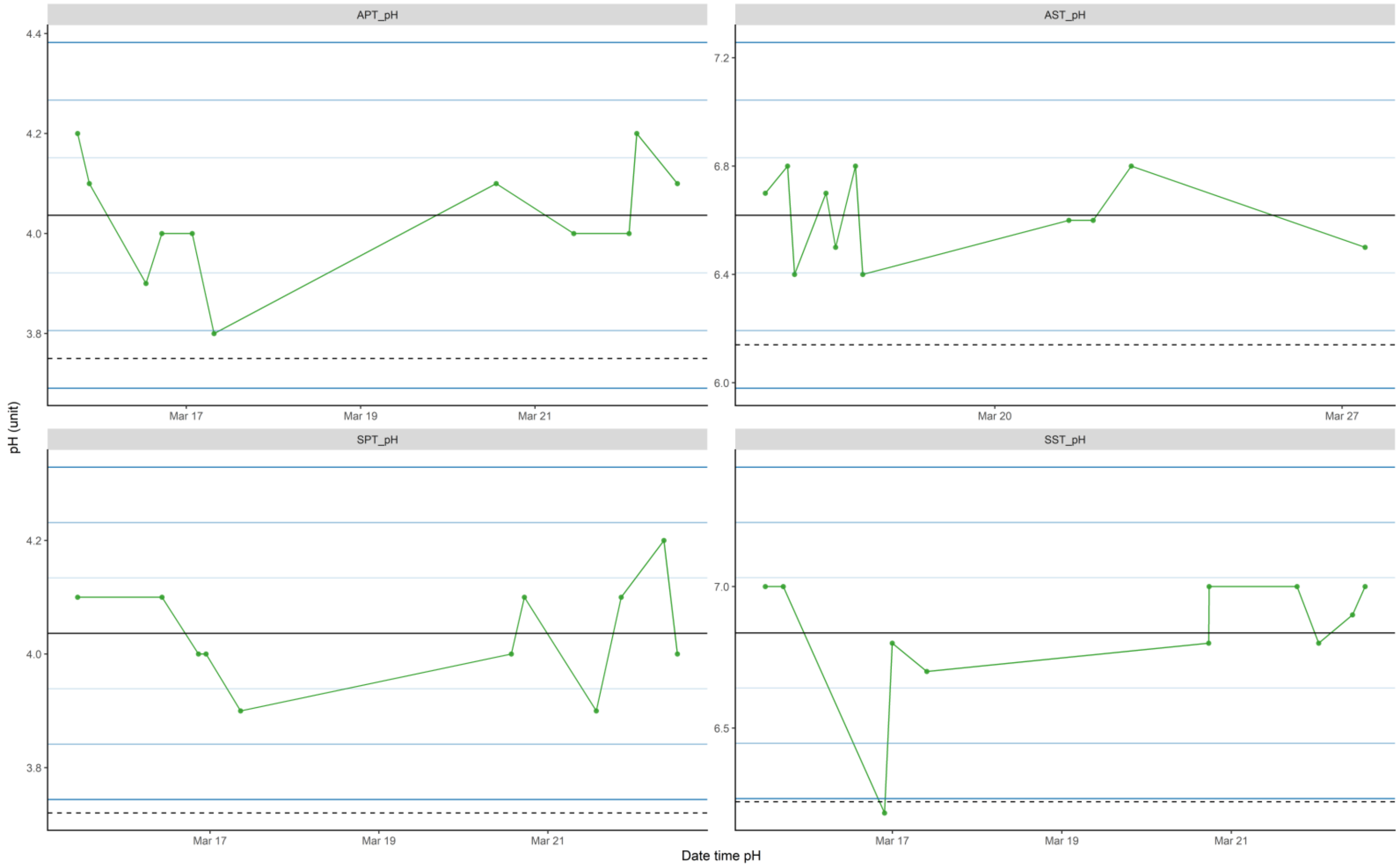


Lead (Pb) sample data IQR: 64.5–172 mg kg^{-1}

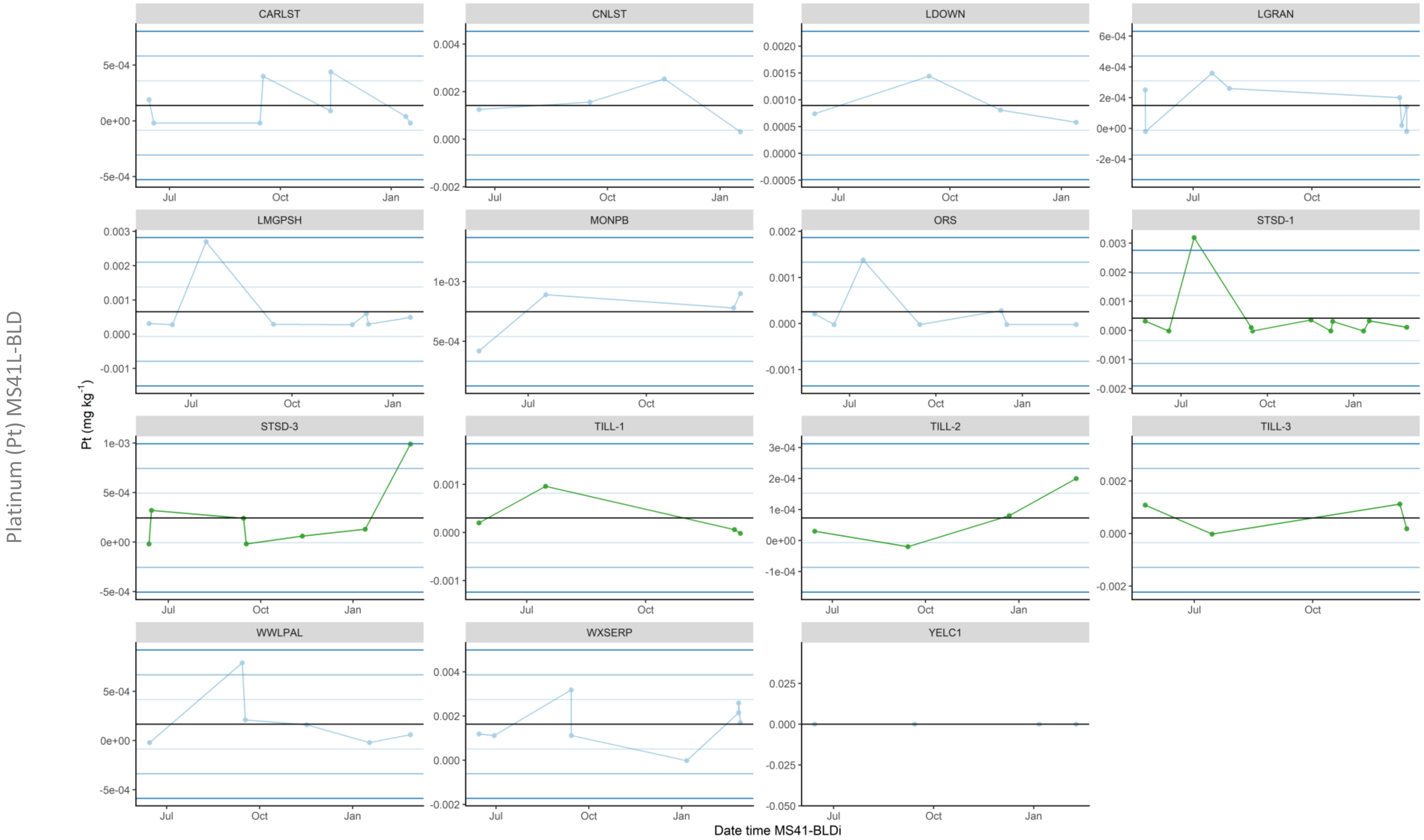


Palladium (Pd) sample data IQR: 0.0000065–0.000161 mg kg^{-1}

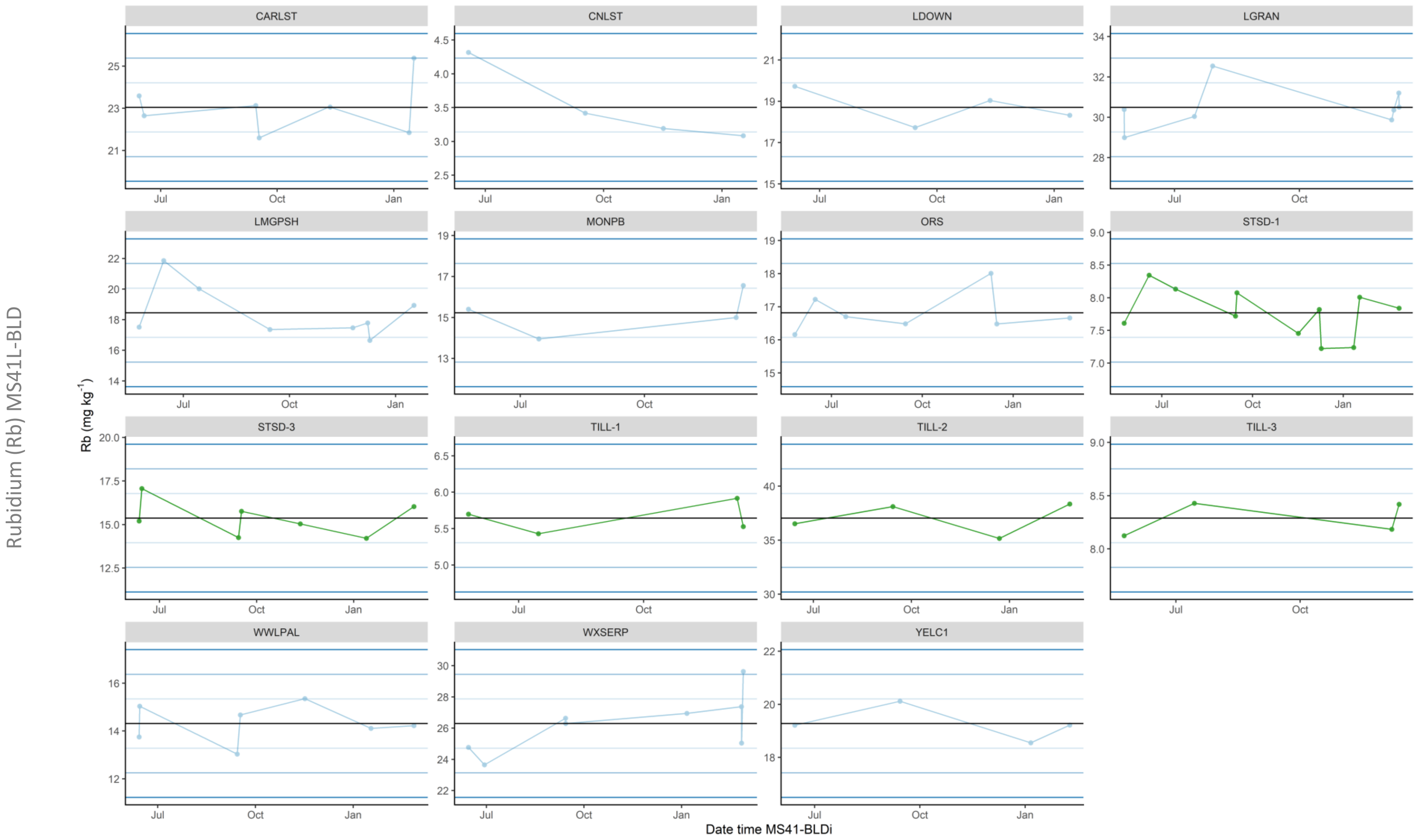
pH $CaCl_2$



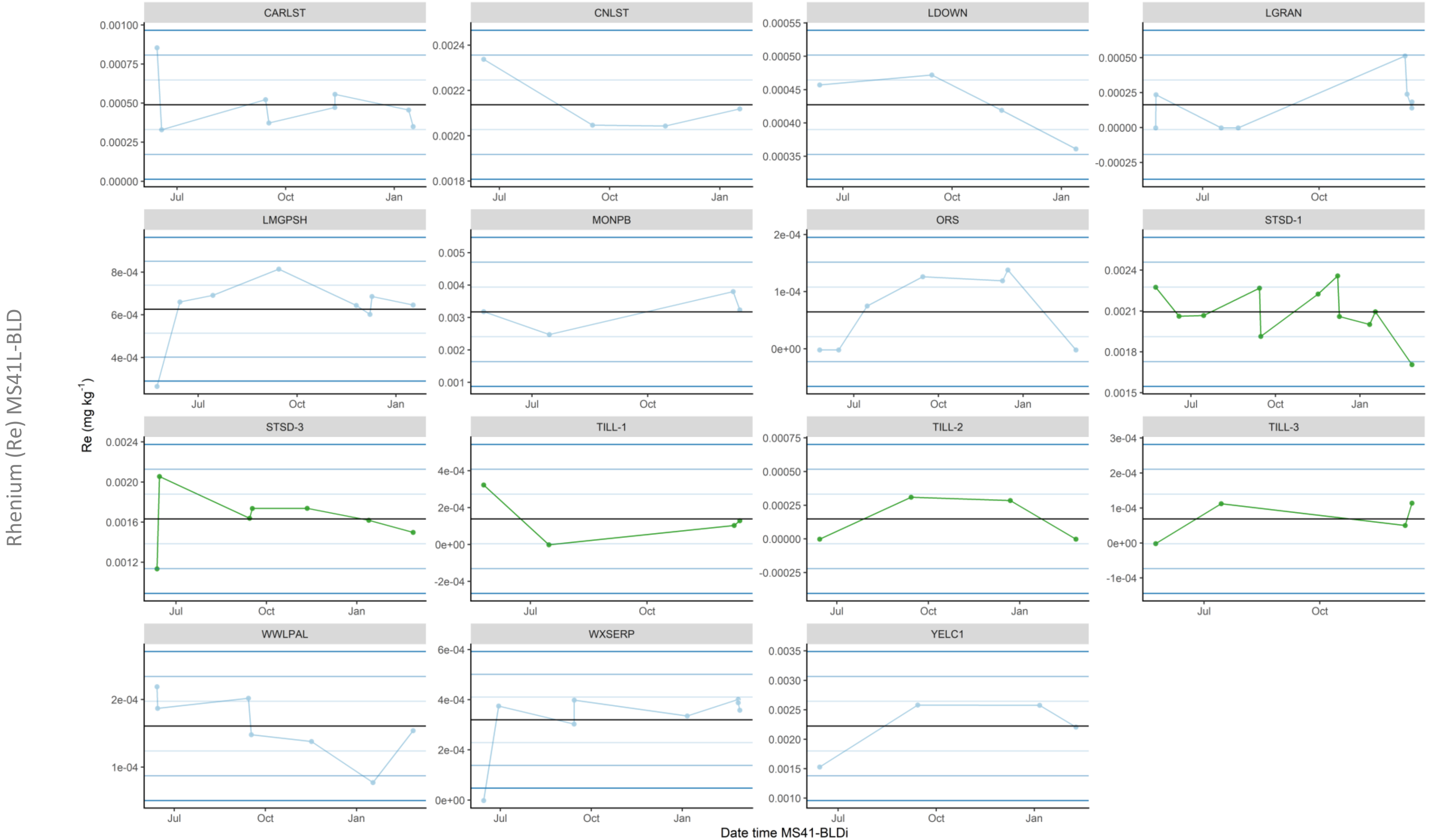
pH sample data IQR: 6.6–7.1



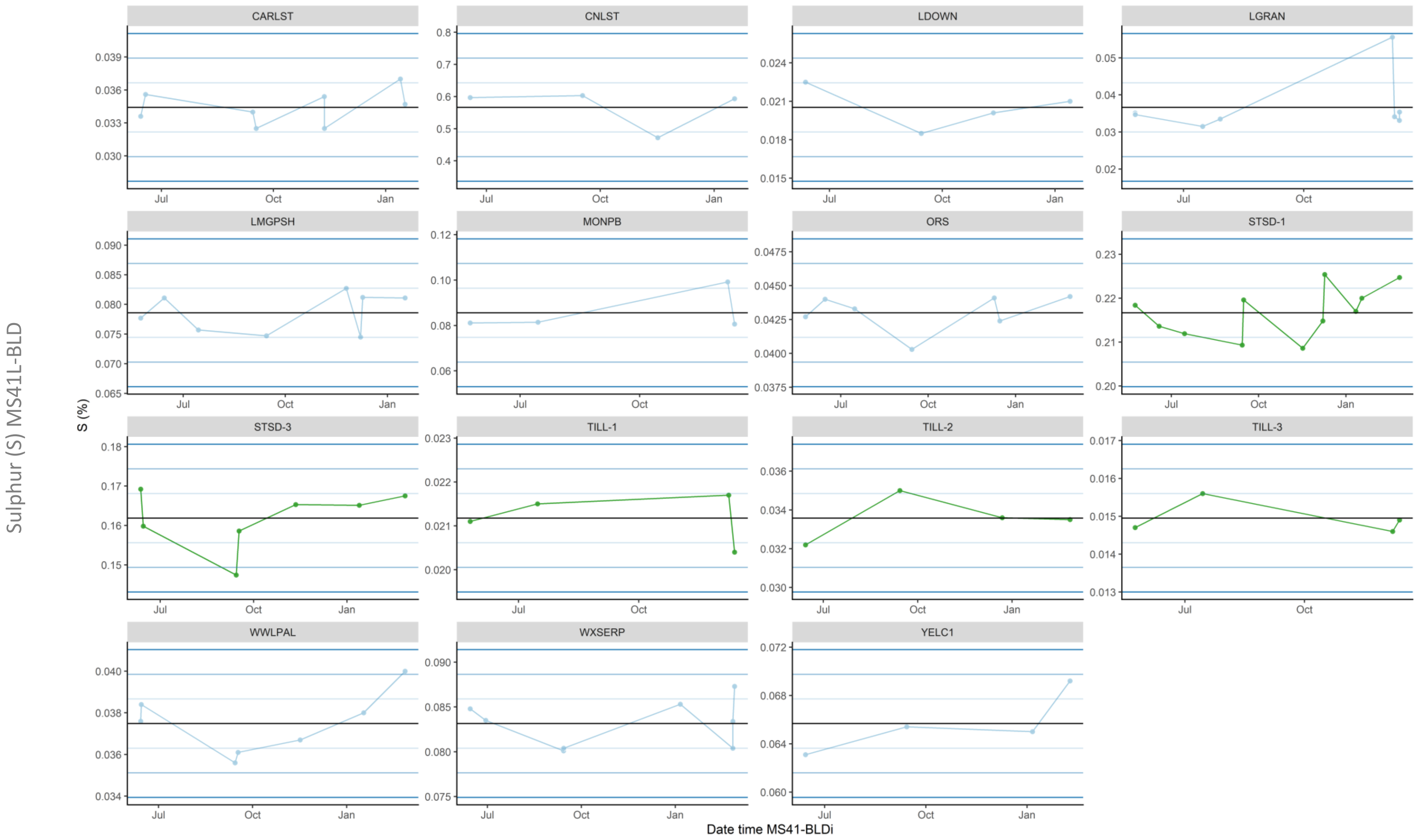
Platinum (Pt) sample data IQR: 0.00044–0.001 mg kg-1



Rubidium (Rb) sample data IQR: 8.01–10.3 mg kg^{-1}

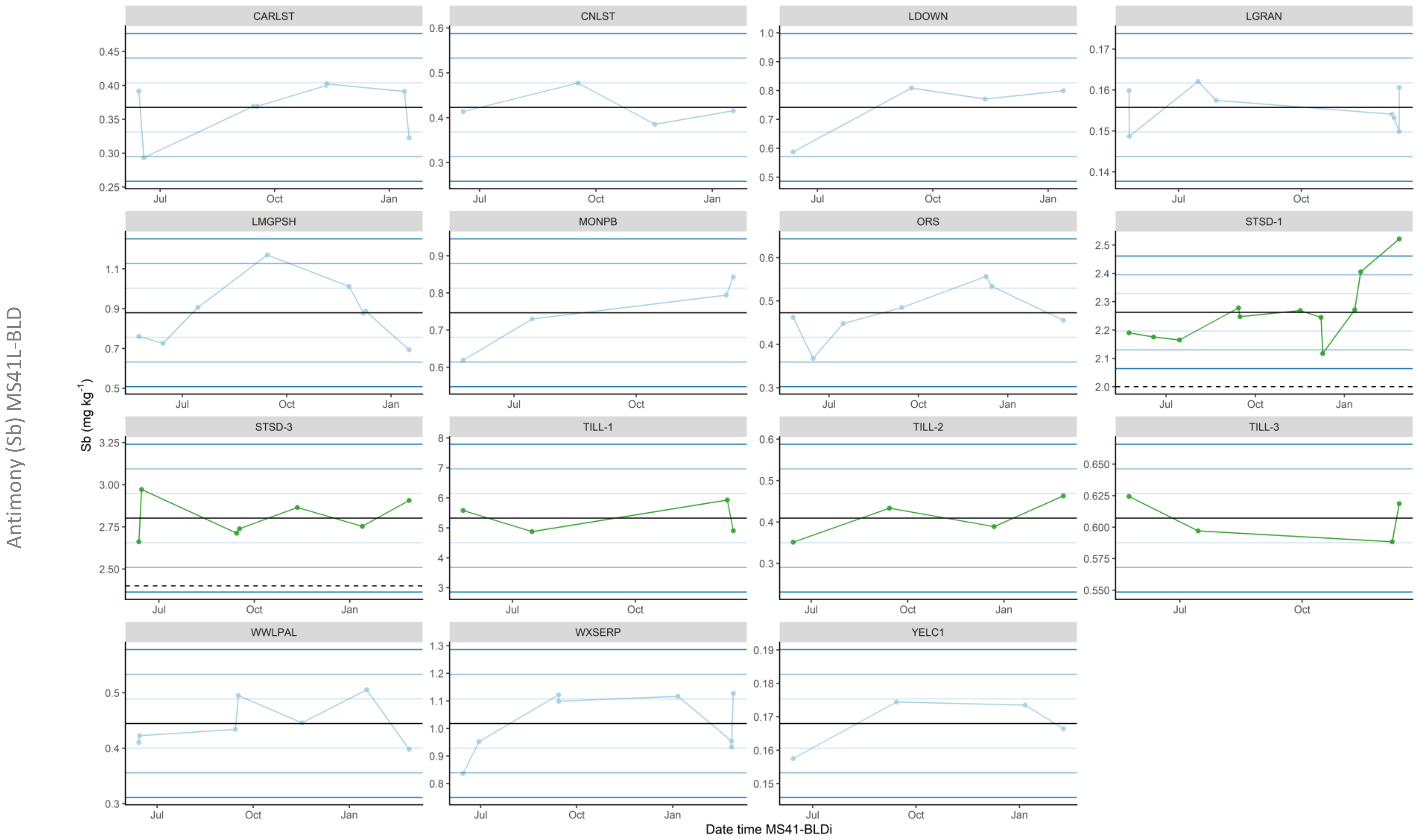


Rhenium (Re) sample data IQR: 0.000722–0.00158 mg kg^{-1}



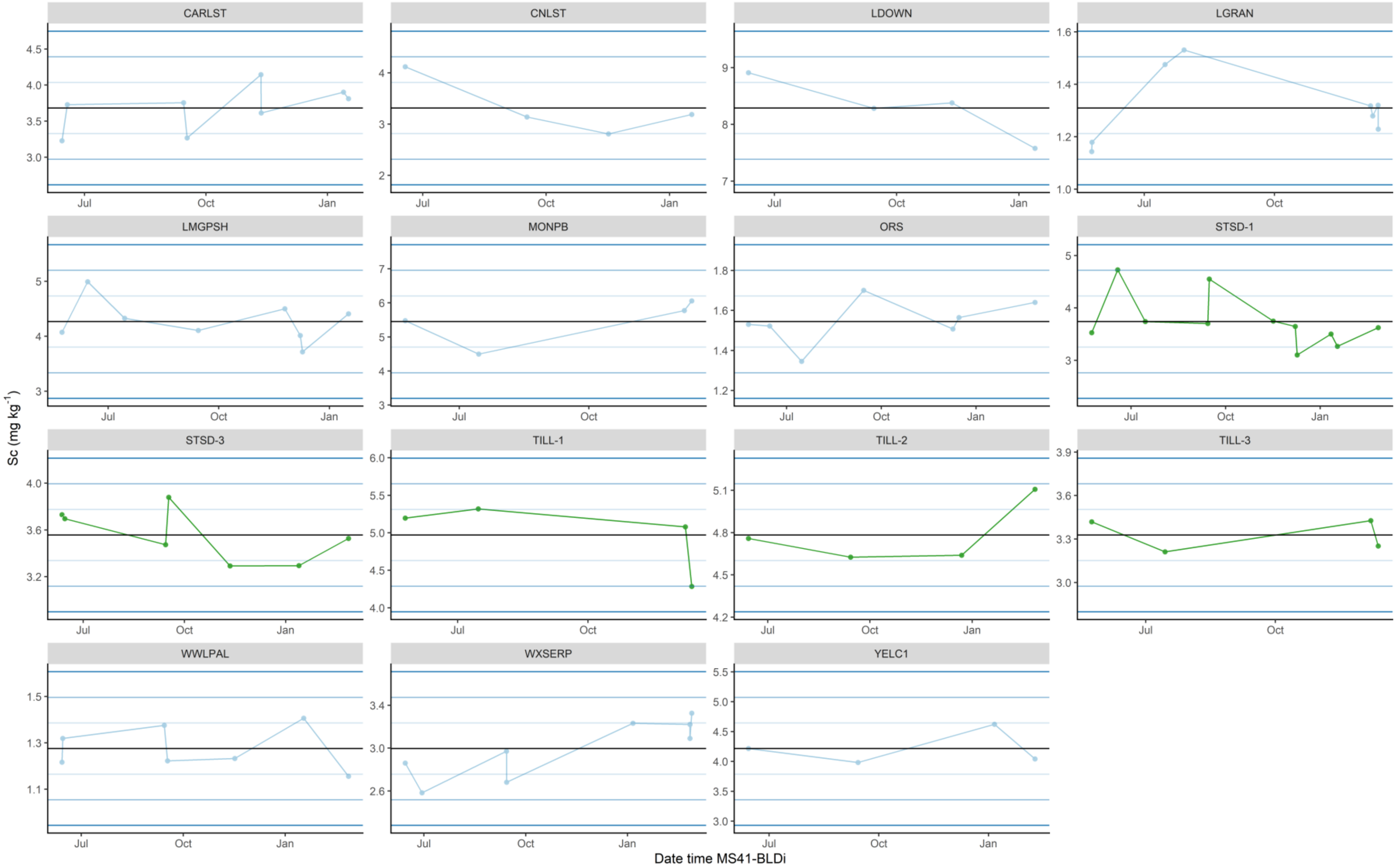
Sulphur (S) sample data IQR: 0.0658–0.093 %

AURUM GLOBAL EXPLORATION



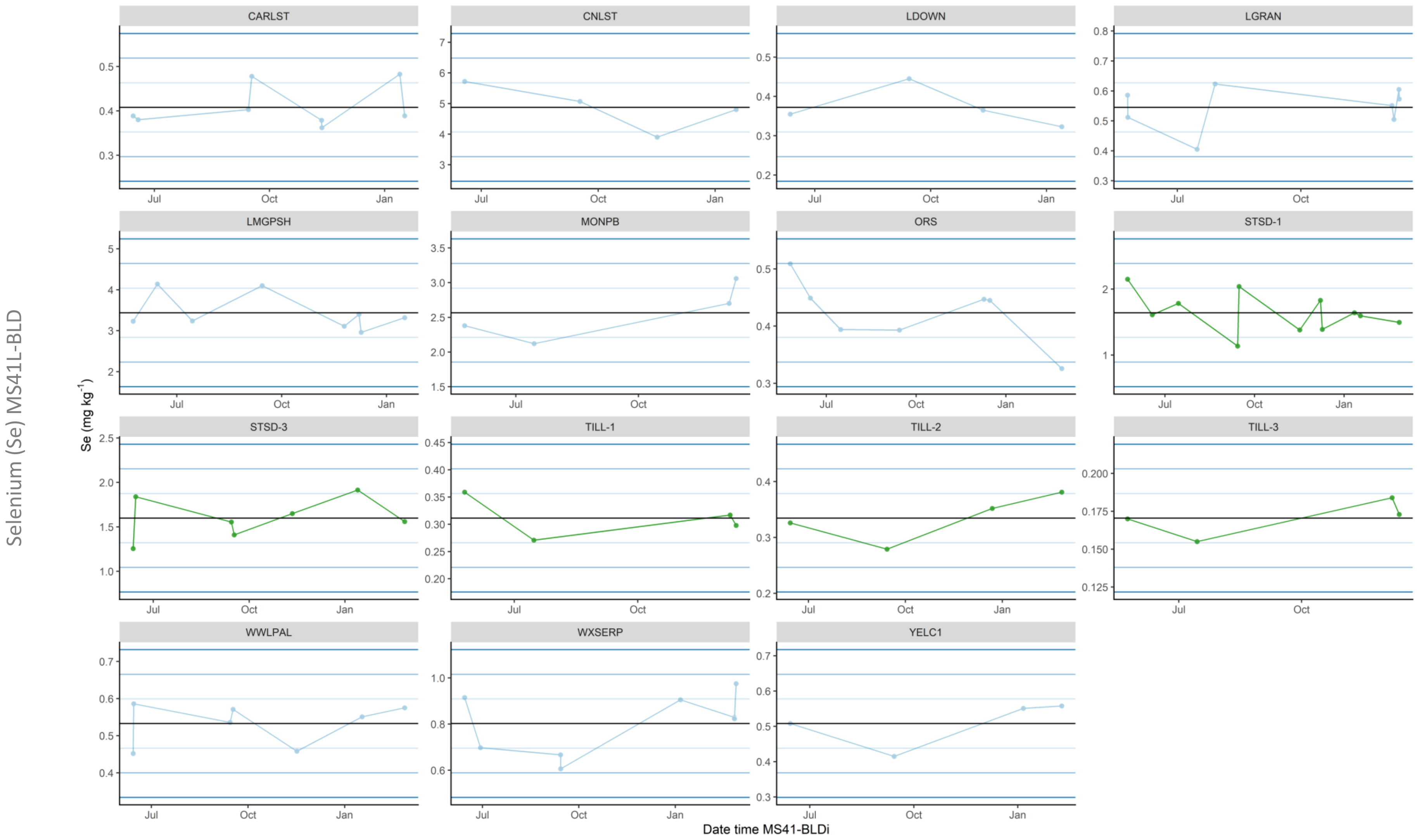
Antimony (Sb) sample data IQR: 1.18–2.16 mg kg^{-1}

Scandium (Sc) MS41L-BLD



Scandium (Sc) sample data IQR: 3.05–3.75 mg kg^{-1}

AURUM GLOBAL EXPLORATION



Selenium (Se) sample data IQR: 0.816–1.14 mg kg^{-1}

Tin (Sn) MS41L-BLD

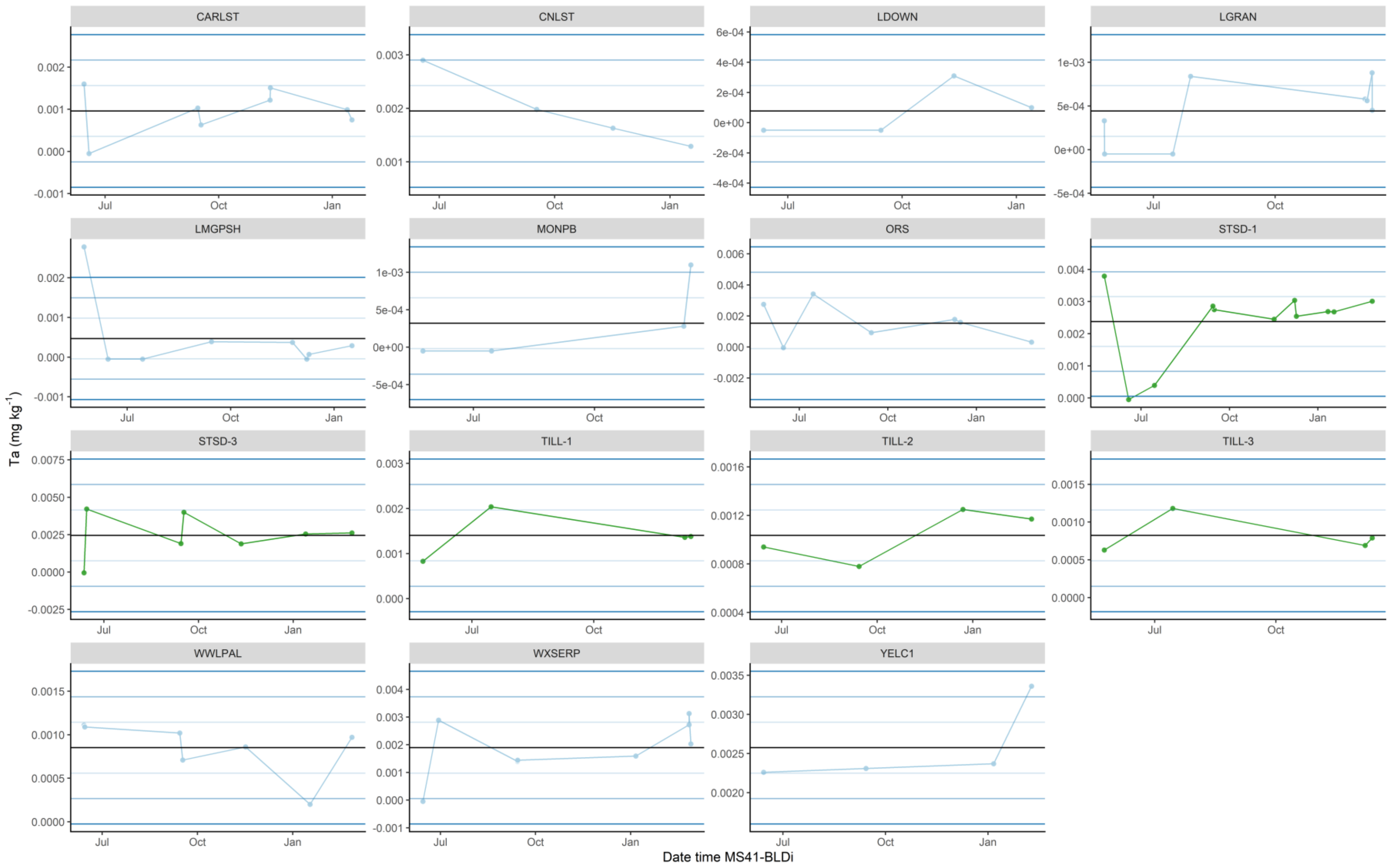
Tin (Sn) sample data IQR: 2.55–8.78 mg kg^{-1}

Strontium (Sr) MS41L-BLD

Strontium (Sr) sample data IQR: 45.1–124 mg kg^{-1}

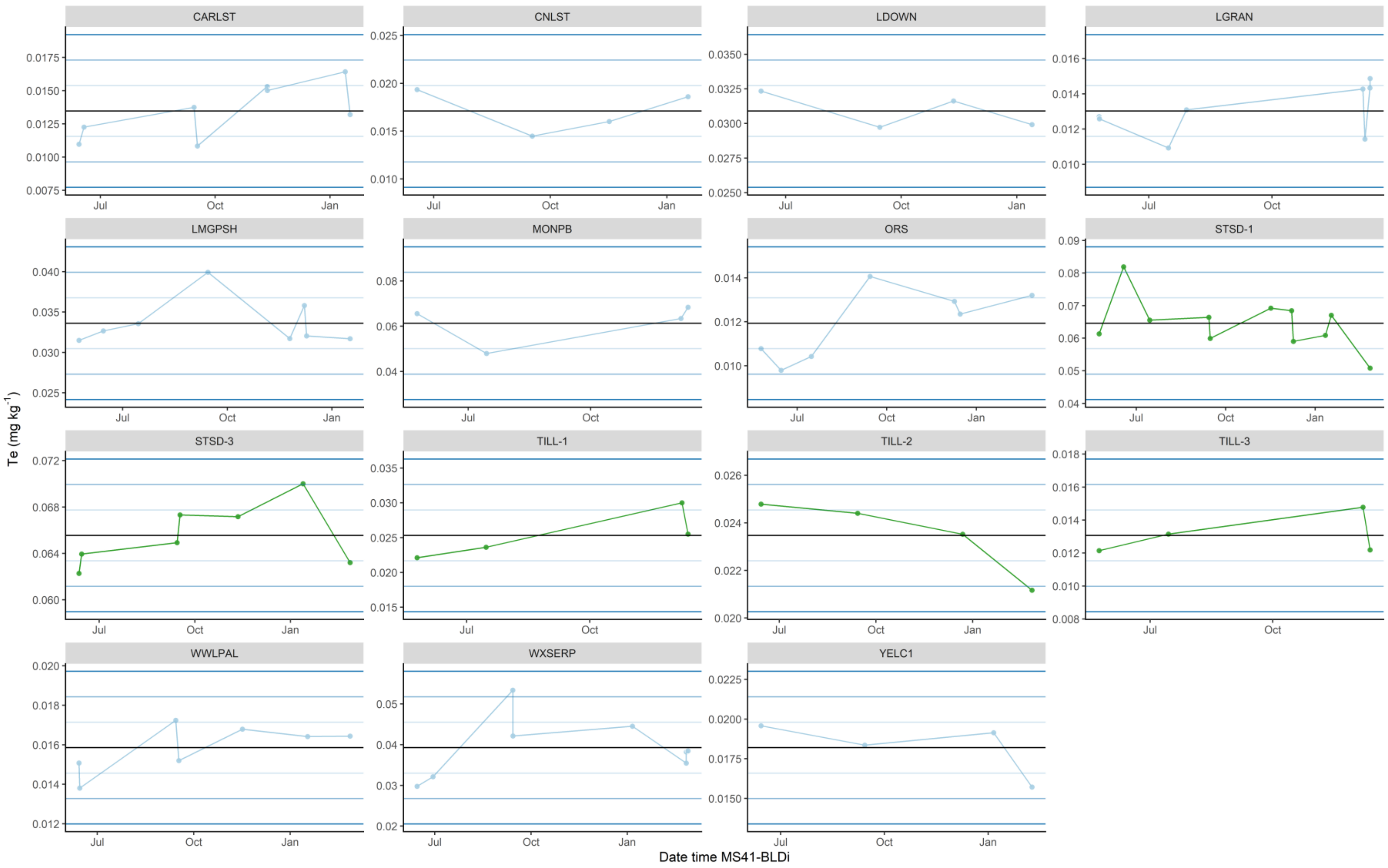
AURUM GLOBAL EXPLORATION

Tantalum (Ta) MS41L-BLD



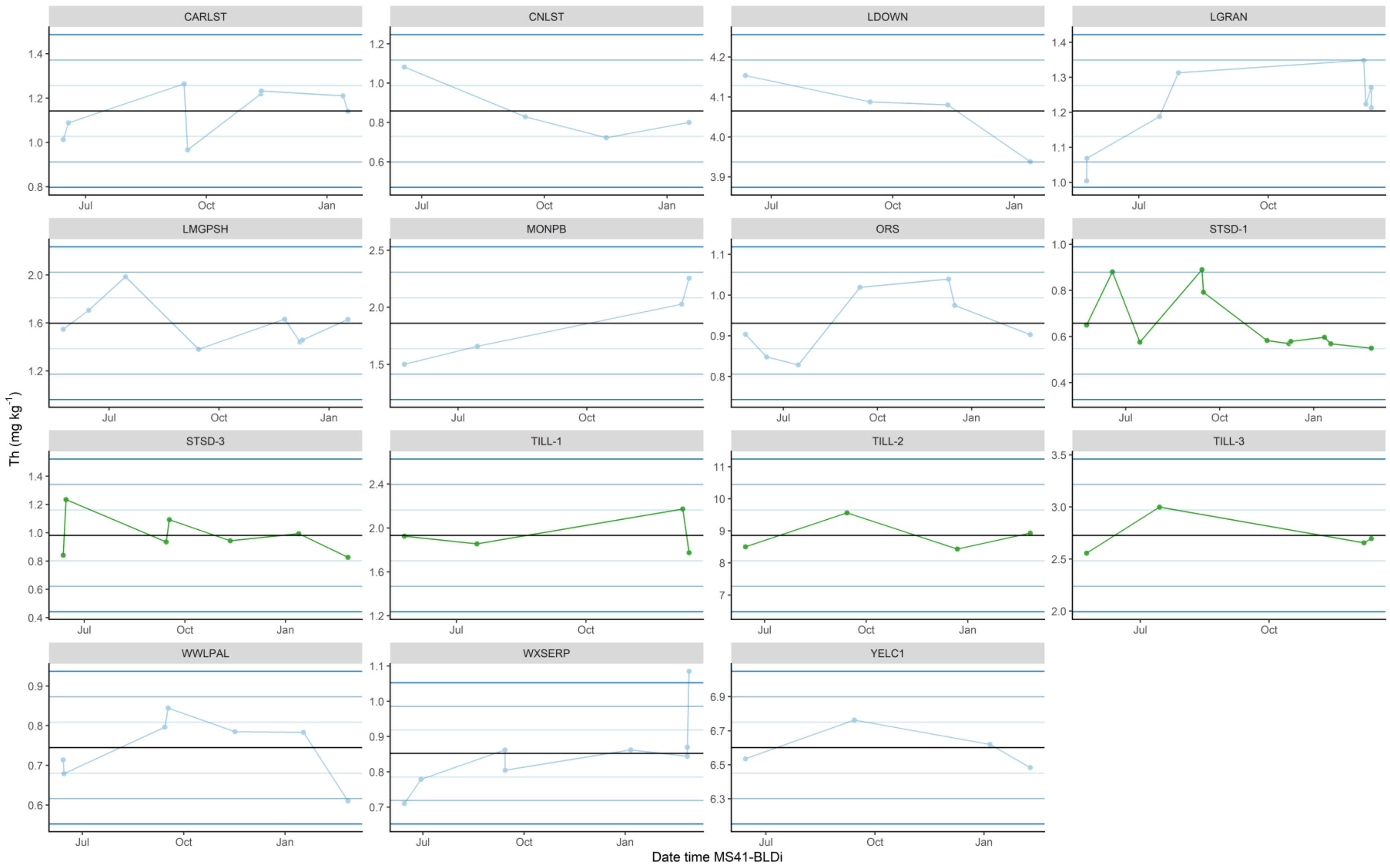
Tantalum (Ta) sample data IQR: 0.00054-0.00101 mg kg^{-1}

Tellurium (Te) MS41L-BLD



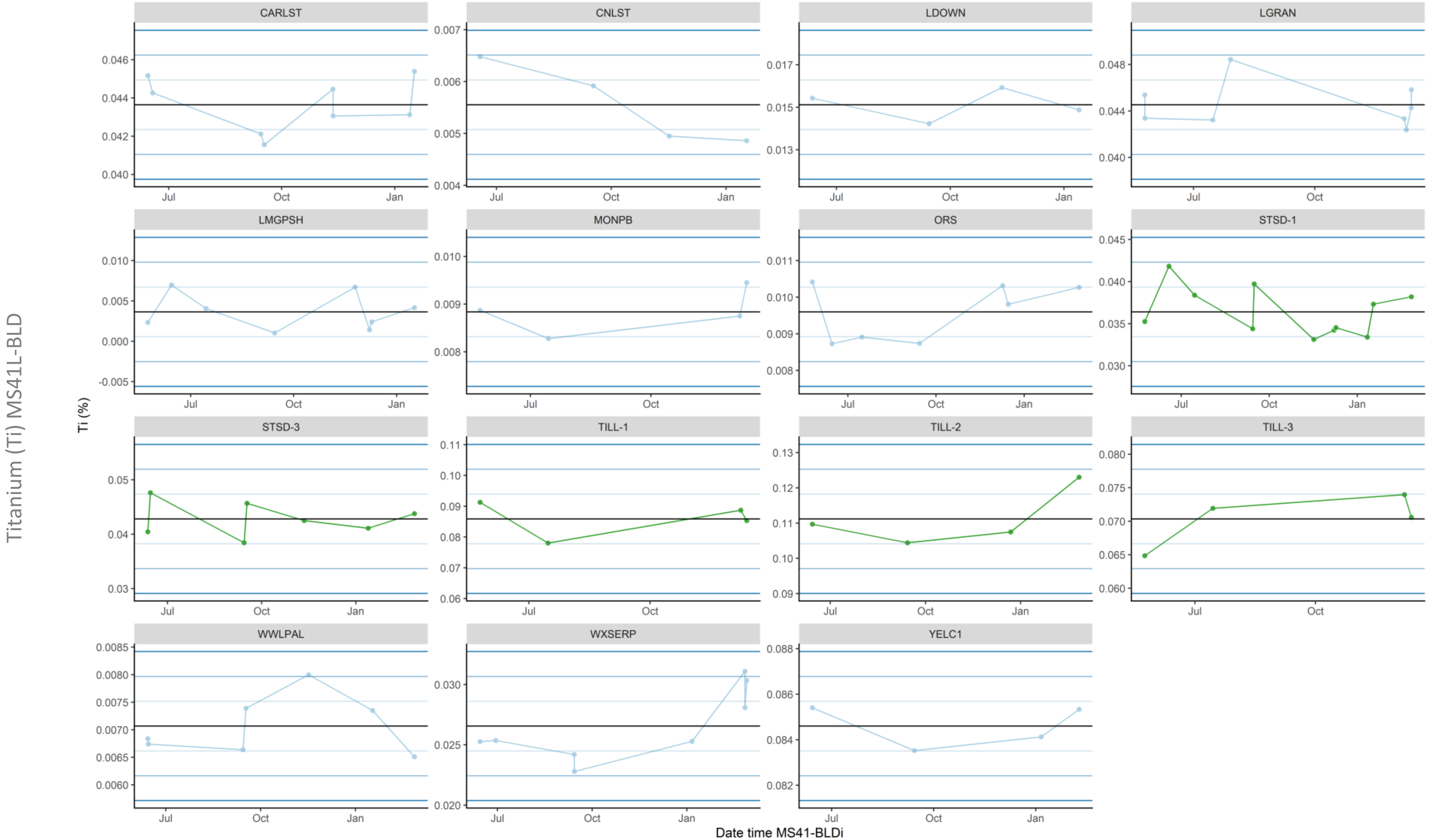
Tellurium (Te) sample data IQR: 0.0257-0.0355 mg kg^{-1}

Thorium (Th) MS41L-BLD

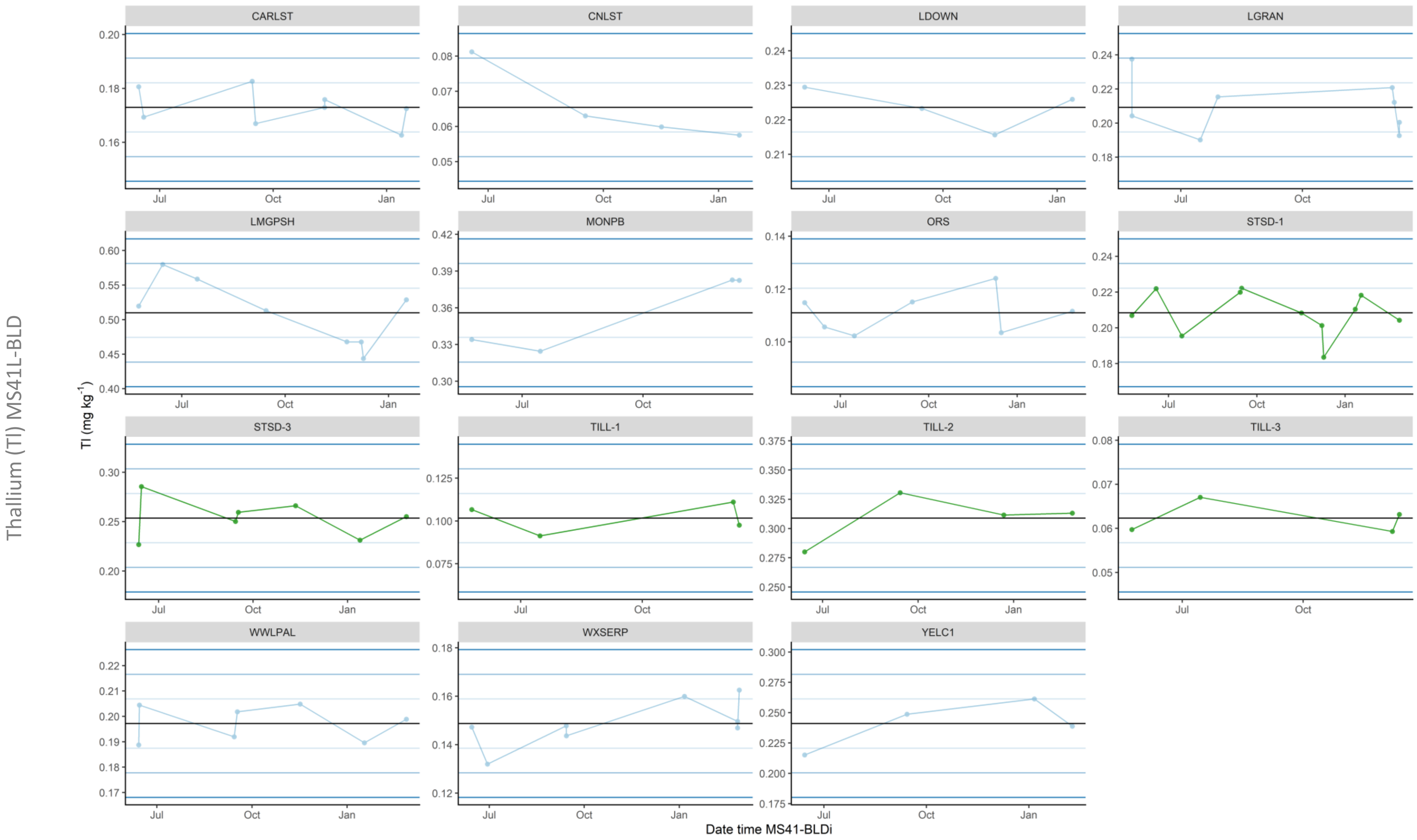


Thorium (Th) sample data IQR: 1.12–1.40 mg kg^{-1}

AURUM GLOBAL EXPLORATION

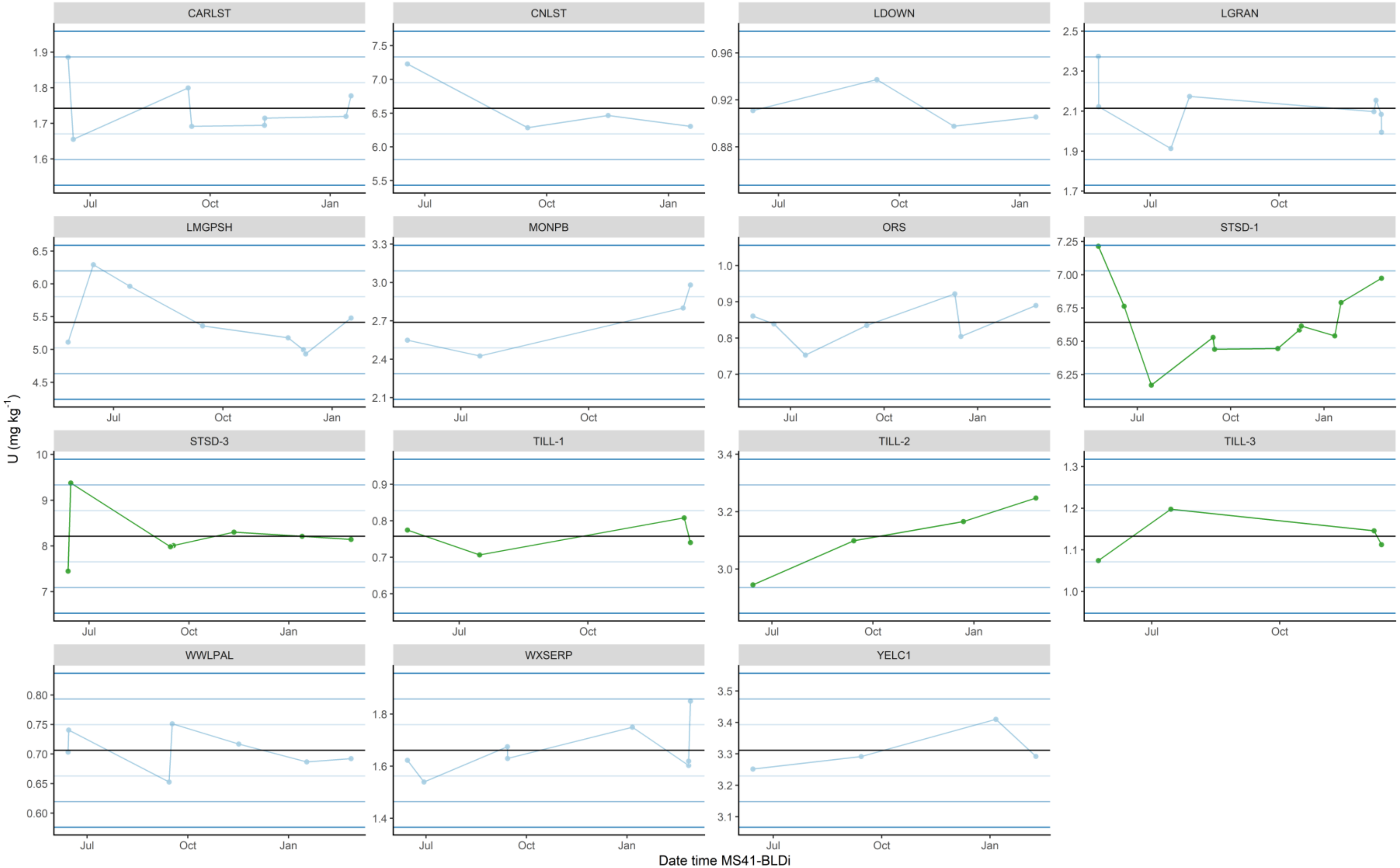


Titanium (Ti) sample data IQR: 0.0042-0.00709 %

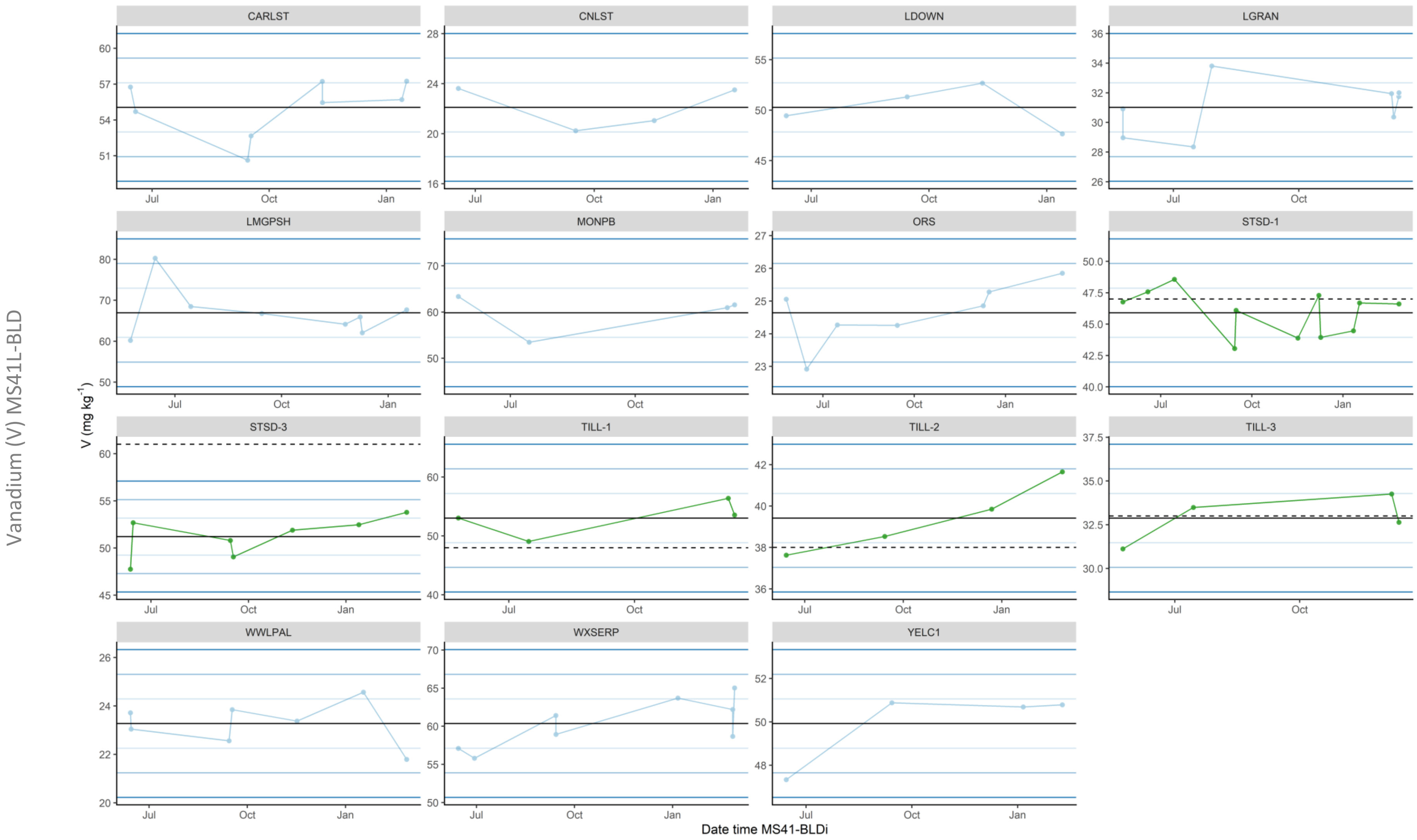


Thallium (Tl) sample data IQR: 0.193–0.239 mg kg^{-1}

Uranium (U) MS41L-BLD

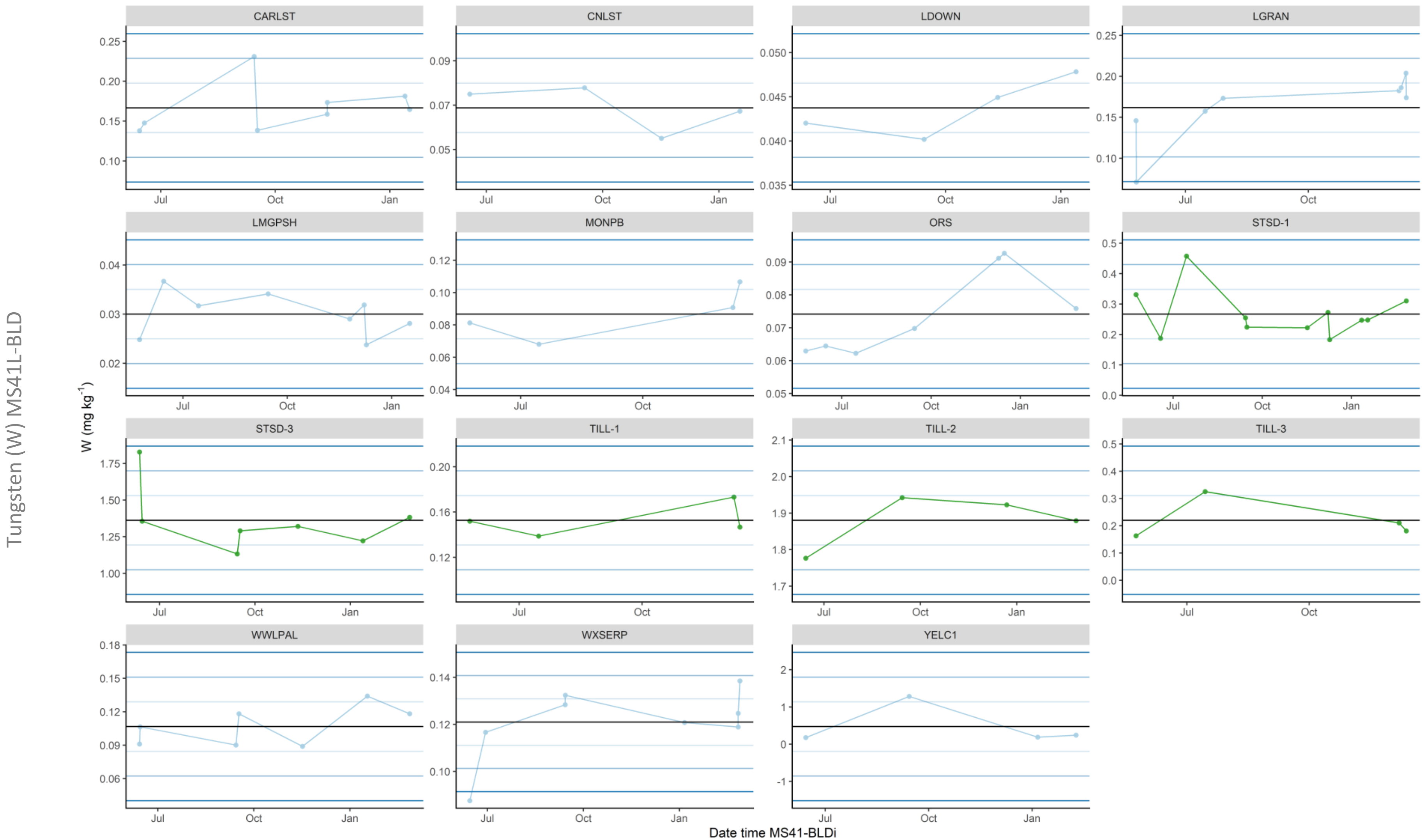


Uranium (U) sample data IQR: 0.781–0.997 mg kg^{-1}



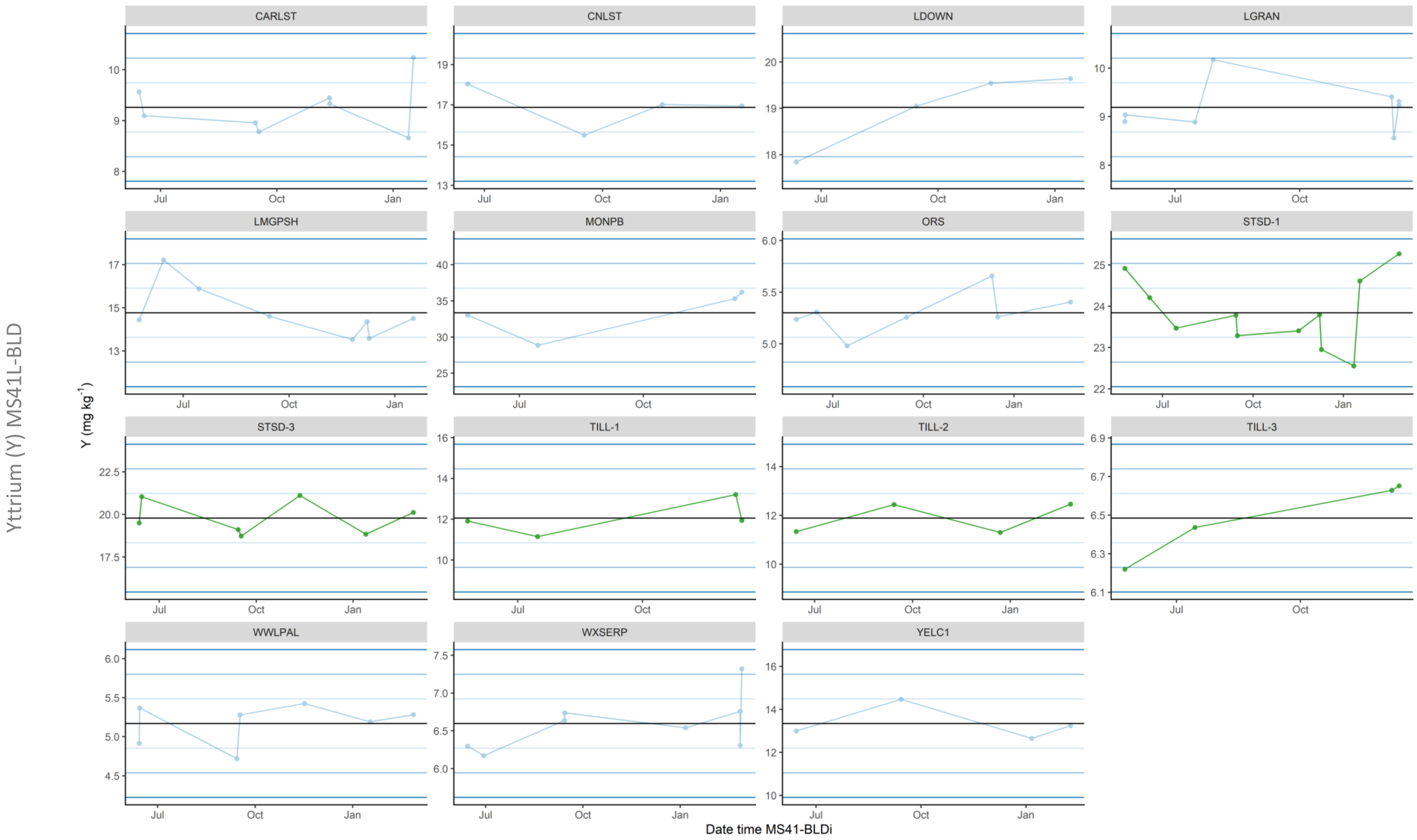
Vanadium (V) sample data IQR: 33.5–41.4 mg kg^{-1}

AURUM GLOBAL EXPLORATION



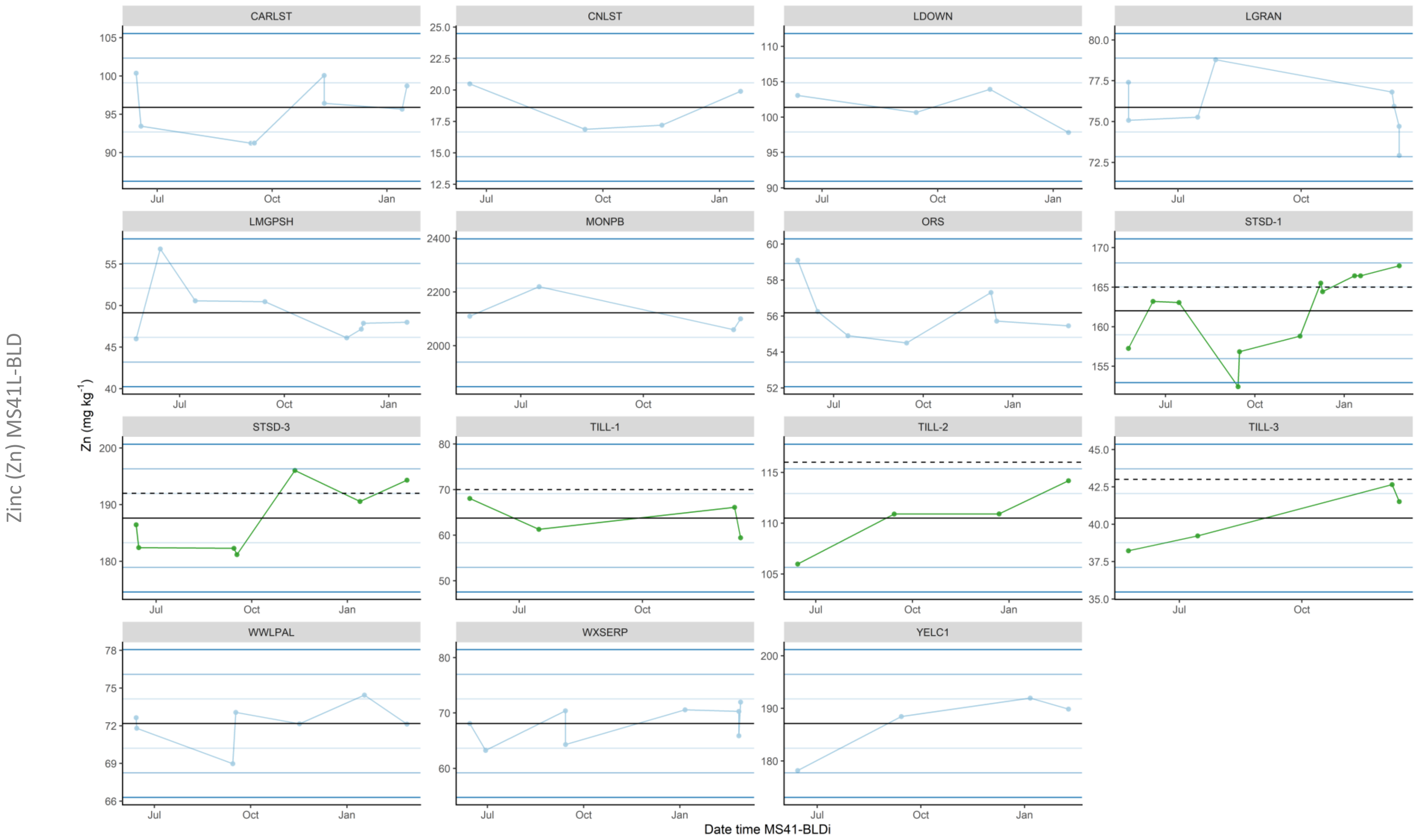
Tungsten (W) sample data IQR: 0.113-0.218 mg kg^{-1}

AURUM GLOBAL EXPLORATION

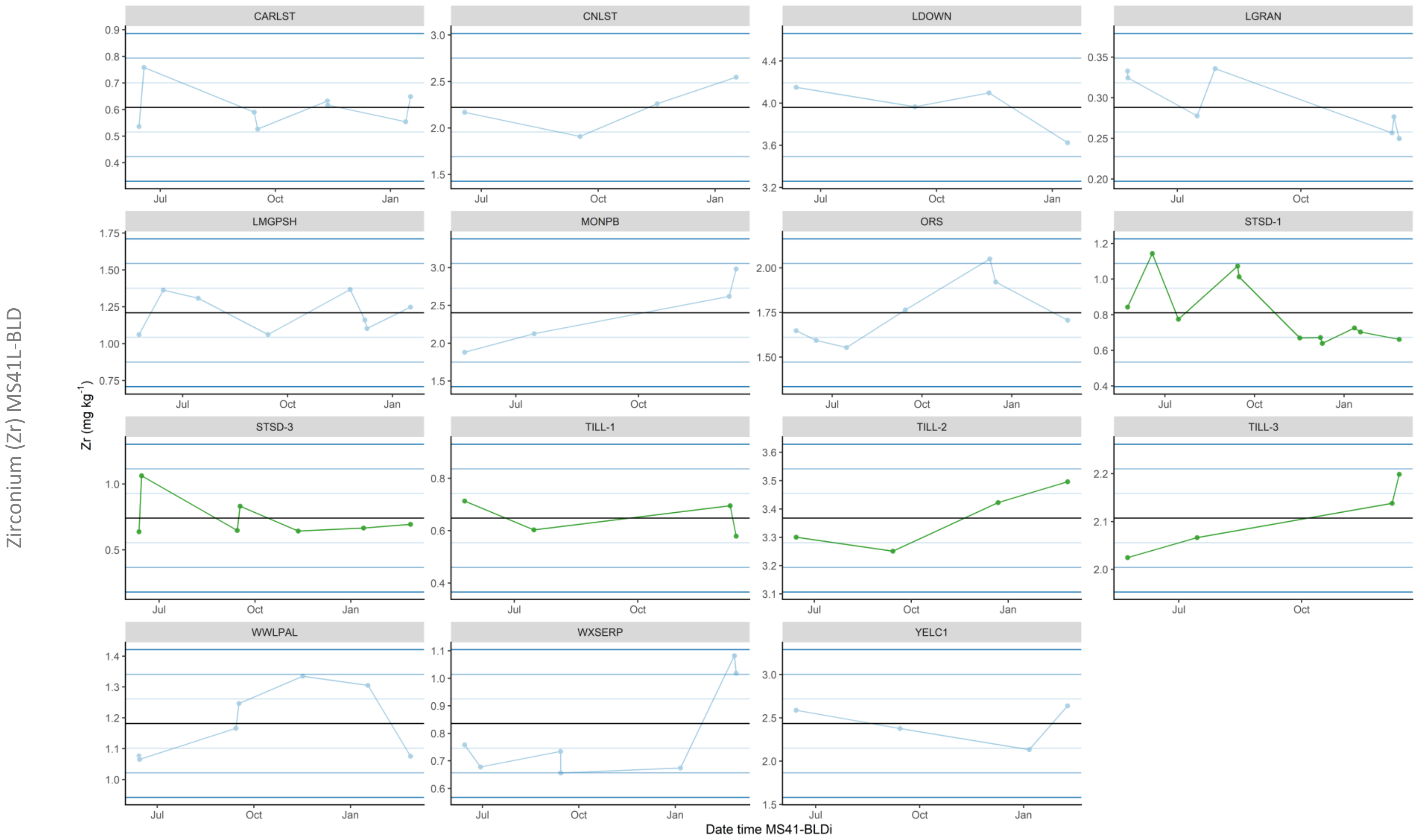


Yttrium (Y) sample data IQR: 14.2–17.3 mg kg^{-1}

AURUM GLOBAL EXPLORATION



Zinc (Zn) sample data IQR: 125–203 mg kg^{-1}



Zirconium (Zr) sample data IQR: 2.76–3.69 mg kg^{-1}

AURUM GLOBAL EXPLORATION

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):

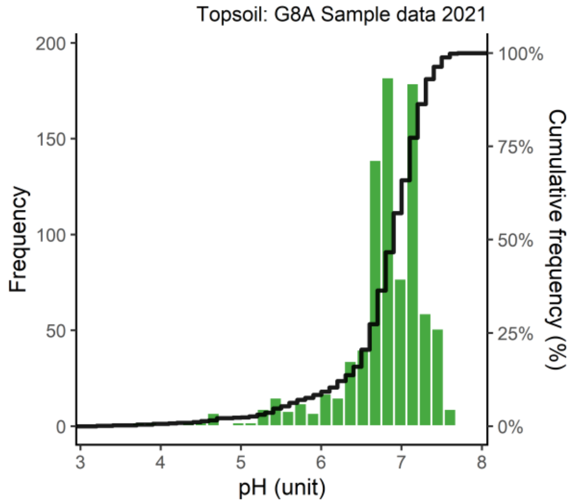
- The first chart (left) is the combined cumulative frequency and histogram. The histogram frequency (y axis left) and the cumulative frequency % (y axis right) are plotted against the analyte concentration (x axis).
- The second chart (right) is the same but data are log_{10} transformed (an exception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

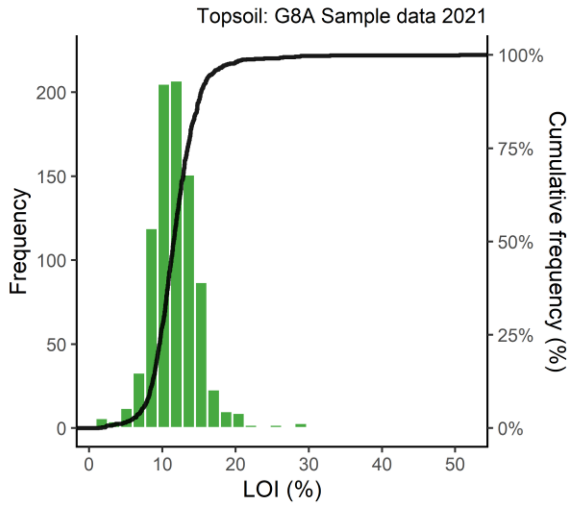
Typically a log transformation results in a less skewed distribution, and geochemical data are broadly log-normal. Censored data will sometimes display as an isolated histogram bar away from the normal data population above the LLD.

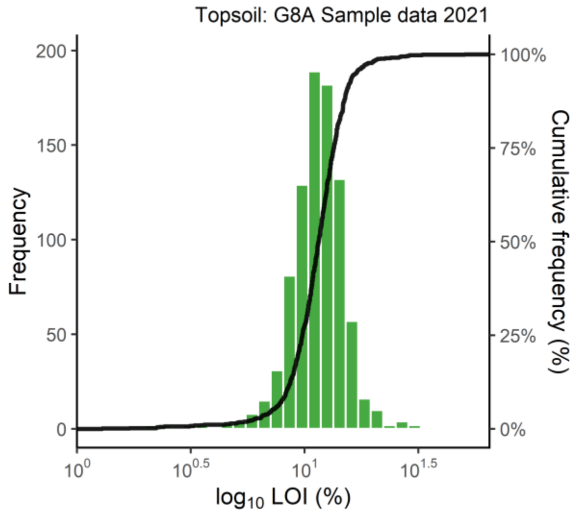
pH and LOI sample site data

Soil pH ($CaCl_2$)

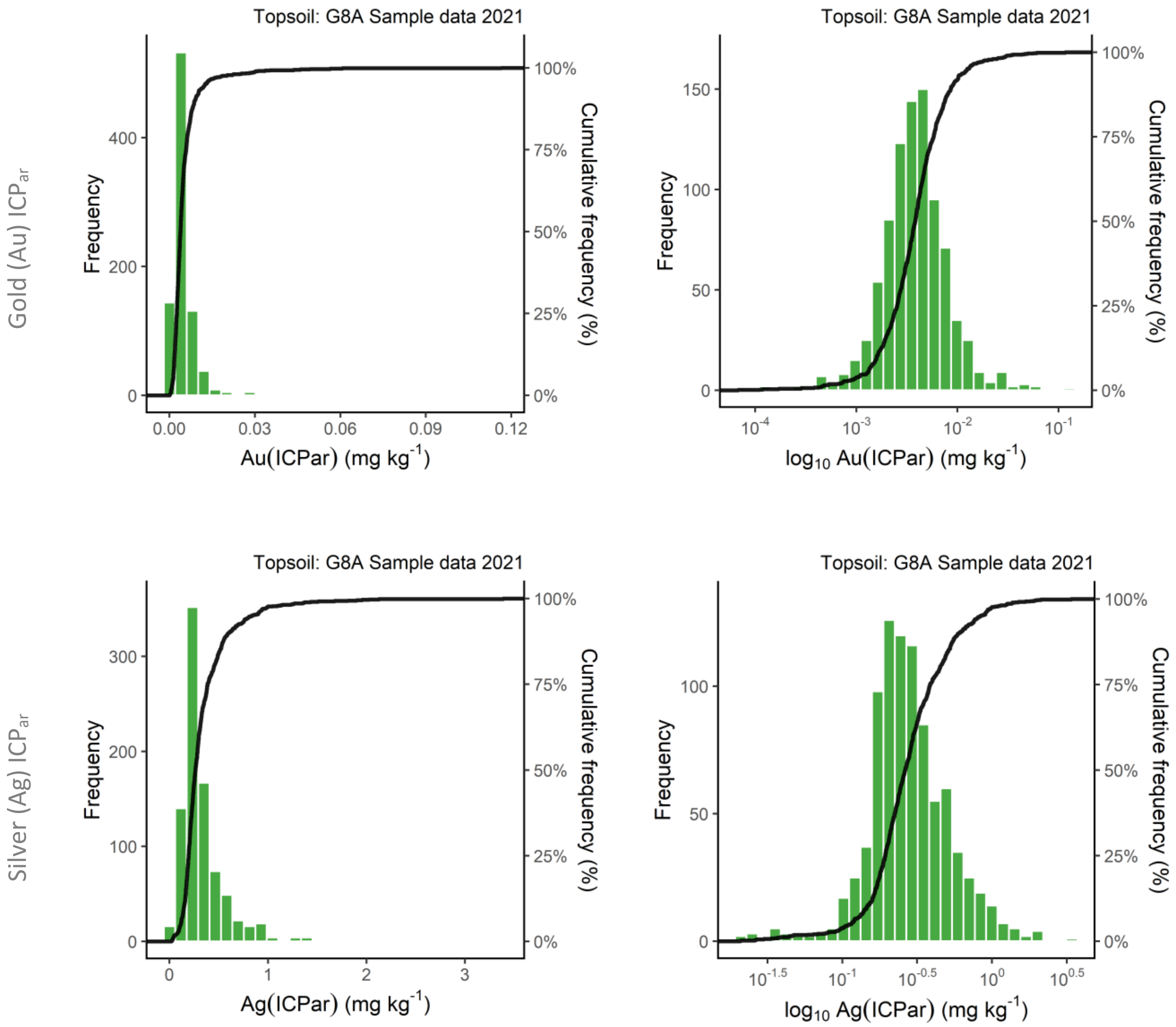


Soil loss-on-ignition (at 450C) %



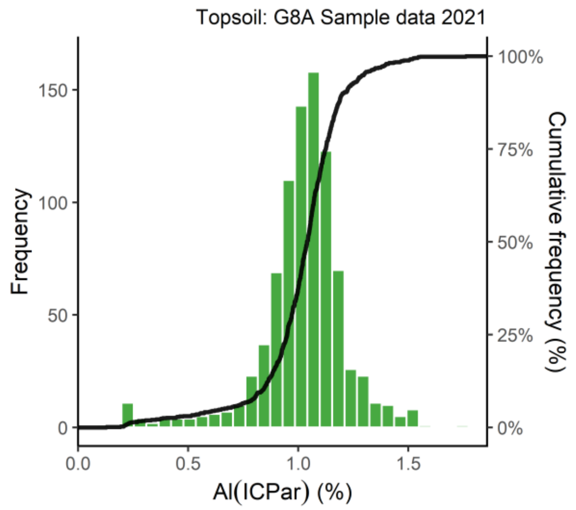


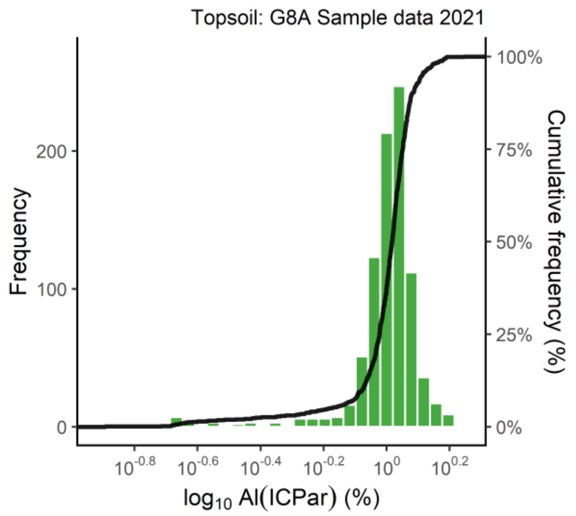
ICP$_{ar}$ sample site data



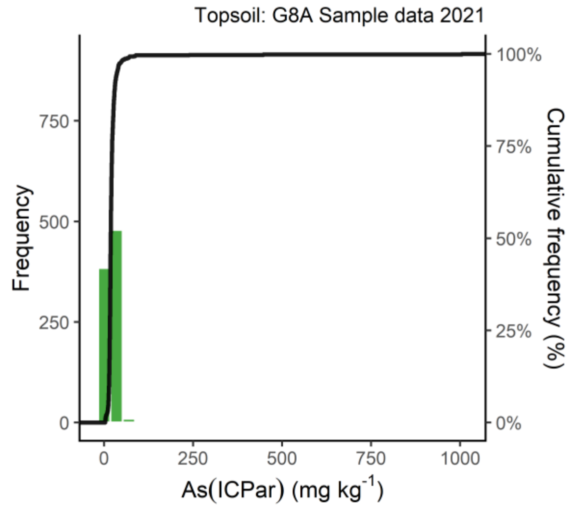
AURUM GLOBAL EXPLORATION

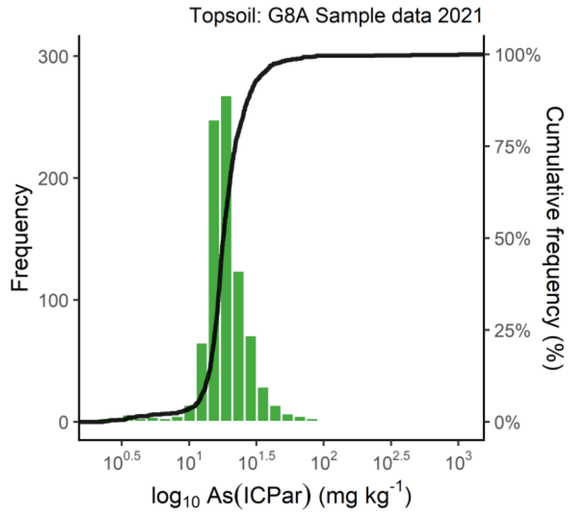
Aluminium (Al) ICP_{ar}



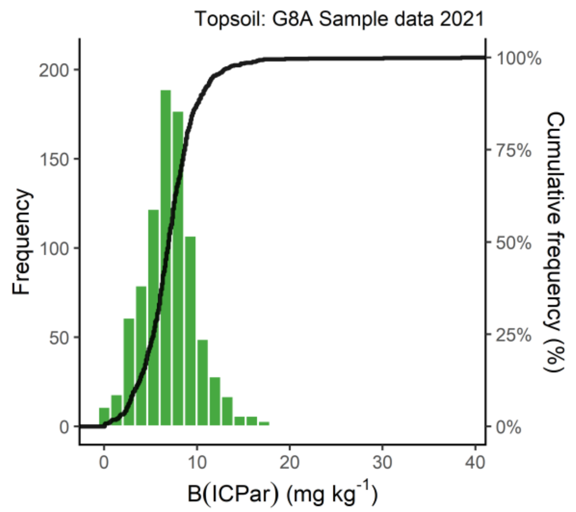


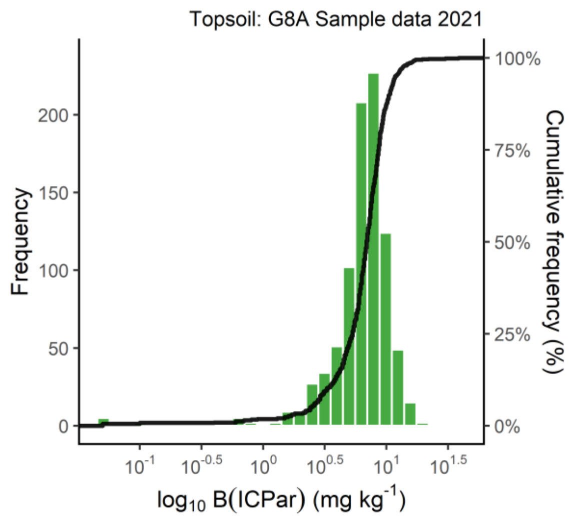
Arsenic (As) ICP_{ar}



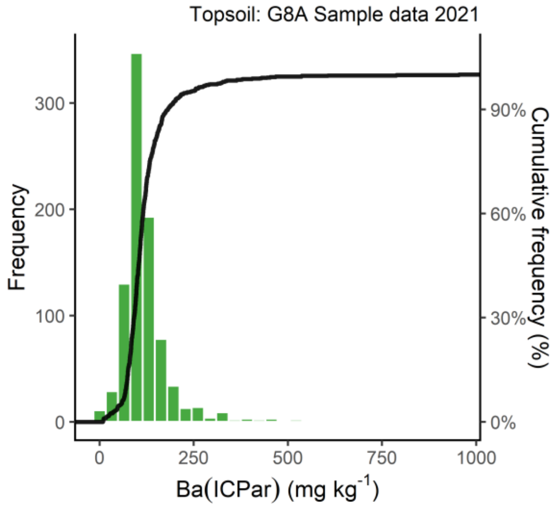


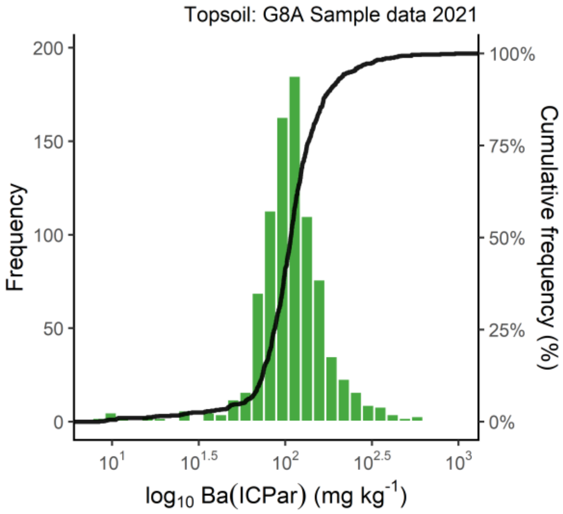
Boron (B) ICP_{ar}



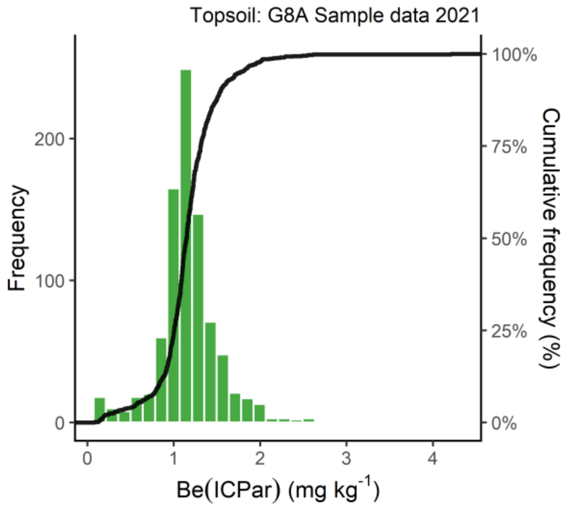


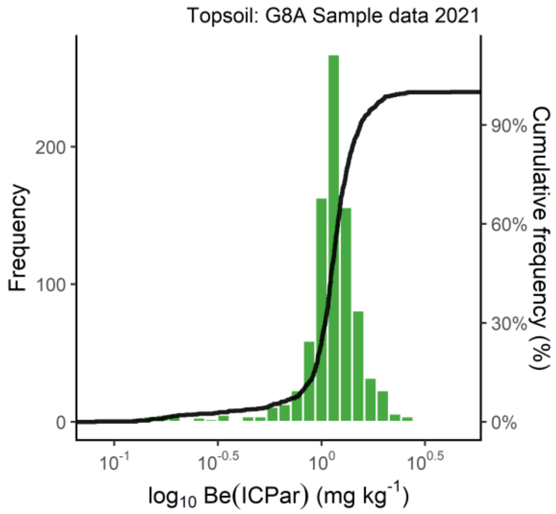
Barium (Ba) ICP_{ar}



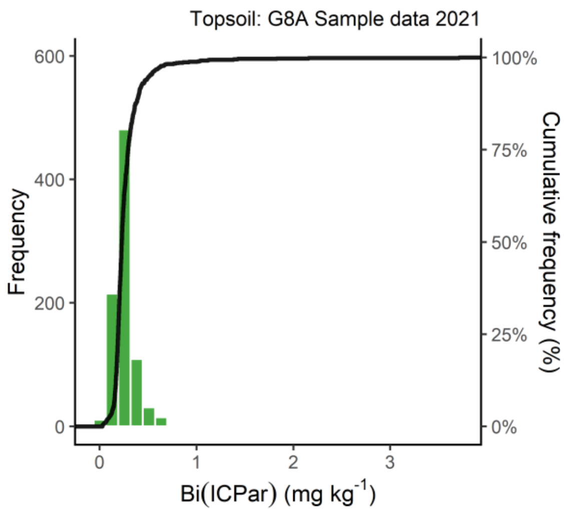


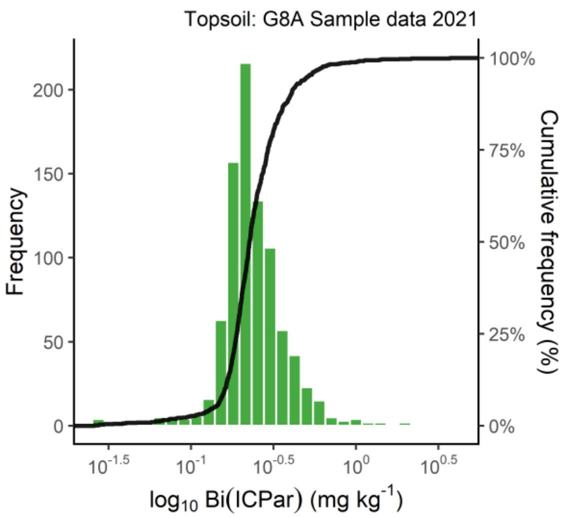
Beryllium (Be) ICP_{ar}



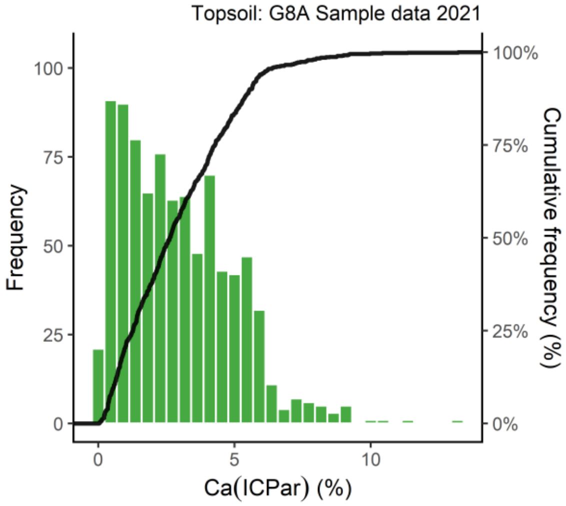


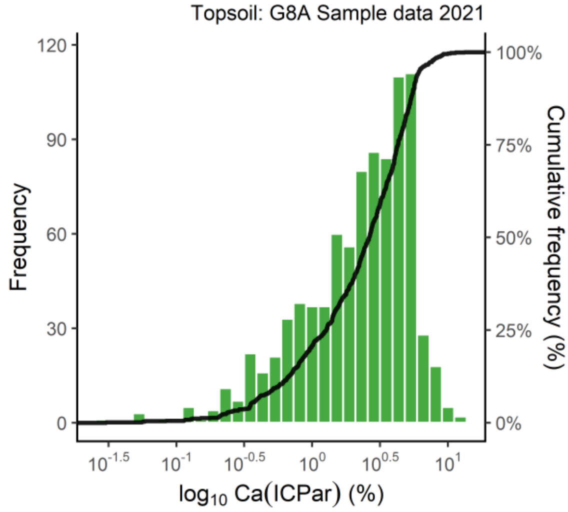
Bismuth (Bi) ICP_{ar}



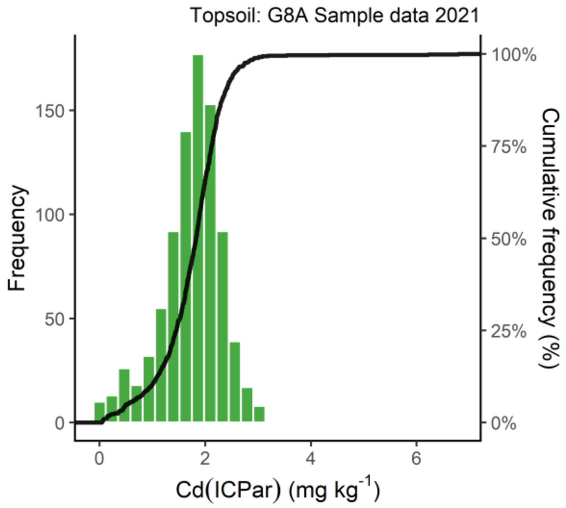


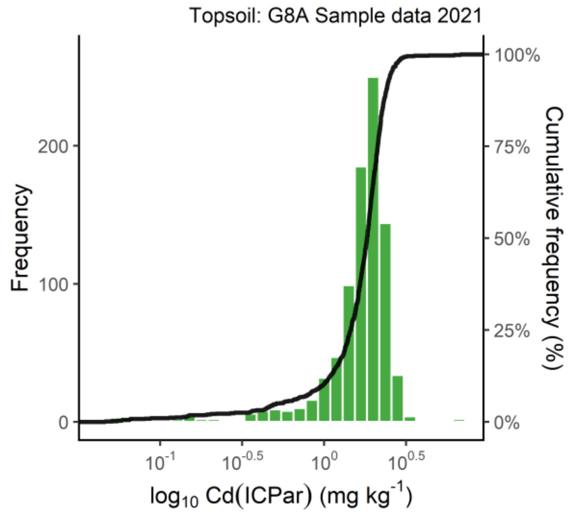
Calcium (Ca) ICP_{ar}



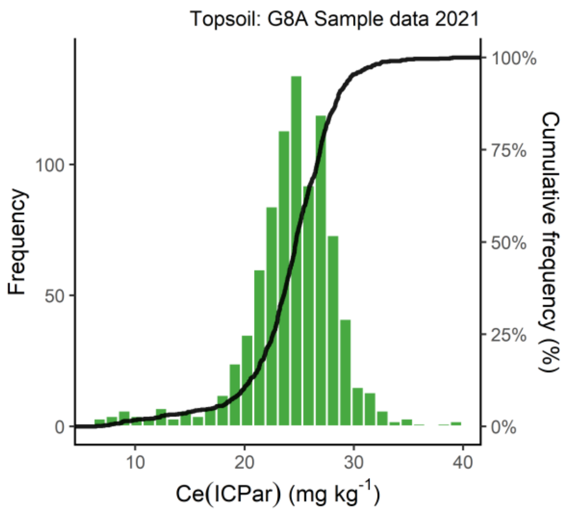


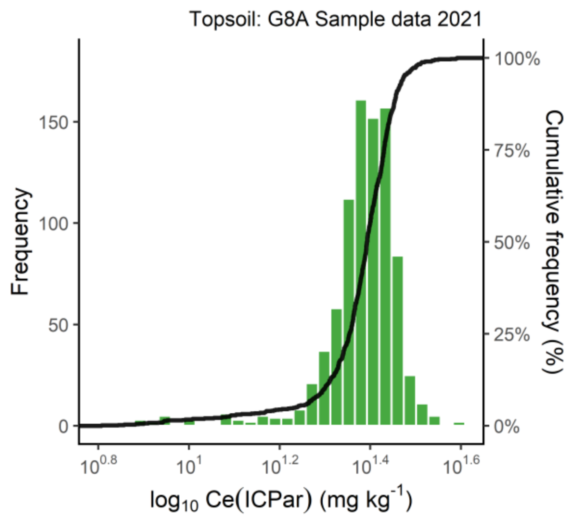
Cadmium (Cd) ICP_{ar}



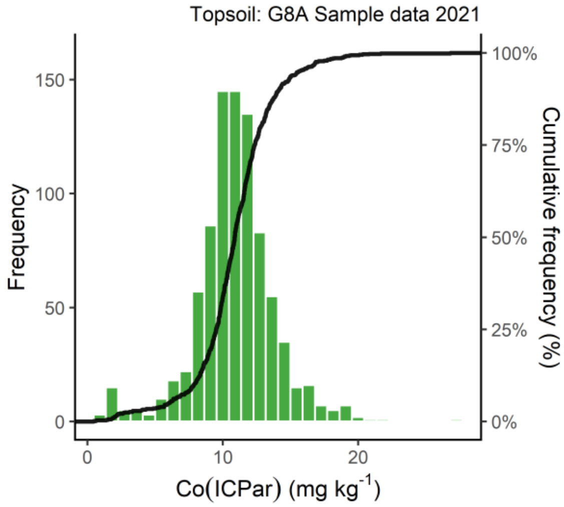


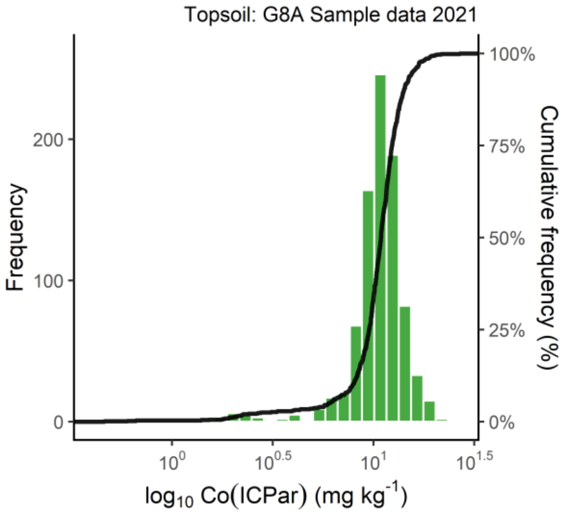
Cerium (Ce) ICP_{ar}



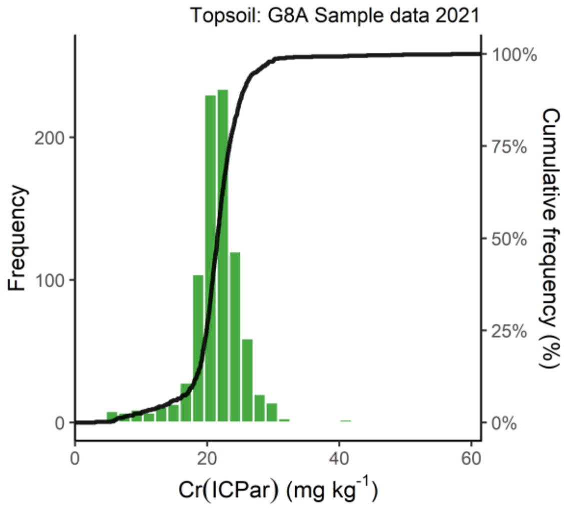


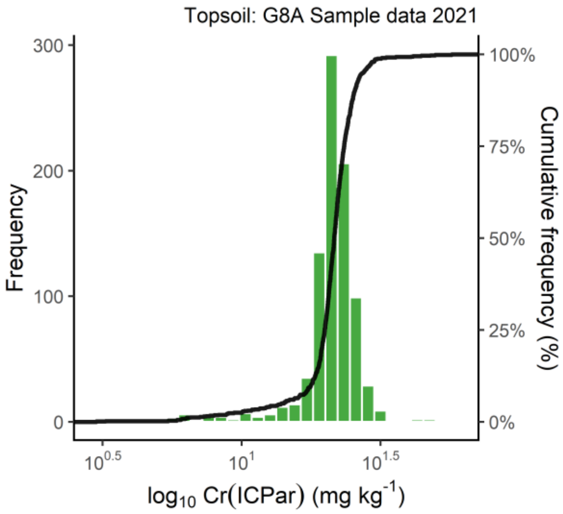
Cobalt (Co) ICP_{ar}



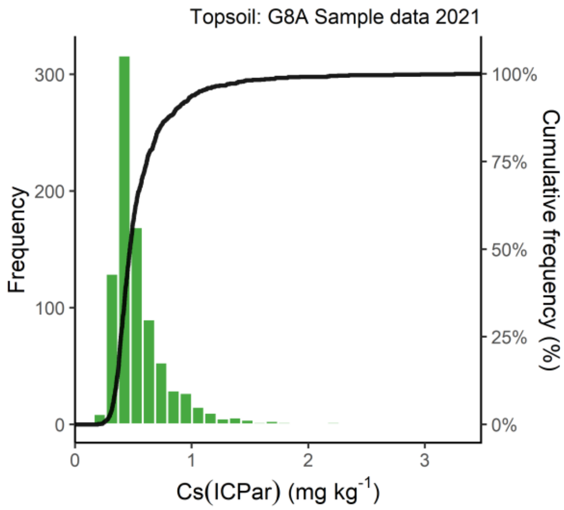


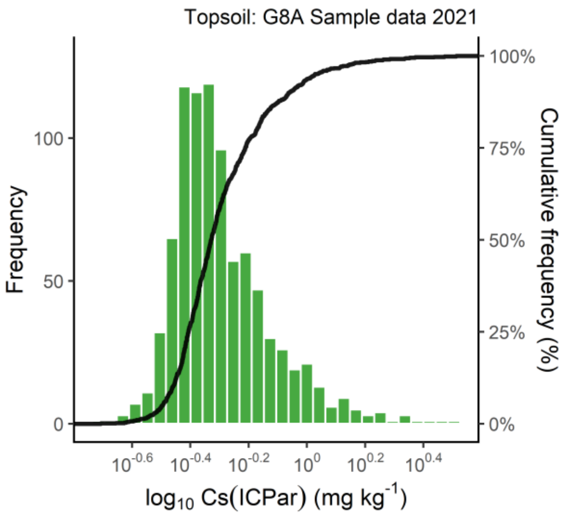
Chromium (Cr) ICP_{ar}



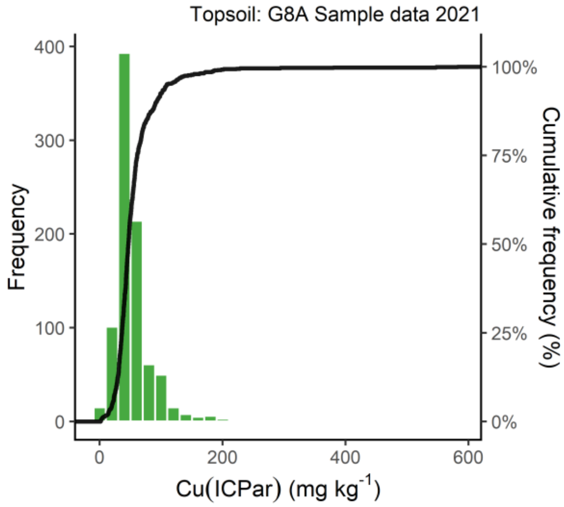


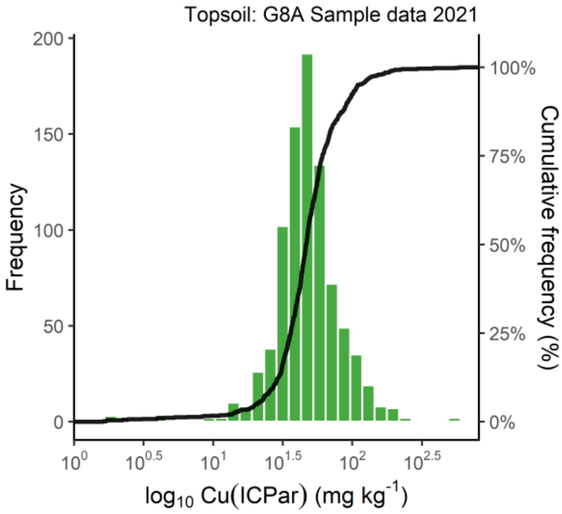
Caesium (Cs) ICP_{ar}



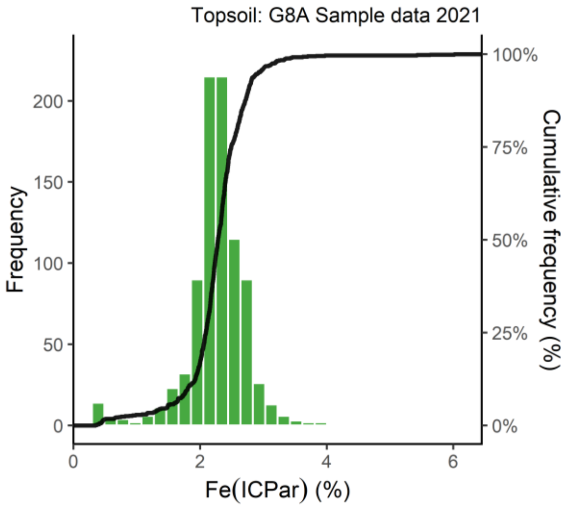


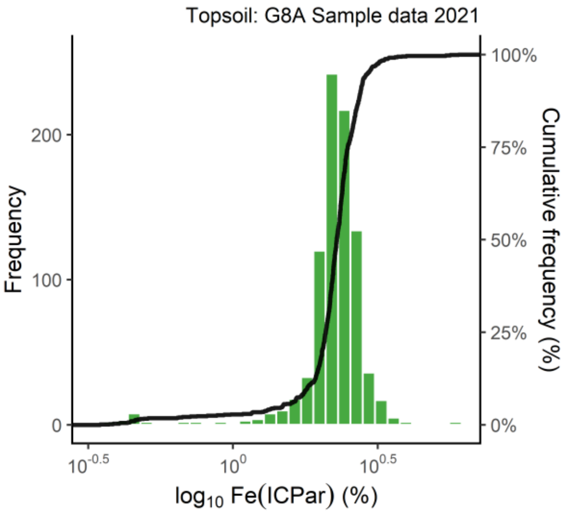
Copper (Cu) ICP$_{ar}$



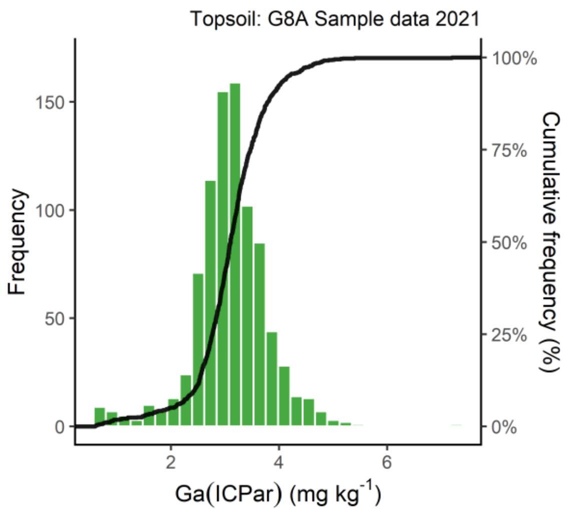


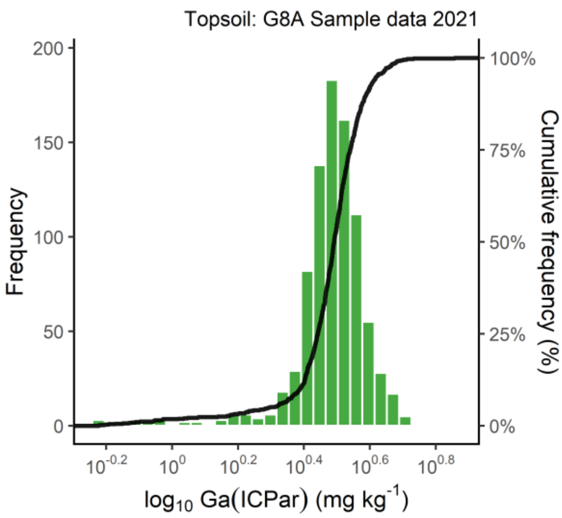
Iron (Fe) ICP$_{ar}$



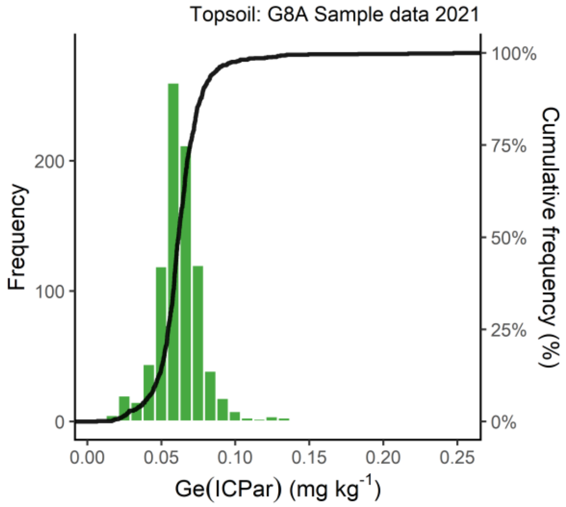


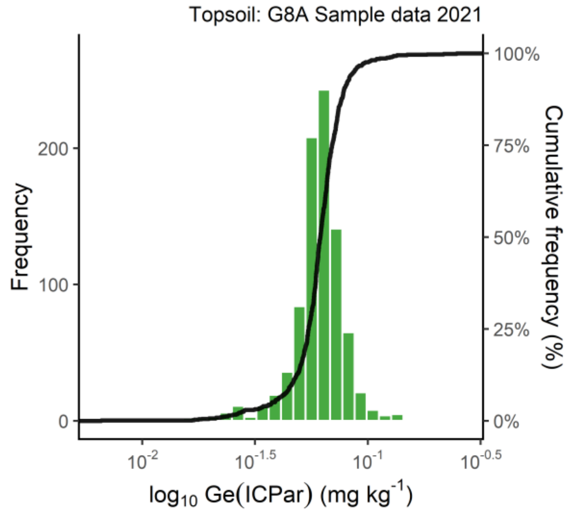
Gallium (Ga) ICP$_{ar}$



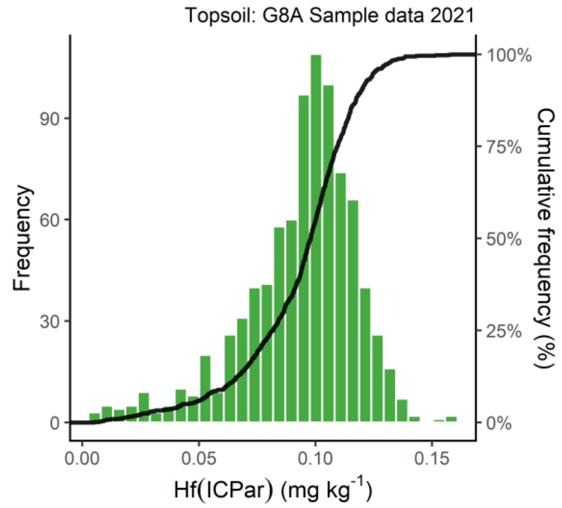


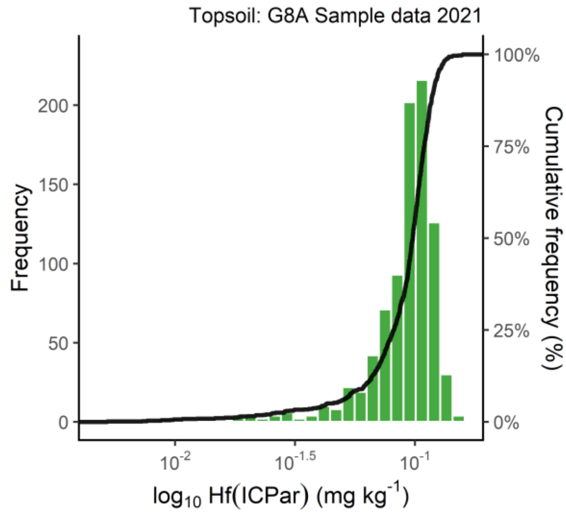
Germanium (Ge) ICP$_{ar}$



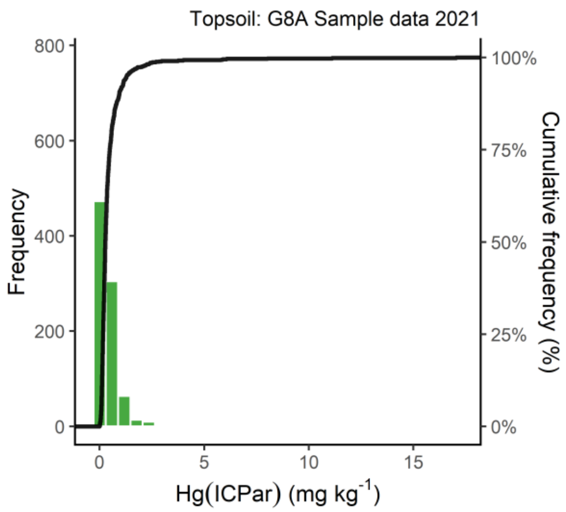


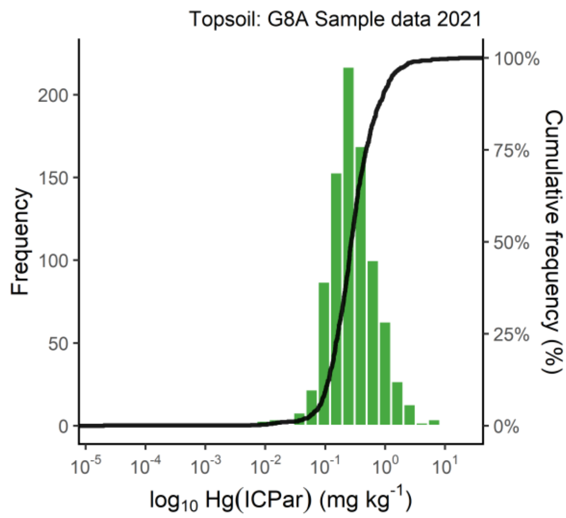
Hafnium (Hf) ICP$_{ar}$



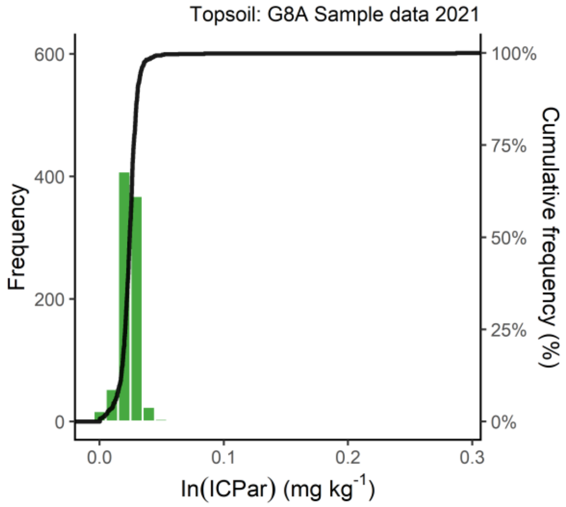


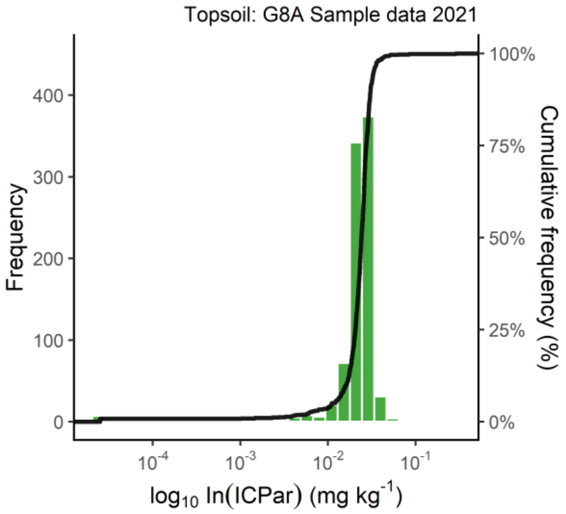
Mercury (Hg) ICP$_{ar}$



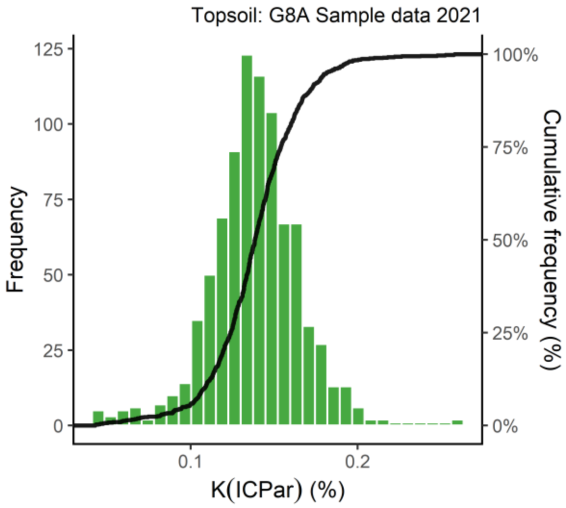


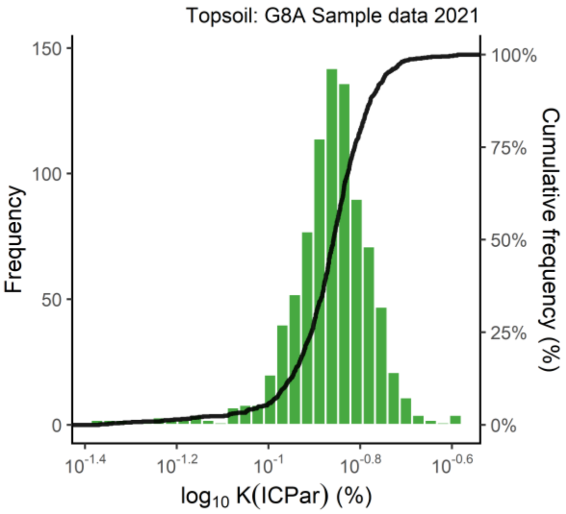
Indium (In) ICP_{ar}



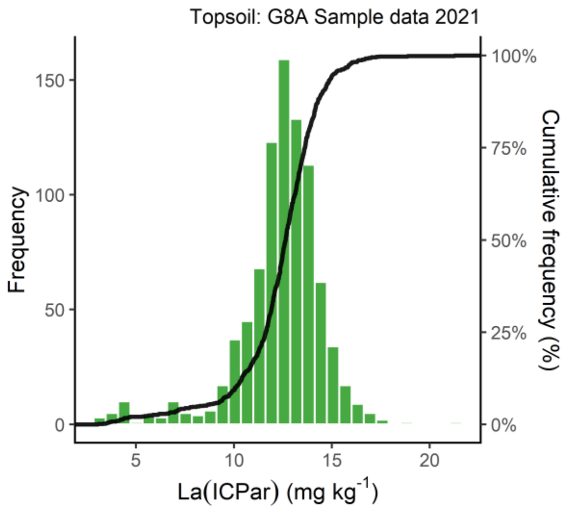


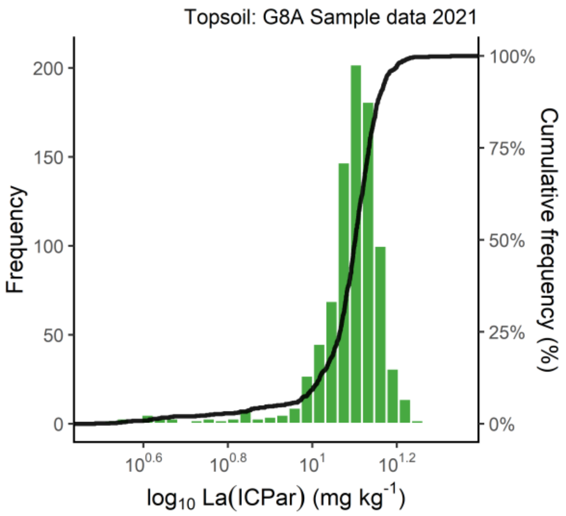
Potassium (K) ICP_{ar}



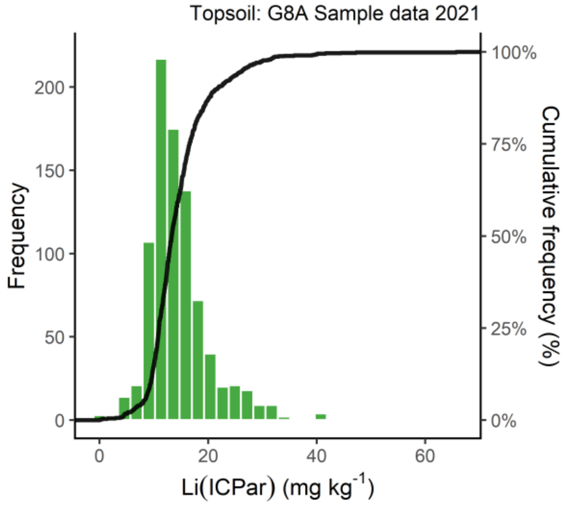


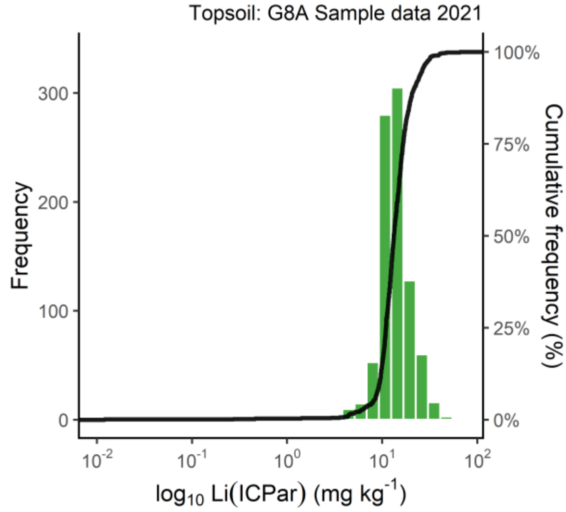
Lanthanum (La) ICP_{ar}



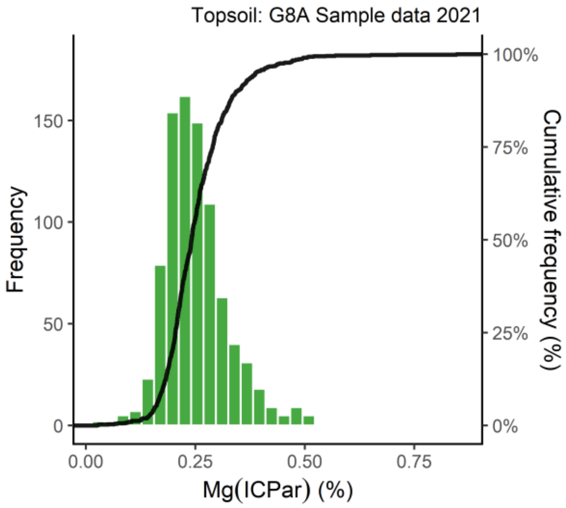


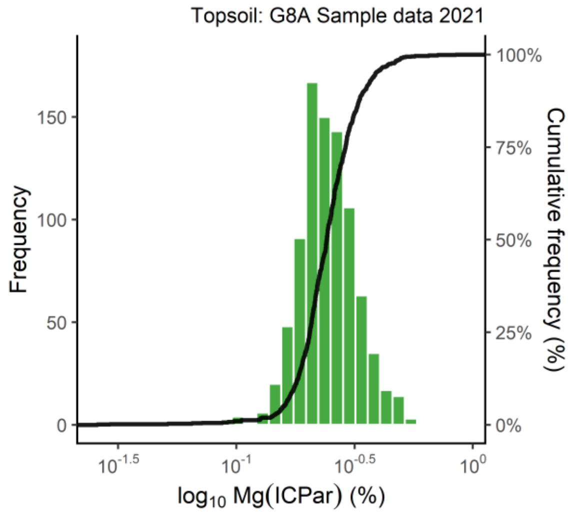
Lithium (Li) ICP_{ar}



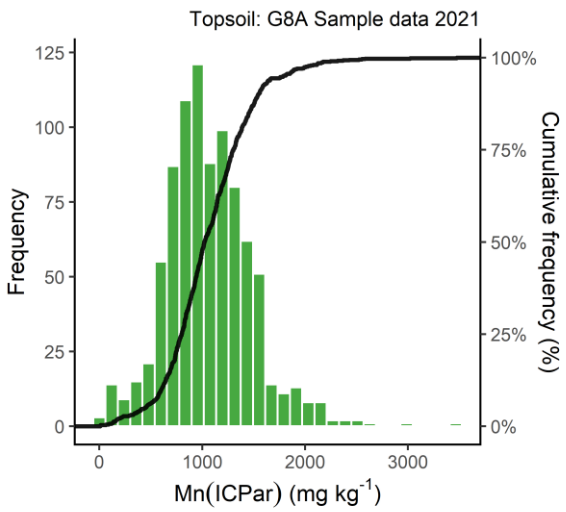


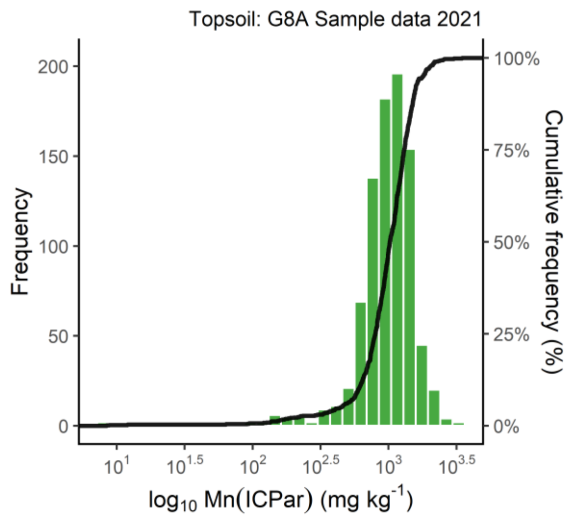
Magnesium (Mg) ICP_{ar}



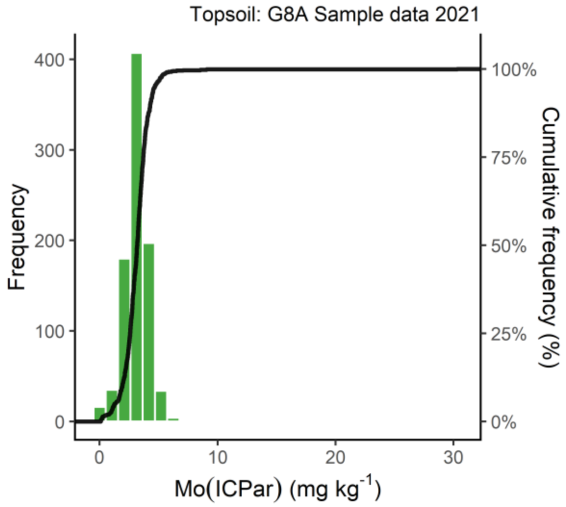


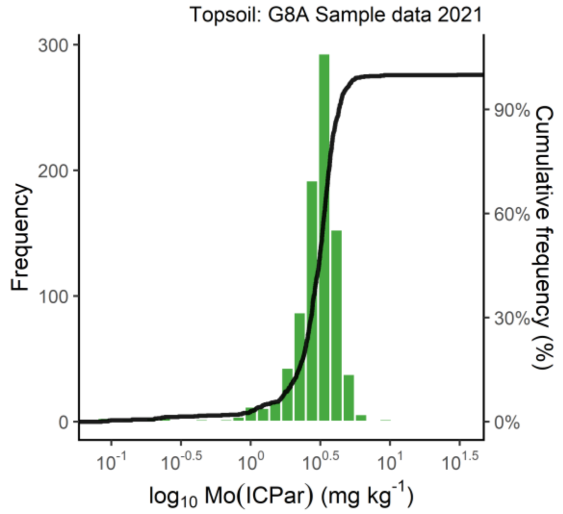
Manganese (Mn) ICP_{ar}



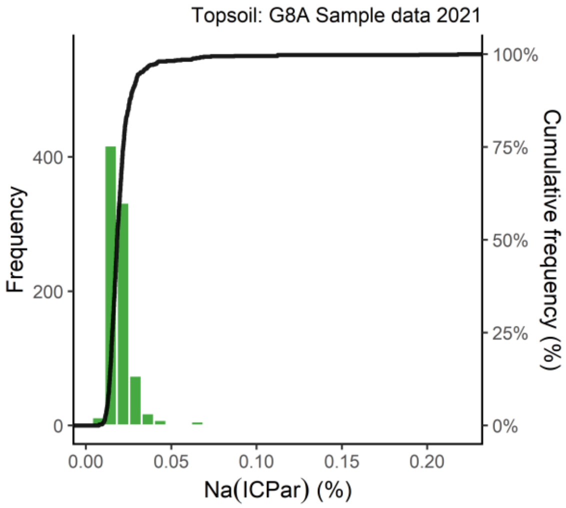


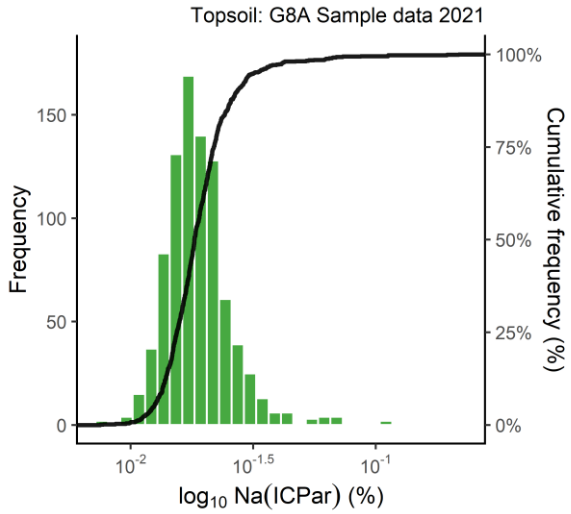
Molybdenum (Mo) ICP_{ar}



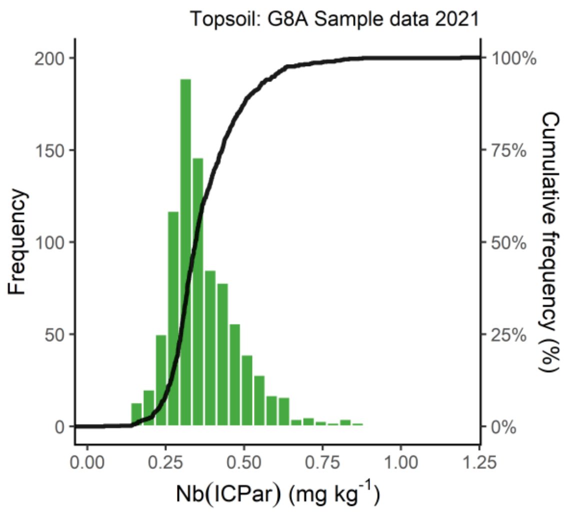


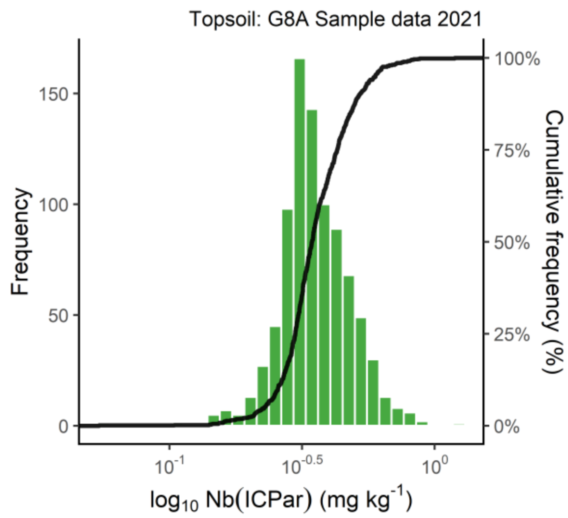
Sodium (Na) ICP_{ar}



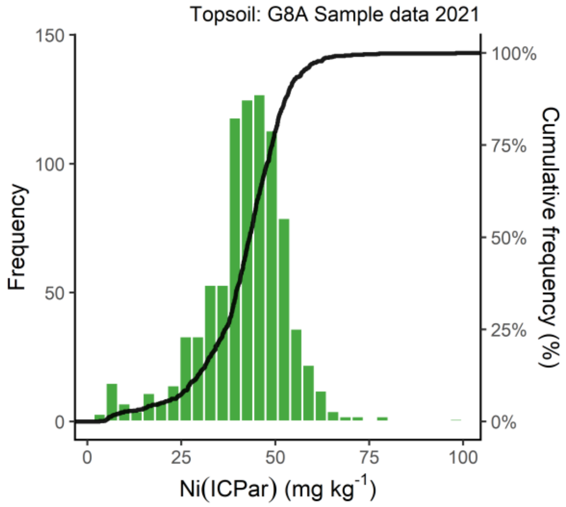


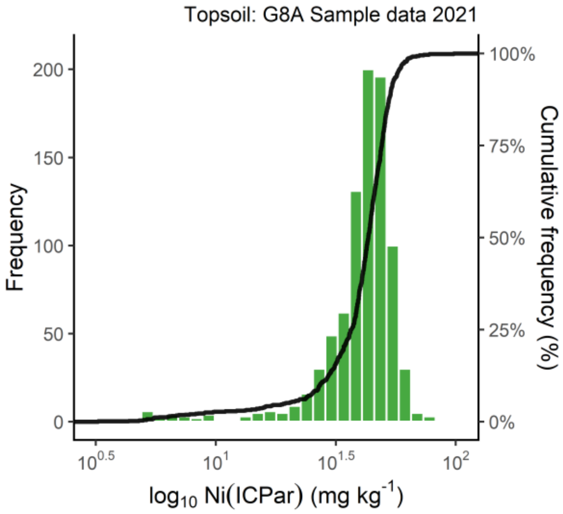
Niobium (Nb) ICP_{ar}



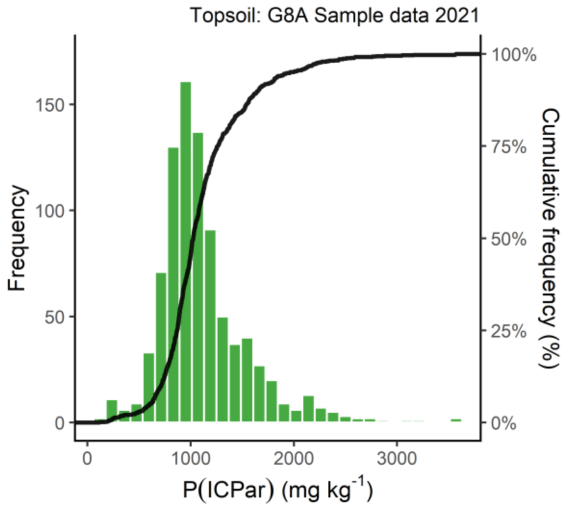


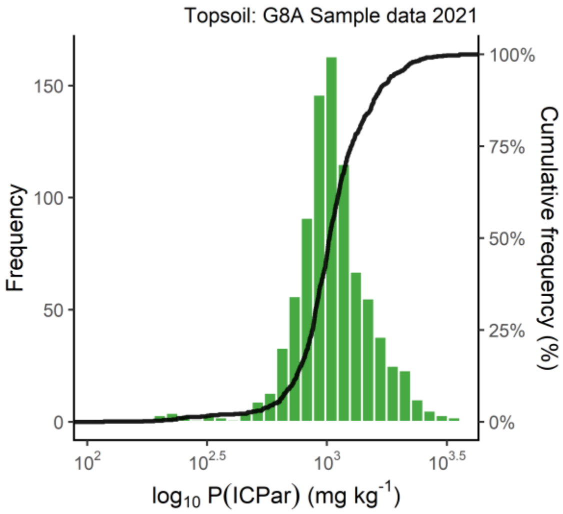
Nickel (Ni) ICP$_{ar}$



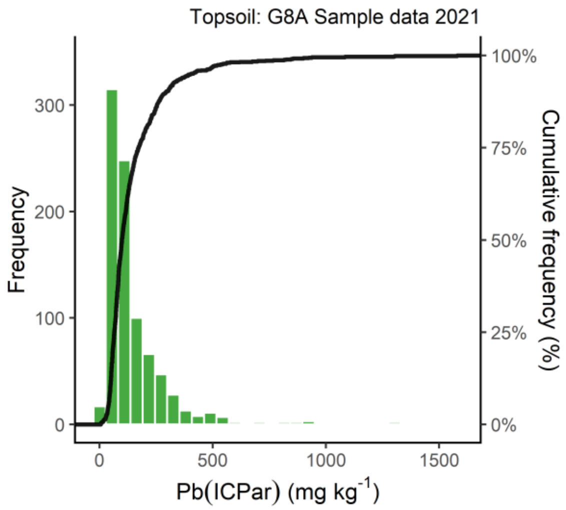


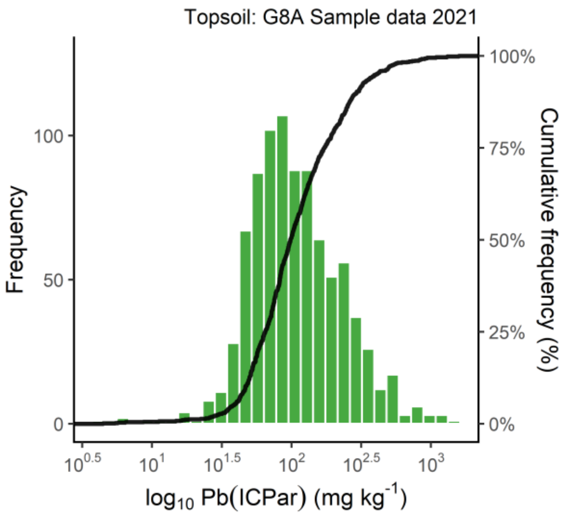
Phosphorus (P) ICP$_{ar}$



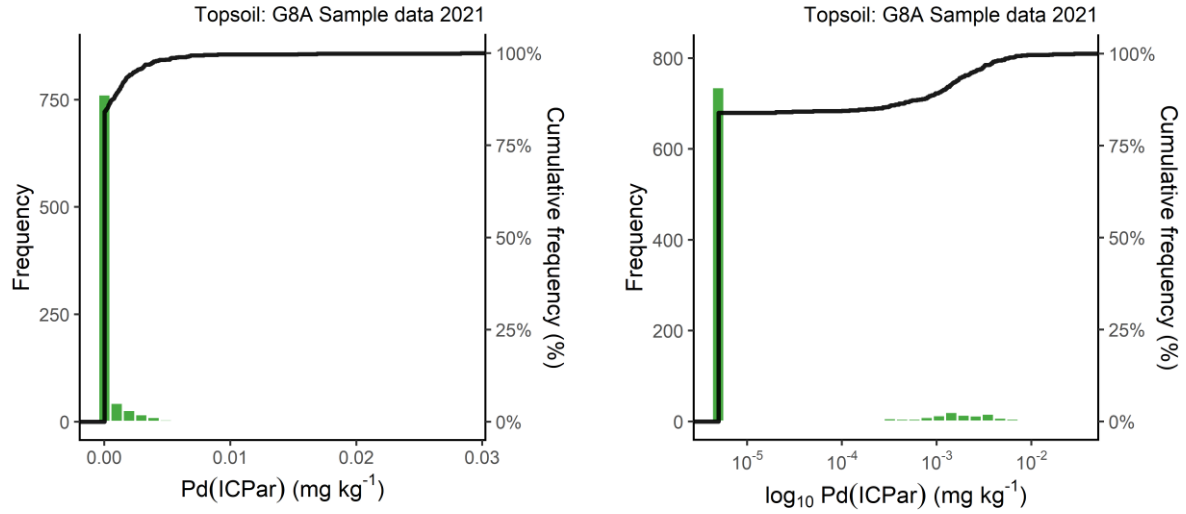


Lead (Pb) ICP$_{ar}$

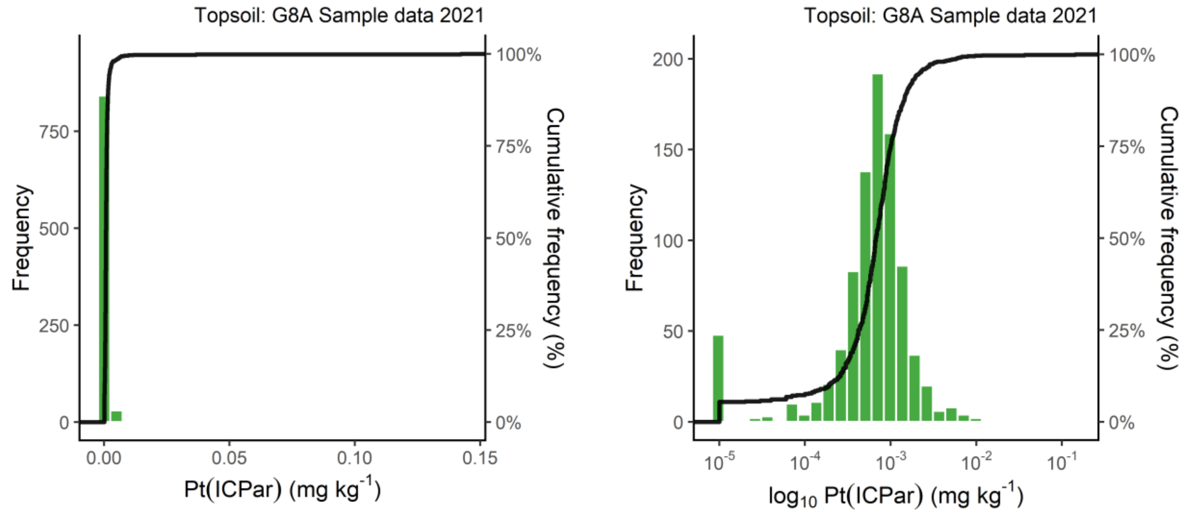




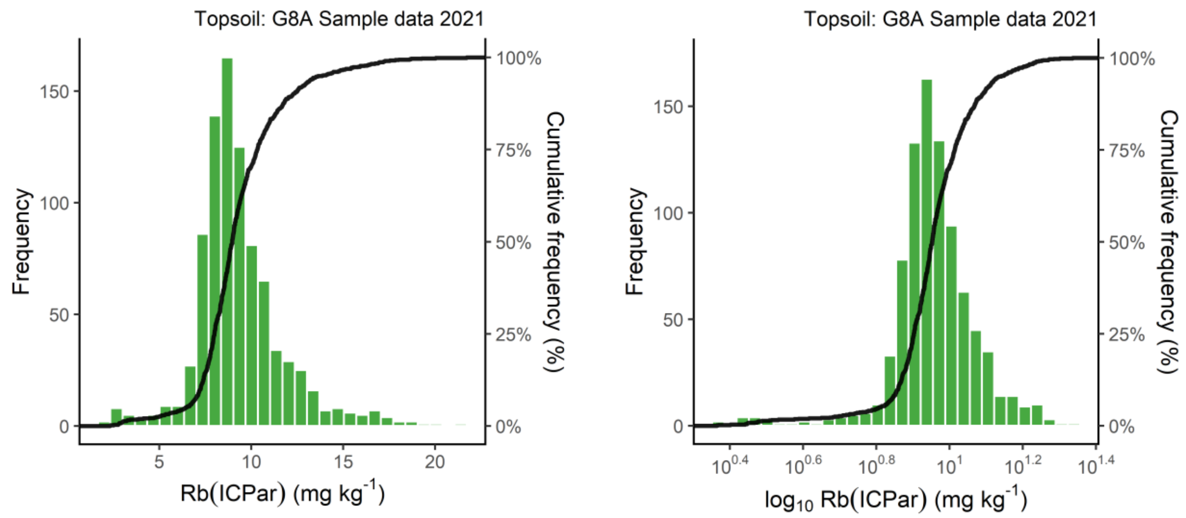
Palladium (Pd) ICP_{ar}



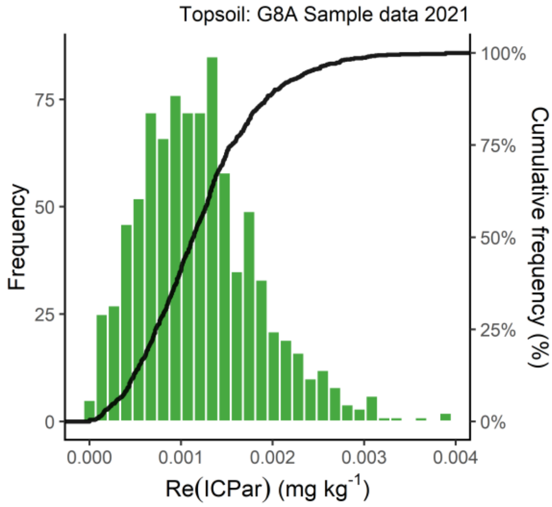
Platinum (Pt) ICP_{ar}

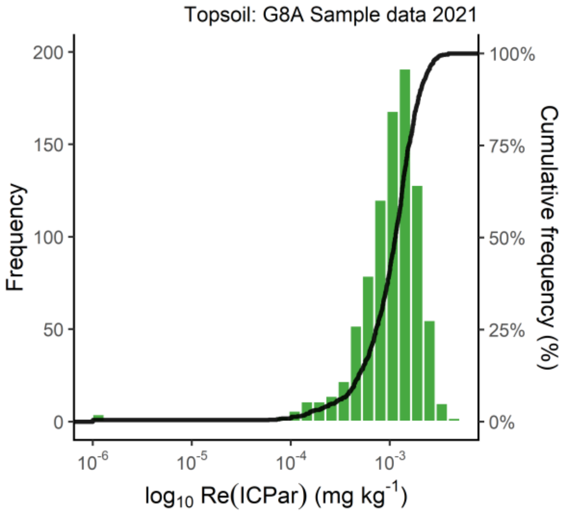


Rubidium (Rb) ICP_{ar}

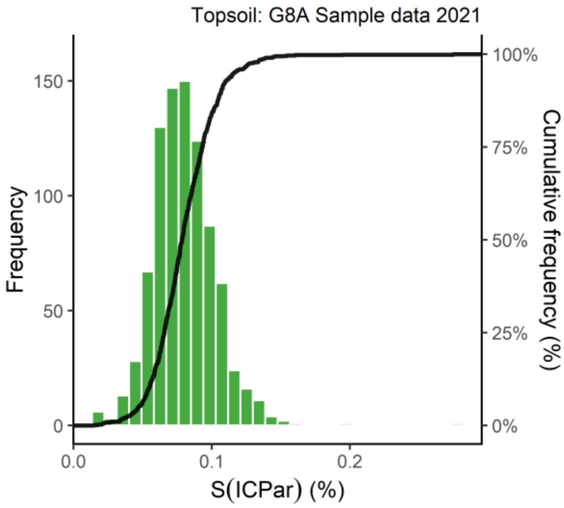


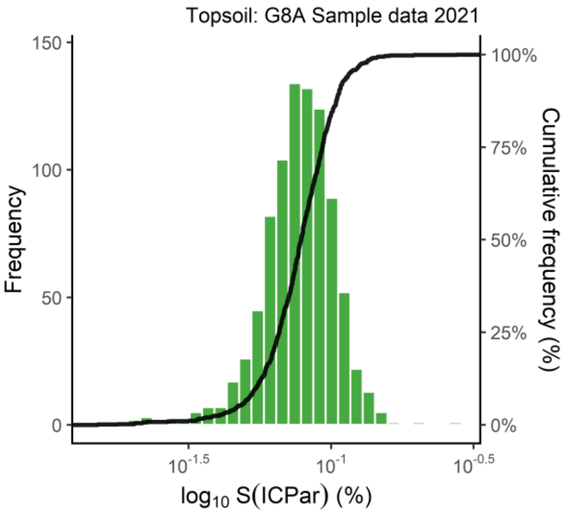
Rhenium (Re) ICP_{ar}



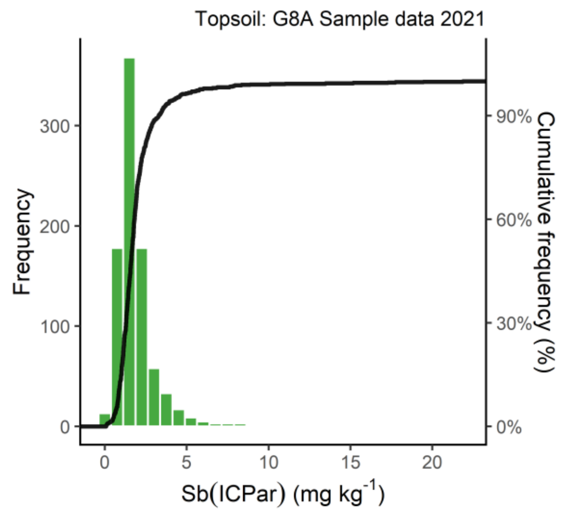


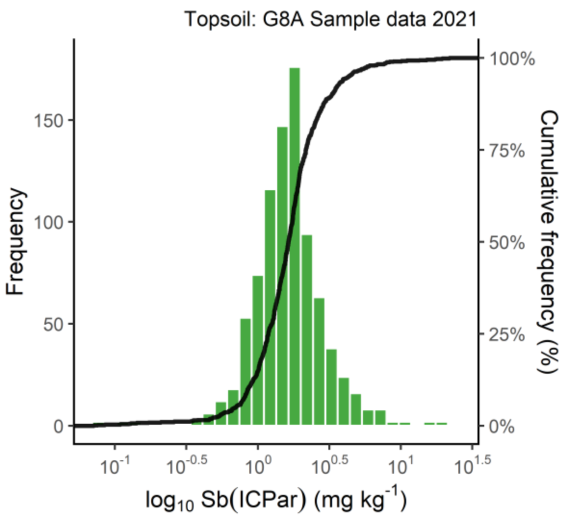
Sulphur (S) ICP_{ar}



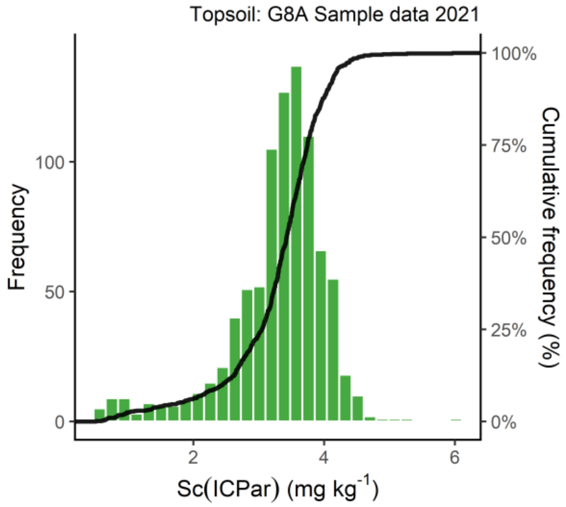


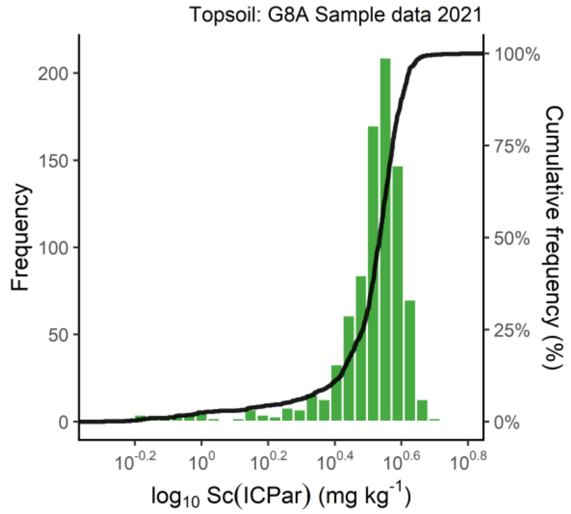
Antimony (Sb) ICP_{ar}



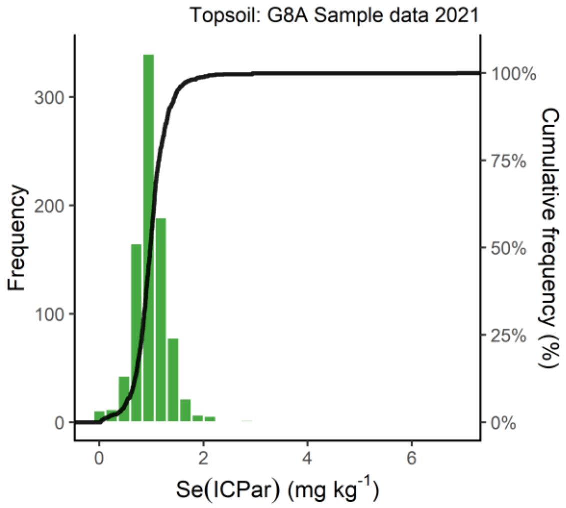


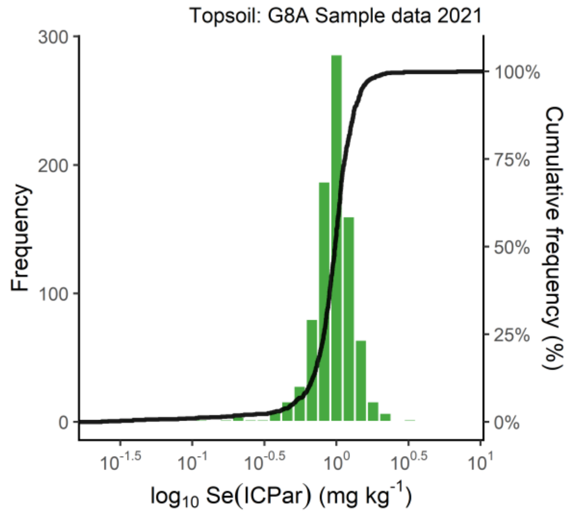
Scandium (Sc) ICP_{ar}



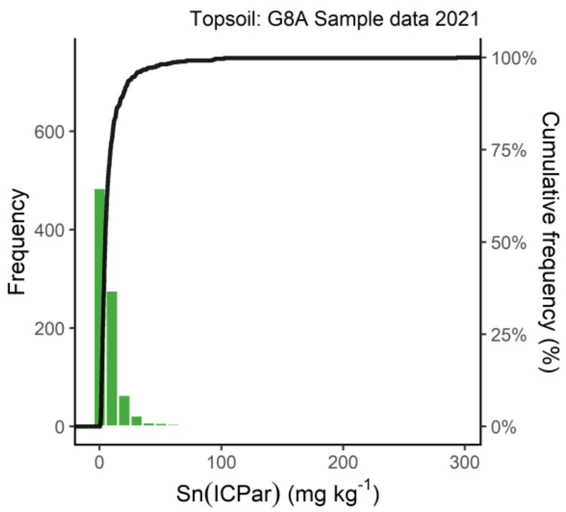


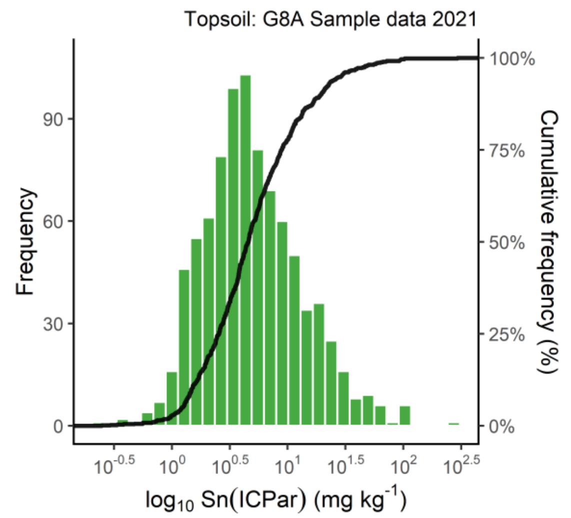
Selenium (Se) ICP_{ar}



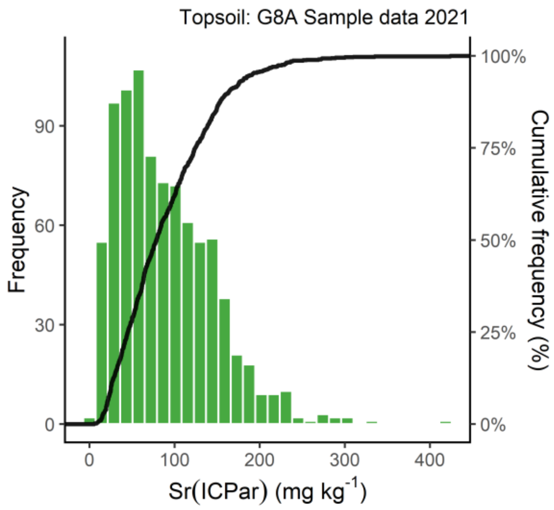


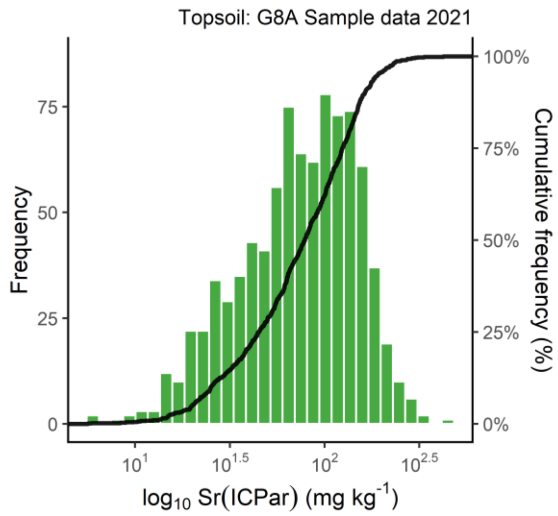
Tin (Sn) ICP_{ar}



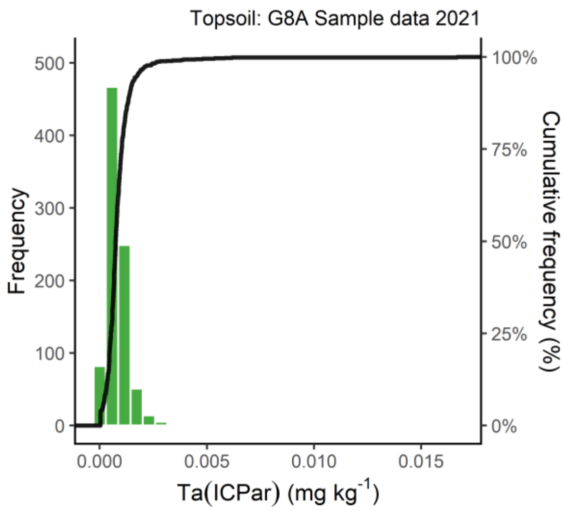


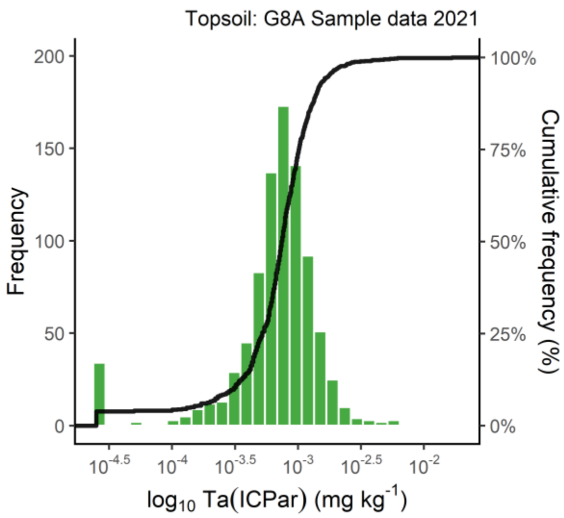
Strontium (Sr) ICP_{ar}



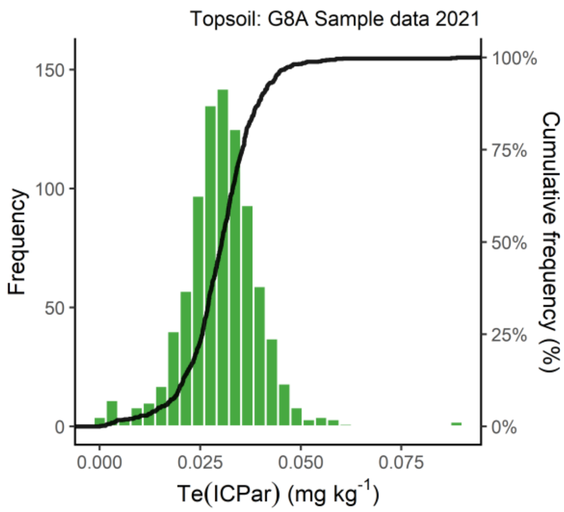


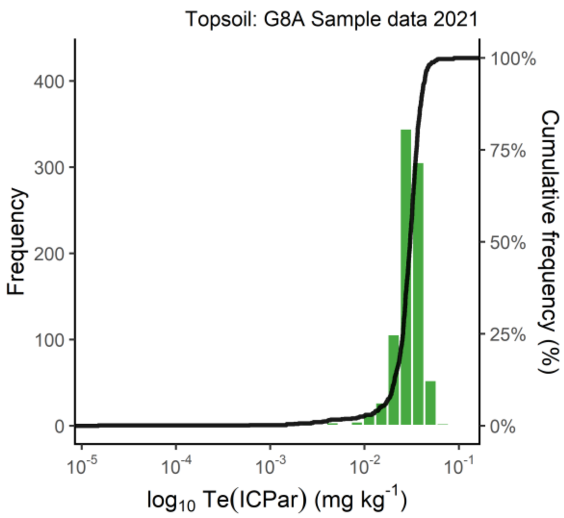
Tantalum (Ta) ICP_{ar}



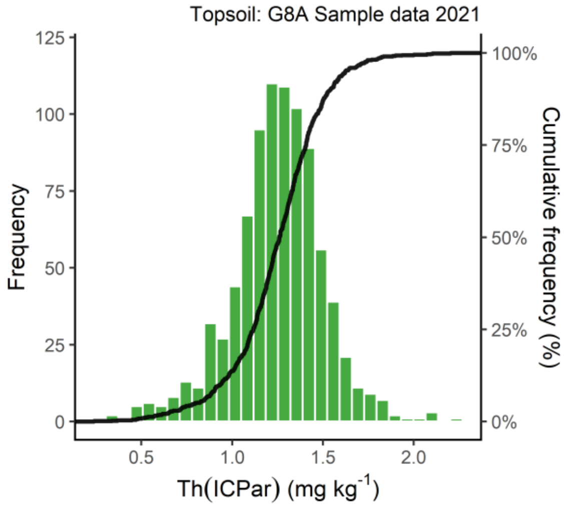


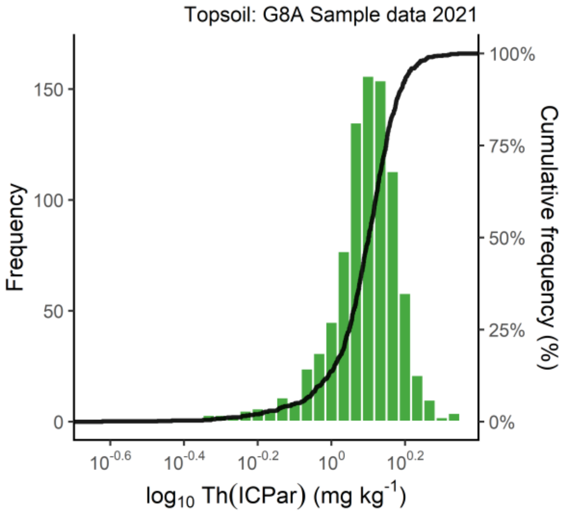
Tellurium (Te) ICP_{ar}



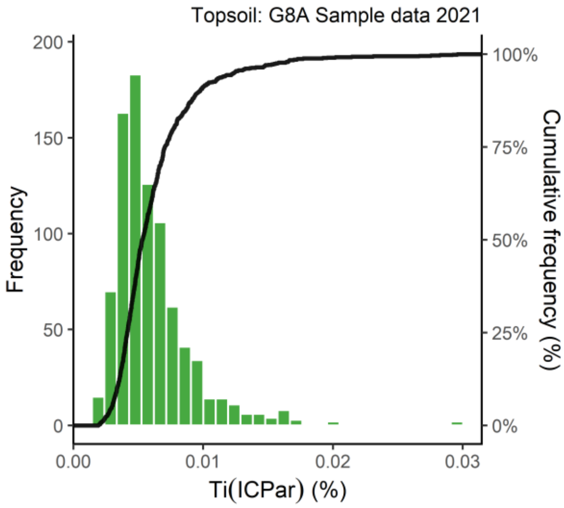


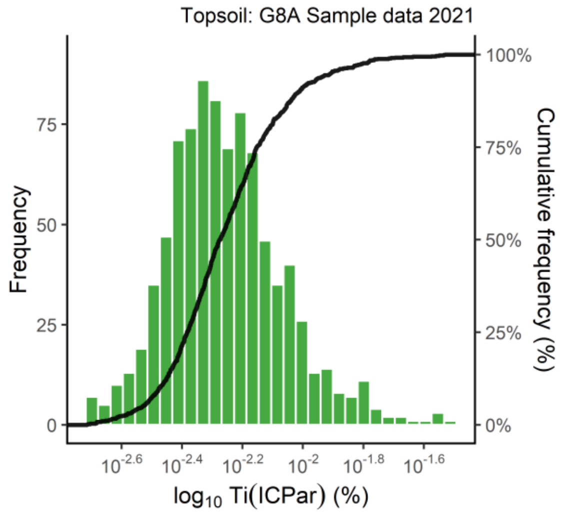
Thorium (Th) ICP_{ar}



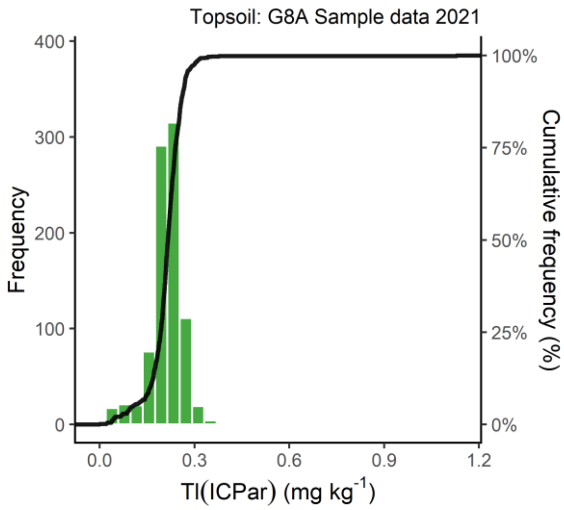


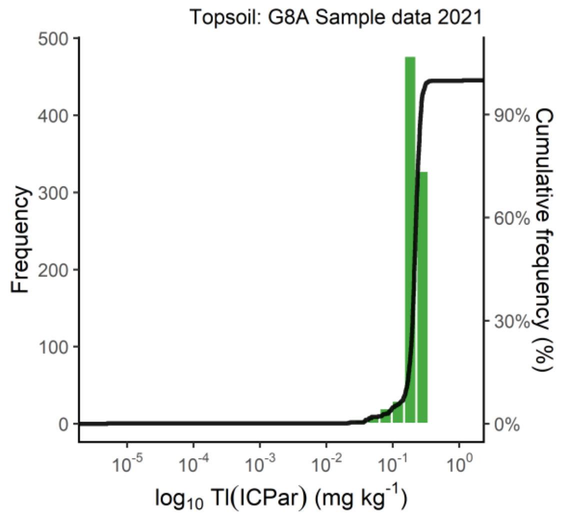
Titanium (Ti) ICP_{ar}

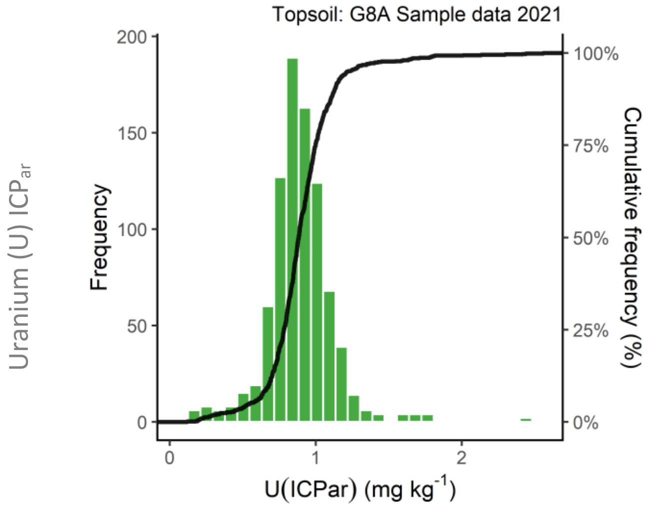


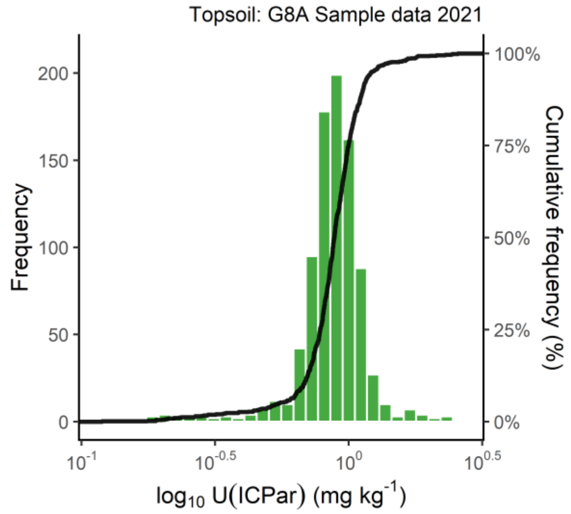


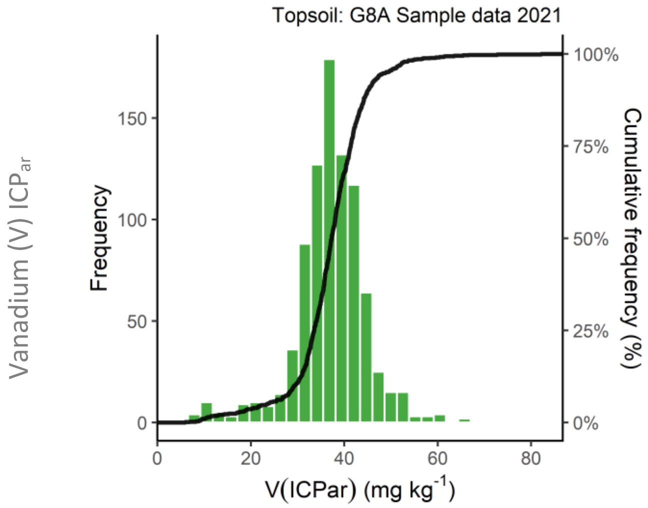
Thallium (Tl) ICP_{ar}

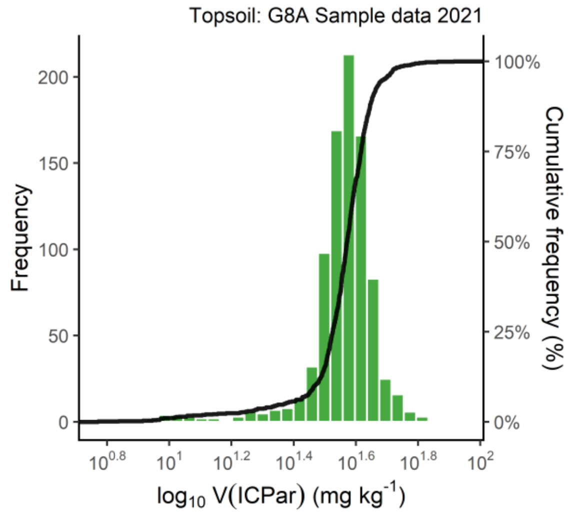


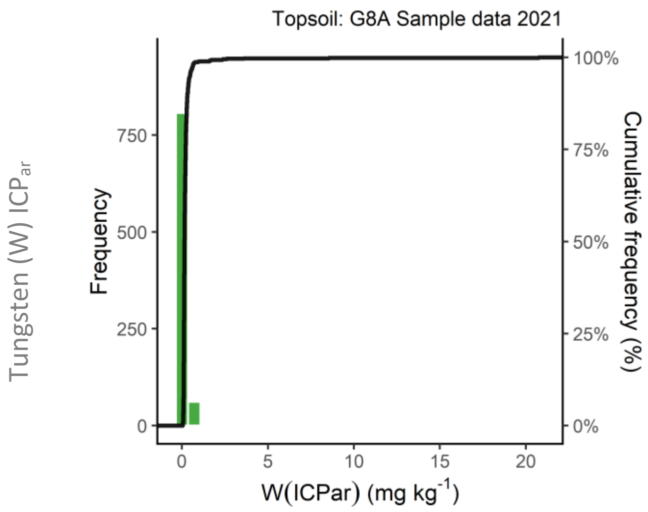


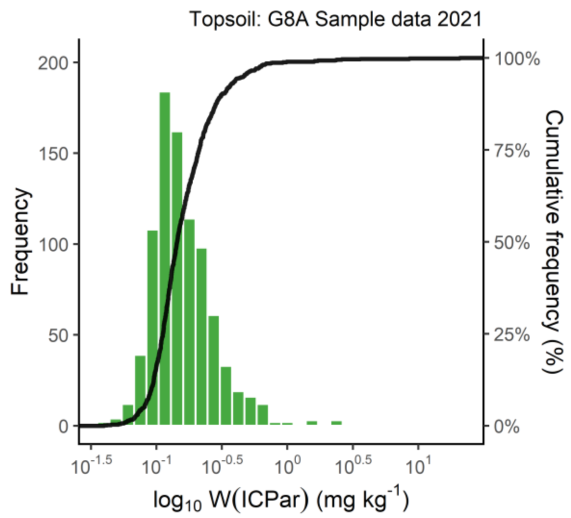

Uranium (U) ICPar
Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
U(ICPar) (mg kg-1)

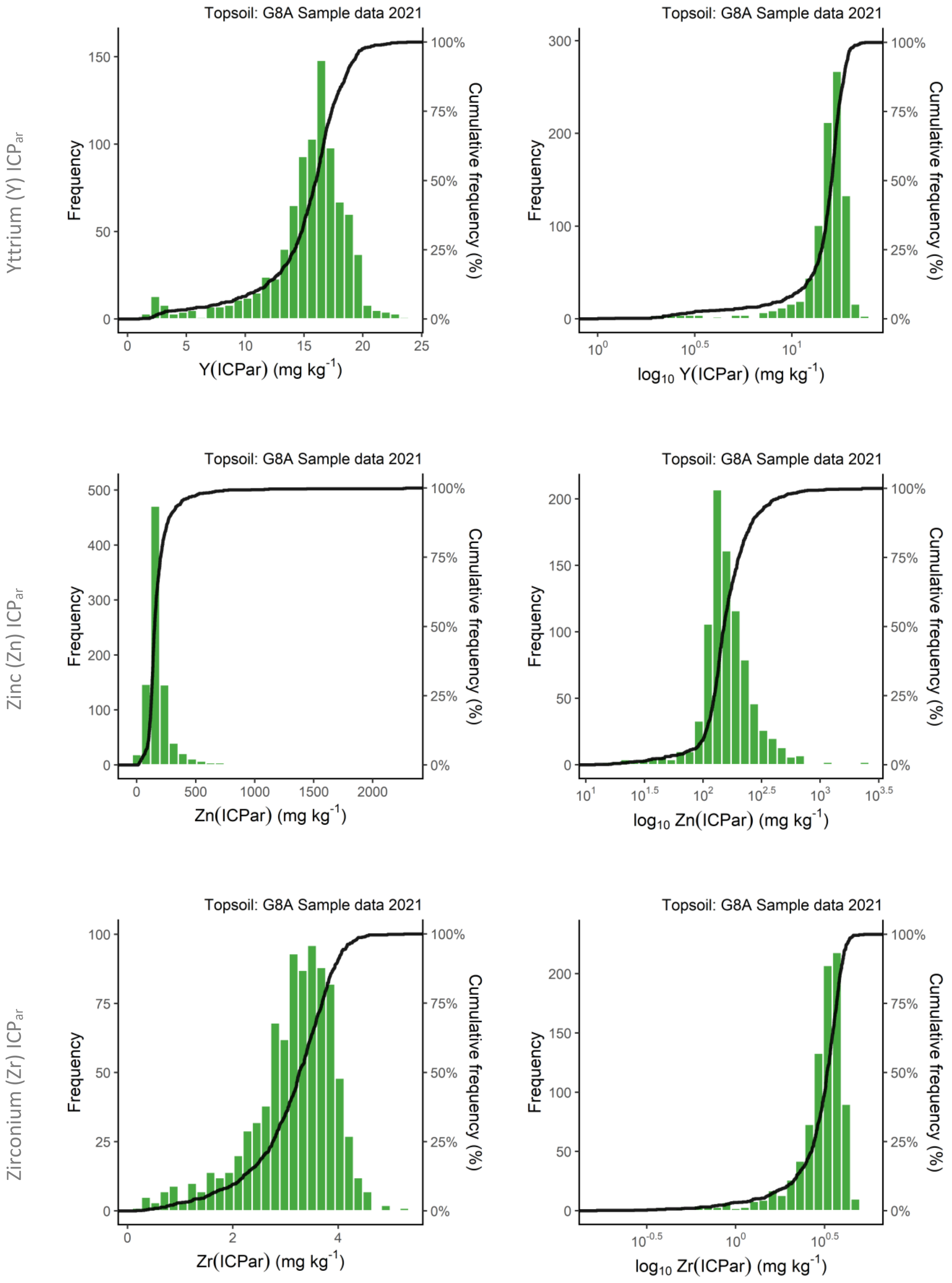

Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
log10 U(ICPar) (mg kg-1)


Vanadium (V) ICPar
Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
V(ICPar) (mg kg-1)


Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
log10 V(ICPar) (mg kg-1)


Tungsten (W) ICPar
Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
W(ICPar) (mg kg-1)


Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
log10 W(ICPar) (mg kg-1)


Yttrium (Y) ICPar
Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
Y(ICPar) (mg kg-1)
log10 Y(ICPar) (mg kg-1)
Zinc (Zn) ICPar
Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
Zn(ICPar) (mg kg-1)
log10 Zn(ICPar) (mg kg-1)
Zirconium (Zr) ICPar
Topsoil: G8A Sample data 2021
Frequency
Cumulative frequency (%)
Zr(ICPar) (mg kg-1)
log10 Zr(ICPar) (mg kg-1)

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.*

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

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

List of Reportable Analytes for ME-MS41L:

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

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

*Please note that the detection limits for the highlighted analytes above Have improved since analysis was carried out on 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

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

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

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 CaCl2 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