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Regional lake sediment geochemical data from northeastern Saskatchewan (NTS 064-E, 074-A and H): re-analysis data and QA/QC evaluation

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Regional lake sediment geochemical data from northeastern Saskatchewan (NTS 064-E, 074-A and H): re-analysis data and QA/QC evaluation

Abstract

This report presents the geochemical data, quality assurance and quality control (QA/QC) results of the re-analysis of lake sediment samples collected from northeastern Saskatchewan (NTS 064-E, 074-A and H). The original lake survey was conducted in 1984 and the re-analysis in 2021. Original survey results are presented in OF 1643. A total of 1,179 lake sediment samples were re-analyzed, covering an area of 18,000 km^2, averaging a density of 1 sample per 13 km^2. Samples were measured for 65 elements via modified aqua-regia – ICP-MS. To ensure high quality data, the geochemical data was evaluated for contamination, accuracy, precision and fitness-for-purpose. QA/QC results have identified a number of elements to be monitored carefully for future analyses. Overall, the data is of good quality.

1 Introduction

Quality assurance and quality control (QA/QC) of geochemical data is an essential process towards the use of any geochemical data. The QA/QC process is designed to identify and where possible, remediate quality issues such that potential users of geochemical data can be fully informed regarding the implications of the quality of the data. This QA/QC report adheres to the methodology presented in McCurdy and Garrett (2016) and analyzes the contamination, accuracy and precision of the data.

In 1984, lake sediment samples were collected in northeastern Saskatchewan and the geochemical data was published in a Geological Survey of Canada (GSC) Open File 1643 by Hornbrook and Friske (1988). With recent improvements in analytical instrumentation, particularly the availability of lower detection limits, the increase in analytical precision and the increase in the diversity of elements for analysis, all original survey samples were re-analyzed. Furthermore, the original survey samples are located in the Athabasca-Wollaston area, a region with known resource potential and thus an area of interest for the Geo-Mapping for Energy and Minerals in Canada's North (GEM-GeoNorth) Program (Geological Survey of Canada, 2018; Lebel, 2020).

Funding for the re-analysis was provided by the GEM-GeoNorth Program. Among other objectives, the GEM-GeoNorth Program aims to advance regional geo-mapping of Canada's North in order to promote sustainable resource exploration and development (Geological Survey of Canada, 2018; Lebel, 2020). Geoscience knowledge produced by the GEM-GeoNorth Program will enable governments and communities to make informed decisions regarding the development of resources (Lebel, 2020). The program (2020-2027) is a continuation of the successful Geo-Mapping for Energy and Minerals (GEM) program (2008-2020). Other partners for this project include the Saskatchewan Geological Survey (SGS).

The survey area is located in northeastern Saskatchewan (NTS 064-E, 074A and H), encompassing a total area of 18,000 km^2 (Hornbrook and Friske, 1988). The area includes the southeastern-most portions of the Paleoproterozoic Athabasca Basin, that hosts one of the most significant uranium deposits in the world by grade, and to a lesser extent production (Kyser, 2014). In addition to uranium potential in the northwest, the region to the southeast has potential for base metals, such as nickel-copper-platinum group elements (e.g. the Rottenstone Mine) and gold (e.g. the Mallard Lake deposit). However, as a whole, the survey area remains largely unexploited.

In this publication, we present the re-analysis data and QA/QC results for a total of 1,179 lake sediment samples. In comparison with the original survey, which included 36 determined elements, this publication presents the results for 65 determined elements, measured at higher precision than the original analysis. We quantify the contamination, accuracy and precision, and fitness-for-purpose for regional mapping of the analytical data using blanks, certified reference materials (CRMs), as well as analytical and field duplicate samples. We also highlight elements of concern. With the publication of this QA/QC report, we hope to make available high quality exploration geochemical data, to facilitate its use in regional exploration.

2 Sampling and analytical techniques

2.1 Description of surveys and sample management

The original lake sediment survey was conducted in the summer of 1984 in northeastern Saskatchewan (Fig. 1). A total of 1,179 (excluding CRMs, analytical duplicates and 1 of the field duplicates) samples were collected covering an area of 18,000 km^2, averaging a density of 1 sample per 13 km^2 (Hornbrook and Friske, 1988). Samples were chemically analyzed for 36 elements and the results were released in 1988 as a Geological Survey of Canada (GSC) Open File 1643.

Survey samples were collected using a hollow-pipe, bottom-valved sampler that was developed by the GSC (Friske and Hornbrook, 1991). During retrieval of the sample, the top few centimeters of sediment were washed out while the remainder, the organic-rich gyttja was retained. Approximately 1 kg of wet lake sediment was collected and placed into high wet-strength paper bags. Samples were then labeled and field observations for each site were recorded on field cards used by the GSC (Garrett, 1974). Samples were then delivered to a commercial laboratory in Ottawa, Golders & Associates, where they were air dried and sieved through a -80 mesh (177 μm) screen before being milled using a ceramic mill with ceramic balls. Typically, 1 kg of organic-rich gyttja yielded about 50 g of material for analysis. After initial analysis in 1988, unused sample material was stored in plastic containers and archived.

To ensure the quality and reproducibility of the data, CRMs and analytical duplicates were added to the survey samples by the GSC. During the survey, samples were numbered consecutively and arranged into blocks (or groups) of 20. Each block of 20 samples contains one site duplicate pair; that is, 2 samples from the same site. A block also contains an analytical duplicate sample pair, where one sample from a single site was split and assigned 2 non-consecutive numbers. Additionally, a CRM was added, at random, into each block.

Samples selected for re-analysis were retrieved from the GSC archival facility in Ottawa and shipped to a commercial laboratory for re-analysis. The samples were already sieved and milled from sample processing conducted during the original survey. The samples' group (or block) structure and quality control measures described in the above paragraph were kept during re-analysis. The only exception was the addition of new CRMs to replace the original ones from the previous analysis. Both lake sediment reference material 2 and 4 (LKSD-2 and LKSD-4) served as the CRMs for this study (Lynch, 1990, 1999; Hechler, 2013).

Before publication, a thorough inspection of the field and analytical data was made to check for any missing and/or mislabeled samples, as well as for any analytical errors. These checks were done both at the laboratory and upon receipt of the data at the GSC.

2.2 Analytical procedures 2021

Samples selected and prepared for re-analysis were analyzed at Bureau Veritas in Vancouver (British Columbia) using a modified aqua regia digestion followed by inductively-coupled plasma-mass spectroscopy (ICP-MS) analysis.

Modified Aqua Regia - ICP-MS analysis   A total of 65 trace elements were determined via ICP-MS (Table 1). A small portion (0.5 g) of the sample was taken and digested using a modified aqua regia solution (1:1:1 HNO$_3$:HCl:H$_2$O) for 1 hour in a heating block. Afterwards, the sample was made up to volume with dilute HCl. The solution was then aspirated into a Perkin ELAN 9000 ICP mass spectrometer for the determination of elements. The commercial laboratory QA/QC protocol included the addition of CRMs (OREAS262, DS11 and BVGEO01) and total procedural blanks. Total procedural blank samples do not contain any sample material (i.e. empty vials), but are brought through the entire digestion and analysis process in the same manner as the remainder of the samples. Analytical results were verified by a British Columbia Certified Assayer prior to being delivered to the GSC.

Legend

- Lake sediment samples

Proterozoic

| Mdd | Diabase dykes and sills |

Paleoproterozoic

PALs	Quartz arenite with pebbly layers
PAMb	Conglorematic quartz arenite ± pebbly quartz arenite
PAMd	Clay intraclast-rich quartz arenite ± mudstone
PAMh	Pebbly quartz arenite ± conglomerate
PAMr	Conglomerate to mudstone, quartz arenite
PAMw	Clay intraclast-rich quarz arenite
PAWq	Quarz arenite ± mudstone ± phosphatic hardgrounds
PCBc	Calcic psammopelite, calc-silicate rocks, minor marble, intermediate volcaniclastic rock
PCBsn	Pelite, psammopelite, minor psamite and wacke
PCMo	Polymicic conglomerate, arkose, wacke

PCMr	Arkose, conglomerate, psammite and derived migmatite
PKsn	Pelitic to psammopelitic gneiss and derived migmatite
PMam	Amphibolite including mafic volcanite, minor gabbro and clastic sedimentary rocks
PMs	Undifferentiated sedimentary and minor volcanic rocks
PPrq	Psammite, feldspathic quartzite, arkose, conglomerate, quartzite and derived migmatite
PTAgd	Granite, granodiorite, tonalite
PTAqd	Diorite to quartz diorite (minor granodiorite)
PTAvf	Felsic to intermediate volcanic, volcaniclastic and minor subvolcanic intrusive rocks
PTAvi	Intermediate to felsic volcanic, volcaniclastic and minor subvolcanic intrusive rocks
PTAvm	Mafic to intermediate (ultramafic) volcanic rocks
PTCg	Syenitegranite, quartz-feldspar porphyry
PTHg	Granite, megacrystic granuite, syenogranite
PTRgn	Undifferentiated granodioritic to gnessis tonalite
PTWg	Megacrystic granite and quartz monzonite
PTam	Amphibolite

PTlg	Leucotonalite to leucogranodiorite
PTWbd	Megacrystic monzonite, diorite and gabbro
PWam	Amphibolite, mafic volcanic rocks, arkose, psammonpelite and calc-silicate rocks
PWc	Mixed calc-silicate rocks, pelitic gneiss, marble
PWo	Conglomerate arkose, bimodal volcanic rocks
PWq	Quartzite, pelite, calc-silicate rocks, minor pebble conglomerate
PWr	Arkose, calcerous arkose, psammite, psammonpelite
PWsn	Pelite to psammonpelite

Neoarchean

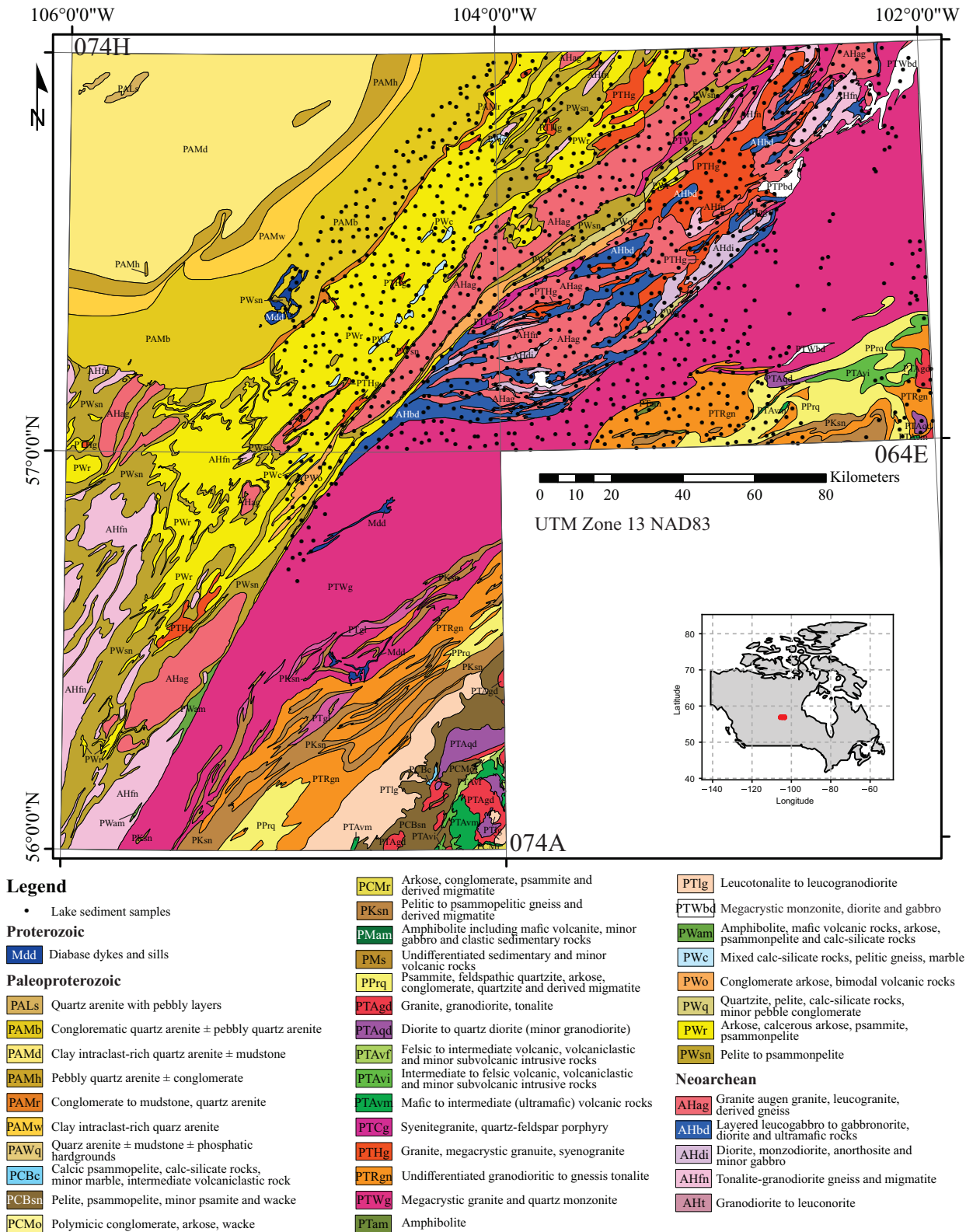| AHag | Granite augen granite, leucogranite, derived gneiss |
AHbd	Layered leucogabbro to gabbronorite, diorite and ultramafic rocks
AHdi	Diorite, monzodiorite, anorthosite and minor gabbro
AHfn	Tonalite-granodiorite gneiss and migmatite
AHt	Granodiorite to leuconorite

Figure 1. *Bedrock geological map of NTS 064-E, 074-A and H, provided by the Saskatchewan Geological Survey. The locations of lake sediment samples collected in 1984 and re-analyzed in this study are shown on the map as black dots.*

Table 1. *Lower detection limits published by Bureau Veritas for 'partial' aqua regia digestion followed by ICP-MS analysis.*

Element	Lower detection limit		Element	Lower detection limit		Element	Lower detection limit	
Ag	2	ppb	Hf	0.02	ppm	S	0.02	%
Al	0.01	%	Hg	5	ppb	Sb	0.02	ppm
As	0.1	ppm	Ho	0.02	ppm	Sc	0.1	ppm
Au	0.2	ppb	In	0.02	ppm	Se	0.1	ppm
B	20	ppm	K	0.01	%	Sm	0.02	ppm
Ba	0.5	ppm	La	0.5	ppm	Sn	0.1	ppm
Be	0.1	ppm	Li	0.1	ppm	Sr	0.5	ppm
Bi	0.02	ppm	Lu	0.02	ppm	Ta	0.05	ppm
Ca	0.01	%	Mg	0.01	%	Tb	0.02	ppm
Cd	0.01	ppm	Mn	1	ppm	Te	0.02	ppm
Ce	0.1	ppm	Mo	0.01	ppm	Th	0.1	ppm
Co	0.1	ppm	Na	0.001	%	Ti	0.001	%
Cr	0.5	ppm	Nb	0.02	ppm	Tl	0.02	ppm
Cs	0.02	ppm	Nd	0.02	ppm	Tm	0.02	ppm
Cu	0.01	ppm	Ni	0.1	ppm	U	0.1	ppm
Dy	0.02	ppm	P	0.001	%	V	1	ppm
Er	0.02	ppm	Pb	0.01	ppm	W	0.1	ppm
Eu	0.02	ppm	Pd	10	ppb	Y	0.01	ppm
Fe	0.01	%	Pr	0.02	ppm	Yb	0.02	ppm
Ga	0.1	ppm	Pt	2	ppb	Zn	0.1	ppm
Gd	0.02	ppm	Rb	0.1	ppm	Zr	0.1	ppm
Ge	0.1	ppm	Re	1	ppb			

3   QA/QC of geochemical data

Blank samples are used to monitor and quantify laboratory contamination. CRMs are used to quantify accuracy, while analytical duplicates are used to quantify precision. The fitness-for-purpose for mapping is determined using variance analyses of in-site versus between-site variability using the analysis of variance (ANOVA) of field duplicate samples.

Project, samples and laboratory metadata is presented in Appendix A. Re-analysis of lake sediment samples is presented in Appendix B in a workbook. Elements in Appendix B are listed in the order that they were reported in the laboratory certificates. Data presented in Appendix B can be used to independently verify the results presented here. QA/QC results for contamination, accuracy, precision and fitness-for-purpose are presented in this report in Tables 3 4, 5, 6 and 7, as well as in Appendix C. Table 2 presents the contents of the Appendix C1 workbook. Elements in Tables 3, 4, 5, 6 and 7, as well as Appendix C are arranged alphabetically for ease of reading.

Table 2. *Appendix C1 workbook. The workbook contain the QA/QC results for this study.*

Worksheet	Contents
C1-1_Contamination	Compares laboratory lower detection limits with results from blank analyses.
C1-2_Accuracy LKSD-2 ICP-MS	Compares accepted values for CRM LKSD-2 with results from re-analysis via ICP-MS.
C1-3_Accuracy LKSD-4 ICP-MS	Compares accepted values for CRM LKSD-4 with results from re-analysis via ICP-MS.
C1-4_Precision ICP-MS	Provides an estimate of precision using analytical duplicate pairs for re-analysis via ICP-MS.
C1-5_ANOVA ICP-MS	Provides an estimate of fitness-for-purpose using field duplicate pairs for re-analysis via ICP-MS.

3.1 Contamination

Blank samples are typically used to quantify contamination and can be introduced at various stages during sampling, sample preparation and analysis. For this study, blanks were used to monitor for any possible contamination stemming from sample preparation (digestion) and analysis during ICP-MS analysis.

To quantify contamination, analyses of blanks can be compared to the lowest detection limit results published by the laboratory (Table 1). Since a number of blank analyses were published along with the survey samples, we can calculate the mean ($\overline{x_i}$; Equation 1) and standard deviation (s_i; Equation 2), respectively, of blank analyses for each determined element (x_i):

$$\overline{x_i} = \frac{\sum_{i=1}^{n} x_i}{n} \tag{1}$$

$$s_i = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x_i})^2}{n}} \tag{2}$$

As an additional measure, we can also calculate the relative standard deviation (RSD), which provides an indication of the precision of the data. Here, we report the RSD in percent (%). For this study, a RSD $<20\%$ is an indication of reliable data, whereas a high ($>20\%$) RSD could indicate contamination issues. The RSD can be calculated via:

$$RSD = \frac{s_i}{\overline{x_i}} \times 100\% \tag{3}$$

The majority of elements published for blank samples have values below the laboratory lower detection limit (e.g. censored). Censored values are denoted by '<' followed by the detection limit appropriate for the element. In accordance with best practices (Grunsky et al., 2014; McCurdy and Garrett, 2016), censored values were replaced by half of their respective lower detection limits (e.g. <2 will be 1).

The contamination results for ICP-MS are presented for each element in Table 3, as well as in Appendix C. Of the 65 elements determined, none has a mean that is above the lower detection limit. However, 8 elements (As, Cu, Hg, Nd, Pb, Th, Y and Zr) have a high RSD ($\leq 20\%$). A detailed analysis of these elements reveals between 0 to 5 data points at or above the detection limit. All 8 elements have at least 1 data point that plots above their detection limit. There are 2 hypotheses that could explain these results: 1) there was an intermittent source of contamination, and/or 2) laboratory detection limits are not as robust as published, on average. It is well known that estimations of lower detection limits are plagued by large random variations as well as other issues (Bernal, 2013). Therefore, some leniency might be required when comparing results to published laboratory detection limits. Additionally, given that the data above the detection limit per element are not substantial outliers (e.g. $\leq 3s_i$), contamination was not a significant factor overall.

Table 3. *Contamination analysis results of 46 blank samples (no material) following 'partial' aqua regia digestion and analysis via ICP-MS. Included in the table are the: published lower detection limits (LDL), minimum (min), maximum (max), number of samples that are at or above the LDL, mean, standard deviation (SD) and relative standard deviation (RSD) of blank samples. Elements with a high RSD (>20%) which could indicate contamination issues are colored light gray.*

Element	Unit	LDL	Min	Max	Number at or above LDL	Mean	SD	RSD%
Ag	ppb	2	1	1		1	0	0
Al	%	0.01	0.005	0.005		0.01	0.00	0.00
As	ppm	0.1	0.05	0.2	9	0.1	0.0	60.5
Au	ppb	0.2	0.1	0.1		0.1	0.0	0.0
B	ppm	20	10	10		10	0	0

Element	Unit	LDL	Min	Max	Number at or above LDL	Mean	SD	RSD%
Ba	ppm	0.5	0.25	0.25		0.3	0.0	0.0
Be	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Bi	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Ca	%	0.01	0.005	0.005		0.01	0.00	0.00
Cd	ppm	0.01	0.005	0.005		0.01	0.00	0.00
Ce	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Co	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Cr	ppm	0.5	0.25	0.5	1	0.3	0.0	15.1
Cs	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Cu	ppm	0.01	0.005	0.02	4	0.01	0.00	56.39
Dy	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Er	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Eu	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Fe	%	0.01	0.005	0.005		0.01	0.00	0.00
Ga	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Gd	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Ge	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Hf	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Hg	ppb	5	2.5	8	3	3	1	42
Ho	ppm	0.02	0.01	0.01		0.01	0.00	0.00
In	ppm	0.02	0.01	0.01		0.01	0.00	0.00
K	%	0.01	0.005	0.005		0.01	0.00	0.00
La	ppm	0.5	0.25	0.25		0.3	0.0	0.0
Li	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Lu	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Mg	%	0.01	0.005	0.005		0.01	0.00	0.00
Mn	ppm	1	0.5	1	1	1	0	15
Mo	ppm	0.01	0.005	0.005		0.01	0.00	0.00
Na	%	0.001	0.0005	0.0005		0.001	0.000	0.000
Nb	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Nd	ppm	0.02	0.01	0.04	5	0.01	0.01	66.38
Ni	ppm	0.1	0.05	0.05		0.1	0.0	0.0
P	%	0.001	0.0005	0.0005		0.001	0.000	0.000
Pb	ppm	0.01	0.005	0.02	2	0	0	44
Pd	ppb	10	5	5		5	0	0
Pr	ppm	0.02	0.01	0.02	1	0.01	0.00	15.07
Pt	ppb	2	1	2	1	1	0	15
Rb	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Re	ppb	1	0.5	0.5		1	0	0
S	%	0.02	0.01	0.01		0.01	0.00	0.00
Sb	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Sc	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Se	ppm	0.1	0.05	0.1	1	0.1	0.0	15.1
Sm	ppm	0.02	0.01	0.02	1	0.01	0.00	15.07
Sn	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Sr	ppm	0.5	0.25	0.25		0.3	0.0	0.0
Ta	ppm	0.05	0.025	0.025		0.03	0.00	0.00
Tb	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Te	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Th	ppm	0.1	0.05	0.2	2	0.1	0.0	44.2
Ti	%	0.001	0.0005	0.0005		0.001	0.000	0.000
Tl	ppm	0.02	0.01	0.01		0.01	0.00	0.00

Element	Unit	LDL	Min	Max	Number at or above LDL	Mean	SD	RSD%
Tm	ppm	0.02	0.01	0.01		0.01	0.00	0.00
U	ppm	0.1	0.05	0.05		0.1	0.0	0.0
V	ppm	1	0.5	0.5		1	0	0
W	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Y	ppm	0.01	0.005	0.02	4	0.01	0.00	45.62
Yb	ppm	0.02	0.01	0.01		0.01	0.00	0.00
Zn	ppm	0.1	0.05	0.05		0.1	0.0	0.0
Zr	ppm	0.1	0.05	0.2	5	0.1	0.0	56.2

3.2   Accuracy

In the context of QA/QC, accuracy is defined as how close a measured value is to a known or accepted value (Piercey, 2014). The known or accepted value in this study consists of a CRM inserted at random within each batch of 20 samples. The CRMs used in this study are lake sediment LKSD-2 and LKSD-4. Specifically, LKSD-2 was prepared using lake sediment from Calabogie Lake in central Ontario combined with lake sediment collected in the east arm of the Great Bear Lake in the Northwest Territories (NTS map sheets 86K and 86L; Lynch, 1990). LKSD-4 was prepared from a mixture of lake sediments from Big Gull Lake (NTS 31C) in Ontario, Key and Seahorse lakes (NTS 74H) in Saskatchewan (Lynch, 1990).

The accepted values for LKSD-2 and LKSD-4 were published by Lynch (1990, 1999) and Hechler (2013). Accepted values published by Lynch (1990, 1999) were derived from analyses at several national and international participating laboratories, where samples were digested using a strong acid (concentrated HNO_3-concentrated HCl) for partial digestion but with varying fuming times, acid ratios and sample weights. It is assumed that the resulting standard deviations of the accepted values reflect variabilities in the analytical methodology across the laboratories. Comparatively, accepted values published by Hechler (2013) were measured at the Geoscience Laboratories of the Ontario Geological Survey (Sudbury). Samples were digested using a modified (nitric acid-rich) aqua regia solution for partial digestion and analyzed via ICP-MS. Since accepted values from Lynch (1990, 1999) and Hechler (2013) were measured from partial digestions and the values are generally in agreement (with the exception for some elements caused by instrument improvements over the last decades), we consider all published certificates to be comparable. Whenever possible, the most recent accepted value was taken for comparison to this study's measured value.

To determine accuracy, we compare the means (Equation 1) and standard deviations (Equation 2) of a CRM to that of the samples for each determined element. We also calculate the RSD (Equation 3), which provides an indication of precision at the stated mean. As an additional measure, we also calculate the relative error (RE) which provides a semi-quantitative indication of how close the measured mean ($\overline{x_i}$) is to the accepted one ($\overline{x_a}$). Here, we report the relative error in percent (%) in Equation 4. Since some of the accepted values are decades old, the relative error can only be used in a semi-quantitative manner. For this study, a RSD <20% is an indication of good precision at the stated mean and thus accuracy, whereas elements with a high (>20%) RSD could indicate accuracy issues.

$$RE = \frac{|\overline{x_i} - \overline{x_a}|}{\overline{x_a}} \times 100\% \tag{4}$$

The accuracy analysis results for LKSD-2 and LKSD-4 are presented for each element in Tables 4 and 5, respectively, as well as in Appendix C. Of 65 elements determined, 6 (B, Ge, Pd, Pt, Re and Ta) and 5 (B, Ge, Pd, Pt and Ta) of these elements are at or below laboratory detection for analyzed samples LKSD-2 and LKSD-4, respectively. Furthermore, a number of elements could have accuracy issues (i.e. RSD >20%). For the CRM LKSD-2, these elements include: Au and Te. For the CRM LKSD-4, the elements of concern include: Au, Be, Hf, Re and Zr.

It should be noted that all elements that are at or below laboratory detection and/or have a high RSD are in low abundance within the CRM (both for accepted and measured values) and are therefore very close to the lower detection limit. This could be caused by these elements being present within insoluble minerals that cannot be dissolved by aqua regia (Crock and Lamothe, 2011). Similarly to Au, the high RSD could be caused by the difficulty in creating a perfectly homogeneous sample, also known as the 'nugget effect' (Harris, 1982; Clark, 2010; Dominy, 2014). Lastly, it should be noted that a number of elements deviate (substantially outside the published standard deviation; i.e. RE >20%) from the accepted value. For LKSD-2, this is limited to the elements Al, Hf, Sb, Ti and W, whereas for LKSD-4, this includes the elements Nb and Ti. It should be noted that the accepted values for these elements were measured in 1990 and hence, substantial improvements in analytical accuracy since then could be the cause for these deviations.

Table 4. *Accuracy results of 36 CRM LKSD-2 samples following 'partial' aqua regia digestion and analysis via ICP-MS. Results are compared to those of Lynch (1990, 1999), in bold, and Hechler (2013). Included in the table are the: published lower detection limits (LDL), mean, standard deviation (SD), relative standard deviation (RSD) and relative error (RE). Elements below or at the laboratory detection limit are shown in gray. Elements with a high RDS (>20%) are shown in light gray.*

Element	Unit	LDL	LKSD-2 accepted values		Saskatchewan lake sediment re-analysis			
			Mean	SD	Mean	SD	RSD (%)	RE (%)
Ag	ppb	2	792	26	778	38	5	2
Al	%	0.01	**1.87**	**0.25**	1.48	0.06	4.18	21.12
As	ppm	0.1	9.5	0.7	9.0	0.5	5.3	5.8
Au	ppb	0.2	3.0	1.0	2.5	2.3	91.8	18.1
B	ppm	20	**65**	**2**	10	0	0	85
Ba	ppm	0.5	206.0	10.0	207.5	9.1	4.4	0.7
Be	ppm	0.1	0.7	0.1	0.7	0.1	17.6	0.5
Bi	ppm	0.02	1.07	0.04	1.15	0.09	8.04	7.17
Ca	%	0.01	**0.67**	**0.06**	0.55	0.03	4.77	17.33
Cd	ppm	0.01	0.83	0.03	0.83	0.05	5.93	0.10
Ce	ppm	0.1	**108.0**	**12.0**	90.4	5.5	6.0	16.3
Co	ppm	0.1	14.7	0.7	15.8	0.8	5.0	7.3
Cr	ppm	0.5	26.0	1.7	29.2	1.3	4.6	12.3
Cs	ppm	0.02	1.22	0.12	1.30	0.10	7.37	6.72
Cu	ppm	0.01	35.10	1.30	34.36	1.51	4.39	2.12
Dy	ppm	0.02	4.94	0.24	4.97	0.38	7.57	0.62
Er	ppm	0.02	2.67	0.14	2.69	0.18	6.76	0.91
Eu	ppm	0.02	1.28	0.07	1.31	0.10	7.73	2.45
Fe	%	0.01	**3.50**	**0.30**	3.20	0.11	3.35	8.48
Ga	ppm	0.1	4.6	0.3	4.9	0.3	6.1	6.0
Gd	ppm	0.02	7.60	0.40	6.66	0.50	7.51	12.40
Ge	ppm	0.1			0.1	0.0	35.6	
Hf	ppm	0.02	0.10	0.02	0.07	0.01	14.19	29.75
Hg	ppb	5	168	17	147	9	6	13
Ho	ppm	0.02	0.95	0.05	0.94	0.07	7.74	0.73
In	ppm	0.02	0.058	0.003	0.06	0.01	12.21	4.29
K	%	0.01			0.21	0.01	5.64	
La	ppm	0.5	**68.0**	**6.0**	54.9	2.7	4.9	19.3
Li	ppm	0.1	14.3	1.0	15.9	0.9	5.5	11.4
Lu	ppm	0.02	0.36	0.02	0.36	0.03	8.55	0.57
Mg	%	0.01	**0.69**	**0.06**	0.60	0.02	3.06	13.61
Mn	ppm	1	**1840**	**180**	1746	50	3	5
Mo	ppm	0.01	1.15	0.07	1.15	0.08	6.75	0.24

Element	Unit	LDL	LKSD-2 accepted values		Saskatchewan lake sediment re-analysis			
			Mean	SD	Mean	SD	RSD (%)	RE (%)
Na	%	0.001			0.026	0.002	7.955	
Nb	ppm	0.02	1.29	0.11	1.26	0.12	9.37	2.67
Nd	ppm	0.02	49.20	2.60	50.31	3.02	6.00	2.25
Ni	ppm	0.1	24.9	1.9	24.9	1.1	4.2	0.1
P	%	0.001	**0.129**	**0.010**	0.117	0.007	6.391	9.496
Pb	ppm	0.01	36.30	2.10	39.08	1.96	5.02	7.67
Pd	ppb	10			5	1	26	
Pr	ppm	0.02	13.20	0.70	13.55	0.81	5.94	2.69
Pt	ppb	2	3	—–	1	0	35	59
Rb	ppm	0.1	15.2	1.3	16.9	1.0	6.1	11.5
Re	ppb	1			1	1	125	
S	%	0.02	**0.14**	**0.04**	0.15	0.01	3.76	4.37
Sb	ppm	0.02	0.65	0.04	0.50	0.04	8.54	22.74
Sc	ppm	0.1	5.3	0.4	5.6	0.3	5.7	6.6
Se	ppm	0.1	0.8	0.3	0.8	0.1	15.2	2.6
Sm	ppm	0.02	8.70	0.50	8.82	0.45	5.15	1.40
Sn	ppm	0.1	1.3	0.1	1.3	0.1	10.4	7.3
Sr	ppm	0.5	22.0	2.0	25.6	1.5	6.0	16.2
Ta	ppm	0.05	0.01	0.00	0.03	0.00	0.00	187.36
Tb	ppm	0.02	0.97	0.05	0.89	0.08	8.42	8.05
Te	ppm	0.02	0.06	0.01	0.05	0.01	23.15	21.59
Th	ppm	0.1	7.7	0.7	8.4	0.7	8.4	8.8
Ti	%	0.001	0.051	0.006	0.068	0.005	6.823	33.454
Tl	ppm	0.02	0.26	0.01	0.27	0.02	5.85	2.80
Tm	ppm	0.02	0.37	0.02	0.38	0.04	9.33	3.07
U	ppm	0.1	6.2	0.2	6.5	0.3	5.3	4.3
V	ppm	1	40	3	42	2	4	4
W	ppm	0.1	0.5	0.1	0.3	0.0	17.0	36.4
Y	ppm	0.01	26.60	1.40	26.69	1.35	5.08	0.33
Yb	ppm	0.02	2.340	0.130	2.44	0.18	7.23	4.23
Zn	ppm	0.1	190.0	12.0	189.8	7.9	4.1	0.1
Zr	ppm	0.1	3.4	0.3	3.4	0.4	11.8	0.2

Table 5. *Accuracy results of 36 CRM LKSD-4 samples following 'partial' aqua regia digestion and analysis via ICP-MS. Results are compared to those of Lynch (1990, 1999), in bold, and Hechler (2013). Included in the table are the: published lower detection limits (LDL), mean, standard deviation (SD), relative standard deviation (RSD) and relative error (RE). Elements below or at the laboratory detection limit are shown in gray. Elements with a high RDS (>20%) are shown in light gray.*

Element	Unit	LDL	LKSD-4 accepted values		Saskatchewan lake sediment re-analysis			
			Mean	SD	Mean	SD	RSD (%)	RE (%)
Ag	ppb	2	235	170	228	13	6	3
Al	%	0.01	**1.44**	**0.19**	1.26	0.04	2.94	12.29
As	ppm	0.1	14.3	0.6	13.7	0.6	4.6	4.3
Au	ppb	0.2	6	11	3.4	8.0	236.8	43.6
B	ppm	20	**22**	**2**	11	3	27	51
Ba	ppm	0.5	132	9	136.1	6.1	4.5	3.1
Be	ppm	0.1	0.43	0.05	0.4	0.1	23.3	2.1
Bi	ppm	0.02	0.481	0.017	0.52	0.05	9.03	8.86
Ca	%	0.01	**0.89**	**0.05**	0.86	0.03	3.21	3.59

Element	Unit	LDL	LKSD-4 accepted values		Saskatchewan lake sediment re-analysis			
			Mean	SD	Mean	SD	RSD (%)	RE (%)
Cd	ppm	0.01	2.04	0.06	2.07	0.11	5.25	1.40
Ce	ppm	0.1	38.6	1.5	38.4	1.7	4.3	0.4
Co	ppm	0.1	8.5	0.5	9.8	0.5	4.7	15.5
Cr	ppm	0.5	19	1.1	21.2	0.9	4.2	11.6
Cs	ppm	0.02	1.03	0.06	1.05	0.06	5.76	2.18
Cu	ppm	0.01	29.9	1.4	30.11	1.04	3.46	0.72
Dy	ppm	0.02	2.9	0.15	2.87	0.20	7.15	1.12
Er	ppm	0.02	1.65	0.07	1.64	0.11	6.91	0.77
Eu	ppm	0.02	0.9	0.04	0.89	0.05	5.89	0.77
Fe	%	0.01	**2.70**	**0.30**	2.41	0.07	3.04	10.73
Ga	ppm	0.1	3.74	0.21	4.0	0.2	5.4	8.1
Gd	ppm	0.02	3.97	0.21	3.51	0.22	6.27	11.64
Ge	ppm	0.1			0.1	0.0	32.4	
Hf	ppm	0.02	0.05		0.03	0.01	43.92	46.67
Hg	ppb	5	210	60	174	11	6	17
Ho	ppm	0.02	0.572	0.024	0.57	0.05	8.36	1.18
In	ppm	0.02	0.0527	0.0022	0.06	0.01	16.10	6.47
K	%	0.01			0.11	0.01	5.72	
La	ppm	0.5	20.8	0.8	21.4	0.9	4.3	2.7
Li	ppm	0.1	8.3	0.7	9.4	0.5	5.5	13.2
Lu	ppm	0.02	0.235	0.011	0.23	0.02	9.72	3.90
Mg	%	0.01	**0.41**	**0.05**	0.36	0.01	2.82	12.33
Mn	ppm	1	**430**	**30**	412	11	3	4
Mo	ppm	0.01	1.74	0.08	1.73	0.12	6.76	0.70
Na	%	0.001			0.017	0.002	9.475	
Nb	ppm	0.02	1.02	0.09	1.20	0.07	5.55	17.57
Nd	ppm	0.02	21.9	0.8	21.81	1.05	4.79	0.42
Ni	ppm	0.1	31.5	1.8	33.6	1.4	4.1	6.8
P	%	0.001	**0.144**	**0.018**	0.125	0.007	5.699	13.175
Pb	ppm	0.01	87	3	92.79	3.86	4.16	6.66
Pd	ppb	10			9	6	60	
Pr	ppm	0.02	5.57	0.19	5.64	0.29	5.18	1.25
Pt	ppb	2	3		1	0	32	65
Rb	ppm	0.1	9.3	0.5	9.9	0.4	4.6	6.1
Re	ppb	1			3	1	29	
S	%	0.02	**0.99**	**0.09**	0.96	0.05	4.68	2.72
Sb	ppm	0.02	1.22	0.06	1.05	0.07	6.66	14.00
Sc	ppm	0.1	3.61	0.31	3.6	0.2	5.5	1.0
Se	ppm	0.1	2.38	0.27	2.2	0.1	5.6	6.2
Sm	ppm	0.02	4.18	0.17	4.14	0.24	5.73	0.93
Sn	ppm	0.1	3.19	0.15	3.4	0.2	6.0	5.6
Sr	ppm	0.5	38.1	1.9	38.9	2.2	5.5	2.0
Ta	ppm	0.05	0.0058	0.0016	0.03	0.00	0.00	331.03
Tb	ppm	0.02	0.546	0.028	0.49	0.04	7.35	9.60
Te	ppm	0.02	0.138	0.013	0.13	0.01	9.67	7.21
Th	ppm	0.1	1.91	0.14	1.7	0.2	13.1	8.5
Ti	%	0.001	0.0412	0.0042	0.052	0.003	5.227	27.225
Tl	ppm	0.02	0.414	0.026	0.41	0.02	5.00	1.64
Tm	ppm	0.02	0.233	0.01	0.24	0.02	9.01	0.86
U	ppm	0.1	**31.0**	**1.6**	30.2	1.6	5.2	2.5
V	ppm	1	30.7	1.5	31	1	3	0
W	ppm	0.1	0.242	0.024	0.2	0.0	13.5	13.9

Element	Unit	LDL	LKSD-4 accepted values		Saskatchewan lake sediment re-analysis			
			Mean	SD	Mean	SD	RSD (%)	RE (%)
Y	ppm	0.01	16.4	0.7	16.25	0.71	4.37	0.88
Yb	ppm	0.02	1.56	0.06	1.51	0.11	7.15	2.92
Zn	ppm	0.1	179	9	186.4	8.2	4.4	4.2
Zr	ppm	0.1	0.77	0.13	1.1	0.4	38.7	47.5

3.3 Precision

Precision is defined as a measure of the reproducibility of a measurement (Piercey, 2014). Analytical duplicate samples were used to provide an estimate of precision. Essentially, a sample, preferably one of the field duplicates, was split into 2 (a pair), with elemental compositions analyzed in one sample (x_i) and the other sample ($x_i^{'}$). To determine precision, we calculate the mean ($\overline{x_p}$) and standard deviation (s_p) of each elemental composition of all n samples as:

$$\overline{x_p} = \frac{1}{n} \sum_{i=1}^{n} \frac{(x_i + x_i^{'})}{2} \qquad (5)$$

$$s_p = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_i^{'})^2}{2n}} \qquad (6)$$

With the mean and standard deviation calculated, we can now calculate the RSD for precision (RSD_p). For this study, a RSD <20% is an indication of good precision, whereas elements with a high (>20%) RSD could indicate precision issues. The RSD can be calculated via:

$$RSD_p = \frac{s_p}{\overline{x_p}} \times 100\% \qquad (7)$$

In circumstances where one or both values for an elemental composition from a pair were below the lower detection limit or above the upper detection limit, the pair was removed before calculations were made for that elemental composition. In cases (not in this study) where there is a significant deviation between pairs of analyses, an entire block (20) of samples may require re-analysis.

The precision analysis results for ICP-MS are presented for each element in Table 6, as well as in Appendix C. Of 65 elements determined, B, Pt and Ta had measured values that were consistently below their detection limits. Thus, no results could be calculated for these elements. Additionally, 4 elements (Ge, Pd, Re and Te) have a high (>20%) RSD value as well as <30 pairs remaining. Another 2 elements (Hf and In) have >30 pairs remaining, but with a low RSD (<20%). Finally, 2 elements (Au and Sb) have a high RSD, but with >30 pairs remaining.

A closer inspection of elements with a high RSD reveal that, on average, a large number of pairs were removed from the calculations. This indicates that the elements with a high RSD had a large number of pairs with concentrations at or slightly above the lower detection limit. As previously mentioned, measurements at or near the detection limit could be caused by these elements being present in the samples at extremely low levels and unable to be measured using current ICP-MS techniques, or existing within insoluble minerals that cannot be dissolved by aqua regia (Crock and Lamothe, 2011). Specifically for Au, the low precision results could be caused by the difficulty obtaining a perfectly homogeneous sample (nugget effect) (Harris, 1982; Clark, 2010; Dominy, 2014). Elements that have both a high RSD combined with <30 pairs remaining are deemed less reliable and therefore less precise (McCurdy and Garrett, 2016).

Table 6. *Precision results for analytical duplicate pairs of lake sediment samples analyzed via ICP-MS. There are a total of 53 pairs included in this dataset. Included in the table are the: published lower detection limits (LDL), percentage of censored samples (% below LDL), duplicate pairs removed, minimum (min), maximum (max), mean and relative standard deviation (RSD%). Elements with <30 pairs remaining are shown in light gray. Elements with >30 pairs remaining and a high RSD (>20%) are shown in gray.*

Element	Unit	LDL	% below LDL	Pairs removed	Min	Max	Mean	Precision RSD%
Ag	ppb	2			25	228	34	19
Al	%	0.01			0.43	2.71	0.44	1.68
As	ppm	0.1	22.64	12	0.1	18.5	4.0	7.9
Au	ppb	0.2	28.3	15	0.3	5.4	1.1	58.0
B	ppm	20	100	53				
Ba	ppm	0.5			32.9	268.2	40.6	2.6
Be	ppm	0.1			0.3	6.4	1.0	14.9
Bi	ppm	0.02			0.02	0.29	0.05	14.75
Ca	%	0.01			0.17	0.69	0.11	1.91
Cd	ppm	0.01			0.14	1.32	0.19	4.66
Ce	ppm	0.1			21.0	371.7	70.3	2.3
Co	ppm	0.1			2.5	27.8	4.0	2.9
Cr	ppm	0.5			9.2	41.5	6.9	2.7
Cs	ppm	0.02			0.11	1.87	0.32	2.69
Cu	ppm	0.01			5.12	39.22	7.28	2.99
Dy	ppm	0.02			1.55	14.61	2.51	3.78
Er	ppm	0.02			0.88	8.37	1.43	3.25
Eu	ppm	0.02			0.28	3.69	0.63	4.41
Fe	%	0.01			0.62	18.37	3.46	2.54
Ga	ppm	0.1			0.7	4.3	0.8	3.8
Gd	ppm	0.02			1.73	20.13	3.52	6.33
Ge	ppm	0.1	75.47	40	0.1	0.3	0.1	25.5
Hf	ppm	0.02	67.92	36	0.02	0.68	0.15	9.24
Hg	ppb	5			52	362	42	13
Ho	ppm	0.02			0.31	2.93	0.49	3.68
In	ppm	0.02	88.68	47	0.02	0.03	0.00	13.86
K	%	0.01			0.02	0.15	0.03	5.96
La	ppm	0.5			10.2	174.4	33.1	2.2
Li	ppm	0.1			0.9	18.3	4.0	3.9
Lu	ppm	0.02			0.12	1.27	0.21	4.45
Mg	%	0.01			0.05	0.34	0.08	3.31
Mn	ppm	1	1.89	1	80	1812	325	2
Mo	ppm	0.01			0.80	22.84	4.09	2.45
Na	%	0.001			0.003	0.019	0.003	10.217
Nb	ppm	0.02			0.73	3.22	0.58	3.71
Nd	ppm	0.02			11.84	163.96	30.48	2.55
Ni	ppm	0.1			6.9	24.5	4.1	2.6
P	%	0.001			0.040	0.316	0.059	3.268
Pb	ppm	0.01			1.22	50.09	6.67	5.79
Pd	ppb	10	98.11	52	13	30	12	56
Pr	ppm	0.02			3.28	47.75	8.69	2.17
Pt	ppb	2	100	53				
Rb	ppm	0.1			1.4	20.4	4.6	3.5
Re	ppb	1	67.92	36	1	355	61	499
S	%	0.02			0.06	0.69	0.11	2.39
Sb	ppm	0.02	1.89	1	0.03	0.59	0.07	54.83
Sc	ppm	0.1			0.4	7.9	1.3	4.7

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Element	Unit	LDL	% below LDL	Pairs removed	Min	Max	Mean	Precision RSD%
Se	ppm	0.1			0.4	2.1	0.3	9.5
Sm	ppm	0.02			2.12	28.62	4.95	4.26
Sn	ppm	0.1	1.89	1	0.2	1.2	0.2	18.8
Sr	ppm	0.5			9.9	38.0	7.6	2.7
Ta	ppm	0.05	100	53				
Tb	ppm	0.02			0.25	2.76	0.47	3.04
Te	ppm	0.02	96.23	51	0.02	0.04	0.01	33.33
Th	ppm	0.1			0.2	24.2	5.0	5.9
Ti	%	0.001			0.007	0.068	0.015	3.250
Tl	ppm	0.02			0.06	0.36	0.06	4.33
Tm	ppm	0.02			0.11	1.24	0.21	4.94
U	ppm	0.1			1.0	58.5	10.8	2.7
V	ppm	1			10	93	15	3
W	ppm	0.1	7.55	4	0.1	2.9	0.5	7.7
Y	ppm	0.01			9.12	82.64	13.60	2.38
Yb	ppm	0.02			0.82	7.96	1.36	3.04
Zn	ppm	0.1			34.2	293.2	44.9	2.9
Zr	ppm	0.1			0.1	26.7	3.9	6.1

3.4 ANOVA

Collection of field duplicate samples at survey sites permits the comparison of the combined variability of the geochemical data due to field sampling procedures, sample heterogeneity and analysis with variability across the survey area. The analyses of the duplicate pairs are used to undertake a one-way random effects Analysis of Variance (ANOVA) model (McKillup and Dyar, 2012; Garrett, 2013a; McCurdy and Garrett, 2016). The hypothesis tested is that the means (μ) at the (n) duplicated sites are equal:

$$H_0 : \mu_1 = \mu_2 = \mu_3 = \mu_4 = ... = \mu_n \tag{8}$$

The desired outcome is a rejection of H$_0$, with the conclusion that there is significant spatial variability across the survey area. In such cases, contour or other iso-concentration maps should be informative in supporting data interpretation. The calculated F-value from the ANOVA is compared with the value of the F distribution with n-1 and n degrees of freedom (DoF) and stated confidence level, α. Commonly the 95% confidence level is chosen, i.e. α = 0.05, implying that the F-ratio could only arise by chance in 1 of 20 occasions. A calculated F-value greater than the value for stated DoF and α, or calculated probability of <0.05, infers a less that 1 in 20 chance the results arose due to chance. If the combined sampling and analytical variability is not significantly smaller than the field survey variability, it cannot be stated that there are statistically significant spatial patterns in the data, and thus the data may be misleading, or at worst, meaningless (Thompson and Howarth, 1973; Garrett, 1983; Reimann et al., 2008).

The critical value of the F-ratio for given α is a function of the DoF, decreasing asymptotically toward unity as the DoF increase. For larger DoF and lower F-ratios it may be prudent to decrease α to increase confidence that any systematic patterns are statistically significant. For example, the F-statistic exceeding that for an α of 0.01, implies that the F-ratio could only arise with a probability of less than 1 in 100.

Any statistical computing software or programming language may be employed to undertake a one-way ANOVA, with the probability associated with the calculated F value being computed internally. Additional steps may also estimate the percentage of the variability in the data that occurs between and at the sample sites. A R (R Code Team, 2022) package, 'rgr' (Garrett, 2013b), developed at the Geological Survey of Canada, contains functions 'anova1' or 'anova2' that undertake the above computations, and other QA/QC computational and graphical display tasks.

If analytical duplicate samples are systematically split from either of the field duplicate pair, the sample site and analytical variabilities, along with the between site variability, can be separately estimated (Garrett, 2013a). This use of an unbalanced staggered ANOVA design is efficient in providing maximum information concerning survey variability at minimum sampling and analytical cost (Garrett, 1983).

In applied geochemical studies where mineral resources or sources of anthropogenic contamination are being sought, systematic spatial variability is not an essential requirement. The data is examined for outliers and/or anomalies, employing a variety of univariate and multivariate tools to support data interpretation. In such cases, symbol maps are likely to be more informative than contour and iso-concentration maps.

For each element, if one or both values from a field duplicate pair were below the lower detection limit or above the upper detection limit, the pair was removed before calculations. A log-transformation ($\log_{10}$) of the data was carried out prior to ANOVA to ensure the homogeneity of variance (homoscedasticity), a requirement of ANOVA (Bartlett, 1947).

The ANOVA results for ICP-MS analysis are presented for each element in Table 7, as well as in Appendix C. Of 65 elements determined, 4 elements (B, Pd, Pt and Ta) have analytical values that are consistently below their detection limits. Thus, no results could be calculated for these elements. Additionally, 5 elements (Ge, Hf, In, Re and Te) have <30 pairs remaining and 1 element (Au) has a low (<4) F-value, combined with a p-value near 0.05.

Elements with a F-value smaller than 4 combined with a p-value near or above 0.05 had a large number of field duplicate pairs removed. In many cases, less than 30 pairs remain for analyses, indicating that the results derived from these elements are less reliable. Values at or near the detection limits could be caused by these elements being present in the sample at extremely low concentrations, such that they cannot be measured using current ICP-MS techniques, or within insoluble minerals that cannot be dissolved by aqua regia (Crock and Lamothe, 2011). The low precision results for Au are typically the result of the difficulty in homogenizing this element in a sample (nugget effect) (Dominy, 2014).

Table 7. *ANOVA results for field duplicate pairs of lake sediment samples analyzed via ICP-MS. There are a total of 53 pairs in this dataset. Included in the table are the: number of duplicate pairs removed, percentage of variation, F-statistic and p-value. Variance components are only estimated where there are >3 pairs left. Elements with <30 pairs remaining are shown in light gray. Elements with >30 pairs remaining and a low F-statistic (<4) are shown in gray.*

Element	Pairs removed	Percentage variation		F-statistic	p-value
		At sites	Between sites		
Ag		14.16	85.84	13.12	0.00
Al		5.37	94.63	36.26	0.00
As	12	8.35	91.65	22.94	0.00
Au	15	68.32	31.68	1.93	0.02
B	53				
Ba		4.26	95.74	45.98	0.00
Be		6.89	93.11	28.02	0.00
Bi		6.05	93.95	32.06	0.00
Ca		6.05	93.95	32.05	0.00
Cd		9.78	90.22	19.45	0.00
Ce		2.12	97.88	93.50	0.00
Co		5.96	94.04	32.55	0.00
Cr		2.99	97.01	65.95	0.00
Cs		2.61	97.39	75.57	0.00
Cu		2.41	97.59	81.99	0.00
Dy		4.42	95.58	44.29	0.00
Er		4.8	95.2	40.67	0.00
Eu		3.4	96.6	57.86	0.00
Fe		3.32	96.68	59.17	0.00

Element	Pairs removed	Percentage variation		F-statistic	p-value
		At sites	Between sites		
Ga		2.98	97.02	66.13	0.00
Gd		3.57	96.43	55.05	0.00
Ge	40	27.54	72.46	6.26	0.00
Hf	36	8.04	91.96	23.87	0.00
Hg		65.24	34.76	2.07	0.00
Ho		4.01	95.99	48.90	0.00
In	47	63.16	36.84	2.17	0.17
K		5.52	94.48	35.21	0.00
La		2.54	97.46	77.79	0.00
Li		1.38	98.62	143.56	0.00
Lu		3.94	96.06	49.75	0.00
Mg		1.75	98.25	113.06	0.00
Mn	1	2.72	97.28	72.55	0.00
Mo		1.3	98.7	152.66	0.00
Na		15.93	84.07	11.56	0.00
Nb		2.09	97.91	94.68	0.00
Nd		3.1	96.9	63.59	0.00
Ni		5.57	94.43	34.92	0.00
P		4.98	95.02	39.19	0.00
Pb		5.94	94.06	32.69	0.00
Pd	52				
Pr		2.76	97.24	71.51	0.00
Pt	53				
Rb		2.02	97.98	97.96	0.00
Re	36	66.57	33.43	2.00	0.08
S		2.97	97.03	66.43	0.00
Sb	1	30.96	69.04	5.46	0.00
Sc		1.79	98.21	110.70	0.00
Se		17.51	82.49	10.42	0.00
Sm		3.44	96.56	57.17	0.00
Sn	1	11.35	88.65	16.62	0.00
Sr		4.85	95.15	40.27	0.00
Ta	53				
Tb		3.63	96.37	54.17	0.00
Te	51	120	-20	0.67	0.62
Th		3.33	96.67	59.04	0.00
Ti		3.54	96.46	55.48	0.00
Tl		5.22	94.78	37.34	0.00
Tm		4.3	95.7	45.51	0.00
U		1.4	98.6	142.09	0.00
V		3.53	96.47	55.74	0.00
W	4	9.5	90.5	20.06	0.00
Y		4.07	95.93	48.17	0.00
Yb		4.06	95.94	48.21	0.00
Zn		8.98	91.02	21.27	0.00
Zr		6.4	93.6	30.26	0.00

4 Conclusion

Conducting a QA/QC program for geochemical data is important prior to the use of the dataset. QA/QC results allow an informed application of geochemical data and a preliminary understanding of the root causes of data quality issues. In this study we quantified the contamination, accuracy, precision and fitness-for-purpose

for prospectivity mapping of a suite of re-analyzed lake sediment samples that were collected in northeastern Saskatchewan (NTS 064-E, 074A and H). Samples were re-analyzed in large part because of a high potential for the area to host uranium and base metals mineralization, as well as recent and significant advances in analytical instrumentation, which allows more elements to be determined, and overall, at a higher precision with lower detection limits than the previous analyses. QA/QC results have identified several elements that need to be monitored carefully for future analyses and for applications of the dataset. Overall, the data is of good quality and can be used within the context of regional geochemical exploration.

Acknowledgements

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Appendix A   Metadata

A.1   Metadata

Title of file: A1_GSC_OF_8871_Metadata.docx

A.2   Bureau Veritas fee schedule

Title of file: A2_Bureau_Veritas_Fee_Schedule-2021.pdf

A.3   Bureau Veritas fee schedule web link

Title of file: A3_Web_Link.txt

Appendix B   Raw Data

B.1   ICP-MS Raw Data

Title of file: B1_GSC_OF-8871_ICP-MS_Raw-Data.xlsx

Appendix C   Edited Data

C.1   QA/QC Results

Title of file: C1_GSC_OF-8871_QAQC-Results.xlsx