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**GEOLOGICAL SURVEY OF CANADA
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**Regional lake sediment geochemical data from north-
central Saskatchewan (NTS 074-A, B, G, and H):
reanalysis data and QA/QC evaluation**

J.E. Bourdeau, M.W. McCurdy, S.J.A. Day, and R.G. Garrett

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Permanent link: <https://doi.org/10.4095/329204>

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Recommended citation

Bourdeau, J.E., McCurdy, M.W., Day, S.J.A., and Garrett, R.G., 2021. Regional lake sediment geochemical data from north-central Saskatchewan (NTS 074-A, B, G, and H): reanalysis data and QA/QC evaluation; Geological Survey of Canada, Open File 8837, 1 .zip file.
<https://doi.org/10.4095/329204>

Publications in this series have not been edited; they are released as submitted by the authors.

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Regional lake sediment geochemical data from north-central Saskatchewan (NTS 074-A, B, G 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 north-central Saskatchewan (NTS 074-A, B, G and H). The original lake survey was conducted in 1986 and the re-analysis in 2021. Original survey results are presented in OF1359. A total of 1,290 lake sediment samples were re-analyzed, covering an area of 17,000 km², averaging a density of 1 sample per 13 km². Samples were measured for 65 elements via modified aqua-regia – ICP-MS and 35 elements via INA analysis. 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 are of good quality.

Introduction

Evaluation of 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 users of geochemical data can be fully informed of the implications of the quality of the data. This QA/QC report adheres to the methodology presented in McCurdy and Garrett (2016) and evaluates the contamination, accuracy, precision and fitness-for-purpose of the data.

In 1986, lake sediment samples were collected in north-central Saskatchewan and the geochemical data were published in Geological Survey of Canada Open File 1359 by Hornbrook and Friske (1987). 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, the original survey samples were selected for re-analysis. Furthermore, the original survey samples are located in the Athabasca-Wollaston area, an area 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).

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). Another partner for this re-analysis project includes the Saskatchewan Geological Survey (SGS).

The survey area is located in north-central Saskatchewan (NTS 074-A, B, G and H), encompassing a total area of 17,000 km² (Hornbrook and Friske, 1987). The area includes the southern-most portions of the Paleoproterozoic Athabasca Basin, that to date, 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 north, the region to the south 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 undeveloped.

In this publication, we present the re-analysis and QA/QC results for a total of 1,290 lake sediment samples. In comparison with the original survey, which included 16 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), and 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.

Sampling and analytical techniques

Description of surveys and sample management

The original lake sediment survey was conducted in the summer of 1986 in north-central Saskatchewan (Fig. 1). A total of 1,286 (excluding CRMs, analytical duplicates and 1 of each of the field duplicate pairs) samples were collected covering an area of 17,000 km², averaging a density of 1 sample per 13 km² (Hornbrook and Friske, 1987). Samples were chemically analyzed for 16 elements and the results were released in 1987 as a Geological Survey of Canada (GSC) Open File 1359.

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, crushed, ball milled (ceramic mill with ceramic balls) and sieved. The -80 mesh (177 µm) fraction was used for subsequent analyses. Typically, 1 kg of organic-rich gyttja yielded about 50 g of material for analysis. After initial analysis in 1986, unused sample material was stored and archived in plastic containers.

To ensure the quality and reproducibility of the data, CRMs and analytical duplicates were added to the survey samples by the GSC. Original 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 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. Re-analyzed 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 obvious errors. These checks were done both at the laboratory and upon reception of the data at the Geological Survey of Canada.

Analytical procedures 2020-2021

Samples selected and prepared for re-analysis were analyzed at Bureau Veritas in Vancouver (British Columbia) and Mississauga (Ontario). Samples were split and analyzed via both inductively-coupled plasma-mass spectroscopy (ICP-MS) and instrumental neutron activation (INA). Details of each procedure are described below.

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 HNO₃:HCl:H₂O) 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 vial), 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.

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			

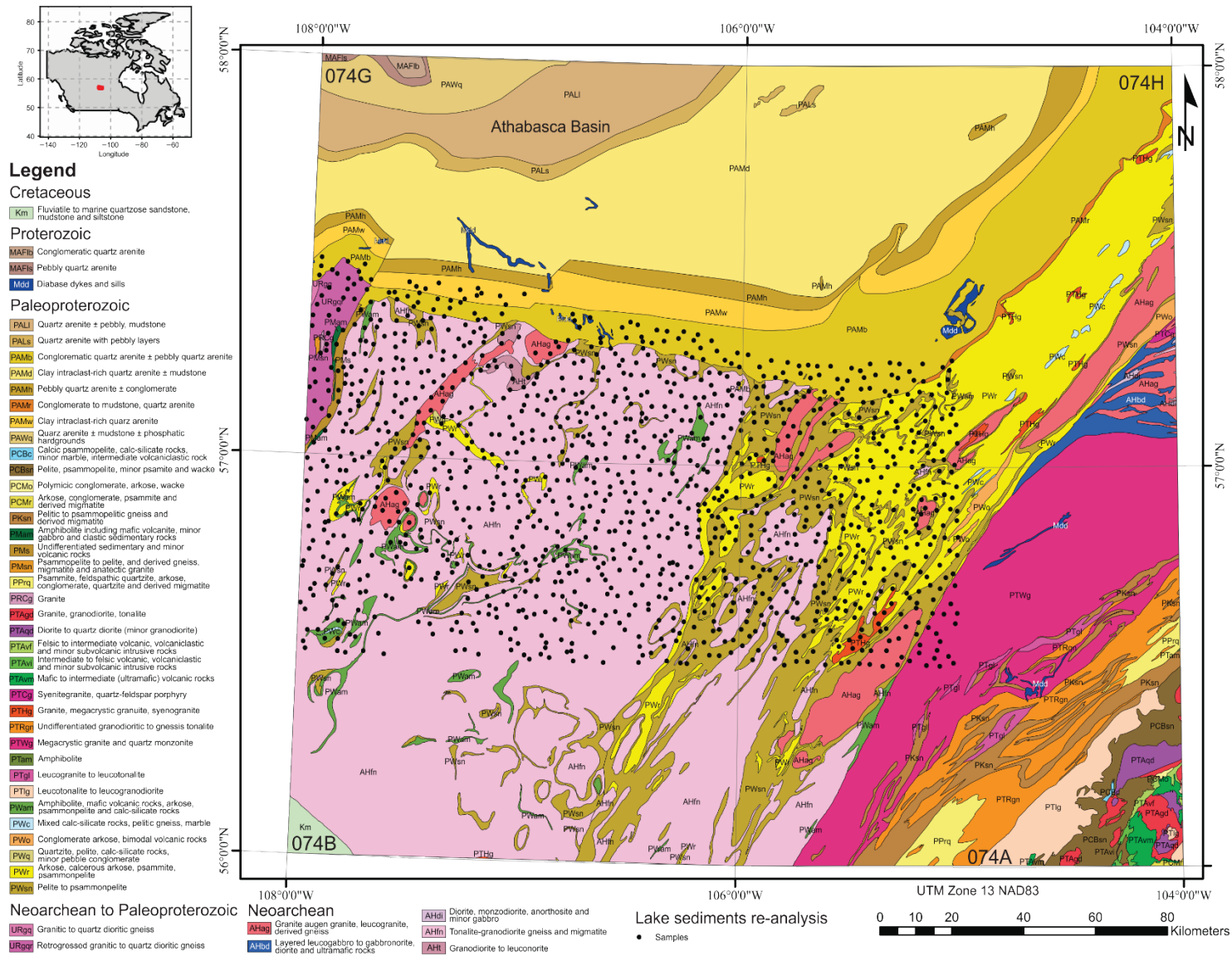


Figure 1. Bedrock geological map of NTS 074-A, B, G and H, provided by the Saskatchewan Geological Survey. Included in the geological map are the locations of lake sediment samples collected in 1986 and re-analyzed in this study (black circles).

INA analysis A total of 35 trace elements were determined via INA (Table 2). In contrast with the ICP-MS analytical procedures, INA required no further sample preparation at the laboratory. Samples were weighed and placed into plastic vials with a flux monitor affixed to each vial. Samples were then stacked into a 'bundle' and exposed to neutron flux. Samples were then placed in front of a detector coupled to a multi-channel analyzer for element 'counting'. The amounts of various isotopes, and hence elements present were determined by comparison of the spectrum energies versus the number of counts at each energy state for the samples and standards. Laboratory QA/QC protocol included the changing of vials (using feedstock) between each sample and the addition of CRMs. Analytical results were verified by a senior analyst prior to being delivered to the GSC.

Table 2. Lower detection limits published by Bureau Veritas for INA analysis.

Element	Lower detection limit	Element	Lower detection limit
Ag	2 ppm	Ni	10 ppm
As	0.5 ppm	Rb	5 ppm
Au	0.002 ppm	Sb	0.1 ppm
Ba	50 ppm	Sc	0.2 ppm
Br	0.5 ppm	Se	5 ppm
Cd	5 ppm	Sm	0.1 ppm
Ce	5 ppm	Sn	100 ppm
Co	5 ppm	Ta	0.1 ppm
Cr	20 ppm	Tb	0.5 ppm
Cs	0.5 ppm	Te	10 ppm
Eu	1 ppm	Th	0.2 ppm
Fe	2000 ppm	Ti	500 ppm
Hf	1 ppm	U	0.2 ppm
Ir	0.05 ppm	W	1 ppm
La	2 ppm	Yb	2 ppm
Lu	0.2 ppm	Zn	100 ppm
Mo	1 ppm	Zr	200 ppm
Na	200 ppm		

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 further determined using variance analyses of in-site versus between-site variability using the analysis of variance (ANOVA) of field duplicate samples.

Re-analysis of lake sediment samples are presented in Appendix B as worksheets titled: "Appendix B1 GSC_OF-1752_ICP-MS_Raw-Data" and "Appendix B2_GSC_OF-1752_INA_Raw-Data", respectively. Included in the worksheets are the data as reported by the laboratory. Elements in Appendix B are listed in the order that they were reported in the laboratory certificates. QA/QC results for contamination, accuracy, precision and fitness-for-purpose accompany this report in Appendix C as a

worksheet titled: "Appendix C1 GSC_OF-1752_QAQC-Results" (see Table 3 for list of worksheets in the appendix). Elements in Appendix C1 are arranged alphabetically for ease of reading.

Table 3. Appendix C1 worksheets. The worksheets contain the edited data (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 - Accuracy LKSD-2 INA	Compares accepted values for CRM LKSD-2 with results from re-analysis via INA.
C1-5 - Accuracy LKSD-4 INA	Compares accepted values for CRM LKSD-4 with results from re-analysis via INA.
C1-6 - Precision ICP-MS	Provides an estimate of precision using analytical duplicate pairs for re-analysis via ICP-MS.
C1-7 - Precision INA	Provides an estimate of precision using analytical duplicate pairs for re-analysis via INA.
C1-8 - ANOVA ICP-MS	Provides an estimate of fit-for-purpose using field duplicate pairs for re-analysis via ICP-MS.
C1-9 - ANOVA INA	Provides an estimate of fit-for-purpose using field duplicate pairs for re-analysis via INA.

Contamination

Blank samples are typically used to quantify contamination and can be introduced at various stages during sampling, sample preparation and analysis. For this analysis, blanks were used by the commercial laboratory to monitor for any possible contamination stemming from sample preparation (digestion) and ICP-MS analysis. Contamination is practically non-existent for INA analysis since no digestion is required and vials are made specifically contaminant-free for laboratory use.

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 (\bar{x}_i Equation 1) and standard deviation (s_i ; Equation 2), respectively, of blank analyses for each determined element (\bar{x}_i):

$$\bar{x}_i = \frac{\sum_{i=1}^n \bar{x}_i}{n} \quad (1)$$

$$s_i = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x}_i)^2}{n}} \quad (2)$$

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,

an RSD <20% is an indication of reliable data, whereas a high (>20%) RSD could indicate contamination issues. The RSD can be calculated via:

$$RSD = \frac{S_i}{\bar{x}_i} \times 100\% \quad (3)$$

The majority of elements published for blank samples fall under 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 (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 Appendix C, worksheet C1-1. Of the 65 elements determined, none has a mean that is above the lower detection limit. However, 13 elements (As, Cd, Cu, Gd, Hg, Mn, Nd, Pb, Pr, Re, Tb, Te, Th and Zr) have a high RSD ($\geq 20\%$). A detailed analysis of these elements reveals between 0 to 8 data points at or above the detection limit. The high RSD for Re and Zr is caused by data at the detection limit and hence, these elements show no sign of contamination or issues with the published detection limit. The remaining 11 elements all have at least 1 data point that plot above their detection limit. There are two 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 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.

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 the Big Gull Lake (NTS 31C) in Ontario, Key and Sea Horse lakes (NTS 74H) in Saskatchewan (Lynch, 1990).

The accepted values for LKSD-2 and LKSD-4 are published in Lynch (1990, 1999) and Hechler (2013). Accepted values published in Lynch (1990) and Lynch (1999) were derived from analyses at several national and international participating laboratories, where samples were digested using a strong acid (concentrated HNO₃-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 (x_i) is to the accepted one (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, an 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.

$$RE = \frac{|\bar{x}_i - \bar{x}_a|}{\bar{x}_a} \times 100\% \quad (4)$$

The accuracy analysis results for ICP-MS are presented for each element in Appendix C, worksheets C1-2 and C1-3 for CRMs LKSD-2 and LKSD-4, respectively. 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 exhibit accuracy issues (i.e., RSD >20%). For the CRM LKSD-2, these elements include: Au, Hf and Te. For the CRM LKSD-4, the elements of concern include: Au, Be, Hf, Re and W.

The accuracy analysis results for INA are presented for each element in Appendix C, worksheets C1-4 and C1-5 for CRMs LKSD-2 and LKSD-4, respectively. Of 35 elements determined, 6 (Au, Cd, Ir, Se, Sn and Te) and 9 (Ag, Au, Cd, Ir, Se, Sn, W, Zn and Zr) of these elements are at or below laboratory detection for analyzed samples LKSD-2 and LKSD-4, respectively. Furthermore, a number of elements could exhibit accuracy issues (i.e., RSD >20%). For the CRM LKSD-2, these elements include: Ag, Eu, Lu, Mo, W and Zr. For the CRM LKSD-4, the elements of concern include: Cr, Eu, Mo, Ta and Yb.

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 in the lake sediment within discrete, often refractory minerals (e.g., spinel, tourmaline, zircon and monazite group minerals, as well as niobates, tungstates, topaz, tantalite and cassiterite; Crock and Lamothe, 2011). As for 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). Lastly, there are also a number of elements in INA analyses that deviate (substantially outside the published standard deviation) from the accepted value. For LKSD-2, this is limited to the element B, whereas for LKSD-4, this includes the elements B, Lu and Tb. 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.

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 (\bar{x}_p) and standard deviation (s_p) of each elemental composition of all n samples as:

$$\bar{x}_p = \frac{1}{n} \sum_{i=1}^n \frac{(x_i + x'_i)}{2} \quad (5)$$

$$s_p = \sqrt{\frac{\sum_{i=1}^n (x_i + x'_i)^2}{2n}} \quad (6)$$

With the mean and standard deviation calculated, we can now calculate the RSD for precision (RSD_p). For this study, an 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:

$$RSD_p = \frac{s_p}{\bar{x}_p} \times 100\% \quad (7)$$

In circumstances where one or both values for an elemental composition from a pair were below or above the 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 Appendix C, worksheet C1-6. Of 65 elements determined, 2 elements (B and Ta) had measured values that consistently fell below detection limits. Thus, no results could be calculated for these elements. Additionally, 5 elements (Ge, In, Pd, Pt and Te) have a high (<20%) RSD value as well as <30 pairs remaining, and 5 elements (Au, Ba, Be, Re and Sn) have a high RSD, but with > 30 pairs remaining.

The precision analysis results for INA are presented for each element in Appendix C, worksheet C1-7. Of 35 elements determined, 6 elements (Ag, Cd, Ir, Sn, Te and Zr) had values that consistently fell below detection limits. Thus, no results could be calculated for these elements. Additionally, 8 elements (Au, Cs, Eu, Mo, Sb, Se, Ta and W) have a high RSD as well as <30 pairs remaining, and 2 elements (Ba and Na) have a high RSD but with more than 30 pairs remaining.

A closer inspection of elements with a high RSD reveals that, on average, a large number of pairs were removed from the calculations. This inspection indicates that the pairs had 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 absent in the samples, or existing in discrete, often refractory minerals (Crock and Lamothe, 2011). Specifically for Au, the low precision results could be caused by the difficulty obtaining a perfectly homogeneous sample (nugget effect). Elements that have both a high RSD combined with <30 pairs remaining are deemed less reliable and therefore less precise (McCurdy and Garrett, 2016).

ANOVA

Applied geochemical surveys generally have two objectives. Firstly, to identify ‘anomalous’ situations related to some process of interest (e.g., mineral concentrations or anthropogenic contamination) and secondly, to map any systematic variability across the survey area. For the latter, if the geochemical patterns are to be reliably mapped, the local (within site) variability must be smaller than the regional (between sites) variability.

To determine if the data are ‘fit-for-purpose’ and regional-scale patterns can be reliably mapped, we employ a one-way ANOVA. Field duplicate samples are collected some small distance apart (within a few meters of each other) at a 5% frequency across the survey area. The analyses of these pairs of

samples quantify the combined local and analytical variability. The hypothesis being tested is that the means of the pairs are equal:

$$H_0: \mu_1 = \mu_2 = \dots = \mu_n$$

where n is the number of field duplicate pairs. For the data to be ‘fit-for-purpose’ we wish that this hypothesis fails (i.e., that there are differences). That is, that the means of the pairs are unequal and that therefore there is regional variability in the samples. Regional site variability, ‘between’ the site pair means taking into account the variability ‘within’ the means due to local sampling and analytical variability.

The variance ratio, or F-statistic (F), is calculated in the ANOVA as the ratio of ‘between’ site variance ($(s_i^b)^2$) and ‘within’ sites variance ($(s_i^w)^2$):

$$F = \frac{(s_i^b)^2}{(s_i^w)^2} \quad (8)$$

The p-value, the probability that the F-statistic could have occurred purely by chance is calculated with $n-1$ and n degrees of freedom. The desired outcome is large F and small p, certainly less than 0.05 (corresponding to an F of 1.45 for 80 pairs) and ideally $<.001$, leading to the rejection of the hypothesis of equal means. The critical value of F is small due to the large number of degrees of freedom and number of multiple mean comparisons being made. This can be accommodated with a Bonferroni correction, essentially ‘raising the bar’ from the 0.95 confidence level:

$$\text{Bonferroni corrected 0.95 confidence level} = 1 - 0.5/n \quad (9)$$

With 80 pairs this leads to a critical value for the 0.988125 confidence level of 1.67, a practically insignificant increase. The F-test is not particularly informative, a more insightful approach would help applied geochemists assess the reliability of any maps prepared.

The magnitude of F, the measure of the ratio ‘between’ sites variance, $(s_i^b)^2$, to ‘within’ sites variance, $(s_i^w)^2$, can be converted to the percentage of the total variability that is due to ‘within’ sites variability through the following relationship:

$$(s_i^w)^2\% = 100 \times \alpha \left[1 - \left(\frac{F}{F+1} \right) \right] \quad (10)$$

where α corresponds to a scale-correction factor (Tidball, 1984):

$$\alpha = \frac{n_p \times n}{n - n_p} \quad (11)$$

where n corresponds to the total number of samples in the study and n_p is the number of points in a pair. In this study, $n = 215$ and $n_p = 2$, yielding a $\alpha \approx 2$. Finally, the percentage of variance between sites ($s_i^{b\%}$) can be given as:

$$(s_i^b)^2\% = 100 - (s_i^w)^2\% \quad (12)$$

For each element, if one or both values from a pair were below or above the detection limits, the pair was removed before calculations. A log-transformation (\log_{10}) of the data was carried out prior to ANOVA to ensure homogeneity of variance (homoscedasticity), a requirement of ANOVA (Bartlett, 1947). Homoscedasticity is when means are independent of variances, when data span more than 1.5 orders-of-magnitude the data are most likely heteroscedastic.

The ANOVA results for ICP-MS analysis are presented for each element in Appendix C, worksheet C1-8. Of 65 elements determined, 2 elements (B and Ta) have values that consistently fell below detection limits. Thus, no results could be calculated for these elements. Additionally, 7 elements (Au, Ge, In, Pd, Pt, Re and Te) have a low (<4) F-value, combined with a p-value above 0.05.

The ANOVA results for INA analysis are presented for each element in Appendix C, worksheet C1-9. Of 35 elements determined, 8 elements (Ag, Au, Cd, Ir, Se, Sn, Te and Zr) have values that consistently fell below detection limits. Thus, no results could be calculated for these elements. Additionally, 1 element (Eu) has a low 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 limit, for factors beyond their absence in the samples, could be caused by these elements being in discrete, often refractory minerals (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).

Conclusions

Conducting a QA/QC program for geochemical data is important prior to the use of the dataset. 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 north-central Saskatchewan (NTS 074-A, B, G 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 are of good quality and can be used within the context of regional geochemical exploration.

Acknowledgments

The authors would like to thank Dr. Danny Wright (GSC) for his support. We thank Beth McClenaghan (GSC) who conceived and manages this GEM re-analysis project. We thank Thomas Love and Dr. Ryan Morelli (Geological Survey of Saskatchewan) for providing detailed geological knowledge and maps of Saskatchewan. Many thanks to Dr. Steven E. Zhang who helped with the creation of a new data QA/QC processing routine in Python. The authors would also like to thank Jean de Chavez, Mayank Nigam and Robert Allen (Bureau Veritas) for providing detailed methodologies for sample analysis. We thank Wendy Spirito (GSC) for providing constructive and critical comments which have improved this report. We also express gratitude to the GSC's Sedimentology Lab staff who managed the archived samples and

prepared them for analyses - a monumental task to undertake during COVID-19 restrictions. Funding for this study was graciously provided by the GEM-GeoNorth program.

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