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Environmental geoscience investigations surrounding the former Aldermac mine, Abitibi, Quebec: interpreting geochemical records of metal contamination in near-shore lake sediments 30 and 70 years after mining

S. Alpay, R.J. McNeil, M.J. Hinton, and A. Grenier

2019

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2019

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Permanent link: <https://doi.org/10.4095/315351>

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Recommended citation

Alpay, S., McNeil, R.J., Hinton, M.J., and Grenier, A., 2019. Environmental geoscience investigations surrounding the former Aldermac mine, Abitibi, Quebec: interpreting geochemical records of metal contamination in near-shore lake sediments 30 and 70 years after mining; Geological Survey of Canada, Open File 8393, 1 .zip file. <https://doi.org/10.4095/315351>

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

SUMMARY

This Geological Survey of Canada (GSC) Open File report presents geochemical datasets from near-shore lake sediments, collected in 1971-72 and 2012, located downstream of the abandoned Aldermac metal mine (Cu-Zn-Ag-Au), 25 km west of Rouyn-Noranda, Quebec. A subset of 25 lake sediment samples, retrieved during a large-scale survey in 1971-72, overlaps geographically with recent investigations of the environmental consequences of metal mining. The archived samples were re-analysed by modern analytical methods. In 2012, these sampling stations were revisited to collect recent sediments, analysed by the same analytical methods. This study evaluates elemental concentrations and their spatial distributions in 1971-72 and 40 years later. Evidence of acid mine drainage persists seven decades after mining operations ended. Although bulk sediment geochemical data can provide qualitative insights into regional distributions for reconnaissance, cautions are advisable when comparing quantitative data from different times, using different sampling techniques, sample treatments, and analytical methods.

SOMMAIRE

Ce dossier public de la Commission géologique du Canada (CGC) présente des données géochimiques provenant de sédiments lacustres recueillis près des rivages en 1971-72 et en 2012, situés en aval de la mine abandonnée, Aldermac (Cu-Zn-Ag-Au), 25 km à l'ouest de Rouyn-Noranda, au Québec. Un sous-ensemble de 25 échantillons de sédiments lacustres, récupérés lors d'un levé à grande échelle en 1971-72, chevauche géographiquement des études récentes portant sur les conséquences environnementales de l'extraction minière. Les échantillons archivés ont été ré-analysés suivant les méthodes analytiques modernes. En 2012, ces stations ont été revisitées pour prélever des sédiments récents, aussi analysés selon les mêmes méthodes analytiques. Cette étude évalue les concentrations élémentaires et leurs distributions spatiales en 1971-72 et 40 ans plus tard. Les indicateurs du drainage minier acide persistent sept décennies après la fin des opérations minières. Bien que les données géochimiques des sédiments en gros puissent fournir un aperçu qualitatif des distributions régionales, des précautions sont recommandées lors de la comparaison de données quantitatives provenant de différentes périodes, en utilisant différentes méthodes d'échantillonnage, de traitement et d'analyse des échantillons.

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INTRODUCTION

The former Aldermac mine, located 25 km west of Rouyn-Noranda in Abitibi, Quebec (Fig. 1), exploited a volcanogenic massive sulphide deposit (copper, zinc, gold and silver), which operated from 1932-43. Mining discharged 1.5 Mt of tailings over an area of 76 hectares (Cyr, 2008). Acid mine drainage was released to the Rivière Arnoux and the adjacent watershed downstream, which includes Lac Dasserat within the Rivière Duparquet sub-catchment of the Rivière Abitibi watershed (Organisme de bassin versant Abitibi-Jamésie (OBVAJ), 2014; Fig. 1). The study site is representative of both a common mineral deposit and the legacy of historical mining practices before the advent of environmental regulations. Scientific reconnaissance studies demonstrated metal contamination and adverse effects on aquatic life downstream (Goulet and Couillard, 2009). In addition, the environmental eyesore at the Aldermac site (Fig. 2) led to public concern and advocacy for site rehabilitation (e.g., Bradley, 2009, Conseil régional de l'environnement de l'Abitibi-Témiscamingue (CREAT), 2007, Doucet, 2005). Consequently, the Government of Quebec initiated environmental restoration of the abandoned Aldermac property in 2008-11 (Cyr, 2008, Cyr *et al.*, 2009, Ednie, 2011, Lafrance *et al.*, 2011). Subsequent exploration (e.g., Alpay, 2016) suggests the possibility of future mining development within the sub-catchment, which would trigger both mine rehabilitation and closure plans, requiring 100% of the financial guarantee to be borne by the operator in advance of mining (Ministère de l'Énergie et des Ressources Naturelles (MERN), 2016). Current legislation necessitates up-to-date environmental risk assessment of both the property and the adjacent waterways with revisions to restoration and closure plans at least every 5 years (MERN, 2016). Industrial proponents will need the science-based knowledge and the practical means to support environmental stewardship of mining developments, to which geoscience can make a significant contribution.

To evaluate contamination caused by historical mining and develop performance measures for environmental mining practices, the Lac Dasserat study initiated several parallel scientific investigations (Alpay, 2016). They included a regional geochemical survey of lake surface water and sediments (McNeil *et al.*, 2015). This report assesses spatial trends in geochemical results from both archived and more recently sampled near-shore lake sediments.

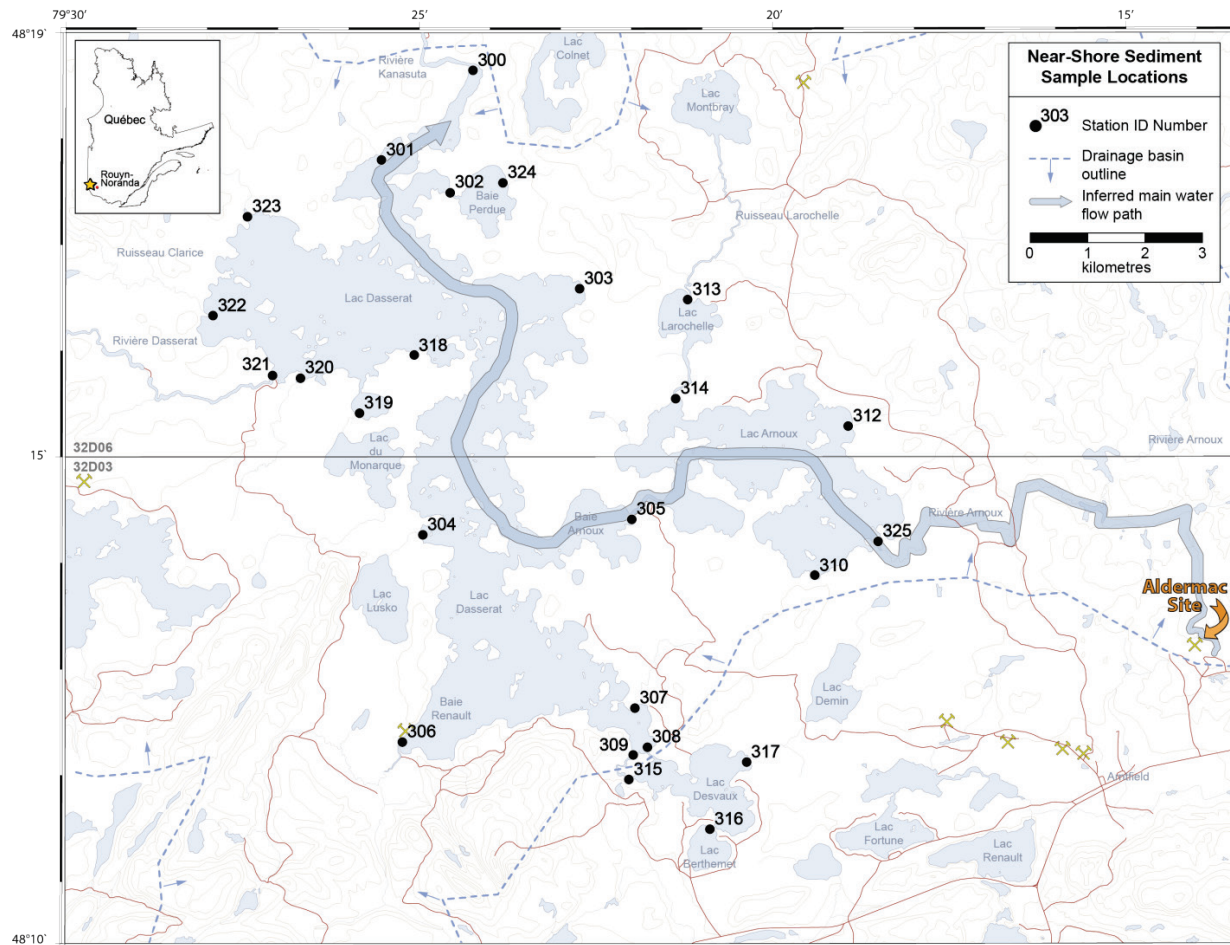


Figure 1. Inset: Location of the Aldermac mine site (yellow star) 25 km west of Rouyn-Noranda, Quebec, near the Ontario border. Map showing subset of sample locations, with designated sample numbers, re-collected from the original 1971-72 sites. Note the inferred main surface water flow path from the Aldermac site to the Rivière Arnoux, Lac Arnoux, Baie Arnoux and to Lac Dasserat to the north, where it eventually discharges to Lac Abitibi and James Bay (OBVAJ, 2014).

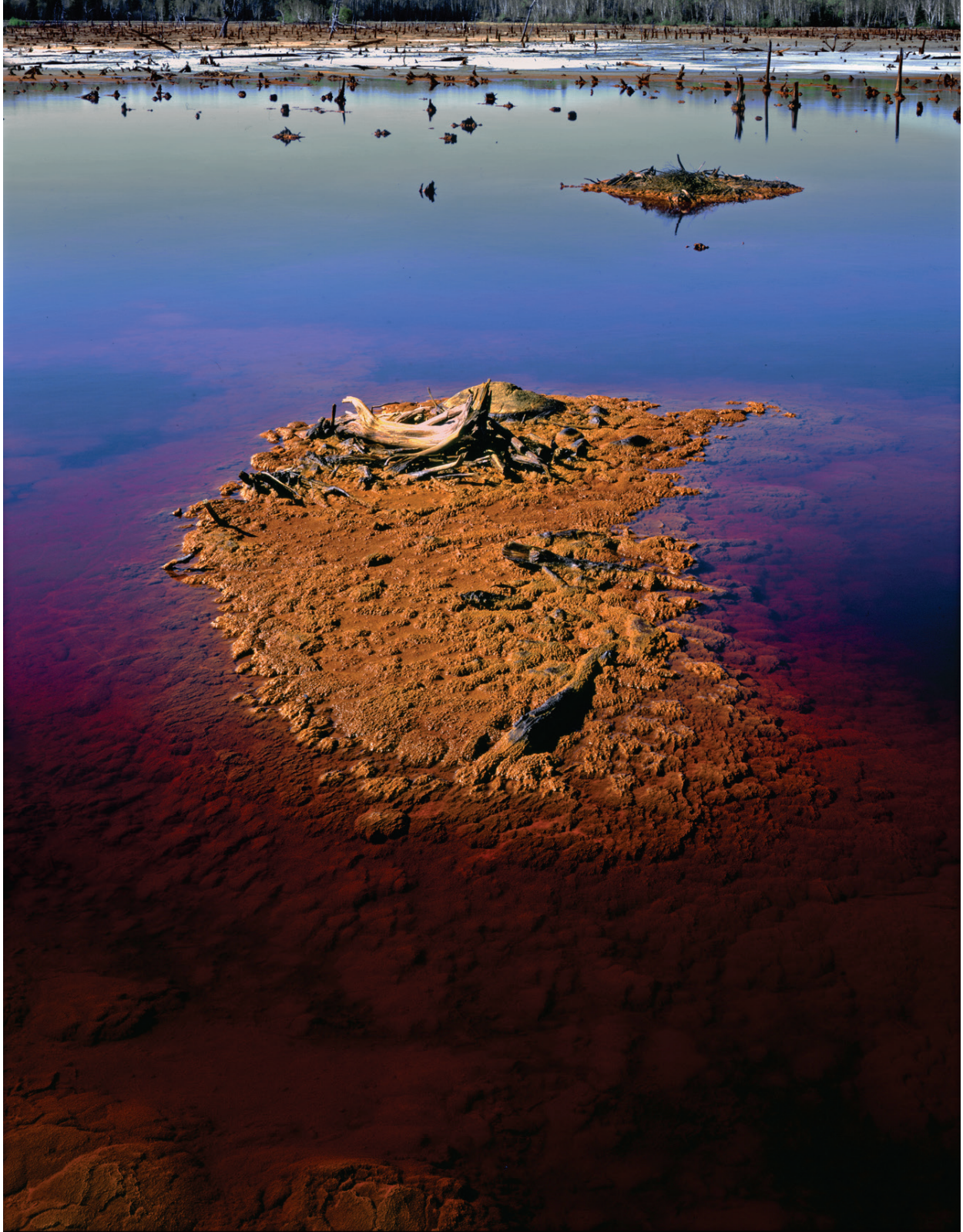


Figure 2: Aldermac site before environmental restoration began in 2008; Photo: Arnold Zageris.

Lac Dasserat study

The Lac Dasserat study (DASS) was initiated to investigate the effects of metal mining on aquatic receiving environments and ecosystems (Alpay, 2016). Its goal was to demonstrate and develop multidisciplinary indicators to form practical tools for environmental risk assessment of downstream responses to metal mining. Indices, such as lake sediment geochemistry, surface water chemistry (e.g., Grenier *et al.*, 2013), and bio-indicators (e.g., Hamilton *et al.*, 2015), serve as criteria to evaluate environmental mining practices throughout the entire mine life cycle, which include pre-development baseline surveys, construction, operation, expansion, adaptive management, decommissioning, restoration, and closure.

One component of the Lac Dasserat study was a regional geochemical survey of surface water and bulk sediment (by grab sampling; McNeil *et al.*, 2015). Shallow sediment cores were also collected at key sampling stations for subsequent analyses. Fortuitously, a separate near-shore lake sediment survey, conducted for mineral exploration in 1971-72, intersected the geographic study area of interest. Both the archived original sediment samples from the early 1970s and their associated geochemical results provided a unique opportunity for a study of lake sediment geochemistry from two distinct times, four decades apart. Given that temporal data are rarely available, this opportunity was pursued in 2012 by collecting new samples from the identical near-shore sampling station locations. The results provide supplementary and independent evidence of spatial contamination trends in metal concentrations emerging from the Lac Dasserat study.

Emergency Gold Mining Assistance project

Nearly 40 years after the Aldermac mine began operating, the GSC took samples of lake-bottom sediment and till for the Emergency Gold Mining Assistance (EGMA; 1971-72) project in the Timmins-Val d'Or corridor of northeastern Ontario and northwestern Quebec (Fig. 3). In addition to stimulating local winter employment, the main scientific objectives were to evaluate regional geochemical exploration techniques for mining development in glaciated Precambrian terrains of the Abitibi region. This was an area where extensive glacial and glaciolacustrine clay-sized deposits proved challenging for the classical geochemical exploration methods at the time (Hornbrook and Gleeson, 1972).

In particular, the aims were to:

- assess the effectiveness of regional geochemical lake-bottom sediment surveys for detecting metal dispersion halos adjacent to the clay belt;
- evaluate the effectiveness of overburden drilling for detecting anomalous dispersion halos in basal till at selected lakes in the clay belt;
- compare the trace element content of lake-bottom sediments with those of lodgement tills and assess their relative suitability as sample media, including evaluation of their respective geochemical dispersion halos, inter-correlation, and links to known mineral occurrences;
- compare the trace element content of selected size fractions in lake-bottom sediments and tills; and
- delineate anomalous target areas worthy of further exploration.

After completing the survey, Hornbrook (1972) reported detection of several areas of metal anomalies, apart from those associated with known mining camps. However, Hornbrook (1972)

also cautioned that, in some zones, snow and ice cover would have obscured visual evidence of mining or other industrial activity. The spatial resolution for sampling density was inadequate for exploration in locations with logistical limitations (no road or snow machine access; no aircraft support). Therefore, the main recommendation was to use the 1971-72 reconnaissance survey as a guide to identify targets for follow-up and re-sampling in advance of further exploration (Hornbrook, 1972).

During the winter months of 1971-72, 2,925 samples were collected, in part, to generate local employment. At all sites, sediment grab samples were collected from the lake bottoms through holes chipped, cut or augered through the ice platform (Hornbrook and Gleeson, 1972). Figure 4 is a modified inset of the original sample map, which includes the 25 stations selected for this study. Hornbrook and Gleeson (1972) targeted near-shore sediments from lake inlets and outlets. The survey was conducted at a time when it was not yet recognized that sampling in deeper lake basins provides a better representation of full-lake sedimentation, a surveying protocol adopted within a couple years (e.g., Davenport *et al.*, 1974).

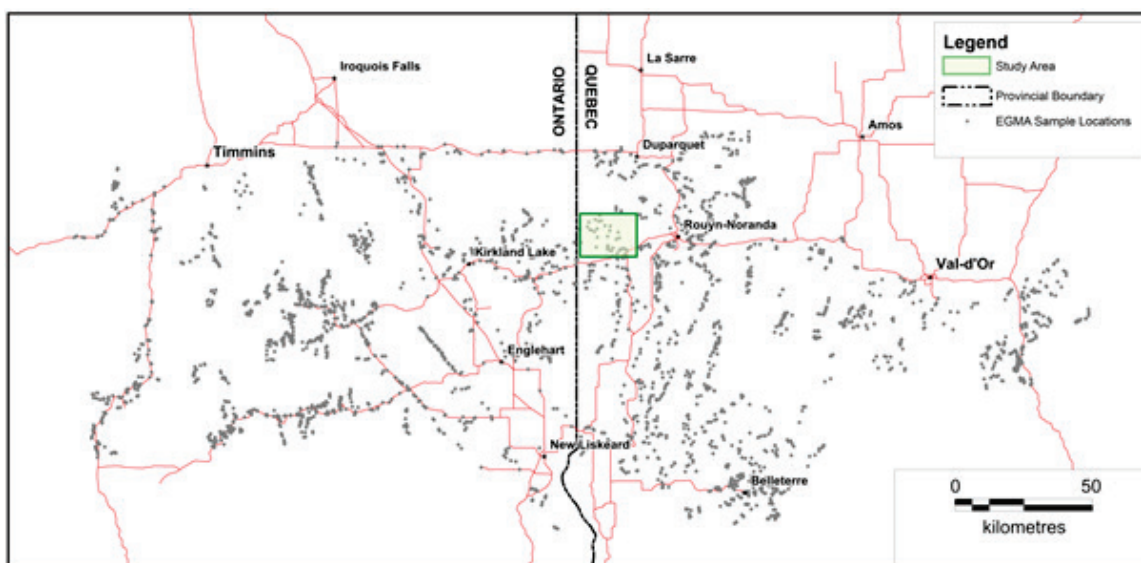
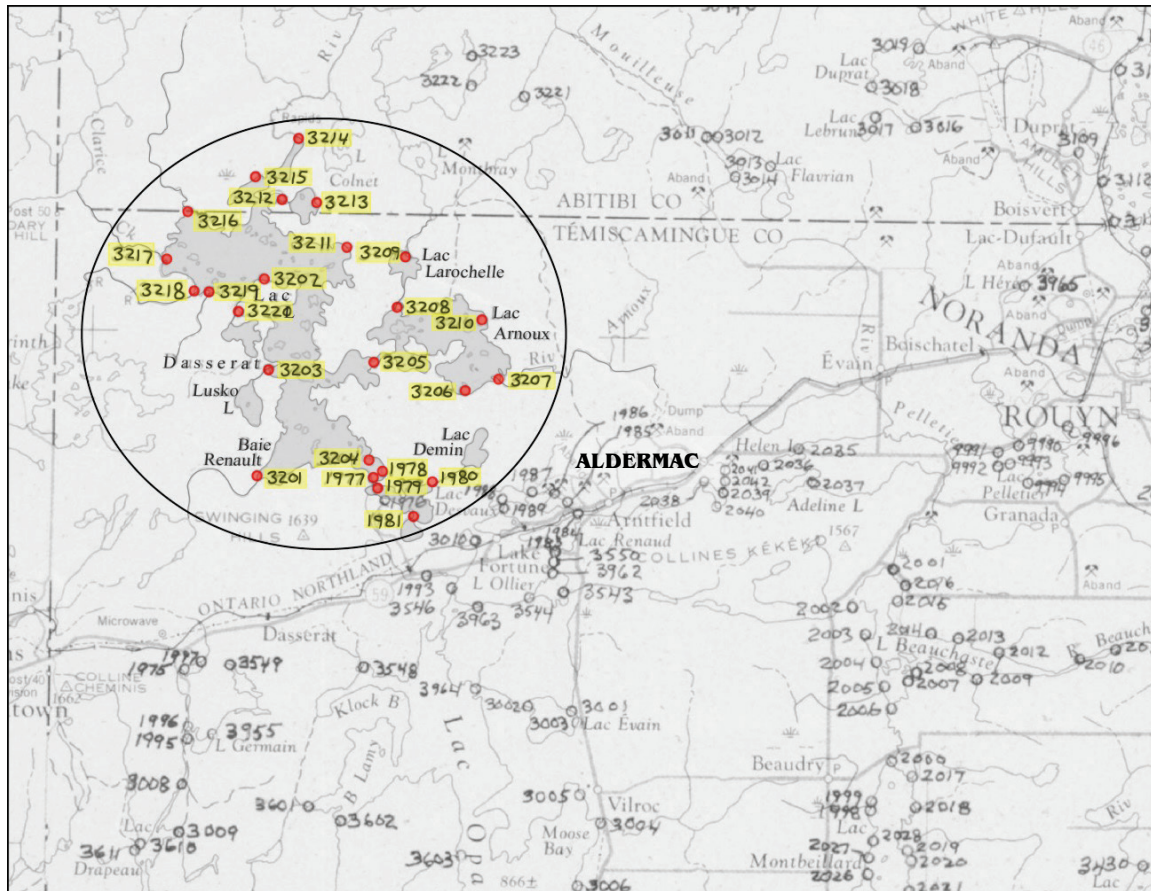


Figure 3. Map showing the geographic extent of near-shore sampling locations collected during the 1971-72 EGMA project; the green outline denotes the Lac Dasserat study area.



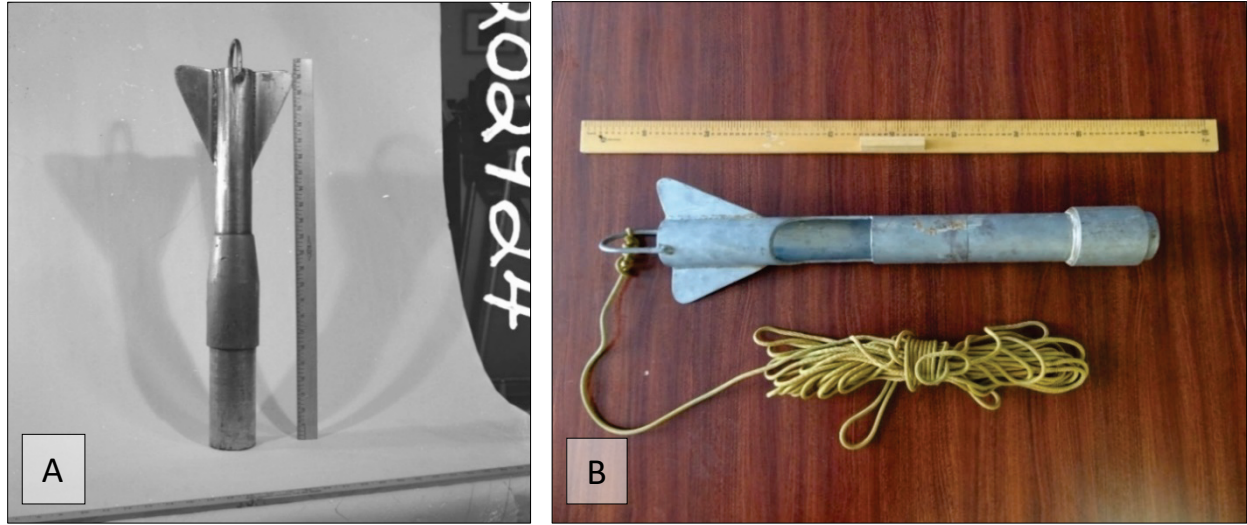


Figure 5: Examples of the Hornbrook or Geological Survey of Canada lake sediment free-falling core-type sampler (described by Coker *et al.*, 1979); 38 cm length, 6.5 cm diameter; **(A)** Photo: GSC archived image number 202924; **(B)** Photo: Government of Canada, 2017.

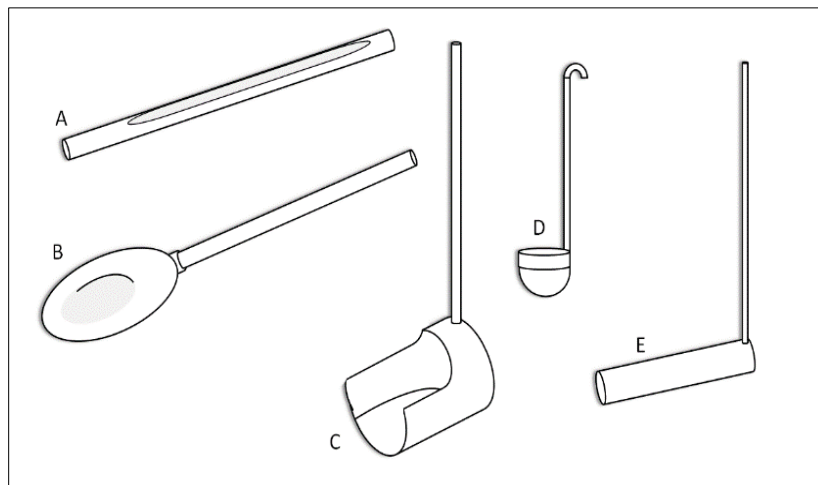


Figure 6. Schematics of improvised sediment samplers for shallow water conceived from Coker *et al.*'s (1979) and anecdotal descriptions (S. Adcock, pers. comm. 2018; S. Day, pers. comm., 2019) **(A)** extension tube sampler, **(B)** spoon sampler, **(C)** telephone scoop sampler, **(D)** ladle, and **(E)** modified sample tube.

METHODS

Re-sampling

In contrast to the original 1971-72 sampling, which took place in the winter on ice by snowmobile, road access or snowshoe traverse (Hornbrook and Gleeson, 1972), the re-sampling was conducted in the fall of 2012 from a 16' aluminum boat. The 25 re-sampled site locations (Fig. 1) were within 10 m of the original coordinates reported by Hornbrook and Gleeson (1972; as UTM coordinates).

At each of the 25 stations in 2012, field scientists collected a bulk grab sample of surface sediment (Fig. 7). The surface sediment samples were taken with a Petite Ponar® grab sampler (Fig. 8; Alpay *et al.*, 2015, Mudroch and MacKnight, 1991) because the Petite Ponar® and variations of it are commonly used in baseline geochemical reconnaissance studies for environmental risk assessment. Field scientists transferred each sediment sample from the Petite Ponar® and transferred it into a clean, thick-walled plastic bag, sealed to retain moisture. Samples were kept cool until sample preparation. The near-shore sediments at most sites were typically clay-sized and exhibited a minor black layer, likely organic. Water depths were relatively shallow, ranging from 0.4 to 2.5 m with the exception of Station 301 in Lac Dasserat, where the water depth was 4.2 m.



Figure 7: Field scientists collecting near-shore sediments using a Petite Ponar® grab sampler at an original 1972 EGMA site. Photo: GSC, 2012; from Station ID 316

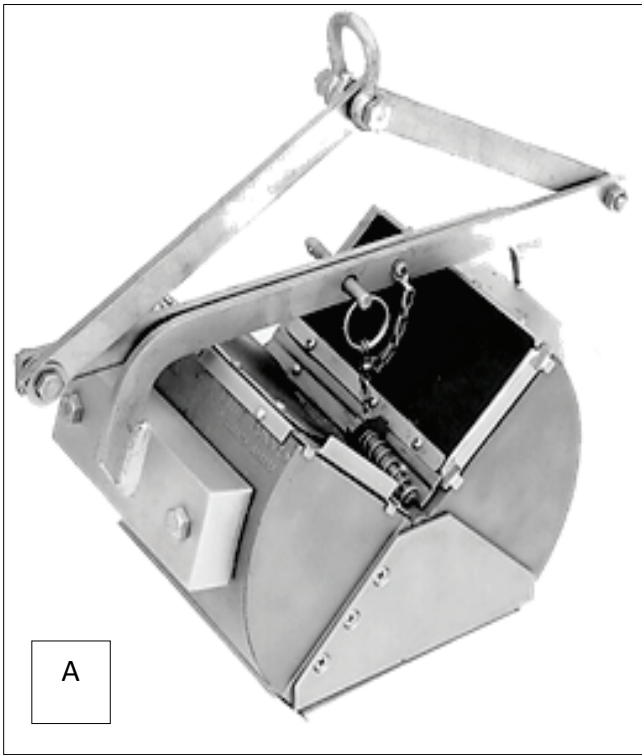


Figure 8. Petite Ponar® (6" x 6") sampler used to collect bulk near-shore surface sediment samples. Maximum sediment depth penetration of 12 cm. **(A)** Photo: Eco Environmental <http://ecoenvironmental.com.au/sales/soil-sampling/ponar-grab-samplers/>, accessed 7 Aug 2019 **(B)** Petite Ponar® about to be deployed; Photo: GSC, May 2012.

For each original sample location revisited, a new station ID was created. Table 1 is an index, linking the original published 1972 EGMA sample number to the re-collected 2012 DASS sample number and the assigned Station ID. Locations are given in Figure 1.

Table 1. Index of sample numbers associated with each Station ID.

Station ID	Original 1972 EGMA Sample Number	Re-collected 2012 DASS Sample Number
300	3214	LD12602-NS101
301	3215	LD12603-NS101
302	3212	LD12604-NS101
303	3211	LD12605-NS101
304	3203	LD12606-NS101
305	3205	LD12607-NS101
306	3201	LD12608-NS101
307	3204	LD12609-NS101
308	1978	LD12610-NS101
309	1977	LD12611-NS101
310	3206	LD12612-NS101
312	3210	LD12615-NS101
313	3209	LD12616-NS101
314	3208	LD12617-NS101
315	1979	LD12618-NS101
316	1981	LD12619-NS101
317	1980	LD12620-NS101
318	3202	LD12622-NS101
319	3220	LD12623-NS101
320	3219	LD12624-NS101
321	3218	LD12625-NS101
322	3217	LD12626-NS101
323	3216	LD12627-NS101
324	3213	LD12628-NS101
325	3207	LD12629-NS101

Sample Preparation

1971-72 EGMA samples

The samples taken in 1971-72 were originally dry-sieved in two size fractions, < 63 μm and < 177 μm . They were stored in sealed plastic vials in the GSC archive collection, from which 25 samples were retrieved within the relevant study area (Figs. 1, 3, and 4) for re-analysis using contemporary methods. To verify effective separation of the < 177- μm fractions in 1971-72, a Beckman Coulter LS 320 Laser Particle Size Analyser provided rapid diagnostic testing.

2012 DASS samples

Lake sediment samples from re-visited stations were prepared for analysis at the GSC Sedimentology Laboratory in Ottawa. Samples were freeze-dried to avoid losing volatile elements during oven- or air-drying. Freeze-drying provided powdered material for analysis instead of the hard aggregated clay obtained after oven- or air-drying (Perttilä and Pedersen, 2008).

Samples were placed in an ultra-low temperature freezer at -60°C until frozen. Frozen samples were then transferred into a freeze-dryer that reached -40°C and a vacuum of less than 170×10^{-3} mBar for approximately 2 to 3 days to remove moisture. An archival sample split was retained and the remaining material dry sieved to < 180 μm and stored in 16-dram vials. The oversize material was discarded. Girard *et al.* (2004) describe the complete methodology.

Analytical Procedures

Carbon content – LOI (2012 DASS)

Carbon content, total and inorganic, was determined by a LECO CR-412 Carbon Analyser® at the GSC Sedimentology Laboratory in Ottawa, according to Girard *et al.* (2004). The total carbon analysis procedure relies on combustion upon volatilization of CO₂ at 1350°C, measured by infrared detection. Inorganic carbon was measured on the residue from a separate sample split after loss-on-ignition (LOI) at 500°C for 1 hour (ashing) to remove the organic content. Organic carbon content was determined by calculating the difference between total carbon and inorganic carbon contents. Results also include the LOI carbon, which is the percentage of mass lost from ashing the sample at 500°C. Two certified reference materials (CRM; LKSD-1, LKSD-4), one standard (Till 2), as well as six duplicates (3 lab; 3 field), were inserted into the sediment sample runs for QA/QC. All analytical results are recorded in GSC OF 8393 All Data.xlsx. The original 1971-72 EGMA dataset did not include analyses of carbon content.

Element concentrations – (1971-72 EGMA)

In 1971-72, the < 177-µm sediment samples were analysed for silver (Ag), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), and zinc (Zn) concentrations by Atomic Absorption Spectrometry (AAS) after a modified aqua regia dissolution (Hornbrook and Gleeson, 1972). At the time, the digestion consisted of a hot solution of hydrochloric (HCl) and nitric (HNO₃) acids; mixing ratios and concentrations were unspecified (Hornbrook and Gleeson, 1972). Arsenic (As) concentrations were determined colorimetrically after digestion by a mixture of HNO₃ and perchloric (HClO₄) acids and treatment with silver diethyldithiocarbonate. (Hornbrook and Gleeson, 1972). Table 2 is a summary of the analytical detection limits from the measurements made in 1971-72. Geochemical data presented in Hornbrook and Gleeson (1972) for the 25 samples are reproduced in the data file accompanying this report (GSC OF 8393 All Data.xlsx).

Table 2. Elements determined by AAS or colorimetry after digestion of near-shore lake sediment samples, 1972 EGMA (after Hornbrook and Gleeson, 1972). ppm: parts per million, mg/kg.

Element	Detection Limit	Units of Measurement	Analytical Method
Cu	1	ppm	AAS
Pb	2	ppm	AAS
Zn	1	ppm	AAS
Mo	0.5	ppm	AAS
Ni	1	ppm	AAS
Mn	10	ppm	AAS
As	0.5	ppm	colorimetry
Ag	0.5	ppm	AAS

Both the original archived (1971-72) and the 2012 samples were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS), using two different digestion procedures prior to analysis, described below.

Element concentrations – ICP-MS (modified aqua regia dissolution; 1972 EGMA and 2012 DASS)

The first sediment digestion was a modified aqua regia "partial" dissolution using package 1F-04 at ACME Analytical Laboratories, Limited (currently Bureau Veritas Mineral Laboratories) in Vancouver, British Columbia. Fifty-three elements were determined. Detection limits are summarized in Table 3. Splits of 0.5-g sediment samples were leached with a 6-ml mixture of hydrochloric (HCl) acid, nitric (HNO₃) acid, and distilled/deionized water (1:1:1 volumetric ratios) at 95°C for one hour. The sample solution was diluted to a 20-ml volume and analysed by ICP-MS.

Element concentrations – ICP-MS (multi-acid dissolution; 1971-72 EGMA and 2012 DASS)

The multi-acid digestion method represents a "near total" dissolution with a 2:2:1:1 mixing ratio of HCl, HNO₃, HClO₄ and hydrofluoric (HF) acids, respectively, using package 1T at ACME Analytical Laboratories Limited (Bureau Veritas Mineral Laboratories) in Vancouver, British Columbia. Sixty elements were determined; Table 4 is a summary of the lower detection limits. Sediment splits of 0.25 g were weighed into Teflon test tubes. A 10-ml aliquot of the acid solution was added, heated on a hot plate until fuming, and taken to dryness. A 4-ml aliquot of 50% HCl was added to the residue and heated using a mixing hot block. After cooling, the solutions were transferred to polypropylene test tubes and made to 10-ml volumes with 5% HCl. Effectively, this method is a total dissolution for most elements. For some (e.g., chromium (Cr), barium (Ba), aluminum (Al), iron (Fe), hafnium (Hf), Mn, tin (Sn), tantalum (Ta), and zirconium (Zr)), it may be a partial dissolution, depending on sample mineralogy. Volatilization during fuming may result in some loss of As, antimony (Sb), and gold (Au). Two CRMs (LKSD-1, LKSD-4), three standards (DS9; OREAS45EA; OREAS24P), as well as five duplicates (a single site sample split, assigned two non-consecutive sample numbers), were inserted into the sediment sample runs for QA/QC. All analytical results are provided in GSC OF 8393 All Data.xlsx.

Table 3. Elements determined by ICP-MS after a modified aqua regia (AR) dissolution of near-shore lake sediment samples (2012 analyses)

Element	Detection Limit	Units of Measurement	Analytical Method
Ag	2	ppb ¹	ICP-MS
Al	0.01	%	ICP-MS
As	0.1	ppm ²	ICP-MS
Au	0.2	ppb	ICP-MS
B	20	ppm	ICP-MS
Ba	0.5	ppm	ICP-MS
Be	0.1	ppm	ICP-MS
Bi	0.02	ppm	ICP-MS
Ca	0.01	%	ICP-MS
Cd	0.01	ppm	ICP-MS
Ce	0.1	ppm	ICP-MS
Co	0.1	ppm	ICP-MS
Cr	0.5	ppm	ICP-MS
Cs	0.02	ppm	ICP-MS
Cu	0.01	ppm	ICP-MS
Fe	0.01	%	ICP-MS
Ga	0.1	ppm	ICP-MS
Ge	0.1	ppm	ICP-MS
Hf	0.02	ppm	ICP-MS
Hg	5	ppb	ICP-MS
In	0.02	ppm	ICP-MS
K	0.01	%	ICP-MS
La	0.5	ppm	ICP-MS
Li	0.1	ppm	ICP-MS
Mg	0.01	%	ICP-MS
Mn	1	ppm	ICP-MS
Mo	0.01	ppm	ICP-MS

Element	Detection Limit	Units of Measurement	Analytical Method
Na	0.001	%	ICP-MS
Nb	0.02	ppm	ICP-MS
Ni	0.1	ppm	ICP-MS
P	0.001	%	ICP-MS
Pb	0.01	ppm	ICP-MS
Pd	10	ppb	ICP-MS
Pt	2	ppb	ICP-MS
Rb	0.1	ppm	ICP-MS
Re	1	ppb	ICP-MS
S	0.02	%	ICP-MS
Sb	0.02	ppm	ICP-MS
Sc	0.1	ppm	ICP-MS
Se	0.1	ppm	ICP-MS
Sn	0.1	ppm	ICP-MS
Sr	0.5	ppm	ICP-MS
Ta	0.05	ppm	ICP-MS
Te	0.02	ppm	ICP-MS
Th	0.1	ppm	ICP-MS
Ti	0.001	%	ICP-MS
Tl	0.02	ppm	ICP-MS
U	0.1	ppm	ICP-MS
V	2	ppm	ICP-MS
W	0.1	ppm	ICP-MS
Y	0.01	ppm	ICP-MS
Zn	0.1	ppm	ICP-MS
Zr	0.1	ppm	ICP-MS

¹ ppb: parts per billion, µg/kg ² ppm: parts per million, mg/kg.

Table 4. Elements determined by ICP-MS after a multi-acid (MA) dissolution of near-shore lake sediment samples (2012 analyses)

Element	Detection Limit	Units of Measurement	Analytical Method
Ag	20	ppb ¹	ICP-MS
Al	0.02	%	ICP-MS
As	0.2	ppm ²	ICP-MS
Au	0.1	ppm	ICP-MS
Ba	1	ppm	ICP-MS
Be	1	ppm	ICP-MS
Bi	0.04	ppm	ICP-MS
Ca	0.02	%	ICP-MS
Cd	0.02	ppm	ICP-MS
Ce	0.02	ppm	ICP-MS
Co	0.2	ppm	ICP-MS
Cr	1	ppm	ICP-MS
Cs	0.1	ppm	ICP-MS
Cu	0.02	ppm	ICP-MS
Dy	0.1	ppm	ICP-MS
Er	0.1	ppm	ICP-MS
Eu	0.1	ppm	ICP-MS
Fe	0.02	%	ICP-MS
Ga	0.02	ppm	ICP-MS
Gd	0.1	ppm	ICP-MS
Hf	0.02	ppm	ICP-MS
Ho	0.1	ppm	ICP-MS
In	0.01	ppm	ICP-MS
K	0.02	%	ICP-MS
La	0.1	ppm	ICP-MS
Li	0.1	ppm	ICP-MS
Lu	0.1	ppm	ICP-MS
Mg	0.02	%	ICP-MS
Mn	2	ppm	ICP-MS
Mo	0.05	ppm	ICP-MS

Element	Detection Limit	Units of Measurement	Analytical Method
Na	0.002	%	ICP-MS
Nb	0.04	ppm	ICP-MS
Nd	0.1	ppm	ICP-MS
Ni	0.1	ppm	ICP-MS
P	0.001	%	ICP-MS
Pb	0.02	ppm	ICP-MS
Pr	0.1	ppm	ICP-MS
Rb	0.1	ppm	ICP-MS
Re	0.002	ppm	ICP-MS
S	0.04	%	ICP-MS
Sb	0.02	ppm	ICP-MS
Sc	0.1	ppm	ICP-MS
Se	0.3	ppm	ICP-MS
Sm	0.1	ppm	ICP-MS
Sn	0.1	ppm	ICP-MS
Sr	1	ppm	ICP-MS
Ta	0.1	ppm	ICP-MS
Tb	0.1	ppm	ICP-MS
Te	0.05	ppm	ICP-MS
Th	0.1	ppm	ICP-MS
Ti	0.001	%	ICP-MS
Tl	0.05	ppm	ICP-MS
Tm	0.1	ppm	ICP-MS
U	0.1	ppm	ICP-MS
V	1	ppm	ICP-MS
W	0.1	ppm	ICP-MS
Y	0.1	ppm	ICP-MS
Yb	0.1	ppm	ICP-MS
Zn	0.2	ppm	ICP-MS
Zr	0.2	ppm	ICP-MS

¹ ppb: parts per billion, µg/kg ² ppm: parts per million, mg/kg.

RESULTS & DISCUSSION

Carbon contents

The organic carbon content (LOI) varied between 2.1 and 44.1% in the sediments sampled in 2012 (Fig. 9). The wide variation in carbon content in near-shore sediments can be affected by many factors, including water depth, boating, storm wave action, local hydrology, productivity, stagnancy of surface water (i.e., backwater), macrophyte growth, and additional site characteristics (e.g., Wetzel, 2001). Organic carbon (LOI) and chalcophile elements are weakly correlated in cross-plots of metals with LOI, with the exceptions of moderate correlations between S and LOI (with 2 outliers) and Hg and LOI. Carbon content was not among the measurements taken in 1971-72. Raw data and cross-plots are in the data files accompanying this report (GSC OF 8393 All Data.xlsx and GSC OF 8393 Data plots).

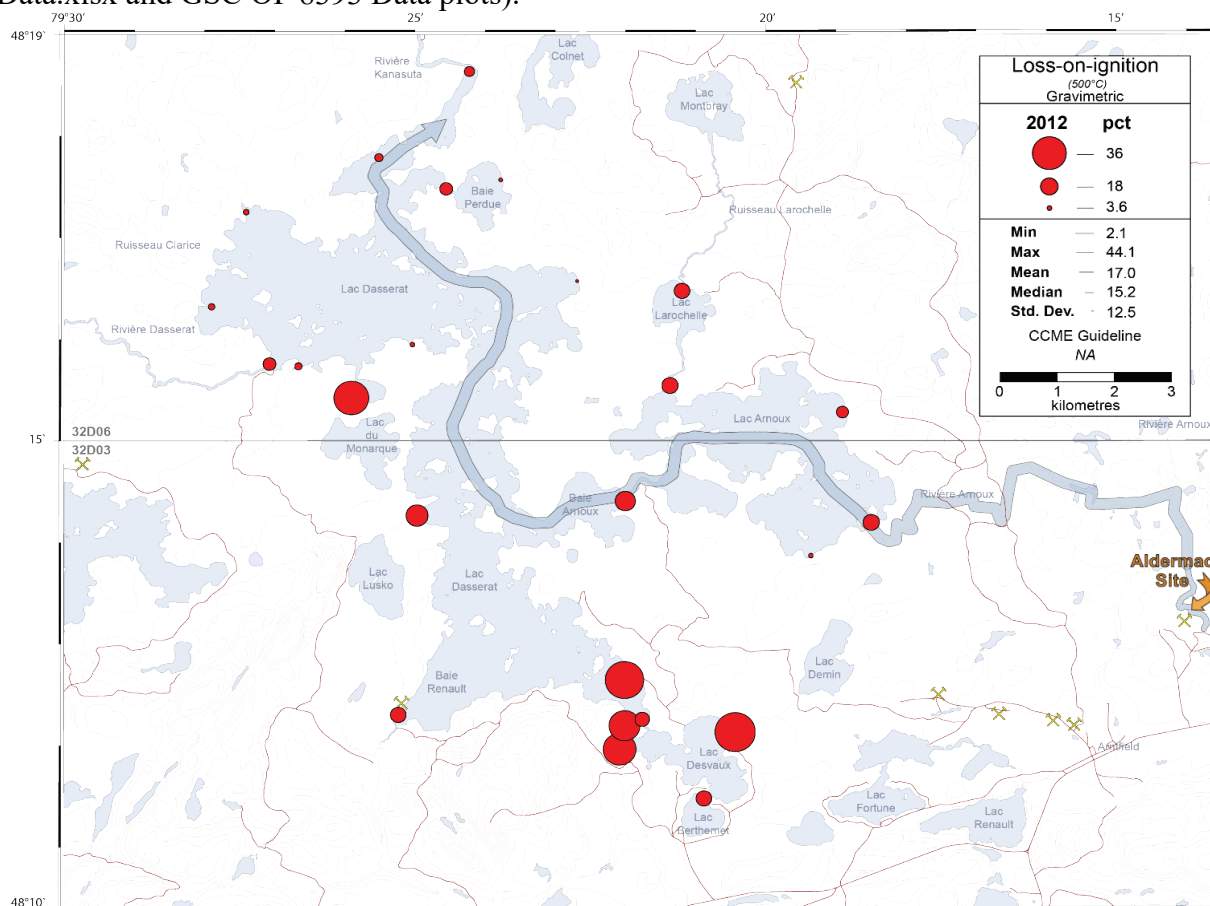


Figure 9. Map showing the distribution and range of carbon contents in lake sediments, measured by LOI (500°C), in the 2012 DASS samples.

Verification of grain size, 1971-72 EGMA samples

Geochemical concentrations are correlated, in part, with grain size, surface area, texture, and mineralogy of different size fractions of earth materials (e.g., Horowitz and Elrick, 1987, Klassen and Knight, 1996, Shilts, 1995). Therefore, it is important to confirm that element concentrations are evaluated on the same sediment grain size fractions. Laser particle size analysis verified that the 1971-72 EGMA samples were < 180 µm.

Comparison of ICP-MS (2012) and AAS, colorimetry (1971-72) results for sediments sampled in 1971-72

Results from the original analyses of eight elements were compared to those from recent ICP-MS analyses of the same sediment material sampled in 1971-72. Linear cross-plots illustrate the results (Fig. 10). Ag and As concentrations analysed by ICP-MS in 2012 versus analysis by AAS (Ag) or colorimetry (As) in 1972 after aqua regia digestion show low correlation because their concentrations are low and detection limits (DLs) for AAS and colorimetry in 1972 were significantly higher than for ICP-MS in 2012. Both the accuracy and precision of measurements are not consistent at, below, or near the limit of detection (low r^2 values). Concentrations of Ag, Mo and Pb are notably lower in the 2012 analyses compared to those in 1972 (i.e., below the 1:1 line). All 2012 analyses of Ag and roughly half of those for Mo are below the 1972 detection limit. Either the 1972 results near the detection limits are in question or the modified aqua regia digestion in 1972 (Hornbrook and Gleeson, 1972) was stronger, resulting in higher concentrations measured in 1972 compared to 2012.

The correlations between analyses of concentrations in 2012 (after aqua regia digest) and 1972 are stronger for Cu, Mn, Ni, Pb, and Zn, which have higher r^2 values, plot closer to the 1:1 line, and are sufficiently above the DLs to register a distinct signal, regardless of the analytical instrument used. Deviations below the 1:1 line for Cu, Mn, Ni, Pb and Zn concentrations are consistently at the same five sampling stations (301, 303, 306, 308, and 318; Fig. 10). Excluding these sites, which were generally outside two standard deviations of the linear regression, brings the results much closer to the 1:1 line, as would be expected for different analytical techniques on the same materials. The five outliers could result from a combination of 40 years of storage that have compromised the integrity of the samples from the early 1970s or inconsistencies in the 1972 samples or analyses.

To investigate further, element concentrations of the 1972 samples, measured after the multi-acid digestion in 2012, were cross-plotted against the concentrations measured after the modified aqua regia digestion in 1972 (Fig. 11). Results for Ag, As, and Mo concentrations are inconsistent near, at or below the analytical detection limits. For the other elements, some correlation is evident, with most results following a general trend parallel to the 1:1 line. This general correlation indicates that the 1972 aqua regia leach was effective at fully extracting these elements (GSC OF 8393 All Data.xlsx). Some, but not all of the outliers identified in Figure 10 appear to be outliers in Figure 11. For most outliers, concentrations measured in 1972 generally exceed the 2012 measurements after both aqua regia and multi-acid digestions. It is implausible that a modified aqua regia digestion in 1972 could be more aggressive than a 'near-total' multi-acid digestion in 2012. Therefore, the rigor of the digestions is not the main controlling factor to explain higher concentrations measured in 1972 on the same sample material. This calls into question whether or not the sample analysed in 1972 is the same material as the archived sample for the same site.

An additional consideration is that the 1971-72 analyses were done soon after sample collection on fresh sediment material with results published in 1972 (Hornbrook and Gleeson, 1972). Storage of archival samples in the intervening four decades between analyses may have compromised sample integrity. However, anecdotally, samples in 1971-72 were likely air-dried ($< 40^\circ\text{C}$) and kept sealed in plastic vials for 40 years. Sample treatment and storage was similar to those in parallel studies with re-analysis of samples archived for 40 years or less (e.g., McNeil and Friske,

2016). Nonetheless, McNeil and Friske (2016) showed better correlation between analyses from 1976 and 1982 compared to those in 2016 ($r^2 \geq 0.923$). Barring errors in sample labeling or an archived sample subset that was not representative of the analysed subsample in 1972, there is no obvious cause for the discordance between results from original and modern analyses of the same materials. Setting aside these factors, further discussion considers the 2012 analytical results of both sample collections.

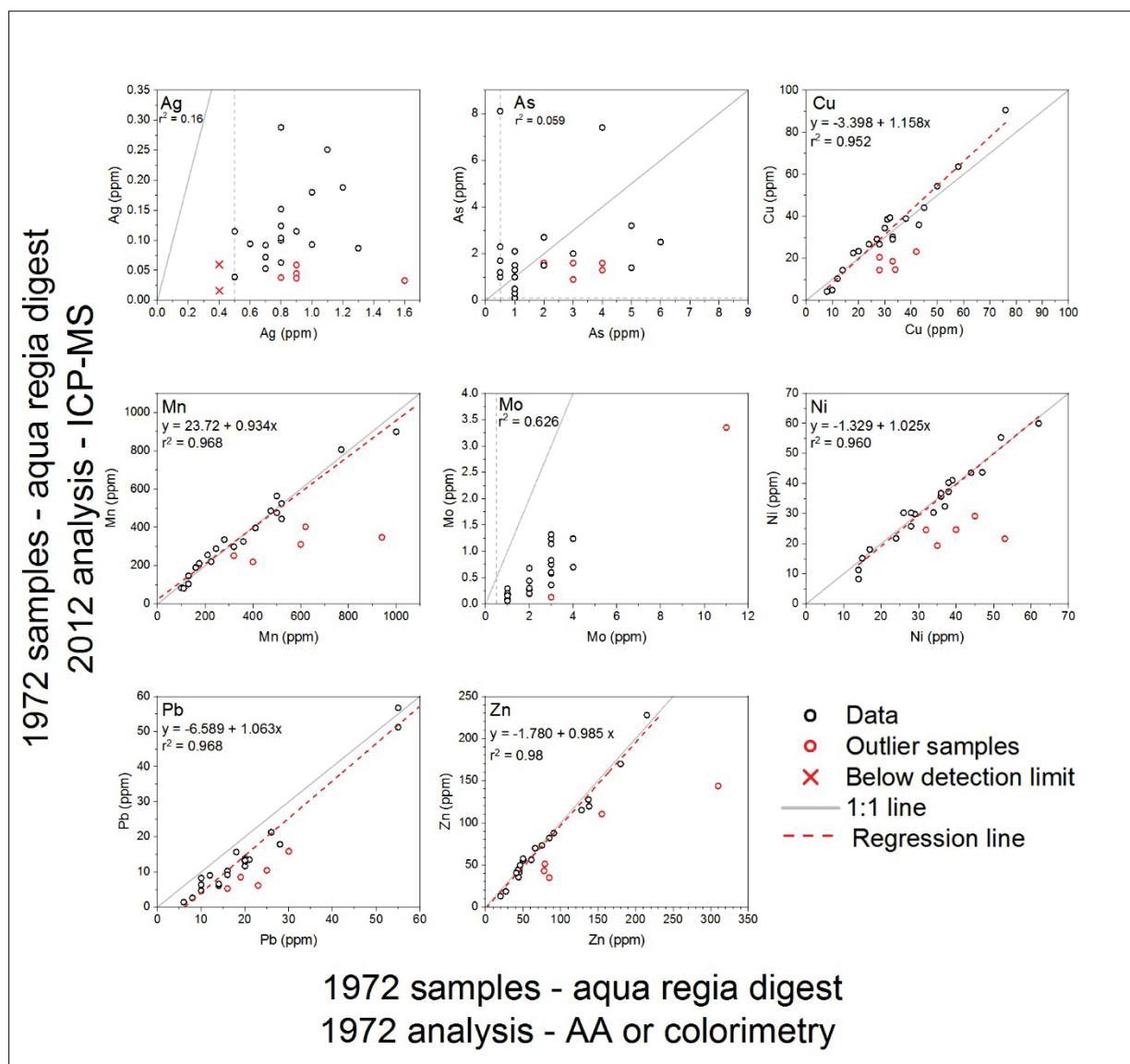


Figure 10. Linear cross-plots of eight elements from 1972 EGMA samples re-analysed in 2012 by ICP-MS after aqua regia dissolution versus original analytical results from 1972 EGMA samples by AAS or colorimetry after modified aqua regia dissolution; note differences in scales; vertical gray dashed lines are detection limits; red circles (outlier samples) were not included in the linear regressions (red dashed lines).

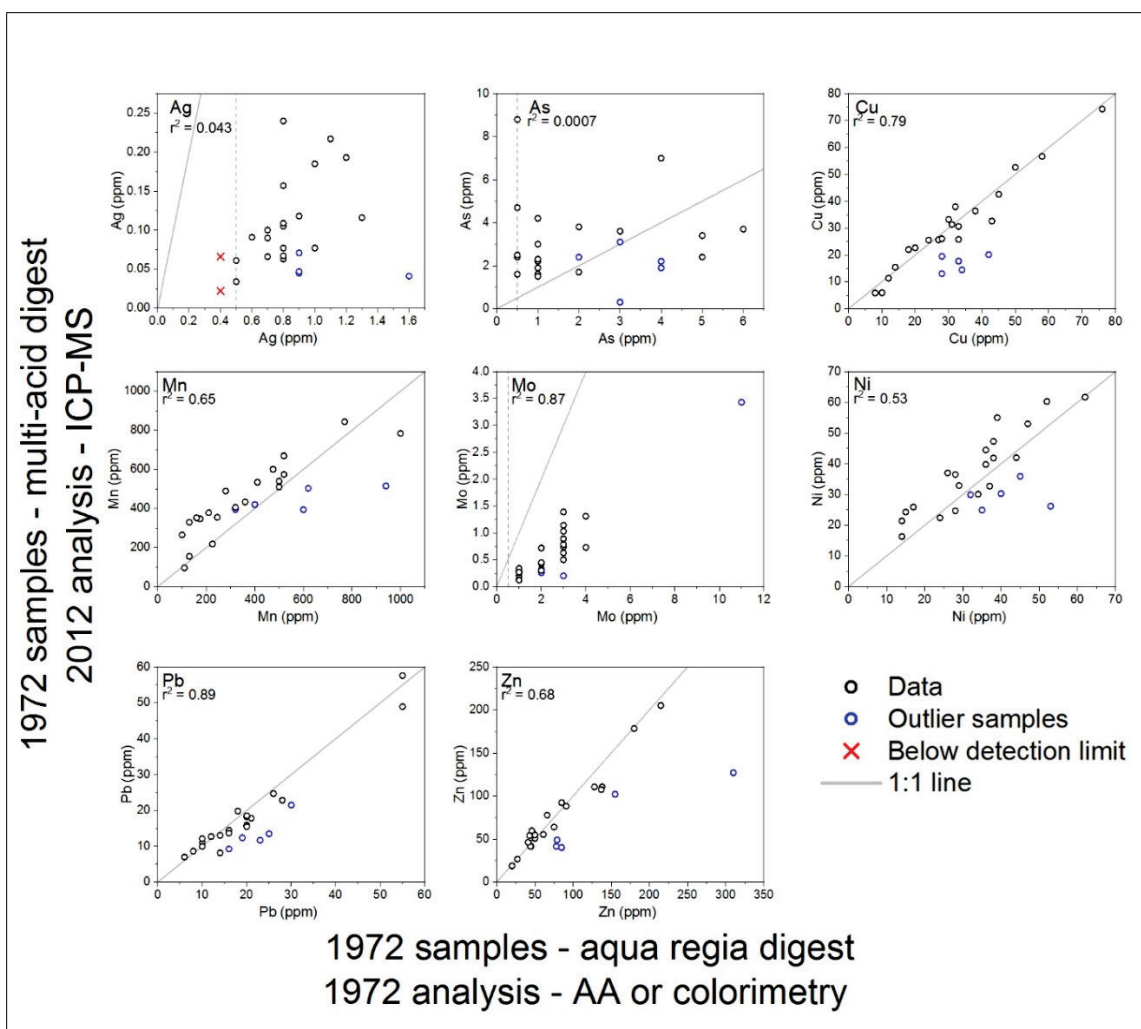


Figure 11. Linear cross-plots comparing the 2012 multi-acid digestion ICP-MS analyses versus the 1972 aqua regia AA and colorimetry analyses of the 1972 samples; note differences in scales; the vertical gray dashed line in the Ag, As, and Mo plots represents the detection limit; blue circles (outlier samples identified in Fig. 10) were included in the linear regression.

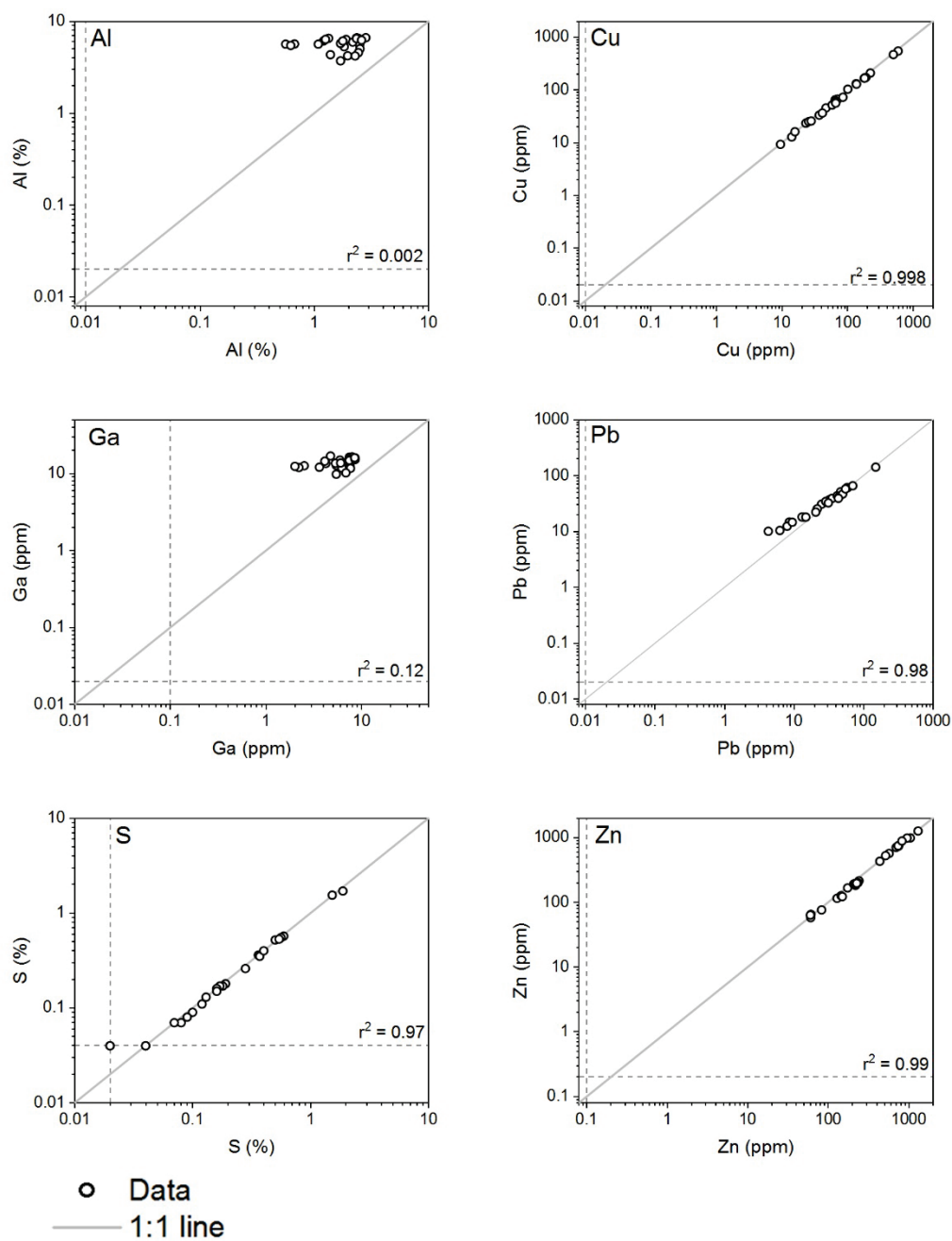
1971-72 EGMA versus 2012 DASS ICP-MS (multi-acid digestion)

Results of ICP-MS analysis after the multi-acid digestion are distinct from those after the aqua regia digestion for some elements. Figure 12 shows the concentration cross-plots of some chalcophile elements (Cu, Pb, S, Zn) and those closely bound in silicates (Al, Ga) after both multi-acid versus aqua regia digestions. Results confirm that most chalcophile elements are put in solution by the aqua regia digestion (1:1 correlation), whereas the more rigorous multi-acid digestion was required to dissolve silicates ($> 1:1$ line).

1971-72 EGMA versus 2012 DASS ICP-MS (aqua regia digestion)

For the purpose of this discussion, the focus will be on ICP-MS results after the aqua regia digestion because some analytes of interest may have volatilized during the multi-acid digestion procedure (e.g., As, Sb, Au). The aqua regia digestion is also a better representation of the more mobile phases, rather than the multi-acid digestion, which is a near-total dissolution.

2012 samples - multi-acid digest - ICP-MS

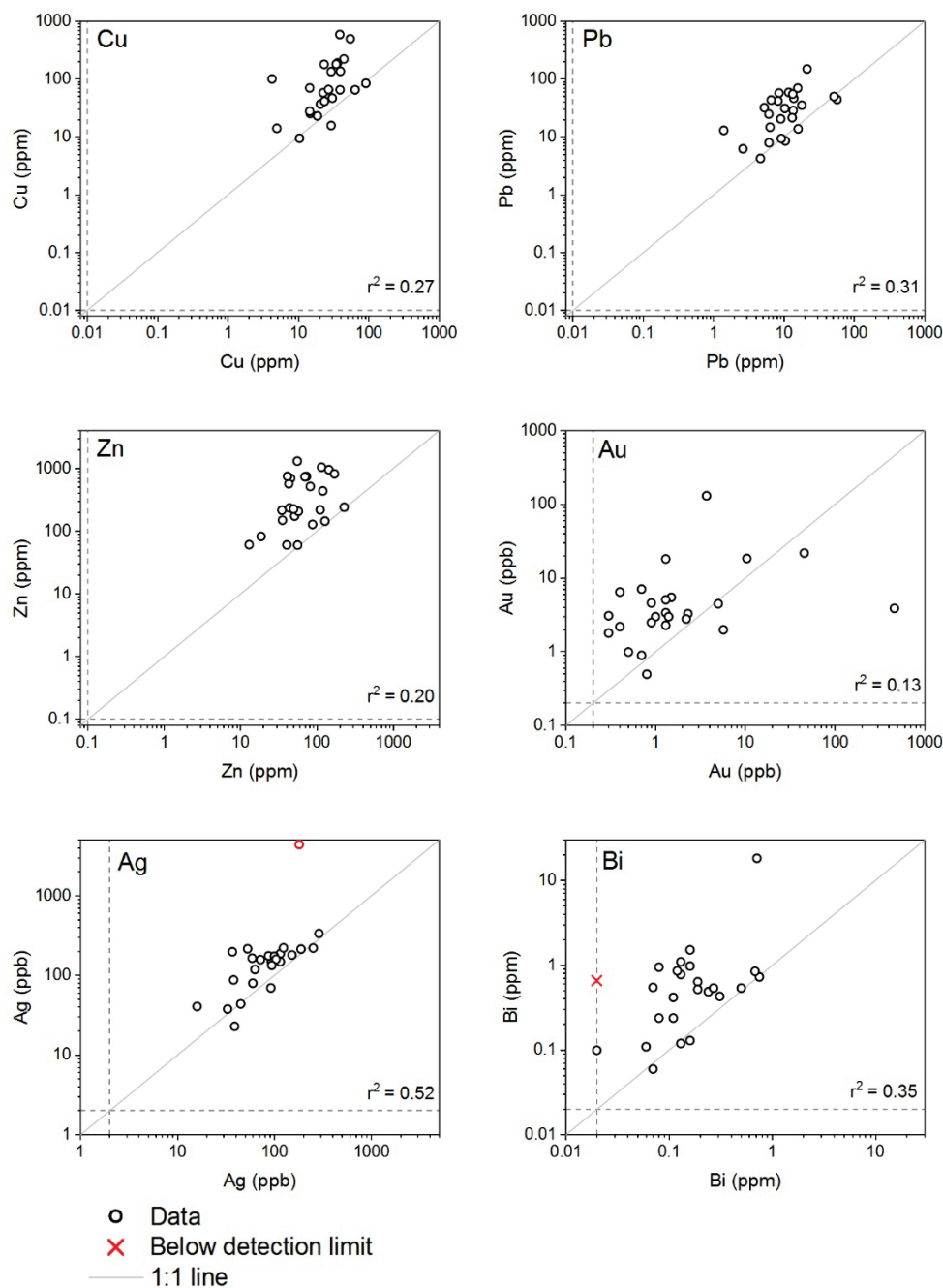


2012 samples - aqua regia digest - ICP-MS

Figure 12. Log¹⁰ reduced major axis - orthogonal regression plots of ICP-MS results after multi-acid digests versus aqua regia digest for some chalcophile elements (Cu, Pb, S, Zn) and those more tightly-bound in silicates (Al, Ga) in 2012 samples; dashed lines represent detection limits; note differences in scales.

The 1971-72 EGMA ICP-MS data are compared with the more recent 2012 DASS ICP-MS data after aqua regia digest using a \log^{10} reduced major axis - orthogonal regression plot (Fig. 13A). At face value, concentrations of known tailings constituents from the Aldermac mine (e.g., Fe, Zn, Cu; Doye and Duchesne, 2005) have apparently increased after the 40-year time interval between samplings, as indicated by the positive concentration shift from the 1:1 line. Concentrations of other elements mined at the Aldermac site, namely, Ag and Au, also appear to have increased in the intervening four decades between sampling. Likewise, Bi, which is associated with the ore deposit at Aldermac (e.g., Barrett *et al.*, 1991), shows an apparent concentration increase over time. Considering chalcophile elements in Figure 13B, there is an apparent increase in the concentrations of As, Co, Cd, Fe, Mn, Mo, S, and Sb from 1971-72 to 2012. Of note are the Cd concentrations in Lac Dasserat, which Goulet and Couillard (2009) found to be in excess of the Canadian water quality guideline for the protection of aquatic life. There is no apparent increase of either Hg or Ni concentrations (also associated with the no. 8 lens of the Aldermac deposit; Barrett *et al.*, 1991). In Figure 13C, In concentrations appear to have increased over time, although values are close to the limit of detection. Nevertheless, the majority of the detectable In concentrations are elevated in 2012 in comparison with 1971-72. The concentrations of Ga and Al (after aqua regia digest) are centred at the 1:1 correlation line, although there is some spread in the data. The concentrations of Ga and Al after the multi-acid digest have a stronger 1:1 correlation than after aqua regia between 1972-71 and 2012 (increase in r^2 values), likely because they were mainly released from terrestrial silicate minerals. (See GSC OF 8393 Data plots accompanying this report). Table 5 shows the comparative summary statistics of both datasets for selected elements.

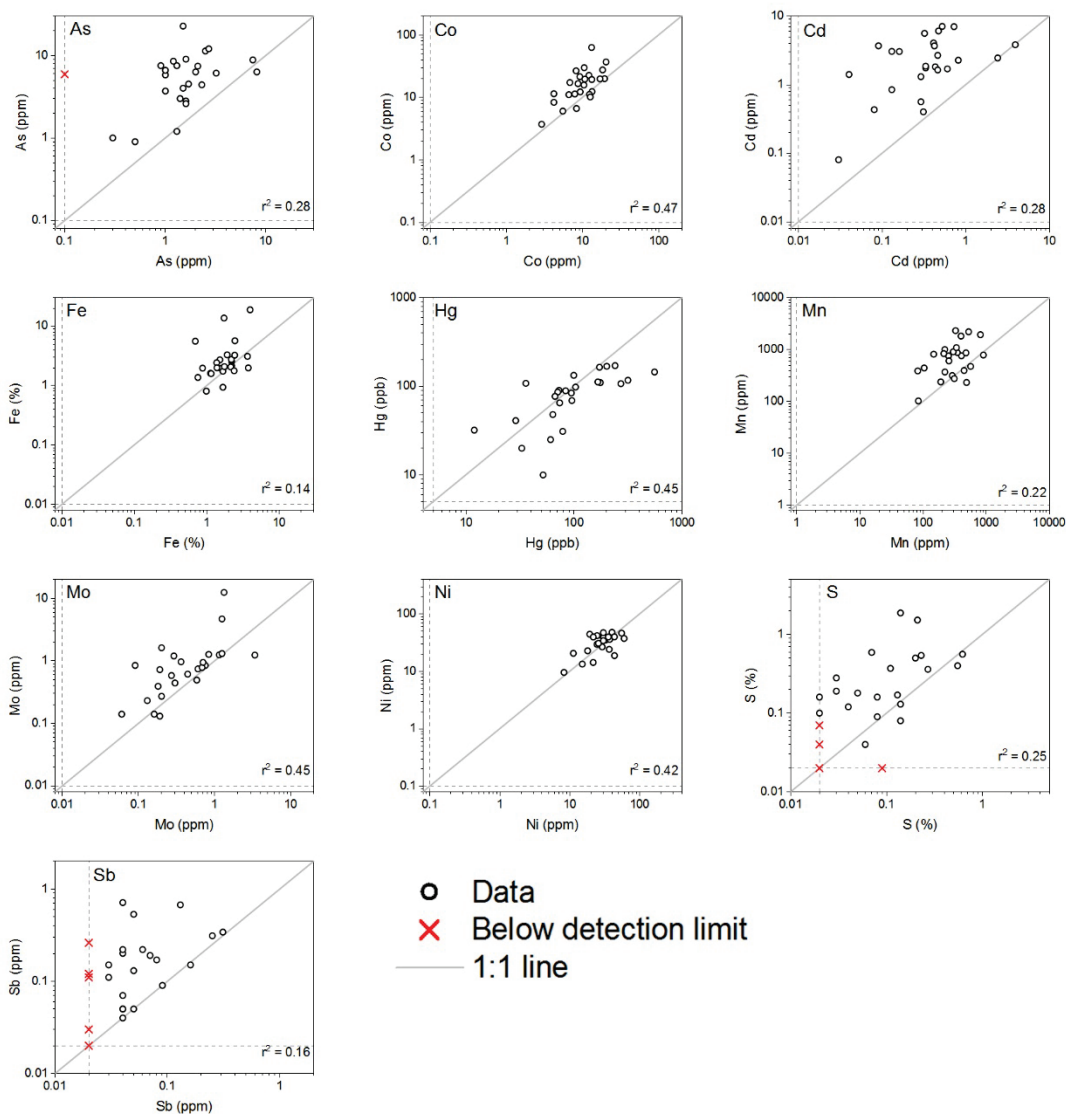
2012 samples - aqua regia digest - ICP-MS



1972 samples - aqua regia digest - ICP-MS

Figure 13 (A) Log¹⁰ reduced major axis—orthogonal regression plots of selected elements for 1972 EGMA re-analysed samples versus 2012 DASS samples analysed by ICP-MS after aqua regia digestion; dashed lines represent detection limits; note differences in scales.

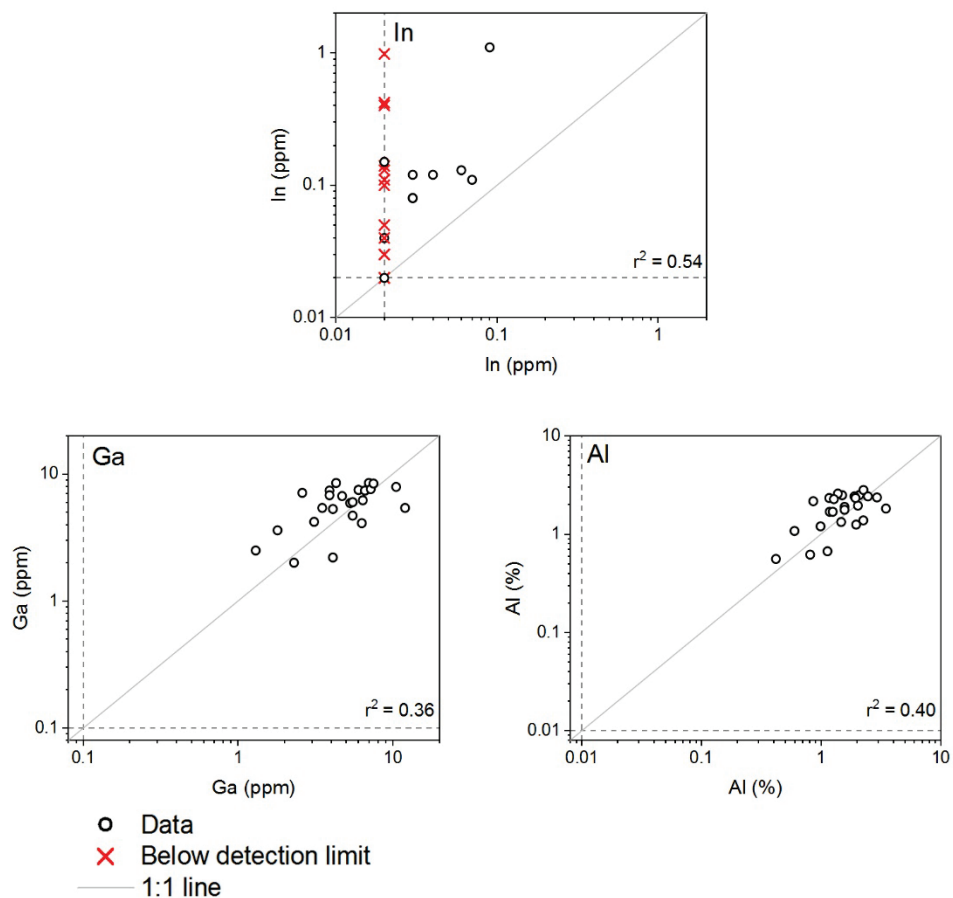
2012 samples - aqua regia digest - ICP-MS



1972 samples - aqua regia digest - ICP-MS

Figure 13 (B) Log^{10} reduced major axis – orthogonal regression plots of selected elements for 1972 EGMA re-analysed samples versus 2012 DASS samples analysed by ICP-MS after aqua regia digestion; dashed lines represent detection limits; note differences in scales.

2012 samples - aqua regia digest - ICP-MS



1972 samples - aqua regia digest - ICP-MS

Figure 13 (C) Log¹⁰ reduced major axis – orthogonal regression plots of selected elements for 1972 EGMA re-analysed samples versus 2012 DASS samples analysed by ICP-MS after aqua regia digestion; dashed lines represent detection limits; note differences in scales.

Table 5. Summary statistics of selected elements from the 1972 EGMA and the 2012 DASS data by ICP-MS after aqua regia dissolution

	Ag		As		Bi		Cu		Fe		In		Mn		Mo		Pb		Sb		Zn	
	1972	2012	1972	2012	1972	2012	1972	2012	1972	2012	1972	2012	1972	2012	1972	2012	1972	2012	1972	2012	1972	2012
LOD	0.002	0.002	0.1	0.1	0.02	0.02	0.01	0.01	100	100	0.02	0.02	1	1	0.01	0.01	0.01	0.01	0.02	0.02	0.1	0.1
Units	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
N	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
# Values <DL	0	0	1	0	1	0	0	0	0	0	15	2	0	0	0	0	0	0	4	1	0	0
Minimum	0.016	0.023	<0.1	0.9	<0.02	0.06	4.22	9.47	6900	8000	<0.02	<0.02	82	102	0.06	0.13	1.40	4.26	<0.02	<0.02	13.0	60.0
Maximum	0.288	4.377	8.1	22.6	0.75	18.24	90.56	586.99	39300	186800	0.09	1.10	899	2308	3.35	12.34	56.72	149.44	0.31	0.71	227.7	1302.9
Mean	0.099	0.317	2.0	6.4	0.22	1.27	30.13	117.56	18880	34880	0.02	0.18	347	830	0.62	1.36	13.55	35.58	0.07	0.20	76.4	430.3
Median	0.092	0.160	1.5	6.1	0.13	0.54	26.74	65.20	17200	20700	0.01	0.11	311	758	0.36	0.78	10.28	31.15	0.04	0.15	56.0	233.7
Std Deviation	0.068	0.849	1.9	4.5	0.21	3.55	19.01	141.70	8739	40420	0.02	0.28	202	615	0.69	2.45	13.09	30.35	0.07	0.19	51.0	356.7
Variance	0.005	0.721	3.5	20.2	0.05	12.63	361.31	20079.71	7.64E+07	1.63E+09	0.00	0.08	40957	378338	0.48	6.01	171.44	921.42	0.01	0.04	2603.3	127239.8
Coeff Var %	67.79	267.9	94.5	70.4	97.80	279.34	63.09	120.54	46	116	95.82	149.84	58	74	111.48	179.92	96.63	85.31	108.15	94.28	66.8	82.9
MAD	0.048	0.080	0.7	3.6	0.09	0.44	17.57	58.95	6968	7265	0.00	0.06	147	489	0.34	0.61	5.84	25.69	0.03	0.12	30.5	256.8
F-test	1.070		0.68		1.070		0.880		1.2		0.850		1.0		1.340		1.070		1.040		0.57	
Prob	0.433		0.83		0.433		0.622		0.3		0.654		0.5		0.236		0.433		0.461		0.91	
T-test	1.306		4.84		1.527		3.211		2.1		3.015		4.2		1.606		3.835		3.675		5.08	
P-value	0.204		0.00		0.140		0.004		0.0		0.006		0.0		0.121		0.001		0.001		0.00	
mean of the differences	0.217		4.40		1.054		87.432		16000.0		0.162		482.8		0.743		22.032		0.131		353.86	

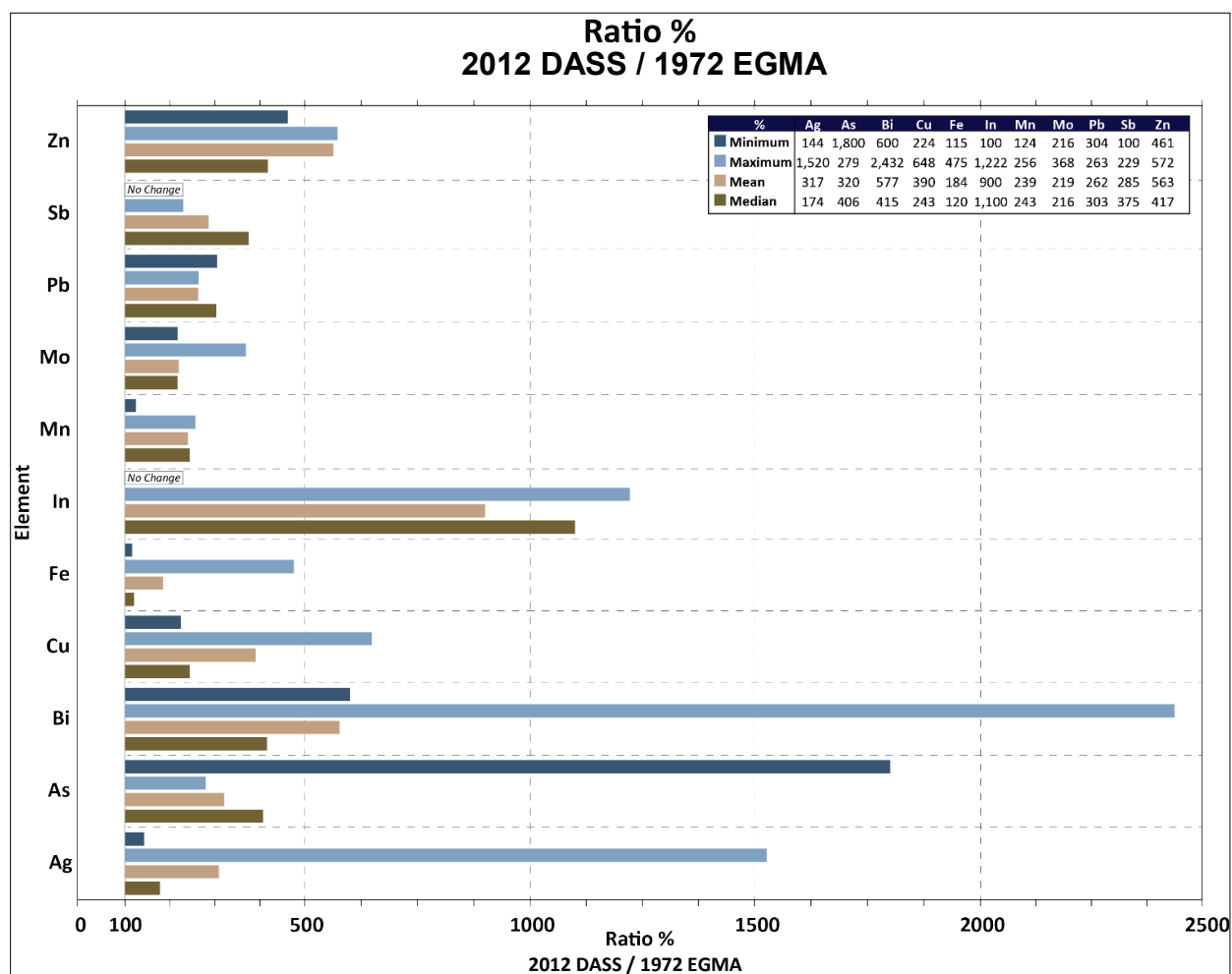


Figure 14. Graph showing the ratios in percent of the change in minima, maxima, means and medians of the 2012 DASS data from the original 1972 EGMA data.

Without delving further, over the 40-year period between measurements there has been an apparent net increase in metal concentrations in bulk surface sediments, as shown in Table 5. Figure 14 shows the change in concentration of selected elements between 1971-72 and 2012 as a calculated ratio in percent for the minimum, maximum, mean and median values of individual elements. The minimum values of each dataset have increased substantially, except for Sb and In, which have not changed statistically because their concentrations are below the DL. Minimum concentrations of Ag, Fe and Mn increased moderately ($\leq 216\%$), whereas As, Bi and Zn concentrations increased substantially ($\geq 461\%$), As, notably by 1800%. Maximum concentrations increased significantly with the highest in Bi, Ag, In, Cu and Zn. Maximum Bi concentration increased by 2400%. As, Bi, In and Zn concentrations recorded the largest increases in the means and medians (320-900% and 406-1100%, respectively), whereas the remaining regional element concentrations increased moderately (means of 184-390%; medians of 174%-375%).

To consider the discrepancy between the older and more recent analyses of samples collected in 1971-72, Figure 15 is a set of \log^{10} reduced major axis - orthogonal cross plots of element concentrations in sediments sampled and analysed in 2012 against those sampled and analysed in

1971-72. Therefore, Figure 15 compares results of samples freshly analysed after their collection. Again, concentrations of Ag, As, and Mo are close to the detection limits. However, concentrations of Cu, Mn, Ni, Pb and Zn are generally higher in 2012 than in the early 1970s (above the 1:1 line), confirming this qualitative observation.

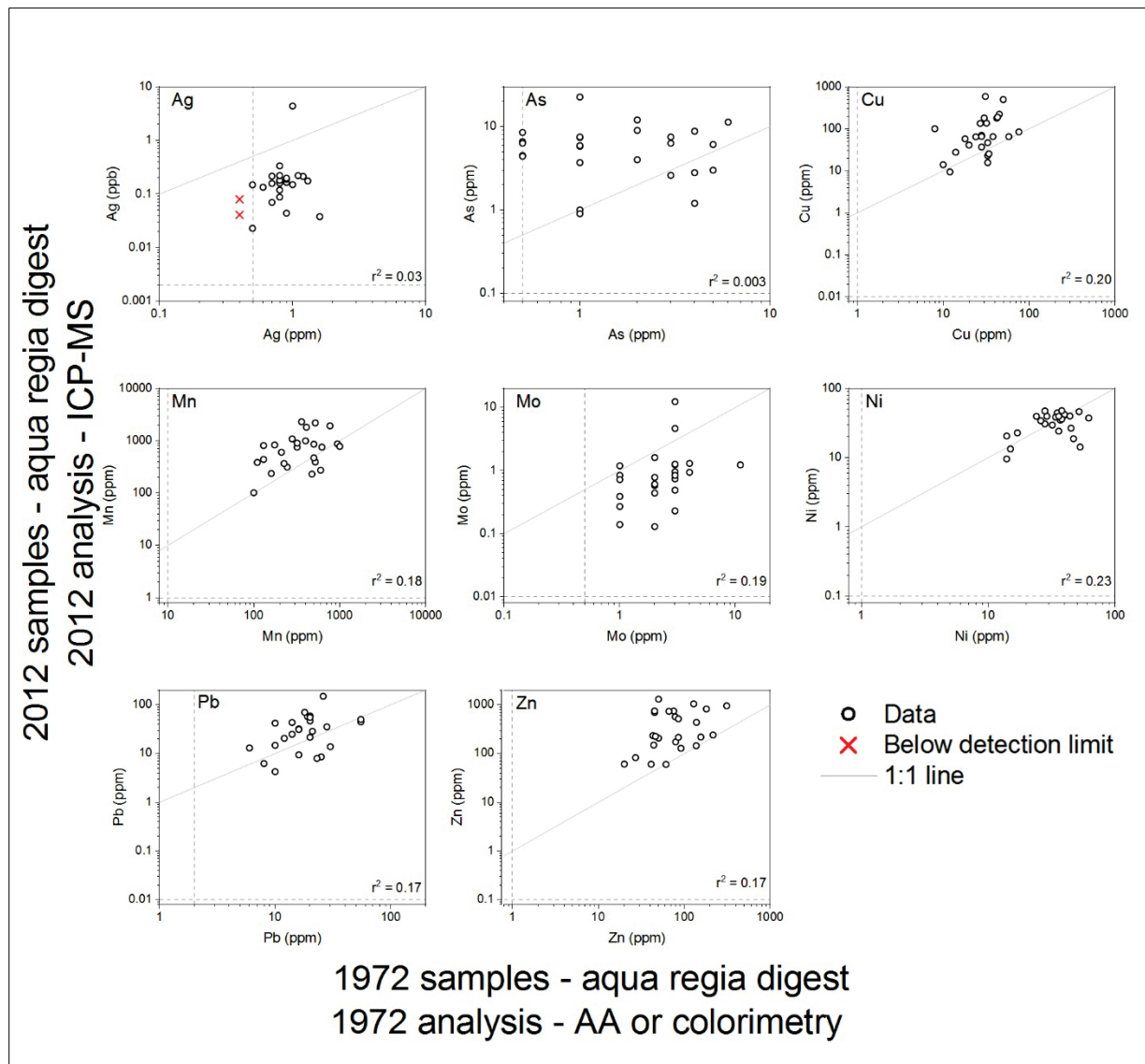


Figure 15. Log^{10} reduced major axis - orthogonal cross plots of element concentrations sampled and analysed in 2012 against element concentrations sampled and analysed in 1971-72; dashed lines represent detection limits; note differences in scales.

Regional distributions

The data presented in Table 5 from both 1971-72 and 2012 show an apparent increase in elemental concentrations with distance down drainage of the Aldermac site. Areas where As, Bi, In and Zn concentrations increased are preferentially distributed along the present-day main flow path of surface water from Rivière Arnoux toward the northern outlet of Lac Dasserat (Fig. 16). Areas outside of the main flow path also exhibit significant increases in metal concentrations, including the southern quadrant of Lac Dasserat, possibly caused by localized effects at stream inlets and outlets or historical changes in flow directions of surface water (AECOM, 2010). Maps of element distributions are included in both Figure 16 and the maps folder accompanying this report (GSC OF 8393 Maps).

In the interval between 1971-72 and 2012, one of the main constituents of the Aldermac tailings, arsenic (As), apparently increased significantly in near-shore sediments along the main surface water flow path from Lac Arnoux through to the north end of Lac Dasserat (Fig. 16A). Sediments of Lac Desvaux had no significant increases in arsenic, although measured increases at Lac Berthemet and the southern end of Lac Dasserat coincide with higher LOI values (Fig. 10). Increases in bismuth (Bi) concentrations are similar to those of As (Fig. 16B). Indium (In) is a tracer of both regional smelter emissions (e.g., from Sudbury and Rouyn-Noranda) and ore processing of massive sulphides (Mayer *et al.*, 2007). Its concentrations increased moderately throughout the drainage system, with the largest increases in sediments proximal to the Aldermac site in Lac Arnoux and Baie Arnoux (Fig. 16C). The increase in In and As concentrations proximal to the Aldermac site reinforces that the abandoned mine site is the dominant local source. Zinc concentrations increased substantially in the sediments along the current main drainage flow path from Lac Arnoux to the northern reaches of Lac Dasserat (Fig. 16D). The southern quadrant of Lac Dasserat, including a site 1 km west of the main surface water flow and about 1 km northeast of Lac Lusko, also demonstrate elevated Zn concentrations. During mining operations, the price of Zn was low (Markewired, 2008) and the Horne smelter in nearby Rouyn-Noranda did not refine Zn (Geocon, 2002). Consequently, the Aldermac mine never produced an economically viable Zn concentrate, Zn was discarded with the tailings, and was never recovered. Therefore, the finding of elevated Zn concentrations proximal to the Aldermac site is consistent with remnant Zn in the Aldermac tailings.

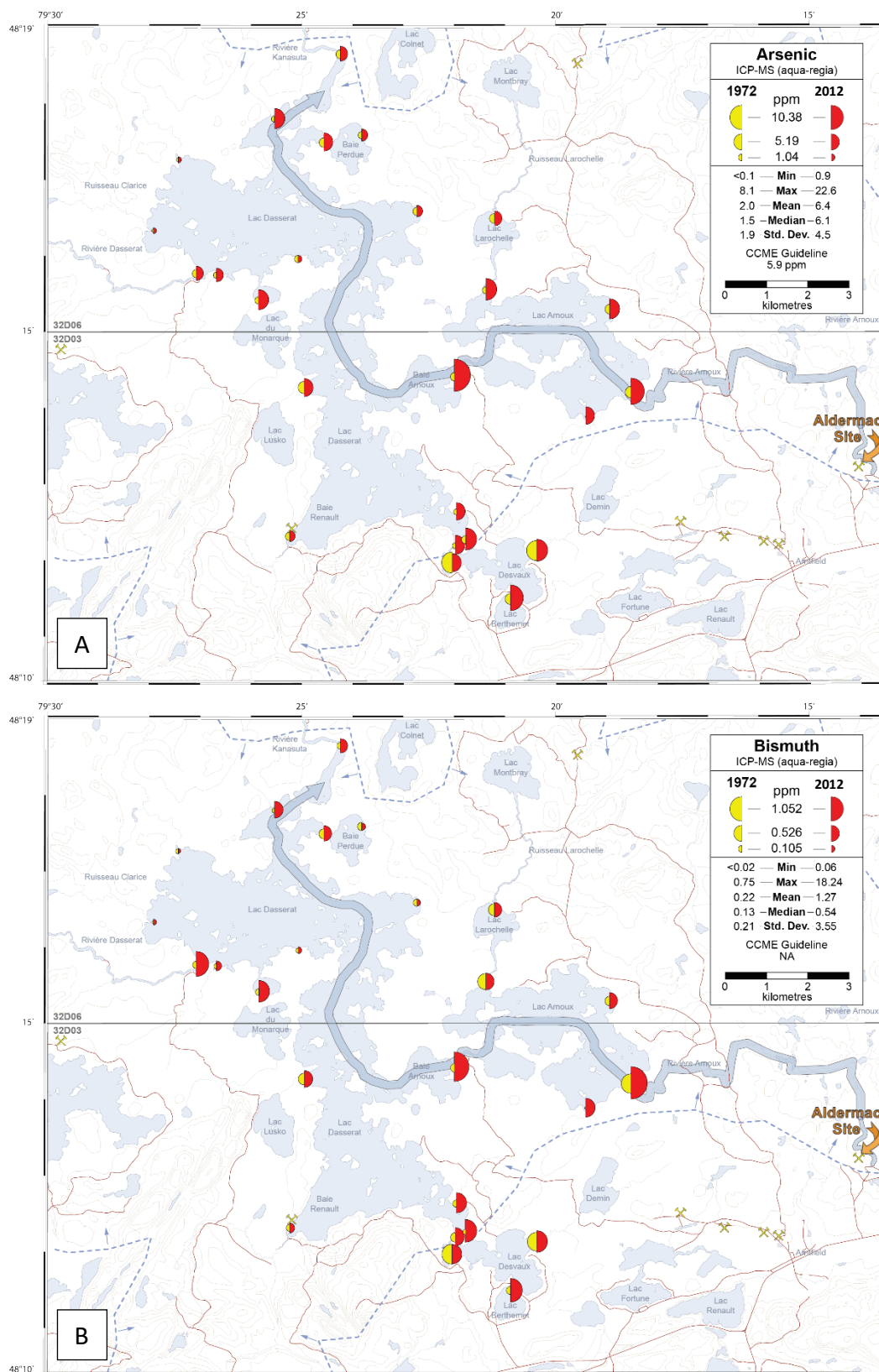


Figure 16. Maps comparing the concentration and distribution of elements (A) arsenic, (B) bismuth, (C) indium, and (D) zinc between the 1972 EGMA and 2012 DASS samples.

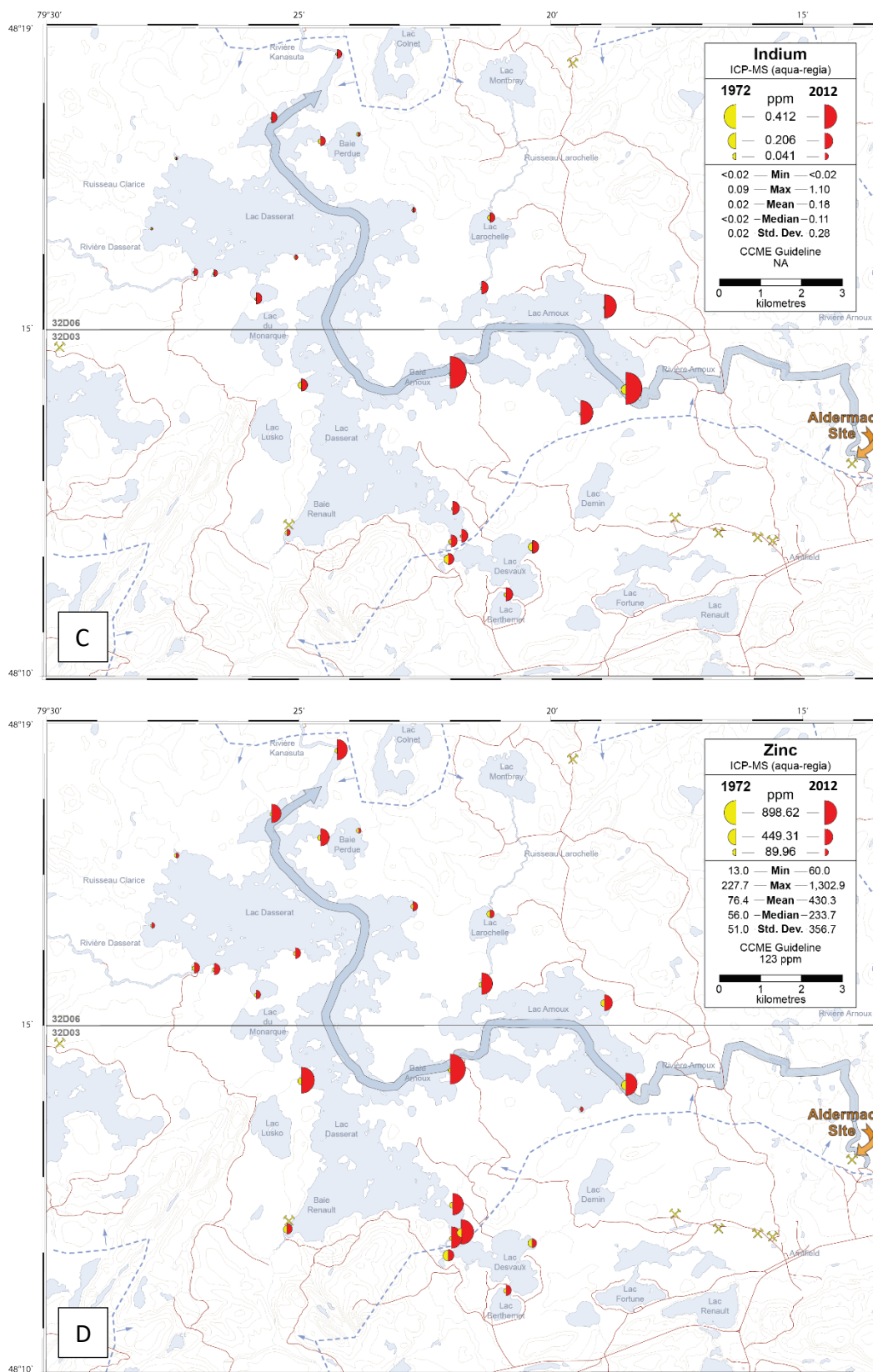


Figure 16 (cont.). Maps comparing the concentration and distribution of elements (A) arsenic, (B) bismuth, (C) indium, and (D) zinc between the 1972 EGMA and 2012 DASS samples.

Inherent differences in sampling

From a cursory glance at the findings of this comparative study, concentrations of metals appear to have increased in the near-shore sediments after the 40-year time gap between samplings. However, when interpreting the geochemistry of bulk sediments and grab samples, it is important to assess what exactly is being measured. Although, the Hornbrook, spoon, and Petite Ponar® lake-sediment samplers are among those widely used in regional geochemical surveys, they are significantly different in their geometries and deployment methods, necessitating caution with interpretations of geochemical results.

It is important to concede that the Hornbrook, improvised spoon, and Petite Ponar® sampling methods generate bulk estimates of sediment geochemistry, which are imprecise in terms of sediment depth and time of deposition. Depth penetration of the samplers into the sediments is dependent on the size and geometry of the sampler, speed of descent of the sampler through the water column, water depth, surface water currents, height of free fall above the sediment-water interface (if used), weather conditions, deployment by different operators, stiffness and nature of the bottom material.

If a gravity coring device was used, it was most likely a prototype of the Hornbrook sampler, a unique Canadian invention, used by the GSC throughout the 1970s and beyond to collect lake sediment samples for large-scale geochemical mapping and mineral exploration (Coker *et al.*, 1979, Davenport *et al.*, 1974, Friske and Hornbrook, 1991, Government of Canada, 2017). The sampler was likely still in development during the beginning of the EGMA project and fully developed before 1974, when deployed in western Newfoundland (Davenport *et al.*, 1974).

A concentration measurement from samples collected by the Hornbrook sampler is an average integrated over the length of the sediment interval collected, providing the sample was well homogenized before analysis. Free-fall of a gravity corer can obliterate the sediment-water interface, making it difficult to estimate the actual sediment penetration depth of the sampler. Incidentally, this was by design, so that recent contamination would not obscure natural metal concentrations required for mineral exploration (Friske and Hornbrook, 1991). Hornbrook and Gleeson (1972) also indicated that recent contamination was not to be sampled to avoid recording false exploration anomalies. In this study, the deepest water depth in 2012 was 4.2 m; the short height of free fall would likely have neither obliterated the interface nor allowed the sampler to become buried and let the sediments overtop the core barrel. As further evidence, in 2016 the Hornbrook sampler was deployed in a parallel study by GSC scientists in Lac Dasserat to retrieve sediments in continuous cores, 30-40 cm deep (Fig. 17; G.R. Brooks, pers. comm., 2017). The high water content at the top of the core (Fig. 17) suggests that the corer could not penetrate much deeper than 30-40 cm, despite a 5-m free-fall to the bottom sediments. Free-fall in 1971-72 would have been from a much shorter height because water depths were shallow, so it is reasonable to estimate a sampling interval from the sediment-water interface to approximately 30 cm depth or less. The physical nature of the bottom sediment material has likely not changed substantially between 1971 and 2016, so core penetration would probably be similar in 2012.

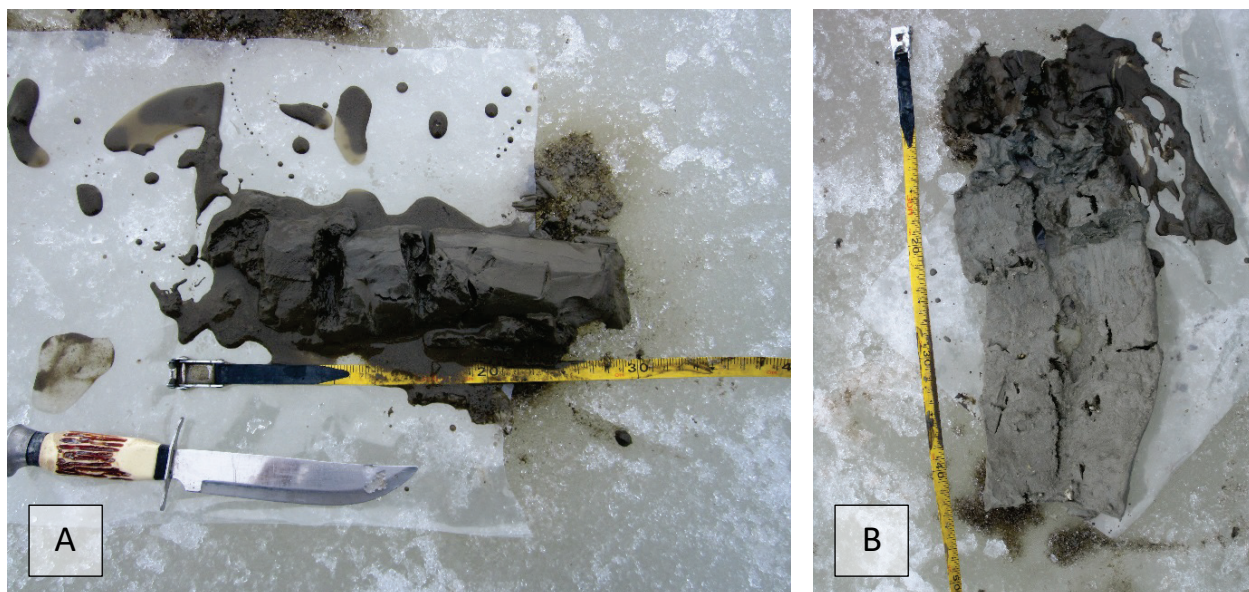


Figure 17. Examples of sediment core from Lac Dasserat taken by a Hornbrook sampler in 2016 **(A)** top of core is on the left; **(B)** top of core is at the top of the image; Note higher water contents at the top of the core samples. Photos: Courtesy of G.R. Brooks, GSC; taken March 2016.

A spoon sampler yields a surface sediment ‘grab’ sample; it is essentially a scoop operated by hand with a short handle in shallow water or attached to the end of a telescoping pole at deeper sites (Fig. 6). There is little control on the depth of sediment sampled, depending on the geometry of the scoop and the nature of the substrate (e.g., State of Ohio Environmental Protection Agency, 2001). Sample volumes are limited with this method and the device is cumbersome when used in deeper water, where Hornbrook and Gleeson (1972) likely opted for the gravity corer or an improvised sampling system. Any improvised sampling tube or device used by the field crew in 1971-72 (Fig. 6) was more than likely irreproducible and imprecise in terms of sediment depth, although the samples represented bulk sediment, perhaps similar to those retrieved by the Hornbrook sampler.

Typically, mining companies and environmental consultants use dredge or grab samples of surface lake sediments, like those taken by the Petite Ponar®, in baseline studies for environmental risk assessment. The Ponar® is simple to operate and has been available since the late 1960s (Grand Valley State University, 2014, Mudroch and MacKnight, 1991). The Petite Ponar® is essentially an open box near the top of the sediment column with jaws at its base that shut around the sample (Mudroch and MacKnight, 1991; Fig. 8). Resultant samples are more representative of recent deposition (up to 12 cm depth) than collected using the Hornbrook sampler because of the sampler’s geometry and operation. In Lac Arnoux, cores retrieved in 2012 showed a distinctive rust-coloured iron precipitate at the surface of the bottom sediments (Figs. 18A and B). This precipitate was also recorded in grab samples taken by Petite Ponar® (Fig. 18C), which indicates that the Petite Ponar® device effectively captured the sediment-water interface and recent sedimentation.

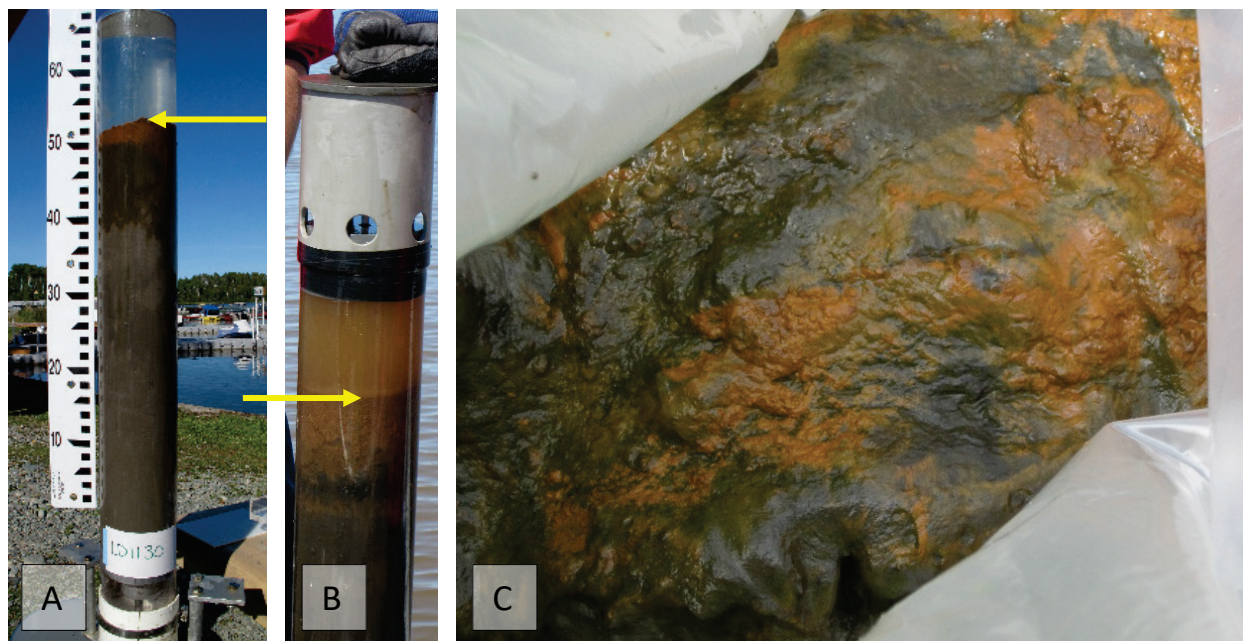


Figure 18. (A) 2011 and (B) 2012 sediment cores taken in Lac Arnoux; yellow arrows mark the sediment-water interface; (C) Petite Ponar® grab sample taken in Lac Arnoux, capturing Fe-precipitate at the sediment-water interface; Photos: GSC, 2011-12

Challenges with quantitative interpretations of element concentrations in bulk sediment samples

Inherent differences in the collection methods for bulk sediment samples strongly influence quantitative interpretations of element concentrations and their temporal trends. Sediment depth penetration of sampling devices incur significant ‘dilution’ of the contamination level by intercepting a combination of contaminated post-industrial sediments and pre-industrial sediments (Fig. 19).

A few simplified calculations help illustrate the challenges of quantitative interpretations. For the purpose of demonstration, assumptions about the sediments retrieved by the different techniques simplify calculations:

- (1) sediment deposition remained constant at a rate of 1 mm/a (Grenier and Kliza, 2005);
- (2) sediment maintained a constant bulk density, i.e., same mass of sediment per unit volume;
- (3) sediment contamination from the Aldermac mine began in 1932 and persisted to 2012;
- (4) there were no additional contaminant sources;
- (5) no post-depositional contaminant mobility occurred, i.e. no diagenetic mobility;
- (6) in 1971-72, the coring methods (Hornbrook or improvised) retrieved a continuous cylindrical sediment sample (6.5 cm diameter), from the sediment-water interface to a depth of 30 cm; and
- (7) in 2012, the Petite Ponar® sampler captured the sediment-water interface and sampled a cuboid of sediment with an area of 15×15 cm, 12 cm deep.

Assumptions are idealized, based on current information. Figure 19 is a schematic representation.

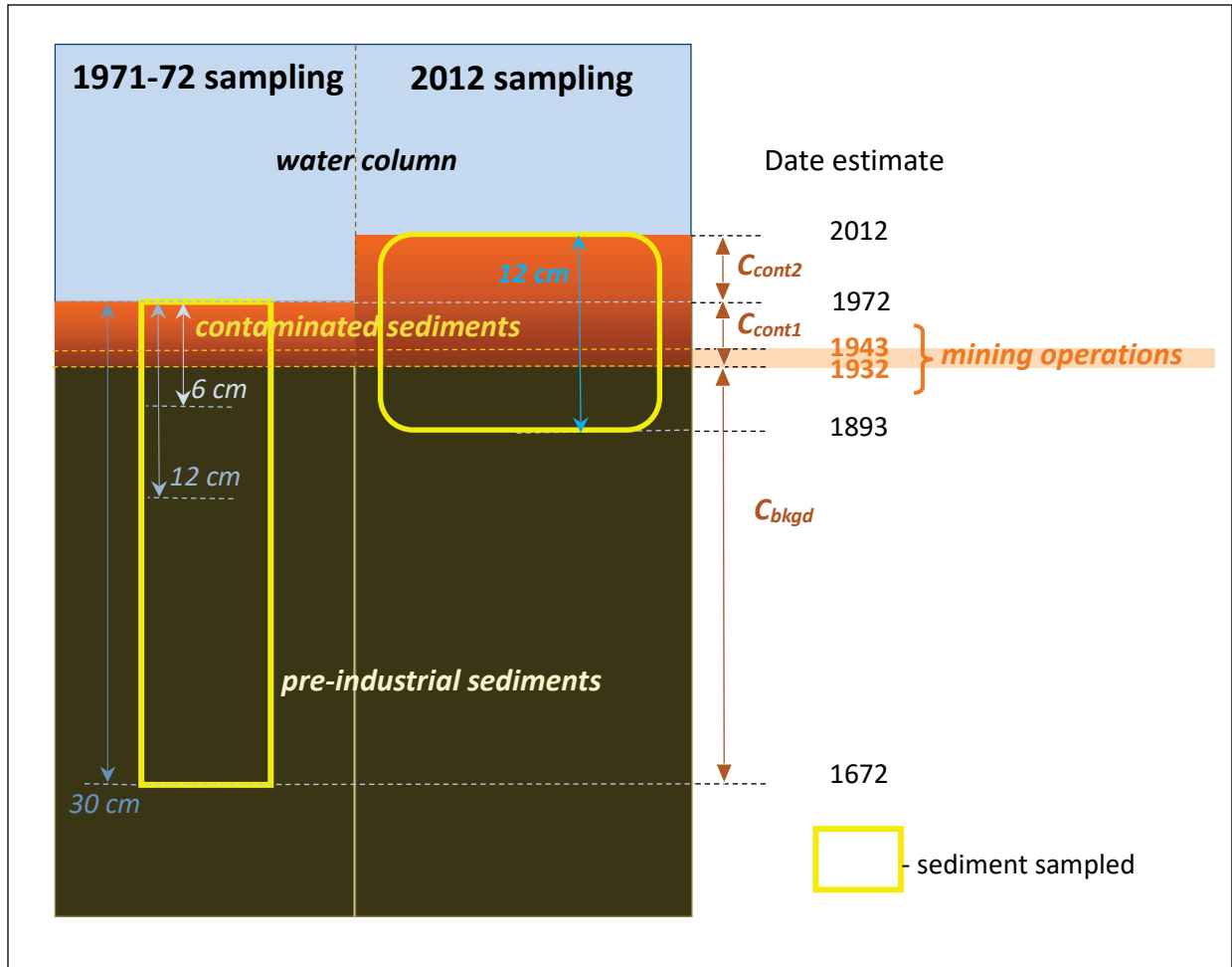


Figure 19. Simplified schematic of sediment sampling in 1971-72 by gravity coring or by ad hoc sampling methods and, in 2012, by Petite Ponar® grab sampling. Sediment age estimated using a constant sedimentation rate of 1 mm/a (Grenier and Kliza, 2005).

Under these idealized assumptions, 85% of a sediment sample volume taken in 1971-72 would represent pre-industrial deposition and 15% would represent contaminated sediments over the 30-cm length of the sample. In contrast, roughly 33% of the sediment volume in 2012 would represent pre-industrial sediments and 66% contaminated. However, even if the sampling methods had been identical in 1971-72 and 2012, after four more decades of contaminated sediments deposited near the same sites, the mean concentrations in 2012 would necessarily be higher than from samples taken in 1971-72.

For a concrete illustration, consider a simplified calculation of an element concentration in 1972:

$$C_{1972}V_{1972} = C_{bkgd}V_{bkgd} + C_{Cont1}V_{Cont1} \quad (1)$$

where:

C_{1972} = total mean concentration of bulk sediments in 1972, measured in EGMA samples;

V_{1972} = total sediment sample volume in 1972, estimated;

C_{bkgd} = 'background' mean concentration, estimated from lowest recorded above DL in 1972 from

near-shore sediments;

V_{bkgd} = volume of pre-industrial sediments sampled in 1972, estimated;

C_{Cont1} = mean concentration of contaminated sediments, 1932-1972, unknown; and

V_{Cont1} = volume of contaminated sediments sampled in 1972, estimated.

Solving the mean concentration of contaminated sediments from 1932 to 1972 in Equation (1) yields:

$$C_{Cont1} = (C_{1972}V_{1972} - C_{bkgd}V_{bkgd})/V_{Cont1}$$

Likewise, the mean concentration of contaminated sediments from 1972 to 2012 (C_{Cont2}) can be calculated according to:

$$C_{2012}V_{2012} = C_{bkgd}V_{bkgdP} + C_{Cont1}V_{Cont1P} + C_{Cont2}V_{Cont2} \quad (2)$$

and solving Equation (2) for C_{Cont2}

$$C_{Cont2} = (C_{2012}V_{2012} - C_{bkgd}V_{bkgdP} - C_{Cont1}V_{Cont1P})/V_{Cont2}$$

where:

C_{2012} = total mean concentration of bulk sediments in 2012, measured;

V_{2012} = total sediment sample volume in 2012, estimated;

V_{bkgdP} = volume of pre-industrial sediments sampled in 2012, estimated;

V_{Cont1P} = volume of contaminated sediments sampled in 2012, representing deposition from 1932-1972, estimated

C_{Cont2} = mean concentration of contaminated sediments, 1972-2012, unknown; and

V_{Cont2} = volume of contaminated sediments sampled in 2012, representing deposition from 1972-2012, estimated

C_{bkgd} ; C_{Cont1} as for Equation (1)

Results of this study show that $C_{2012} > C_{1972}$ in mean concentrations. However, if $C_{Cont2} > C_{Cont1}$, then contamination has increased since 1972 and reflects more than the additional 4 decades of the same level of metal contamination emanating from the Aldermac site. If $C_{Cont2} \leq C_{Cont1}$, then the contamination level has either remained the same or decreased.

In this simplified calculation, Bi, In, and Zn are the elements in Figure 15, which register an increase in contamination after the 40-year interval ($C_{Cont2} > C_{Cont1}$; Table 6). However, the calculation is highly dependent on the assumptions made, particularly the sampling depth estimated in 1972, which is a poorly constrained parameter. Perhaps a more realistic estimate of the sediment depth sampled in 1971-72 is 12 cm (or 6 cm for spoon sampling), instead of 30 cm. For 12- and 6-cm depth penetrations, the calculated concentrations of the elements in Figure 15 indicate temporal increases from 1932 to 1972 and 1972 to 2012 (Table 6). Even for qualitative assessment of metal concentrations over time in bulk sediments, it would be critical to record the sampling depth. Another assumption in the calculations is the value of the background or pre-industrial concentration. Although most of the lowest detectable values came from two sites of the 25 sampled (310, 322; Fig. 7; GSC OF 8393 All Data.xlsx), this exercise did not consider their authenticity as local control sites.

Table 6. Results of calculated mean element concentrations for three assumed sediment depth penetrations in 1971-72; Calculation of C_{cont1} from Equation 1; calculation of C_{cont2} from Equation 2, under the assumptions provided.

Element	Assumed sediment depth sampled in 1971-72 (cm)	C_{cont1} (1932-1972)	C_{cont2} (1972-2012)	$C_{cont2} - C_{cont1}$
Ag (ppb)	30	645	289	-356
	12	268	667	399
	6	142	793	651
As (ppm)	30	13.6	5.29	-8.29
	12	5.61	13.6	7.64
	6	2.96	15.9	12.9
Bi (ppm)	30	1.41	2.34	0.93
	12	0.60	3.15	2.55
	6	0.33	3.42	3.09
Cu (ppm)	30	198	150	-48.4
	12	82.0	267	185
	6	43.1	305	262
Fe (%)	30	9.66	0.12	-9.54
	12	4.28	5.50	1.21
	6	2.49	7.29	4.81
In (ppm)	30	0.18	0.42	0.24
	12	0.09	0.51	0.42
	6	0.06	0.54	0.48
Mn (ppm)	30	2070	340	-1730
	12	877	1530	653
	6	478	1920	1448
Mo (ppm)	30	4.26	*-0.12	*--
	12	1.74	2.40	0.66
	6	0.90	3.24	2.34
Pb (ppm)	30	92.9	12.5	-80.3
	12	38.0	67.4	29.4
	6	19.7	85.7	66.0
Sb (ppm)	30	0.42	0.17	-0.25
	12	0.19	0.41	0.22
	6	0.11	0.48	0.38
Zn (ppm)	30	488	790	302
	12	203	1075	872
	6	108	1170	1062

*In the simplified calculation of Mo at a sediment depth of 30 cm, $C_{cont1}V_{cont1P} > C_{2012}V_{2012}$, which yields negative C_{cont2} , an invalid result.

The distributions of metals before and after a 40-year time span recorded by analyses of bulk near-shore sediments suggest that the Aldermac site remained a persistent source of metal contamination decades after the last landowner left in 1946 (Cyr *et al.*, 2009). There are several mechanisms for perpetuating metal contamination from the Aldermac property, likely dominated by acid mine drainage.

Acid mine drainage (AMD) from the Aldermac mine was left unconstrained for nearly eight decades before the site was declared abandoned and the Government of Quebec assumed

responsibility for its restoration. The oxidation of sulphide minerals upon exposure to atmospheric oxygen generates AMD, for example, when water levels recede, or when tailings are discarded on land in the unsaturated zone. Oxidation of sulphides perpetuates the release of acid and metals (oxidation products) into the environment indefinitely if left untreated and exposed, providing that reactants persist (e.g., Akcil and Koldas, 2006, Moncur *et al.*, 2005). Mine tailings, or residual waste from the Aldermac mine, consist of 50% sulphides (Cyr *et al.*, 2009), including 20-30% pyrite and 25% pyrrhotite (Geocon, 2002). Measurements of tailings chemistry from the Aldermac property in January 1995 (Conсор Inc., 1995) include a pH range of 2.0 to 5.2 (mean of 3.5; n=12) with high contents of Pb (≤ 218 ppm), Zn ($\leq 13\,613$ ppm), Cu (≤ 4185 ppm), Cd (≤ 29 ppm), Mo (≤ 19.4 ppm), and As (≤ 90 ppm), confirming AMD potential. Doye and Duchesne (2005) verified that the tailings from the Aldermac mine were net acid generating with leachate concentrations of Fe, Zn, and Cu, exceeding the provincial environmental regulations, as well as an acidic pH of 2.3 to 3.1. Sporadic measurements of lake-water pH also confirm sustained acidity in Lac Arnoux (range of 3.5 in 1973 to 6.9 in 1985, at unspecified lake locations; Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP), 2012) and from additional pH measurements in 2011-13 (Alpay, unpublished data)). In the time between 1971-72 and 2012, continuing AMD could sustain the metal concentration patterns detected in grab samples of near-shore sediments at locations in the current drainage flow path from the Aldermac site, particularly for elements, which are constituents of the tailings.

In addition to AMD, physical transport and flow direction of surface water likely contribute to the spatial metal distributions observed downstream of the Aldermac property. Other land-use activities, physical sediment perturbations, and atmospheric fallout are possible causes of some elevated concentrations observed in near-shore sediments, not necessarily linked to effluent from the Aldermac site.

There would be an expected lag time before environmental recovery could be detectable in the sediments, if present, after the restoration of the Aldermac site, and as contaminated sediments become buried. However, with an estimated sediment deposition rate of 1 mm/a in boreal lakes (e.g., Grenier and Kliza, 2005), the resolution of the Petite Ponar® sediment sampler would not be able to detect potential environmental recovery for several more decades. Furthermore, if the chemical gradient in the sediments before and after restoration is sharp, evidence of recovery may also become obscured by diagenetic metal mobility, e.g., from diffusion or reductive dissolution and subsequent re-precipitation at a different depth within the sediment profile.

Two separate bulk sediment samplings, four decades apart, provided a qualitative basis to evaluate metal contents and spatial trends. However, exercising caution is essential when comparing time-series datasets, which are not generated by the same sampling methods with variability or uncertainty in the sediment depths retrieved. Mechanisms, which generate the observed element concentrations and distributions in near-shore sediments, will be explored beyond the two snapshot measurements in 1971-72 and 2012 in tandem with emerging results from ^{210}Pb -dated lake sediment cores, which represent longer, more continuous temporal archives spanning from pre-colonial and pre-industrial to modern times (e.g., Alpay, unpublished data, Hamilton *et al.*, 2015).

CONCLUSIONS

Two measurements of near-shore lake sediment geochemistry over 1971-72 and in 2012 demonstrated that acid mine drainage and metal contamination from the Aldermac mine have persisted long after it was abandoned and for at least seven decades. The historical data and samples from 1971-72 provide qualitative concentration distributions at a regional scale, against which modern concentration patterns can be compared. However, the differences in sampling methods, sample treatment and analytical techniques prohibit quantitative temporal comparison of element concentrations in sediments. Bulk sediment sampling and analysis yield qualitative spatial geochemical trends for environmental risk assessment, but are insufficient to represent absolute baseline geochemical conditions at a given time.

Regardless of the original purpose to aid mineral exploration in 1971-72, the resultant EGMA survey data and samples formed a spatial record of the environmental effects of metal mining. Although the free-fall coring, improvised sediment samplers, and Petite Ponar® devices are different in geometry and operation, they each retrieve a representation of metal deposition in shallow sediments. In fact, the geochemistry of bulk sediment samples is a routinely used parameter in environmental risk assessment as a first approximation of distribution patterns and as a possible datum for retrospective and future comparison. Although most baseline studies examine lake sediment geochemistry from the centre of the lake basin or in the profundal zone, data from bulk near-shore sediments generally concurred with findings from short cores and bulk sediment samples at deeper sites (McNeil *et al.*, 2015). The two sets of results indicated the main point source of metal contamination, spatial metal distributions, and localized variations in metal concentrations. If near-shore bulk sediment geochemical data are the only results available, they can serve a reconnaissance purpose for environmental risk assessment. In parallel to Hornbrook's (1972) recommendation for mineral exploration, geochemical surveys of bulk near-shore sediments from the past provide a preliminary basis for further investigation. For environmental risk, surveys give guidance to explore anomalies, additional sources of contamination, transport, and processes of metal sequestration (e.g., with organic carbon) near stream inlets and outlets to lake systems.

However, continuous sediment cores provide more accurate and precise data than bulk sediment samples, particularly if the environmental risk assessment necessitates further investigation than the reconnaissance-level information gleaned from regional grab sampling of bottom sediments (Alpay *et al.*, 2015). Dated sediment cores, with high-resolution sub-sampling, allow for more relevant, precise data to aid in quantifying historical contamination and assessing natural variability of metal concentrations. For monitoring rapid change in aquatic systems, water quality analyses provide relevant snapshots of pH and element concentrations (e.g., Grenier *et al.*, 2013), particularly if done as a time series or continuous recording, to track environmental recovery or deterioration on shorter time scales.

ACKNOWLEDGMENTS

This study received support from the Environmental Geoscience Program and the Geological Survey of Canada, Lands and Minerals Sector of Natural Resources Canada. A. Plouffe is gratefully acknowledged for his valuable scientific review of this Open File Report. S. Adcock and S. Day provided critical contextual information about the original sampling methods used in 1971-72. M. McCurdy offered discussion about sample integrity during four decades of archival storage. G.R. Brooks provided field images of coring using the Hornbrook device, in addition to anecdotal evidence of sediment stiffness and coring experiences in Lac Dasserat. The GSC-Ottawa Sedimentology Lab is also acknowledged for sample preparation and analytical results for particle size and carbon content. M. Szadurski graciously provided the vintage image of the Hornbrook sampler from GSC archives.

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