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**GEOLOGICAL SURVEY OF CANADA
OPEN FILE 7595**



**Environmental geoscience investigations
surrounding the former Aldermac mine,
Abitibi, Quebec:
Regional surveys of surface water
and sediment geochemistry**

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

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Environmental geoscience investigations surrounding the former Aldermac mine, Abitibi, Quebec: Regional surveys of surface water and sediment geochemistry

Summary

Geoscience investigations are fundamental for environmental risk assessment of metal mining. This Geological Survey of Canada Open File presents regional geochemical surveys of surface water and sediments from lakes and streams collected during 2011-13. The data form the basis to identify environmental metal contamination in the vicinity of the former Aldermac mine site (Cu, Zn, Au and Ag) in Abitibi, Quebec, in addition to tracking potential recovery of aquatic systems.

Current practices for baseline studies of sites to be developed for mining include temporal surface water sampling and surface grab sampling of sediments in aquatic receiving environments. In addition to surface sediment sampling, vertical sediment coring is a universal tool of paleolimnological research. This report presents data from surface water, sediment grab sampling and sediment coring in the vicinity of the Aldermac site.

The former Aldermac mine (Cu, Zn, Au and Ag), 25 km west of Rouyn-Noranda in Abitibi, Quebec, operated from 1932-1943 and discharged acid mine drainage to the watershed downstream which includes Lac Arnoux and Lac Dasserat (Figure 1). The study site is representative of both a common mineral deposit and the legacy of historical mining practices in the area (Goulet and Couillard, 2009). Contamination and adverse effects on aquatic habitats were demonstrated to the point at which the Government of Quebec led an environmental restoration of the Aldermac property in 2008-11. Given current active exploration, further mining development within the watershed is foreseeable.

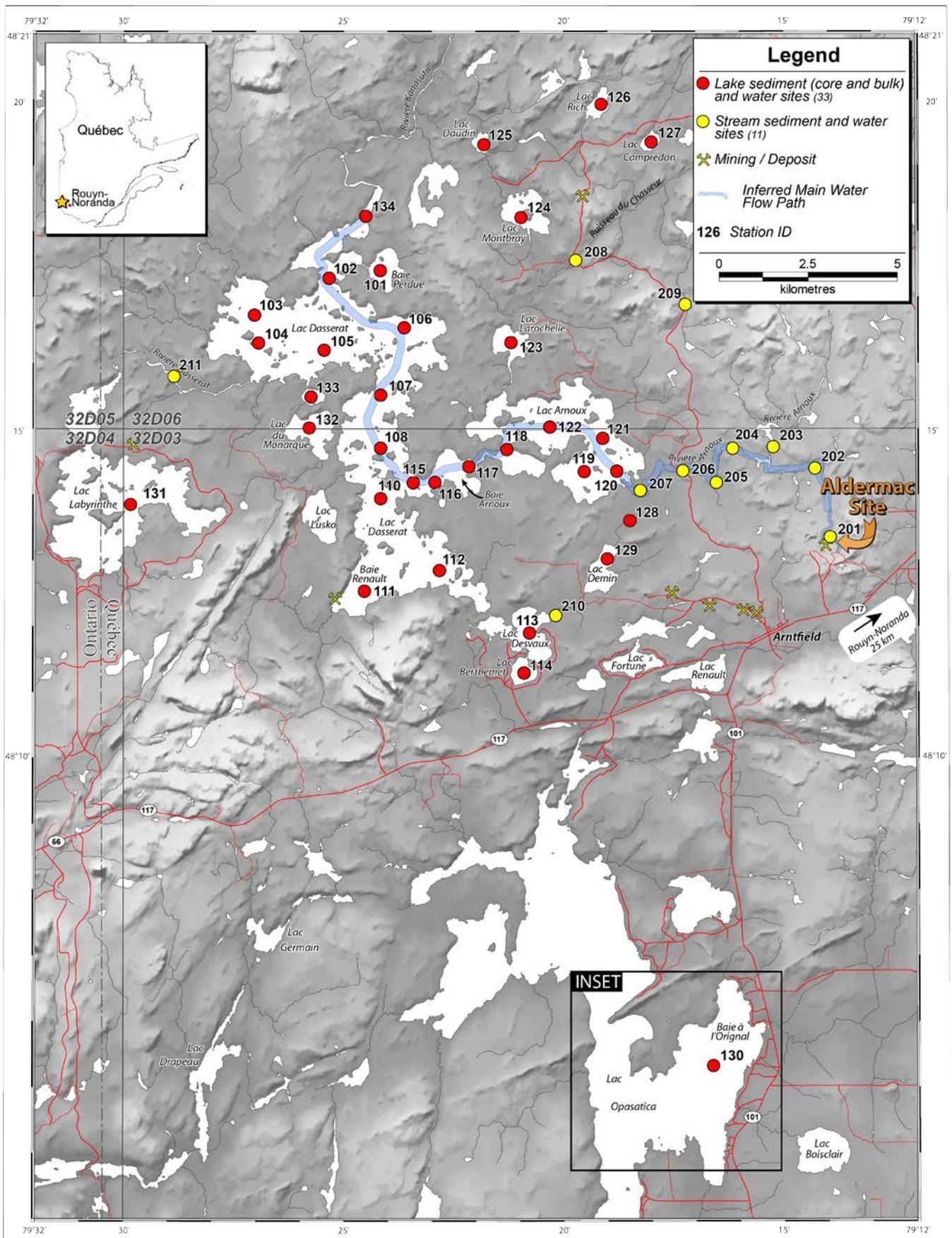


Figure 1. Digital elevation map of the Lac Dasserat study area, 25 km west of Rouyn-Noranda; sampling stations are indicated.

Regional survey design

The regional survey was based on a 2 x 2 km sampling grid. The grid was generated using GIS software and was overlain on the study area map. The objective was to collect a minimum of one sample per grid cell where the cell was predominantly surface water (Figure 2). A sampling density of 1 sample per 4 km² was suitable to identify and map geochemical gradients down drainage of the Aldermac mine site. For a regional survey of this type, grid sizes can be modified and scaled to fit the need of the project (i.e., for a larger survey area, the grid sizes can be made larger) so that the total number of stations is representative and not prohibitive.

There were a few exceptions to the spatial density of sampling. For example, in areas where a higher geochemical gradient was suspected, usually at the inflow or outflow of a lake, additional sampling stations were added to document variations more rigorously.

In the field, selection of sampling stations was determined by depth sonar to evaluate the lake bottom and ensure the selected sampling station was representative of the surrounding area within the grid cell. An exception was made to target sites of sediment focussing in deeper basins, where present, such as stations 105, 108 and 111.

Sample Collection Methodologies

Lake water, lake sediment cores and bulk lake sediment samples were collected at each lake site. Surface water and sediments in streams were also sampled according to suitability of the sites. Some of the planned sites, mainly streams, were not sampled because they were compromised by the presence of beavers and their activities. Sample collection was undertaken from a 16' aluminum boat on larger lakes where access permitted. The smaller regional lakes were accessed by a 12' Zodiac®. All stream sites were accessed by truck with the exception of stations near the mouth of the Rivière Arnoux where boat access was possible.

Regional samples were collected from 33 lake stations and 11 stream stations for a total of 33 bulk surface lake sediments, 32 lake sediment cores, 11 stream sediments, 44 surface waters (from lakes and streams) and 25 lake bottom water samples in a 400 km² area (Figure 1).

The following is a description of the sampling methodologies.

Water

Lake Water

Using a 4.2-l Kemmerer® sampler (Figure 3), a set of surface water samples was collected at a depth of 0.5 m and a set of bottom water samples at approximately 0.5 m above the sediment-water interface. All sampling sites have a set of surface water samples. The bottom water sample set was only collected at sites where the water depth was greater than 4 m. Where water depths were shallow (≤ 4 m), only the surface water sample was retrieved because shallow waters were unlikely to reflect chemical stratification as verified by chemical profiles.



Figure 3. Kemmerer® surface water sampler.

Each set of water samples collected was comprised of three bottles:

- 1- Filtered and Acidified (FA),
- 2- Unfiltered and Acidified (UA)
- 3- Filtered and Unacidified (FU)

On-site, 60 ml of water were filtered through a single-use Millipore Sterivex-HV® 0.45- μ m filter unit attached to a 60-ml sterile plastic syringe into each of the triple-rinsed FA and FU 60-ml Nalgene® bottles (Figure 5). The UA bottle was filled with 60 ml of unfiltered sample water.

The FA and the UA samples were collected for trace and major element analysis by inductively coupled plasma mass spectrometry and emission spectrometry (ICP-MS and ES). The FU samples were analyzed for anions (Dionex ICS 2100 Ion Chromatograph), alkalinity (by titration) and dissolved organic carbon (DOC; Shimadzu TOC-L analyser). In-situ water column measurements (HL) were also retrieved for temperature, pH, conductivity, dissolved oxygen, Eh and turbidity at 0.5 m intervals within the water column by a Hydrolab® DS5X water multi-probe datasonde (Figure 4). See Analytical Procedures section for more details.



Figure 4. Hydrolab® DS5X Datasonde.

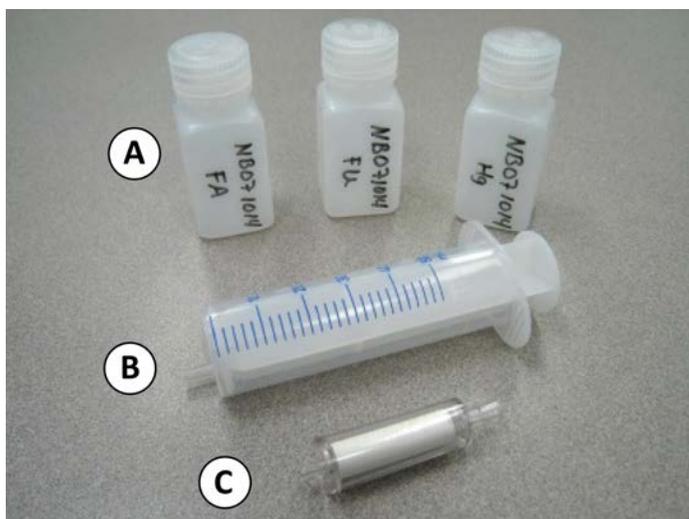


Figure 5. Equipment used for filtering lake water samples on site. A) 50-ml Nalgene® bottles B) 60-ml syringe and C) Millipore® 0.45-µm capsule filter

Stream water

Stream stations also have a set of three water samples (FA, UA and FU). They were collected by filling the syringe from the active part of the stream channel where 50 ml of water were filtered on site into triple-rinsed 60-ml Nalgene® bottles. The samples were also preserved by acidifying to 0.4% with high-purity 8M HNO₃.

Sediment

Lake Sediment

Grab

At each lake-sediment coring station, an accompanying grab sample of surface sediment was collected. The surface sediment grab samples were taken by a Petite Ponar® grab sampler (6" X 6"; Figure 6) at 33 sites with a penetration depth of up to 10 cm, depending on sediment stiffness. The entire sediment sample was emptied into a thick-walled plastic bag, sealed to retain moisture and kept cool until sample preparation.

Cores

Sediment cores were taken with a modified gravity corer at 32 sampling stations. A 10-cm diameter gravity corer was modified with threaded rod extensions on the head assembly to allow hand-taken push cores from the water surface. This method preserves the nepheloid layer (sediments in suspension at the sediment-water interface) and can be deployed at sites with water depths up to 15 m (Figure 7). Depth penetration of the core tube into the sediments was controlled by a perforated disk mounted on the outside of the coring assembly (Figure 8; Grenier *et al.*, in prep). The length of the recovered core varied between 35 and 90 cm with most being approximately 40 cm. Core tubes were carefully kept upright in the boat after collection with a custom core rack holder. Cores were extruded and sub-sampled in camp at discreet intervals ranging from 1.0 to 5.0 cm thickness using either a mechanical extruder or a hydraulic extruder with water pressure advancing the core. Sediments cored in this study were either organic-rich (e.g., Lac Arnoux gyttja) or mixed glaciolacustrine clays from glacial Lake Barlow-Ojibway.

Stream Sediment

A silt sediment sample was collected into a spun-bonded polyester fabric bag filled with silt and/or fine grained clastic material from the active stream channel after the water collection was completed. The sediments were gathered by hand from several points in the active channel while moving upstream, typically over a distance of 5 to 15 m.

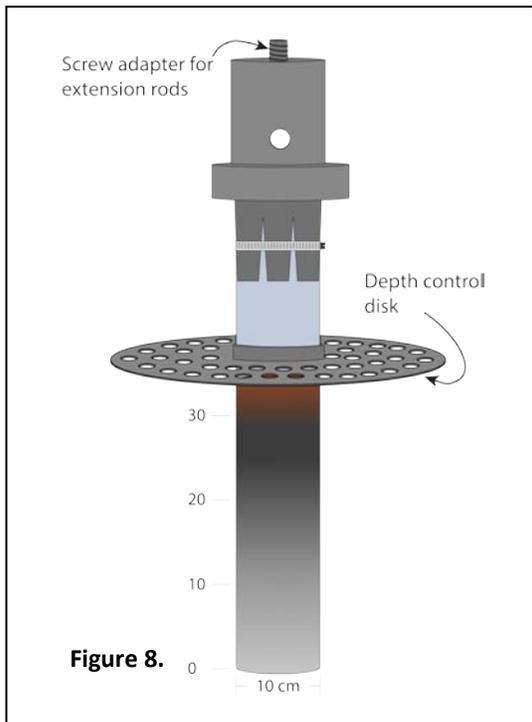
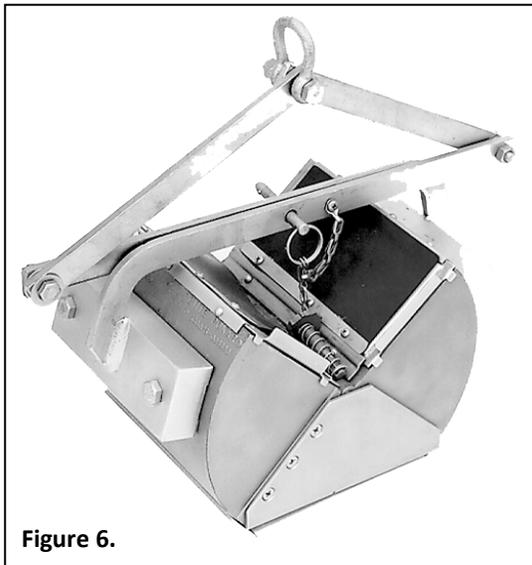


Figure 6. Petite Ponar® (6" x 6") sampler used to collect bulk surface sediment samples.

Figure 7. Field sampling crew preparing the modified sediment push corer.

Figure 8. Schematic of gravity corer with adjustable depth control disk.

Sample Numbering / Labeling System

There was a total of 33 lake, 11 stream and 9 near-shore lentic sampling stations. At each sampling station (Station ID), multiple samples were collected throughout the duration of the study. Each of these samples was assigned a unique identifier (Unique ID). The Unique ID is comprised of a seven digit Site ID and a five digit Sample ID.

Station ID

A unique three digit number assigned to each sampling station (e.g., 111).

The 1xx series represents lake stations, the 2xx series are stream stations and the 4xx series are near-shore lentic lake stations.

Unique ID

A concatenation of the Site ID followed by the Sample ID

e.g. **LD12272-LS109**

LD12272-LW109FA

Site ID: Comprises three components e.g. LD12272);

- i. First two characters: project name (LD = Lac Dasserat)
- ii. Next two characters: year of collection (12 = 2012)
- iii. Last three characters: unique site identifier (272)

Sample ID: Comprises three components (e.g. LS109);

- i. First two characters: sample type (See list of sample types below).
- ii. Third character: core identifier (1). Increases sequentially when more than one core is collected
- iii. Last two characters : sub-sample number (09 – core sample slice #9)

Sample types

Sediment samples: **LS** – slice of lake sediment core
 BS – bulk surface lake sediment
 SS – stream sediment

Water samples: **LW** – lake water
 SW – Stream water

Additional suffix for water sample type:

FA - filtered and acidified
UA – unfiltered and acidified
FU – filtered and un-acidified

In-situ measurements: **HL** – in-situ physico-chemical measurements by Hydrolab®

Field data collection

Site locations, field observations, lake water physico-chemical measurements, sample type, and any specific comments were recorded on a lake sediment and water field card at each sampling station (Figure 9). The field card was adapted from the lake sediment and water survey field data collection developed by Garrett (1974) for the Geological Survey of Canada (GSC) National Geochemical Reconnaissance program.

Sample Preparation

Water

After collection, lake and stream water samples were kept cool until acidified for preservation. Within 24 hours of collection the FA and UA samples were acidified to 0.4% by adding 0.5 ml of UltraPure 8M nitric acid (HNO_3) using an Eppendorf® pipette repeater with disposable plastic tips (Figure 10). There is no preparation for analysis on the FU sample.

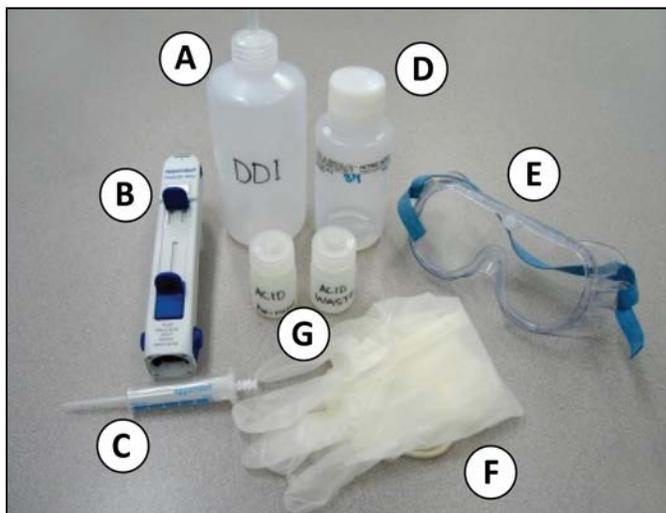


Figure 10. Equipment used to acidify water samples. A) Distilled de-ionized water B) pipette C) 10-ml pipette tip D) High-purity 8M nitric acid E) protective goggles F) protective gloves G) container for acid waste disposal

Sediment

All lake and stream sediment samples were prepared for analysis at the GSC Sedimentology Laboratory in Ottawa.

The sediments were freeze dried to lower the risk of losing the more volatile elements when analysed for trace-element geochemistry and to provide a powdered material for analysis, rather than a hard aggregated clay when oven- or air-dried (Pertilla and Pedersen, 2007).

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, until the samples were completely dry. An archived split of the sample was retained and the remaining material was sieved through an 80-mesh ($177 \mu\text{m}$) screen and stored into 16-dram vials. The oversize material was discarded. Girard *et al.* (2004) present the complete methodology. The 1-cm, 2.5-cm and 5-cm core slices yielded approximately 5-10 g, 20-25 g and upwards of 40 g of material, respectively.

Certified reference materials (CRMs; LKSD-1 and LKSD-4), as well as blind duplicates (a single site sample split and assigned two non-consecutive sample numbers) were inserted into a group of sediment samples for QA/QC. See the quality control of geochemical results section for more detail.

Analytical Procedures

Sediment (lake core, bulk lake and stream sediment)

Samples were analyzed by ICP-MS and ICP-ES, the latter for more abundant major elements (e.g. Ca, Mg, Na, K and Fe), whereas the more sensitive ICP-MS technique focused on measurement of trace element concentrations. Two different digestion procedures were used prior to analysis.

ICP-MS/ES (modified aqua-regia dissolution - "partial")

The first dissolution was a modified aqua-regia "partial" dissolution. Fifty three elements are determined and lower detection limits are summarized in Table 1. Pulp-splits of 0.5-g samples were leached with a 6-ml mixture of HCl, HNO₃, and distilled/deionized water (2:2:2 volume to volume ratio) at 95°C for one hour. The sample solution was diluted to 20 ml and analysed by ICP-MS (Perkin-Elmer Elan instrument) and by ICP-ES (Jarell-Ash instrument). Analyses were carried out at ACME Analytical Laboratories, Limited, Vancouver, in British Columbia.

Element	Detection Limit	Units of Measurement	Analytical Method
Ag	2	PPB ¹	ICP-MS
Al	0.01	PCT ²	ICP-MS
As	0.1	PPM ³	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	PCT	ICP-ES
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	PCT	ICP-ES
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	PCT	ICP-ES
La	0.5	PPM	ICP-MS
Li	0.1	PPM	ICP-MS
Mg	0.01	PCT	ICP-ES
Mn	1	PPM	ICP-ES
Mo	0.01	PPM	ICP-MS

Element	Detection Limit	Units of Measurement	Analytical Method
Na	0.001	PCT	ICP-MS
Nb	0.02	PPM	ICP-MS
Ni	0.1	PPM	ICP-MS
P	0.001	PCT	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	PCT	ICP-ES
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	PCT	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/kg² PCT: percent, %³ PPM: parts per million, mg/kg

Table 1. Elements determined after a modified aqua-regia by ICP-MS/ES analysis of lake and stream sediment samples.

ICP-MS/ES (4-acid dissolution - "near total")

The 4-acid dissolution method is a "near total" dissolution using HCl, HNO₃, HClO₄ and HF mixed in the ratio of 2:2:1:1, respectively. Sixty elements are determined and lower detection limits are summarized in Table 2. Pulp 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. This method is effectively a total

dissolution for most elements, although for some (e.g., Cr, Ba, Al, Fe, Al, Hf, Mn, Sn, Ta and Zr) it may be a partial dissolution, depending on sample mineralogy. Also, volatilization during fuming may result in some loss of As, Sb and Au. Analyses were carried out at ACME Analytical Laboratories, Limited, Vancouver, British Columbia.

Element	Detection Limit	Units of Measurement	Analytical Method
Ag	20	PPB ¹	ICP-MS
Al	0.02	PCT ²	ICP-MS
As	0.2	PPM ³	ICP-MS
Au	100	PPB	ICP-MS
Ba	1	PPM	ICP-MS
Be	1	PPM	ICP-MS
Bi	0.04	PPM	ICP-MS
Ca	0.02	PCT	ICP-ES
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	PCT	ICP-ES
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	PCT	ICP-ES
La	0.1	PPM	ICP-MS
Li	0.1	PPM	ICP-MS
Lu	0.1	PPM	ICP-MS
Mg	0.02	PCT	ICP-ES
Mn	2	PPM	ICP-ES
Mo	0.05	PPM	ICP-MS

Element	Detection Limit	Units of Measurement	Analytical Method
Na	0.002	PCT	ICP-MS
Nb	0.04	PPM	ICP-MS
Nd	0.1	PPM	ICP-MS
Ni	0.1	PPM	ICP-MS
P	0.001	PCT	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	PCT	ICP-ES
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	PCT	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 PCT: percent, %

³ PPM: parts per million, mg/kg

Table 2. Elements determined after 4-acid "near- total" dissolution by ICP-MS/ES analysis of lake and stream sediment samples.

Carbon

At the GSC Sedimentology Laboratory in Ottawa, the carbon content, organic and inorganic, was determined by using a LECO CR-412 Carbon Analyser®. The 'total' carbon content is first determined on a split, and the inorganic carbon determined on another split after low-temperature (<500°C) ashing to remove the organic content. The organic carbon content is deduced by subtracting the inorganic carbon from the total. The total carbon and inorganic carbon were measured at 1,350°C. Loss-on-ignition (LOI) was measured at 500°C for 1 hour. Girard *et al.*, 2004 provide a complete description of the methodology.

Water (lakes and streams)

All water samples were analyzed at the GSC Inorganic Geochemistry Research Laboratory for trace metals, major cations and anions. Physico-chemical measurements were recorded in-situ. All methods used for analysis of water samples are described below. A list of trace elements analyzed by ICP-MS/ES is presented in Table 3.

ICP-MS

Trace metal analysis was performed on the filtered-acidified and unfiltered-acidified (FA and UA) samples using a Thermo X Series 2 quadrupole ICP-MS with Xt cones, PlasmaScreen fitted, standard concentric nebulizer and Peltier-cooled conical impact bead spray chamber (3°C) using rhodium and iridium as internal standards. Most isotopes measured and corrections for spectral interferences are detailed in Hall *et al.* (1995; 1996). Data for hafnium and zirconium are not published because these elements are not sufficiently stabilized by the addition of nitric acid to waters.

Element	Lower Detection Limit	Units of Measurement	Analytical Method
Ag	0.005	ppb	ICP-MS
Al	2	ppb	ICP-MS
As	0.1	ppb	ICP-MS
B	0.5	ppb	ICP-MS
Ba	0.2	ppb	ICP-MS
Be	0.005	ppb	ICP-MS
Br	0.05	ppm	ICP-ES
Ca	0.02	ppm	ICP-ES
Cd	0.02	ppb	ICP-MS
Ce	0.01	ppb	ICP-MS
Cl	0.1	ppm	ICP-ES
Co	0.05	ppb	ICP-MS
Cr	0.1	ppb	ICP-MS
Cs	0.01	ppb	ICP-MS
Cu	0.1	ppb	ICP-MS
Dy	0.005	ppb	ICP-MS
Er	0.005	ppb	ICP-MS
Eu	0.005	ppb	ICP-MS
Fe	0.005	ppm	ICP-ES
Ga	0.01	ppb	ICP-MS
Gd	0.005	ppb	ICP-MS
Ge	0.02	ppb	ICP-MS
Ho	0.005	ppb	ICP-MS
In	0.01	ppb	ICP-MS
K	0.05	ppm	ICP-ES
La	0.01	ppb	ICP-MS
Li	0.02	ppb	ICP-MS
Lu	0.005	ppb	ICP-MS
Mg	0.005	ppm	ICP-ES
Mn	0.1	ppb	ICP-MS
Mo	0.05	ppb	ICP-MS
Na	0.05	ppm	ICP-ES
Nb	0.01	ppb	ICP-MS
Nd	0.005	ppb	ICP-MS
Ni	0.2	ppb	ICP-MS
P	0.05	ppm	ICP-ES
Pb	0.01	ppb	ICP-MS
Pr	0.005	ppb	ICP-MS
Rb	0.05	ppb	ICP-MS
Re	0.005	ppb	ICP-MS
S	0.05	ppm	ICP-ES
Sb	0.01	ppb	ICP-MS
Se	1	ppb	ICP-MS
Si	0.02	ppm	ICP-ES
Sm	0.005	ppb	ICP-MS
Sn	0.01	ppb	ICP-MS
Sr	0.5	ppb	ICP-MS
Ta	0.01	ppb	ICP-MS
Tb	0.005	ppb	ICP-MS
Te	0.02	ppb	ICP-MS
Ti	0.5	ppb	ICP-MS
Tl	0.005	ppb	ICP-MS
Tm	0.005	ppb	ICP-MS
U	0.005	ppb	ICP-MS
V	0.1	ppb	ICP-MS
W	0.02	ppb	ICP-MS
Y	0.01	ppb	ICP-MS
Yb	0.005	ppb	ICP-MS
Zn	0.5	ppb	ICP-MS

Table 3. Major and trace elements determined by ICP-MS/ES for filtered-acidified and unfiltered-acidified water samples.

ICP-ES

Major element analysis was also performed on the FA and UA samples using an axial Spectro Arcos, ICP-ES with a 1% CsNO₃ buffer (1:5 ratio) as a matrix modifier, Burgener Teflon Mira Mist Nebulizer (uptake rate 1 ml/min), and a cyclonic spray chamber. The argon flow rates were: coolant 14.5 l/min, auxiliary 0.9 l/min, and nebulizer 0.8 l/min. The RF power was 1500 watts. Inter-element correction factors were applied as required to correct for various spectral interferences. Data for scandium are not published because of inadequate detection limits and/or precision. A list of major elements analyzed by ICP-MS/ES is presented in Table 3.

TXRF

A new field-portable total reflection X-ray fluorescence spectrometer (TXRF), the Bruker S2 PICOFOX, was tested to verify its use and effectiveness to produce quality analytical water data in a field camp environment (Figures 11 A and B). The S2 PICOFOX Spectrometer has a built-in air-cooled 50 Kv X-ray Mo tube which allows the instrument to be transported easily and used outside of a laboratory. Filtered-acidified samples were used for analysis. After acidification, as described above, the samples were well mixed and left to rest for at least one hour prior to sub-sampling so that any precipitates or metals which adhered to the walls of the sample bottle were returned into solution. An aliquot of 1 ml was sub-sampled, spiked with gallium to a concentration of 1 ppm and mixed using a vortex mixer. The Ga-spiked water samples were mounted on individual acrylic disks by transferring 10 µl of the solution onto it with a polypropylene pipette tip (Figure 11 C). The disks were heated to 65°C until dry. Two additional 10-µl aliquots were applied onto the disk and dried.

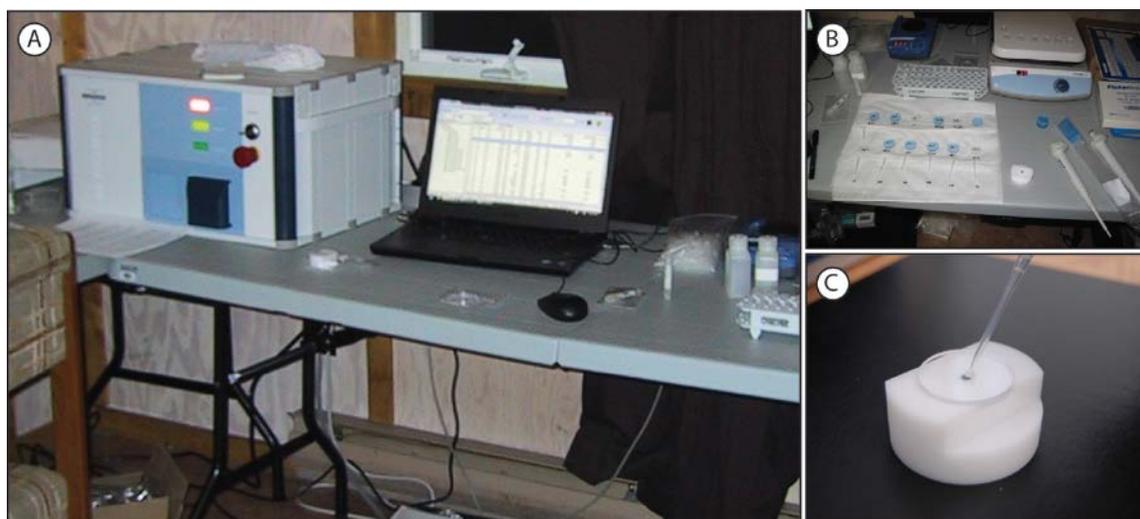


Figure 11. A) Field setup of the Total X-ray fluorescence spectrometer S2 PICOFOX; **B)** Sample preparation (spiking, mixing, applying and drying) spiked samples; **C)** Transferring spiked sample onto acrylic disk

The disks were then loaded into the 25-space sample holder for automated analysis with an acquisition time of 1000 seconds. A full suite of elements is reported from the analysis. However, as a testing exercise, only the elements listed in Table 4 were verified and are reported in this Open File. The resulting data were de-convoluted using profile bytes (normal fit).

Element	Lower Detection Limit	Units of measurement	Analytical Method
Ca	NA	ppm	TXRF
Cu	NA	ppb	TXRF
Fe	NA	ppm	TXRF
K	NA	ppm	TXRF
Mn	NA	ppb	TXRF
S	NA	ppm	TXRF
Zn	NA	ppb	TXRF

Table 4. Elements analyzed in the field and reported by TXRF in filtered-acidified surface water samples.

Anions

Anion analysis was done by a Dionex ICS 2100 Ion Chromatograph fitted with an AS-AP auto-sampler. Operating conditions are listed in Table 5. Bromide, chlorine, fluoride, nitrate, phosphate and sulphate were separated using a three-step gradient elution (12 to 52 mm potassium hydroxide eluant) with an AS-18 column. The anion concentrations were quantified using conductivity in comparison with known concentration calibration standards and Dionex Chromeleon software. Table 6 lists the anions reported with the corresponding lower detection limit.

Operating conditions of Dionex ICS2100	
Guard column - Dionex AG18 4mm	Separator column - Dionex AS 18 4mm
Anion Suppressor - Dionex ASRS-300, 4mm	Current - 127 mA
DS6 heated Conductivity Detector cell	Eluent - 12 to 52mm KOH
Column Temp. - 30°C	Sample loop - 25µL
Eluant flow rate - 1.0 ml/min	

Table 5. Details on operating conditions of Dionex ICS2100 for anion analysis.

Anions	Lower Detection Limit	Units of Measurement	Analytical Method
Br	0.02	ppm	Ion Chromatography (ICS-2100)
Cl	0.01	ppm	Ion Chromatography (ICS-2100)
F	0.01	ppm	Ion Chromatography (ICS-2100)
NO ₃	0.02	ppm	Ion Chromatography (ICS-2100)
PO ₄	0.02	ppm	Ion Chromatography (ICS-2100)
SO ₄	0.02	ppm	Ion Chromatography (ICS-2100)

Table 6. Anions determined by Ion Chromatography in filtered-unacidified (FU) surface water samples.

Dissolved organic carbon

Total Organic Carbon (TOC) analysis (Table 7) was completed with a Shimadzu TOC-L analyser using a 680°C combustion catalytic oxidation method combined with NDIR detection. This is reported as DOC on a 0.45-µm Durapore®-filtered (FU) sample. In environmental and water samples where the inorganic carbon (IC) concentration may be high, the (total or dissolved) organic carbon is measured by a non-purgeable organic carbon (NPOC) method. This method is the same as the TOC combustion measurement method with the addition of acidification and sparging to remove the inorganic carbon (IC) in the sample prior to TOC analysis.

	Lower Detection Limit	Units of Measurement	Analytical Method
DOC	1	ppm	Combustion

Table 7. Dissolved organic carbon determined by combustion on filtered-unacidified (FU) surface water samples.

Alkalinity

Alkalinity measurements (Table 8) were done using a Man-Tech PC-Titrate™ system with a Titra-Sip™ Module on the FU samples. The total alkalinity was measured by potentiometric titration with 0.02N sulphuric acid. The software determined the volume of acid required to reach the bicarbonate equivalence point. Alkalinity results are reported as equivalents of CaCO₃ in ppm.

	Lower Detection Limit	Units of Measurement	Analytical Method
Alkalinity	1	ppm	Titration

Table 8. Alkalinity determined by titration of filtered-unacidified (FU) surface water samples.

In-situ (physicochemical) parameters

In-situ water column measurements were completed using a Hydrolab® DS-5X multi-parameter datasonde. The instrument simultaneously measures temperature, pH, conductivity, luminescent dissolved oxygen (LDO), oxidation-reduction potential (ORP), turbidity, and depth with automatic temperature compensation for pH and dissolved oxygen. Water colour measurements were done using a Lamotte TC-3000i meter. Accuracy and units of measurements of each parameter are listed in Table 9.

Parameter	Accuracy	Units of Measurement
Temperature	-	°C
pH	±0.2	pH units
Conductivity	±0.5% of reading	µS/cm
LDO	±0.2	mg/L
ORP	±20	mV
Turbidity	±3% of reading	NTU
Depth	0.01	m
Colour	±0.5	CU

Table 9. Summary of determined water variables using the Hydrolab® DS-5X multi-parameter data sonde. Colour was determined using a Lamotte TC-3000i

Table 12 below provides information on the number of each quality control sample type included within the sample suite.

Control Reference Material		Analytical Duplicate Pairs
LKSD-1	LKSD-4	
20	19	

Table 12. Total number of Certified Reference Material samples and analytical duplicate pairs included within the sample suite.

Accuracy

Accuracy of the analytical data was evaluated for systematic error (bias or 'drift') by inserting established lake sediment CRMs, LKSD-1 and LKSD-4 (Appendix 1), in random positions throughout the sample suite. LKSD-1 is a combination of lake sediments from two lakes located in central Ontario (Brady Lake, 31M and Joe Lake, 31F). Sediment from three lakes, Big Gull Lake (31C) in Ontario and Key Lake and Seahorse Lake (74H) in Saskatchewan, were combined to prepare LKSD-4 (Lynch, 1990, 1999).

Certified Reference Material

Appendix 1A contains the analytical data for each CRM after aqua-regia and 4-acid digestions. The table in Appendix 1B lists all the elements by analytical method with their respective lower detection limits along with the data generated as part of this study (Project Values). The table includes the provisional values (mean and standard deviations) published by Lynch (1990, 1999) and unpublished values from GSC projects.

Elements for which provisional means have been estimated are generally within two standard deviations of the published value. The provisional means and associated standard deviations are taken, where available, from Lynch (1990, 1999). Otherwise, values (highlighted in grey) are derived from the compilation of unpublished CRM data ($n \geq 40$) from recent GSC projects. Elements of possible concern, as indicated by a relatively high, $> 20\%$, Percent Relative Standard Deviation (%RSD), are shown in bold type. In many cases a relatively high %RSD, suggesting poor repeatability, is related to elemental values which are close to the lower detection limit.

Description of fields in Appendix 1B CRM - Accuracy

Analytical Method: AR (aqua-regia) and 4A (4-acid)

Provisional values: from Lynch (1990, 1999)

Mean: Estimated mean value of individual element for each Certified Reference Material.

Standard Deviation: Estimated standard deviation of individual element for each Certified Reference Material.

Project values:

% of Samples <LDL: Percentage of samples where the analytical value is below the lower detection limit. * <LDL values are halved for calculation of statistics. (e.g., -5 ppm = >2.5 ppm)

Range (min-max): Range of analytical values for each element

Mean: Mean of all reported values for each element

Standard Deviation: standard deviation of all reported values for each element

% RSD: Relative Standard Deviation expressed as percentage

Precision

Precision is considered in terms of the closeness of agreement between analytical duplicate samples analyzed by the same method, Appendix 2A-1 and 2A-2, i.e., independent test results obtained using the same equipment within short intervals of time on duplicate project samples (Reimann *et al.*, 2008). In order to provide an estimate of precision for each element, the squared difference between two analytical duplicates was calculated for $N = 28$ duplicate pairs. The sum of these values was divided by the number of samples ($(2*N) = 56$) to estimate a measure of variability (variance). Standard deviation was then obtained by calculating the square root of this variance (Garrett, 1969). The resulting numerical estimates of precision are shown in Appendix 2B, represented by the Percent Relative Standard Deviation (Reimann *et al.*, 2008).

Elements with precisions poorer than 15% in Appendix 2B, tend towards generally low concentrations in samples, as indicated by the range, the mean and the percentage of data below the detection limit. Such is the case for the following elements highlighted in grey: Au, Be, Ge, Hf, In, Pd, Pt, Re, Sb, Se, Ta, Te, and W (after aqua-regia), and Ag, As, Au, Be, Bi, Re, S, Se, Te and Tm (after 4-acid digestion).

Description of fields in Appendix 2B Precision

Analytical Method: AR (aqua-regia) and 4A (4-acid)

Project values:

% of Samples <LDL: Percentage of samples where the analytical value is below the lower detection limit. * <LDL values are halved for calculation of statistics

Range (min-max): Range of analytical values for each element

Mean: Mean of all reported values for each element

Standard Deviation: Standard deviation of all reported values for each element

Precision - % RSD: Relative Standard Deviation expressed in percentage

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References

- Garrett, R.G., 1969. The determination of sampling and analytical errors in exploration geochemistry; *Economic Geology* 64(4): 568-569.
- Garrett, R.G., 1974. Field data acquisition methods for applied geochemical surveys at the Geological Survey of Canada; Geological Survey of Canada, Paper 74-52.
- Garrett, R.G., 2013. The GSC Applied Geochemistry EDA Package, <http://cran.r-project.org/web/packages/rgr/index.html>
- Girard, I, Klassen, R.A., Laframboise, R.R., 2004. Sedimentology laboratory Manual, Terrain Sciences Division, Geological Survey of Canada, Open File 4823, CD-ROM.
- Goulet, R.R. and Couillard, Y., 2009. Weight-of-evidence assessment of impacts from an abandoned mine site to the Dasserat Lake Watershed, Quebec, Canada. In: *Lake Pollution Research Progress*. Ed: F.R. Miranda and L.M. Bernard. Nova Science Publishers, Inc, 355-369 pp.
- Grenier, A., McNeil, R.J., and Alpay, S. *In prep*. Environmental geoscience investigations surrounding the former Aldermac mine, Abitibi, Quebec: Modifications to a classic gravity corer for greater control of sediment depth penetration. Geological Survey of Canada Open File.
- Hall, G.E.M., Vaive, J.E. and McConnell, J.W., 1995. Development and Application of a sensitive and rapid analytical method to determine the rare earth elements in surface water; *Chem. Geol.*, 120, p. 91-109.
- Hall, G.E.M., Vaive, J.E. and Pelchat, J.C., 1996. Performance of ICP-MS methods used in the determination of trace elements in surface waters in hydrogeochemical surveys. *J. Anal. At. Spectrom.*, 11, p.779-786.
- Lynch, J.J., 1990. Provisional elemental values for eight new geochemical lake sediment and stream sediment reference materials, LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4; *Geostandards Newsletter*, v. 14, no. 1, p. 153-167.
- Lynch, J.J., 1999. Additional provisional elemental values for LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4; *Geostandards Newsletter*, Vol. 23 (2), p. 251-260.
- Perttita, M. and Pedersen, B., 2007. Quality assurance of sediment sampling. In: *Quality Assurance in Environmental Monitoring: Sampling and Sample Pre-treatment*, Ed. Quevauviller, P., John Wiley & Sons, 113-128 pp.
- Reimann, C., Filzmoser, P., Garrett, R.G. and Dutter, R., 2008. *Statistical Data Analysis Explained: Applied Environmental Statistics with R*, Wiley & Sons, 335 pages.