



**GEOLOGICAL SURVEY OF CANADA
OPEN FILE 6433 (revised)**

**Soil Geochemical, Mineralogical, Radon and Gamma Ray Spectrometric Data
from the 2007 North American Soil Geochemical Landscapes Project in New
Brunswick, Nova Scotia and Prince Edward Island**

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2014

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doi:10.4095/293020

This publication is available for free download through GEOSCAN (<http://geoscan.ess.nrcan.gc.ca/>).

Recommended citation

Friské, P.W.B., Ford, K.L., McNeil, R.J., Pronk, A.G., Parkhill, M.A., and Goodwin, T.A., 2014. Soil Geochemical, mineralogical, Radon and Gamma Ray Spectrometric Data from the 2007 North American Soil Geochemical Landscapes Project in New Brunswick, Nova Scotia, and Prince Edward Island; Geological Survey of Canada, Open File 6433 (revised). doi:10.4095/293020

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

Soil Geochemical, Mineralogical, Radon and Gamma Ray Spectrometric Data from the 2007 North American Soil Geochemical Landscapes Project in New Brunswick, Nova Scotia and Prince Edward Island

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Introduction

Chemical elements in soil support and affect human, animal and plant life. Naturally-occurring levels of elements may vary by several orders of magnitude. Understanding the range and causes of natural variability is vital for the assessment and management of risks to human health and the environment.

Currently there is no systematic continent-wide data on background variations in soil composition. There is a critical need for data for a wide spectrum of elements and compounds in mineral- and organic-based soils based on up-to-date field and laboratory techniques. In addition, outside the earth sciences world there is little awareness of the enormous amount of natural variability, and the value of this information for evaluating risk potential.

To address the above issues the North American Soil Geochemical Landscapes Project (NASGLP) - a tri-national initiative between the United States, Canada and Mexico - was established to meet the need for soil geochemical data by providing a consistent national- and continental-scale framework and database. It was undertaken jointly by Natural Resources Canada-Geological Survey of Canada (GSC) (Environment and Health Program), the United States Geological Survey (USGS) and the Servicio Geológico Mexicano (SGM).

A Canada-United States pilot study consisting of two sampling transects (E-W and N-S) was carried out in 2004 to test field sampling and analytical protocols and data applications. Since then, a methodology for the collection, preparation and analysis of soil samples for the NASGLP Project has been formulated (Friske et al., 2010) and in 2007 systematic sampling began. With the assistance of personnel from the provincial Geological Surveys and soil scientists from Agriculture and Agri-Food Canada (AAFC) (Figure 1), sampling was completed in New



Brunswick, Nova Scotia and Prince Edward Island (Figure 2). This Open File presents results from the 2007 field season. NASGLP activities continued during the 2008 and 2009 field season

Figure 1. Field meeting near Fredericton, June 14, 2007 to finalize protocols and commence surveys. Standing left to right: Jim Kilburn (USGS), Dave Smith (USGS), Laurel Woodruff (USGS), Rex Boldon (NBDNR), Rita Mroz (EC), Rick McNeil (GSC), Parish Arnott (NBDNR), Brad Harvey (GSC), Toon Pronk (NBDNR), Mike Parkhill (NBDNR), Martin McCurdy (GSC), Peter Friske (GSC); Kneeling left to right: Sheldon Hann (AAFC), Sherif Fahmy (AAFC), Ken Ford (GSC) and Marc Desrosiers (NBDNR) (Photo by A. Rencz).

and results will be similarly released. Results from the pilot study and protocol development can be found in various publications including Garrett et al. (2008), Friske et al. (2008), Kettles et al. (2008), Garrett (2009), Klassen (2009), Smith et al. (2009), Woodruff et al. (2009), Friske et al. (2010).

A significant part of the Canadian component of the NASGLP included the collection of soil gas radon, permeability and gamma ray spectrometric analysis. These data, along with the soil geochemical data, will support assessment of radon potential, a key element of Health Canada's National Radon Program

(http://www.hc-sc.gc.ca/ewh-semt/radiation/radon/guidelines_lignes_directrice-eng.php), particularly in areas where no indoor radon survey data is available (<http://www.hc-sc.gc.ca/ewh-semt/radiation/radon/survey-sondage-eng.php>).

The reader is referred to the “Data” directory where files containing all included data are located.

North American Geochemical Soil Landscapes Project Maritimes 2007 Sample Collection



**Sample Locations
with Ecoregions**
GSC Open File 6433

Sampled Sites	
	n
New Brunswick:	115
Nova Scotia:	54
Prince Edward Island:	9
Total:	178

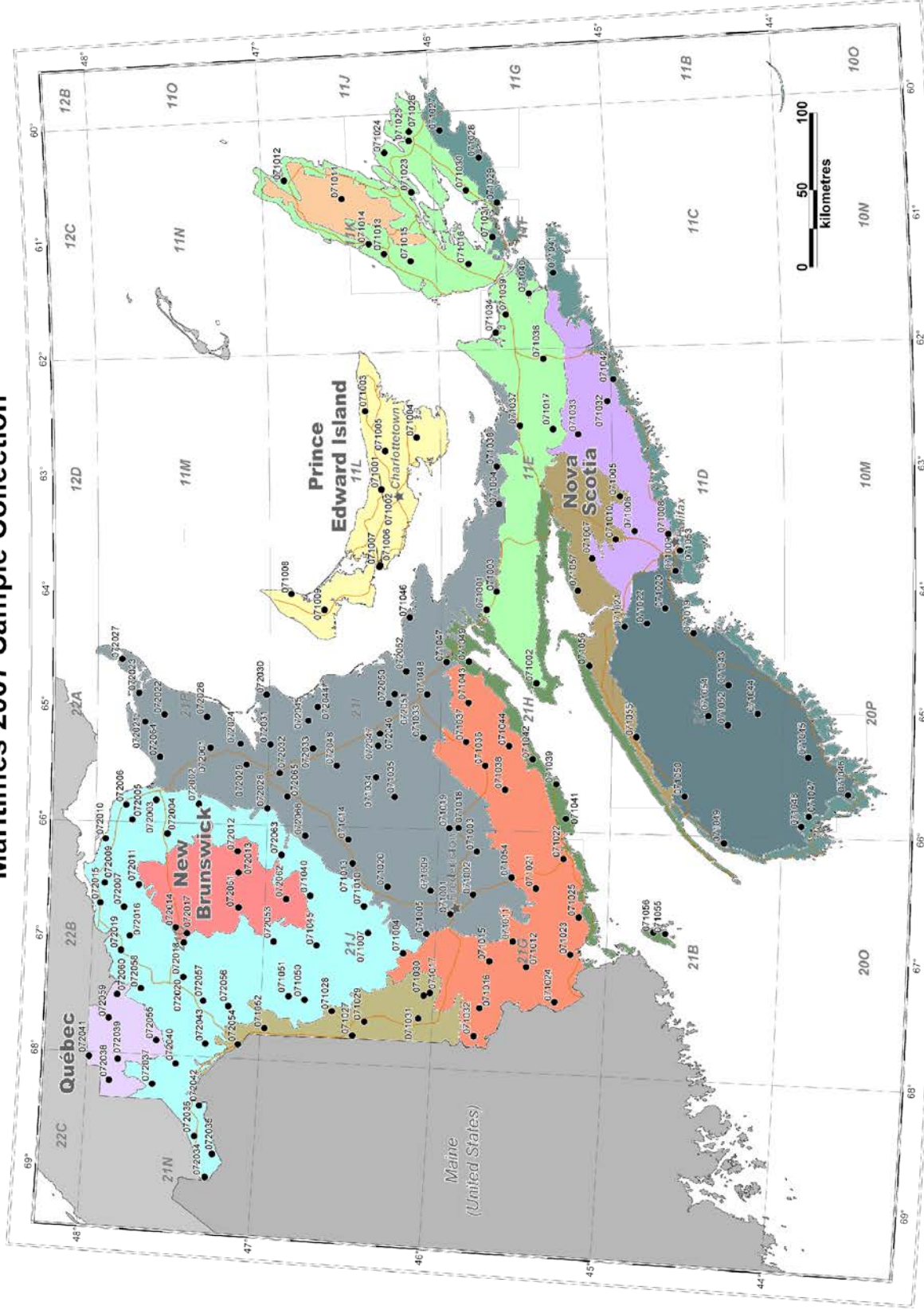
Sample ID	
Province	Year Number
New Brunswick:	NB 07 1001
Nova Scotia:	NS 07 1001
Prince Edward Island:	PE 07 1001
data listing e.g. NB071001 ● 071001	

Ecoregions	
Common sites	
5/5	Appalachians
32/32	Northern New Brunswick Highlands
6/6	New Brunswick Highlands
10/10	Saint John River Valley
16/17	Southern New Brunswick Uplands
45/47	Maritime Lowlands
7/7	Fundy Coast
12/14	Southwest Nova Scotia Uplands
9/9	Atlantic Coast
6/6	Annapolis-Minas Lowlands
2/3	South-Central Nova Scotia Uplands
18/18	Nova Scotia Highlands
1/1	Cape Breton Highlands
0/51	Prince Edward Island

Reference:
Ecological Stratification Working Group 1995. A National
Ecological Framework for Canada. Agriculture and Agri-Food
Canada. Report and national map at 1:7,500,000 scale.



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Figure 2. Sample sites for 2007 TriNational survey in the Maritimes with Ecoregions in the background.

Summary of Office and Field Procedures

Site Selection

Office

The project was based on low density sampling (within a 40 km x 40 km grid). There were 6,018 potential sites in Canada and a total of 13,487 potential sites across North America (Figure 3). Details of the sampling design and site selection procedure are given by Garrett and Kettles (2009). A brief description follows.

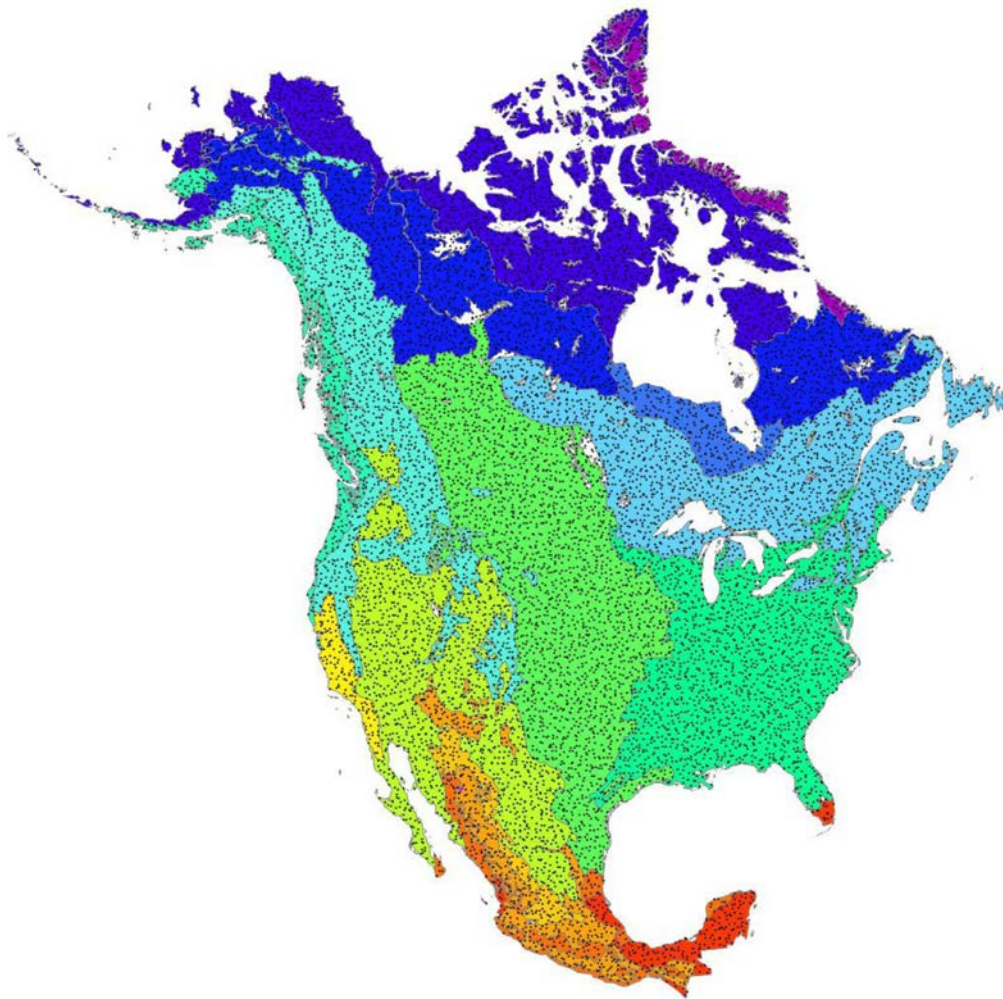


Figure 3. Distribution of sample sites (black dots) over North America. Ecozones for North America are shown in colour (after Commission for Environmental Co-operation, 1997).

The TriNational soil sites were pre-selected using the US-EPA Generalized Random Tessellated Stratified (GRTS) design procedure (Stevens and Olsen, 2004) based on a 40 x 40 km grid. Each 40 x 40 km cell contained, on average, 64 possible sites allowing sampling density up to 1 per 25 km². During routine TriNational sampling the objective was to collect, from each 40 x 40 km

cell, one random sample from the 64 possible sites. To do this the following procedure was employed.

A table of random numbers between 1 and 4 was used to define a 10 x 10 quadrant from which the TriNational site was selected. Starting at any point in the table two consecutive numbers were selected. The first was used to define a 20 x 20 km quadrant within the 40 x 40 km cell and the second to define a 10 x 10 quadrant in the 20 x 20 cell. By definition the numbers 1 to 4 represented the northwest, southwest, northeast and southeast quadrants. For example if the two consecutive random numbers selected were 2 and 4 then the final 10 x 10 km cell (target quadrant) from which the site was selected was the southeast quadrant of the southwest quadrant of the initial 40 x 40 km cell. If the target quadrant was not suitable (e.g. occurred over water in coastal areas) further sets of random numbers were selected until a suitable target quadrant was identified.

Generally within the target quadrant there were 3 to 5 GRTS sites. All else being equal the site with the highest GRTS site number was selected as the sample site. If however this site was not suitable the other sites within the target quadrant were evaluated (in order from highest to lowest GRTS site number) until a site was selected.

Field

In the field the final sample site selection was based on information determined in the office and what the sampling crew encountered in the field. The objective was to get within 500 m of the pre-selected site and sample from a site that was representative of landscape characteristics of the 1 km² target area. For example, in the office a site was selected that, based on background information, was an upland area associated with Podzolic soils. However in the field "ground zero" was a low lying area of Gleysolic soil surrounded by the expected upland Podzolic soils. In this case the site of collection was moved to a surrounding upland area, provided it was still within 500 m of the original site.

On Site Soil Collection Protocols

Following is a brief overview of the on site protocols for the collection of soil samples. More detailed instructions after Friske et al., 2010 are given in Appendix A-1 (field soil collection procedures), and Appendix A-2 (soil field card).

To accommodate QA/QC procedures, samples were collected in blocks of 20. For every block of 20 consecutive field numbers there were 17 routine field samples (Replicate Status (RS = 0), one control reference sample (RS = 9), one blind (analytical) duplicate sample (RS = 8) and one pair of field duplicate samples (RS = 1 and 2).

At the duplicate sample site, two immediately adjacent separate samples were collected to provide a site duplicate. Their numbers would be, for example, 1048 with the RS code “1” and 1049 with the RS code “2” on the field card. The choice of which of the 17 sites in a block of 20 to duplicate was random and left to the judgement of the traverse planner and/or the sampling team.

A field sample number in each block (e.g., 1043) was reserved for the control reference sample. A randomly generated list of reserved field numbers, one field number for each block of 20 field sample numbers was generated in advance of field work. The corresponding field card for the control reference sample contained only the field sample number and the RS code “9”.

At an ideal mineral soil site the following was collected: Public Health (PH) sample; A-horizon sample; B-horizon sample; C-horizon sample; separate samples from each of the four aforementioned intervals/horizons for bulk density and moisture content determinations (Figure 4).

Sampling began by digging a rectangular shaped pit, at least 60 cm wide and 70 cm long. The pit depth depended on the distance to the top of C-horizon layer, but a minimum depth of 60 cm was specified. One side of the pit was for collecting samples of A-horizon and B-horizon materials, and also bulk density samples (Figure 9). Disturbance or compaction of the area around the side to be sampled was avoided.



Figure 4. Photo showing samples collected at one tri-national site. A five gallon plastic pail is used to transport the material and is usually filled at each site.

The first samples were collected from the C-horizon; they were a bulk density sample and a sample for chemical analysis. The latter was collected from a depth >75 cm (if possible), by boring into the bottom of the pit using a “Dutch” soil auger.

Subsequently, bulk density samples for the public health (0-5 cm) layer and samples for chemical analyses of A- and B-horizon materials were collected from the undisturbed side of the pit by systematically exposing layers and collecting samples from a cut made into the undisturbed wall of the pit.

NOTE: 1) Ae-horizon (eluviated) soil material was not included as part of the A-horizon sample; 2) If the A-horizon was <2 cm thick, an attempt was made to collect a combined H and A sample, estimating relative proportion of each (e.g., 30% H and 70% A) and noting this information on the field card.

Complete documentation of field observations were recorded on a field sheet (Appendix A-2) and a series of photographs taken.

On Site Measuring of Soil Gas Radon and Natural Radioactivity: Methods and Protocols

Soil gas radon (SGR), soil permeability and in-situ gamma ray spectrometry (GGRS) measurements were conducted at NASGLP sites in Canada. Normally for each site, 5 GGRS measurements, 5 SGR and 2 direct permeability measurements were conducted.

In 2007 soil gas radon concentrations were measured on soil gas samples normally extracted from a depth of 80 cm as recommended by the manufacturer (Radon v.o.s., 2007b, c). In subsequent years the sample depth was raised to 60 cm because of difficulty in reaching the target depth at most sites due to the boulder-rich nature of most glacial tills. Soil gas samples were collected using small-diameter hollow steel probes with a removable, sharpened lower end (lost-tip) combined with a 150 ml syringe (Radon v.o.s., 2007b). Soil gas samples collected with the syringe were transferred to an evacuated ionization chamber. As recommended by the manufacturer the ionization chamber was measured using an RM-2 Radon detector after a period of approximately 15 minutes (Radon v.o.s., 2007c). Normally an ionization chamber was only used if the background radon concentration was less than 0.7 kBq/m^3 .

For each probe the following radon information is presented (refer to “Data” directory): site ID; depth to bottom of probe (m); the resistance encountered during the first pull on the syringe recorded as maximum pull (ml) versus resting volume (ml); the final sample volume collected, usually 150 ml; the actual radon concentration in kBq/m^3 and the corrected radon concentration if the sample volume was less than 150 ml. If the actual radon concentration measured was less than 0.7 kBq/m^3 , a value of 0.35 kBq/m^3 was recorded for the corrected radon concentration. For each site the mean, median, min, max and mean radon for values of 0.7 kBq/m^3 or greater are also presented along with any pertinent comments or observations.

Soil gas permeability was measured using a RADON-JOK apparatus (Radon v.o.s., 2007a). The soil gas was pumped from the soil under constant pressure through the same probes used for later radon collection, from a constant active area created at the bottom of the probe using special, “long lost tips” (Radon v.o.s., 2007a). The gas permeability was calculated using the known air

flow through the probe defined by the known air volume (2000 cc) in the time recorded. For sites having very low permeability, determined by no movement on the RADON-JOK apparatus after 5 minutes, a minimum permeability value of $2 \times 10^{-14} \text{ m}^2$ was recorded due to time constraints in the field. For those probes where only a soil gas sample for radon was collected a subjective description as either, easy, moderate or hard, for the resistance was recorded as an indicator of relative permeability.

For each probe the following permeability information was recorded: site ID; depth to bottom of probe (m); number of weights used to pump the soil gas through the probe (1 or 2); the time (sec) required to pump 2000 cc of soil gas; calculated air flow (m^3/s); calculated permeability (m^2) including a default minimum permeability of $2 \times 10^{-14} \text{ m}^2$ if no movement was observed after 5 minutes. An estimate of the permeability determined from the syringe resistance was recorded as either “Easy or High” for high permeability, “Moderate or Medium” for intermediate permeability or “Hard or Low” for low permeability, with any pertinent comments or observations.

Studies elsewhere have shown that SGR concentration and soil permeability are two important factors to determine the radon availability from soil to air (Neznal et al., 2004). The soil radon potential (SRP), a derived value used to characterize radon availability from soil to air is defined as:

$$\text{SRP} = (C - C_0) / (-\log P + \log P_0)$$

Where C is the soil gas radon concentration (kBq/m^3), and P is the soil permeability (m^2). C_0 and P_0 are set to $1 \text{ kBq}/\text{m}^3$ and $1 \times 10^{-10} \text{ m}^2$, respectively. Neznal et al., (2004) have demonstrated the use of SRP index values for building site radon risk assessment.

For each probe the following information required to determine the SRP index value was recorded: site ID; corrected Rn concentration (kBq/m^3), and an estimated permeability determined from resistance encountered on the syringe during collection of the soil gas sample. Three values for permeability are provided in the data listing. Firstly, the calculated permeability for those probes where a direct measurement, using the RADON-JOK apparatus was conducted are listed. Secondly for those probes where a direct measurement was attempted but where no movement was observed after 5 minutes a minimum permeability default value of $2 \times 10^{-14} \text{ m}^2$ is recorded. Thirdly, for those probes where only an estimated permeability was recorded, a value

determined from comparison of those probes where both direct measurements and estimated observations were recorded is used. During three years of field work (2007 to 2009) 1259 direct and corresponding estimated permeability measurements were made. Table 1 and Figure 5 show the results of the comparison of these duplicate measurements.

	Mean	Median	Std	Min	Max	Count
Low	1.07E-13	2.00E-14	5.58E-13	1.73E-14	8.13E-12	273
Medium	7.13E-13	1.32E-13	3.27E-12	1.15E-14	3.60E-11	229
High	8.63E-12	5.34E-12	8.78E-12	1.94E-14	3.60E-11	757

Table 1. Statistical summary of direct versus estimated permeability measurements.

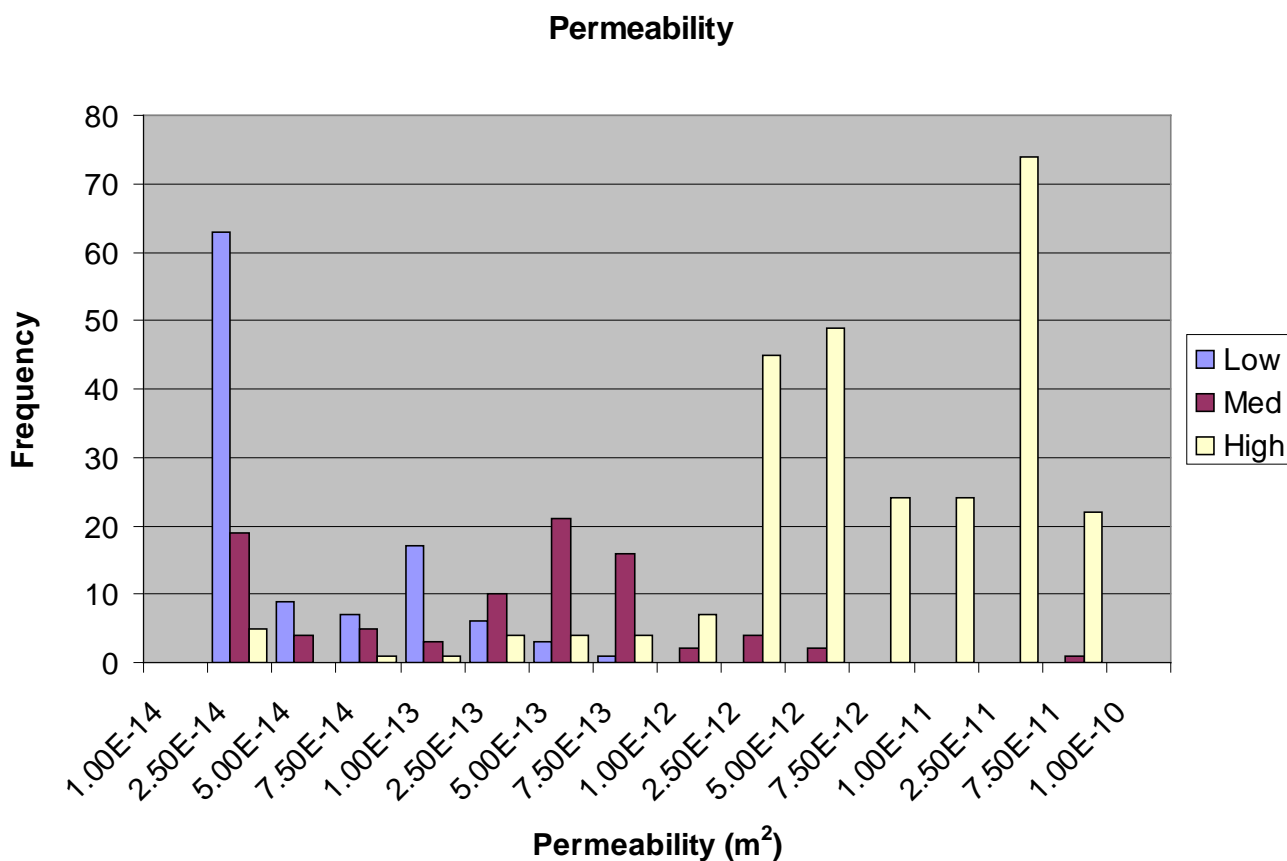


Figure 5. Comparison of direct and estimated permeability measurements. Includes 2007 to 2009

At each probe location a 5 minute in-situ, ground gamma ray spectrometry analysis was conducted. At all 2007 sites a GR-320 gamma ray spectrometer (Terraplus, 2011b) was used. Each GR-320 spectrometer utilizes a single 21 cubic inch sodium-iodide detector and is calibrated on the Geological Survey of Canada's transportable calibration pads (Grasty et al., 1991) to ensure accurate determination of potassium (pct), equivalent uranium (ppm) and

equivalent thorium (ppm). Prior to the first spectrometer measurement each site was quickly scanned with a total count scintillometer (Terraplus, 2011a). For each measurement the following information was recorded: site ID, percent potassium (K), ppm equivalent uranium (eU), ppm equivalent thorium (eTh) and the mean values for K (%), eU (ppm) and eTh (ppm)

Following is a quick overview of required field procedures for radon and natural radioactivity field measurements. More detailed instructions after Friske et al., 2010 are given in Appendix B-1 (soil radon-gas sampling protocols), and Appendix B-2 (field card).

1) At each site an area of approximately 10 m by 10 m was scanned to check for anomalous radioactive variations. This was accomplished using the GR-110 scintillometer. Areas for subsequent spectrometric analysis or soil gas measurements where localized anomalies such as radioactive boulders are detected were avoided. Sites that are representative of the general background radiation levels were selected.

2) The field crew member inserted the first probe using a short, lost-tip and tested the availability of soil gas using the 150 ml syringe, and then set up the spectrometer to start the first spectrometer measurement. If time permitted, the remaining 4 probes were inserted before the first spectrometer measurement was completed.

3) The crew member returned to record the spectrometer measurements and relocated the spectrometer for the next measurement. If the RADON-JOK permeability apparatus (Radon v.o.s., 2007a) was being used, it was necessary to take measurements on probes inserted with the long lost-tips. NASGLP protocols suggest that 2 of the 5 probes be measured with the RADON-JOK permeability apparatus. For a direct permeability measurement using the RADON-JOK apparatus, the time required to fill the 2 litre air bladder was recorded. If little or no movement was noticed after 5 minutes, “minimum permeability” was noted for that probe and the apparatus was moved to the next probe. An estimate of the permeability from the other 3 probes was also recorded by describing the relative resistance encountered during the first pull of the syringe to collect the soil gas sample. A comment was recorded on the field sheet as either “Easy” for high permeability, “Moderate” for intermediate permeability or “Hard” for low permeability. If the permeability apparatus was not being used, there was often sufficient time to collect the soil gas at some probes and transfer it to the ionization chambers during the 5 minute counting periods needed for the spectrometer measurements.

4) The priority was to finish the 5 surface spectrometer measurements first because the measuring of soil gas radon is time-sensitive. The soil gas in the ionization chamber was measured within 13 to 17 minutes after the soil gas was transferred from the syringe to the IC.

5) The soil gas was collected in syringes and transferred to the ionization chambers (Radon v.o.s., 2007b, 2007c). Once transferred, the measurement was made using the ERM-3 electrometer after a wait time of 13 to 17 minutes.

Soil Sample Preparation and Archiving

Soil samples were sent from the field to the sample preparation laboratory at the GSC. In the laboratory, the samples were prepared following the procedures summarized in Table 2 and Figure 6 described below.

	PH	A-horizon	B-horizon	C-horizon	Site Specific
<2.0mm fraction	✓	✓	✓	✓	
<2.0 mm (milled)	✓	✓	✓	✓	
<63um fraction	*	*	✓	✓	
4acid -ICP on <2.0 mm fraction (milled)	✓	✓	✓	✓	
aqua-regia - ICP on <2.0 mm fraction (not milled)	✓	✓	✓	✓	
aqua-regia - ICP on <63 um fraction	*	*	✓	✓	
4acid - ICP on <63 um fraction	*	*	✓	✓	
INAA on <2.0 mm fraction (milled)	✓	*	*	✓	
water leach - ICP on <2.00 mm fraction	✓	*	*	✓	
carbon & LOI <2.0 mm fraction milled	✓	✓	✓	✓	
carbon & LOI <63 um fraction	*	*	✓	✓	
soil pH on <2.00 mm fraction	✓	✓	✓	✓	
soil conductivity on <2.00 mm fraction	*	*	✓	✓	
munsell color (lab)	*	✓	✓	✓	
moisture content	✓	✓	✓	✓	
bulk density	✓	✓	✓	✓	
size fraction analysis	*	*	✓	✓	
x-ray diffraction	*	✓[s]	*	✓[s]	
bioaccessibility on <2.00 mm fraction	✓[s]	*	✓[s]	✓[s]	
gamma ray spectrometry analysis (laboratory at GSC)	✓	✓	✓	✓	
radon/gamma ray spectrometry analysis					✓
detailed field notes					✓

✓ *Determined/prepared*
 * *Not determined/prepared*
 [s] *Selected samples*

Table 2. Summary of sample preparations and analyses applied to the PH interval and soil horizons collected under the auspices of the NASGLP. X-Ray diffraction and bioaccessibility data not included in this Open File.

North American Soil Geochemical Landscapes Project Preparation and Analytical Procedures



Figure 6. Flow chart of TriNational sample preparation and analytical protocols summary.

Samples were removed from pails and left to air dry in the Kraft paper bags used for field collection in a warm, dry and uncontaminated storage area (Figure 7). The drying process took from several weeks to several months depending on the type of sample. Sample bag numbers were compared with manifest lists and field data submitted by the sampling crew. Errors or omissions were resolved through discussions with the field crew and project leader.



Figure 7. TriNational sample drying area with some 2007 Maritime samples laid out.

When dry the samples were moved to the sample preparation laboratory. There were generally two Kraft bags of material from each of the soil horizons or depth intervals sampled at each field site. Soil materials from one type of sample (e.g., A-horizon) were processed together.

The slab-cake method was used for sub sampling (Gy, 1992; Pitard, 1993). All material for a given sample was poured into a pile on a large clean sheet of Kraft paper. A large spatula and/or rubber mallet was used to break down aggregated materials until there were no pieces larger than 5 mm. The material was then shaped into a uniform elongated pile across the Kraft paper. For the archived sub-sample, stored in plastic containers, two flat-bottomed plastic scoops were used to scoop 5 diagonal bands across the elongated pile (Figure 8). This procedure was repeated to obtain the various splits as outlined in Figure 6. The radiometric split for



Figure 8. Sub sampling of a TriNational soil sample using the slab-cake method.

laboratory gamma ray spectrometry analysis (LGRS) was wrapped in plastic wrap before being placed in an 8 oz shallow seamless tin to avoid possible trace metal contamination so that the sample could be used for chemical analysis if required. Any excess material from each step was placed in a labelled Ziploc bag and archived.

Two size fractions, a <2 mm and <0.063 mm, were prepared. Before sieving large pebbles were removed and clumps of dried sample were gently disaggregated using a porcelain pestle. The collected sieved material was transferred to a spinning riffler equipped with a 16 tube carousel from which splits of proper size/weight were created. With the 0.063 mm sieve, a coarse sieve (2.0 mm) was used to protect the fine mesh from damage. Between each sample the sieves were wiped down with Kim wipes that had been dampened with distilled water. Also as required, the sieves were cleaned by placing them into an ultrasound bath for 5 minutes, rinsing them with distilled water and drying them in a 105°C oven for 10 to 15 minutes.

Portions of various splits (Figure 6) of the <2 mm fraction were ball milled prior to the 4 acid digestion. This was done at a commercial lab using a ceramic mill. Samples were ground until the final grain size was <0.063 mm.

Chemical and Physical Analysis Methods

Soil samples were analysed for a wide range of variables using different size fractions and dissolution procedures as summarized in Figure 6 and Table 2. With the exception of the ICP-MS/ES and INA analysis these data were determined by laboratories at the Geological Survey of Canada. A description for each procedure is given below. More detailed description of many of the physical analysis methods can be found in Girard et al. (2004).

Inductively Coupled Plasma Mass Spectrometry/Atomic Emission Spectrometry (ICP-MS/AES)

Data available for:

- *PH; A, B and C-horizons - 4-acid digestion - milled <2mm fraction*
- *PH; A, B and C-horizons - modified 3050B digestion - unmilled <2 mm fraction*
- *B and C-horizons - 4-acid digestion - unmilled <63 um fraction*
- *B and C-horizons - modified 3050B digestion - unmilled <63 um fraction*

Samples were analysed by the complementary techniques of ICP-MS and ICP-AES, the latter being used for the more abundant elements (e.g. Ca, Mg, Na, K, Fe) whereas the more sensitive MS technique focuses on the determination of the trace elements. Two different digestion procedures were used prior to analysis.

The first digestion method is a "near total" 4-acid digestion using HCl, HNO₃, HClO₄ and HF mixed in the ratio of 2:2:1:1. Elements determined and lower detection limits are summarized in Table 3.

Pulp splits of 0.25 g were weighed into Teflon test tubes. A 10 mL aliquot of the acid solution was added, heated until fuming on a hot plate and taken to dryness. A 4 mL aliquot of 50% HCl is added to the residue and heated using a mixing hot block. After cooling the solutions were transferred to polypropylene test-tubes and made to a 10 mL volume 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 only be partial depending on sample mineralogy. Also volatilization during fuming may result in some loss of As, Sb and Au.

The second dissolution is a "partial" extraction akin to an "aqua regia" digestion. Elements determined and lower detection limits are summarized in Table 4. As part of protocol development for the Tri-National project a test comparing five digestion protocols (aqua regia (*senso stricto*), Lefort (reverse aqua regia), 1:1 HCl-HNO₃, 1:1:1 HCl-HNO₃-H₂O, and the HNO₃-H₂O₂ variant of US-EPA 3050B) was undertaken (Garrett et al., 2008). Based on results from this study and other considerations it was decided that a modified procedure based on US-EPA 3050B be used (USEPA, 1996).

EPA method 3050B describes "two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS)". The digestion procedure

4acid ICP-MS/AES Precision Summary

		<u>Blind Duplicates Summary</u>					<u>TILL-1 (n = 20)</u>				<u>LKSD-4 (n = 12)</u>				<u>SoNE-1 (n = 16)</u>				<u>2711 (n = 11)</u>			
Element	LDL	< DL	Pairs (N)	Mean	SD	%RSD	< DL	Mean ⁺	SD	%RSD	< DL	Mean	SD	%RSD	< DL	Mean	SD	%RSD	< DL	Mean	SD	%RSD
Ag	20 ppb	0	41	255	38.3	15.1%	0	432	61.5	14.2%	0	285	30.4	10.7%	0	261	39.7	15.2%	0	3857	154	4.0%
Al	0.02 %	0	41	5.29	0.199	3.8%	0	6.80	0.486	7.1%	0	2.97	0.145	4.9%	0	6.08	0.298	4.9%	0	6.17	0.265	4.3%
As	0.2 ppm	0	41	7.28	0.487	6.7%	0	16.8	0.800	4.8%	0	12.5	0.688	5.5%	0	11.2	0.801	7.1%	0	95.9	5.28	5.5%
Au	100 ppb	82	0	< 100			18	< 100			12	< 100			16	< 100			10	< 100		
Ba	1 ppm	0	41	282	11.6	4.1%	0	623	42.2	6.8%	0	265	26.7	10.1%	0	651	35.5	5.4%	0	635	52.9	8.3%
Be	1 ppm	33	23	1.83	0.466	25.5%	0	1.5	0.513	34.2%	11	< 1			1	1.5	0.562	36.7%	0	2.0	0.447	22.4%
Bi	0.04 ppm	0	41	0.249	0.026	10.6%	0	1.90	0.127	6.7%	0	0.503	0.052	10.3%	0	0.272	0.029	10.8%	0	2.33	0.255	11.0%
Ca	0.02 %	0	41	0.271	0.015	5.4%	0	1.81	0.103	5.7%	0	1.28	0.032	2.5%	0	0.608	0.044	7.2%	0	2.75	0.090	3.3%
Cd	0.02 ppm	0	41	0.251	0.031	12.5%	0	0.367	0.058	15.8%	0	2.03	0.147	7.2%	0	0.503	0.048	9.5%	0	42.1	3.44	8.2%
Ce	0.02 ppm	0	41	46.0	2.65	5.8%	0	61.7	4.46	7.2%	0	42.6	2.99	7.0%	0	67.7	3.59	5.3%	0	61.1	4.05	6.6%
Co	0.2 ppm	0	41	9.62	0.420	4.4%	0	18.2	0.646	3.5%	0	11.3	0.555	4.9%	0	12.5	0.403	3.2%	0	10.3	0.571	5.6%
Cr	1 ppm	0	41	48.6	3.86	7.9%	0	54.9	3.74	6.8%	0	30.3	1.14	3.8%	0	56.7	3.50	6.2%	0	37.8	3.16	8.3%
Cs	0.1 ppm	0	41	3.67	0.147	4.0%	0	0.910	0.064	7.0%	0	1.34	0.067	5.0%	0	4.06	0.150	3.7%	0	6.06	0.452	7.5%
Cu	0.02 ppm	0	41	13.4	0.664	4.9%	0	49.0	2.10	4.3%	0	32.8	2.413	7.3%	0	23.0	1.71	7.4%	0	111	5.83	5.2%
Dy	0.1 ppm	0	41	2.01	0.194	9.7%	0	4.65	0.433	9.3%	0	3.15	0.235	7.5%	0	3.56	0.196	5.5%	0	3.98	0.289	7.3%
Er	0.1 ppm	0	41	1.12	0.178	15.9%	0	2.53	0.207	8.2%	0	1.78	0.217	12.2%	0	1.83	0.161	8.8%	0	2.12	0.223	10.5%
Eu	0.1 ppm	1	40	0.656	0.064	9.8%	0	1.35	0.100	7.4%	0	0.983	0.119	12.1%	0	1.01	0.089	8.7%	0	0.891	0.094	10.6%
Fe	0.02 %	0	41	2.68	0.067	2.5%	0	4.56	0.160	3.5%	0	2.74	0.109	4.0%	0	2.72	0.075	2.8%	0	2.72	0.098	3.6%
Ga	0.02 ppm	0	41	13.6	0.454	3.3%	0	16.7	0.635	3.8%	0	7.46	0.262	3.5%	0	13.8	0.592	4.3%	0	15.0	0.778	5.2%
Gd	0.1 ppm	0	41	2.52	0.260	10.3%	0	5.18	0.402	7.8%	0	3.83	0.235	6.1%	0	4.59	0.225	4.9%	0	4.69	0.348	7.4%
Hf	0.02 ppm	0	41	2.68	0.134	5.0%	0	4.28	0.217	5.1%	0	1.35	0.068	5.0%	0	3.27	0.170	5.2%	0	2.44	0.156	6.4%
Ho	0.1 ppm	2	39	0.403	0.058	14.3%	0	0.930	0.086	9.3%	0	0.633	0.065	10.3%	0	0.675	0.058	8.6%	0	0.782	0.075	9.6%
K	0.02 %	0	41	1.40	0.112	8.0%	0	1.69	0.155	9.2%	0	0.661	0.037	5.6%	0	1.81	0.202	11.2%	0	2.25	0.202	8.9%
La	0.1 ppm	0	41	22.8	1.32	5.8%	0	25.4	2.23	8.8%	0	24.0	1.75	7.3%	0	35.7	2.59	7.2%	0	33.6	3.02	9.0%
Li	0.1 ppm	0	41	42.1	1.98	4.7%	0	15.8	0.718	4.5%	0	12.5	0.613	4.9%	0	29.4	1.37	4.7%	0	27.0	0.871	3.2%
Lu	0.1 ppm	10	35	0.209	0.029	14.0%	0	0.400	0.032	8.1%	0	0.283	0.039	13.7%	0	0.313	0.034	10.9%	0	0.345	0.052	15.1%
Mg	0.02 %	0	41	0.539	0.013	2.5%	0	1.21	0.045	3.7%	0	0.533	0.017	3.1%	0	0.595	0.018	3.0%	0	0.969	0.033	3.4%
Mn	2 ppm	0	41	556	16.8	3.0%	0	1444	54.4	3.8%	0	479	17.6	3.7%	0	605	18.2	3.0%	0	628	26.9	4.3%
Mo	0.05 ppm	0	41	0.642	0.093	14.5%	0	0.871	0.066	7.6%	0	1.86	0.117	6.3%	0	1.12	0.056	5.0%	0	1.54	0.086	5.6%
Na	0.002 %	0	41	0.720	0.031	4.3%	0	2.06	0.100	4.8%	0	0.556	0.013	2.3%	0	0.740	0.049	6.7%	0	1.14	0.054	4.7%
Nb	0.04 ppm	0	41	9.93	0.409	4.1%	0	9.01	0.584	6.5%	0	3.91	0.236	6.0%	0	12.0	0.674	5.6%	0	16.7	1.16	6.9%
Nd	0.1 ppm	0	41	21.1	1.47	7.0%	0	29.0	1.95	6.7%	0	25.3	1.00	4.0%	0	32.8	1.92	5.9%	0	29.7	2.15	7.2%
Ni	0.1 ppm	0	41	24.6	0.840	3.4%	0	25.4	1.31	5.2%	0	35.0	1.59	4.6%	0	29.9	1.26	4.2%	0	19.5	0.854	4.4%
P	0.001 %	0	41	0.058	0.003	5.2%	0	0.095	0.006	6.5%	0	0.142	0.005	3.5%	0	0.052	0.005	10.1%	0	0.085	0.014	16.1%
Pb	0.02 ppm	0	41	26.8	2.32	8.7%	0	23.1	1.789	7.7%	0	93.1	8.75	9.4%	0	22.4	1.86	8.3%	0	1103	45.6	4.1%
Pr	0.1 ppm	0	41	5.39	0.356	6.6%	0	6.89	0.469	6.8%	0	6.08	0.374	6.1%	0	8.43	0.559	6.6%	0	7.62	0.583	7.6%
Rb	0.1 ppm	0	41	72.3	6.19	8.6%	0	39.2	4.07	10.4%	0	23.5	1.31	5.6%	0	81.8	6.91	8.5%	0	99.8	10.4	10.4%
S	0.04 %	48	16	0.065	0.003	3.8%	20	< 0.04			0	0.968	0.038	3.9%	16	< 0.04			11	< 0.04		
Sb	0.02 ppm	0	41	0.685	0.037	5.4%	0	7.14	0.435	6.1%	0	1.52	0.114	7.5%	0	1.29	0.095	7.4%	0	19.1	1.59	8.3%
Sc	0.1 ppm	0	41	7.01	0.315	4.5%	0	11.3	0.803	7.1%	0	5.81	0.264	4.6%	0	7.28	0.488	6.7%	0	7.78	0.546	7.0%
Sm	0.1 ppm	0	41	3.40	0.337	9.9%	0	5.33	0.401	7.5%	0	4.33	0.263	6.1%	0	5.46	0.253	4.6%	0	5.06	0.372	7.4%
Sn	0.1 ppm	0	41	2.23	0.119	5.3%	0	1.74	0.114	6.6%	0	3.54	0.31	8.8%	0	1.54	0.145	9.5%	0	3.44	0.280	8.2%
Sr	1 ppm	0	41	66.9	2.12	3.2%	0	297	15.1	5.1%	0	124	6.27	5.1%	0	131	5.13	3.9%	0	236	9.07	3.8%
Ta	0.1 ppm	2	40	0.599	0.049	8.1%	0	0.395	0.039	10.0%	0	0.208	0.029	13.9%	0	0.613	0.050	8.2%	0	0.891	0.083	9.3%
Tb	0.1 ppm	5	38	0.357	0.041	11.6%	0	0.775	0.064	8.2%	0	0.517	0.039	7.5%	0	0.619	0.066	10.6%	0	0.645	0.052	8.1%
Th	0.1 ppm	0	41	7.22	0.508	7.0%	0	5.23	0.458	8.8%	0	4.69	0.403	8.6%	0	10.95	0.980	9.0%	0	12.6	1.27	10.1%
Ti	0.001 %	0	41	0.328	0.015	4.5%	0	0.494	0.024	4.8%	0	0.169	0.011	6.6%	0	0.324	0.025	7.7%	0	0.275	0.011	4.1%
Tm	0.1 ppm	13	34	0.200	0.030	14.9%	0	0.400	0.046	11.5%	0	0.258	0.051	19.9%	0	0.294	0.025	8.5%	0	0.355	0.052	14.7%
U	0.1 ppm	0	41	1.91	0.144	7.5%	0	1.74	0.198	11.4%	0	29.4	2.94	10.0%	0	2.91	0.253	8.7%	0	2.45	0.298	12.2%
V	1 ppm	0	41	64.6	2.73	4.2%	0	96.3	7.03	7.3%	0	39.9	2.39	6.0%	0	95.7	6.10	6.4%	0	74.5	4.30	5.8%
W	0.1 ppm	0	41	0.978	0.084	8.6%	0	0.565	0.067	11.9%	0	0.550	0.067	12.3%	0	1.14	0.136	11.9%	0	2.77	0.174	6.3%
Y	0.1 ppm	0	41	10.4	1.30	12.5%	0	24.5	1.66	6.8%	0	18.7	1.15	6.2%	0	19.4	1.21	6.2%	0	22.6	1.51	6.7%
Yb	0.1 ppm	0	41	1.29	0.094	7.3%	0	2.73	0.205	7.5%	0	1.86	0.090	4.8%	0	2.12	0.098	4.6%	0	2.25	0.151	6.7%
Zn	0.2 ppm	0	41	66.1	3.49	5.3%	0	90.4	3.44	3.8%	0	182	5.31	2.9%	0	81.2	4.84	6.0%	0	326	15.9	4.9%

* For purposes of Mean calculation: <LDL values set to ½ LDL if more than 50% of values >LDL; Mean set to <LDL if >50% of values <LDL

Table 3. Precision summary for blind duplicate and control reference material data generated by the 4-acid ICP-MS/AES analytical method.

used for the Tri-National as outlined below (G.E.M. Hall pers. comm., 2008) is a modified version of the first variant, FLAA/ICP-AES.

Digestion protocol for <2.0 mm sieved fraction (not milled)

1) To 10.0 g of sample in a beaker, add 25 ml of reagent-grade concentrated HNO₃ and 100 ml of reagent-grade concentrated HCl and cover with a watch-glass to aid in refluxing during

3050B Precision Summary

Element	LDL	<u>Blind Duplicates Summary</u>					<u>TILL-1 (n = 12)</u>				<u>LKSD-4 (n = 12)</u>			
		< LDL	Pairs (N)	Mean	SD	%RSD	< LDL	Mean	SD	%RSD	< LDL	Mean	SD	%RSD
Ag	2 ppb	0	40	111	8.35	7.5%	0	201	11.6	5.8%	0	205	13.6	6.6%
Al	0.01 %	0	40	1.62	0.078	4.8%	0	1.86	0.065	3.5%	0	1.34	0.040	3.0%
As	0.1 ppm	0	40	6.05	0.453	7.5%	0	16.6	1.36	8.2%	0	13.6	0.846	6.2%
Au	0.2 ppb	19	23	0.730	0.364	49.9%	0	12.8	4.51	35.4%	0	3.13	1.48	47.2%
B	1 ppm	11	31	3.32	1.15	34.6%	0	2.71	1.60	59.1%	0	10.3	1.61	15.6%
Ba	0.5 ppm	0	40	63.5	3.34	5.3%	0	79.4	5.21	6.6%	0	134	8.07	6.0%
Bi	0.02 ppm	0	40	0.255	0.023	9.1%	0	2.10	0.194	9.3%	0	0.558	0.055	9.8%
Ca	0.01 %	0	40	0.132	0.011	8.0%	0	0.353	0.035	9.8%	0	0.879	0.034	3.8%
Cd	0.01 ppm	2	39	0.191	0.025	13.2%	0	0.248	0.026	10.3%	0	2.30	0.254	11.0%
Co	0.1 ppm	0	40	8.59	0.658	7.7%	0	14.1	0.533	3.8%	0	10.5	0.758	7.2%
Cr	0.5 ppm	0	40	23.8	1.32	5.6%	0	31.8	2.00	6.3%	0	22.7	1.63	7.2%
Cu	0.01 ppm	0	40	11.1	0.784	7.1%	0	50.9	3.64	7.1%	0	33.4	2.12	6.4%
Fe	0.01 %	0	40	2.49	0.102	4.1%	0	3.45	0.100	2.9%	0	2.56	0.103	4.0%
Ga	0.1 ppm	0	40	5.20	0.277	5.3%	0	6.38	0.316	4.9%	0	4.08	0.262	6.4%
Hg	5 ppb	1	39	84.2	6.936	8.2%	0	125	24.0	19.1%	0	169	13.4	7.9%
K	0.01 %	0	40	0.082	0.011	13.9%	0	0.061	0.008	13.0%	0	0.113	0.006	5.5%
La	0.5 ppm	0	40	13.3	0.768	5.8%	0	20.2	1.57	7.8%	0	21.7	1.81	8.4%
Mg	0.01	0	40	0.375	0.023	6.0%	0	0.597	0.024	4.0%	0	0.384	0.016	4.1%
Mn	1 ppm	0	40	496	34.5	7.0%	0	1140	25.5	2.2%	0	430	13.0	3.0%
Mo	0.01 ppm	0	40	0.499	0.036	7.1%	0	0.713	0.037	5.2%	0	1.67	0.101	6.1%
Na	0.001 %	0	40	0.006	0.000	5.6%	0	0.030	0.004	11.9%	0	0.018	0.002	9.2%
Ni	0.1 ppm	0	40	20.9	1.19	5.7%	0	18.7	0.656	3.5%	0	33.3	1.99	6.0%
P	0.001 %	0	40	0.049	0.002	4.8%	0	0.091	0.007	8.2%	0	0.138	0.011	8.1%
Pb	0.01 ppm	0	40	22.6	1.20	5.3%	0	14.6	1.50	10.2%	0	93.6	6.79	7.3%
S	0.02 %	25	24	0.084	0.026	30.9%	0	0.035	0.050	143.9%	0	1.06	0.064	6.0%
Sb	0.02 ppm	0	40	0.354	0.037	10.5%	0	4.60	1.02	22.2%	0	0.972	0.156	16.1%
Sc	0.1 ppm	0	40	1.97	0.170	8.7%	0	4.57	0.416	9.1%	0	2.85	0.326	11.4%
Se	0.1 ppm	0	40	0.769	0.207	26.9%	0	0.417	0.195	46.7%	0	2.95	0.247	8.4%
Sr	0.5 ppm	0	40	12.5	0.746	6.0%	0	11.7	0.906	7.7%	0	40.7	3.47	8.5%
Te	0.02 ppm	35	17	0.033	0.013	38.3%	0	0.033	0.017	52.7%	0	0.134	0.027	20.5%
Th	0.1 ppm	5	37	3.10	0.242	7.8%	0	2.28	0.290	12.7%	0	0.750	0.100	13.3%
Ti	0.001%	0	40	0.030	0.003	9.3%	0	0.129	0.017	13.5%	0	0.067	0.006	8.2%
Tl	0.02 ppm	0	40	0.111	0.011	10.1%	0	0.126	0.009	7.2%	0	0.473	0.068	14.4%
U	0.05 ppm	0	40	0.659	0.046	7.0%	0	0.950	0.080	8.4%	0	31.1	2.41	7.7%
V	2 ppm	0	40	31.8	3.12	9.8%	0	61.8	4.05	6.6%	0	38.8	6.25	16.1%
W	0.05 ppm	31	23	0.283	0.047	16.5%	0	0.217	0.039	18.0%	0	0.317	0.039	12.3%
Zn	0.1 ppm	0	40	57.4	2.60	4.5%	0	73.6	3.21	4.4%	0	199	10.5	5.3%

Table 4. Precision summary for blind duplicate and control reference material data generated by the modified 3050B ICP-MS/AES analytical method.

digestion. Heat at 95±2 °C (on a hot-plate, heating block or in a water bath) for 1 hour. Swirl several times during the digestion. Allow to cool.

Note: If the sample is organic-rich, first carry out a predigestion (to reduce this organic component) with 20 ml of concentrated HNO₃ at 95±2 °C for 30 min. Swirl several times during this digestion.

2) With DDI water, rinse the watch glass, adding the rinse to the digestate. Add ~ 50 ml of H₂O to the digestate, mix and transfer to a polypropylene 500-ml volumetric flask (or other suitably graded container). Rinse the beaker thoroughly several times with H₂O and add all washes to the volumetric flask. Make up to 500 ml with H₂O [The volume of the residue is deemed to be insignificant].

3) Mix digestate thoroughly in the volumetric flask and allow to settle. Withdraw an aliquot for analysis (without disturbing the residue) and dilute by a factor of 10 with 1% HNO₃ ready for analysis by ICP-AES or ICP-MS. The latter technique may require further dilution. Overall dilution factor is 500.

Digestion protocol for <63 µm sieved fraction or milled samples

1) To 1.0 g of sample in a 50-ml polypropylene Falcon tube, add 2.5 ml of reagent-grade concentrated HNO₃ and 10.0 ml of reagent-grade concentrated HCl. Heat at 95±2 °C (in a heating block or water bath) for 1 hour. Vortex several times during the digestion. Allow to cool.

Note: If the sample is organic-rich, first carry out a predigestion (to reduce this organic component) with 2 ml of concentrated HNO₃ at 95±2 °C for 30 min. Vortex several times during this predigestion.

2) Make up to 50 ml with H₂O. Shake thoroughly or vortex and allow to settle. Remove an aliquot, taking care to avoid any remaining residue, and dilute tenfold with 1% HNO₃ ready for analysis by ICP-AES or ICP-MS. The latter technique may require further dilution. Overall dilution factor is 500.

Instrumental Neutron Activation Analysis (INAA)

Data available for:

- *PH and C-horizon - milled <2 mm fraction*

Weighed and encapsulated samples, normally in the 30 g range, were packaged for irradiation along with internal standards and international reference materials. Samples and standards were irradiated together with neutron flux monitors in a two-megawatt pool type reactor. After a seven-day decay period, samples were measured with a high-resolution germanium detector.

Typical counting times were 500 seconds. Elements determined by INAA and lower detection limits are listed in Table 5.

INAA Precision Summary

Element	LDL	<u>Blind Duplicate Summary</u> (n = 20 pairs)					<u>TILL-1 (n = 7)</u>				<u>LKSD-4 (n = 7)</u>				<u>SoNE-1 (n = 7)</u>				<u>2711 (n = 5)</u>			
		< DL	Pairs (N)	Mean	SD	%RSD	< DL	Mean	SD	%RSD	< DL	Mean	SD	%RSD	< DL	Mean	SD	%RSD	< DL	Mean	SD	%RSD
Ag	2 ppm	40	0	< 2			7	< 2			7	< 2			7	< 2			2	3400	2510	73.8%
As	0.5 ppm	0	20	8.3	0.522	6.3%	0	18.4	0.535	2.9%	0	15.9	0.690	4.4%	0	11.3	0.951	8.4%	0	99.6	7.38	7.4%
Au	2 ppb	33	1	2.5	0.707	28.3%	0	25.0	25.7	103%	7	< 2			2	6.57	7.18	109%	0	34.8	5.97	17.2%
Ba	50 ppm	0	20	354	25	7.1%	0	713	52.2	7.3%	0	327	43.5	13.3%	0	710	52.3	7.4%	0	712	41.5	5.8%
Br	0.5 ppm	0	20	8.8	0.391	4.4%	0	6.21	0.376	6.1%	0	49.5	1.35	2.7%	0	7.90	0.451	5.7%	0	5.50	0.394	7.2%
Cd	5 ppm	40	0	< 5			7	< 5			7	< 5			7	< 5			0	37.6	3.97	10.6%
Ce	5 ppm	0	20	62.7	3.42	5.5%	0	69.7	6.42	9.2%	0	46.6	6.60	14.2%	0	81.6	12.7	15.6%	0	69.0	5.24	7.6%
Co	5 ppm	11	14	14.8	1.15	7.8%	0	19.3	1.38	7.2%	0	11.9	1.86	15.7%	0	12.7	1.11	8.8%	1	8.10	3.88	47.9%
Cr	20 ppm	0	20	64.8	6.76	10.4%	0	60.1	5.79	9.6%	3	22.7	14.0	61.5%	0	72.3	14.9	20.7%	1	49.8	32.9	66.1%
Cs	0.5 ppm	0	20	4.3	0.260	6.0%	0	1.14	0.315	27.6%	2	1.13	0.636	56.4%	0	4.29	0.445	10.4%	0	6.20	0.604	9.7%
Eu	1 ppm	30	3	1.8	0.408	22.3%	4	< 2			3	1.21	0.756	62.3%	6	< 1			5	< 1		
Fe	0.2 %	0	20	2.9	0.158	5.4%	0	4.87	0.275	5.6%	0	2.94	0.113	3.9%	0	2.83	0.214	7.6%	0	2.98	0.228	7.7%
Hf	1 ppm	0	20	7.2	0.689	9.6%	0	13.1	1.21	9.2%	2	2.29	1.35	59.0%	0	11.7	0.756	6.5%	0	7.00	1.22	17.5%
Ir	50 ppm	40	0	< 50			7	< 50			7	< 50			7	< 50			5	< 50		
La	2 ppm	0	20	29.9	1.1	3.6%	0	28.7	1.25	4.4%	0	25.6	1.51	5.9%	0	40.4	2.07	5.1%	0	37.2	2.59	7.0%
Lu	0.2 ppm	3	18	0.5	0.060	13.0%	0	0.671	0.125	18.7%	4	< 0.2			0	0.614	0.121	19.8%	0	0.46	0.114	24.8%
Mo	1 ppm	38	0	< 1			7	< 1			5	< 1			5	< 1			3	< 1		
Na	0.02 %	0	20	0.8	0.064	7.7%	0	2.03	0.102	5.0%	0	0.581	0.023	3.9%	0	0.749	0.072	9.6%	0	1.14	0.055	4.8%
Ni	10 ppm	13	12	43.1	7.75	18.0%	0	21.1	12.4	58.8%	3	19.7	14.7	74.7%	2	23.3	12.9	55.3%	3	< 10		
Rb	5 ppm	0	20	88	6.0	6.8%	0	37.2	17.1	46.0%	2	20.0	13.0	64.8%	0	86.6	5.71	6.6%	0	103	10.1	9.8%
Sb	0.1 ppm	0	20	0.8	0.039	5.0%	0	7.53	0.415	5.5%	0	1.74	0.098	5.6%	0	1.39	0.090	6.5%	0	19.3	0.953	4.9%
Sc	0.2 ppm	0	20	10.3	0.561	5.4%	0	13.7	0.756	5.5%	0	7.11	0.609	8.6%	0	9.14	0.890	9.7%	0	9.50	0.686	7.2%
Se	5 ppm	40	0	< 5			7	< 5			7	< 5			7	< 5			5	< 5		
Sm	0.1 ppm	0	20	4.9	0.143	2.9%	0	6.11	0.318	5.2%	0	4.79	0.168	3.5%	0	6.34	0.207	3.3%	0	5.76	0.270	4.7%
Sn	100 ppm	40	0	< 100			7	< 100			7	< 100			7	< 100			5	< 100		
Ta	0.5 ppm	3	17	1.4	0.216	15.1%	0	0.779	0.271	34.8%	5	< 0.5			0	0.950	0.409	43.1%	0	1.76	0.313	17.8%
Tb	0.5 ppm	14	11	0.8	0.130	15.8%	0	0.929	0.180	19.4%	3	0.507	0.254	50.1%	0	1.01	0.195	19.2%	0	0.860	0.152	17.6%
Te	10 ppm	40	0	< 10			7	< 10			7	< 10			7	< 10			5	< 10		
Th	0.2 ppm	0	20	9.1	0.396	4.4%	0	5.47	0.482	8.8%	0	5.14	0.230	4.5%	0	11.9	0.690	5.8%	0	13.4	0.548	4.1%
Ti	0.05 %	0	20	0.474	0.017	3.5%	0	0.590	0.031	5.3%	0	0.211	0.018	8.4%	0	4043	374	9.2%	0	0.314	0.024	7.7%
U	0.2 ppm	0	20	2.4	0.153	6.5%	0	1.99	0.195	9.8%	0	30.73	0.974	3.2%	0	3.56	0.230	6.5%	0	2.74	0.483	17.6%
W	1 ppm	12	11	2.1	0.603	28.8%	6	< 1			7	< 1			3	1.50	1.00	66.7%	1	3.10	1.52	48.9%
Yb	2 ppm	10	13	2.7	0.439	16.5%	0	4.00	0.577	14.4%	3	1.86	0.900	48.4%	0	3.00	0.816	27.2%	1	3.00	1.41	47.1%
Zn	100 ppm	36	1	125	7.1	5.7%	5	< 100			2	146	68.5	47.0%	7	< 100			0	320	43.0	13.4%
Zr	200 ppm	31	3	343	41.2	12.0%	4	< 200			7	< 200			5	< 200			5	< 200		

Table 5. Precision summary for blind duplicate and control reference material data generated by INAA.

Water Leach

Data available for:

- PH and C-horizon - unmilled <2 mm fraction

Determinations of total metal content overestimates the amount of an element that is easily accessible through solubilization to flora or fauna. The issue of bioavailability is of increasing importance as data from regional geochemical surveys are increasingly being used to support environmental and human health exposure and risk assessments. The following water leach method was developed during the pilot studies to estimate bioaccessibility of elements in soils (Garrett et al., 2009).

Procedure:

- 1) Weigh out 1.0 g of sample into new precleaned (Reversed Osmosis – Deionized (RO-DI) water rinsed) 50 mL polypropylene (PP) centrifuge tubes.
- 2) Add 40 mL of RO-DI water, cap and shake by hand to suspend.
- 3) Shake samples horizontally for 20 hours (on a mechanical shaker) @ 160 shakes per minutes.
- 4) Centrifuge samples for 10 minutes @ 3800 RPM (Relative Centrifugal Force (RCF) of 3230).
- 5) Decant supernatant into new pre-cleaned 50 mL PP tubes.
- 6) Decant an aliquot of approximately 5 mL that will be used for Br and I dilutions and pH.
- 7) Re-centrifuge the supernatant for 20 minutes at a RCF of 3230.
- 8) Dilute samples twofold with 2% HNO₃ into 15 mL PP centrifuge tubes, mix by vortexing and centrifuge immediately for 20 minutes at a RCF of 4200.
- 9) Analyse by inductively coupled plasma–atomic emission spectrometry (ICP–AES) and inductively coupled plasma–mass spectrometry (ICP–MS) the same day.

Elements determined and lower detection limits are summarized in Table 6.

Water Leach Precision Summary

Element	LDL	Blind Duplicate Summary (n = 20 pairs)					TILL-1 (n = 8)				LKSD-4 (n = 8)			
		< DL	UQ pairs	Mean	SD	%RSD	< DL	Mean	SD	%RSD	< DL	Mean	SD	%RSD
Ag	0.4 ppb	37	1	0.650	0.085	13.1%	0	1.16	0.158	13.6%	3	0.653	0.431	66.0%
Al	0.2 ppm	0	20	23.9	1.81	7.6%	0	7.15	2.33	32.5%	0	92.8	3.38	3.6%
As	8 ppb	19	10	53.0	3.02	5.7%	0	33.8	1.91	5.7%	0	401	88.2	22.0%
B	40 ppb	14	10	197	9.4	4.8%	0	153	13.1	8.6%	0	2738	87.6	3.2%
Ba	10 ppb	0	20	358	27	7.6%	0	276	15.5	5.6%	0	2633	38.1	1.4%
Be	0.4 ppb	1	19	1.3	0.142	10.8%	6	< 0.4			0	4.36	0.396	9.1%
Bi	2 ppb	40	0	< 2			8	< 2			8	< 2		
Br	2 ppm	39	0	< 2			8	< 2			1	2.48	0.794	32.1%
Ca	2 ppm	0	20	27	2.27	8.5%	0	123	5.01	4.1%	0	3029	51.1	1.7%
Cd	1 ppb	9	14	2.8	0.779	28.3%	2	1.13	0.582	51.8%	0	63.5	0.756	1.2%
Ce	0.8 ppb	0	20	17	2.20	13.0%	0	19.4	5.98	30.8%	0	104	4.23	4.1%
Cl	8 ppm	9	13	35.3	1.39	3.9%	0	14.1	1.48	10.5%	0	23.2	2.60	11.2%
Co	4 ppb	5	17	18.6	1.46	7.8%	0	7.88	0.991	12.6%	0	562	22.6	4.0%
Cr	8 ppb	8	15	43.1	1.67	3.9%	0	13.4	1.92	14.4%	0	105	4.46	4.3%
Cs	1 ppb	28	6	2.00	0.408	20.4%	8	< 1			0	5.00	0.000	0.0%
Cu	8 ppb	10	14	48.21	6.71	13.9%	0	239	11.9	5.0%	0	218	7.00	3.2%
Dy	0.4 ppb	4	18	2.04	0.314	15.4%	0	3.52	0.552	15.7%	0	11.9	0.585	4.9%
Er	0.4 ppb	15	12	1.26	0.175	13.9%	0	1.99	0.302	15.2%	0	8.10	0.305	3.8%
Eu	0.4 ppb	21	8	0.97	0.137	14.2%	0	0.938	0.151	16.1%	0	3.22	0.098	3.1%
Fe	0.4 ppm	1	19	14.8	1.68	11.3%	0	5.72	2.410	42.1%	0	44.7	5.32	11.9%
Ga	1 ppb	19	10	6.95	0.671	9.7%	2	1.13	0.582	51.8%	0	6.13	0.354	5.8%
Gd	0.4 ppb	4	18	2.53	0.442	17.5%	0	4.22	0.675	16.0%	0	13.6	0.524	3.8%
Ge	2 ppb	37	1	< 2			8	< 2			0	11.8	0.707	6.0%
Hf	0.8 ppb	26	7	1.84	0.144	7.8%	8	< 0.8			0	3.95	0.798	20.2%
Ho	0.4 ppb	30	5	0.82	0.099	12.1%	0	0.710	0.113	15.9%	0	2.59	0.122	4.7%
In	1 ppb	40	0	< 1			8	< 1			8	< 1		
K	4 ppm	9	15	64	3.2	5.0%	0	28.5	0.292	1.0%	0	81.3	11.1	13.6%
La	0.8 ppb	0	20	7.38	1.04	14.1%	0	17.09	3.05	17.9%	0	59.7	2.04	3.4%
Li	2 ppb	0	20	31.75	1.95	6.1%	8	< 2			0	62.0	1.51	2.4%
Lu	0.4 ppb	40	0	< 0.4			8	< 0.4			0	1.63	0.044	2.7%
Mg	0.4 ppm	2	19	9.93	0.519	5.2%	0	42.1	1.21	2.9%	0	308	3.59	1.2%
Mn	8 ppb	0	20	4576	474	10.4%	0	8760	758	8.7%	0	93070	3057	3.3%
Mo	4 ppb	30	5	7.6	0.63	8.3%	0	7.38	0.518	7.0%	0	35.25	0.707	2.0%
Na	4 ppm	0	20	22	1.58	7.1%	0	40.33	0.433	1.1%	0	35.6	4.83	13.6%
Nb	1 ppb	25	7	4.8	0.463	9.7%	8	< 1			0	4.13	0.354	8.6%
Nd	0.4 ppb	0	20	10.0	1.45	14.5%	0	21.5	3.44	16.0%	0	68.6	2.40	3.5%
Ni	16 ppb	17	11	46	2.29	5.0%	6	< 16			0	1138	38.3	3.4%
P	4 ppm	25	7	53	3.13	5.9%	8	< 4			0	22.8	0.785	3.4%
Pb	0.8 ppb	2	19	60	4.89	8.2%	0	10.4	5.24	50.4%	0	384	17.6	4.6%
pH	0.1 unit	0	20	4.8	0.135	2.8%	0	6.81	0.394	5.8%	0	4.84	0.056	1.2%
Pr	0.4 ppb	2	18	2.5	0.360	14.6%	0	4.97	0.828	16.7%	0	16.2	0.579	3.6%
Rb	4 ppb	0	20	121	16.6	13.7%	0	46.0	3.07	6.7%	0	247	10.6	4.3%
Re	0.4 ppb	40	0	< 0.4			8	< 0.4			0	1.05	0.031	3.0%
S	4 ppm	1	19	26	1.26	4.8%	0	19.7	1.36	6.9%	0	2788	64.2	2.3%
Sb	1 ppb	24	8	4.9	0.500	10.3%	0	79.4	5.34	6.7%	0	132	3.33	2.5%
Sc	0.08 ppm	40	0	< 0.08			8	< 0.08			8	< 0.08		
Se	80 ppb	40	0	< 80			8	< 80			8	< 80		
Si	2 ppm	0	20	21	1.87	8.9%	0	47.0	4.00	8.5%	0	106	9.77	9.2%
Sm	0.4 ppb	4	18	2.7	0.350	13.2%	0	4.48	0.700	15.6%	0	14.3	0.582	4.1%
Sn	1 ppb	28	6	2.75	0.289	10.5%	1	2.31	1.16	50.3%	0	5.00	0.000	0.0%
Sr	40 ppb	10	14	216	14	6.4%	0	236	18.6	7.9%	0	9249	220	2.4%
Ta	0.8 ppb	38	1	1.4	0.021	1.5%	8	< 0.8			8	< 0.8		
Tb	0.4 ppb	30	5	0.84	0.123	14.6%	0	0.638	0.103	16.2%	0	2.00	0.068	3.4%
Te	2 ppb	40	0	< 2			8	< 2			8	< 2		
Th	2 ppb	16	12	9.6	1.50	15.7%	6	< 2			0	16.00	3.59	22.4%
Ti	40 ppb	9	14	379	41	10.9%	0	169	73.0	43.2%	0	405	24.5	6.1%
Tl	0.4 ppb	26	7	1.8	0.190	10.7%	0	0.845	0.044	5.2%	0	33.2	0.725	2.2%
Tm	0.4 ppb	38	1	0.46	0.035	7.8%	8	< 0.4			0	1.28	0.043	3.4%
U	0.4 ppb	1	19	1.95	0.189	9.7%	0	2.23	0.263	11.8%	0	212	10.1	4.8%
V	8 ppb	14	12	100	4.4	4.4%	0	22.4	3.70	16.5%	0	483	22.4	4.6%
W	2 ppb	34	2	4.0	0.000	0.0%	8	< 0.2			0	4.38	1.06	24.2%
Y	0.8 ppb	0	20	8.0	1.35	16.8%	0	18.5	2.63	14.2%	0	74.3	1.55	2.1%
Yb	0.4 ppb	16	12	1.1	0.131	12.4%	0	1.83	0.243	13.3%	0	9.37	0.324	3.5%
Zn	40 ppb	17	12	402	35	8.7%	7	< 40			0	12187	754	6.2%
Zr	4 ppb	4	18	21	2.83	13.5%	0	7.63	1.06	13.9%	0	87.8	3.77	4.3%

Table 6. Precision summary for blind duplicate and control reference material data generated by the water leach ICP-MS/AES analytical method.

Carbon and Loss on Ignition (LOI)

Data available for:

- PH; A, B and C-horizons - milled <2 mm fraction
- B and C-horizons - unmilled <63 μm fraction

Organic and inorganic carbon soil analysis was done using a Leco CR-412 Carbon Analyser®.

The method involves sample combustion and measurement of the released CO₂ by infrared detection.

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 carbon. The organic carbon is deduced by subtracting the inorganic carbon from the total. The results also include the LOI at 500°C.

Carbon Related Variables - Precision Summary

Variable	LDL	Blind Duplicate Summary					LKSD-4 (n = 24)				SoNE-1 (n = 12)				2711 (n = 10)			
		< DL	Pairs (N)	Mean	SD	%RSD	< DL	Mean	SD	%RSD	< DL	Mean	SD	%RSD	< DL	Mean	SD	%RSD
Total Carbon		0	41	9.5	0.089	0.90%	0	18.5	0.076	0.41%	0	1.87	0.014	0.7%	0	1.71	0.018	1.1%
Organic Carbon		0	41	9.5	0.12	1.3%	0	18.0	0.47	2.6%	0	1.83	0.049	2.7%	0	1.20	0.046	3.8%
Inorganic Carbon		31	41	0.1	0.098	72.6%	0	0.577	0.47	82.3%	4	0.042	0.048	114%	0	0.52	0.041	7.8%
Loss-on-Ignition (500° C)		0	41	21.2	0.32	1.5%	0	38.1	1.07	2.8%	0	7.2	0.58	8.0%	0	5.00	0.49	9.7%

Table 7. Precision summary for blind duplicate and control reference material data for carbon generated by the GSC Sedimentology Laboratory.

pH

Data available for:

- PH; A, B and C-horizons - unmilled <2mm fraction

Procedure:

1. In a 50 ml beaker, place a magnetic stirring bar. Weigh 10 g of soil into the beaker. For organic soils, use 2 g.
2. Add 20 ml of 0.01M CaCl₂ solution. Place onto the magnetic stirrer.
3. Stir for 30 minutes, fast enough to create a vortex, then let stand for 30 minutes to allow the bulk of the sample to settle.
4. Measure pH. For detailed description see Girard et al. (2004).

Conductivity

Data available for:

- *B and C-horizons - unmilled <2mm fraction*

Procedure:

1. The soil sample is air dried and passed through a 2 mm sieve.
2. In a labelled 16 dram plastic vial, put a magnetic stirrer bar. Weigh 20 g (± 0.03 g) of sample into the vial.
3. Add 40.0 ml of ultra pure water. Set on magnetic stirrer.
4. Stir fast enough to create a vortex for at least 30 minutes.
5. Remove from stirrer. Allow solution to reach equilibrium for a minimum of 4 hours, or overnight.
6. Measure conductivity.

Moisture Content

Data available for:

- *PH; A, B and C-horizons - unmodified separate field sample*

Moisture, or water content, is the ratio of the weight of water in a given mass of soil to the weight of the dried sample expressed as a percentage. Because the percentage is expressed as a ratio to the dry weight (by convention) of the sample, percentages $>100\%$ are possible.

Procedure:

1. Record the weight of a clean, dry container and lid (W1).
2. Place a crumbled sample loosely in the container and replace the lid. Weigh the container, lid and content (W2).
3. Remove the lid and place the container, content and lid in an oven at 105°C to dry for 24 hours.
4. After drying, remove container, lid and content from the oven, replace the lid and allow to cool in a desiccator until temperature equilibrium is reached (approximately 2 hours).
5. Record the weight of the container with lid and content (W3).

$$\% \text{ moisture} = ((W2 - W1)/(W3 - W1)) * 100 (W3 - W1)$$

Bulk Density

Data available for:

- *PH; A, B and C-horizons - unmodified separate field sample*

Soil bulk density is defined as the ratio of the mass of an oven-dry soil sample to the volume of that sample at a specified moisture condition. It provides a measure of soil porosity and can be correlated to other physical soil properties (Carter, 1993).



Figure 9. Photo showing collected sample for bulk density and moisture determinations using a clear acrylic tube.

A separate undisturbed core sample was collected in the field using a clear lexan cylinder that had a bevelled cutting edge (Figure 9). The sample was extruded into a tin container on which the length and diameter of the core was recorded. In the lab the sample was oven dried at 105°C for 1 to 2 days, until the weight was constant.

$$\text{Bulk Density (g/cc)} = ((\text{core dry weight (g)})/(\text{volume core (mL)}))$$

Particle Size Analysis

Data available for:

- *B and C-horizons - original unmodified material*

The procedure for grain size analysis includes sand-silt-clay and complete grain size analysis. The classes of sizes greater than 0.063 mm are determined by wet sieving through a stack of appropriately sized sieves. The classes of sizes less than 0.063 mm are determined using a

Lecotrac LT-100® Particle Size Analyser. The definition of clay size varies amongst fields of research but for the NASGLP it was defined as <0.002 mm. There are modifications to the procedure for low weight samples, not discussed here, that are documented in Girard et al. (2004).

Sample preparation:

- 1) Split ~ 200 to 300 g of the original sample.
- 2) Take a quarter of this split and place it in a 16 dram vial. Set this vial aside for the particle size analyser (split B).
- 3) Let the remaining sample air dry in a weigh boat (split A).
- 4) If the sample weight is low (<50 g), place the whole sample in the vial and follow the procedure for low weight samples.

Grain size sieving procedure:

- 1) Once the sample is dry (split A), record the dry sample weight.
- 2) Add a 5% Na hexametaphosphate solution and mix in milkshake mixer.
- 3) Decant into a stack of sieves, (2.0, 0.063, and 0.045 mm) and wet sieve under running tap water, discarding the <0.045 mm fraction.
- 4) Dry the sieves containing the samples in an oven at 105°C for 15 to 30 minutes.
- 5) Record the dry weight of the >2.0 and >0.063 mm fractions.
- 6) Pour the >0.063 mm fraction onto a stack of sieves (2.0, 1.4, 1.0, 0.71, 0.50, 0.35, 0.25, 0.18, 0.12, 0.088, and 0.063 mm).
- 7) Set the sieves on the RO-tap® mechanical sieve shaker, and sieve for 15 minutes.
- 8) Transfer the sieved fractions into metal weighing boats, and record the weight for each fraction.

Procedure for determination of silt and clay sized fractions (<0.063 mm)

- 1) To the vial containing split B, add hexametaphosphate solution (50 g/l) and let it soak for a minimum of three days.
- 2) Decant sample into bucket and mix in milkshake mixer.
- 3) Using a 0.090 mm sieve, wet sieve with distilled water into a 1 litre beaker. If the sample contains a lot of coarse fraction, use a 0.5 mm sieve on top of the 0.090 mm sieve to protect it. Discard the >0.090 mm material.
- 4) Suspend the sample contained in the 1 litre beaker using a propeller, fast enough to create a vortex.

- 5) Draw a 3 to 5 ml aliquot from the side of the beaker, away from the vortex, at mid-height, using a 5 ml disposable syringe. Run the aliquot on the Lecotrac LT-100® particle size analyser.

Laboratory Gamma-ray Spectrometry analysis for K (%), eU (ppm) and eTh (ppm)

The GSC maintains a laboratory spectrometer system for analysis of rock, till and soil samples. The spectrometer system measures radioelement concentrations of potassium (%), equivalent uranium (ppm) and equivalent thorium (ppm). The term “equivalent” is used for U and Th concentrations as they are determined indirectly from their daughter products (Bi^{214} and Tl^{208} respectively) that are assumed to be in equilibrium with their parent isotope. Potassium concentration is determined directly from K^{40} .

The spectrometer system is composed of two, lead-shielded, 14 cm by 14 cm NaI detectors. Calibration of the spectrometer is accomplished using potassium (RGK-1), equivalent uranium (RGU-1), and equivalent thorium (RGTh-1) standards recognized by the International Atomic Energy Agency (IAEA, 1987). The laboratory utilizes 8-oz (400mm x 102mm) shallow, seamless steel cans. The can is lined with plastic wrap to prevent trace element contamination from the sample can in the event subsequent chemical analysis is required. Each sample can is completely filled with bulk (all size fractions), air dried sample material. The weight of the sample can, empty and full is recorded. The can is then sealed and stored for 21 days to allow the radon and Bi^{214} to reach equilibrium.

Procedures for Analytical Quality Control (QC)

Laboratory Gamma Ray Spectrometry (LGRS) Analyses

As part of quality control for LGRS analysis the following procedures are followed:

- Samples are analyzed in batches of 20
- Control reference material (3 - IAEA standards) in addition to a background (distilled water) sample are analyzed before and after each batch.
- Repeat analysis is performed on randomly selected samples at a rate of 1 per every 10 samples.
- Samples and standards are counted for 20 minutes.

For 2007, using the twice daily repeated measurements of the 3 - IAEA reference standards (RGK-1; RGU-1 and RGTh-1) 58 measurements are available. The means and standard deviations of these measurements are as follows (numbers in brackets are Certificate of Analysis values (IAEA, 1987)):

IAEA/RGK-1 – 44.8 +/- 0.36% (44.8 +/- 0.3%)

IAEA/RGTh-1 – 803.9 +/- 4.59 ppm (800 +/- 16 ppm)

IAEA/RGU-1 – 399.98 +/- 1.82 ppm (400 +/- 2 ppm).

The % RSD may be used to assess the general elemental precision for a batch of samples. Figure 10 shows scatter-plots of calculated % RSD from blind duplicate data for the LGRS analysis of percent K and ppm eU and eTh. For K, eU and eTh concentrations below approximately 0.3%, 1.7 ppm and 4.5 ppm respectively the % RSD is slightly above the accepted value of 20% and therefore readers should be cognisant of the fact that analysis at or below these levels will exhibit more variability. Duplicate analysis of samples under approximately 100g tend to display %RSD's that exceed 20%. These low weights result in lower count rates that result in higher than expected statistical variations. In house processing software normalizes sample count rates to 200g. So for samples with low weights, predominantly PH and A-horizon samples, expected statistical counting errors may be amplified resulting in increased variability.

Soil Analyses

As part of the quality control (QC) for the project soil analytical data, the following procedures were followed:

- 1) Field duplicates were collected at a frequency of ~5%.
- 2) Control reference materials (CRMs) were inserted at an overall rate of ~5%.
- 3) Analytical duplicates, generally prepared from one of the field duplicate samples, were prepared at a rate of ~5%.
- 4) Several elements were determined by more than one analytical method and the resultant data plotted on scatter plots, element by element. Visual inspection of these plots provided an additional measure of QC.

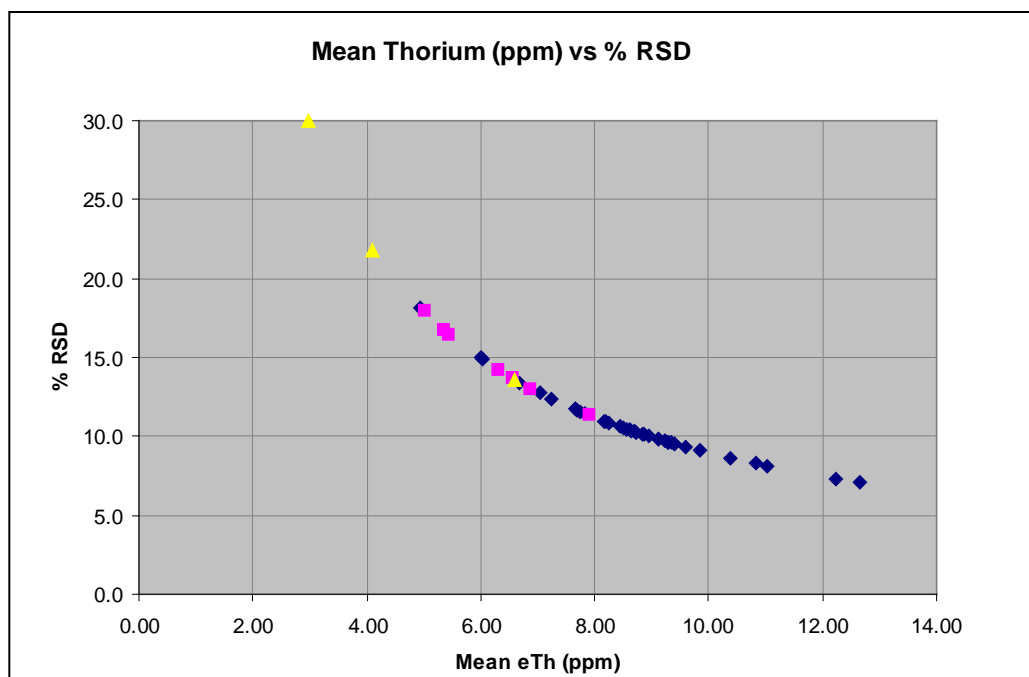
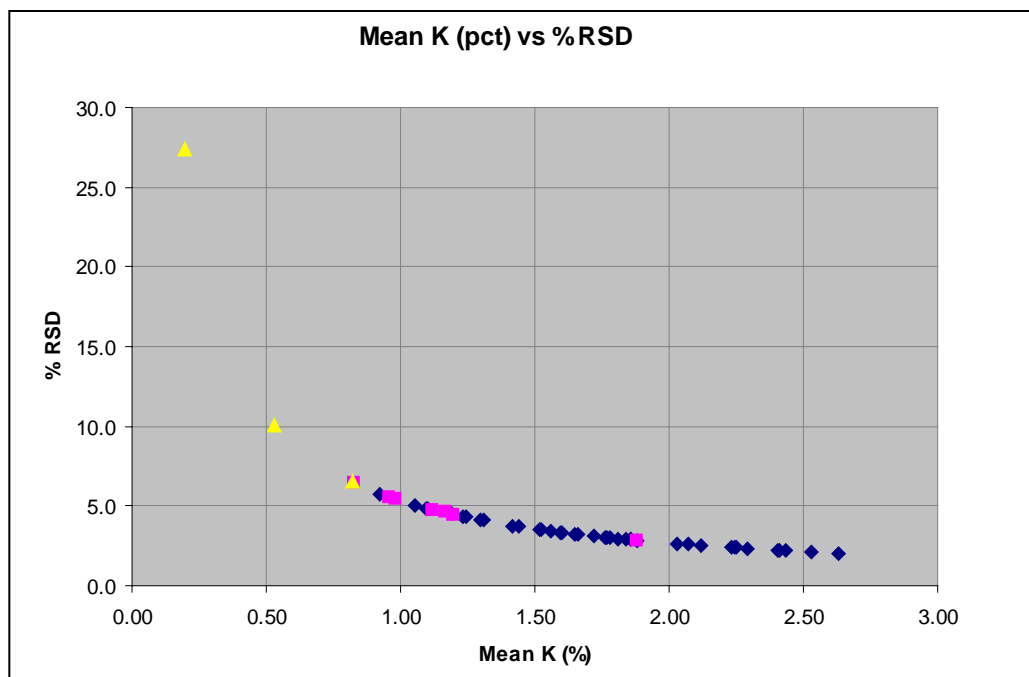
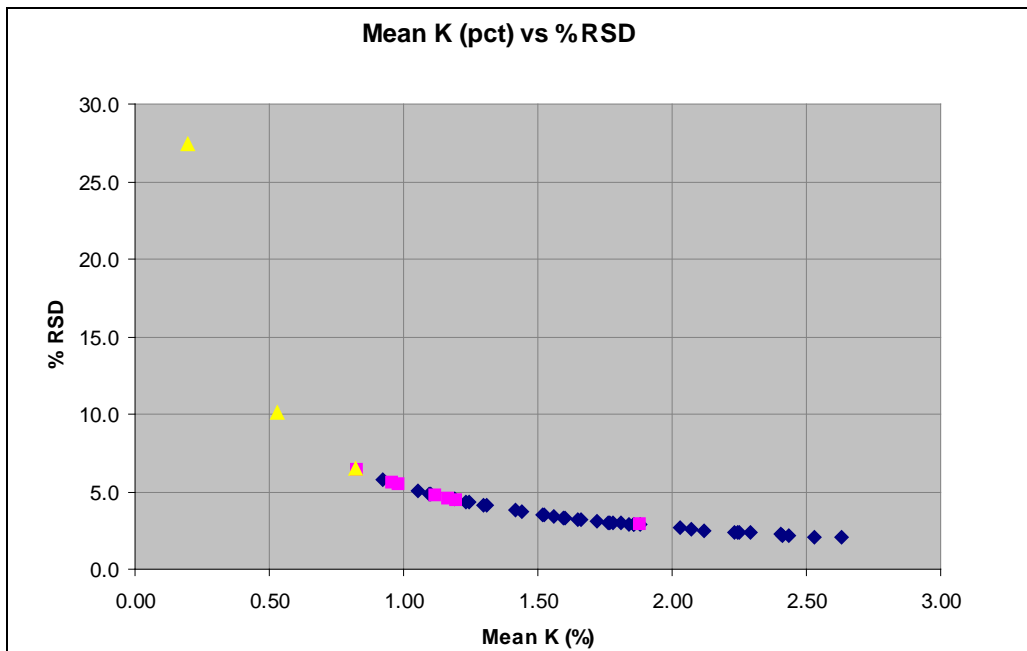


Figure 10. Mean K (pct), eU (ppm) and eTh (ppm) analysis for 49 duplicate analysis for 2007 NASGLP samples analyzed by laboratory gamma ray spectrometry. Sample weights less than 100g shown with yellow triangles, sample weights between 100g and 200g shown with red squares and sample weights above 200g shown with blue diamonds.

- 5) To facilitate the QC process, samples were collected and prepared in blocks of 20 according to the design used since the early 1970s for the National Geochemical Reconnaissance (NGR) program (Garrett, 1974, 1983; Friske and Hornbrook, 1991). As described earlier, each block consisted of 17 routine field samples, a control reference, a laboratory blind duplicate and a field duplicate. The field duplicate is a complete and separate set of samples collected within 10 meters of the main site. There is no set procedure for choosing which of the 17 sites in each block of 20 to duplicate; it is decided by the sampling team. In the field, the first number in each block of 20 is reserved for later use as a laboratory duplicate. A second number within the block is also reserved at random for the CRM sample. Back at the laboratory the blind duplicate is prepared by splitting one sample from the 18 field samples, preferably one of the field duplicates.
- 6) The precision and accuracy of the data were determined and evaluated. In some cases also, as described below, element concentrations were measured using more than one method.

Statistical summaries of blind duplicate and standard reference materials are given in Tables 3 to 11 that are divided based on the five analytical methods used for which QC data are available: 4-acid ICP-MS/AES; 3050B ICP-MS/AES; INA; water leach ICP-MS/AES and carbon analyses. Figures 11 and 12 are examples of Time-Charts of CRM data that were used to monitor accuracy and drift of the data, both within and between analytical batches. Following are a few general comments on the precision and accuracy of the project data primarily using the 4-acid data for illustrative purposes.

It was decided to release the data for all elements even though some have a significant percentage of values that are at or below the lower detection limit. Users of these data need to be cognisant of the limitations of these data and ensure that any interpretation respects these limitations.

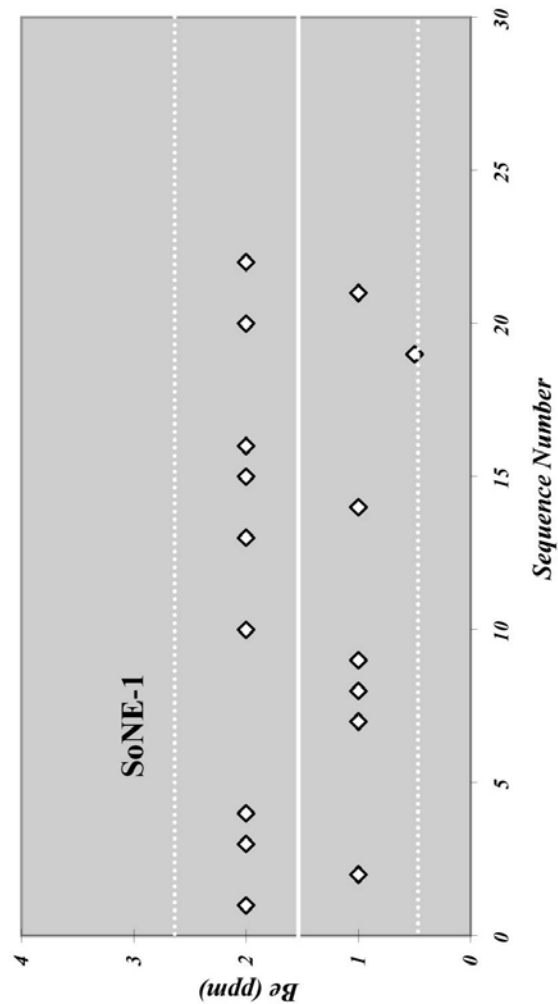
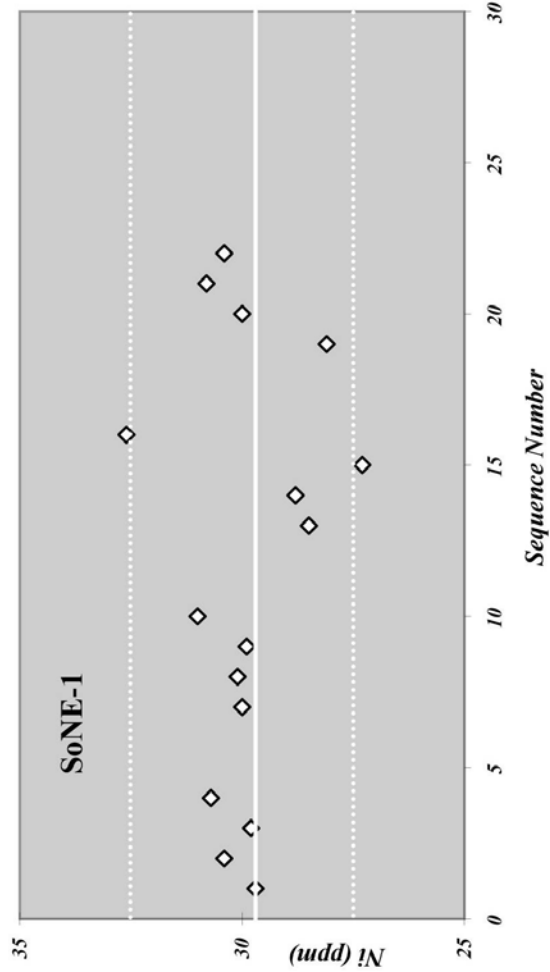
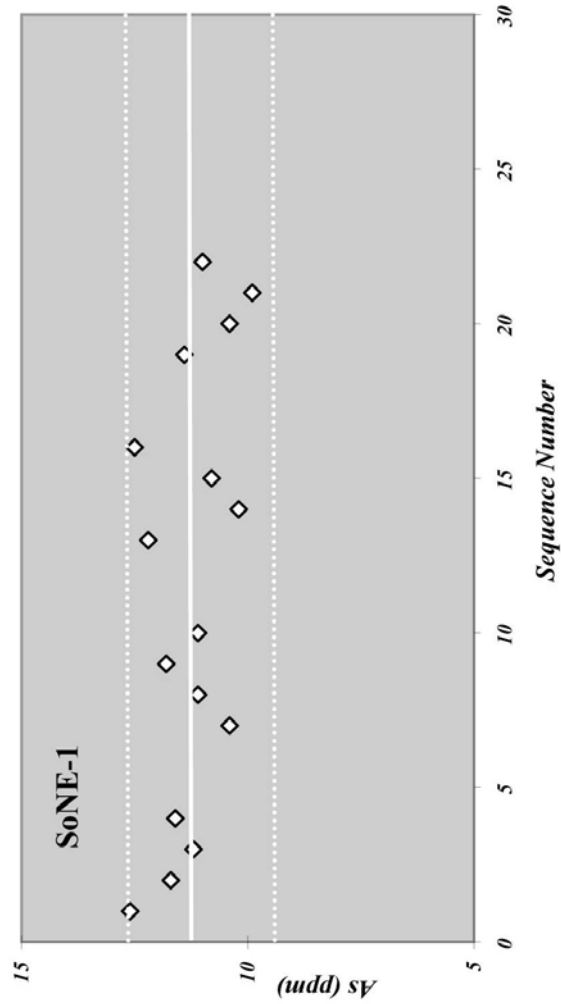


Figure 11. Time charts for Be, Ni and As data generated for SoNE-1 from 5 separate analytical batches (sequence numbers 1-4 = batch 1; 6-10 = batch 2; 13-16 = batch 3; 19-22 = batch 4 and 25-28 = batch 5). These data were obtained for the <2mm fraction of the C-horizon using a 4-acid dissolution.

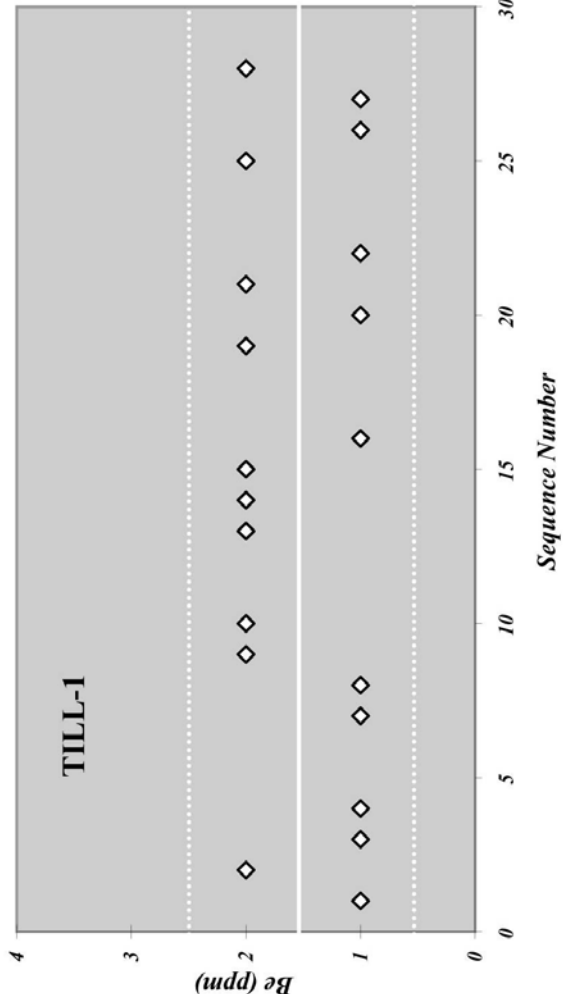
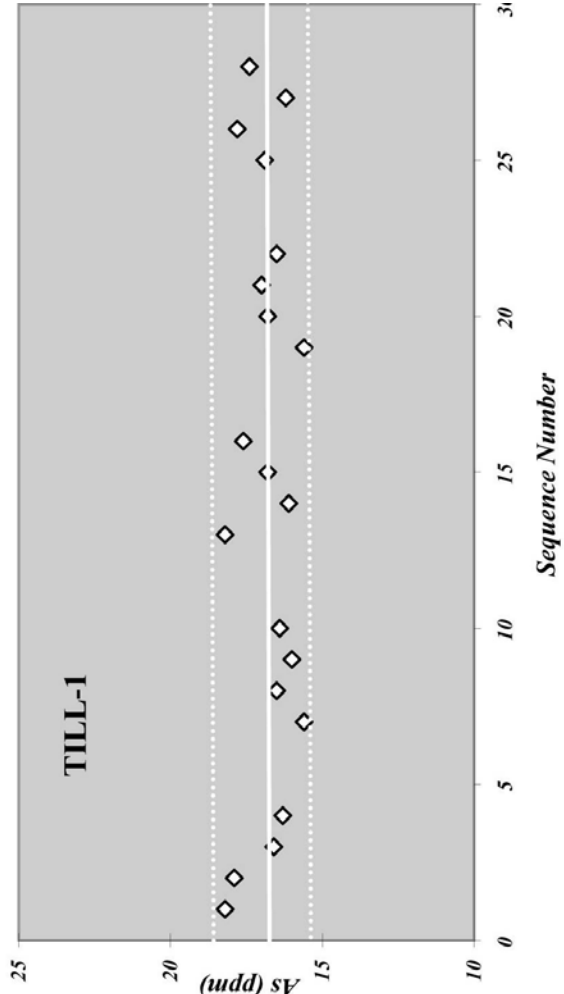
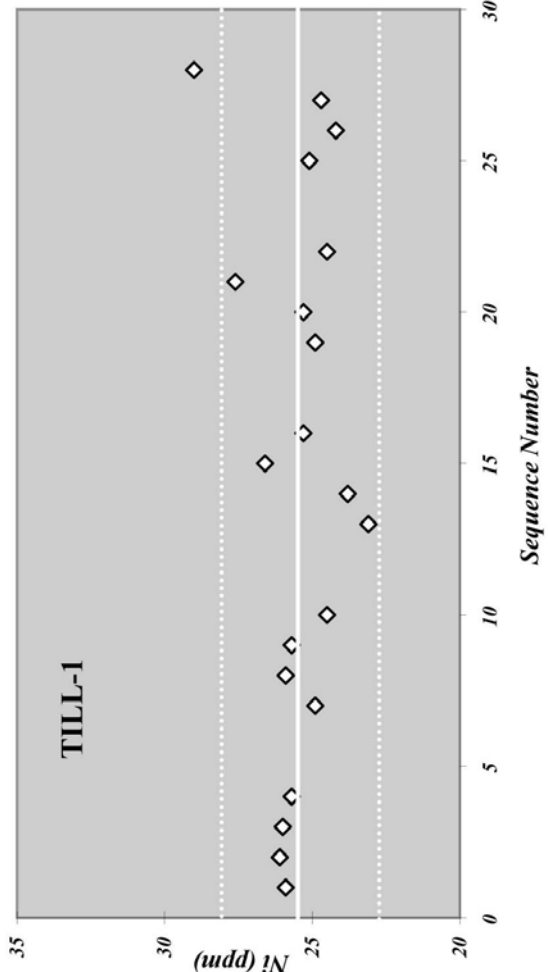


Figure 12. Time charts for Be, Ni and As data generated for TILL-1 from 5 separate analytical batches (sequence numbers 1-4 = batch 1; 6-10 = batch 2; 13-16 = batch 3; 19-22 = batch 4 and 25-28 = batch 5). These data were obtained for the <2mm fraction of the C-horizon using a 4-acid dissolution.

Determination of Data Precision

“Precision is the closeness of agreement between independent test results obtained under stipulated conditions” as stated by Reimann *et al.*(2008). For the NASGLP analytical data, precision was estimated primarily by the evaluation of the blind duplicate sample pairs and, to a lesser extent, by replicate analysis of CRMs. Standard deviations for blind duplicate samples and replicate analysis of control reference materials were calculated as follows.

Standard deviation calculation for blind duplicates

$$s = \sqrt{\frac{\sum d^2}{2k}}$$

d = difference of duplicate measurements

k = number of sets of duplicate measurements

Note: Where the concentration of elements in one or both blind duplicates was lower than the detection limit, they were not included in the calculation.

Standard deviation calculation for replicate control reference analysis

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

x_i = each individual value

\bar{x} = mean of all values

n = number of values

For purposes of calculating the mean, values below the lower detection level were set to one half the limit of detection, but only if more than 50% of the samples had values above the limit. If the values for more than 50% were below the limit, the mean was set to less than detection limit and no standard deviation was calculated.

Percent relative standard deviation (%RSD) calculation:

$$\%RSD = 100 * (s / \bar{x})$$

s = standard deviation

\bar{x} = mean

In general, for sample batches where the mean is more than 5 times greater than the reported detection limit, elemental precision is considered acceptable if the calculated RSD for the duplicate samples is no greater than 20%. However, where concentrations approach the detection limit, there is in most cases a trend of decreasing precision as illustrated by Figure 13. In Figure 13, blind duplicate data obtained using the 4-acid and 3050B digestions from NASGLP samples from 2007 are used as an example. The scatter plots show the calculated %RSD plotted against the ratio of the mean to lower detection limit for each element. For the 3050B data, 5 elements (Au, B, S, Se and Te) have calculated RSDs of greater than 20% (Table 4). Except for Se (mean/LDL = 7.7), all have mean values for the blind duplicate pairs less than 5 times the lower detection limit. This suggests that the lower detection limit for Se may actually be higher than the stated value. For the 4-acid results only Be has a %RSD greater than 20% at 25.5% (mean/LDL = 1.8; Table 3). In addition to the data values being close to the detection limit, the poor precision for Be may also reflect data rounding.

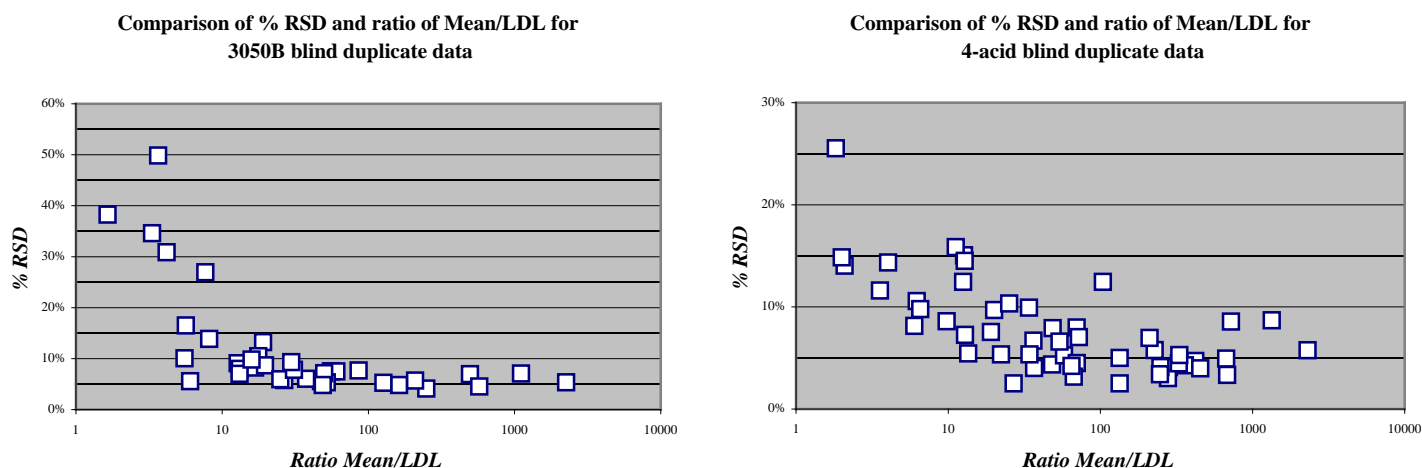


Figure 13. Scatter plots illustrating the relationship between calculated % RSD and ratio of mean to lower detection limit (LDL) for the 4-acid and 3050B blind duplicate data, as per Tables 3 and 4.

Determination of Data Accuracy

Simply defined, accuracy is the agreement between an observed value and an accepted reference value. For the NASGLP, four CRMs were used to monitor the accuracy of the data, both within and between analytical batches. The first two - *TILL-1* and *LKSD-4* - composed respectively of till and lake sediment, were prepared and characterized at GSC. They are two of a series of 12 standards consisting of tills (4), stream sediments (4) and lake sediments (4), all available for purchase from Natural Resource Canada - CANMET. For these standards, Lynch (1990, 1996, 1999) summarized the recommended total and partial concentrations with standard deviations for

a wide range of elements. The third - *SRM 271* - is a spiked soil moderately enriched in As and other elements and is available from the American National Institute of Standards and Technology (NIST). Certified values of total element concentrations (with no standard deviations) are provided and also non-certified values obtained using the USEPA Method 3050 (NIST, 2002). The fourth - *SoNE-1* - is composed of Nebraska soil and is uncertified. It was prepared and analyzed in-house at the USGS specifically for the NASGLP and the recommended element levels, excluding standard deviations, were made available to NASGLP participants. All *SoNE-1* values are considered to be total concentrations because elements such as Cr, Ti, and Nb that are resistant to the 4-acid solubilisation were also determined using a fusion technique (David Smith, personal comm.). *SoNE-1* is a common standard being used for the NASGLP in Canada and the United States to allow for comparison and integration of the two data sets (Smith *et al.*, 2009).

Tables 8, 9, 10 and 11 summarize the CRM project data compared to proposed values for the standards. In the case of the 4-acid data the proposed values whether they be certified, provisional or recommended are total values. Although the 4-acid digestion is often considered a total extraction it is in fact total for some elements and partial for others. Moreover, for a given element it may be total or partial depending on mineralogy. In general most silicates dissolve but values for elements such as REEs, Al, Ba, Ta, Nb, Hf, Cr and Zr are often not total as they can occur in oxides and other refractory minerals. Also volatilization during fuming may result in some loss of As, Sb and Au. Because of these uncertainties, the importance of the project 4-acid values for many of the elements summarized in Table 8 is in providing bench marks to which other data generated by the same method for the same CRMs can be compared, more so than providing an estimate of data trueness. To a lesser extent there are also uncertainties associated with the 3050B accuracy data because of differences in the implementation of “aqua-regia” digestions. The carbon and INA data are total; *sensu-stricto*.

To monitor the accuracy (hence drift) of the data, both within and between analytical batches, new CRM data were plotted in a series of time charts as illustrated by Figures 11 and 12. On these charts element data are plotted against a sequence of numbers that corresponds, time-wise, to the order in which individual samples were analysed. The solid line represents the average for all samples and the dashed lines the mean ± 2.0 standard deviations. Data for a block of samples were considered acceptable, based on the CRMs, if the value for a given element was within

±2.0 standard deviations of the mean. Figures 11 and 12 show 4-acid data for SoNE-1 and TILL-1 generated in 5 distinct batches. The sequence numbers 1 to 4 correspond to the first batch of data, 6 to 10 the second, 13 to 16 to the third, 19 to 22 to the fourth and 25 to 28 to the fifth. There are no SoNE-1 data for the fifth batch. As is evident from these figures, there is no significant drift in concentrations levels for As, Ni and Be over time. The last Ni value for TILL-1 in Batch 5 is slightly outside the defined limits but the block of data was accepted because BD and other CRM data in the vicinity of this sample were within limits.

4acid ICP-MS/AES Accuracy Summary

Element	LDL	TILL-1 (n = 20)					LKSD-4 (n = 12)					SoNE-1 (n = 16)					2711 (n = 11)				
		Proposed value		Project value			Proposed value		Project value			Proposed value		Project value			Proposed value		Project value		
		Value	SD	<DL	Mean	% Rcvry	Value	SD	<DL	Mean	% Rcvry	Value	SD	<DL	Mean	% Rcvry	Value	SD	<DL	Mean	% Rcvry
Ag	20 ppb			0	432		< 500		0	285		< 1000		0	261		4630	390	0	3857	83%
Al	0.02 %	7.3	0.08	0	6.80	93%	3.12	0.21	0	2.97	95%	6.28	0	6.08	97%		6.53	0.09	0	6.17	95%
As	0.2 ppm	18	1	0	16.8	93%	16	1	0	12.51	78%	11	0	11.2	102%		105	8	0	95.9	91%
Au	100 ppb	13	4	18	< 100		2	2	12	< 100				16	< 100		30		10	< 100	
Ba	1 ppm	702	59	0	623	89%	330	55	0	265	80%	730	0	0	651	89%	726	38	0	635	87%
Be	1 ppm	2.4	0.6	0	1.50	63%	1	0.03	11	< 1		1.6	1	1.53	96%				0	2.00	
Bi	0.04 ppm	< 5		0	1.90				0	0.503		0.29	0	0.272	94%				0	2.33	
Ca	0.02 %	1.94	0.09	0	1.81	93%	1.29	0.14	0	1.28	99%	0.61	0	0.608	100%		2.88	0.08	0	2.75	95%
Cd	0.02 ppm			0	0.367		2	0.2	0	2.03	101%	0.4	0	0.503	117%		42	0.25	0	42.1	100%
Ce	0.02 ppm	71	6	0	61.7	87%	48	6	0	42.6	89%	71	0	67.7	95%		69		0	61.1	89%
Co	0.2 ppm	18	2	0	18.2	101%	11	1	0	11.3	102%	12	0	12.5	104%		10		0	10.3	103%
Cr	1 ppm	65	6	0	54.9	84%	33	6	0	30.3	92%	69	0	56.7	82%		47		0	37.8	80%
Cs	0.1 ppm	1	0.2	0	0.910	91%	1.7	0.6	0	1.34	79%	4.6	0	4.06	88%		6.1		0	6.06	99%
Cu	0.02 ppm	47	4	0	49.0	104%	31	4	0	32.8	106%	22	0	23.0	105%		114	2	0	111	97%
Dy	0.1 ppm			0	4.65		3.7	0.2	0	3.15	85%			0	3.56		5.6		0	3.98	71%
Er	0.1 ppm			0	2.53				0	1.78				0	1.83				0	2.12	
Eu	0.1 ppm	1.3	0.5	0	1.35	103%	1.1	0.3	0	0.983	89%			0	1.01		1.1		0	0.891	81%
Fe	0.02 %	4.81	0.22	0	4.56	95%	2.9	0.2	0	2.74	94%	2.89	0	2.72	94%		2.89	0.06	0	2.72	94%
Ga	0.02 ppm			0	16.7				0	7.46		14	0	13.8	98%		15		0	15.0	100%
Gd	0.1 ppm			0	5.18				0	3.83				0	4.59				0	4.69	
Hf	0.02 ppm	13	1	0	4.28	33%	2.8	0.5	0	1.35	48%			0	3.27		7.3		0	2.44	33%
Ho	0.1 ppm			0	0.930				0	0.633				0	0.675		1		0	0.782	78%
K	0.02 %	1.84	0.09	0	1.69	92%	0.66	0.05	0	0.661	100%	1.86	0	1.81	97%		2.45	0.08	0	2.25	92%
La	0.1 ppm	28	2	0	25.4	91%	26	2	0	24.0	92%	36	0	35.7	99%		40		0	33.6	84%
Li	0.1 ppm	15	1	0	15.8	106%	12	2	0	12.5	104%	27	0	29.4	109%				0	27.0	
Lu	0.1 ppm	0.6	0.1	0	0.400	67%	0.5	0.1	0	0.283	57%			0	0.313				0	0.345	
Mg	0.02 %	1.3	0.05	0	1.21	93%	0.56	0.04	0	0.533	95%	0.62	0	0.595	96%		1.05	0.03	0	0.969	92%
Mn	2 ppm	1420	75	0	1444	102%	500	30	0	479	96%	630	0	605	96%		638	28	0	628	98%
Mo	0.05 ppm	2	1	0	0.871	44%	< 5		0	1.86		1.2	0	1.12	93%		1.6		0	1.54	96%
Na	0.002 %	2.01	0.08	0	2.06	102%	0.52	0.015	0	0.556	107%	0.74	0	0.740	100%		1.14	0.03	0	1.14	100%
Nb	0.04 ppm	10	2	0	9.01	90%	9	7	0	3.91	43%	21	0	12.01	57%				0	16.7	
Nd	0.1 ppm	26	2	0	29.0	112%	25	2.4	0	25.3	101%			0	32.8				0	29.7	
Ni	0.1 ppm	24	4	0	25.4	106%	31	5	0	35.0	113%	24	0	29.9	125%		20.6	1.1	0	19.5	94%
P	0.001 %	0.093	0.006	0	0.095	103%	0.144	0.013	0	0.142	98%	0.051	0	0.052	103%		0.086	0.007	0	0.085	99%
Pb	0.02 ppm	22	3	0	23.1	105%	91	6	0	93.1	102%	23	0	22.4	97%		1162	31	0	1103	95%
Pr	0.1 ppm			0	6.89				0	6.08				0	8.43				0	7.62	
Rb	0.1 ppm	44	6	0	39.2	89%	28	10	0	23.5	84%	88	0	81.8	93%		110		0	99.8	91%
S	0.04 %	< 0.05		20	< 0.04		0.99	0.09	0	0.968	98%	0.03	16	< 0.04			0.042	0.001	11	< 0.04	
Sb	0.02 ppm	7.8	0.5	0	7.14	92%	1.7	0.1	0	1.52	89%	1.3	0	1.29	99%		19.4	1.8	0	19.1	98%
Sc	0.1 ppm	13	2	0	11.3	87%	7	1	0	5.81	83%	9	0	7.28	81%		9		0	7.78	86%
Sm	0.1 ppm	5.9	0.4	0	5.33	90%	5	0.9	0	4.33	87%			0	5.46		5.9		0	5.06	86%
Sn	0.1 ppm			0	1.74		5	1	0	3.98	80%	1.7	0	1.54	90%				0	3.44	
Sr	1 ppm	291	10	0	297	102%	110	38	0	124	113%	130	0	131	101%		245	0.7	0	236	97%
Ta	0.1 ppm	0.7	0.1	0	0.395	56%	0.4	0.04	0	0.208	52%			0	0.613				0	0.891	
Tb	0.1 ppm	1.1	0.2	0	0.775	70%	1.2	0.7	0	0.517	43%			0	0.619				0	0.645	
Th	0.1 ppm	5.6	0.5	0	5.23	93%	5.1	0.7	0	4.69	92%	12	0	11.0	91%		14		0	12.6	90%
Ti	0.001 %	0.599	0.021	0	0.494	82%	0.227	0.047	0	0.169	74%	0.40	0	0.324	81%		0.306	0.023	0	0.275	90%
Tm	0.1 ppm			0	0.400				0	0.258				0	0.294				0	0.355	
U	0.1 ppm	2.2	0.3	0	1.74	79%	31	1.8	0	29.4	95%	2.8	0	2.91	104%		2.6		0	2.45	94%
V	1 ppm	99	10	0	96.3	97%	49	8	0	39.9	81%	110	0	95.7	87%		81.6	2.9	0	74.5	91%
W	0.1 ppm	< 1		0	0.565		< 4		0	0.550		1	0	1.14	114%		3		0	2.77	92%
Y	0.1 ppm	38	4	0	24.5	64%	23	10	0	18.7	81%	30	0	19.4	65%		25		0	22.6	90%
Yb	0.1 ppm	3.9	0.4	0	2.73	70%	2	0.2	0	1.86	93%			0	2.12		2.7		0	2.25	84%
Zn	0.2 ppm	98	10	0	90.4	92%	194	19	0	182	94%	83	0	81.2	98%		350	4.8	0	326	93%
Zr	0.2 ppm	502	58	0	149	30%	105	17	0	45.7	44%			0	114		230		0	75.0	33%

* For purposes of Mean calculation: < LDL values set to 1/2 LDL if more than 50% of values >LDL; Mean set to < LDL if > 50% of values < LDL.

Table 8. Accuracy summary of control reference material data generated by the 4-acid ICP-MS/AES analytical method.

3050B Accuracy Summary

Element	LDL	<u>TILL-1 (n = 12)</u>					<u>LKSD-4 (n = 12)</u>				
		<u>Proposed value</u>			<u>Project value</u>		<u>Proposed value</u>			<u>Project value</u>	
		Value	SD	< DL	Mean	% Rcvry	Value	SD	< DL	Mean	% Rcvry
Ag	2 ppb	200	100	0	201	100%	200	100	0	205	102%
Al	0.01 %			0	1.86		1.44	0.19	0	1.34	93%
As	0.1 ppm	13	4	0	16.6	128%	12	3	0	13.6	113%
Au	0.2 ppb			0	12.8				0	3.13	
B	1 ppm			0	2.71				0	10.3	
Ba	0.5 ppm	84	6	0	79.4	94%	135	4	0	134	99%
Bi	0.02 ppm	< 3		0	2.10				0	0.558	
Ca	0.01 %			0	0.353		0.89	0.05	0	0.879	99%
Cd	0.01 ppm	< 0.2		0	0.248		1.9	0.5	0	2.30	121%
Co	0.1 ppm	12	1	0	14.1	118%	11	1	0	10.5	95%
Cr	0.5 ppm	30	3	0	31.8	106%	21	2	0	22.7	108%
Cu	0.01 ppm	48	2	0	50.9	106%	30	3	0	33.4	111%
Fe	0.01 %	3.1	0.2	0	3.45	111%	2.7	0.3	0	2.56	95%
Ga	0.1 ppm			0	6.38				0	4.08	
Hg	5 ppb	92	11	0	125	136%	190	17	0	169	89%
K	0.01 %			0	0.061				0	0.113	
La	0.5 ppm			0	20.2				0	21.7	
Mg	0.01			0	0.597		0.41	0.05	0	0.384	94%
Mn	1 ppm	950	70	0	1140	120%	430	30	0	430	100%
Mo	0.01 ppm	< 2		0	0.713		2.0	0.6	0	1.67	83%
Na	0.001 %			0	0.030				0	0.018	
Ni	0.1 ppm	18	2	0	18.7	104%	32	5	0	33.3	104%
P	0.001 %			0	0.091		0.144	0.018	0	0.138	96%
Pb	0.01 ppm	12	1	0	14.6	122%	93	8	0	93.6	101%
S	0.02 %			0	0.035				0	1.06	
Sb	0.02 ppm			0	4.60		1.5	0.6	0	0.972	65%
Sc	0.1 ppm			0	4.57				0	2.85	
Se	0.1 ppm			0	0.417				0	2.95	
Sr	0.5 ppm			0	11.7		41	5	0	40.7	99%
Te	0.02 ppm			0	0.033				0	0.134	
Th	0.1 ppm			0	2.28				0	0.750	
Ti	0.001%			0	0.129		0.066	0.0086	0	0.067	102%
Tl	0.02 ppm			0	0.126				0	0.473	
U	0.05 ppm			0	0.950				0	31.1	
V	2 ppm	48	8	0	61.8	129%	32	10	0	38.8	121%
W	0.05 ppm			0	0.217				0	0.317	
Zn	0.1 ppm	70	7	0	73.6	105%	189	10	0	199	105%

Table 9. Accuracy summary of control reference material generated by the modified 3050B ICP-MS/AES analytical method.

The ideal way to minimize drift would be to analyse all samples from a given project at the same time as one large batch. However the desire of stakeholders to see data as soon as possible,

unexpected fluctuations in funding and the undertaking of multi-year projects most often necessitates generating project data in multiple batches. Hence having and monitoring CRM data is critical.

INAA Accuracy Summary

Element	LDL	<u>TILL-1 (n = 7)</u>					<u>LKSD-4 (n = 7)</u>					<u>SoNE-1 (n = 7)</u>					<u>2711 (n = 5)</u>				
		<u>Proposed value</u>		<u>Project Values</u>			<u>Proposed value</u>		<u>Project Values</u>			<u>Proposed value</u>		<u>Project Values</u>			<u>Proposed value</u>		<u>Project Values</u>		
		Value	SD	<DL	Mean	% Rcvry	Value	SD	<DL	Mean	% Rcvry	Value	SD	<DL	Mean	% Rcvry	Value	SD	<DL	Mean	% Rcvry
Ag	2 ppm			7	<2		<500		7	<2000		<1	7	<2			4630	390	2	3400	73%
As	0.5 ppm	18	1	0	18	102%	16	1	0	15.86	99%	11	0	11.3	103%		105	8	0	99.6	95%
Au	2 ppb	13	4	0	25	192%	2	2	7	<2		2	2	6.57			30	0	0	34.8	116%
Ba	50 ppm	702	59	0	713	102%	330	55	0	327	99%	730	0	710	97%		726	38	0	712	98%
Br	0.5 ppm	6.4	0.6	0	6.2	97%			0	49.5			0	7.90				5	0	5.5	
Cd	5 ppm			7	<5		2	0.2	7	<5		0.4	7	<5			42	0.25	0	37.6	90%
Ce	5 ppm	71	6	0	70	98%	48	6	0	46.6	97%	71	0	81.6	115%		69	0	0	69.0	100%
Co	5 ppm	18	2	0	19	107%	11	1	0	11.9	108%	12	0	12.7	106%		10	1	1	8.10	81%
Cr	20 ppm	65	6	0	60	93%	33	6	3	22.7	69%	69	0	72.3	105%		47	1	1	49.8	106%
Cs	0.5 ppm	1	0.2	0	1.14	114%	1.7	0.6	2	1.13	66%	4.6	0	4.29	93%		6.1	0	0	6.20	102%
Eu	1 ppm	1.3	0.5	4	<2		1.1	0.3	3	1.21	110%		6	<1			1.1	5	5	<1	
Fe	0.2 %	4.81	0.22	0	4.9	101%	2.9	0.2	0	2.94	101%	2.89	0	2.83	98%		2.89	0.06	0	2.98	103%
Hf	1 ppm	13	1	0	13	101%	2.8	0.5	2	2.29	82%		0	11.7			7.3	0	0	7.00	96%
Ir	50 ppm			7	<50				7	<50			7	<50				5	5	<50	
La	2 ppm	28	2	0	29	103%	26	2	0	25.6	98%	36	0	40.4	112%		40	0	0	37.2	93%
Lu	0.2 ppm	0.6	0.1	0	0.671	112%	0.5	0.1	4	<0.2			0	0.614				0	0	0.460	
Mo	1 ppm	2	1	7	<1		<5		5	<1		1.2	5	<1			1.6	3	3	<1	
Na	0.02 %	2.01	0.08	0	2.03	101%	0.52	0.015	0	0.581	112%	0.74	0	0.749	101%		1.14	0.03	0	1.14	100%
Ni	10 ppm	24	4	0	21	88%	31	5	3	19.7	64%	24	2	23.3	97%		20.6	1.1	3	<10	
Rb	5 ppm	44	6	0	37	85%	28	10	2	20.0	71%	88	0	86.6	98%		110	0	0	103	94%
Sb	0.1 ppm	7.8	0.5	0	7.5	97%	1.7	0.1	0	1.74	103%	1.3	0	1.39	107%		19.4	1.8	0	19.3	100%
Sc	0.2 ppm	13	2	0	13.7	105%	7	1	0	7.1	102%	9	0	9.14	102%		9	0	0	9.50	106%
Se	5 ppm			7	<5				7	<5		0.5	7	<5			1.52	0.14	5	<5	
Sm	0.1 ppm	5.9	0.4	0	6.1	104%	5	0.9	0	4.79	96%		0	6.34			5.9	0	0	5.76	98%
Sn	100 ppm			7	<100		5	1	7	<100		1.7	7	<100				5	5	<100	
Ta	0.5 ppm	0.7	0.1	0	0.779	111%	0.4	0.04	5	<0.5			0	0.950				0	0	1.76	
Tb	0.5 ppm	1.1	0.2	0	0.929	84%	1.2	0.7	3	0.507	42%		0	1.01				0	0	0.860	
Te	10 ppm			7	<10				7	<10		<0.1	7	<10				5	5	<10	
Th	0.2 ppm	5.6	0.5	0	5.5	98%	5.1	0.7	0	5.14	101%	12	0	11.9	99%		14	0	0	13.4	96%
Ti	0.05 %	0.599	0.021	0	0.590	98%	0.227	0.047	0	0.211	93%	0.40	0	0.404	101%		0.306	0.023	0	0.314	103%
U	0.2 ppm	2.2	0.3	0	2.0	90%	31	1.8	0	30.7	99%	2.8	0	3.56	127%		2.6	0	0	2.74	105%
W	1 ppm	<1		6	<1		<4		7	<1		1	3	1.50	150%		3	1	1	3.10	103%
Yb	2 ppm	3.9	0.4	0	4.0	103%	2	0.2	3	1.86	93%		0	3.00			2.7	1	1	3.00	111%
Zn	100 ppm	98	10	5	<100		194	19	2	146	75%	83	7	<100			350	4.8	0	320	91%
Zr	200 ppm	502	58	4	<200		105	17	7	<200			5	<200			230	5	5	<200	

Table 10. Accuracy summary of control reference material generated by INAA.

Carbon Related Variables - Accuracy Summary

	<u>LKSD-4 (n = 24)</u>					<u>SoNE-1 (n = 12)</u>					<u>2711 (n = 10)</u>				
	<u>Proposed value</u>		<u>Project Values</u>			<u>Proposed values</u>		<u>Project Values</u>			<u>Proposed values</u>		<u>Project Values</u>		
	Value	SD	<DL	Mean	% Rcvry	Value	SD	<DL	Mean	% Rcvry	Value	SD	<DL	Mean	% Rcvry
Total Carbon	17.7	0.8	0	18.5	105%	1.96	0	1.87	95%		2.0	0	1.71	86%	
Organic Carbon			0	18.0			0	1.83				0	1.20		
Inorganic Carbon			0	0.58			4	0.042				0	0.52		
Loss-on-Ignition (500 °C)	40.8	0.7	0	38.1	93%		0	7.2				0	5.00		

Table 11. Accuracy summary for blind duplicate and control reference material data for carbon generated by the GSC Sedimentology Laboratory.

Elements Determined by Two or More Methods

Improvements in the instrumentation for generating geochemical data in the last 20 years have led to data being acquired at relatively low cost. Hence, it is often within the project budget to have samples analyzed by more than one method. Having more than one set of data with common and different elements adds tremendously to the worth of the project. These data serve as an additional check on quality control, bringing to light, for example, the mislabelling of sample splits and the effectiveness of one analytical method compared to another. Interpretation of these data may also lead to a better understanding of mineralogical and other factors controlling element distribution in soil materials.

Figure 14 shows a scatter plot of U data generated by INAA and by ICP-MS after a 4-acid digestion. The data were generated at different commercial laboratories using two splits from the same set of C-horizon samples. Because both methods are considered to be “total” it is possible to compare these data directly. The strong correlation ($r = 0.96$) corroborates the quality of the data from both laboratories. The plot also shows that there were no sample mix-ups at either laboratory.

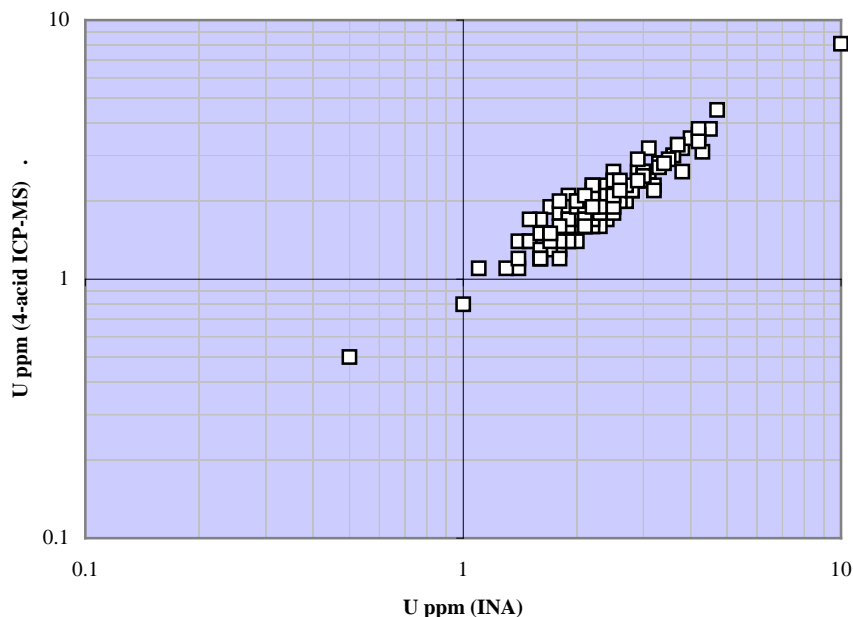


Figure 14. Scatter plot of U data obtained for the <2mm fraction of C-horizon samples using two different analytical methods - ICP-MS after a near-total 4-acid dissolution and INAA.

Any significant deviation from the trend would be investigated with a mix-up in samples being considered first as the possible cause. Depending on the number of samples and their location in

the blocks of 20 relative to the blind duplicates and CRMs, there is a small chance that errors due to sample misnumbering might not be detected using other QC procedures.

The validity of the 4-acid method for obtaining reliable As and Sb data was also confirmed by having data from more than one source. The 4-acid digestion involves a fuming step which may cause volatilization of As and Sb if not carried out properly. The binary plots of As and Sb data determined by INAA and 4acid-ICP-MS analysis in Figure 15 clearly show that As and Sb were not lost when analyzed after the 4-acid digestion.

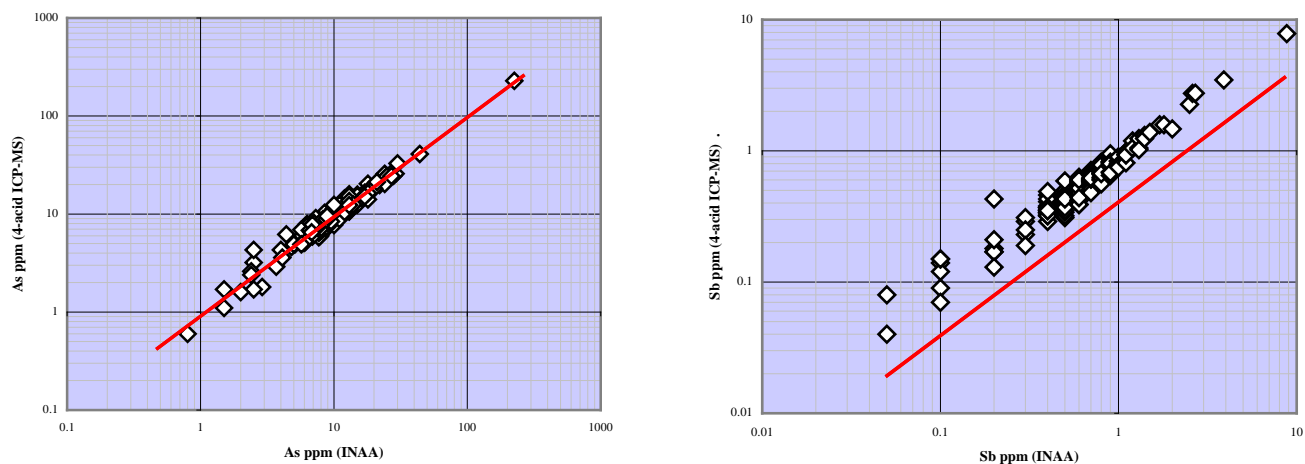


Figure 15. Scatter plots of As and Sb data for the <2mm fraction of C horizon samples obtained using two different analytical methods - ICP-MS after a near-total 4-acid dissolution and INAA.

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Acknowledgments

The authors wish to thank: Andy Rencz, for his leadership on the Canadian part of the North American Soil Geochemical Landscapes Project; Robert Garrett for his helpful advice and contribution to the sample site selection procedures; Dave Kroetsch (AAFC) for his insightful knowledge of soil and soil processes; Dave Smith and Laurel Woodruff (USGS) for their input into NASGLP field protocol development; the contributions of the many students without who's assistance the sample collection could not have been completed in a timely and efficient manner.

Figure Captions

- Figure 1. Field meeting near Fredericton, June 14, 2007 to finalize protocols and commence surveys. Standing left to right: Jim Kilburn (USGS), Dave Smith (USGS), Laurel Woodruff (USGS), Rex Boldon (NBDNR), Rita Mroz (EC), Rick McNeil (GSC), Parish Arnott (NBDNR), Brad Harvey (GSC), Toon Pronk (NBDNR), Mike Parkhill (NBDNR), Martin McCurdy (GSC), Peter Friske (GSC); Kneeling left to right: Sheldon Hann (AAFC), Sherif Fahmy (AAFC), Ken Ford (GSC) and Marc Desrosiers (NBDNR) (Photo by A. Rencz).
- Figure 2. Sample sites for 2007 TriNational survey in the Maritimes with Ecoregions in the background.
- Figure 3. Distribution of sample sites (black dots) over North America. Ecozones for North America are shown in colour (after Commission for Environmental Co-operation, 1997).
- Figure 4. Photo showing samples collected at one tri-national site. A five gallon plastic pail is used to transport the material and is usually filled at each site.
- Figure 5. Comparison of direct and estimated permeability measurements. Includes 2007 to 2009 data.
- Figure 6. Flow chart of TriNational sample preparation and analytical protocols summary.
- Figure 7. TriNational sample drying area with some 2007 Maritime samples laid out.
- Figure 8. Sub sampling of a TriNational soil sample using the slab-cake method.
- Figure 9. Photo showing collected sample for bulk density and moisture determinations using a clear acrylic tube.
- Figure 10. Mean K (pct), eU (ppm) and eTh (ppm) analysis for 49 duplicate analysis for 2007 NASGLP samples analyzed by laboratory gamma ray spectrometry. Sample weights less than 100g shown with yellow triangles, sample weights between 100g and 200g shown with red squares and sample weights above 200g shown with blue diamonds.
- Figure 11. Time charts for Be, Ni and As data generated for SoNE-1 from 5 separate analytical batches (sequence numbers 1-4 = batch 1; 6-10 = batch 2; 13-16 = batch 3; 19-22 = batch 4 and 25-28 = batch 5). These data were obtained for the <2mm fraction of the C-horizon using a 4-acid dissolution.
- Figure 12. Time charts for Be, Ni and As data generated for TILL-1 from 5 separate analytical batches (sequence numbers 1-4 = batch 1; 6-10 = batch 2; 13-16 = batch 3; 19-22 = batch 4 and 25-28 = batch 5). These data were obtained for the <2mm fraction of the C-horizon using a 4-acid dissolution.
- Figure 13. Scatter plots illustrating the relationship between calculated % RSD and ratio of mean to lower detection limit (LDL) for the 4-acid and 3050B blind duplicate data, as per Tables 3 and 5.
- Figure 14. Scatter plot of U data obtained for the <2mm fraction of C-horizon samples using two different analytical methods - ICP-AES after a near-total 4-acid dissolution and INAA.
- Figure 15. Scatter plots of As and Sb data for the <2mm fraction of C horizon samples obtained using two different analytical methods - ICP-AES after a near-total 4-acid dissolution and INAA.

Table Captions

Table 1. Statistical summary of direct versus estimated permeability measurements.

Table 2. Summary of sample preparations and analyses applied to the PH interval and soil horizons collected under the auspices of the NASGLP. X-Ray diffraction and bioaccessibility data not included in this Open File.

Table 3. Precision summary for blind duplicate and control reference material data generated by the 4-acid ICP-MS/AES analytical method.

Table 4. Precision summary for blind duplicate and control reference material data generated by the modified 3050B ICP-MS/AES analytical method.

Table 5. Precision summary for blind duplicate and control reference material data generated by INAA.

Table 6. Precision summary for blind duplicate and control reference material data generated by the water leach ICP-MS/AES analytical method.

Table 7. Precision summary for blind duplicate and control reference material data for carbon generated by the GSC Sedimentology Laboratory.

Table 8. Accuracy summary of control reference material data generated by the 4-acid ICP-MS/AES analytical method.

Table 9. Accuracy summary of control reference material generated by the modified 3050B ICP-MS/AES analytical method.

Table 10. Accuracy summary of control reference material generated by INAA.

Table 11. Accuracy summary for blind duplicate and control reference material data for carbon generated by the GSC Sedimentology Laboratory.