



**PROCEEDINGS OF THE 24<sup>TH</sup>  
INTERNATIONAL APPLIED GEOCHEMISTRY SYMPOSIUM  
FREDERICTON, NEW BRUNSWICK, CANADA**



**JUNE 1<sup>ST</sup>-4<sup>TH</sup>, 2009**

**EDITED BY**

**DAVID R. LENTZ, KATHLEEN G. THORNE, & KRISTY-LEE BEAL**



**VOLUME II**



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# **NORTH AMERICAN SOIL GEOCHEMICAL LANDSCAPES PROJECT**

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## The landscape geochemistry of the Sacramento Valley, California

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**ABSTRACT:** We have conducted a holistic 'geochemical landscape' study of the Sacramento Valley (the northern portion of the Great Valley of California, U.S.A). Our data sets consist of regional soil and ground-water chemical analyses coupled with more focused geochemical studies comprising smaller portions of the area. Both the soil and ground-water data exhibit systematic distribution patterns reflecting geologic, geomorphic, hydrologic, and anthropogenic processes. Sacramento Valley soil samples are differentiated east to west due to the effect of a levee along the Sacramento River, which bisects the valley. Eastern valley soils reflect inputs of glacial debris from the Sierra Nevada as well as material washed down to the valley from extensive placer gold mining. Western valley soils contain a significant chemical signature derived from ultramafic rocks in the Coast Ranges to the west of the valley. Ground water is similarly differentiated east to west in part reflecting this geologic differentiation of valley fill materials. Chromium in the (VI) oxidation state (a potentially toxic constituent) is present in somewhat elevated concentrations, particularly in the western valley. This elevated ground-water Cr content also may reflect the relative abundance of Cr in western valley soil.

**KEYWORDS:** *Geochemical landscapes, chromium, California, soil geochemistry*

### INTRODUCTION

The field of Landscape Geochemistry (LG) deals with the study of the environment that occurs at or near the surface of the earth. As a discipline, LG integrates the interactions of the lithosphere with the hydrosphere, atmosphere and biosphere. As described in a series of papers and a book by Fortescue (1992), LG was conceptually developed largely in the former Soviet Union. The evolution of a geochemical landscape involves the interaction of processes occurring over a range of time and spatial scales. Humans are increasingly intervening and even dominating these processes, making LG studies especially relevant to understanding global environmental change. We have conducted an LG study of a large portion of the Sacramento Valley, in the state of California, U.S.A. This study originated as a pilot project for the soil geochemical survey of North America (North American Soil Geochemical Landscapes Project) and links regional soil and rock geochemistry, hydrochemistry, geophysics, and remote

sensing with existing geomorphic, geologic and land use studies. Our research encompasses regional-scale studies, supplemented by research on specific processes at the local and microscopic scales.

### Overview of study area

Most of the study area is located in the drainage basin of the Sacramento River, which flows near the center of the Sacramento Valley in the northern third of the Great Valley, or Central Valley, of California. This valley was extensively transformed during the past 150 years of human settlement through urbanization, agriculture, mining, and flood control activities (Kelley 1998). The Central Valley is one of the great agricultural regions of the world (Johnson *et al.* 1993) and has rapidly expanding urban and suburban population centers.

The Sacramento Valley is a tectonically controlled basin bounded on the east by the Sierra Nevada, on the west by the Coast Ranges, and on the north by the Klamath Mountains. The alluvium of the valley reflects inputs from these bounding

source areas. Useful geochemical tracers are derived from the chemically and mineralogically distinctive ultramafic rocks (e.g., serpentinite) that crop out extensively in both the Coast Range and Sierra Nevada. These rocks, and the soils derived from them, have particularly high concentrations of Cr and Ni.

#### **Methodology**

Our study uses archived samples supplemented by newly collected material. The archived sample set consists of more than 1300 soil samples collected on a 1-km grid spacing throughout the 1:250,000-scale Sacramento Quadrangle during the late 1970s and early 1980s by the U.S. Department of Energy's National Uranium Resource Evaluation Hydrogeochemical and Stream Sediment Reconnaissance (NURE HSSR) Program (Smith 1997). Each sample represents the upper 10-15 cm of soil. We reanalyzed these archived samples using ICP-MS and ICP-AES. Details on the methods and the analytical results are available in Morrison *et al.* (2008). We also collected soil and rock samples along the western and eastern drainages feeding the valley to characterize potential sources of alluvium.

In addition, chemical data for 661 ground-water and 627 surface-water samples were obtained from the USGS National Water Information System database. Only subsets of all available data that included analyses for major cations, anions, and pH, and had cation-anion charge balances within  $\pm 20\%$  were utilized.

## **RESULTS**

### **Soil Geochemistry**

The soil geochemical results segregate broadly into distinct element groups whose distribution reflects the interplay of geologic, hydrologic, geomorphic, and anthropogenic factors. One group includes the elements Cr, Ni, V, Co, Cu, and Mg associated with mafic and ultramafic rocks. Using Cr as an example, elevated concentrations occur in soils overlying ultramafic rocks in the foothills of the Sierra Nevada (median Cr = 3500 mg/kg) as well as in the northern Coast Ranges.

Low concentrations of these elements occur in soils located further upslope in the Sierra Nevada, where they overly Tertiary volcanic, metasedimentary and plutonic rocks (granodiorite and diorite). Eastern Sacramento Valley soil samples, defined as those collected east of the Sacramento River, are lower in Cr (median Cr = 150 mg/kg) and are systematically lower in the ultramafic suite of elements compared to soils from the west side of the Sacramento Valley (median Cr = 250 mg/kg). A second group of elements showing a coherent pattern, including Ca, K, Sr, and rare earth elements (REE), is derived from relatively silicic rock types. This group occurs at elevated concentrations in soils overlying volcanic and plutonic rocks at higher elevations in the Sierras (e.g., median La = 28 mg/kg). The same elements are elevated on the east side of the Sacramento Valley (median La = 20 mg/kg) compared to soils overlying ultramafic rocks in the Sierra Nevada foothills (median 15 mg/kg) and the western Sacramento Valley (median 14 mg/kg). The segregation of soil geochemistry into distinctive groupings separated by the Sacramento River arises from the former presence of a natural levee (now replaced by an artificial one) along the banks of the river. This levee has been a barrier to cross-valley sediment transport. Sediment transport to the valley by glacial outwash from higher elevations in the Sierra Nevada and, more recently, debris from placer gold mining in the Sierra foothills has dominated sediment sources in the eastern valley. High content of mafic elements (and low content of silicic elements) in surface soils of the west side of the valley is due to the transport of ultramafic rock material from the Coast Ranges and input of sediment from the late Mesozoic marine Great Valley Group. The Great Valley Group lies between the Coast Range ultramafic rocks and the Sacramento Valley and is itself enriched in mafic elements.

The distribution pattern of a third group of elements, including Zn, Cd, As, and Cu, reflects the impact of historical mining.

Soil with elevated content of these elements occurs along the Sacramento River in both levee and adjacent flood basin settings. We interpret that transport of sediment impacted by large metal sulfide mines located in the Klamath Mountains at the north end of the Valley has caused this pattern.

Lead and, to some extent, Zn distribution patterns are strongly affected by anthropogenic inputs. Elevated soil Pb content is localized around major cities and along major highways due to inputs from leaded gasoline. Zinc has a similar distribution pattern, but the likely source is tire wear.

#### **Ground-water Geochemistry**

Ground water on the west side of the Sacramento Valley contains greater concentrations of Na, Ca, Mg, B, Cl, and SO<sub>4</sub>, while the east-side ground water contains greater concentrations of Si and K. These differences in ground-water composition result, in part, from chemical reactions between water and aquifer materials. As such, they reflect the chemical differences of the sediments that fill the western Sacramento Valley, which are higher in Mg and lower in K than eastern valley sediments. The elevated Na, B, and Cl may, in part, reflect input from saline thermal springs that are common along the west side of the Sacramento Valley.

Ground water on the west side of the Sacramento Valley has particularly high concentrations of dissolved Cr ranging up to 50 µg/L and averaging 16.4 µg/L. We interpret that this pattern reflects the enrichment in soil/alluvium Cr content on the west side of the Valley.

#### **Mechanism of Cr(VI) Generation**

Chromium occurs in both the Cr(III) and Cr(VI) valence states. The rock and soil Cr reported in this study is dominantly insoluble and non-toxic Cr(III), whereas the aqueous Cr reported in ground water is soluble and potentially toxic Cr(VI). We have analyzed core material (up to ~30 m depth) from an area of the valley that exhibits elevated Cr(VI) concentrations in

ground water. This core material contains up to 2200 mg/kg total Cr of which only a minute fraction is Cr(VI) (up to 42 µg/kg). Our data suggests that the majority of the total Cr is contained in the refractory spinel mineral chromite, which is the dominant residence of Cr in ultramafic rocks. The core samples contain abundant Mn oxides, an oxidizing agent for Cr(III), and are able to oxidize up to 26 mg of added Cr(III) (as CrCl<sub>3</sub>) per kg of soil. The relative insolubility of chromite in the pH range of ~7 to 9 inhibits the dissolution of Cr(III) from this mineral and its resulting transport to Mn-oxide surfaces. We are currently performing laboratory investigations into possible roles of microbial activity and anthropogenic inputs in the mobilization of Cr(III) and its subsequent oxidation by native Mn oxides.

#### **CONCLUSIONS**

(1) We have studied the interaction of geologic, geochemical, geomorphic, hydrologic, and anthropogenic processes in the Sacramento Valley of north-central California, U.S.A.

(2) Our results demonstrate significant spatial differentiation in the geochemistry of Sacramento Valley soil between the eastern and western sides of the valley that is related to the geomorphic separation of the valley by a levee along the Sacramento River. The western valley contains an elevated component of material derived from ultramafic rocks compared to the eastern side.

(3) This east-west difference reflects dominance in sediment source in the eastern valley by material derived from glacial debris and placer mining, and the presence of ultramafic rocks in the headwaters of western streams and ultramafic constituents in sediments on the west side of the valley.

(4) Ground water in the Sacramento Valley likewise has an east-west differentiation that reflects the geologic differentiation in valley materials

(5) Chromium in ground water is elevated in parts of the Sacramento Valley, particularly the western side.

(6) The rate of Cr(VI) formation is limited by the insolubility of Cr(III) oxides.

#### ACKNOWLEDGEMENTS

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## The North American Soil Geochemical Landscapes Project: preliminary results from Nova Scotia

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**ABSTRACT:** The North American Soil Geochemical Landscapes Project (NASGLP) is a tri-national initiative that involves the federal, provincial and state geological surveys of Canada, the United States and Mexico. Soil samples were collected, prepared and analyzed using a common set of field and analytical protocols. One outcome of this initiative will be the release of the first-ever continental-scale map of the soil geochemistry of North America. Preliminary results for Nova Scotia indicate maximum arsenic soil concentrations are associated with the Meguma Supergroup, host to the majority of the province's gold districts, while maximum uranium and radon concentrations are associated with highly evolved leucomonzogranite. This type of information is required for land-use planners and policy makers to ensure effective land-use planning minimizes human health risks by identifying areas where the natural background elemental concentrations are elevated.

**KEYWORDS:** *Nova Scotia, soil, geochemical surveys, arsenic, uranium, radon, human health*

### INTRODUCTION

Nova Scotia is a small province located on the east coast of Canada and is characterized by a relatively complex bedrock and surficial geologic history. As a result, large regions of the province are known to contain naturally elevated background concentrations of various elements. In addition to areas of naturally elevated background, significant sub-economic to economic mineralization also exists for a wide variety of elements. Anthropogenic inputs also contribute to the variation in the geochemical landscape at both local and regional scales.

### FIELD SAMPLING

In order to assess natural soil geochemical background concentrations, samples were collected from various soil horizons and discrete depth intervals from hand-dug pits. A total of 72 sites were sampled during the 2007 and 2008 field seasons yielding an average density of approximately 1 site per 800 km<sup>2</sup> that is double the nominal density of a site per 1600 km<sup>2</sup> for the NASGLP. Samples were collected from the surface layer (0 to 5

cm) as well as the A, B and C soil horizons. At each site, (1) soil gas radon (kBq/m<sup>3</sup>); (2) K (pct), eU (ppm) and eTh (ppm) concentrations by in situ gamma ray spectrometry; and (3) soil permeability values were also determined.

### SAMPLE PREPARATION AND ANALYSIS

Soil samples were sieved to two size fractions: <63 µm and <2 mm. Samples were analyzed for multi-element geochemistry by inductively coupled plasma/mass spectrometry (ICP/MS) following a "near total" 4-acid digestion.

Radon concentrations were determined using an RM-2 portable soil radon monitoring system while in situ soil permeability values were determined using Radon-JOK portable sampling equipment.

### RESULTS – ARSENIC

Preliminary results for As in the <63-µm fraction indicate C-horizon soil concentrations range from a low of 2.2 ppm to a high of 345 ppm with a mean of 22.3 ppm (Fig. 1). The highest As sample site is located within the Late Neoproterozoic/Cambrian Meguma



**Fig. 1.** Arsenic concentrations (ppm) in C-horizon soil samples, Nova Scotia.



**Fig. 2.** Uranium concentrations (ppm) in C-horizon soil samples, Nova Scotia.

Supergroup, a deepwater succession of marine metasandstones fining upwards into slate. This site also reported the highest arsenic in the <2-mm fraction of the A-horizon (229 ppm), B-horizon (284 ppm) and the C-horizon (228 ppm). The Meguma Supergroup hosts the majority of the province's gold districts that are characterized by the regional presence of arsenopyrite and locally by gold-arsenopyrite mineralization.

### URANIUM

Uranium concentrations in the <63- $\mu$ m fraction of C-horizon soil range from a low of 1.3 ppm to a high of 12.5 ppm with a mean of 3.0 ppm (Fig. 2). The highest U concentration is associated with highly evolved Middle-to-Late Devonian leucomonzogranite of the South Mountain Batholith, one of the largest granitoid bodies in eastern North America and occupying an area of approximately 7300 km<sup>2</sup>. Several other highs are associated with Middle-to-Late Devonian leucomonzogranite or Carboniferous age Horton Group sedimentary rocks.

### RADON

Radon in soil gas is present everywhere throughout the province in all geologic terrains. Soil gas Rn concentrations range from a low of 0.1 kBq/m<sup>3</sup> to a high of 207.0 kBq/m<sup>3</sup> with a mean of 25.3 kBq/m<sup>3</sup> (Fig. 3). The highest Rn soil gas concentrations are also associated with Middle-to-Late Devonian leucomonzogranite of the South



**Fig. 3.** Mean soil gas radon concentrations (kBq/m<sup>3</sup>), Nova Scotia.

Mountain Batholith and, to a lesser degree, with sedimentary rocks of the Carboniferous age Horton and Pictou groups.

### DISCUSSION

All results represent regional, natural background soil concentrations unaffected by obvious anthropogenic influences such as garbage or proximity to industrial, residential or transportation sources.

Exposure to elements such as As, U and Rn may represent an increased human health risk, particularly in areas where the natural background concentrations are elevated.

In order to ensure effective land-use planning, geochemical sampling and mapping are required to identify areas where the natural background concentrations are elevated so that

human exposure to these elements can be minimized.

The identification of elevated U in the C-horizon soil and elevated Rn in the soil gas associated with the Middle-to-Late Devonian leucomonzogranite of the South Mountain Batholith are examples of the type of information generated by the

NASGLP for predicting areas of potential natural geologic hazards.

#### **ACKNOWLEDGEMENTS**

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## Testing the variants of aqua regia digestion using certified reference materials

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**ABSTRACT:** The North American Soil Geochemical Landscapes Project requires an analytical protocol that will: 1) provide consistent data across North America; and 2) provide data that would be to the greatest extent possible compatible with current data holdings. The primary method involves a near-total digestion using hydrochloric, nitric, perchloric, and hydrofluoric acids followed by ICP-AES and ICP-MS. The project is also investigating the use of an aqua regia digestion because environmental regulatory agencies frequently use this “total recoverable” extraction to set soil action levels and remediation levels. To select the specific aqua regia protocol, eight Certified Reference Materials (CRMs) were analyzed, in triplicate random order, for 53 elements by four “aqua regia” digestion protocols and the EPA 3050B digestion method. From the results, we have concluded that there are few significant differences among the different aqua regia extractions for the elements of greatest environmental concern (e.g., As, Cd, Co, Cu, Hg, Ni, Pb, U, and Zn). Elements where agreement among the protocols is significantly lacking include Cr, Mn, Mo, Sb, and Zr. The final decision was to use the “aqua regia” variant of the US EPA 3050B protocol.

**KEYWORDS:** *aqua regia digestion, certified reference materials, analysis of variance, Tri-national soil survey*

### INTRODUCTION

A variety of strong acid dissolutions, e.g., 4-acid (near-total) extraction and aqua regia (total recoverable) extraction, are used by different agencies for the purpose of determining trace-element concentrations in environmental materials.

The North American Soil Geochemical Landscapes Project requires an analytical protocol that will: 1) provide consistent data across North America; and 2) provide data that would be to the greatest extent possible compatible with current data holdings. In a 2003 workshop decision, a near-total extraction using hydrochloric, nitric, perchloric, and hydrofluoric acids followed by ICP-AES and ICP-MS was chosen as the core analytical protocol for the continental-scale survey. However, it was also recognized that many environmental regulatory agencies use some variety of aqua regia extraction in setting soil action levels and remediation levels. For this reason, an experiment was devised to select an aqua regia extraction that would be optimum for the project.

Eight Certified Reference Materials (CRMs) (Table 1) were analyzed, in triplicate random order, for 53 elements by five digestion protocols (Table 2) as shown in the experimental design (Table 3). All final determinations were by ICP-AES and -MS in a single batch using a randomized ordering of the prepared digestions.

### RESULTS

Of the 53 elements determined, 48 had useful values above the method detection limits. The data for As and Cr are shown as dotplots (Figs. 1 and 2) as examples of metals and metalloids that occur in both soluble and acid-resistant mineral phases. Dotplots highlight the varying analytical precision for each material and each analytical protocol.

Chromium (Fig. 2) shows the greatest variability across the CRMs, which is consistent with the presence of Cr in both strong-acid soluble minerals and as acid-resistant chromite. On the other hand, As shows good repeatability for the range of

**Table 1.** Certified Reference Materials

Certified Reference Material	Description
LKSD-1	GSC-CCRMP lake sediment
LKSD-4	GSC-CCRMP lake sediment
STSD-1	GSC-CCRMP stream sediment
STSD-4	GSC-CCRMP stream sediment
TILL-1	GSC-CCRMP glacial till (diamicton)
TILL-4	GSC-CCRMP glacial till (diamicton)
SoNE-1	USGS Nebraska soil
2711	USGS Montana soil

**Table 2.** Variants of strong-acid digestion.

**M1 [AR-111]**

1 g sample in a test-tube digest with 3 ml of 1:1:1 HCl-HNO<sub>3</sub>-H<sub>2</sub>O in a heated shaker block at 95° C for an hour, then make up to 10 ml volume with 5% diluted HCl and homogenize the solution with a shaker.

**M2 [AR31] Classical AR digestion**

1 g sample in a test-tube, cold digest with 0.75 ml of HNO<sub>3</sub> for half an hour to oxidize any excess organic matters; follow by adding 2.25 ml of HCl. Place the samples in a heated shaker block at 95° C for an hour. Make up to 10 ml volume with 5% diluted HCl and homogenize the solution with a shaker.

**M3 [AR13] Reverse classical AR digestion (Lefort)**

1 g sample in a test-tube, cold digest with 2.25 ml of HNO<sub>3</sub> for half an hour to oxidize any excess organic matters, follow by adding 0.75 ml of HCl. Place the samples in a heated shaker block at 95° C for an hour. Make up to 10 ml volume with 5% diluted HCl and homogenize the solution in a shaker.

**M4 [AR11]**

1:1 HCl-HNO<sub>3</sub>. Cold digest 0.5 g sample in a test tube with 1.5 ml of conc. HNO<sub>3</sub> until reaction subsides. Further oxidize the sample in a hot water bath at 95° C until brown fumes almost disappear. Remove samples and cool, then add 1.5 ml of conc. HCl and mix. Place the samples in a heated shaker block at 95° C for an hour. Make up to 10 ml volume with 5% diluted HCl and homogenize the solution in a shaker.

**M5 [EPA3050] Modified US-EPA 3050B**

1 g sample in a test-tube, digest with 1 ml of 1:1 HNO<sub>3</sub>-H<sub>2</sub>O in a hot water bath until no brown fumes given off. Allow the samples to cool, add further 0.5 ml of conc. HNO<sub>3</sub> and place samples back to hot water bath and continue heating until no brown fumes are given off. Cool the samples and add 0.5 ml of 30% H<sub>2</sub>O<sub>2</sub>, reheat the samples in hot water bath until the reaction subsides, cool the samples and continue adding another 0.5 ml of 30% H<sub>2</sub>O<sub>2</sub> and repeat the heating until the reaction subsides. Cool the sample and make up to 10 ml volume with 5% diluted HCl and mix the solution well by shaking.

**CRMs and analytical protocols.**

Figures 3 and 4 display what are known as, “interaction plots”, where the mean of triplicate analyses is plotted with respect to CRM and analytical protocol. Where all methods extract a similar amount of the element, the lines representing CRMs will be parallel. In cases where the lines cross, there is an “interaction” between the mineralogy of the CRM and the analytical protocols. For Cr, this latter effect is clearly demonstrated, whereas for As, the methods consistently extract proportionally similar amounts.

ANOVA (ANalysis Of VAriance) provides a formal statistical procedure for analyzing the data arising from the experimental design used here (Table 3).

The details, beyond the model, are not presented, however, the key conclusions are for some of the elements there is no statistical difference between the standard Aqua Regia digestions analytical protocols and a significant difference for some elements with the EPA 3050B digestion. These differences are shown in the interaction plots of Figure 4.

**CONCLUSIONS**

From the experiment undertaken, it is concluded that there are few significant differences between the results yielded by the aqua regia-based extractions for the elements of greatest environmental concern (e.g., As, Cd, Co, Cu, Hg, Ni, Pb, U, and Zn). Elements where agreement between the protocols is significantly lacking include Cr, Mn, Mo, Sb and Zr. Clearly, US-EPA 3050B, an all-oxidizing reagent, HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>, protocol, ([www.epa.gov/epawaste/hazard/testmeth ods/sw846/pdfs/3050b.pdf](http://www.epa.gov/epawaste/hazard/testmeth ods/sw846/pdfs/3050b.pdf)) extracts, in almost all instances, less of the metals and metalloids than the various HCl-HNO<sub>3</sub> strong-acid mixtures, including “classic” aqua regia (M2 - AR31). Notable exceptions are Hf, Nb, Th, and Zr, where US-EPA3050B extracts more of these elements than the “aqua regias”.

Our objective was to select an analytical

**Table 3.** Experimental design and statistical model.

Table 3. Experimental Design and Statistical Model

CRM	Extraction Method				
	1	2	3	4	5
1	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
2	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
4	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
5	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
6	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
7	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
8	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3

Analysis of Variance Model:

Two-Way with Interaction and Replication within CRMs

$$Y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \gamma_{jk} + \epsilon_{ijk}$$

Where:

Y<sub>ijk</sub> = the k-th replicate analysis by the i-th Method of the j-th CRM

μ = the grand mean

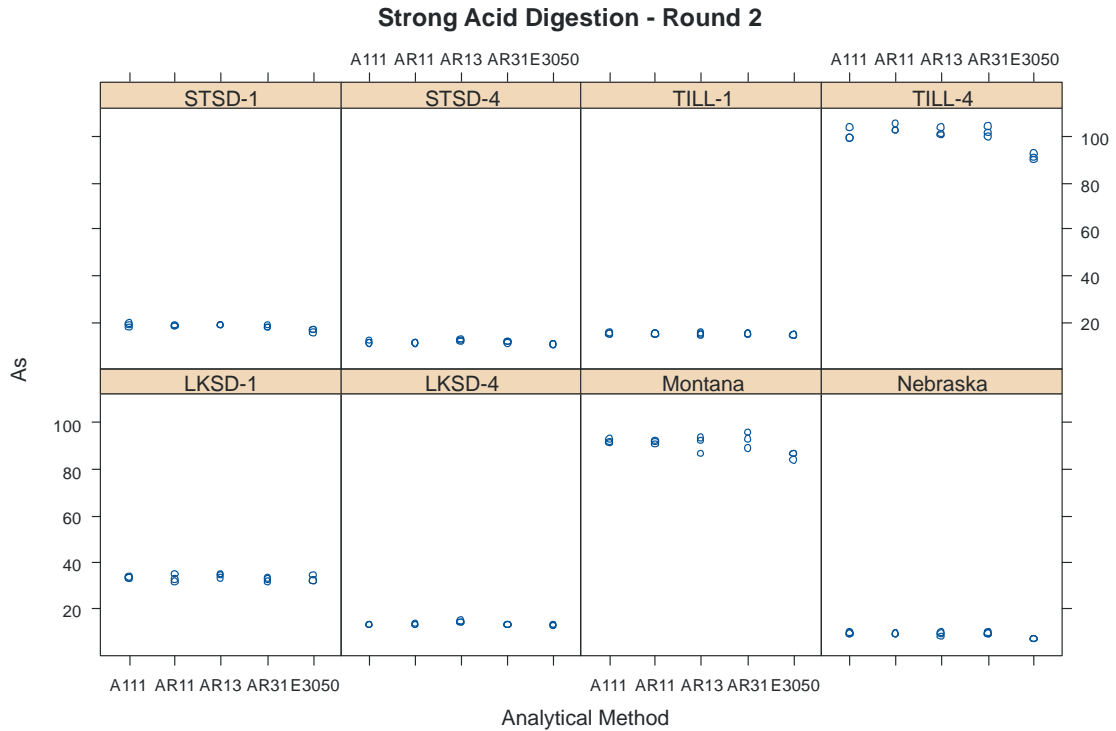
α<sub>i</sub> = the main effect due to the i-th Method

β<sub>j</sub> = the effect due to the j-th CRM (Sample)

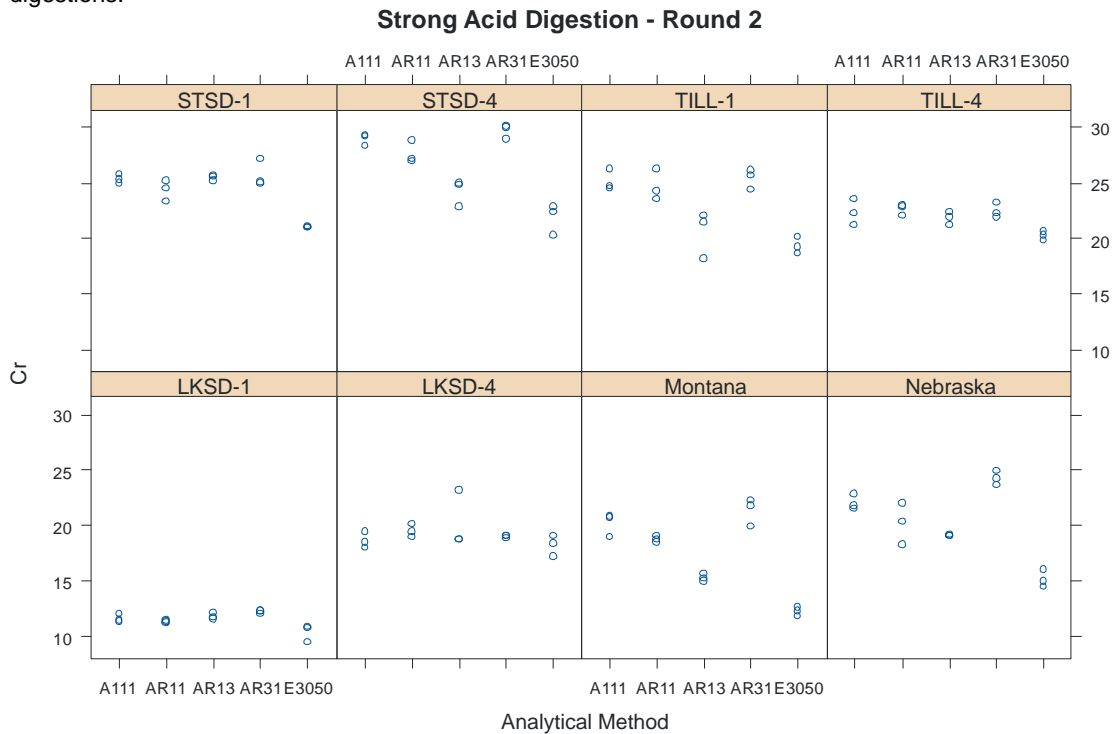
(αβ)<sub>ij</sub> = the interaction effect between the i-th Method and j-th CRM

γ<sub>jk</sub> = the effect due to the k-th analysis of the j-th CRM

ε<sub>ijk</sub> = the pooled residual variability



**Fig. 1.** Dotplot for arsenic factored by certified reference material. The x-axis represents the different digestions.



**Fig. 2.** Dotplot for chromium factored by certified reference material. The x-axis represents the different digestions.

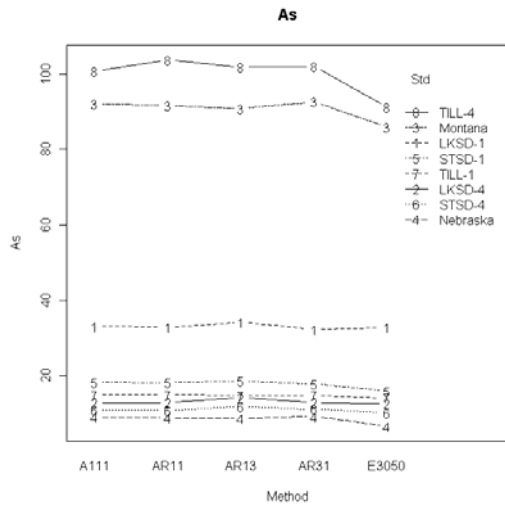


Fig. 3. Interaction plot for As.

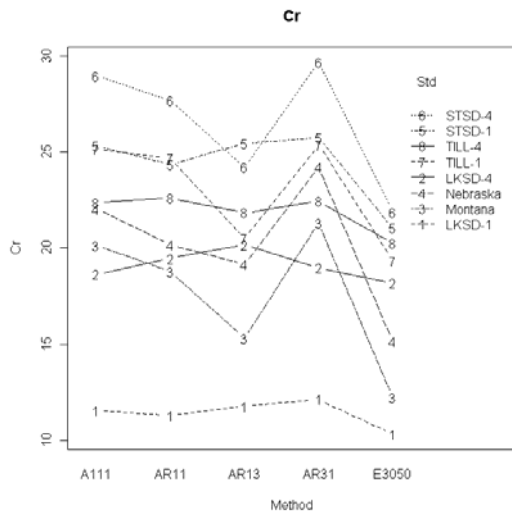


Fig. 4. Interaction plot for Cr.

protocol that will yield data that are consistent with both the majority of the regulatory regimes and the existing data holdings. The “classic” aqua regia (M2 – AR31) protocol meets this requirement. However, this may not be widely accepted in the environmental community. Therefore, we recommend that the aqua regia variant of US-EPA 3050B (i.e. without H<sub>2</sub>O<sub>2</sub>) be the basis of an analytical protocol for use in the North American Soil Geochemical Landscapes. This procedure uses a 4:1 HCl-HNO<sub>3</sub> mix rather than the 3:1 of “classical” aqua regia. However, on the basis of this study, we expect that this change in reagent ratio will not cause any geochemically significant variation.

## Preliminary results of the North American Soil Geochemical Landscapes Project, northeast United States and Maritime Provinces of Canada

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**ABSTRACT:** The results of a soil geochemical survey of the Canadian Maritime provinces and the northeast states of the United States are described. The data presented are for the <2-mm fraction of the surface layer (0-5 cm depth) and C horizons of the soil. Elemental determinations were made by ICP-MS following two digestions, aqua regia (partial dissolution) and a strong 4-acid mixture (near-total dissolution). The preliminary results show that Hg and Pb exhibit elevated abundances in the surface layer, while As and Ni exhibit abundances that can be attributed to the geological provenance of the soil parent materials.

**KEYWORDS:** *soil geochemistry, Northeast United States, Maritime Provinces of Canada, As, Hg, Ni, Pb, Zn*

### INTRODUCTION

Initial results of the North American Soil Geochemical Landscapes project (NASGLP) are presented from the Northeast United States (Maine, New Hampshire, Vermont, Massachusetts, Connecticut, Rhode Island and New York) and the Maritime provinces of Canada (Nova Scotia, New Brunswick and Prince Edward Island).

Soil sampling was conducted across the Canadian Maritime provinces and the US states during 2007 using an established field protocol by the United States Geological Survey (USGS), the Geological Survey of Canada (GSC) and the New Brunswick and Nova Scotia provincial surveys.

The surface layer (0-5 cm depth), A, B and C soil horizons were sampled where available. The B horizon was not sampled by the USGS. Due to the thin and relatively discontinuous nature of the A horizon at many of the Canadian sites and difficulty in distinguishing between H- and A-horizon material, some of the A-horizon samples have organic content greater than the >17% upper pedological limit. Reclassification based on the organic content and other factors will be done

before any detailed interpretation is undertaken on these "A-horizon" samples.

The Canadian maritime component of the NASGLP consists of 171 sites and the US component is comprised of 180 sites. Nominal sample densities were one site per 1600 km<sup>2</sup> in the United States and one site per 800 km<sup>2</sup> in Canada. Not all sites provided sufficient material to undertake chemical analyses for all horizons.

The results presented here are for As, Hg, Ni, and Pb, which are elements of interest for issues in human health.

Results are plotted on a base map of Ecoprovinces, which reflect geological, pedological, meteorological and topographic conditions (<http://sis.agr.gc.ca/cansis/nsdb/ecostrat/intro.html>).

### FOUR-ACID DIGESTION RESULTS FOR 0-5-CM AND C-HORIZON SOILS

Figure 1 presents As in 0-5-cm soils. Elevated levels occur along the eastern shore of Nova Scotia (Meguma terrane), in the Belledune area of northern New Brunswick, the northeast part of Maine, southwest New Hampshire, and south eastern New York State. The elevated values of As may also reflect

compositional differences in the 0-5-cm layer (e.g., carbon content, Fe, Mn). Further evaluation is required.

Figure 2 presents As in C-horizon soil. Elevated levels are probably more closely related to bedrock such as the Meguma terrain of Nova Scotia and in northern New Brunswick. Isolated elevated concentrations of As occur throughout Maine, New Hampshire, and Vermont.

Figure 3 presents Pb in 0-5-cm soils. Elevated levels occur throughout the populated areas of the Northeast United States and the Maritime provinces, suggesting anthropogenic sources. Elevated concentrations of Pb also occur in northern New Brunswick geographically near the Bathurst mining camp and the Belledune smelter.

Figure 4 presents Pb in C-horizon soils, it is noticeably low in abundance throughout the region, with the exception of the New York City area, Fredericton,

New Brunswick and the Sydney area of Nova Scotia.

Figure 5 presents Ni in 0-5-cm soils. There are no notable elevated concentrations of Ni in the region, with the exception of northern Maine and north-central New Brunswick. Figure 6 displays Ni in the C-horizon where there is a distinctive elevated Ni signature spatially correlative with the mafic rocks of northern New Brunswick that host mineralization at the Bathurst mining camp.

### CONCLUSIONS

The initial results of this survey indicate that there is variation of element abundances that can be attributed to both underlying geological factors, regional climatological/glacial events and possibly more recent anthropogenic activity.

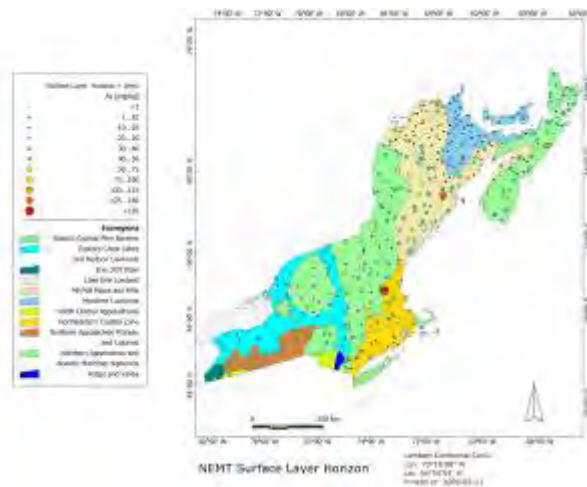


Fig. 1. As in 0-5-cm soils; 4-acid digestion, < 2mm size fraction, ICP-MS.

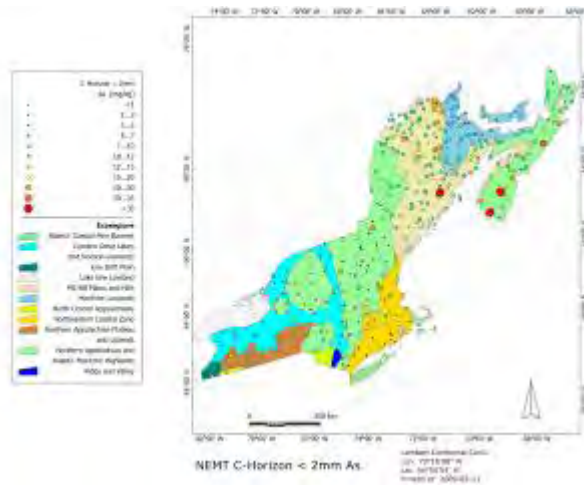


Fig. 2. As in C horizon; 4-acid digestion, < 2mm size fraction, ICP-MS.

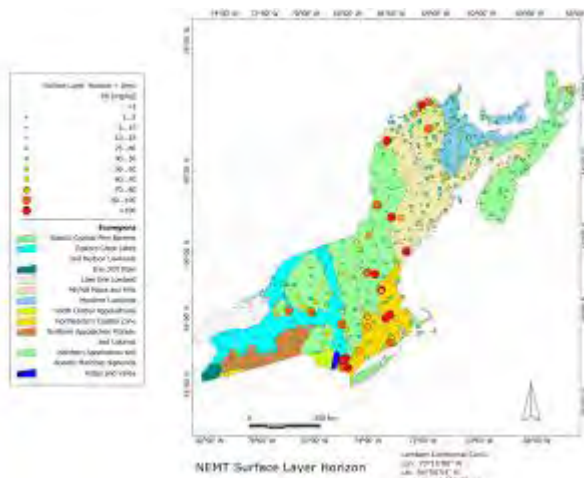


Fig. 3. Pb in 0-5-cm soils; 4-acid digestion, < 2mm size fraction, ICP-MS.

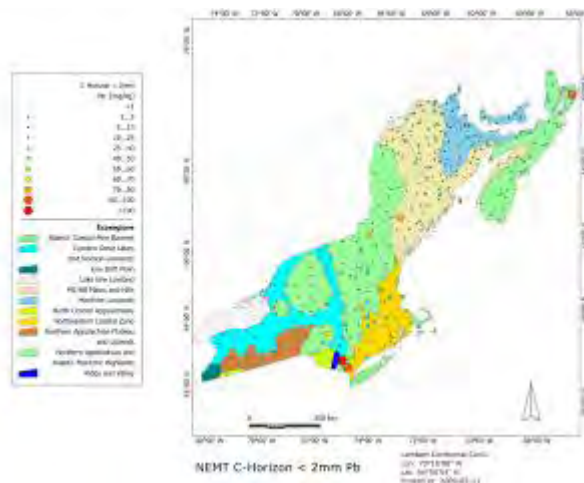


Fig. 4. Pb in C horizon; 4-acid digestion, < 2mm size fraction, ICP-MS.

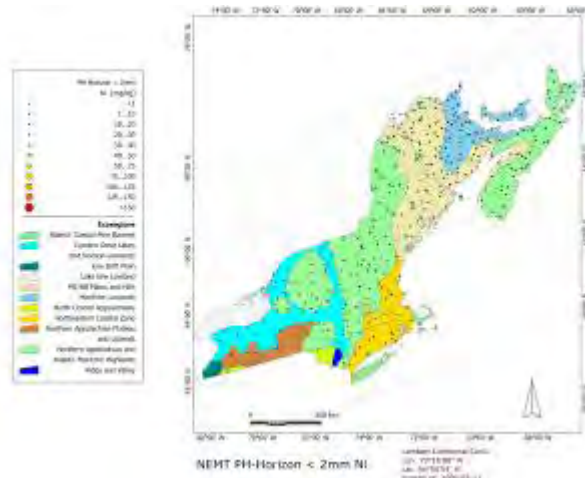


Fig. 5. Ni in 0-5-cm soils; 4-acid digestion, < 2mm size fraction, ICP--MS.

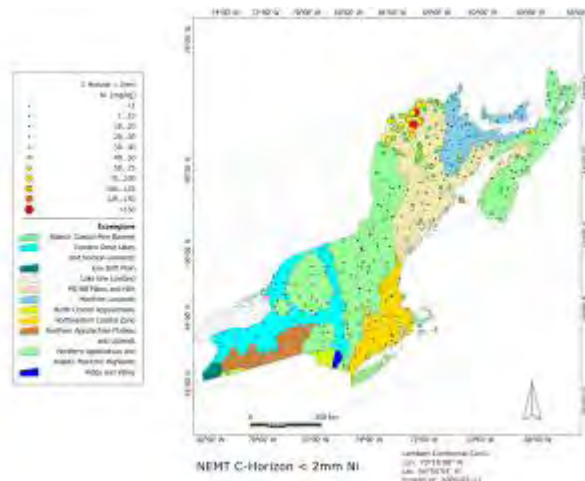


Fig. 6. Ni in C horizon; 4-acid digestion, < 2mm size fraction, ICP-MS.



## The North American Soil Geochemical Landscapes Project in New Brunswick

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**ABSTRACT:** The New Brunswick field component of the North American Soil Geochemical Landscapes Project (NASGLP) was carried out in 2008. A total of 118 sites were sampled following the NASGLP sampling protocol for Canadian projects. A total of 19 different samples for 7 separate government agencies were collected at each site. Initial analytical results indicate consistent regional patterns that largely follow geological and ecosystem boundaries. The cross-disciplinary aspect of the project has attracted collaborators from environment, health and resource sectors. The existence of large till, stream, and water geochemical databases provides background information for ongoing research, data extrapolation, and possibly spin-off map products that can be used for health, environmental and land use planning studies.

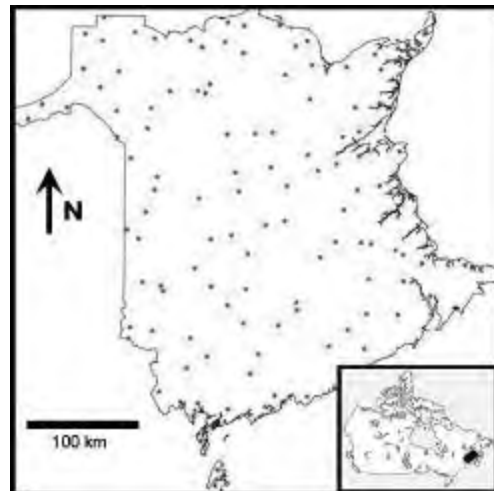
**Keywords:** *New Brunswick, soil chemistry, environment, radon, health, background values*

### INTRODUCTION

New Brunswick's diverse geology, excellent accessibility, and extensive geochemical database, make it a logical place to start 'testing' the protocols and methodology of the North American Soil Geochemical Landscapes Project (NASGLP) within Canada. Cooperation and coordination between the federal and provincial geological surveys, as well as Health Canada (HC), Environment Canada - Atlantic (ECA), and Agriculture Canada (AAFC) assured methodological continuity across the country and involvement of the user groups from the project outset.

New Brunswick Quaternary geologists have dug more than 18,000 soil pits during the last 25 years in all parts of the province and have an intimate knowledge of the landscape and its soils. New Brunswick's diverse geology and relatively small areal extent led us to sample at double the national/continental density, i.e. two sample sites per 1600 km<sup>2</sup> (Fig. 1). The second site within each sample block was taken at a National Forest

Inventory (NFI) site and will thus help link the newly acquired data with that database. Partly because of the "pilot" aspect of the project and partly because of all the partners involved (7 different departments/ agencies), a large number (19) of samples from various soil horizons was collected at each site (Fig. 2). Such



**Fig. 1.** Distribution of NASGLP sample sites in New Brunswick.



**Fig. 2.** Array of samples collected for 7 different agencies at each NASGLP site. Soil gas radon concentration and radiometric measurements were recorded at each site as well.

thorough sampling will make the resulting database a very robust one that will undoubtedly form the base of many future research projects and play an important role in decision making processes related to environment, health, and more general chemical background questions.

For agriculture and environment related projects, the <2-mm soil fraction is routinely analyzed and used as a standard, whereas for mineral exploration the <63- $\mu$ m fraction is used. The latter better reflects bio-accessibility and both fractions are analyzed using different chemical digestions.

### **GEOLOGICAL SETTING**

New Brunswick's bedrock geology is well mapped and largely well understood. Because of NB's mineral wealth, a great deal of mineral exploration work has been carried out since the 1950s. The bedrock in NB is also diverse in age. The oldest Precambrian rocks can be found in the Saint John area, whereas some of the younger ones, in the form of Triassic basalts, occupy more than half of the Island of Grand Manan. Most of NB's rocks are of Middle Paleozoic age. The triangle between Moncton, Fredericton, and Bathurst is occupied by a thick sequence of Carboniferous rocks that host

economic quantities of salt, potash, oil and gas, as well as numerous uranium occurrences. This diverse bedrock geology is covered by a generally thin layer of Quaternary glacial and glacio-fluvial and minor fluvial, aeolian, and marine deposits. Few areas of the province are dominated by bedrock outcrop and soil composition is thus often a mixture of several lithological components. The chemistry and texture of our soils is a reflection of New Brunswick's complex geological history.

The chemistry of the earth's surface, or active layer, influences our health and well being. Natural background variation of surface chemistry is rather high because of the variety in age and depositional environment of our bedrock. This variety is captured by the New Brunswick component of the NASGLP.

### **SAMPLING METHODOLOGY**

Sampling was carried out by two field parties, one in the north and one in the southern part of the province. Several times during the campaign, crews got together in the 'overlap' area and confirmed sampling was consistent between the two crews.

Sample locations (Fig. 1) were selected by using the methodology developed by the Geological Survey of Canada (Geological Survey of Canada Report, in prep.) during the start-up of the NASGLP. Canadian protocols differ somewhat from the American and Mexican protocols, partly because our sampling environments differ and partly because in the Canadian context several add-on projects were developed in cooperation with other interested agencies. Target sample sites were randomly generated by the GSC's generalized random tessellation stratified (GRTS) sampling design (Garrett 1983), but sampling crews had the option to reject a site if it was not representative of the area or if access was extremely difficult. The latter was a logistical issue as the sample gear and instrumentation were rather voluminous and heavy, and could only be carried from roads for a short distance. If the target site was rejected,

the next randomly generated site was evaluated in the same manner. It was only necessary once to go to a third option. In addition to the core Canadian sampling protocol, New Brunswick crews gathered soil radon data for Health Canada and composite surface and mineral soil samples for use by Environment Canada - Atlantic for toxicology studies.

### **SELECTED RESULTS**

One of the most revealing results is the chromium plot, which shows high values over part of the sedimentary cover rocks in the northwestern corner of the province. This regionally elevated area has been investigated in the past when stream sediment geochemical surveys revealed highly anomalous Cr-Ni-Co values. It was never satisfactorily explained and it was concluded that higher than normal background levels were responsible for the anomalies. The present survey seems to confirm that conclusion. The two sample sites on Grand Manan gave us some of the highest values (369 ppm in C-horizon parent material) which is not surprising in light of the bedrock geology represented by Triassic basalts. Several other elements (e.g., Se) are also highest at the Grand Manan sites.

There is also (as expected) a strong regional correlation between the uranium and radon soil gas concentrations in general, though not always site-to-site. Arsenic distribution is of special interest because of its toxicological effects and the fact that there are a couple of areas within New Brunswick that historically have high arsenic levels in drinking water and soils. These include areas underlain by Carboniferous volcanic rocks near Harvey, and the Bathurst/Belledune area in northern New Brunswick. The Harvey area seemingly defies detection at the scale NASGLP sampling because of the low sample density.

Comparisons of the chemistry of different soil horizons (Fig. 3) will reveal some of the natural variability and may highlight areas of potential health concern. If we compare the lead values for the <2-mm fraction for the surficial 0-5-cm, layer,

which is the horizon typically looked at for health studies, and the C horizon, we can detect some interesting differences. Lead in the C horizon has a generally 'flat' appearance with slightly elevated background over the northern part of the Miramichi Highlands, especially the Bathurst base-metal camp. The 0-5-cm material shows a more diverse distribution, which may be partly related to the higher organic content of that layer and/or to anthropogenic sources.

### **RADON FOLLOW-UP STUDY IN THE FREDERICTON – NEW MARYLAND AREA**

A follow-up study on soil radon gas and indoor radon gas was carried out in the Fredericton area. It was found that the individual correlation between soil gas radon and indoor radon on individual properties was not very high, but there was definitely a regional correlation. The reasons for the low individual correlation can be traced to other important variables such as age and type of construction of the homes.

### **TOXICOLOGY STUDY (ENVIRONMENT CANADA - ATLANTIC)**

Toxicology and environmental health studies often lack a firm foundation of baseline data, and the NASGLP is a perfect starting point for a baseline data survey. During the field component of the survey, the crews collected two composite samples. One represented the top 5 cm of the soil directly below the litter layer (which will include a lot of the airborne components if they are present), and a second came from the 0-30-cm interval, independent of which soil horizon this may represent. Within this interval (the active layer), most of the interactions between biota and the non-living soil components take place, and thus is the important interval for this type of study. Environment Canada's Biological Methods Division selected one of the northern New Brunswick sites to collect a bulk sample in an attempt to create reference sites across Canada for standardized toxicity test methods.



**Fig. 3.** Podzol profile at NASGLP sample site NB072009. Podzols were the soil type at approximately 100 of the 118 sites.

#### **ACKNOWLEDGEMENTS**

We would like to thank Ken Ford, Rick McNeil and other staff at the GSC for their

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## The North American Soil Geochemical Landscapes Project: overview, goals, progress

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**ABSTRACT:** In 2002, the U.S. Geological Survey (USGS), the Geological Survey of Canada (GSC), and the Mexican Geological Survey (Servicio Geológico Mexicano, or SGM) initiated a long-term effort called the North American Soil Geochemical Landscapes Project to map the geochemistry of North American soils using standardized sample collection and analytical protocols. The purpose of this geochemical survey is to improve our understanding of the baseline concentrations of chemicals and elements that are normally found in soil and the location and causes of elevated or depleted concentrations. Protocols were developed through recommendations of stakeholders at a series of workshops in 2002 – 2004 and tested and refined during a 3-year pilot phase from 2004 – 2006. Sampling for the continental-scale survey, initiated in 2007, will be done at a density of 1 site per 1,600 km<sup>2</sup> (13,500 sites).

**KEYWORDS:** *soil geochemistry, low-density geochemical mapping, geochemical background, continental-scale geochemical mapping, soil*

### INTRODUCTION

Soil is a critical natural resource that plays a key role in determining human health and ecosystem integrity, supporting food production, and the natural recycling of carbon and essential nutrients in the environment. On the other hand, many communities dispose of solid and liquid wastes from households and from agricultural and industrial processes by dumping them onto, or burying them in, the soil. Either through ingestion, inhalation, or dermal absorption, soil can be a pathway for potentially toxic chemicals of natural or anthropogenic origin to enter the human body (Oliver 1997; Abrahams 2002; Plumlee & Ziegler 2003). Although soil is so important in our everyday lives, our knowledge of the concentration and distribution of naturally occurring and man-made chemicals in the soils of North America is limited. At present, agencies involved with human health and environmental risk assessment and management have no common

understanding of soil geochemical background variation for the continent of North America and the processes that control this variation.

In 2002, the North American Soil Geochemical Landscapes Project, a tri-national initiative among the United States, Canada, and Mexico, was initiated with the goals to (1) develop a continental-scale framework for generating soil geochemical data and (2) provide soil geochemical data that are useful for a wide range of applications and disciplines.

### PROJECT DEVELOPMENT

A series of three workshops held in 2002 – 2004 included stakeholders representing about 50 North American governmental agencies, academia, environmental consultancies, and the medical community. The workshops resulted in a set of recommended sampling and analytical protocols for a soil geochemical survey that would meet the needs of this diverse set of customers. The Project is

based on low-density sample collection over a spatially balanced array of 13,500 sites for the North American continent (1 sample site per approximately 1,600 km<sup>2</sup>). There is a core set of samples to be taken at each site, and each country may add additional sample types to meet the needs of users.

The core sampling protocols represent both depth-based and horizon-based samples. One depth-based sample is taken from 0-to-5 cm, regardless of what soil horizon this represents. A composite of the A horizon (the uppermost mineral soil) and a composite of the C horizon (usually the weathered parent material of the overlying soil) are also collected at each site. The 0-5-cm and A-horizon samples are more likely to represent anthropogenic influence on soil composition, and the C-horizon sample is more representative of geologic influence. Each sample is sieved to <2 mm and then ground to <150 µm prior to chemical analysis for over 40 major and trace elements. The core analytical protocol, consistent among the three countries, involves a near-total 4-acid (hydrochloric, nitric, perchloric, and hydrofluoric) digestion followed by inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry. Mercury is determined by cold-vapor atomic absorption spectrometry (AAS) and Se and As are determined by hydride generation AAS. Total carbon is determined by combustion at 1370°C and carbonate carbon is determined as CO<sub>2</sub> by coulometric titration. Organic carbon can then be determined by difference. Each country may include additional analytical methods as desired.

In addition to the standard geochemical protocols, the survey has a microbiological

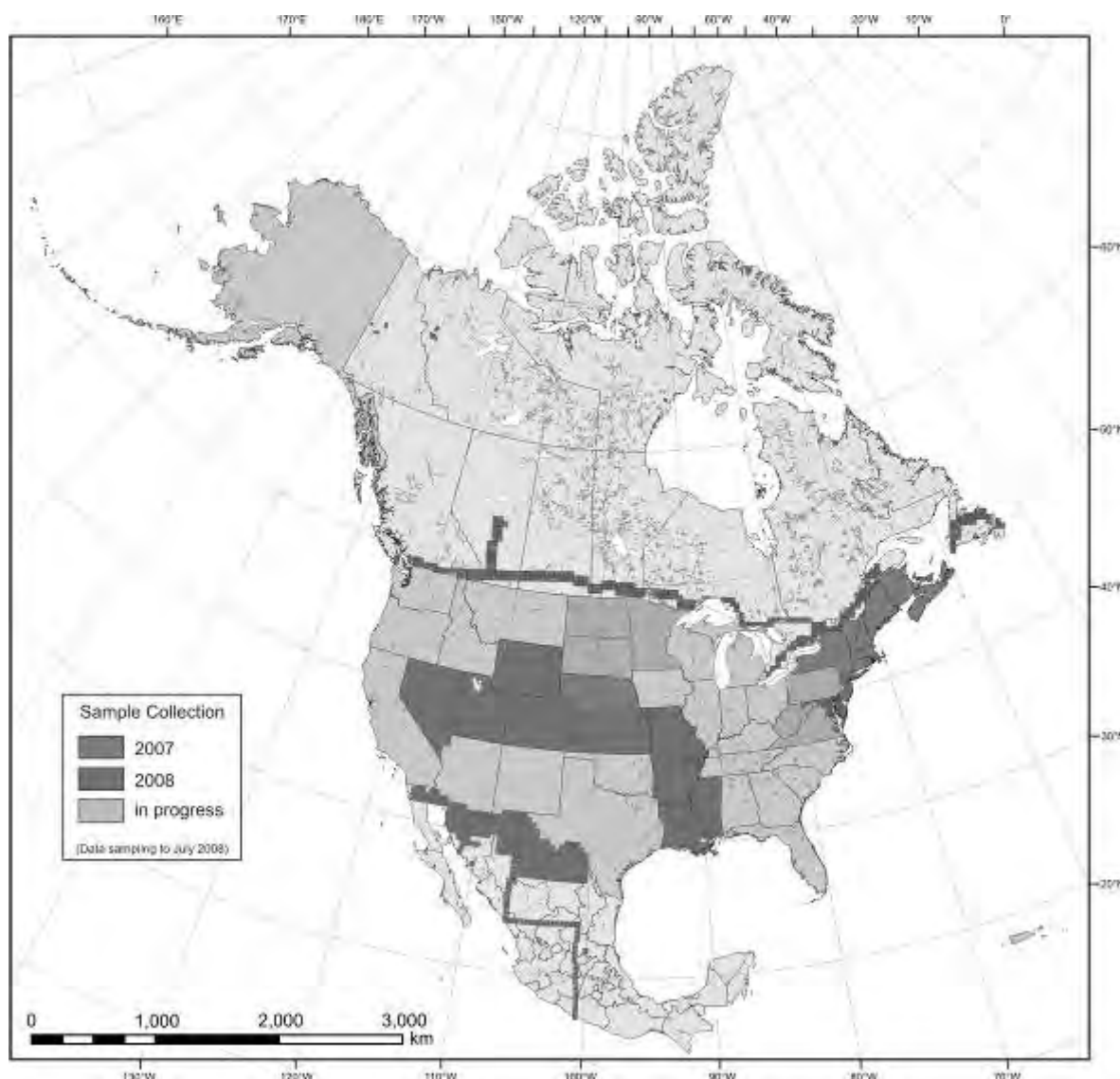
component. A separate sample of 0-5-cm soil is collected at each site for the determination of *Bacillus anthracis* (anthrax).

### PILOT STUDIES

A three-year pilot phase was conducted from 2004 – 2006 to test and refine the sampling and analytical protocols and to optimize logistics for the survey. This pilot phase was conducted at both a continental- and a regional-scale. The continental-scale pilot study consisted of sampling at approximately 40-km intervals along two transects across the US, Canada, and Mexico. A north-south transect extended from northern Manitoba to the Pacific coast of Mexico west of Acapulco. An east-west transect followed the 38<sup>th</sup> parallel from just north of San Francisco, California to the Virginia shore (Smith *et al.* 2005). The regional-scale study, designed to represent a more detailed follow-up investigation of an area of interest identified from the larger scale study, was conducted in an area of northern California located just north of San Francisco and extending from the Pacific coast to the California-Nevada border (Morrison *et al.* 2008).

### INITIATION OF CONTINENTAL-SCALE SAMPLING

The full-scale sampling of North American soils was initiated in 2007 with completion of the Maritime Provinces of New Brunswick, Nova Scotia, and Prince Edward Island in Canada and the New England states and New York in the US. Sample coverage at the end of 2008 is shown in Fig. 1. It is anticipated that this project will take approximately ten years to complete.



**Fig. 1.** Map showing status of sampling for the North American Soil Geochemical Landscapes Project as of December 31, 2008.

**ACKNOWLEDGEMENTS**

We thank the many stakeholders who participated in the various workshops and provided valuable guidance in the design of the continental-scale soil geochemical survey. We also thank all the people who have, to date, participated in sampling in all three countries.

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## Continental-scale patterns in soil geochemistry and mineralogy: results from two transects of the United States and Canada

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**ABSTRACT:** In 2004, the U.S. Geological Survey and the Geological Survey of Canada initiated a pilot study that collected more than 1,500 soil samples along two transects across Canada and the United States. The two transects crossed a wide array of soil types, surficial materials, soil ages, climatic conditions, landforms, land covers, and land uses. Geochemical and mineralogical data for the transect samples display coherent, robust regional and continental-scale patterns that are the result of broad-scale geochemical processes acting at the scale of mapping. The patterns can often be related to profound differences in soil parent material and to hemisphere-wide climate effects. The geochemical data also demonstrate that at the continental-scale changes can occur in the dominance of any of the major factors that control soil geochemistry, abruptly in some regions. The transect study served as a pilot project to develop and refine field and analytical protocols for a comprehensive North American soil geochemistry sampling project.

**KEYWORDS:** *continental-scale, soil geochemistry, soil mineralogy, transects*

### INTRODUCTION

In the United States, a large-scale soil geochemical survey was conducted from 1961 through 1974 (Shacklette & Boerngen 1984), but a continental-scale database of soil geochemistry for North America using consistent protocols and modern analytical methods is currently not available. To address this, the U.S. Geological Survey (USGS), the Geological Survey of Canada (GSC), and the Mexican Geological Survey (SGM) are collaborating on a soil geochemical survey of the entire North American continent (Smith *et al.* 2009). As a pilot study for this effort, the USGS and GSC sampled soils along two transects across the US and Canada in 2004.

The two transects crossed multiple, complex environments with widely diverse surficial materials, topography, climate, landforms, land covers, and land uses. A north-to-south (N-S) transect extended from northern Manitoba, Canada, to the US-Mexico border near El Paso, Texas. A west-to-east (W-E) transect followed the 38<sup>th</sup> parallel from just north of San

Francisco, California, to the Virginia shore (Fig. 1).

At each site, soils representing 0-to-5 cm depth, and the A, and C horizons, if present, were collected and analyzed for more than 40 major and trace elements. Soils from 0-to-5 cm depth also were analyzed of a suite of organic compounds.

The W-E transect crosses significant gradients in precipitation, with generally humid conditions along the west coast, arid to semiarid conditions in the interior



Fig. 1. Location of two transects.

western half of the US, and increasingly humid conditions in the eastern half of the country. The N-S transect has less dramatic precipitation changes, but does have significant differences in mean annual temperature from very cold in the north to very hot in the south.

Despite the highly variable settings of the sample sites, transect soil data show regional- to continental-scale patterns in mineralogy and geochemistry that can be related to soil-forming factors and processes acting at broad scales (Woodruff *et al.* 2009). To illustrate large-scale patterns revealed by transect soils, geochemical results have been grouped into ten coherent, sub-continental areas based on physiographic characteristics, including commonalities of surficial processes, climate, landform, soil parent materials, and soil age.

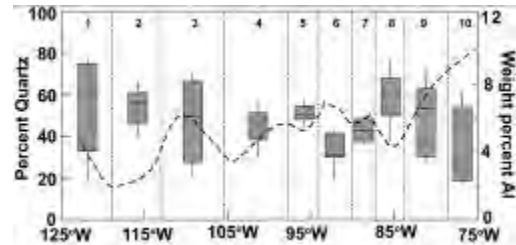
#### CONTINENTAL-SCALE MINERALOGY AND GEOCHEMISTRY

At the continental- to subcontinental-scale the relative proportions of major minerals in soils are largely controlled by parent material and climate factors. In turn, the distributions of many major and trace elements are strongly influenced by soil mineralogy, especially the presence or absence of quartz (Eberl & Smith 2009; Bern 2009).

##### West to East Transect

Mineralogy and soil geochemistry along the W-E transect reflect both the influence of soil parent materials and effect of hemispheric climate gradients. The quartz dilution effect described by Bern (2009) dominates the distribution of a number of elements; Al is given as an example in Figure 2.

Higher quartz contents in soils occur in areas where the soil parent materials include quartz-rich materials, such as sandstone bedrock or eolian deposits (area 3; Fig. 2) and in regions where high precipitation accelerates soil weathering and leaching, resulting in high contents of residual, inert quartz (areas 9 and 10; Fig. 2). In Fig. 2 the distribution of Al is nearly

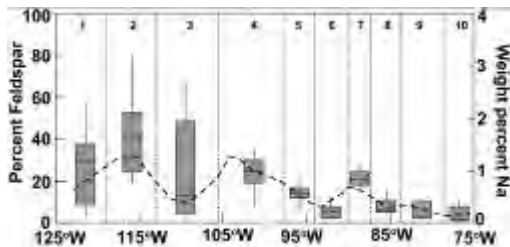


**Fig. 2.** Percent quartz in C horizon (dashed trend line) and weight percent Al (filled boxes) in C horizon soils along the W-E transect (truncated box plot; boxes include 50% of data, extent of lines include 80% of data; solid line is the median). Geochemical data shown by the box plots were grouped into 10 areas (vertical dashed lines, numbers at top of plot) defined by commonalities of physiographic features.

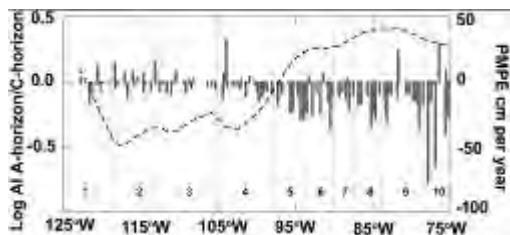
a mirror image of the distribution of quartz as the presence of quartz dilutes the presence of other minerals or elements other than Si.

The continental pattern for Na matches the pattern for total feldspar percentages, as Na values are primarily correlated with plagioclase (Eberl & Smith 2009). Feldspars are much more susceptible to chemical dissolution than quartz and, with sufficient time and precipitation, will weather mainly to clay minerals. As a result, total feldspar contents and Na contents decrease with increasing precipitation from west to east (Fig. 3).

Interpreting vertical chemical trends in soils along the transects is complicated by the diverse combination of parent materials, soil age, and climate, which all influence vertical element distributions. However, there is a common pattern for a number of elements in vertical soil profiles along the W-E transect that is apparently reflective of the strong west to east gradient in precipitation along the 38th parallel. The variability of mean annual precipitation minus mean annual potential evapotranspiration (PMPE) provides an index of relative moisture conditions at the ground surface (McCabe & Wolock 2002). Positive PMPE values indicate water in excess of climate demands, and negative values indicate a scarcity of water for climate demands (McCabe & Wolock 2002). Along the W-E transect, these hydrologic landscape-derived climate



**Fig. 3.** Percent feldspar in C horizon (dashed trend line) and weight percent Na in C horizon soils along the W-E transect (filled boxes). Plot specifics as in Figure 2.



**Fig. 4.** Trend line for PMPE (dashed line) plotted with a bar anchor plot of the log A-horizon/C-horizon Al ratios (dark boxes) for the W-E transect.

conditions roughly correspond to the general west (arid) to east (humid) pattern of increasing precipitation. In Figure 4, the log A-horizon/C-horizon ratio for Al is plotted as individual values with a base of 0 (ratio of 1). Also shown is a trend line for PMPE values for each sample site.

The log Al A-horizon/C-horizon ratio is variable for sites in the western half of the transect, but east of ~ 103.5°W longitude, the ratio becomes consistently <0, indicating that Al is higher in the C horizon than the A horizon. The vertical distributions for a diverse group of elements, including Fe, Ce, Cr, Cs, Ga, In, La, Ni, Rb, Sc, Th, and V, match the pattern observed for Al with a transition to log ratios consistently <0 east of the break point near 103.5°W longitude. This agreement for multiple elements suggests that this pattern represents a profound characteristic of soil geochemistry along the transect that appears independent of the very diverse soil parent materials and soil ages. The west-to-east shift in the A-horizon/C-horizon ratios for these elements corresponds with the west-to-east climatic shift from drier, more arid

conditions to wetter, more humid conditions. Where PMPE values are positive, excess surface soil moisture and its consequences, such as enhanced plant activity, soil leaching, and formation of secondary minerals, apparently dominate over the influence of soil parent material and soil age, and strongly influence the vertical distributions of many elements.

### North to South Transect

Data from the N-S transect reveal complex patterns for soil mineralogy and geochemistry. Marked transitions in both mineralogy and chemistry are noted where the N-S transect crosses the southern glacial limit. North of the glacial limit, soils record mixed glacial provenances while south of the limit, soils from a number of sites developed on transported and sorted parent materials, including loess and alluvium. An increase in clay content in loess south of the glacial limit compared to tills and outwash north of the glacial limit results in markedly higher concentrations of a number of elements in loess, including Al, Sc, Ti, Ba, Be, Bi, Ce, Cs, Ga, La, Nb, Pb, Rb, Sb, Sn, Th, U, and W.

Seventy-three soil samples from 0-to-5 cm depth along the N-S transect collected by ultraclean methods were analyzed for selected organochlorine pesticides. Only three of the samples had pesticide concentrations greater than the detection limit of the analytical method.

### CONCLUSIONS

Lessons learned from the field sampling for the transects and recognized in the geochemical data lead to the following:

- (1) A 40-km x 40 km sample spacing for the North American project will provide soil geochemical and mineralogical data that will display coherent and robust regional to continental-scale patterns, as also demonstrated by Smith and Reimann (2008).
- (2) Collecting soils from the A and C horizons eliminates variability resulting from mixing of soil horizons in random

percentages when using only a depth-based sampling. This provides the greatest chance for success in relating soil geochemistry to pedogenic processes. A 0-to-5 cm depth sample represents soils with a high potential of human contact.

(3) The distribution of Al and a number of other elements in soil profiles across the W-E transect appears to be strongly dependant on climate gradients rather than significant changes in soil parent materials and soil age. This observation provides important information about the relative importance of a number of geochemical processes that are not revealed in studies at more detailed (local) scales.

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