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Environment and Health

North American Soil Geochemical Landscapes Project

Sampling, Analytical and Data Handling Protocols for the North American Soil Geochemical Landscape Project

INTRODUCTION

Soil geochemical properties are critical to the health of the environment and virtually all organisms. The natural concentrations of elements differ among soil constituents and vary markedly between geologically distinct terranes. There is a requirement for soil geochemical data to assess the spatial variability related to issues of environment and health protection.

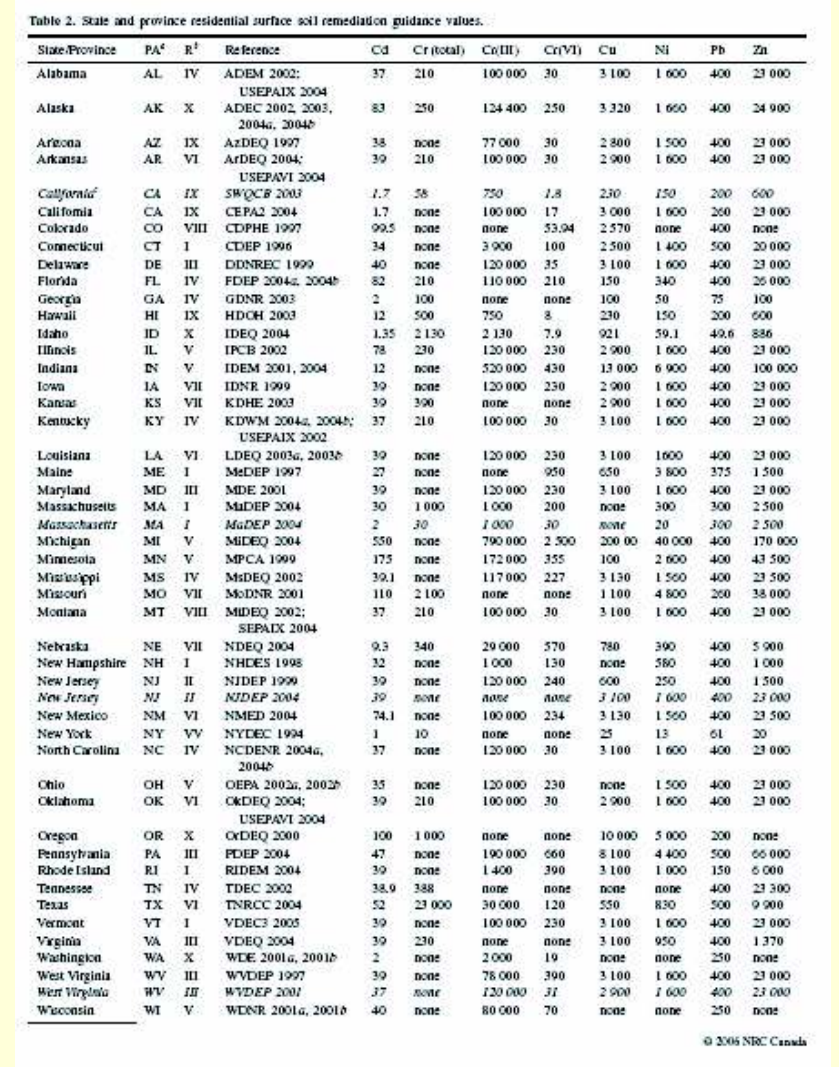
At present there is no common understanding of the amount and origin of variation in soil geochemistry, no consistent methodology for determining variation, and no national-scale set of soil geochemical data for Canada.

The North American Soil Geochemical Landscapes Project is a tri-national initiative between United States, Canada and Mexico. It was established to meet the need for standard geochemical data.
It provides: (1) consistent geochemical data for Canada and North America which characterizes background chemistry and sources of variation; (2) standard field and laboratory protocols.

The total land surface area covered by the Tri-national survey is nearly 40 times the size of France. The collection of soil samples to generate the geochemical database is only possible through the establishment of partnerships. These include federal, provincial and state geological surveys and organizations related to agriculture and forestry. Sampling and data generation will continue for an estimated decade. Use of consistent protocols ensures that the resultant data sets will stitch together to produce a final seamless geochemical database.

Variability of North American Regulatory Guidance

As shown below there is at present no common understanding of acceptable element levels in soils. Jennings & Petersen (2006) compiled a list of currently accepted residential surface soil remediation guidance values for provinces and states in Canada and United States.



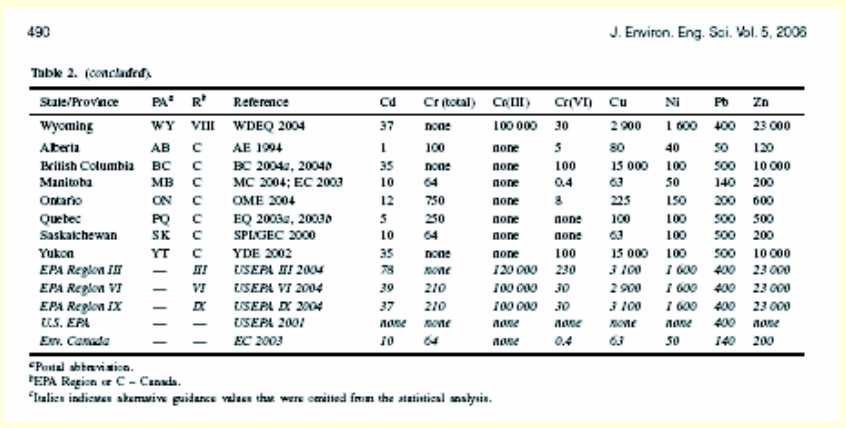


Table 2. State and province residential surface soil remediation guidance values.

State/Province	PA[a]	R[b]	Reference	Cd	Cr (total)	Cr(III)	Cr(VI)	Cu	Ni	Pb	Zn
Alabama	AL	IV	ADEM 2002; USEPAIX 2004	37	210	100 000	30	3 100	1 600	400	23 000
Alaska	AK	X	ADEC 2002, 2003, 2004a, 2004b	83	250	124 400	250	3 320	1 600	400	24 900
Arizona	AZ	IX	AzDEQ 1997	38	none	77 000	30	2 800	1 500	400	23 000
Arkansas	AR	VI	ArDEQ 2004; USEPAVI 2004	39	210	100 000	30	2 900	1 600	400	23 000
California[c]	*CA*	*IX*	*SWQCB 2003*	*1.7*	*58*	*750*	*1.8*	*230*	*150*	*200*	*600*
California	CA	IX	CEPA2 2004	1.7	none	100 000	17	3 000	1 600	260	23 000
Colorado	CO	VIII	CDPHE 1997	99.5	none	none	53.94	2 570	none	400	none
Connecticut	CT	I	CDEP 1996	34	none	3 900	100	2 500	1 400	500	20 000
Delaware	DE	III	DDNREC 1999	40	none	120 000	35	3 100	1 600	400	23 000
Florida	FL	IV	FDEP 2004a, 2004b	82	210	110 000	210	150	340	400	26 000
Georgia	GA	IV	GDNR 2003	2	100	none	none	100	50	75	100
Hawaii	HI	IX	HDOH 2003	12	500	750	8	230	150	200	600
Idaho	ID	X	IDEQ 2004	1.35	2 130	2 130	7.9	921	59.1	49.6	886
Illinois	IL	V	IPCB 2002	78	230	120 000	230	2 900	1 600	400	23 000
Indiana	IN	V	IDEM 2001, 2004	12	none	520 000	430	13 000	6 900	400	100 000
Iowa	IA	VII	IDNR 1999	39	none	120 000	230	2 900	1 600	400	23 000
Kansas	KS	VII	KDHE 2003	39	390	none	none	2 900	1 600	400	23 000
Kentucky	KY	IV	KDWM 2004a, 2004b; USEPAIX 2002	37	210	100 000	30	3 100	1 600	400	23 000
Louisiana	LA	VI	LDEQ 2003a, 2003b	39	none	120 000	230	3 100	1600	400	23 000
Maine	ME	I	MeDEP 1997	27	none	none	950	650	3 800	375	1 500
Maryland	MD	III	MDE 2001	39	none	120 000	230	3 100	1 600	400	23 000
Massachusetts	MA	I	MaDEP 2004	30	1 000	1 000	200	none	300	300	2 500
Massachusetts	*MA*	*I*	*MaDEP 2004*	*2*	*30*	*1 000*	*30*	*none*	*20*	*300*	*2 500*
Michigan	MI	V	MiDEQ 2004	550	none	790 000	2 500	200 00	40 000	400	170 000
Minnesota	MN	V	MPCA 1999	175	none	172 000	355	100	2 600	400	43 500
Mississippi	MS	IV	MsDEQ 2002	39.1	none	117 000	227	3 130	1 560	400	23 500
Missouri	MO	VII	MoDNR 2001	110	2 100	none	none	1 100	4 800	260	38 000
Montana	MT	VIII	MtDEQ 2002; SEPAIX 2004	37	210	100 000	30	3 100	1 600	400	23 000
Nebraska	NE	VII	NDEQ 2004	9.3	340	29 000	570	780	390	400	5 900
New Hampshire	NH	I	NHDES 1998	32	none	1 000	130	none	580	400	1 000
New Jersey	NJ	II	NJDEP 1999	39	none	120 000	240	600	250	400	1 500
New Jersey	*NJ*	*II*	*NJDEP 2004*	*39*	*none*	*none*	*none*	*3 100*	*1 600*	*400*	*23 000*
New Mexico	NM	VI	NMED 2004	74.1	none	100 000	234	3 130	1 560	400	23 500
New York	NY	VV	NYDEC 1994	1	10	none	none	25	13	61	20
North Carolina	NC	IV	NCDENR 2004a, 2004b	37	none	120 000	30	3 100	1 600	400	23 000
Ohio	OH	V	OEPA 2002a, 2002b	35	none	120 000	230	none	1 500	400	23 000
Oklahoma	OK	VI	OkDEQ 2004; USEPAVI 2004	39	210	100 000	30	2 900	1 600	400	23 000
Oregon	OR	X	OrDEQ 2000	100	1 000	none	none	10 000	5 000	200	none
Pennsylvania	PA	III	PDEP 2004	47	none	190 000	660	8 100	4 400	500	66 000
Rhode Island	RI	I	RIDEM 2004	39	none	1 400	390	3 100	1 000	150	6 000
Tennessee	TN	IV	TDEC 2002	38.9	388	none	none	none	none	400	23 300
Texas	TX	VI	TNRCC 2004	52	23 000	30 000	120	550	830	500	9 900
Vermont	VT	I	VDEC3 2005	39	none	100 000	230	3 100	1 600	400	23 000
Virginia	VA	III	VDEQ 2004	39	230	none	none	3 100	950	400	1 370
Washington	WA	X	WDE 2001a, 2001b	2	none	2 000	19	none	none	250	none
West Virginia	WV	III	WVDEP 1997	39	none	78 000	390	3 100	1 600	400	23 000
West Virginia	*WV*	*III*	*WVDEP 2001*	*37*	*none*	*120 000*	*31*	*2 900*	*1 600*	*400*	*23 000*
Wisconsin	WI	V	WDNR 2001a, 2001b	40	none	80 000	70	none	none	250	none

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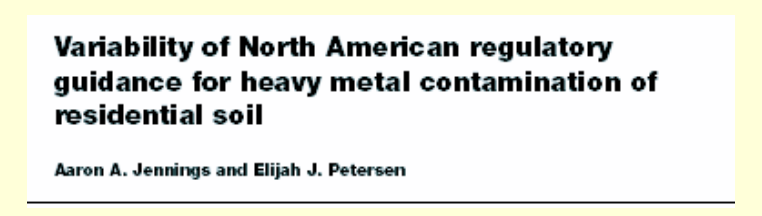
Table 2. (*concluded*).

State/Province	PA[a]	R[b]	Reference	Cd	Cr (total)	Cr(III)	Cr(VI)	Cu	Ni	Pb	Zn
Wyoming	WY	VIII	WDEQ 2004	37	none	100 000	30	2 900	1 600	400	23 000
Alberta	AB	C	AE 1994	1	100	none	5	80	40	50	120
British Columbia	BC	C	BC 2004a, 2004b	35	none	none	100	15 000	100	500	10 000
Manitoba	MB	C	MC 2004; EC 2003	10	64	none	0.4	63	50	140	200
Ontario	ON	C	OME 2004	12	750	none	8	225	150	200	600
Quebec	PQ	C	EQ 2003a, 2003b	5	250	none	none	100	100	500	500
Saskatchewan	SK	C	SPI/GEC 2000	10	64	none	none	63	100	500	200
Yukon	YT	C	YDE 2002	35	none	none	100	15 000	100	500	10 000
EPA Region III	*—*	*III*	*USEPA III 2004*	*78*	*none*	*120 000*	*230*	*3 100*	*1 600*	*400*	*23 000*
EPA Region VI	*—*	*VI*	*USEPA VI 2004*	*39*	*210*	*100 000*	*30*	*2 900*	*1 600*	*400*	*23 000*
EPA Region IX	*—*	*IX*	*USEPA IX 2004*	*37*	*210*	*100 000*	*30*	*3 100*	*1 600*	*400*	*23 000*
U.S. EPA	*—*	*—*	*USEPA 2001*	*none*	*none*	*none*	*none*	*none*	*none*	*400*	*none*
Env. Canada	*—*	*—*	*EC 2003*	*10*	*64*	*none*	*0.4*	*63*	*50*	*140*	*200*

[a] Postal abbreviation.
[b] EPA Region or C – Canada.
[c] Italics indicates alternative guidance values that were omitted from the statistical analysis.



Variability of North American regulatory guidance for heavy metal contamination of residential soil

Aaron A. Jennings and Elijah J. Petersen

Journal of Environmental Engineering , v. 5, p. 485-508.

TRI-NATIONAL PROJECT PROTOCOLS

- The Tri-national protocols are comprehensive for field, laboratory, archiving samples and data, and undertaking quality control and assurance.
- They are based on up-to-date methodology and new testing.
- Their use provides data that meet a standard for comparison in North America
- Development of a protocol manual is a major focus of the Tri-national documentation is detailed for all phases of field, laboratory, and data handling.
- Project has a database framework and protocols manual designed to accommodate new data and new protocols as needed.
- We cannot say that these are the only protocols needed. However, they do provide one standard for comparison that is nationally and internationally consistent.

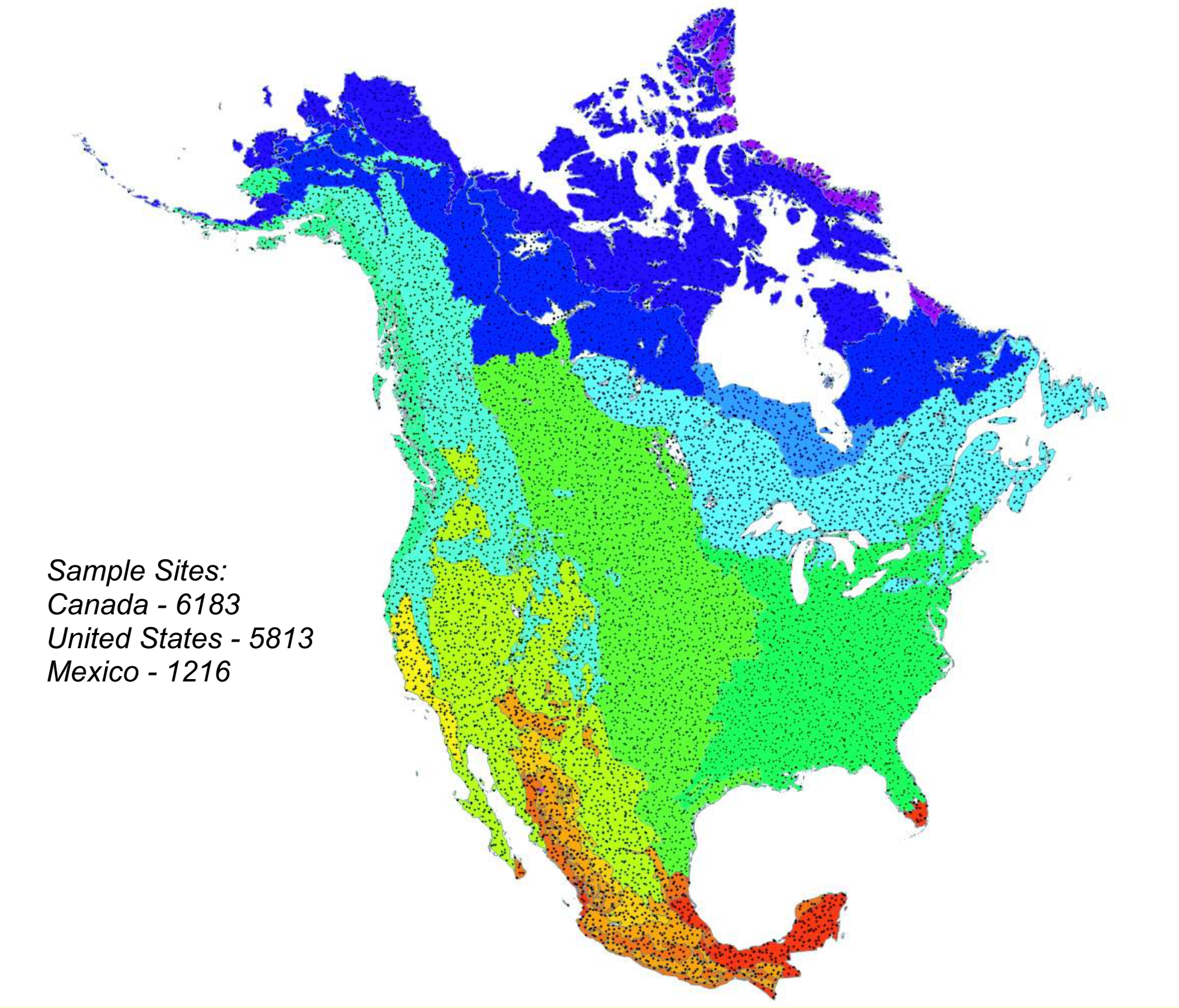
A soil sample pit near Ottawa, Canada

Work on Tri-national samples at GSC, Ottawa

THE CHALLENGES

Developing a set of protocols to ensure a consistent data set for North America is not without its challenges, some of which are noted as follows: (1) the enormous size of the continent; (2) three international and 95 state and provincial jurisdictions; (3) the complexity of the operation in that sampling is horizon- and depth-based and involves numerous types of analyses, all requiring field, laboratory, quality assurance, archiving, and data handling protocols; (4) the many types of mineral and organic soils and field situations (e.g. peatland, permafrost, desert, mountain, urban, and agriculture areas) that require diverse equipment and procedures; and (5) the need to anticipate and accommodate possible future requirements. From the outset of the Project, attention has been paid to developing and documenting the protocols necessary to provide a data set that serves as a common national and international standard.

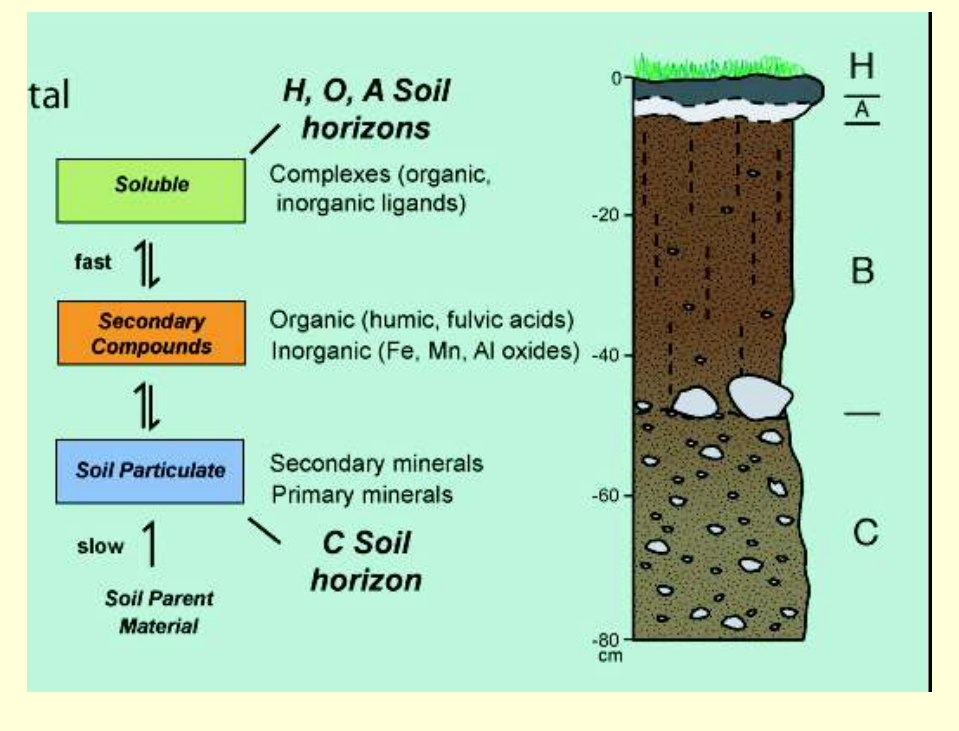
SAMPLE SITE SELECTION



Sample Sites:
Canada - 6183
United States - 5813
Mexico - 1216

Project sampling is based on a spatially balanced array known as a generalized random tessellation stratified (GRTS) sampling design (Garrett 1983; Stevens & Olsen 2004). It was chosen for its added flexibility. With this design it is possible to locally increase the sampling density in areas of special concerns within the context of the continental sampling framework.

CORE SOIL ANALYSES



Soil sampling is horizon-based. Diagram shows characteristics of individual soil horizons.

At each site in areas of mineral soils, samples are collected from a depth of 0-5 cm (referred to as the "public health" layer) and from the A- and C- soil horizons.

The <2 mm fraction (an agricultural and environmental standard) is analyzed for a suite of more than 40 major, minor and trace elements, following a near-total (4-acid) digestion.

A separate sample from the 0-5-cm depth interval from each site will be analyzed for the presence of *Bacillus anthracis* (anthrax).

Splits of each soil sample are archived and will be made available for future investigations.

ADDITIONAL SOIL SAMPLING AND ANALYSES IN 3 COUNTRIES

Each country will carry out certain other procedures and analyses that are particular to its environmental and/or policy needs.

Canada

The extra procedures include the following: collection and analysis of B-horizon samples; analyses of the <63 µm fractions of A-, B-, and C-horizon samples using total (4-acid) and partial (USA-EPA 3050B) digestions; and analysis of 0-5 cm and C-horizon samples after a water leach (G.E.M. Hall, Geological Survey of Canada, 2008, unpublished report). Another major addition to the Canadian project is the in-situ measurement of soil gas radon and natural radioactivity.

Use of the <63 µm (silt-plus clay-sized) fraction and partial leaches allow for a more detailed understanding of bioaccessibility. In addition, this fraction of soil and till samples is commonly analyzed in Canada for mineral exploration and geological mapping purposes and there is a large body of existing geochemical data for this size fraction for comparison.

United States

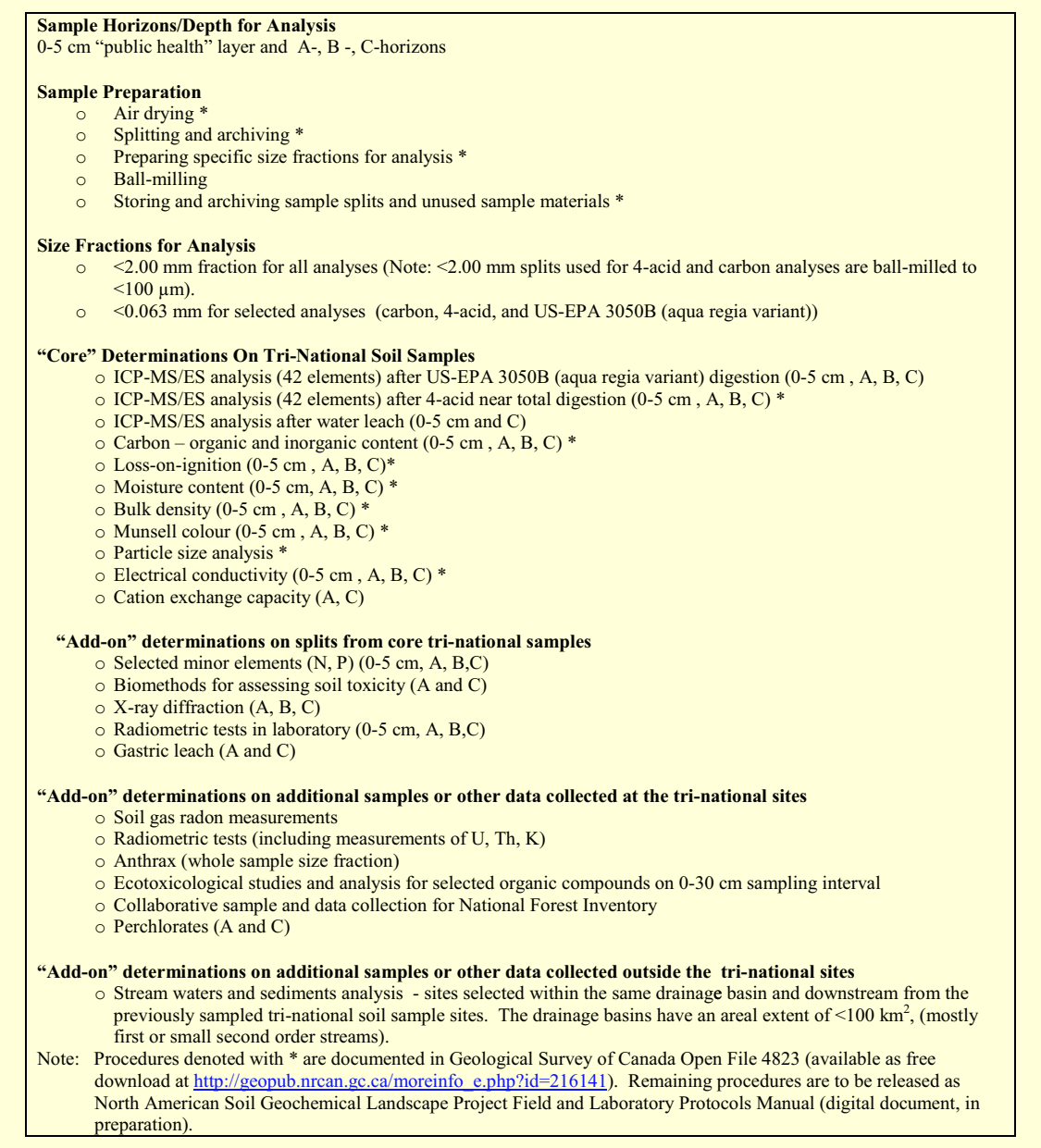
Samples of each of the three depths/horizons at 10% of the sites are being collected for additional microbial characterization. Physiological-based extraction techniques, such as digestion with simulated human gastric and lung fluids, are conducted on a subset of the 0-5 cm soils.

Mexico

The bioaccessibility of selected potentially toxic elements are being measured in 0-5 cm interval and A-horizon samples. The mobility of a broad suite of elements is being tested in C-horizon and some B-horizon soil samples.

The in-situ measurement of soil gas radon and natural radioactivity is a major value-added feature of the Canadian project.

Standard sampling and analytical procedures for the Canadian Project



Sample Horizons/Depth for Analysis
0-5 cm "public health" layer and A-, B -, C-horizons

Sample Preparation
- Air drying *
- Splitting and archiving *
- Preparing specific size fractions for analysis *
- Ball-milling
- Storing and archiving sample splits and unused sample materials *

Size Fractions for Analysis
- <2.00 mm fraction for all analyses (Note: <2.00 mm splits used for 4-acid and carbon analyses are ball-milled to <100 µm).
- <0.063 mm for selected analyses (carbon, 4-acid, and US-EPA 3050B (aqua regia variant))

"Core" Determinations On Tri-National Soil Samples
- ICP-MS/ES analysis (42 elements) after US-EPA 3050B (aqua regia variant) digestion (0-5 cm , A, B, C)
- ICP-MS/ES analysis (42 elements) after 4-acid near total digestion (0-5 cm , A, B, C) *
- ICP-MS/ES analysis after water leach (0-5 cm and C)
- Carbon – organic and inorganic content (0-5 cm , A, B, C) *
- Loss-on-ignition (0-5 cm , A, B, C)*
- Moisture content (0-5 cm, A, B, C) *
- Bulk density (0-5 cm , A, B, C) *
- Munsell colour (0-5 cm , A, B, C) *
- Particle size analysis *
- Electrical conductivity (0-5 cm , A, B, C) *
- Cation exchange capacity (A, C)

"Add-on" determinations on splits from core tri-national samples
- Selected minor elements (N, P) (0-5 cm, A, B,C)
- Biomethods for assessing soil toxicity (A and C)
- X-ray diffraction (A, B, C)
- Radiometric tests in laboratory (0-5 cm, A, B,C)
- Gastric leach (A and C)

"Add-on" determinations on additional samples or other data collected at the tri-national sites
- Soil gas radon measurements
- Radiometric tests (including measurements of U, Th, K)
- Anthrax (whole sample size fraction)
- Ecotoxicological studies and analysis for selected organic compounds on 0-30 cm sampling interval
- Collaborative sample and data collection for National Forest Inventory
- Perchlorates (A and C)

"Add-on" determinations on additional samples or other data collected outside the tri-national sites
- Stream waters and sediments analysis - sites selected within the same drainage basin and downstream from the previously sampled tri-national soil sample sites. The drainage basins have an areal extent of <100 km^2, (mostly first or small second order streams).

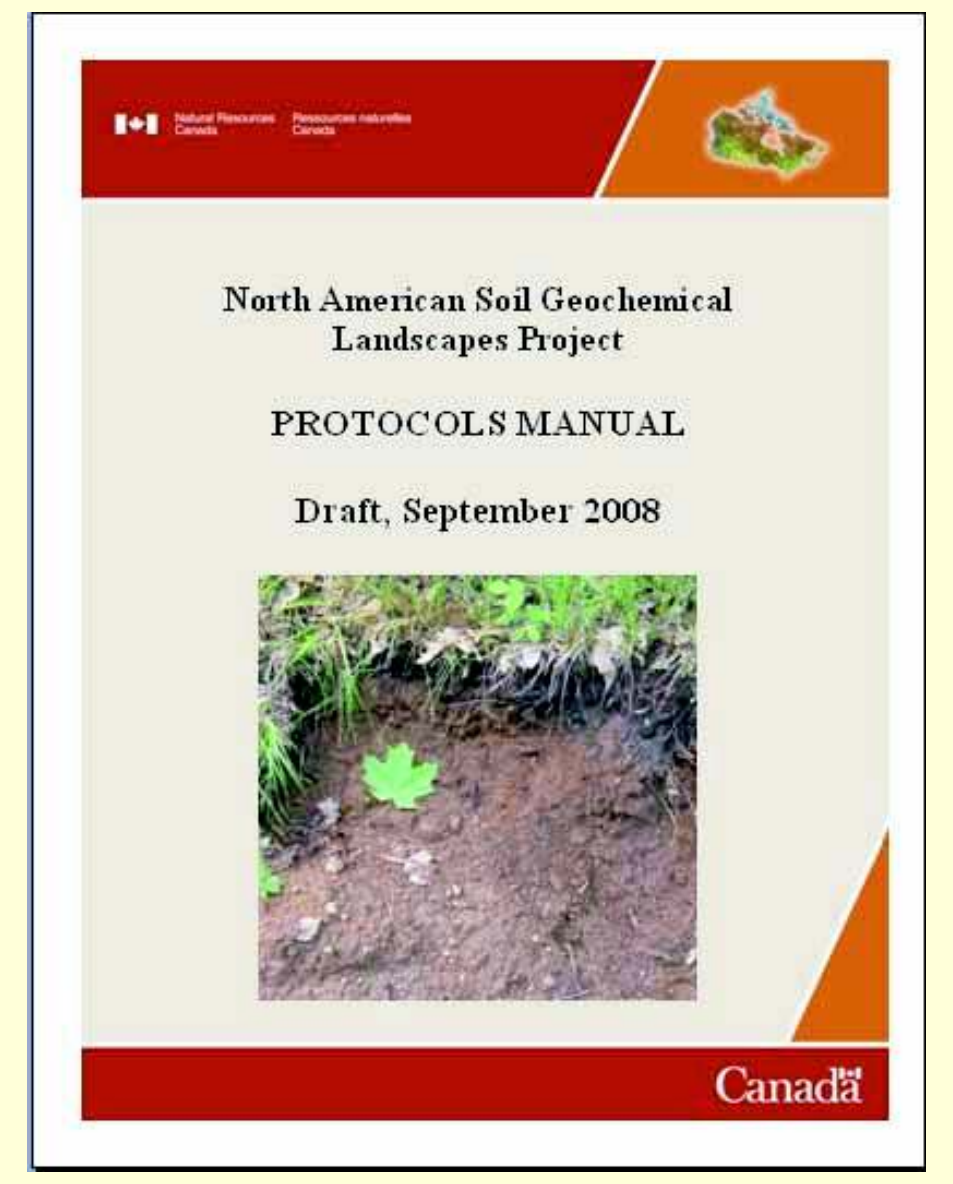
Note: Procedures denoted with * are documented in Geological Survey of Canada Open File 4823 (available as free download at http://geopub.nrcan.gc.ca/moreinfo_e.php?id=216141). Remaining procedures are to be released as North American Soil Geochemical Landscape Project Field and Laboratory Protocols Manual (digital document, in preparation).

PROTOCOL DEVELOPMENT AND DOCUMENTATION

A major part of the Tri-national Project is the development and documentation of protocols for soil sample collection and analysis to ensure consistent geochemical data.

The protocol manual being constructed has sufficient background information and detail to provide guidance to individuals from the user community who are seeking advice on procedures. There are recommended protocols related to the national data base.

To determine "optimal" methodology for the purpose of establishing a Tri-national protocol it is sometimes necessary to test a variety of analytical methods. One such case was the partial extraction experiment where aqua regia and its variants were tested in order to select the best technique for the Tri-national Project.



North American Soil Geochemical Landscapes Project

PROTOCOLS MANUAL

Draft, September 2008

Canada

Standard field and laboratory protocols are documented in a protocols manual.

PROTOCOLS FOR DATA MANAGEMENT, ANALYSIS AND PRESENTATION

- Integrated relational database management systems for all Tri-national data
- Geographic referencing for all data
- Toolkit (rgr) for analyzing analytical results
- Presentation of data and results of data analysis in both data and geographic contexts.

SUMMARY

A major part of the Tri-national Project is the development and documentation of protocols for soil sample collection and analysis to ensure consistent geochemical data.

To determine "optimal" methodology for the purpose of establishing a Tri-national protocol it is sometimes necessary to test a variety of analytical methods.

The Project framework is sufficiently flexible to incorporate additional protocols and new types of data when required in the future.

The protocol manual being constructed has background information and details to provide guidance to individuals from the user community who are seeking advice on procedures. There are recommended protocols related to the Tri-national data base