

Abstract

Ecological and human health risk assessments at active and abandoned metal mines require accurate geochemical data for earth materials, including soils, sediments, dusts, and mine wastes. Reliable data on metal(loid) concentrations are also important for establishing geochemical baselines and to support environmental monitoring activities. However, the reported concentration for an element in a given sample can be affected by many factors, including mineralogy, grain size, laboratory digestion conditions (reagents, temperature, time), and the instrument(s) used for elemental analysis. In particular, aggressive multi-acid digestion methods used to provide “near-total” data for some metals of environmental interest (e.g. chromium (Cr), uranium (U)) may result in the loss of other elements (e.g. antimony (Sb), arsenic (As), sulfur (S)) through volatilization prior to analysis. When comparing data from different studies or sampling periods, it is crucial to ensure that the analytical protocols used are consistent and that changes in element concentrations over time are not simply due to variations in sample processing or laboratory procedures.

The purpose of this study is to compare common digestion protocols used in the analysis of geological materials and provide recommendations on the most appropriate techniques for use in environmental risk assessments. We analyzed samples of lake sediments, stream sediments, soils, and mine tailings collected at metal mine sites across Canada. These samples were digested using two of the most commonly employed procedures in exploration and environmental geochemistry: a modified *aqua regia* digestion and a 4-acid digestion. All solutions were analyzed using ICP-ES/MS, and certified reference materials (CRMs) and duplicate samples were used to monitor analytical accuracy and precision. The concentration of elements (e.g. Cr) hosted in relatively insoluble mineral phases are consistently higher following 4-acid digestions as compared to digestions using *aqua regia*, but generally lower than total values measured using direct methods of analysis (e.g. Instrumental Neutron Activation Analysis). In contrast, the concentrations of As are often higher in samples following *aqua regia* versus 4-acid digestions and generally in good agreement with total values in CRMs. The behaviour of other elements (e.g. Sb, copper (Cu), lead (Pb), S, zinc (Zn)) was more variable and for many samples, the results following 4-acid and *aqua regia* digestions were statistically indistinguishable. Variations in the mineralogy of different samples play a key role in determining the fraction of different metal(loid)s released by these digestion techniques. This poster highlights some of the advantages and disadvantages of using each of these digestion protocols for risk assessment and environmental monitoring purposes, and provides recommendations for using geochemical data to help guide environmental decision-making at both active and abandoned metal mines.

Motivation for Study

- Reliable geochemical data for metals and metalloids are an essential component of environmental and human-health risk assessments (Rencz et al. 2011), especially in mineralized areas with naturally elevated metal(loid) concentrations and/or contamination from mining activities.
- Geochemical data are often compared to regulatory guidelines (e.g. CCME 2018) to evaluate potential risks, to distinguish the effects of anthropogenic contamination from natural geological variability, and to establish realistic remediation targets for the clean-up of contaminated sites.
- Regulatory agencies across Canada and around the world use various analytical protocols for the determination of metals and metalloids in environmental samples, which may produce very different concentrations for a given element depending on the sample mineralogy, laboratory digestion conditions (reagents, temperature, time), and analytical technique.
- The main objective of this study is compare geochemical results from two commonly employed digestion protocols used in the analysis of geological materials in Canada and provide recommendations on the most appropriate techniques for use in environmental risk assessments.

Typical disclaimers from contract labs regarding multi-acid digestions:

4-Acid “Near Total” Digestion

“This acid attack is the most vigorous digestion used in geochemistry. It will employ hydrochloric, nitric, perfluoric and hydrofluoric acids. Even with this digestion, certain minerals (barite, galena, chromite, cassiterite, etc.) may only be partially dissolved or stable in solution. Other minerals including zircon, sphene and magnetite may not be totally dissolved. Most other silicates will be dissolved, however some elements will be erratically volatilized, including As, Sb, Cr, U and Au. Near-Total digestion cannot be used to obtain accurate determinations of REE, Ta, Nb, As, Sb, Sn, Hg, Cr, Au and U.”

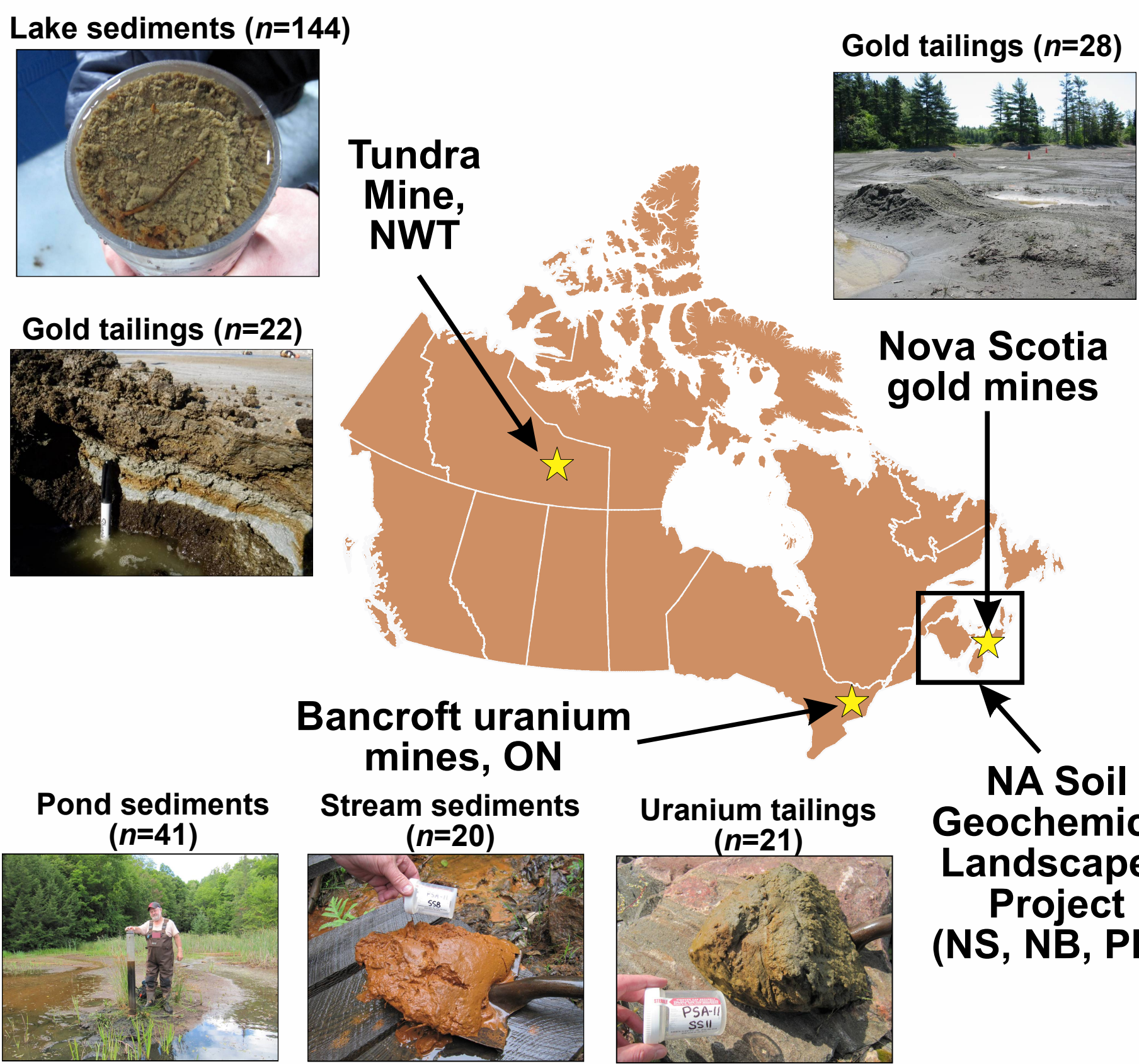
- Actlabs (2018)

Multi Acid Digestion

In multi-acid digestion packages, “a 0.25 g soil is heated in HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>-HF to fuming and taken to dryness. The residue is dissolved in HCl. While multi-acid digestion is considered to be a near total digestion, this digestion is only partial for some Cr and Ba minerals and oxides of Al, Fe, Hf, Mn, Sn, Ta, Zr and REEs. Additionally volatilization during fuming may result in some loss of As, S and Sb.”

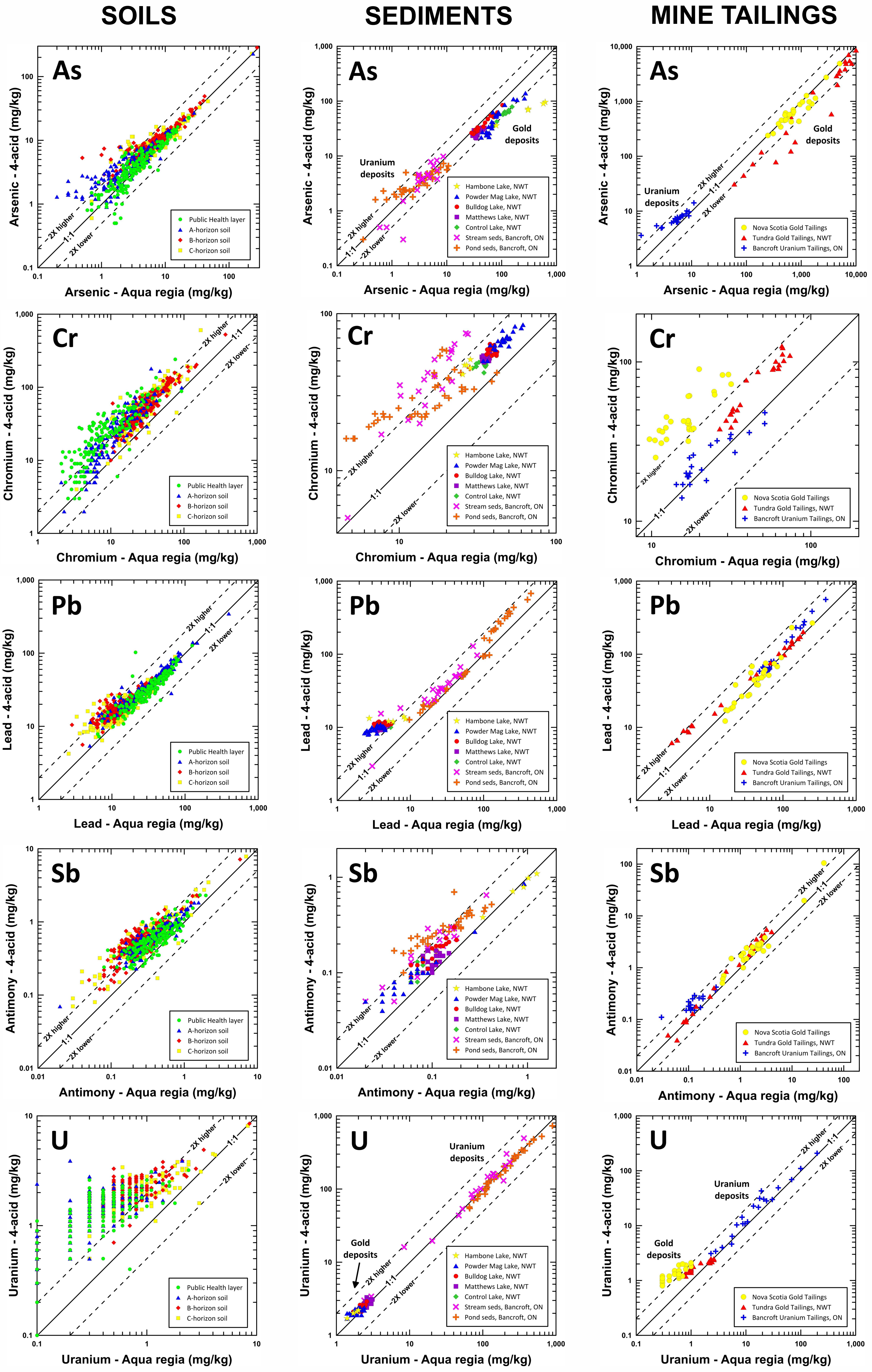
- Bureau Veritas (2018)

Sample Selection and Laboratory Methods



- Geochemical data for sediments and mine tailings were selected from previous studies by the authors at the former Tundra Gold Mine, NWT, historical gold mines in Nova Scotia (Corriveau, 2006), and at decommissioned uranium mines near Bancroft, ON.
- Air dried sediments and tailings samples were sieved to <177 µm, then digested using both a modified *aqua regia* digestion (equal parts HNO<sub>3</sub>:HCl:H<sub>2</sub>O at 95°C for one hour) and a 4-acid digestion (HF-HClO<sub>4</sub>-HNO<sub>3</sub> heated to fuming and taken to dryness; residue dissolved in HCl). All solutions were analyzed using ICP-ES/MS, and CRMs and duplicate samples were used to monitor analytical accuracy and precision.
- Soil geochemistry data were chosen from the 2007 North American Soil Geochemical Landscapes Project in New Brunswick, Nova Scotia and Prince Edward Island (n=177; Friske et al. 2014).
- Soil samples were air dried, sieved to <2 mm, then digested with the same 4-acid protocol described above, and a modified *aqua regia* digestion using 1 part HNO<sub>3</sub> to 4 parts HCl at 95°C for one hour (Garrett et al. 2008; Friske et al. 2014).

Comparison of 4-Acid and Aqua Regia Digestions



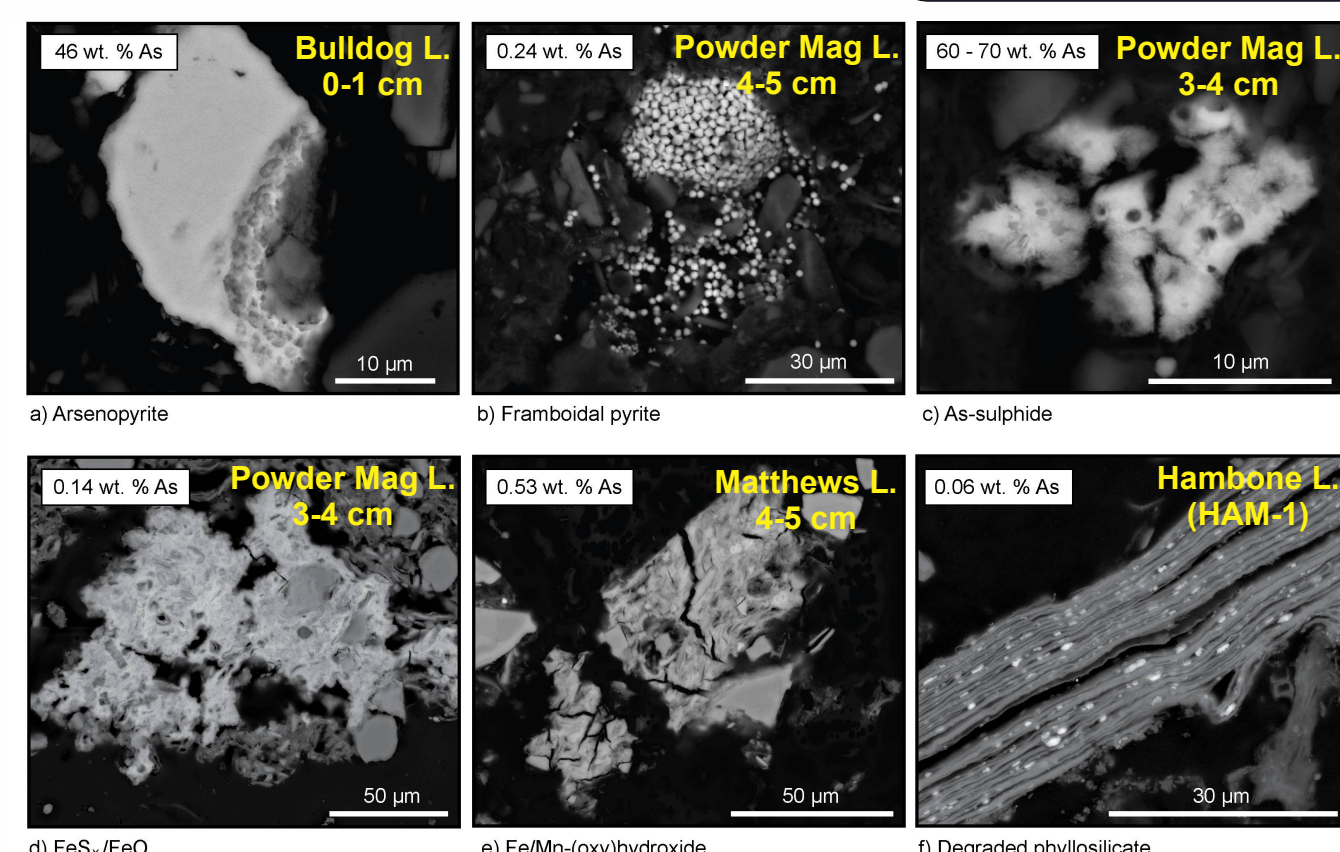
Summary Statistics: Percentage Change - 4-acid vs. Aqua Regia

	SOILS				SEDIMENTS				MINE TAILINGS			
	Min	Max	Median	n	Min	Max	Median	n	Min	Max	Median	n
As	-240%	91%	18%	677	-552%	70%	-25%	139	-501%	67%	-9%	69
Cd	-181%	95%	29%	655	-24%	77%	9%	143	-60%	86%	16%	71
Cr	-115%	87%	47%	678	-5%	71%	34%	143	-25%	78%	36%	71
Cu	-117%	86%	14%	678	-41%	21%	-1%	143	-68%	41%	-4%	71
Ni	-409%	82%	13%	678	-37%	53%	4%	143	-24%	49%	7%	71
Pb	-129%	87%	15%	678	-23%	79%	55%	143	-33%	52%	7%	71
S	-280%	100%	-56%	240	-68%	50%	-2%	142	-140%	70%	-7%	44
Sb	-153%	81%	43%	677	-15%	100%	38%	143	-50%	73%	24%	71
U	-88%	96%	67%	671	-48%	48%	4%	143	-20%	75%	40%	71
Zn	-90%	82%	8%	678	-17%	64%	7%	143	-14%	63%	15%	71

Positive values = 4-acid > aqua regia Negative values = 4-acid < aqua regia Medians ≥ ±20% are shaded

In general, the concentrations of elements (e.g. Cr, Sb, U) hosted in relatively insoluble mineral phases are higher following 4-acid digestions as compared to digestions using *aqua regia*. The concentrations of As in sediments and mine tailings, and S in soils, are on average lower following 4-acid digestions as compared to digestions using *aqua regia*, which may result from volatilization of these elements (e.g. as volatile AsF<sub>3</sub> or SO<sub>2</sub>) during fuming with HF and boiling to dryness prior to analysis.

Mineralogical Controls



Arsenic-hosting solid phases identified in near-surface lake sediments from the Tundra Mine region, NWT (from Miller et al., submitted). The crystallinity, grain size, and solubility of these phases varies, which leads to differences in the amount of As released in 4-acid vs. aqua regia digestions.

- In soils, sediments, and mine tailings, metal(loid)s are hosted by a range of primary and secondary minerals that reflect the underlying bedrock geology, soil-forming processes, and degree of weathering.
- These minerals have varying solubilities, which contributes to the differences between the 4-acid and *aqua regia* results for a given element in the table above.
- For ecological and human health risk assessments, strong acid digestions should be supplemented with analyses of metal speciation and bioaccessibility tests to determine the true risks associated with elevated metal(loid) concentrations in geological materials.

Conclusions and Recommendations

- Digestion protocols used for the determination of near-total metal(loid) concentrations in earth materials, including soils, sediments, dusts, and mine wastes, should be chosen carefully to provide the most accurate data possible. For multi-element surveys, more than one digestion may be required for each sample to provide quantitative data for metal(loid)s hosted by both labile and insoluble phases. Most contract labs are pleased to help clients select methods that are fit-for-purpose. End-users should also submit blind duplicates and Certified Reference Materials as an independent check on laboratory QA/QC.
- For surveys where As and mercury (and potentially sulphur in the case of soils) are the main elements of interest, *aqua regia* digestions are recommended to minimize the loss of these elements via volatilization during sample processing.
- 4-acid digestions are recommended when the main elements of concern are typically hosted in silicate minerals or oxide phases (e.g. Cr, U). Fusion methods may be required to obtain accurate total concentrations for some elements (e.g. Cr, Ba, REEs).
- When comparing data from different studies or sampling periods, it is crucial to ensure that analytical protocols are consistent and that changes in element concentrations over time are not due to variations in sample processing or laboratory procedures.

References

Canadian Council of Ministers of the Environment (CCME) (2018) Canadian Environmental Quality Guidelines. Available online at: <http://ceqg-rceq.ccmec.ca/>

Corriveau, M.C. (2006) Characterization of arsenic-bearing near-surface and airborne particulates from gold mine tailings in Nova Scotia, Canada. M.Sc. (Eng.) Thesis, Queen's University, 124 p.

Friskes, 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), 50 p., doi: 10.4095/293020.

Garrett, R.G., Grunsky, E.C., and Friske, P.M.B. (2008) Comparison of soil data obtained using aqua regia variants on 8 standard reference materials. Geological Society of America, Abstracts with Programs, v. 40, no. 6, p. 490 (poster presented at GSA annual meeting in Houston, Texas, October 2008).

Miller, C.B., Parsons, M.B., Jamieson, H.E., Swindles, G.T., Nasser, N.A., and Galloway, J.M. (submitted) Lake-specific controls on the long-term stability of mining-related, legacy As contamination and geochemical baselines in a changing northern environment, Tundra Mine, Northwest Territories, Canada.

Rencz, A.N., Garrett, R.G., Kettles, I.M., Grunsky, E.C., and McNeil, R.J. (2011) Using soil geochemical data to estimate the range of background element concentrations for ecological and human-health risk assessments. Geological Survey of Canada, Current Research 2011-9, 22 p., doi:10.4095/288746.

Acknowledgements & Contact Information

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