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Introduction

A variety of analytical protocols are employed by environmental agencies in North America, there are no consistent national or international protocols. Aqua Regia (AQ), or similar, digestions are common. To determine whether an AQ, or some other hot acid, digestion would be used to determine near-total metal and metalloid levels in soil materials for the Tri-National survey an experiment comparing five digestion protocols, Aqua Regia, Lefort (reverse AQ), 1:1 HCl-HNO₃, 1:1:1 HCl-HNO₃-H₂O, and the HNO₃-H₂O variant of US-EPA 3050B was undertaken. Eight control reference materials, two each of soils, tills, and stream and lake sediments, were analysed, with appropriate randomization, in triplicate by the five methods. Analyses of Variance were undertaken to determine which protocols yielded similar data. These indicated that the HNO₃-H₂O variant of US-EPA 3050B generally extracts significantly less metals and metalloids, with the exception of Hf, Nb, Th and Zr, than AQ and similar digestions. For the remaining protocols, AQ and three HCl-HNO₃ variants, the results are similar, even when results are statistically (p<0.05) different between protocols an inspection indicates that most differences are likely insignificant in a geochemical context. Considering the volume of AQ and US-EPA AQ-variant data existing in North America and internationally, and that the AQ-like variants yield very similar results for most elements, it is recommended that the Tri-National project employ the US-EPA 3050B AQ-variant digestion. This procedure used a 4:1 HCl-HNO₃ mix rather than the 3:1 of "classical" AQ. The Geological Survey of Canada has prepared a protocol defining the procedures to be used for Tri-National analyses. These include the choices of 1 g (<63 μm) or 10 g (<2 mm) aliquots and a 1:12.5 solid:reagent ratio.

Table 1

Province/Territory	Sample Type	Sample Preparation	Digestion	Elements
CCME	Depth not specified, uppermost 1.5 m suggested; samples are either coarse (>75 μ) or fine (<75 μ)		US EPA, Method 3050B for GFAA/ICP-MS HCl/HNO ₃ /H ₂ O ₂	
Ontario	composite, 10-15 cores collected within 2 m radius; 0-5 cm depth	dry composite sample at 40°C; grind & sieve through 2 mm screen; grind and sieve through 355 μ screen	0.5 g digested with conc. HNO ₃ /conc. HCl; heated for two hours at 120°C	Cd, V, Pb, Cr, Mo, Ba, Co, Ni, Cu, Zn
British Columbia	Discrete or composite; depends on purpose	dry composite sample at 60°C; sieve through 2 mm screen; do not grind	to 1.0 g dry sample is added equal volumes of conc. HNO ₃ and HCl. Digest for two hours at 90°C	Metals
Yukon Territory	For background samples, one sample taken up to 0.5 m below surface, per 50 m ² soil	Methods approved by BC Ministry of Water, Land and Air Protection	Methods approved by BC Ministry of Water, Land and Air Protection	
Saskatchewan	composite, 0-5 cm depth	sample is dried and sieved to extract the <63 micron fraction	digested with conc. HCl, conc. HNO ₃ and perchloric acid	
New Brunswick	composite, 0-5 cm depth	sample is homogenized (stirred) and a portion is removed and dried at 56°C overnight	0.5 g digested with conc. HNO ₃ /30% H ₂ O ₂ , diluted to 50 ml	As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn
Nova Scotia	Composite	dry composite sample at 60°C; sieve through -180 μm screen	aqua regia	Metals
Manitoba	Depends on nature of site		US EPA, Methods	

Table 2
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 (diamiction)
TILL-4	GSC-CCRMP glacial till (diamiction)
SoNE-1	USGS Nebraska soil
2711	USGS Montana soil

Table 3
Analytical Protocols

M1 [AR-111] 1 g sample in a test-tube digest with 3 ml of 1:1:1 HCl-HNO ₃ -H ₂ 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 ₃ 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 ₃ 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 ₃ . Cold digest 0.5 g sample in a test tube with 1.5 ml of conc. HNO ₃ 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 ₃ -H ₂ 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 ₃ , 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 ₂ O ₂ , reheat the samples in hot water bath until the reaction subsides, cool the samples and continue adding another 0.5 ml of 30% H ₂ O ₂ 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.

Table 4
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	1, 2, 3
2	1, 2, 3	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	1, 2, 3
4	1, 2, 3	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	1, 2, 3
6	1, 2, 3	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	1, 2, 3
8	1, 2, 3	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
 $Y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \gamma_k + \epsilon_{ijk}$
 Where:
 Y_{ijk} = the k-th replicate analysis by the i-th Method of the j-th CRM
 μ = the grand mean
 α_i = the main effect due to the i-th Method
 β_j = the effect due to the j-th CRM (Sample)
 $(\alpha\beta)_{ij}$ = the interaction effect between the i-th Method and j-th CRM
 γ_k = the effect due to the k-th analysis of the j-th CRM
 ϵ_{ijk} = the pooled residual variability

Results - 1

Of the 53 elements determined, 48 had useful values above the method detection limits. The data for four elements, As, Cr, Cu and Zr, are presented, as examples of metals and metalloids that occur in both soluble and acid-resistant mineral phases. See Panel 1, which shows the variability of the elemental determinations given CRM and method protocol using dotplots. These plots highlight the varying analytical precision for each material and each analytical protocol. Chromium shows the greatest variability over 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 CRMs and analytical protocols. The variability of Cu lies between these two extremes, exhibiting higher variability only for TILL-4.

Results - 2

Panel 2, to the right, shows 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 and Zr, this latter effect is clearly demonstrated, whereas for As and Cu, the methods consistently extract proportionally similar amounts.

ANOVA Results

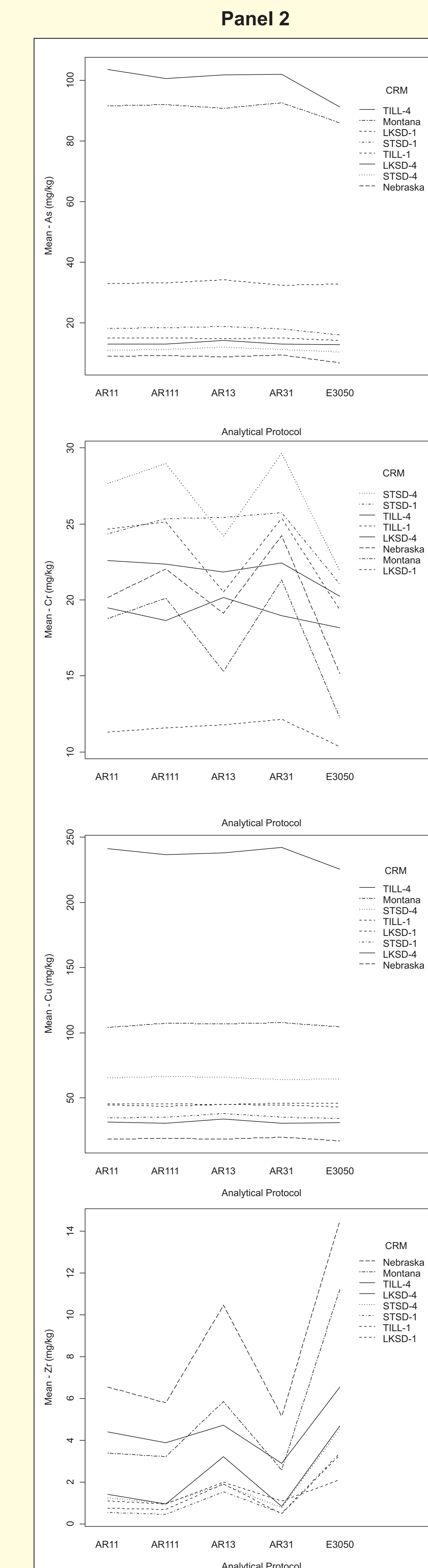
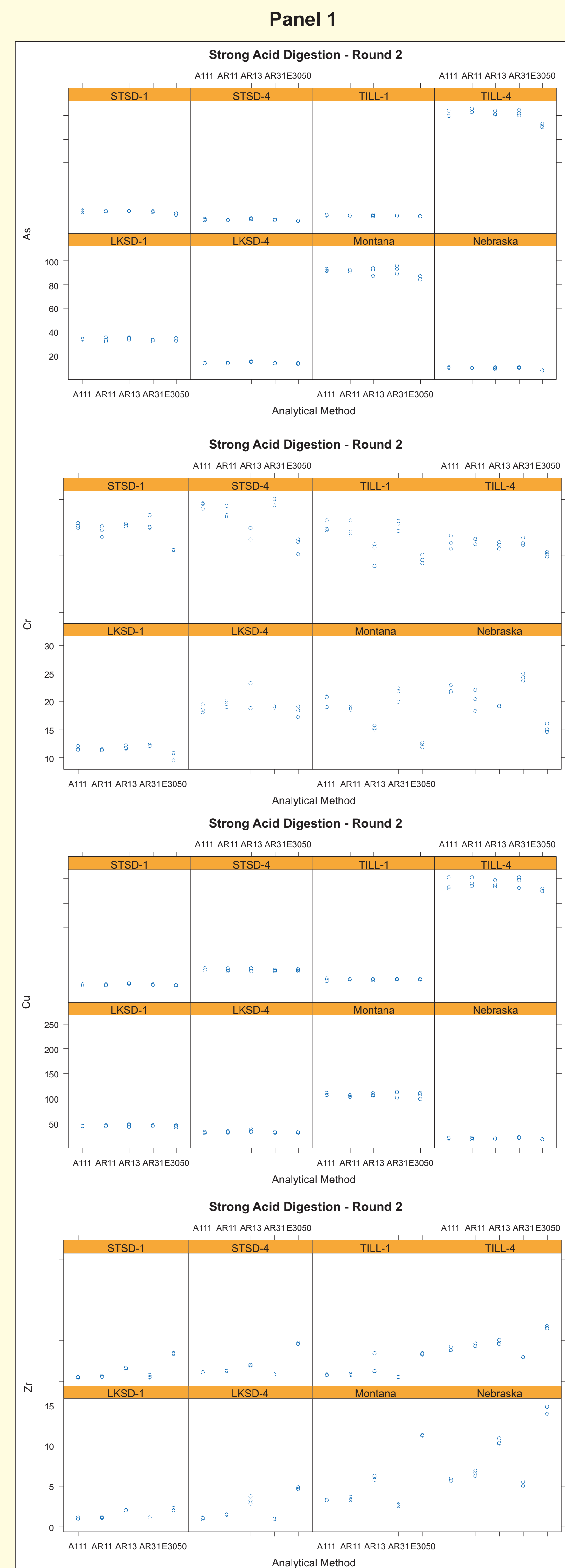
ANOVA (ANalysis Of VAriance) provides a formal statistical procedure for analyzing the data arising from the experimental design used here. The details, beyond the model, (see Table 4) are not presented. The key conclusions are presented in Table 5, below. Where the same letter (a,b,c,d,e) is used there is no statistical difference (p < 0.05) between the analytical protocols. Where differences do occur, they are attributed to interaction effects as described above, with examples in Panel 2.

Table 5
Table of Equivalences of Results

Element	Equivalence of Analytical Methods ¹				
	AR31	AR13	AR11	AR111	E3050 ²
Ag	a	a	a	a	b
Al	b	b	b	a	c
As	a	a	a	a	b
Au	a	a, b	a, b	a, b	b
Ba	a	a	a	a	a
Be	a	a	a	a	a
Bi	a, b	a, b	a, b	a	a, b
Cd	a	a	a	a	a
Ce	a	b	a	a	d
Co	a	a	a	a	b
Cr	a	c	b	a, b	d
Cr	c	a	b, c	a, b	d
Cu	a	a	a, b	a, b	d
Fe	a	c	b	a, b	d
Ga	a	b	b	a	c
Hf	d	b	c	c, d	a
Hg	a	a	a	a	a
In	a	a	a, b	a, b	b
K	a	a	a	a	b
La	a	b	c	a	d
Li	a	a, b	b	a, b	c
Mg	a	a	a	a	b
Mn	a, b	a	c	a, b, c	b, c
Mo	a, b	c	b	a	d
Na	a	d	c	b	e
Nb	a, b	c	c	b	a
Ni	a	a	a	a	b
P	b	a	b	b	a
Pb	a	a	a	a	a
Rb	a	a, b	b	a	c
Re	a	a	a	a	a
S	b	a	a, b	a, b	a
Sb	b	d	c	a	e
Sc	a	a	a	a	a
Se	a	a	a	a	b
Sn	a	b	a, b	a	c
Sr	a	a, b	a, b	a	b
Te	a	a	a	a	a
Th	d	b	c	c	a
Ti	a	d	c	b	e
Tl	a	a	a	a	b
U	a	a	a	a	d
V	a	c	b	b	c
W	a	b	c, c	a, b	b, c
Y	a, b	a, b	a, b	a, b	c
Zn	a, b	a, b	b, c	b, c	c
Zr	e	b	c	d	a

¹For methods with the same letter there is no significant difference (p < 0.05) between the analytical results. The letter 'a' indicates the greatest amount of an element extracted, and thence in decreasing order, 'b', 'c', etc.

²This is the HNO₃-H₂O variant of US-EPA 3050B with an all 'oxidising reagent' digestion



Conclusions

From the experiment we have undertaken, we have concluded that there are few significant differences between the results yielded by the strong-acid extractions for the elements of greatest 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, the US-EPA 3050B (an all-oxidizing reagent protocol) extracts less of the metals and metalloids, in almost all instances, than the various HCl-HNO₃ strong-acid mixtures, including "classical" Aqua Regia (M2 - AR31). Notable exceptions are Hf, Nb, Th and Zr.

Our objective has been to select an analytical protocol that will yield data that are consistent with both the majority of the regulatory regimes and the existing data holdings. The "classical" 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 H₂O₂) be the basis of an analytical protocol for use in the Tri-National project. This procedure uses a 4:1 HCl-HNO₃ 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.

The Geological Survey of Canada is preparing a protocol document defining the procedures to be used for the Tri-National analyses. These include the choices of 1 g (<63 μm) or 10 g (<2 mm) aliquots and a 1:12.5 sample weight - to - volume ratio, followed by elemental determinations employing ICP-OES and ICP-MS.