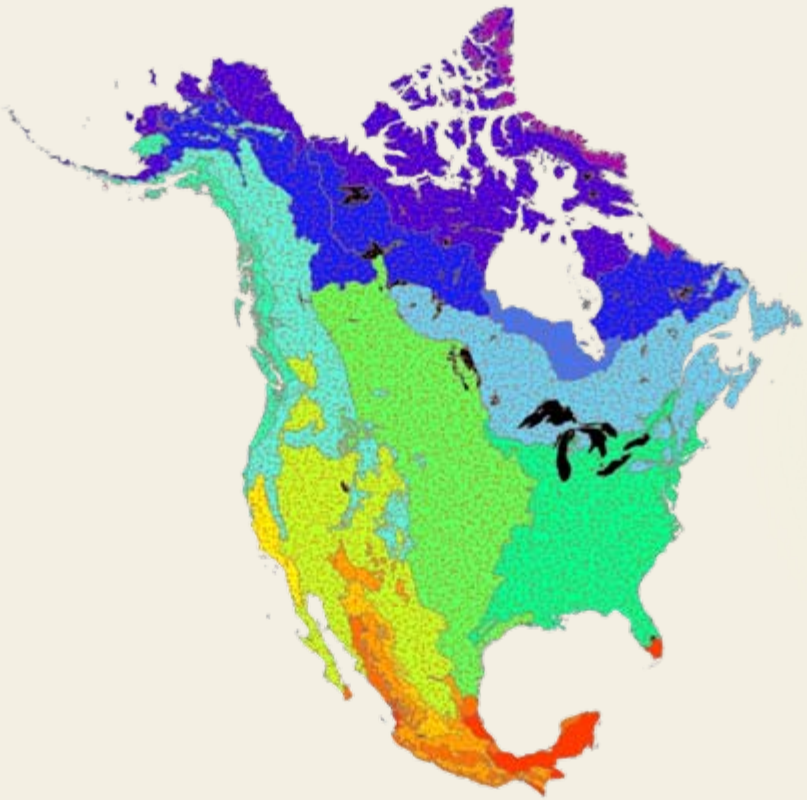
North American Soil Geochemical Landscapes Project



To Aqua Regia or not … that is the question

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Background

- Different regulatory agencies across Canada and North America use different analytical protocols, frequently Aqua Regia or variants, for the determination of metals and metalloids in environmental samples;
- What protocol should the North American Soil Geochemical Landscapes Project employ to meet the needs of various client groups?

Objectives

- To identify a protocol that will generate data the same as, or equivalent to, that used by different regulatory agencies across Canada and North America; and furthermore,
- The data should be compatible with the extensive data holdings, held nationally, continentally and internationally, accumulated over the last three, or so, decades during studies of the surface environment.

Methodology

- Eight Control Reference Materials (CRMs) were analysed in triplicate by each of five different analytical protocols. For each protocol the 24 aliquots were digested in random order. Following completion of the 120 digestions the solutions were randomized again prior to elemental determinations by ICP-OES and -MS;
- The results were analysed using Analysis of Variance procedures. If required, data were log transformed to ensure homogeneity of variance, an ANOVA requirement.

Materials

- CRMs: LKSD-1, LKSD-4, STSD-1, STSD-4, TILL-1 & TILL-4 (all GSC-CCRMP materials), and SoNE-1 & 2711 (USGS Nebraska & Montana soil CRMs)
- Dissolution protocols:
  - 1:1:1 HCl-HNO_3-H_2O, AR111[1]
  - 3:1 HCl-HNO_3, AR31[1] - classical Aqua Regia
  - 1:3 HCl-HNO_3, AR13[1] - Lefort, reverse Aqua Regia
  - 1:1 HCl-HNO_3, AR11[2]
  - US-EPA 3050, HNO_3-H_2O_2 variant, E3050
  - [1] 1 g sample aliquot, 3 ml of reagent, digestion at 95 °C for 1 hour, and dilution to 10 ml with 5% HCl
  - [2] 0.5 g sample aliquot, 3 ml of reagent, digestion at 95 °C for 1 hour, and dilution to 10 ml with 5% HCl

The ANOVA Model

Two-Way with Interaction and Replication within CRMs

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

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

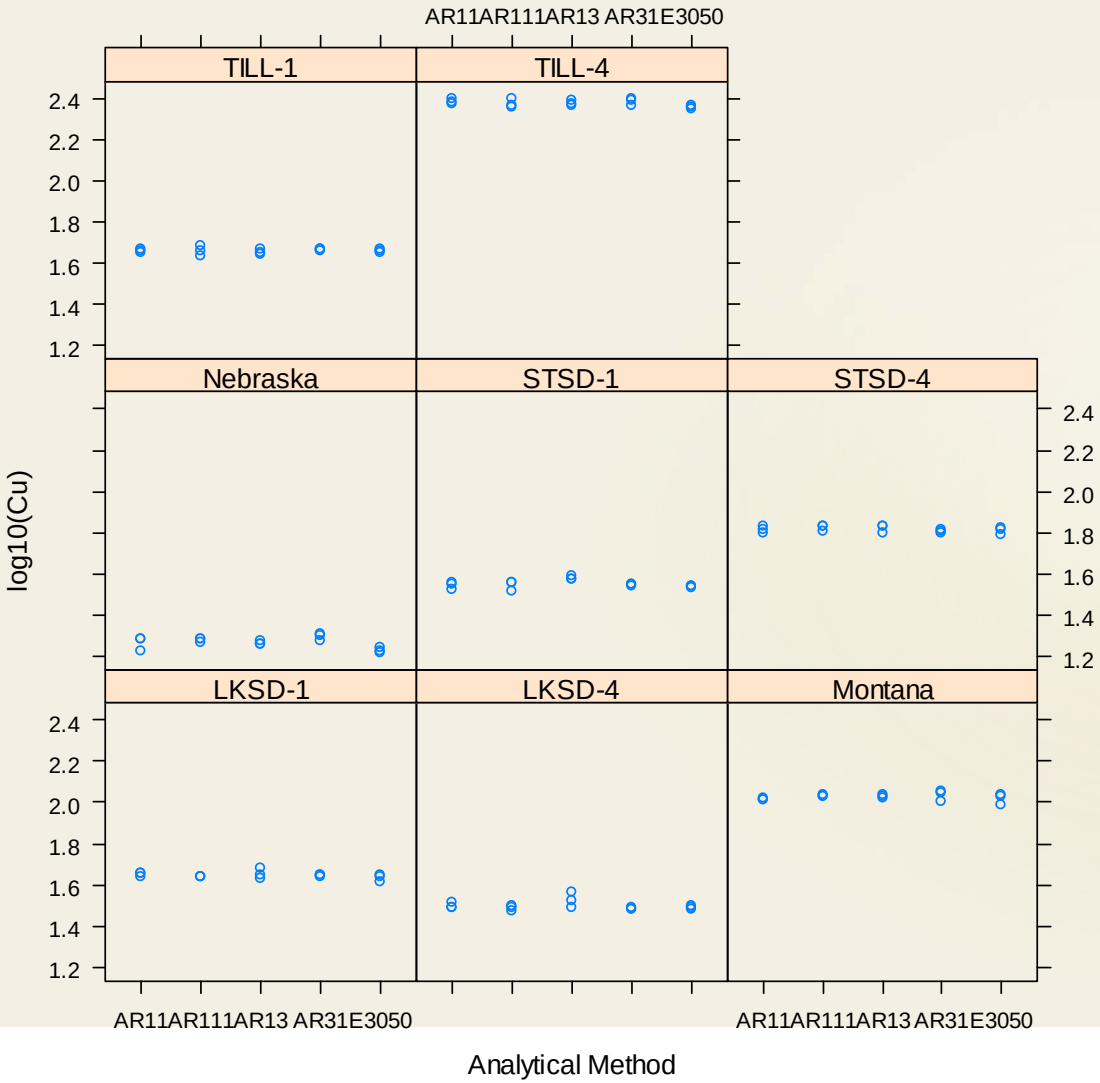
β_j = the effect due to the j-th CRM (Sample)

$(\alpha\beta)_{ij}$ = the interaction effect between the i-th Method and j-th CRM

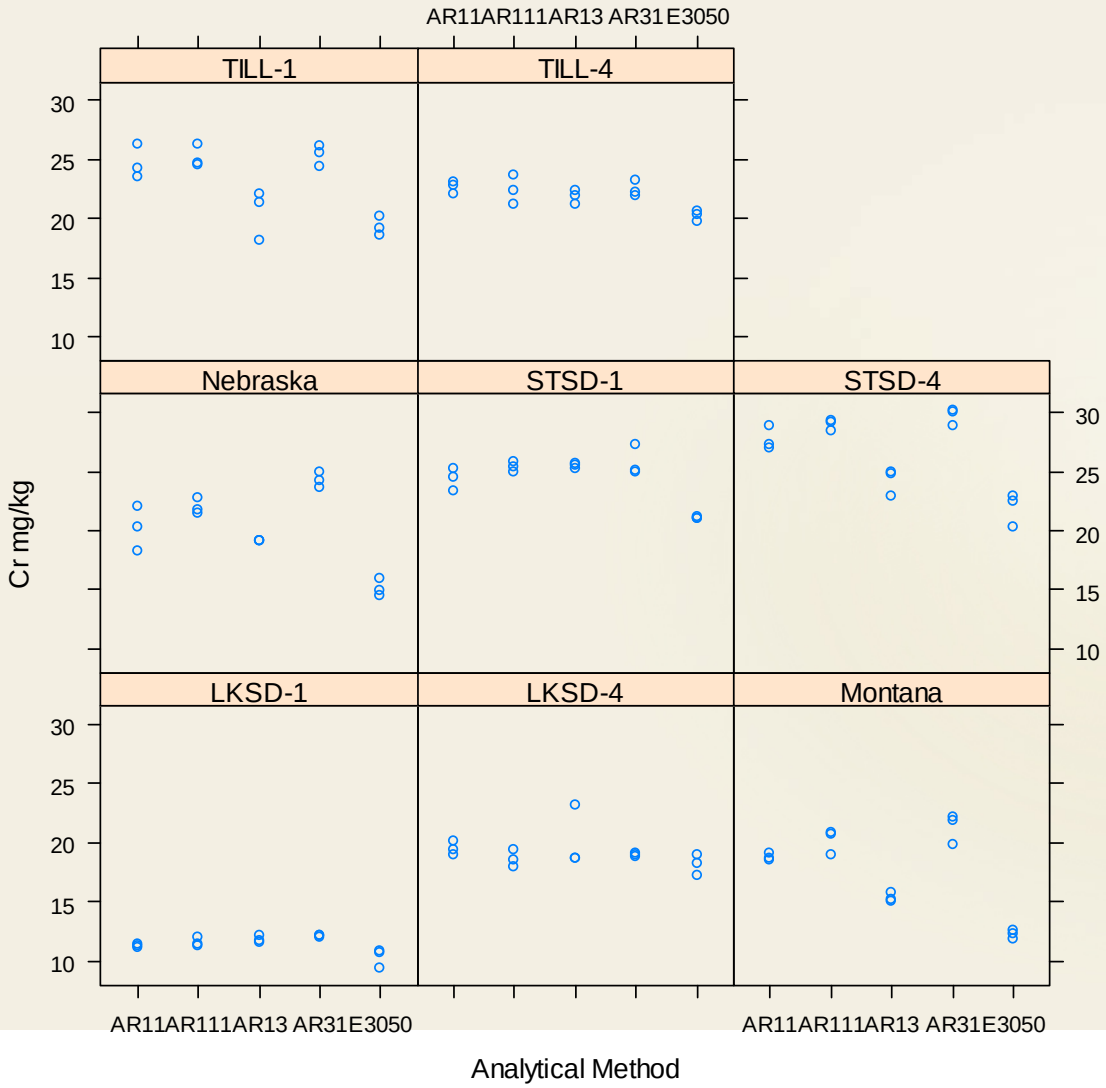
γ_{jk} = the effect due to the k-th analysis of the j-th CRM

ε_{ijk} = the pooled residual variability

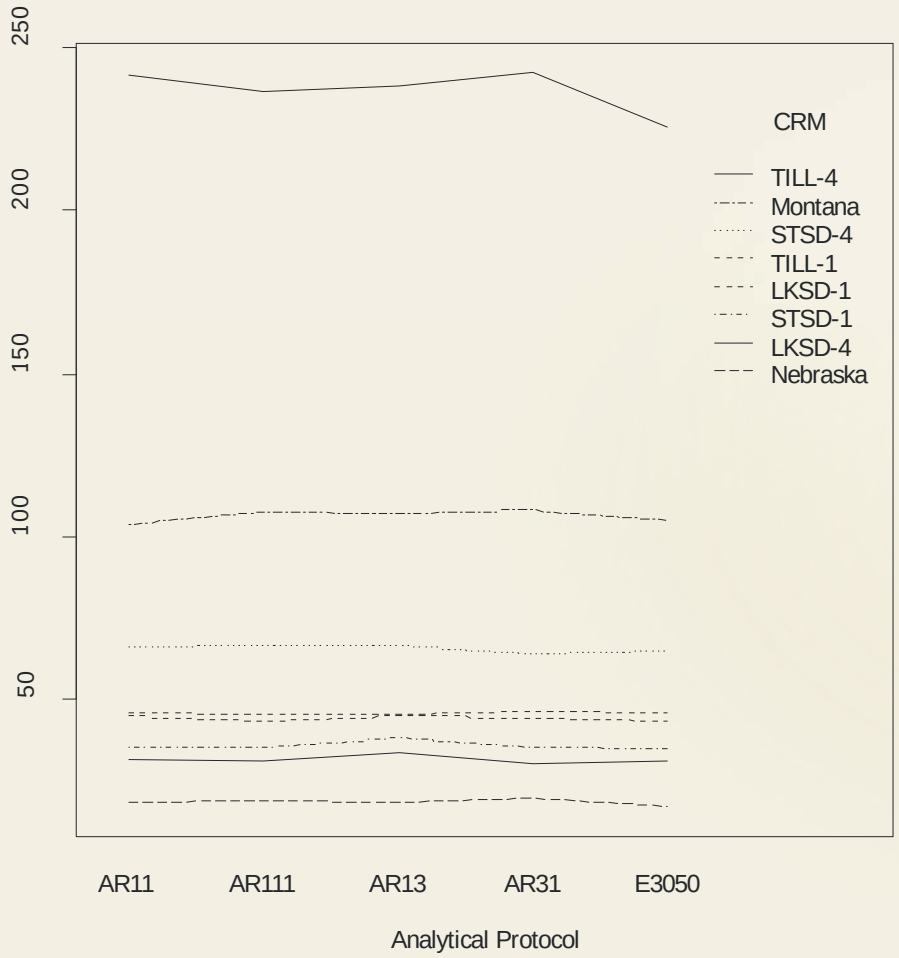
Graphical Results - Cu



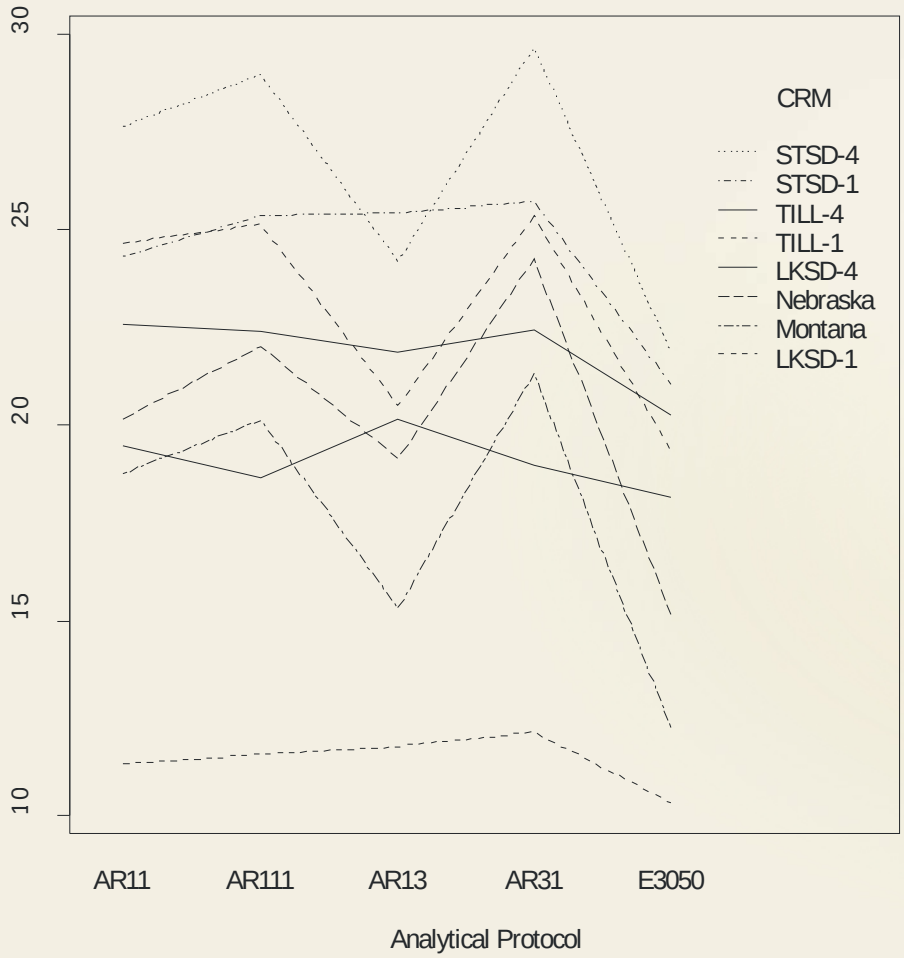
Graphical Results - Cr



Interaction Plot - Cu



Interaction Plot - Cr



ANOVA Results

Element	Equivalence of Analytical Methods[1]				
	AQ	Rev-AQ	1:1	1:1:1	3050[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
Ca	a	a	a	a	a
Cd	a, b	a, b	a, b	b	a
Ce	a	c	b	a	d
Co	a	a	a	a	b
Cr	a	c	b	a, b	d
Cs	c	a	b, c	a, b	d
Cu	a	a	a, b	a, b	b
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

Element	Equivalence of Analytical Methods[1]				
	AQ	Rev-AQ	1:1	1:1:1	3050[2]
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	b
V	a	c	b	b	d
W	a	c	b, c	a, b	b, c
Y	a, b	a	b, c	a, b	c
Zn	a	a, b	a, b	a	c
Zr	e	b	c	d	a

Footnotes:
[1] For 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.
[2] This is the HNO_3-H_2O_2 variant of US-EPA 3050 with an all 'oxidising reagent' digestion

Conclusions

- The ANOVA results indicate that US-EPA 3050, the HNO_3-H_2O_2 variant, generally extracts significantly less metals and metalloids than Aqua Regia and the Aqua Regia-like digestions. Notable exceptions are Hf, Nb, Th and Zr;
- For the remaining four analytical protocols, Aqua Regia and three HCl-HNO_3 variants, the results are very similar, if not identical; and
- Even when results are significantly ($p<0.05$) different between some protocols, an inspection of the data indicates that these differences are likely not significant in a geochemical/engineering context.

Recommendation

- Considering the vast amounts of Aqua Regia and US-EPA Aqua Regia variant data that are extant in North America and internationally, and the fact that the Aqua Regia-like variants extract very similar amounts of elements as “classical” Aqua Regia for most elements, it is recommended that the North American Soil Geochemical Landscapes Project, the Tri-National, employs the US-EPA 3050B Aqua Regia variant digestion.

US-EPA 3050B

- The Aqua Regia variant is outlined in the "flow chart" on Page 12 of the December 1996 Revision 2 of the US-EPA 3050B protocol under 7.5 et seq.
- This procedure uses a 4:1 HCl-HNO_3 mix rather than the 3:1 of "classical" Aqua Regia; and
- The Geological Survey of Canada is preparing a protocol document better 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.