

Elemental concentrations and in vitro bioaccessibility in Canadian background soils

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Received: 28 September 2015 / Accepted: 23 June 2016 / Published online: 28 June 2016
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Abstract Elemental concentrations and bioaccessibility were determined in background soils collected in Canada as part of the North American Geochemical Landscapes Project. The concentrations of As, Cr, Cu, Co, Ni and Zn were higher in the C-horizon (parent material) compared to 0–5 cm (surface soil), and this observation along with the regional distribution suggested that most of the variability in concentrations of these elements were governed by the bedrock characteristics. Unlike the above-stated elements, Pb and Cd concentrations were higher in the surface layer reflecting the potential effects of anthropogenic deposition. Elemental bioaccessibility was variable

decreasing in the order $Cd > Pb > Cu > Zn > Ni > Co > As > Cr$ for the surface soils. With the exception of As, bioaccessibility was generally higher in the C-horizon soils compared to the 0–5 cm soils. The differences in metal bioaccessibility between the 0–5 cm and the C-horizon and among the provinces may reflect geological processes and speciation. The mean, median or 95th percentile bioaccessibility for As, Cr, Cu, Co, Ni and Pb were all below 100 %, suggesting that the use of site-specific bioaccessibility results for these elements will yield more accurate estimation of the risk associated with oral bioavailability for sites where soil ingestion is the major contributor of human health risk.

Electronic supplementary material The online version of this article (doi:[10.1007/s10653-016-9846-9](https://doi.org/10.1007/s10653-016-9846-9)) contains supplementary material, which is available to authorized users.

Keywords Bioaccessibility · Arsenic · Lead · Metals · Canadian soils

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Introduction

The concentrations of naturally occurring elements in soils depend on the prevailing geology and may be highly variable (Rencz and Garrett 2006; Rencz et al. 2011). Occasionally, the natural levels can exceed generic environmental quality guidelines such as the Canadian Council of Ministers of the Environment (CCME) soil quality guidelines without representing anthropogenic impacts (Richardson 2002). Understanding the magnitude and causes of natural

variability is therefore important for ecological and human health risk assessment. In Canada, remediation of sites anthropogenically contaminated with metals is generally not required where similar or higher levels of natural origin are found in local soils (Health Canada 2010, 2012). Due to the lack of systematic continent-wide data on background soil composition, the North American Soils Geochemical Landscapes Project (NASGLP) was initiated to provide a soil geochemical database for a broad-based group of users in the field of environmental and human health (Smith et al. 2009; Friske et al. 2010). The project was a collaborative effort among Natural Resources Canada—Geological Survey of Canada (GSC), the United States Geological Survey (USGS) and the Mexican Geological Survey and was based on low-density sampling (approximately one sample per 1600 km²). The long-term goals of the NASGLP were: to produce a continental-scale set of field and analytical protocols for generating geochemical data; provide a baseline soil geochemical database with a broad spectrum of inorganic and selected biological and organic parameters; and provide a coordinated common approach for human and ecological risk assessment that is based on sound scientific principles.

A Canada–United States pilot study consisting of two sampling transects (E–W and N–S) was carried out in 2004 to test field sampling and analytical protocols and data applications (Smith et al. 2009). Subsequently, methodology for the collection, preparation and analysis of soil samples for the NASGLP in Canada was formulated (Friske et al. 2010), and from 2007 to 2009, systematic sampling was undertaken. Sampling and analysis for the NASGLP were initiated in 2004. The core field program involved the collection of soil samples from depths of 0–5 cm (surface layer), A, B and C-horizons at each selected sampling location using standardized protocols. Laboratory analyses included over 40 elements and other physicochemical characteristics such as particle size, pH, total organic carbon (TOC), inorganic carbon (IC) and loss on ignition (LOI).

Not only are the relative levels of anthropogenic and natural source metals in soil relevant to risk assessment, but also the relative oral bioaccessibility of anthropogenic versus natural forms of these metals. Therefore, in addition to the core NASGLP program, additional analyses were performed for a select number of samples to estimate bioaccessibility of

naturally sourced elements in soil in the USA (Morman et al. 2009) and Canada. This paper presents the results of the assessment of total elements and their oral bioaccessibility in a subset of the samples collected in Canada.

Exposure to metal contaminants in soils can occur through inhalation of suspended dust, dermal contact with soils and soil ingestion. This study is limited to the risk associated with oral ingestion and bioavailability. At many sites where metal soil contamination exists, the inhalation and dermal pathways tend to be minor routes of exposures and risks. Nevertheless, a full consideration of all pathways is typically required at contaminated sites and consideration of only the incidental ingestion route is not sufficient. It remains possible that the inhalation and dermal routes will become dominant contributors of risks where the *in vitro* bioaccessibility results are only applied to oral intake. Moreover, it should be recognized that there could be scenarios such as air emissions near certain industries where soil contamination is typically a relatively minor route and consideration of *in vitro* oral bioavailability is likely to have very little effect on overall risk estimates.

In the absence of any evidence to the contrary, it is often conservatively assumed that 100 % of the measured concentration of the metals in soil is bioavailable after exposure. However, the oral bioavailability of ingested soil contaminants depends on the complex physical, chemical and biological interactions that control partitioning within the gastrointestinal tract. Depending on the form of the metal, anywhere from 0 to 100 % can be solubilized within the gastrointestinal tract and may then be available for absorption into systemic circulation (i.e., become bioaccessible which is a prerequisite for a substance to be absorbed across the gastrointestinal tract, or bioavailable). Site-specific oral bioavailability estimates of metals in soils can be used to make adjustments in human health risk assessment to provide realistic estimates of exposure [United States Environmental Protection Agency (USEPA) 2007a; Richardson et al. 2006; Health Canada 2010]. Metal bioavailability in contaminated soils can be determined through either *in vivo* animal assay or estimated as bioaccessibility via *in vitro* digestion models (Basta and Juhasz 2014; Ruby 2004). *In vitro* testing involves an assay of the ratio of the mass of the metal dissolved into a volume of simulated gastric/intestinal fluid to

the total mass of contaminant in the soil sample. Bioaccessibility refers to the fraction of the contaminant in soil that is solubilized in the simulated gastric fluid and would be potentially available for absorption (Ruby 2004). In this manner, bioaccessibility is not a direct measurement of oral bioavailability and actual oral bioavailability could be appreciably lower (i.e., only the solubilized metal will be available for absorption; however, not all that is solubilized will necessarily be absorbed). Nevertheless, the measurement of oral bioaccessibility has provided important information particularly when the values from soil are quite different than the fractions that would have been solubilized in the toxicity study. The *in vitro* bioaccessibility assay (IVBA) described by the USEPA (2012) was applied to assess metal oral bioaccessibility in this study.

The objectives of the investigations presented in this paper include the assessment of: (a) the variation in metal bioaccessibility in selected background soils collected in Canada as part of the North American Geochemical Landscapes Project from ten provinces, (b) differences between the 0–5 cm (surface layer) and the C-horizon based on the physicochemical characteristics and (c) the relationship between metal bioaccessibility and geochemical data including total metals, soil pH and TOC. The present study is limited to the physicochemical characterization of the soil samples only since data on geological origin of the soil samples from the two horizons at each location were not obtained. Metal speciation was also not investigated. The samples were analyzed for over 30 elements; however, 8 metals or metalloids comprising As, Cd, Cr, Co, Cu, Pb, Ni, and Zn were selected for discussion in this paper. These elements are contaminants commonly found at waste sites, abandoned mines, military installations and marine navigation sites (light stations) in Canada (Federal Contaminated Sites Inventory 2015) and are listed as target analytes by the CCME (1993).

Materials and methods

Sampling

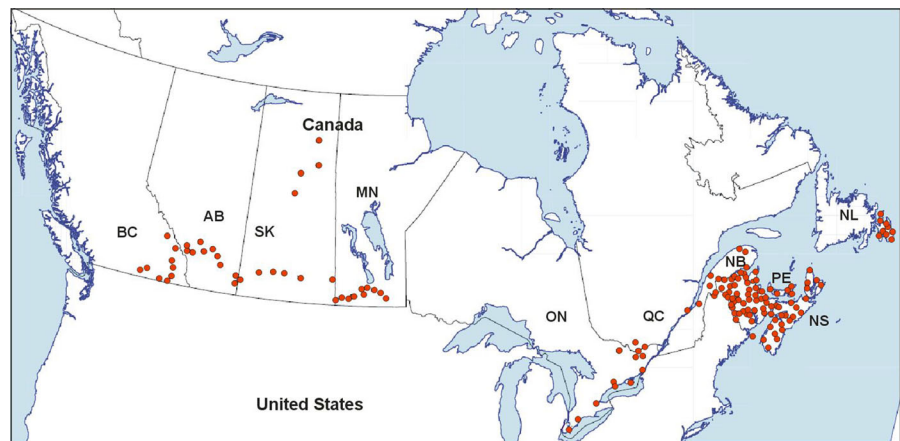
Site selection and soil sampling were based on the NASGLP protocols (Smith et al. 2009; Friske et al. 2010). Briefly, a 40 km × 40 km grid was set up over

the entire continent (Canada, Mexico and the USA). A 1-km² target area was chosen at random within each grid, and a sample site was selected from the most representative landscape within the most common soil type. A soil pit was dug to bedrock, water table or C-horizon depending on which was encountered first. Samples were then collected from 0 to 5 cm (surface layer) and the A, B and C-horizons. The 0–5 cm layer is assumed to be the materials that humans are most exposed to during daily activities and likely to provide human exposure risk estimates from anthropogenic sources, while the C-horizon represented the layer least affected by soil-forming processes and the most representative of soil parent material and background conditions. A subset of samples comprising a minimum of ten locations (where available) from each province of Canada—British Columbia (BC), Alberta (AB), Saskatchewan (SK), Manitoba (MB), Ontario (ON), Quebec (QC), New Brunswick (NB), Nova Scotia (NS), Prince Edward island (PE) and Newfoundland and Labrador (NL)—were randomly selected for the IVBA analysis. Sampling locations are shown in Fig. 1.

Soil characterization

Soil characterization was conducted using the <2 mm soil size fraction as this is the fraction most commonly used for environmental site investigations and, consequently, in human health risk assessment. To obtain this fraction, the soil sample was air-dried, large pebbles were removed, and clumps of dried materials were gently disaggregated using a porcelain pestle. The sample was then sieved through a 2-mm mesh sieve. The collected sieved material was transferred to a spinning riffler equipped with a 16-tube carousel from which splits of the proper size/weight were created for subsequent analysis. Soil pH was measured in 0.01 M CaCl₂ at a soil:solution ratio of 1:2 (w/v) except for organic soils where a ratio of 1:10 (w/v) was used. Soils were analyzed for organic and inorganic carbon using a Leco CR-412 Carbon Analyser[®] (Girard et al. 2004). This method involved sample combustion and the measurement of the released CO₂ using infrared detection. The total content of carbon was determined on one split, and the inorganic carbon on a second split after the second had been ashed at low temperature (<500 °C) to remove the organic carbon. The amount of organic carbon was calculated

Fig. 1 Sampling locations. *BC* British Columbia, *AB* Alberta, *SK* Saskatchewan, *MB* Manitoba, *ON* Ontario, *QC* Quebec, *NB* New Brunswick, *NS* Nova Scotia, *PE* Prince Edward Island and *NL* Newfoundland and Labrador



by subtracting the inorganic carbon from the total. Total elemental concentrations in the soils were determined using USEPA 3050B aqua regia variant (USEPA 1996). Briefly, 10.0 g of the sample was digested in a beaker with 25 ml of concentrated HNO_3 and 100 ml concentrated HCl . The digestate was analyzed for metals by ICP-AES or ICP-MS. Element concentrations, pH, TOC and IC data are included as a supplement.

In vitro extraction (IVBA)

The IVBA methodology was based on USEPA standard operating protocols (USEPA 2012). Soil samples selected for the IVBA were sieved to $<250 \mu\text{m}$ as this fraction is considered most representative of the soil particle size that adheres to children's hands (USEPA 1994). A 1-g portion of the sieved soil was extracted by end-to-end rotation for 1 h in 100 ml of 30 g/L glycine adjusted to a pH of 1.5 with concentrated HCl (Fisher Scientific, trace metal grade). The extract was filtered through $0.45 \mu\text{m}$ cellulose acetate syringe filter. The filtered extract was analyzed for total metals by ICP-MS based on USEPA Method 200.8 (USEPA 1994).

Percent elemental bioaccessibility was calculated for each sample by dividing the concentration in the extract by the total elemental concentration in the $<250 \mu\text{m}$ soil fraction as determined by acid digestion and ICP-MS analysis. Bioaccessibility was not calculated for the samples with extract concentrations below the limits of detection. The data quality

assurance/quality control program included the use of NIST 2711 control samples, procedure and reagent blanks and duplicates to ensure reproducibility and minimal contamination from filters, vessels and sample containers.

Statistical analyses

Statistical analyses were performed using Minitab[®] 15 and ProUCL version 5.0.00 (USEPA 2013). Total metals and bioaccessibility data were tested for distribution using goodness-of-fit test statistics. The data for the majority of the metals did not follow a discernible distribution, and as such nonparametric statistics including Wilcoxon Mann–Whitney and Kruskal–Wallis tests were used for quantitative comparisons of metal concentrations and bioaccessibility data at the 5 % significance level. The effects of soil properties on bioaccessibility were initially explored via scatter plots and Pearson correlation coefficients using metal bioaccessibility as the dependent variable and soil properties including the total metal concentrations, major elements (e.g., Fe, Al, S, P) concentrations, pH and TOC as independent variables. Parameters with the strongest linear relationship and $p < 0.05$ were subsequently used in a best subset regression analysis to determine the factors which best explained the dataset. To permit the comparison of on-site contamination to the background data presented in this paper, the mean, standard deviation, median, 95 percentile and the 95 % upper confidence limit (95 % UCL) concentrations were also determined.

Results and discussions

Soil properties

Total element concentrations, pH, inorganic carbon (IC) and total organic carbon (TOC) in the <2 mm fraction for the 0–5 cm and C-horizon soil samples are summarized in Tables 1 and 2, respectively. Total organic carbon was higher in the 0–5 cm samples (mean 12 %, median 7.2 %) compared to the C-horizon (mean 0.70 %, median 0.49 %). In contrast to TOC, soil pH was lower in the 0–5 cm layer (mean 4.73, median 4.14) compared to the C-horizon (mean 5.78, median 5.07). The lower pH in the 0–5 cm soils may reflect anthropogenic contributions as well as the influence of the organic acid components of the higher TOC content. Soil pH in the surface soils was variable among the provinces with the eastern provinces (QC, NB, NS, PE and NL) showing lower pH compared to the western provinces.

The mean and median total element concentrations were below the CCME (1999) soil quality guidelines for residential/parkland use (SQG R/P); however, the maximum concentrations for As, Cr, Cu, Ni and Pb exceeded the guidelines. Variations in metal concentrations among the provinces and samples that exceeded the guidelines are discussed further below under individual elements.

There were differences in concentrations between the <2 mm and the <250 μm soil fractions for some of the metals with no consistent patterns between the 0–5 cm and C-horizon samples: The concentrations of As did not show statistically significant differences between the soil fractions for both soil layers; for the 0–5 cm soils Cd, Co, Pb and Zn were slightly higher while Cu was lower in the <2 mm fraction; for the C-horizon, Cd and Pb were slightly higher in the <2 mm fraction; however, this difference was not statistically significant. These results are consistent with observations by Bright et al. (2006) that there is variability in the distribution of contaminants across different particle size fractions. Despite the differences in metal distribution among the two soil fractions, there were significant correlations in metal concentrations between the <2 mm and the <250 μm fractions (R^2 of 0.5–0.9) except for Cu in the C-horizon samples ($R^2 = 0.386$) as shown in the scatter plots in Fig. 2. These relationships suggest that in the estimation of risk using default values for

bioaccessibility (USEPA 2007a), the use of the total metal concentrations data for the <2 mm particle size fraction, which is the fraction analyzed for most environmental site investigations in Canada, may be appropriate.

Elemental bioaccessibility

Descriptive summary statistics including mean, standard deviation, median and 95 percentile of elemental bioaccessibility are presented in Table 3. The maximum bioaccessibility for Cd, Cu, Ni and Zn exceeded 100 %. An examination of the data indicated the samples with calculated bioaccessibility values exceeding 100 % contained elements at concentrations close to the limit of quantitation in the IVBA extract (i.e., less than five times the limit of detection). The elevated bioaccessibility was attributed to analytical constraints. Turner and Simmonds (2006) reported bioaccessibility over 100 % for Cu, Pb and Zn in their study of elemental bioaccessibility in UK dust samples and attributed this to analytical constraints. Cadmium bioaccessibility in excess of 100 % was also reported for the United States NASGLP samples (Morman et al. 2009). Since the total elemental concentrations in the soil samples with metal bioaccessibility exceeding 100 % were fairly low (well below the applicable Canadian environmental soil quality guidelines), and the masses of extractable fractions were fairly low, the risks associated with oral ingestion of the metals in these soils were deemed fairly low.

Bioaccessibility for each element was variable among the provinces and between the 0–5 cm layer and the C-horizon as shown in Fig. 2. Bioaccessibility for the eight elements decreased in the order Cd > Pb > Cu > Zn > Ni > Co > As > Cr for the 0–5 cm layer. This trend was comparable to the bioaccessibility data for surface samples collected from two transects across the USA and Canada as part of the NASGLP (Morman et al. 2009). The trend for the C-horizon samples was slightly different (Cd > Cu > Pb > As > Co > Zn > Ni > Cr); however, as with the surface layer, Cd had the highest bioaccessibility, while Cr had the lowest. The differences in the trend between the two layers may be attributed to elemental speciation, the influence of soil physicochemical properties, origin of the metal (natural or anthropogenic) and surface precipitation and

Table 1 Statistical summary of total metal concentrations (mg/kg), iron (%) pH and total organic carbon (%) in 0–5 cm soil samples

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Fe	pH	TOC
British Columbia (<i>n</i> = 10)											
Mean	7.0	0.47	6.3	14	11	14	34	91	1.7	5.47	5.9
SD	6.8	0.73	2.1	12.5	5.5	7.7	50.4	51.9	0.5	0.81	6.9
Median	4.8	0.17	6.5	9.4	9.1	11	18	97	1.5	5.69	2.9
Maximum	23	2.5	10	49	23	30	175	193	2.7	6.93	20
95 %ile	19	1.6	9.4	34	19	28	114	163	2.5	6.53	19
95 % UCL	11 ^a	1.2 ^c	7.5 ^a	2.3 ^c	14 ^a	20 ^d	103 ^b	121 ^a	2.0 ^a	5.94 ^a	13 ^c
Alberta (<i>n</i> = 32)											
Mean	5.7	0.60	7.4	16	17	17	11	83	1.5	5.88	7.7
SD	1.8	0.44	2.4	5.6	6.3	6.5	3.3	34	0.44	0.90	5.9
Median	5.5	0.49	6.9	15	17	15	11	82	1.5	5.64	5.8
Maximum	9.1	2.5	13	31	34	32	20	171	2.5	7.43	29
95 %ile	8.6	1.2	12	25	28	30	17	151	2.3	7.30	18
95 % UCL	6.2 ^a	0.73 ^c	8.1 ^a	17 ^a	18 ^a	19 ^c	12 ^a	95 ^a	1.6 ^a	6.16 ^c	8.1 ^c
Saskatchewan (<i>n</i> = 65)											
Mean	5.0	0.33	6.7	20	14	14	8.9	57	1.5	5.96	4.2
SD	3.1	0.19	4.3	12.8	9.4	10.5	4.2	34.5	0.9	1.55	4.68
Median	5.3	0.3	6.8	17	14	14	9.2	62	1.4	6.58	2.9
Maximum	11	1.0	16	53	37	41	19	131	3.6	7.83	27
95 %ile	9.5	0.6	15	48	33	37	17	112	3.3	7.60	10
95 % UCL	4.8 ^b	0.37 ^b	9.1 ^b	27 ^b	19 ^b	20 ^b	11 ^b	64 ^a	2.0 ^b	6.28 ^b	4.8 ^b
Manitoba (<i>n</i> = 20)											
Mean	5.5	0.50	7.2	19	19	18	12	72	1.5	6.68	5.3
SD	2.7	0.21	3.7	11.5	11.6	10.2	4.8	28.2	0.7	0.68	2.9
Median	5.3	0.51	6.2	16	17	16	11	73	1.4	6.85	4.7
Maximum	10	1.0	14	42	40	37	22	121	2.8	7.57	13
95 %ile	9.5	0.8	14	41	39	37	19	109	2.6	7.54	12
95 % UCL	6.5 ^a	0.59 ^a	8.6 ^a	23 ^a	24 ^a	22 ^a	14 ^a	82 ^a	1.8 ^a	6.94 ^a	6.8 ^c
Ontario (<i>n</i> = 110)											
Mean	4.3	0.45	7.1	20	18	16	23	82	1.8	6.27	5.6
SD	3.3	0.36	3.9	9.5	11.6	9.8	14.5	54.8	0.7	0.95	4.6
Median	3.7	0.3	7.1	20	15	15	19	75	1.8	6.46	4.9
Maximum	24	2.8	19	51	80	42	105	519	3.7	7.42	34
95 %ile	8.9	1.0	14	34	38	35	50	134	3.0	7.35	13
95 % UCL	4.8 ^c	0.49 ^d	7.7 ^a	21 ^a	20 ^c	18 ^c	25 ^d	89 ^d	1.9 ^a	6.42 ^a	6.3 ^d
Quebec (<i>n</i> = 39)											
Mean	4.3	0.47	5.0	13	13	11	39	59	1.3	4.08	16
SD	6.6	0.39	5.6	10.8	14.1	10.3	27.6	29.4	0.9	0.85	11.5
Median	2.5	0.39	3.4	9.2	10	8.1	34	57	1.2	3.85	11
Maximum	42	1.8	31	50	88	51	143	121	3.9	6.70	44
95 %ile	8.0	1.4	13	33	28	29	88	107	2.7	5.45	42
95 % UCL	5.7 ^c	0.58 ^c	6.7 ^c	16 ^c	16 ^d	14 ^c	47 ^c	67 ^c	1.6 ^a	4.31 ^a	20 ^a

Table 1 continued

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Fe	pH	TOC
New Brunswick (<i>n</i> = 115)											
Mean	4.0	0.49	3.2	11	8.2	8.6	38	53	1.0	3.58	21
SD	4.0	0.49	3.2	11.2	8.2	8.6	38.0	53.3	1.0	3.53	21.3
Median	2.9	0.39	1.6	7.3	7.8	5.4	35	43	0.71	3.48	19
Maximum	23	2.4	23	76	23	49	125	182	4.4	5.20	46
95 %ile	11	1.1	9.2	32	15	26	69	122	3.1	4.47	43
95 % UCL	4.5 ^d	0.55 ^c	4.6 ^b	16 ^b	8.8 ^a	12 ^b	41 ^c	59 ^c	1.2 ^c	3.611 ^a	23 ^c
Nova Scotia (<i>n</i> = 67)											
Mean	6.1	0.21	4.5	13	9.3	7.7	27	46	1.2	3.51	12
SD	4.9	0.21	5.8	12.9	8.9	7.6	13.6	40.1	1.3	0.50	10.8
Median	4.4	0.14	2.5	11	7.7	5.4	23	33	1.6	3.37	8.0
Maximum	25	1.3	28	92	73	44	77	245	7.1	4.98	48
95 %ile	15	0.56	14	30	16	24	53	113	3.8	4.37	42
95 % UCL	7.1 ^c	0.25 ^d	6.2 ^d	16 ^c	10 ^d	9.1 ^c	30 ^a	53 ^c	2.0 ^a	3.62 ^c	18 ^b
Prince Edward Island (<i>n</i> = 9)											
Mean	2.6	0.22	3.6	9.7	6.7	7.1	23	36	1.8	3.93	11
SD	0.6	0.22	2.2	3.7	2.3	3.3	18.2	24.9	0.5	0.98	9.2
Median	2.6	0.17	3.2	9.1	5.6	6.6	16	29	1.3	3.50	8.8
Maximum	3.5	0.62	7.9	17	11	13	61	84	7.1	5.66	28
95 %ile	3.3	0.60	6.9	15	10	12	54	79	3.8	5.58	27
95 % UCL	3.0 ^a	0.50 ^a	4.9 ^a	12 ^a	8.2 ^a	9.1 ^a	34 ^a	52 ^a	1.5 ^a	4.53 ^a	29 ^a
Newfoundland and Labrador (<i>n</i> = 66)											
Mean	2.2	0.30	2.5	9.3	7.5	5.9	27	41	0.82	3.49	25
SD	2.6	0.19	4.0	12.2	7.5	7.8	26.8	20.4	0.80	0.66	11.5
Median	1.3	0.25	1.2	5.2	6.2	3.4	23	38	0.53	3.29	21
Maximum	14	1.1	29	85	45	52	228	105	3.3	6.24	42
95 %ile	5.5	0.63	8.5	23	24	15	43	84	2.5	4.95	41
95 % UCL	2.9 ^d	0.34 ^c	3.0 ^d	15 ^b	13 ^b	7.0 ^d	41 ^b	45 ^c	1.2 ^d	3.6 ^a	29 ^a
All sites (<i>n</i> = 532)											
Mean	4.5	0.40	5.1	15	12	12	26	60	1.4	4.73	12
SD	4.0	0.3	4.5	12	9.8	9.8	21	41	0.9	1.55	11
Median	3.7	0.32	3.9	12	9.8	8.5	20	54	1.3	4.14	7.2
Maximum	42	2.8	31	92	88	52	228	519	7.1	7.83	48
95 %ile	11	0.97	14	37	31	34	61	122	3.1	7.34	41
95 % UCL	5.2 ^b	0.47 ^b	5.9 ^b	17 ^b	13 ^d	13 ^b	27 ^d	63 ^c	1.6 ^b	4.85 ^b	14 ^b

SD standard deviation, 95 % UCL 95 % upper confidence limit

^a 95 % student's t UCL

^b 95 % Chebyshev (mean, SD) UCL

^c 95 % adjusted gamma UCL

^d 95 % H-UCL

leaching. Surface precipitation and leaching in concert with absorption, and adsorption can lead to metals species that are not readily soluble. Thus, metals of mainly anthropogenic sources which have presumably

not been on the site long enough to undergo the processes described above tend to be more soluble and therefore more bioaccessible compared to those of natural origin (Ljung et al. 2007).

Table 2 Statistical summary of total metal concentrations (mg/kg), iron (%), pH, and total organic carbon (%) in the C-horizon soil samples

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Fe	pH	TOC
British Columbia (<i>n</i> = 10)											
Mean	5.8	0.11	7.3	17	19	16	16	45	2.0	6.88	0.58
SD	5.7	0.08	2.8	19	9.5	7.8	15	21	0.6	1.33	0.48
Median	5.2	0.10	6.8	12	17	14	11	35	1.9	7.43	0.48
Maximum	20	0.26	12	69	33	33	54	94	3.2	8.32	1.6
95 %ile	15	0.25	11	46	32	28	40	81	2.8	8.08	1.3
95 % UCL	9.1 ^a	1.6 ^a	8.9 ^a	30 ^d	24 ^a	20 ^a	24 ^a	58 ^a	2.3 ^a	7.57 ^a	0.90 ^a
Alberta (<i>n</i> = 32)											
Mean	7.6	0.37	10	20	22	27	12	68	2.0	8.32	1.5
SD	1.6	0.44	3	7.0	7.7	7.9	5.3	23	0.8	0.76	0.31
Median	7.8	0.30	10	19	21	26	11	65	1.9	7.65	0.55
Maximum	10	2.68	15	38	37	47	35	146	5.1	9.23	1.7
95 %ile	9.8	0.56	14	32	35	40	18	95	3.0	8.86	1.1
95 % UCL	8.1 ^a	0.72 ^b	11 ^a	23 ^a	25 ^a	29 ^a	14 ^c	74 ^a	2.3 ^c	7.81 ^a	0.68 ^d
Saskatchewan (<i>n</i> = 65)											
Mean	6.7	1.23	8.3	22	17	19	8.4	45	1.5	7.13	0.41
SD	3.3	0.17	4.0	14	11	10	4.3	28	0.8	1.28	0.29
Median	6.5	0.28	7.2	18	16	19	7.3	42	1.4	7.79	0.32
Maximum	12	0.67	17	79	66	44	17	118	3.5	8.40	1.1
95 %ile	11	0.52	16	50	36	39	16	103	3.2	8.22	1.1
95 % UCL*	7.8 ^b	0.35 ^b	9.5 ^b	29 ^b	23 ^b	24 ^b	8.4 ^a	60 ^b	2.0 ^b	7.39 ^a	0.47 ^c
Manitoba (<i>n</i> = 20)											
Mean	6.7	0.32	7.5	19	15	20	8.0	49	1.6	7.55	0.42
SD	2.6	0.2	4.3	14	12	12	4.6	30	0.9	0.57	0.19
Median	6.3	0.33	6.6	16	14	18	7.1	40	1.5	7.73	0.38
Maximum	11	0.82	17	53	39	45	17	106	3.4	8.08	0.86
95 %ile	10	0.54	14	45	35	38	15	101	3.1	8.04	0.71
95 % UCL*	7.7 ^a	0.39 ^a	9.1 ^a	26 ^c	20 ^a	25 ^a	9.8 ^a	61 ^a	2.0 ^a	7.8 ^a	0.50 ^d
Ontario (<i>n</i> = 110)											
Mean	5.1	0.16	9.5	24	20	22	9.6	52	2.2	6.97	0.41
SD	6.3	0.18	6.1	18	14	17	8.5	41	1.2	0.83	0.37
Median	2.9	0.11	8.9	20	18	18	8.2	46	2.0	7.24	0.37
Maximum	39	1.16	28	145	64	81	51	227	5.2	7.96	2.3
95 %ile	16	0.43	20	51	44	53	20	125	4.3	7.75	1.0
95 % UCL*	6.0 ^c	0.24 ^b	11 ^c	26 ^c	23 ^c	25 ^c	11 ^c	59 ^c	2.4 ^c	7.10 ^a	0.48 ^d
Quebec (<i>n</i> = 39)											
Mean	8.3	0.11	14	35	24	44	15	65	3.1	4.98	0.63
SD	9.2	0.06	6.6	25	14	41	19	26	1.2	0.69	0.33
Median	6.4	0.10	14	32	22	36	13	62	3.2	4.76	0.55
Maximum	54	0.26	30	139	60	234	119	122	6.4	7.29	1.7
95 %ile	18	0.21	25	73	51	103	25	111	4.8	6.31	1.1
95 % UCL	11 ^c	0.12 ^c	16 ^a	43 ^c	28 ^a	56 ^c	28 ^b	72 ^a	3.5 ^a	5.17 ^a	0.72 ^a

Table 2 continued

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Fe	pH	TOC
New Brunswick (<i>n</i> = 115)											
Mean	8.5	0.09	14	39	19	40	13	66	3.1	4.48	0.89
SD	5.4	0.07	5.6	24	12	29	6.4	24	1.0	0.34	0.79
Median	7.0	0.08	14	30	17	28	12	62	3.1	4.49	0.69
Maximum	28	0.45	35	169	74	213	41	153	6.0	5.75	4.6
95 %ile	21	0.21	23	81	37	82	26	106	4.7	5.06	2.4
95 % UCL*	11 ^b	0.10 ^c	15 ^c	41 ^b	21 ^b	52 ^b	14 ^a	70 ^c	3.3 ^a	4.53 ^a	1.0 ^c
Nova Scotia (<i>n</i> = 67)											
Mean	10	0.07	12	25	24	23	16	68	2.9	4.58	0.82
SD	28.1	0.06	6.5	14	38	14	12	48	1.3	0.51	0.74
Median	7.7	0.06	11	24	18	23	13	59	2.8	4.49	0.59
Maximum	228 ^e	0.28	32	112	316	74	73	286	7.0	6.44	3.4
95 %ile	28	0.19	25	36	43	48	34	115	5.3	5.48	2.6
95 % UCL	13 ^d	0.09 ^c	15 ^b	32 ^b	45 ^b	26 ^c	18 ^c	94 ^b	3.2 ^a	4.68 ^a	1.0 ^b
Prince Edward Island (<i>n</i> = 9)											
Mean	2.7	0.06	10	22	12	22	8.4	45	2.4	4.55	0.12
SD	0.7	0.04	2.5	5.8	3.1	4.2	3.6	10	0.3	0.57	0.10
Median	2.7	0.05	9.2	19	9.9	19	6.5	40	2.2	4.28	0.10
Maximum	3.8	0.14	14	31	18	29	16	62	2.9	5.80	0.36
95 %ile	3.8	0.12	14	29	16	28	14	60	2.9	5.52	0.28
95 % UCL	3.2 ^a	0.09 ^a	12 ^a	25 ^a	13 ^a	24 ^a	11 ^a	51 ^a	2.6 ^a	4.90 ^a	0.25 ^c
Newfoundland and Labrador (<i>n</i> = 66)											
Mean	9.7	0.11	13	34	24	33	10	55	2.9	4.94	1.23
SD	0.11	8.0	29	24	45	6.7	26	1.2	0.8	1.27	15.2
Median	4.4	0.08	11	29	20	20	8.9	51	2.8	4.78	0.75
Maximum	103	0.52	43	166	180	333	39	129	7.4	7.11	5.9
95 %ile	31	0.34	28	86	56	76	22	103	5.0	6.72	4.2
95 % UCL	12 ^d	0.14 ^d	15 ^c	41 ^d	28 ^c	39 ^d	12 ^c	60 ^a	3.2 ^a	5.1 ^a	1.5 ^d
All sites (<i>n</i> = 532)											
Mean	7.6	0.15	11	28	21	29	12	58	2.5	5.78	0.70
SD	13	0.2	6.3	21	19	27	9.5	34	1.2	1.47	0.74
Median	6.3	0.10	10	23	17	23	10	55	2.5	5.07	0.49
Maximum	228 ^e	2.7	43	169	316	333	119	286	7.4	9.23	5.9
95 %ile	21	0.44	22	64	43	72	24	109	4.6	7.95	2.0
95 % UCL	9.1 ^b	0.19 ^b	12 ^b	32 ^b	24 ^b	34 ^b	13 ^b	65 ^b	2.8 ^b	5.89 ^b	0.76 ^d

SD standard deviation, 95 % UCL 95 % upper confidence limit

^a 95 % student's t UCL

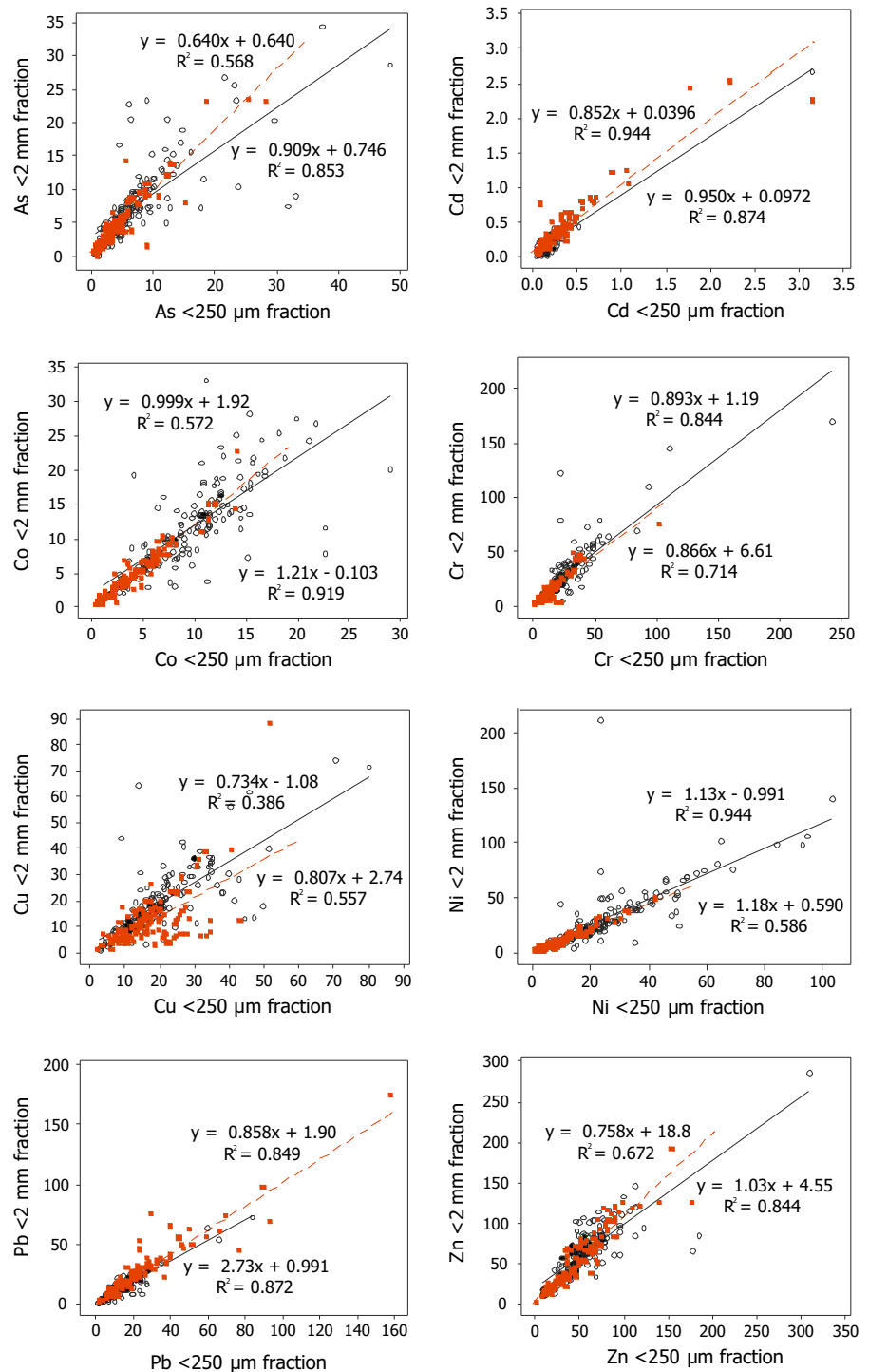
^b 95 % Chebyshev (mean, SD) UCL

^c 95 % adjusted gamma UCL

^d 95 % H-UCL

^e This sample was treated as an outlier and excluded from statistical analyses

Fig. 2 Relationship between total metal concentrations in mg/kg in the <2 mm and <250 μm soil particle size fractions in the surface layer (white circle) and C-horizon (orange square)



Arsenic

Arsenic concentrations in the <2 mm soil samples ranged from <0.1 to 42 mg/kg for the 0–5 cm layer

and <0.2 to 228 mg/kg for the C-horizon. The highest concentration (228 mg/kg) was detected in a sample collected from a location 100 m off an old logging road. An abandoned household refuse disposal area

Table 3 Statistical summary of metal bioaccessibility (%) in select Canadian soil samples

	As	Cd	Cr	Cu	Co	Pb	Ni	Zn
0–5 cm (<i>n</i> = 114)								
Mean	11	86	3.6	44	24	54	31	40
SD	7.8	15	1.7	20	15	15	22	29
Median	9.3	88	3.1	42	20	52	28	31
Minimum	1.1	12	0.9	4.4	3.0	20	1.5	4.2
Maximum	44	116	7.8	95	79	93	111	115
95 %ile	32	107	6.5	84	59	81	67	100
95 % UCL	12 ^c	89 ^a	3.8 ^a	47 ^c	27 ^c	56 ^c	35 ^c	45 ^c
C-horizon (<i>n</i> = 164)								
Mean	16	60	7.3	35	14	26	10	11
SD	13	25	7.1	23	10	18	14	7.6
Median	12	57	5.0	31	12	29	2.8	8.4
Minimum	0.3	7.4	0.6	0.2	1.8	0.2	0.2	0.7
Maximum	58	116	40	112	51	72	79	52
95 %ile	42	104	21	78	34	54	35	24
95 % UCL	10 ^c	64 ^a	8.3 ^c	44 ^b	16 ^b	34 ^b	15 ^b	11 ^d

95 % UCL 95 % upper confidence limit

^a 95 % student's t UCL

^b 95 % Chebyshev (mean, SD) UCL

^c 95 % adjusted gamma UCL

^d 95 % H-UCL

was later discovered 20 m south of the sampling location, and as such the elevated concentration could be attributed to anthropogenic sources. This data point was treated as an outlier and excluded from statistical calculations. Elevated As concentrations were found in samples from Nova Scotia, New Brunswick and Newfoundland and Labrador; 18 % of the samples collected from the C-horizon in these provinces exceeded the CCME SQG R/P for As (12 mg/kg). It has long been known that some areas in these provinces have natural As concentrations exceeding human health risk-based guideline levels due to bedrock and natural soil enrichment (Klassen et al. 2009). The data are also consistent with previous investigations that show As to be a common constituent in Nova Scotia soil, with till samples at concentrations which often exceeded the CCME SQG R/P (Goodwin et al. 2010).

The provincial mean As concentrations (Tables 1, 2) were within the range (4.8–13.6 mg/kg) reported for several uncontaminated soils in Canada (Wang and

Mulligan 2006). The mean As concentration for all the samples (surface layer and C-horizon combined) was 6.2 mg/kg which compared well with the world soil average of 6.8 mg/kg (Kabata-Pendias 2011). Statistically significant lower As concentrations were detected in the surface layer (median 4.7 mg/kg) compared to the C-horizon (median 6.3 mg/kg). The higher concentrations in the C-horizon along with the regional distribution suggested that most of the As variability was controlled by the bedrock characteristics (i.e., natural weathering of As-rich parent materials may be a significant contributing source). The potential leaching of the metals of natural origin from surface soil could also be a factor.

Arsenic bioaccessibility ranged from 1.1 to 44 % (mean 11 %, median 9.3 %) for the 0–5 cm layer and from 0.3 to 58 % (mean 16 %, median 12 %) for the C-horizon. In comparison, the range of As bioaccessibility for the surface soils from the NASGLP transect across the USA and Canada studied by Morman et al. (2009) was <0.9–11.3 % (median 4.8 %). The 95th percentile bioaccessibility for the 0–5 cm layer (32 %) and the C-horizon (42 %) were lower than that for data compiled from various contaminated sites (59 %) (Jacques Whitford 2006).

There were differences in As bioaccessibility among the provinces, as depicted in Fig. 2, with the values generally lower in the 0–5 cm layer compared to the C-horizon. It has been suggested that properties that affect As bioaccessibility include total As, iron oxide, pH, TOC and phosphate (Ruby 2004; Cave et al. 2011; Basta and Juhasz 2014). Soluble phosphate has been shown to increase As bioaccessibility through the desorption of As from Fe oxide surfaces (Basta and Juhasz 2014), increasing pH increased As bioaccessibility, while organic carbon did not significantly influence As bioaccessibility (Cave et al. 2011). Since metal oxides and phosphates were not analyzed in this study, Fe and phosphorus (P) were used as pseudo-measures (surrogates), respectively. The Pearson product-moment correlation coefficients for the regression analysis between As bioaccessibility and soil physicochemical properties (Table 4) indicated that bioaccessibility increased with soil pH and P and decreased with total Fe and As concentrations, while TOC had negligible effects. The best subset regression analysis suggested P had the most influence on As bioaccessibility and may account for the higher bioaccessibility of As from the C-horizon soils.

Table 4 Pearson product-moment correlation coefficients for regression analysis between metal bioaccessibility versus pH, organic carbon (TOC), total iron (Fe_T), aluminum (Al_T), phosphorus (P_T) Mn and total metal (Met_T)

	pH	TOC	Met _T	Al _T	Fe _T	P _T
Arsenic bioaccessibility						
0–5 cm	0.350*	ns	−0.245	0.230	ns	0.404*
C-horizon	0.237	ns	−0.367*	ns	−0.358	0.268
Cadmium bioaccessibility						
0–5 cm	n.s.	0.259	n.s.	n.s.	−0.237*	n.s.
C-horizon	0.681	n.s.	ns	−0.247*	−0.371	n.s.
Cobalt bioaccessibility						
0–5 cm	–	0.521	n.s.	−0.252	−0.432	n.s.
C-horizon	0.402	n.s.	n.s.	n.s.	−0.246	n.s.
Chromium bioaccessibility						
0–5 cm	−0.411*	0.282*	n.s.	n.s.	n.s.	n.s.
C-horizon	−0.237	0.620	n.s.	0.197*	n.s.	n.s.
Copper bioaccessibility						
0–5 cm	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
C-horizon	0.455*	n.s.	−0.509	−0.450	−0.452	n.s.
Nickel bioaccessibility						
0–5 cm	n.s.	0.532	n.s.	−0.276*	−0.462*	n.s.
C-horizon	0.710	0.236*	−0.356	−0.402*	−0.474	n.s.
Lead bioaccessibility						
0–5 cm	−0.214*	0.433	0.325*	−0.335*	−0.443	n.s.
C-horizon	0.660	n.s.	−0.214	−0.333	−0.328	0.226
Zinc bioaccessibility						
0–5 cm	−0.522	0.732	−0.289*	−0.556*	−0.595*	n.s.
C-horizon	n.s.	n.s.	−0.327	−0.222	−0.307	n.s.

All coefficients are significant at the $p < 0.001$ level, with the exception of those marked with an asterisk (*), which are significant at the $p < 0.05$. *n.s.* not significant at the $p > 0.05$

Cadmium

Cadmium levels were generally low (<0.1–2.8 mg/kg) in relation to the CCME SQG R/P of 10 mg/kg with mean concentrations of 0.4 mg/kg for the 0–5 cm layer and 0.2 mg/kg for the C-horizon (Tables 1, 2). The difference in concentrations between the two layers was statistically significant (median 88 and 57 %, respectively). The major sources of Cd in soils include atmospheric deposition mainly from metal mining and smelters (Pb and Zn production in particular) and fertilizers (Kabata-Pendias 2011, p. 293), as well as combustion of fossil fuels and weathering of galvanized metal (CCME 1999). The higher Cd concentrations in the surface layer may reflect anthropogenic inputs from atmospheric sources: Samples with the highest Cd concentrations in this investigation also contained relatively high concentrations of Zn and Pb.

There were no statistically significant differences in Cd concentrations among the provinces with the range falling within data for Canadian background soils (CCME 1999) and comparable to values reported for continental crust and surface soils (Kabata-Pendias 2011). The median of 0.3 mg/kg for the 0–5 cm soils was similar to the median for the soils from the NASGLP transect across the USA and Canada (Morman et al. 2009).

Cadmium bioaccessibility ranged from 12 to 116 % (mean 86 %; median 88 %) for the 0–5 cm layer soils and 7.4–116 % (mean 60 %; median 57 %) for the C-horizon. The range of Cd bioaccessibility in this study was within the values reported for soils from the NASGLP transect across the USA and Canada, which was 29–140 % (Morman et al. 2009). Cadmium generally had the highest bioaccessibility compared to the other elements covered in this study (Fig. 3). It has been suggested that during weathering processes cadmium

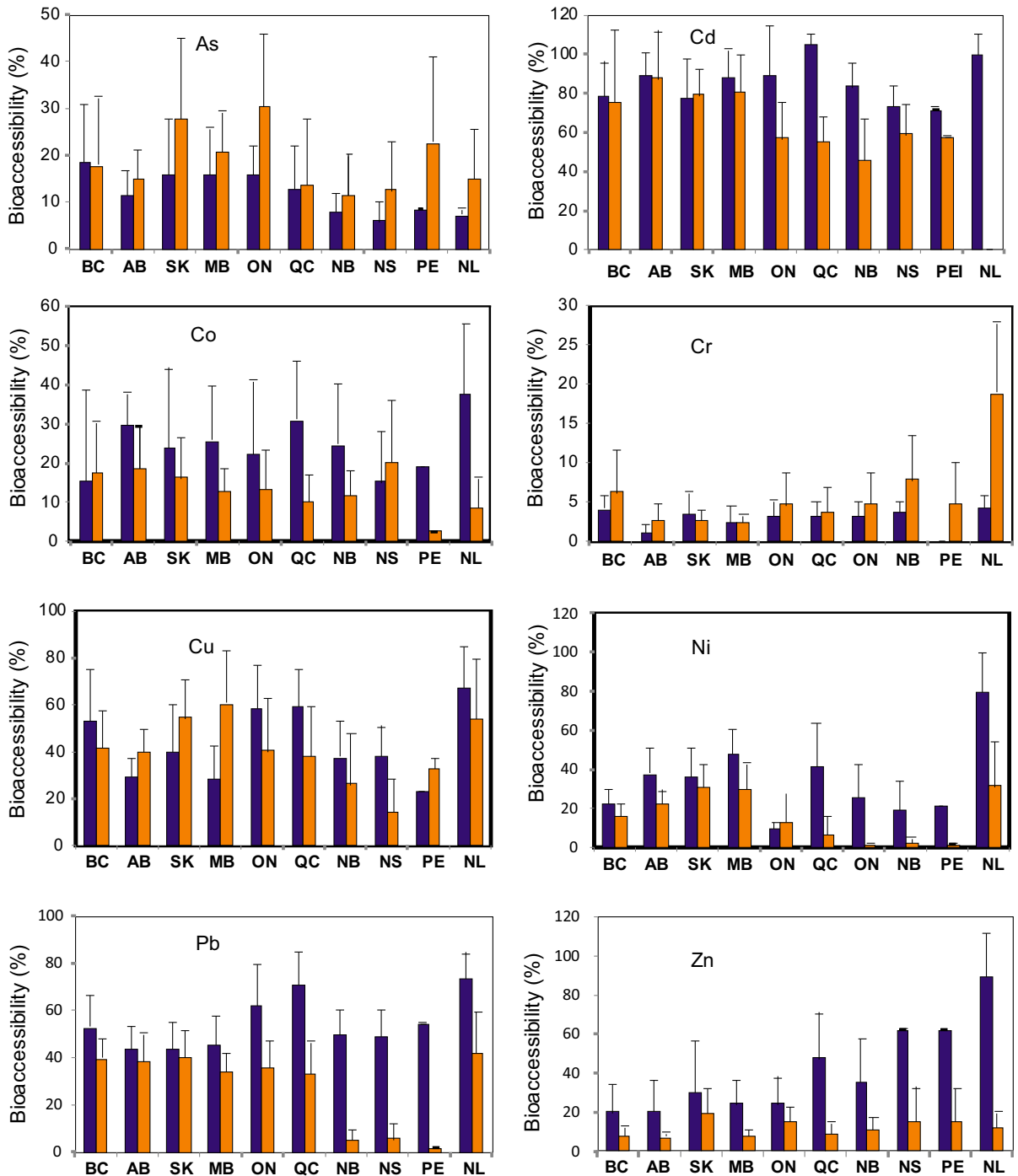


Fig. 3 Mean metal bioaccessibility (%) for the 0–5 cm and (blue bar) and C-horizon (orange bar) for each province. Error bars represent one standard deviation. BC British Columbia, AB

Alberta, SK Saskatchewan, MB Manitoba, ON Ontario, QC Quebec, NB New Brunswick, NS Nova Scotia, PE Prince Edward Island and NL Newfoundland and Labrador

forms simple compounds such as CdO, Cd(OH)₂ and CdCl₂ that are readily mobile (Kabata-Pendias 2011) leading to the high bioaccessibility. The solubility of the Cd species appeared to have the most influence on bioaccessibility in the 0–5 cm layer soils as there were no strong relationships between the soil properties studied in this investigation and bioaccessibility for this element (Table 4). Soil pH appeared to be significantly correlated with Cd bioaccessibility for the C-horizon soils.

Chromium

Chromium concentrations (Tables 1, 2) were higher in the C-horizon (mean 28 mg/kg, median 23 mg/kg) compared to the 0–5 cm layer soils (mean 15 mg/kg, median 12 mg/kg). Both mean concentrations were lower than the world soil average of 59.7 mg/kg for surface soils (Kabata-Pendias 2011). The median Cr concentration for the 0–5 cm layer soils (12 mg/kg) was lower than the median value (39 mg/kg) for soils from the NASGLP transect across the USA and Canada (Morman et al. 2009). As per previous investigations (McKeague and Wolynetz 1980; CCME 1999), Cr concentrations varied regionally with the highest levels occurring in the C-horizon soils from NL and NB. Higher Cr concentrations in the C-horizon may reflect weathering and other natural soil-forming processes of the parent materials as the major sources and consistent with the literature data, indicating that Cr in soils is generally inherited from parent materials (Kabata-Pendias 2011; CCME 1999).

The bioaccessibility of Cr in both the 0–5 cm layer (mean 3.6 %, median 3.1 %) and C-horizon (mean 7.3 %, median 5.0 %) was low. Similarly low Cr bioaccessibility values were detected for the samples from the NASGLP transect across the USA and Canada (range 0.5–7.5 %) (Morman et al. 2009). The low bioaccessibility of Cr may be attributed to its occurrence mainly in immobile form in soils (Kabata-Pendias 2011).

Cobalt

Cobalt concentrations in all the samples were below the CCME SQG R/P with a mean of 5.1 mg/kg for the 0–5 cm layer and 11 mg/kg for the C-horizon. The mean concentrations were lower than the mean (20 mg/kg) reported for 173 Canadian background soils (McKeague and Wolynetz 1980). The mean for

the 0–5 cm layer was also lower than the world soil average of 11.3 mg/kg (Kabata-Pendias 2011).

Cobalt bioaccessibility was variable among the provinces (Fig. 3) with the 0–5 cm samples having a higher mean (24 %) and median (20 %) compared to the C-horizon (mean 14 %, median 12 %): The difference was statistically significant. Cobalt distribution and availability in soils may be governed by pH, TOC and hydrous oxides of Fe and Mn (Kabata-Pendias 2011). There was a strong linear correlation between Co and Fe for both the 0–5 cm layer ($R^2 = 0.589$, $p < 0.001$) and C-horizon ($R^2 = 0.701$) while pH, Mn and TOC showed weaker association. Bioaccessibility for Co decreased with increasing Fe concentration and decreasing soil pH (Table 4), and as such the lower Co bioaccessibility in the C-horizon may be attributed to its higher pH and Fe content compared to the 0–5 cm layer.

Copper

The mean concentration of Cu in the C-horizon (21 mg/kg) was higher than that of the 0–5 cm layer (12 mg/kg) with minor variation in concentrations among the provinces. The mean for the C-horizon compared well to the estimated average of 20 mg/kg Cu in Canadian background soils (CCME 1999). As with Cr and Co, parent materials governed Cu concentrations in soils (Kabata-Pendias 2011, p. 253).

Copper bioaccessibility was variable among the provinces (Fig. 3) with no consistent pattern of differences between the 0–5 cm layer (mean 44 %, median 42 %) and C-horizon soils (mean 35 %, median 31 %). Factors that influence the solubility and bioavailability of copper in soils include pH, cation exchange capacity, organic matter content, presence of oxides of Fe, Mn and Al, oxidation–reduction potential and mineralogy (CCME 1999; Kabata-Pendias 2011). There were no strong correlations between soil properties such as pH, TOC, Fe and Mn with bioaccessibility for the 0–5 cm layer, whereas some relationships were observed for the C-horizon (Table 4), suggesting Cu speciation may be the dominant property that influenced bioaccessibility for the study soils.

Nickel

No significant differences in Ni concentrations were found among the provinces for the 0–5 cm layer soils

with the mean (12 mg/kg) comparably lower than the world soil average for surface soils (29 mg/kg) as reported by Kabata-Pendias (2011). The median Ni concentration (8.5 mg/kg) was also lower than the median (14 mg/kg) for the soils from the NASGLP transect across the USA and Canada (Morman et al. 2009). Soils from the C-horizon had relatively higher Ni concentrations (mean 29 mg/kg, median 23 mg/kg) compared to the 0–5 cm layer (mean 12 mg/kg, median 9.8 mg/kg). In particular, the C-horizon soils from Quebec (mean 44 mg/kg) and New Brunswick (mean 40 mg/kg) had high Ni concentrations with over 28 % of the samples from these two provinces exceeding the CCME SQG R/P for Ni (50 mg/kg). Ontario and Newfoundland and Labrador also had a number of samples that exceeded the guidelines. These elevated concentrations may be due to the presence of naturally nickel-enriched bedrock in Canada (CCME 1999).

Nickel was more bioaccessible in the 0–5 cm layer soils (mean 31 %, median 28 %) compared to the C-horizon (mean 10 %, median 2.8 %) and variable among the provinces (Fig. 3). The highest Ni bioaccessibility values were obtained for the 0–5 cm soils from Newfoundland and Labrador (Fig. 3) which also had high TOC and low pH. According to the CCME (1999) factors that influence Ni cycling in the environment include pH, organic matter, clay minerals, Fe and Mn oxides. There was some association between bioaccessibility and TOC, Fe and pH (Table 4). Higher bioaccessibility in the surface soils is consistent with observations that Ni is much more mobile in organic-rich surface soils due to the formation of relatively soluble chelates and also strongly associated with Fe and Mn oxides (CCME 1999; Kabata-Pendias 2011 p. 240).

Lead

The distribution of Pb was variable among the provinces (Tables 1, 2) with significantly higher concentrations in the 0–5 cm layer soils (mean 26 mg/kg, median 20 mg/kg) compared to the C-horizon (mean 12 mg/kg, median 10 mg/kg). The mean values were comparable to the background levels for total Pb in Canadian soils (12–25 mg/kg) as reported by the CCME (1999), while the mean Pb concentration in the 0–5 cm layer was comparable to the world soil average (27 mg/kg) for surface soils (Kabata-Pendias

2011). The median for the 0–5 cm layer (20 mg/kg) was slightly higher than the median (17 mg/kg) for the soils from the NASGLP transect across the USA and Canada (Morman et al. 2009). Even though Pb may be inherited from parent rocks, due to the widespread anthropogenic introduction of Pb from leaded gasoline in the past and other atmospheric sources, most soils are likely to be enriched in the top horizon (Kabata-Pendias 2011). In addition, anthropogenic lead is accumulated near the surface due to its affinity for soil organic matter (CCME 1999). Thus, anthropogenic influence and the higher organic matter content of the surface soils are the most likely explanation for the higher concentration and distribution of Pb in the surface soils in this study.

There was a small variation in Pb bioaccessibility among the provinces as depicted in Fig. 3 with the surface soils (mean 54 %, median 52 %) showing statistically significant higher bioaccessibility compared to the C-horizon (mean 26 %, median 29 %). Factors which influence the mobility and bioavailability of Pb include pH, soil texture, organic matter content and speciation (CCME 1999; Ruby 2004): Increasing acidity, formation of lead–organic matter complexes and oxidized species may increase Pb solubility. The higher bioaccessibility of Pb in the 0–5 cm layer soils in this study may be attributed to the presence of the oxidized forms, higher TOC, lower pH and anthropogenic origin. As suggested previously, metals of mainly anthropogenic origin tend to be more soluble and therefore more bioaccessible compared to those of natural origin (Ljung et al. 2007).

The median Pb bioaccessibility for the 0–5 cm layer soils (52 mg/kg) was higher than the median (18 %) for the NASGLP transect (Morman et al. 2009), while the 95th percentile for the 0–5 cm layer (81 %) was comparable to that obtained for the data compiled from various contaminated sites (Jacques Whitford 2006).

Zinc

In general, Zn was found to be evenly distributed between the two soil profiles with mean concentrations of 60 mg/kg and 58 mg/kg for the 0–5 cm layer and C-horizon, respectively (Tables 1, 2); a mean of 74 mg/kg was reported for Zn in Canadian soils by McKeague and Wolynetz (1980), while the world soil average for Zn in surface soils was given as 70 mg/kg

by Kabata-Pendias (2011). Zinc concentrations in the surface soils from BC (mean 91 mg/kg), Alberta (mean 83 mg/kg) and Ontario (mean 82 mg/kg) were relatively higher compared to the other provinces.

Zinc bioaccessibility (Table 3) was higher in the 0–5 cm layer (mean 40 %, median 31 %) compared to the C-horizon (mean 11 %, median 8.4 %). Variation in bioaccessibility among the provinces was more pronounced in the 0–5 layer soils with samples from the eastern provinces (Quebec, New Brunswick, Prince Edward Island, Newfoundland and Labrador) showing relatively higher bioaccessibility. Soil pH has been identified as one of the main factors affecting Zn mobility and sorption in soils, with Zn becoming more soluble as pH decreases (CCME 1999; Kabata-Pendias 2011). Zinc bioaccessibility increased with decreasing pH for the surface soils (Table 4), and the higher bioaccessibility of Zn in surface samples from the eastern provinces may be attributed to their relatively lower pH.

Implications for human health risk assessment in Canada

Human health risk assessment based on generic environmental quality guidelines generally conservatively assumes 100 % bioavailability of the soil-borne contaminant after ingestion in the absence of any evidence to the contrary. To provide more realistic estimates of exposure, site-specific oral bioavailability of the soil-borne contaminant can be used to make adjustments in the risk assessment (USEPA 2007a; Richardson et al. 2006; Health Canada 2010). Bioavailability is best assessed with in vivo assays; however, in vitro bioavailability assays (bioaccessibility) have been shown to be suitable surrogates (Basta and Juhasz 2014; Ruby 2004; USEPA 2007a). This study has shown that with the exception of Cd, the mean or median bioaccessibility of the elements, and therefore the resultant bioavailability, are considerably less than 100 %. Thus, the use of site-specific bioaccessibility results for these elements will yield more accurate estimation of the risk associated with the oral bioavailability for sites where soil ingestion is the major contributor of human health risk.

The IVBA protocol used to determine bioaccessibility in the study (USEPA 2012) has been validated for As and Pb through studies that show good

correlation between the in vivo and in vitro assays (Basta and Juhasz 2014; Drexler and Brattin 2007; Juhasz et al. 2014). The USEPA recommends site-specific IVBA, but in cases where the development of site-specific relative bioavailability (RBA) for arsenic in soil is not feasible in screening level risk assessment, the USEPA recommends a default As RBA value of 60 % based on a review of soil results which showed that less than 5 % of the RBA estimates exceeded 60 % (USEPA 2012). Using the in vivo/in vitro regression model described by Juhasz et al. (2014) for As bioaccessibility based on a range of soil types and contamination scenarios, the relative oral bioavailability of As from soil can be expressed as:

$$RBA = 0.84(IVBA, \%) + 3.56$$

where RBA = relative bioavailability adjustment (expressed as %) and IVBA = in vitro bioaccessibility assay result (expressed as %). Substituting the Canada-wide 95th percentile IVBA result of 32 % for soils in the top 5 cm, the relative oral bioavailability of As when ingested from such soil is estimated to be 30 %. In Canadian assessments, the RBA results are typically used without the need for testing the bioaccessibility in the media of concern evaluated in the development of the toxicity reference value (i.e., RBA of As in water is assumed to be 100 % for the toxicity study). As a result, oral bioavailability of As in soil can reasonably be assumed to be 30 % of the bioavailability of As when present in water, which is appreciably lower than the default USEPA As RBA of 60 %.

A default Pb oral bioavailability value of 60 % is prescribed by the USEPA (2007b) and Health Canada (2009). Health Canada (2009) also supports use of site-specific IVBA for federal sites contaminated with Pb, with derivation of relative bioavailability (RBA) based on the following USEPA (2007b) equation for Pb:

$$RBA = 0.878(IVBA, \%) - 2.8$$

When the Canada-wide 95th percentile IVBA result of 81 % for surface soils (see Table 3) is used in the above equation, the relative oral bioavailability of Pb when ingested from such soil is estimated to be 68 %.

The bioaccessibility of As in soils at contaminated mine sites is typically greater than that reported here for background soils, whereas the bioaccessibility from mine tailings is much lower. For example, at

Giant Mine in Yellowknife, NT, the bioaccessibility of As from surface soils ranged between approximately 30 and 40 % (Ollson 2003; Bromstad 2011), while bioaccessibility from tailings was only 1–3 % (Ollson 2003). The mean bioaccessibility of As for the background soils investigated herein was 11 % (see Table 3). Similar variation between soils and tailings was also observed for gold mining sites in Nova Scotia (Meunier et al. 2010). Therefore, it will be important to differentiate contaminated soils from tailings or other mining waste materials when assessing human exposures and risks at mine sites contaminated with arsenic.

At the current time, Canadian agencies are generally reluctant to use IVBA results for substances other than Pb and As. Nevertheless, there could be tremendous cost savings if IVBA or in vivo bioavailability testing was extended to additional metals and organic substances such as polycyclic aromatic hydrocarbons (PAHs). At a typical Canadian cost of approximately \$200 per sample for IVBA, and in vivo swine testing cost in the range \$6000–\$9500 per sample, a cost savings to the Canadian Federal Contaminated Sites Action Plan of approximately \$2 billion have been postulated (Richardson and Fast 2014). Depending on the results obtained from the testing, the consideration of these results could lead to a substantial reduction in remediation costs since risk-based soil standards would be correspondingly increased for substances where soil ingestion is the major contributor of human health risk. In addition, consideration of such testing will result in improvements to more accurately identify environmental priorities and thereby support governments directing limited resources to sites in a more defensible manner (e.g., all other aspects assumed to be equal, a site with an As soil concentration of 200 mg/kg and IVBA of 5 % would be properly ranked to be less of a concern than a site with a soil concentration of 80 mg/kg and IVBA of 60 %).

Conclusion

This study indicated some differences in elemental concentrations between the 0–5 cm (surface soil) layer and the C-horizon (parent material) and among the provinces with the mean concentrations comparable to the data for Canadian soils for the majority of the elements. The concentrations of As, Cr, Cu, Co, Ni and

Zn were higher in the C-horizon, and this observation along with the regional distribution suggested that most of the variability in concentrations of these elements was governed by the bedrock characteristics and potential leaching of the metals of natural origin from surface soil. Unlike the above-stated elements, Pb and Cd concentrations were higher in the surface layer, likely reflecting the potential effects of anthropogenic deposition. The strong affinity of Pb and Cd for organic matter is also a contributing factor. Elemental bioaccessibility was variably decreasing in the order Cd > Pb > Cu > Zn > Ni > Co > As > Ni > Cr. With the exception of As, bioaccessibility was generally higher in the C-horizon soils compared to the 0–5 cm soils. The differences in metal bioaccessibility between the 0–5 cm and the C-horizon and among the provinces may reflect geological processes and speciation. The mean, median or 95th percentile bioaccessibility for As, Cr, Cu, Co and Pb were below 100 %, and the consideration of these results will yield more accurate estimation of the risk associated with the oral bioavailability for these elements for sites where soil ingestion is the major contributor of human health risk.

Acknowledgments The authors thank Health Canada's Contaminated Sites Division and the Federal Contaminated Sites Action Plan (FCSAP) for funding. We also thank D. Lee for her review and valuable comments.

References

- Basta, N., & Juhasz, A. (2014). Using in vivo bioavailability and/or in vitro gastrointestinal bioaccessibility testing to adjust human exposure to arsenic from soil ingestion. *Reviews in Mineralogy and Geochemistry*, 79, 451–472.
- Bright, D. A., Richardson, G. M., & Dodd, M. (2006). Do current standards of practice measure what is relevant to human exposure at contaminated sites? I: A discussion of soil particle size and contaminant partitioning in soil. *Human and Ecological Risk Assessment*, 12, 591–605.
- Bromstad, M. J. (2011). *The characterization, persistence, and bioaccessibility of roaster-derived arsenic in surface soils at giant mine, yellowknife, NT*. A thesis submitted to the Department of Geological Sciences and Geological Engineering in conformity with the requirements for the Degree of Master of Science, Queen's University. November 2011.
- Canadian Council of Ministers of the Environment (CCME). (1993). *Guidance manual on sampling, analysis and data management for contaminated sites, volume I: Main report, CCME EPC-NCS62E (p. 2)*. Winnipeg, Manitoba.
- Cave, M. R., Wragg, J., Denys, S., Jondreville, C., & Feidt, C. (2011). Oral bioavailability. In F. A. Swartjes (Ed.),

- Dealing with contaminated sites* (pp. 287–324). New York: Springer.
- CCME. (1999). *Canadian environmental quality guidelines*.
- Drexler, J. W., & Brattin, W. J. (2007). An in vitro procedure for estimation of lead relative bioavailability: With validation. *Human and Ecological Risk Assessment*, 13, 383–401.
- Federal Contaminated Sites Inventory. (2015). <http://www.tbs-sct.gc.ca/fcsi-rscf/home-accueil-eng.aspx>. Accessed 15 September 2015.
- Friske, P. W. B., Ford, K. L., Kettles, I. M., McCurdy, M. W., McNeil, R. J., & Harvey, B. A. (2010). North American soil geochemical landscapes project: Canadian field protocols for collecting mineral soils and measuring soil gas radon and natural radioactivity. *Geological Survey of Canada*, Open File 6282; 177 p.
- Girard, I., Klassen, R. A., & Laframboise, R. R. (2004). *Sedimentology laboratory manual*, Terrain Sciences Division. Geological Survey of Canada, Open File 4823.
- Goodwin, T. A., Parker, L., Fisher, B. E. & Dummer, T. J. B. (2010). *Mineral resources branch, report of activities 2009*. Nova Scotia Department of Natural Resources, Report ME 2010-1, pp. 41–44.
- Health Canada. (2009). *Memorandum: Interim CSD guidance on a TRV for lead (Pb) and interpretation of Pb bioaccessibility data for federal contaminated site human health risk assessment in Canada*. Contaminated Sites Division, Health Canada, Ottawa, ON Canada. Dated December 2009.
- Health Canada. (2010). *Federal contaminated site risk assessment in Canada, part V: Guidance on human health detailed quantitative risk assessment of chemicals (DQRA_{Chem})*. Report H128-1/11-639E-PDF, Health Canada, Ottawa, ON, Canada.
- Health Canada. (2012). *Federal contaminated site risk assessment in Canada, part I: Guidance on human health preliminary quantitative risk assessment (PQRA), version 2.0*. Report H128-1/11-632E-PDF, Health Canada, Ottawa, ON, Canada.
- Jacques Whitford. (2006). *Ingestion bioavailability of arsenic, lead and cadmium in human health risk assessments: Critical review, and recommendations*. Submitted to Health Canada, Ottawa, ON. <http://www.bioavailabilityresearch.ca/Health%20Canada%20Bioavailability.final.pdf>. Accessed 15 September 2015.
- Juhasz, A. L., Herde, P., Herde, C., Boland, J., & Smith, E. (2014). Validation of the predictive capabilities of the SBRC-G in vitro assay for estimating arsenic relative bioavailability in contaminated soils. *Environmental Science and Technology*, 48, 12962–12969.
- Kabata-Pendias, A. (2011). *Trace elements in soils and plants* (4th ed.). Boca Raton: CRC Press.
- Klassen, R. A., Douma, S. L., Ford, A., Rencz, A. & Grunsky, E. (2009). Geoscience modeling of relative variation in natural arsenic hazard in potential in New Brunswick. *Geological Survey of Canada, Current Research 2006–7*.
- Ljung, K., Oomen, A., Duits, M., Selinus, O., & Berglund, M. (2007). Bioaccessibility of metals in urban playground soils. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 42(9), 1241–1250. doi:10.1080/10934520701435684.
- McKeague, J. A., & Wolynetz, M. S. (1980). Background levels of minor elements in some Canadian soils. *Geoderma*, 24, 299–307.
- Meunier, L., Walker, S. R., Wragg, J., Parsons, M. B., Koch, I., Jamieson, H. E., & Reimer, K. J. (2010). Effects of soil composition and mineralogy on the bioaccessibility of arsenic from tailings and soil in gold mine districts of Nova Scotia. *Environmental Science and Technology*, 44(7), 2667–2674.
- Morman, S. A., Plumlee, G. S., & Smith, D. B. (2009). Application of in vitro extraction studies to evaluate element bioaccessibility in soils from a transect across the United States and Canada. *Applied Geochemistry*, 24, 1454–1463.
- Ollson, C. A. (2003). *Arsenic risk assessments: The importance of bioavailability*. Ph.D. thesis, Faculty of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, ON. 377 p.
- Rencz, A., Garrett, R. G., Adcock S. W. & Bonham-Carter G. F. (2006). Geochemical background in soil and till. *Geological Survey of Canada, Open File 5084*. Natural Resources Canada, Ottawa, ON.
- Rencz, A., Garret, R. G., Kettle, I. M., Grunsky, E. C., & 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*. doi:10.4095/288746.
- Richardson, G. M. (2002). *Determining natural (background) arsenic soil concentrations in Yellowknife NWT, and deriving site-specific human health-based remediation objectives for arsenic in the Yellowknife area*. Final report, submitted by Risklogic Scientific Services Inc. to the Yellowknife Arsenic Soils Remediation Committee (YASRC), Yellowknife, April 2002.
- Richardson, G. M., Bright, D. A., & Dodd, M. (2006). Do current standards of practice measure what is relevant to human exposure at contaminated sites? II. Oral bioaccessibility of contaminants in soil. *Human and Ecological Risk Assessment*, 12, 606–616.
- Richardson, G. M., & Fast, A. (2014). *Bioaccessibility and bioavailability: The great opportunity not realized (so far)*. Presented at the 35th Annual Meeting of SETAC North America, Vancouver, BC, 11 November 2014.
- Ruby, M. V. (2004). Bioavailability of soil-borne chemicals: Abiotic assessment tools. *Human and Ecological Risk Assessment*, 10, 647–656.
- Smith, D. B., Woodruff, L. G., O’Leary, R. M., Cannon, W. F., Garrett, R. G., Kilburn, J. E., & Goldhaber, M. B. (2009). Pilot studies for the North American Soil Geochemical Landscapes Project—Site selection, sampling protocols, analytical methods, and quality control protocols. *Applied Geochemistry*, 24, 1357–1368.
- Turner, A., & Simmonds, L. (2006). Elemental concentrations and metal bioaccessibility in UK Household dust. *Science of the Total Environment*, 371, 74–81.
- USEPA. (1994). *Method 200.8 determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry, Revision 5.4*. <https://www.epa.gov/sites/production/files/2015-06/documents/epa-200.8.pdf>.
- USEPA. (1996). Method 3050B acid digestion of sediments, sludges, and soils. *EPA SW-846, test methods for evaluating solid waste, physical/chemical methods*.

- USEPA. (2007a). *Guidance for evaluating the oral bioavailability of metals in soils for use in human health risk assessment*. May 2007, OSWER 9285.7-80. Office of Solid Waste and Remedial Response, Washington, DC, USA.
- USEPA. (2007b). *Estimation of relative bioavailability of lead in soil and soil-like materials using in vivo and in vitro methods*. Office of Solid Waste and Emergency Response 9285.7-77. <http://www.epa.gov/superfund/health/contaminants/bioavailability/guidance.htm>. Accessed 15 September 2015.
- USEPA. (2012). *Standard operating procedure for an in vitro bioaccessibility assay for lead in soil*, EPA 9200.2-86.
- USEPA. (2013). *Statistical Software ProUCL 5.0.00 for Environmental Applications for Data Sets with and without Nondetect Observations*. <http://www.epa.gov/osp/hstl/tsc/software.htm>. Accessed 15 September 2015.
- Wang, S., & Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. *Science of the Total Environment*, 366(2–3), 701–721.