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Distribution and In Vitro Bioaccessibility of Potentially Toxic Metals in Soils at Select Urban Parks at Eastern Canadian Cities

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Abstract: This study investigated the human health risks associated with exposure to potentially toxic metals, including arsenic, barium, cadmium, chromium, cobalt, copper, lead, nickel, and zinc, at select parks in Eastern Canadian cities. Except for arsenic in Halifax, the mean metal concentrations in the cities, including Saint John, Fredericton, Ottawa, Toronto, London, Windsor, Woodstock, Kitchener, Guelph, Chatham, and Montreal, were below the Canadian Council of Ministers of Environment soil quality guideline for parkland use. Metal distribution reflected either the regional natural-occurring concentrations or anthropogenic sources such as industrial activities, historical land use, and heavy traffic corridors. In vitro bioaccessibility values were variable and in the order chromium < nickel < cobalt < arsenic < zinc < copper < lead < cadmium. The risk associated with incidental soil ingestion for children, incorporating bioaccessibility, indicated unacceptable levels of non-carcinogenic effects for 6 out of the 101 samples analyzed. For adults, unacceptable non-carcinogenic effects were noted for only one sample. Lead was the leading contributor to the non-carcinogenic risk. Carcinogenic risk for arsenic was limited to two samples. The overall risks associated with exposure to metals in soils in most of the parks studied were deemed low except for arsenic and lead at a few parks.

Keywords: urban parks; playgrounds; metals; in vitro bioaccessibility

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1. Introduction

Core ideas:

- Potentially toxic metals distribution in surface soils at select parks and playgrounds in 12 Canadian cities reflect natural and anthropogenic sources.
- In vitro bioaccessibility values are variable due to different soil physicochemical properties.
- The risk which is associated with incidental ingestion of potentially toxic metals in soils incorporating bioaccessibility is low except for arsenic and lead at a few parks.

Urban green spaces, including playgrounds and sports fields, often have bare patches that can serve as potential deposition points for contaminants. The world's population is increasingly becoming urbanized, and according to the United Nations World Urbanization Prospects 2018, 81.4% of Canadians live in urban areas [1]. This rise in urbanization likely leads to the increasing use of outdoor green spaces by urban residents with the corresponding potential increase in exposure to soils through dermal contact, incidental ingestion, and inhalation of suspended particles. Incidental soil ingestion is typically an exposure pathway, especially for young children during recreational activities at these parks and playgrounds, due to their playing on the ground and frequent mouthing of hands, toys, and other objects [2]. Characterization and mapping of potentially toxic metals and metalloids in soils at urban parks and playgrounds is thus an important first step in the evaluation of ecological and human health risks toward the overall achievement of the United Nations Sustainable Development Goal 3: Good Health and Well-Being.

Surrounding land use affects metal and metalloid (collectively referred to as metals) distribution in urban surface soils, and, in general, samples collected from locations close to roads with heavy traffic have higher metal concentrations compared to soils farther from roads [3]. Vehicular traffic has been shown to contribute to the environmental loading of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) [4–6]. Studies in urban parks and playgrounds have also identified elemental contamination from treated wood structures in addition to natural sources, industry, and traffic [7]. Five out of twenty-four sites that were surveyed in Istanbul, Turkey, had systematically higher As, Cu, Cr, or Zn concentrations, compared to the backgrounds that were attributed to leaching from wooden structures [7]. Data from European and American cities surveyed indicated moderate to heavy contamination with Cd, Cu, Pb, and Zn, which were attributed to anthropogenic sources [8]. Geostatistical and multivariate statistical analyses indicated that the two principal sources of trace elements, especially Cu, Pb, and Zn, in the urban soils in China were industrial discharges and traffic emissions, while As and mercury (Hg) primarily originated from coal combustion, partly for home-heating activities [8]. Other activities identified as potential sources of metals include incineration of municipal, medical, and other wastes (As, Cd, Cr, Pb, Ni, and Zn), metal works (Cd, Cr, Cu, Ni, Pb, and Zn), oil refining (As, Co, Cr, Cu, Ni, Pb, and V), glassworks (As, Cd, Co, Cu, Ni, Pb, and Zn), battery production (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) and pesticide production and use (As, Cd, Cu, Hg, Pb, and Zn) [3,8].

Various studies have incorporated bioaccessibility data in human health risk assessment of metals in urban environments [7–10]. The inclusion of the bioaccessibility data resulted in a more realistic estimation of the human health risk associated with incidental soil ingestion. These studies have shown that bioaccessibility varies widely among different metals and soils from different cities and that metals of natural origin generally have lower solubility and bioaccessibility than those from anthropogenic sources.

In light of the potential toxicity of metals, especially to children through inadvertent soil ingestion, it is pertinent to identify and quantify the concentration of contaminants in soils at parks and playgrounds while utilizing urban green spaces. Due to the lack of data on the distribution of metals in Canadian urban parks, this study was conducted as an initial scoping survey; it provides the first regional overview of the metal distribution and potential health risks associated with incidental exposure to soils at select parks in Eastern Canada. It involves the meta-analysis of metal concentrations in surface soil samples collected from select parks and playgrounds at 12 urban centers in Eastern Canada. Eight potentially toxic metals, including As, Cd, Co, Cr, Cu, Ni, Pb, and Zn, were selected for the meta-analysis based on their potential to be introduced into the urban environment from various anthropogenic sources. The relationships between soil metal concentrations and traffic, surrounding land use, and site history were explored. The influence of soil pH and total organic carbon on bioaccessibility was also investigated and the potential risk associated with exposure to the metal contaminants was estimated.

2. Methodology

2.1. Soil Sampling and Preparation

Sampling was conducted at select parks in eight cities, including Halifax (10), Ottawa (8), London (4), Windsor (4), Woodstock (4), Kitchener (4), Guelph (4), and Chatham (4) (Figure 1). Data for samples collected from previous investigations, including Toronto (15) [11], Saint John (10) [12], Fredericton (10) [12], and Montreal (16) [13], were included in the meta-analysis. The geographical coordinates of the sampling locations are given in Table S1 in the Supplemental Material. The parks were selected to reflect different surroundings, such as residential, industrial, educational institutes, and commercial. Travel volumes in the vicinities as well as historical land use of adjacent areas were also considered. One composite soil sample was collected from the top 0–5 cm layer from visibly disturbed patches due to human activities in easily accessible areas in each park, including picnic areas and near play structures. Samples were placed into Ziploc bags and transported to the laboratory. Each sample was air-dried in a paper sandwich bag at ambient temperatures (~20 °C) in a fume hood in the laboratory. The dried sample was sieved to <250 μm [14].

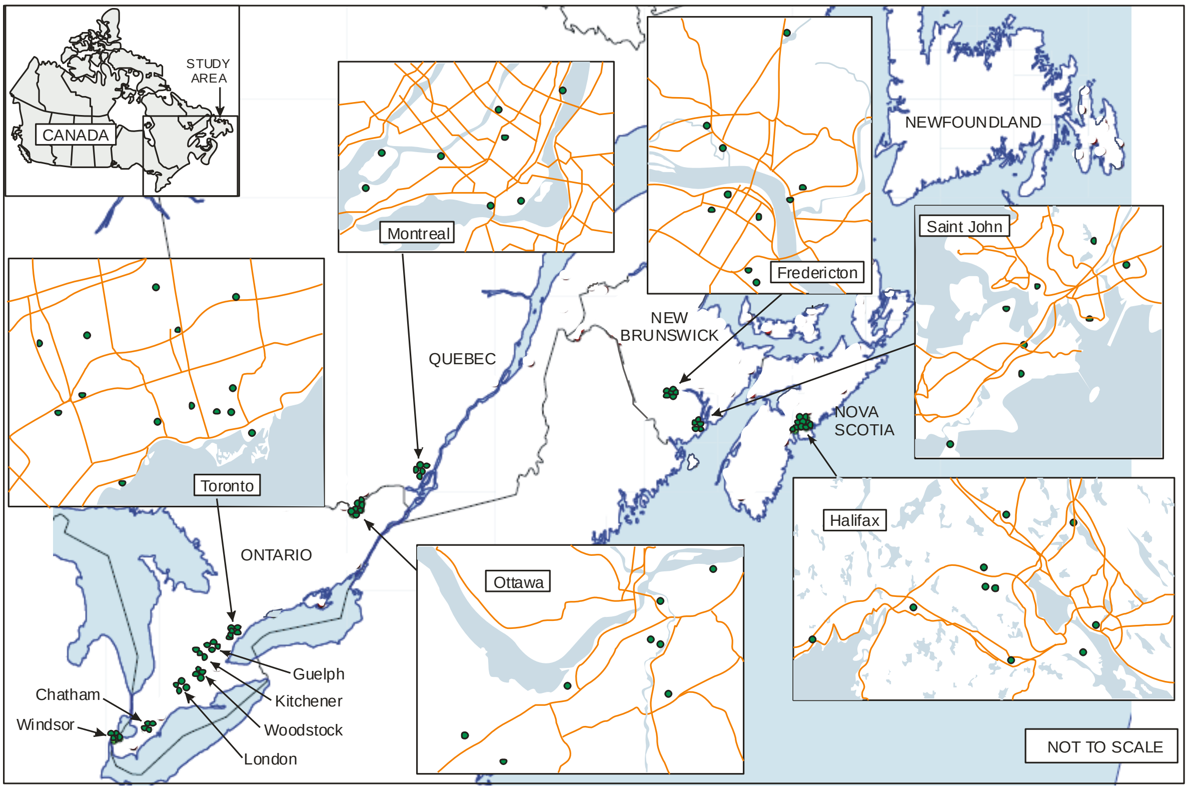

Figure 1. Sampling locations. Green dots represent sampling locations at each city.

2.2. Soil pH, Carbon Content and Total Metal Content

Soil pH was measured using a soil-to-deionized water ratio of 1:2 (*w/v*). Approximately 10 g of sieved soil sample was measured into a 50 mL beaker, and 20 mL of water was added. The suspension was allowed to settle for 1 h, following which the pH of the supernatant was measured using a standardized pH meter. Total carbon was determined using the loss-on-ignition (LOI) method in two sequential phases to estimate the organic matter (OM) and carbonate content of the soils [13]. Samples were analyzed in triplicate for this procedure. Total metal concentrations in the soils were determined by ICP-MS using the USEPA 3050B aqua regia variant [15].

2.3. In Vitro Extraction Assay (IVBA)

The IVBA methodology was based on the United States Environmental Protection Agency (USEPA) Method 1340 [16]. One gram 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. The extract was filtered through a 0.45 µm cellulose acetate syringe filter and analyzed for total metals by ICP-MS. Percent metal bioaccessibility was calculated for each sample by dividing the concentration in the IVBA extract by the total metal concentration as determined by aqua regia variant digestion and ICP-MS analysis. The QA/QC program included procedure blanks, certified reference materials (NIST 2711a). and duplicates. Concentrations obtained for the procedure blanks indicated minimal interferences from the extraction solution and equipment. The IVBA values for the reference materials were within the control limits while the relative percent difference for the duplicates were generally less than 30%, suggesting good reproducibility.

2.4. Statistical Analysis and Data Evaluation

Total metal concentrations were evaluated using the Canadian Council of Ministers of Environment (CCME) soil quality guidelines for residential/parkland use. The guidelines provide concentrations of contaminants in soil, at or below which no appreciable human health risk is expected [17]). The potential impact of anthropogenic sources on metal concentrations was evaluated using enrichment factor (EF) while the geoaccumulation index (Igeo) was used to assess the level of pollution [18]. Enrichment factor (EF) was calculated as follows:

$$\mathrm{EF} = \left(\frac{\mathrm{Ms}}{\mathrm{Fes}}\right) / \left(\frac{\mathrm{Mb}}{\mathrm{Feb}}\right) \tag{1}$$

where Ms and Fes are the concentrations of metal and Fe in the soil sample while Mb and Feb are the relevant background concentrations of the metal and Fe. Regional elemental background concentrations reported by Dodd et al. [5] were used in this study. An EF < 2 indicates deficiency to minimal enrichment; 2–5 moderate enrichment; 5–20 implies significant enrichment; 20–40 implies very high enrichment, and >40 extremely high enrichment [18].

The geoaccumulation index (Igeo) was calculated using Equation (2):

$$\mathrm{Igeo} = \log_2\left[\frac{\mathrm{Ms}}{\mathrm{I.5Mb}}\right] \tag{2}$$

The Igeo data were evaluated using the following descriptive classes: ≤ 0 = unpolluted; 0–1 = unpolluted to moderately polluted; 1–2 = moderately polluted; 2–3 = moderately to highly polluted; 3–4 = highly polluted; 4–5 = highly to extremely high polluted; and 5–6 extremely high polluted [18].

2.5. Human Health Exposure Assessment

Although exposure to contaminants in soil at the urban parks and playgrounds can occur through ingestion, dermal contact, and inhalation, the human health exposure assessment was conducted for the oral ingestion route, since this was deemed the most important risk pathway relative to the others [19,20]. The risk estimate was based on equations described by Health Canada [14].

The chemical daily intake (CDI) due to incidental ingestion of contaminated soil was calculated using Equation (3):

$$\mathrm{CDI} = \frac{\mathrm{Cs} \times \mathrm{IRs} \times \mathrm{RAForal} \times \mathrm{ET}}{\mathrm{BW} \times \mathrm{LE}} \tag{3}$$

where CDI = chemical daily intake (mg kg^{-1} day^{-1}); Cs = concentration of metal in soil (mg kg^{-1}); IRs = ingestion rate of soil (0.00002 kg day^{-1}); RAForal = relative absorption factor from the gastrointestinal tract (unitless); ET = exposure term (unitless) = days/week x weeks/year (x years for carcinogens); BW = body weight (32.9 kg for a child and 70.7 kg for an adult) and LE = life expectancy for assessment of carcinogens (75 years) [21]). The metal bioaccessibility value was used as a surrogate for the absorption factor from the gastrointestinal tract, incorporating RBA/IVBA regression equations where available [22]. The CDI was divided by the tolerable daily intake (TDI) (mg kg^{-1} d^{-1}) to obtain the hazard quotient (HQ) for non-cancer risk (Equation (4)).

$$\text{Hazard Quotient HQ} = \frac{\mathrm{CDImetal}}{\mathrm{TDI}} \tag{4}$$

The TDI values used were As: 0.0003 mg kg^{-1} d^{-1}; Cd: 0.0008 mg kg^{-1} d^{-1}; Co: 0.03 mg/kg-day; Cr: 0.001 mg kg^{-1} d^{-1}; Cu: 0.426 mg kg^{-1} d^{-1}; Ni; 0.011 mg kg^{-1} d^{-1}; Pb: 0.0005 mg kg^{-1} d^{-1}; and Zn: 0.48, 0.48, and 0.57 mg kg^{-1} d^{-1} [23,24]. The HQ for the individual metals (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) were summed to obtain the overall hazard index (HI) (Equation (5)).

$$\mathrm{HI} = \sum \mathrm{HQi} \tag{5}$$

Carcinogenic risk (CR) was determined for As, since it was the only carcinogenic substance that exceeded the CCME guideline using Equation (6):

$$CR = CDI \times SF \tag{6}$$

where SF = oral slope factor $(mg/kg\ d)^{-1}$. The oral slope factor used for As was 1.80 $(mg/kg\ d)^{-1}$ (Health Canada, 2021).

Statistical analyses were performed using Minitab® 19 Statistical Software and ProUCL version 5.1 [25]. Summary statistics, including the mean, median, standard deviation, and 95 percentiles were compiled to allow for a comparison of the data among the cities. Pearson correlation analysis was used to determine the relationship between soil pH, OM, metal concentrations and IVBA while principal component analysis (PCA) was conducted to explore the sources of elemental concentration after the data were transformed using varimax rotation.

3. Results and Discussion

3.1. Summary Statistics

Descriptive statistics of soil pH, organic matter (OM), and metal concentrations, including median, mean, standard deviation, 95 percentiles, and maximum for the urban centers, are given in Table 1. The entire dataset is shown in Table S2 in the Supplemental Material.

Table 1. Descriptive statistics of total metal concentrations (mg/kg), pH, and organic matter (OM%).

City		As	Cd	Co	Cr	Cu	Ni	Pb	Zn	pH	OM
CCME R/P		**12**	**10**	**50**	**64**	**63**	**50**	**140**	**200**		
Halifax (*n* = 10)	Mean	***36***	0.21	6.7	16	25	15	53	85	4.59	9.8
	Median	9.9	0.21	7.4	16	23	16	17	48	4.51	8.5
	Std Dev	68	0.12	2.2	3.3	13	4.9	71	65	0.68	5.1
	95% tile	***154***	0.35	8.9	21	47	21	174	187	5.50	16.8
	Maximum	***218***	0.37	9.0	21	49	22	***234***	***204***	5.59	17.6
Saint John (*n* = 10)	Mean	8.9	0.27	9.3	21	32	19	46	96	6.99	12.5
	Median	7.6	0.17	9.2	22	29	19	22	84	6.80	8.3
	Std Dev	3.7	0.21	2.5	4.2	14	6.6	53	53	0.71	10.1
	95% tile	***15***	0.65	13.0	28	54	30	148	196	8.13	29.8
	Maximum	***17***	0.78	13.3	29	63	33	175	199	8.38	38.0
Fredericton (*n* = 10)	Mean	10	0.19	10.8	31	23	32	35	79	6.54	7.1
	Median	11	0.16	9.3	29	19	29	28	80	6.37	7.6
	Std Dev	3.9	0.10	3.3	6.6	9	13	22	25	1.13	3.2
	95% tile	***16***	0.35	16.3	41	38	54	69	115	7.96	11.0
	Maximum	***17***	0.42	19.3	44	48	***67***	74	138	8.15	11.0
Montreal (*n* = 16)	Mean	5.1	0.33	8.7	24	35	22	35	88	7.68	8.9
	Median	3.7	0.34	8.7	22	36	22	28	88	7.85	8.8
	Std Dev	2.6	0.19	3.7	11	15	10	22	32	0.43	4.3
	95% tile	10	0.60	14.6	48	60	36	73	146	8.16	14.1
	Maximum	11	0.63	16.6	48	68	49	78	162	8.53	18.2
Ottawa (*n* = 8)	Mean	2.7	0.26	6.9	30	19	17	29	74	6.49	12.0
	Median	1.6	0.22	6.5	29	18	15	11	59	6.43	11.0
	Std Dev	2.3	0.14	3.3	17	8	9.2	33	38	0.43	4.5
	95% tile	6.5	0.48	11.9	56	30	32	84	129	7.08	18.9
	Maximum	6.9	0.57	13.1	69	31	37	89	134	7.11	20.4
Toronto (*n* = 15)	Mean	3.5	0.59	4.7	19	28	12	107	97	7.63	10.7
	Median	3.3	0.29	4.2	13	21	10	41	72	7.65	10.1
	Std Dev	1.5	1.06	1.8	21	23	7.1	165	77	0.50	4.2
	95% tile	6.6	1.80	7.1	40	***79***	26	***354***	198	8.25	16.8
	Maximum	6.7	4.60	9.3	***98***	***88***	33	***690***	***350***	8.85	21.7

Table 1. *Cont.*

City		As	Cd	Co	Cr	Cu	Ni	Pb	Zn	pH	OM
CCME R/P		**12**	**10**	**50**	**64**	**63**	**50**	**140**	**200**		
Windsor (n = 4)	Mean	4.7	0.54	4.4	17	24	15	39	112	6.28	13.5
	Median	4.7	0.47	4.7	16	20	16	38	80	6.30	12.1
	Std Dev	1.1	0.24	1.5	3.0	11	5.0	17	74	0.51	5.1
	95% tile	5.7	0.82	5.8	20	37	20	57	***201***	6.79	19.6
	Maximum	5.7	0.88	5.9	21	40	21	59	***222***	6.84	20.7
Guelph (n = 4)	Mean	4.8	0.44	4.1	11	14	8.4	40	122	7.01	10.7
	Median	3.4	0.42	4.1	11	14	8.2	43	123	7.09	10.8
	Std Dev	3.4	0.15	0.3	0.6	2	1.1	15	39	0.21	1.0
	95% tile	8.9	0.59	4.4	11	16	10	53	161	7.14	11.7
	Maximum	9.8	0.61	4.4	11	17	10	53	164	7.15	11.8
Kitchener (n = 4)	Mean	2.3	0.27	3.2	10	13	7.7	27	67	7.29	7.8
	Median	2.2	0.30	3.6	12	12	8.4	29	71	7.29	6.9
	Std Dev	1.1	0.06	1.1	3.6	5	2.0	14	14	0.09	3.3
	95% tile	3.3	0.31	3.9	13	17	9.1	39	77	7.38	11.7
	Maximum	3.3	0.31	3.9	13	18	9.1	40	78	7.39	12.5
Woodstock (n = 4)	Mean	3.4	0.24	4.0	12	24	8.5	27	55	6.91	10.2
	Median	3.0	0.24	3.8	12	20	8.1	26	58	6.93	9.5
	Std Dev	1.5	0.08	0.9	2.1	12	1.5	14	12	0.17	1.7
	95% tile	5.2	0.32	5.0	14	39	10	42	64	7.07	12.3
	Maximum	5.5	0.33	5.2	14	42	11	45	64	7.09	12.7
London (n = 4)	Mean	2.8	0.23	3.4	11	14	8.2	15	46	6.84	10.6
	Median	2.2	0.23	3.4	11	12	8.2	12	46	7.12	9.7
	Std Dev	1.5	0.04	0.6	2.4	8	1.7	9	10	0.63	4.8
	95% tile	4.6	0.28	4.0	13	24	10	26	56	7.21	16.0
	Maximum	5.0	0.28	4.1	13	26	10	28	56	7.22	16.8
Chatham (n = 4)	Mean	3.3	0.20	5.1	13	14	13	15	48	7.21	9.4
	Median	3.0	0.19	5.0	14	15	13	13	46	7.25	9.3
	Std Dev	1.0	0.03	1.5	3.2	4	4.4	6	19	0.09	2.3
	95% tile	4.5	0.24	6.5	16	18	17	22	68	7.27	11.8
	Maximum	4.8	0.25	6.6	16	18	17	23	71	7.27	11.9

Values in bold italics exceed the CCME soil quality guideline for residential/parkland use (CCME R/P). Std Dev = standard deviation.

Soil pH and OM were variable among the cities in Halifax showing more acidic pH (mean of 4.59) compared to the other cities. The lower pH in Halifax is consistent with previous observations of low pH in the region [15]. The maximum concentrations of select metals exceeded the CCME guideline, including: As, Pb, and Zn in Halifax; As in Saint John; As and Ni in Fredericton; Cr, Cu, Ni, Pb, and Zn in Toronto; and Zn in Windsor. Metal concentrations in samples collected from Montreal, Ottawa, Guelph, Kitchener, Woodstock, London, and Chatham were all below the CCME guidelines. Out of the 101 samples analyzed, the percentages of samples that exceeded the guidelines were 7% for As, 2% for Cr, 4% for Cu, 1% for Ni, 6% for Pb, and 3% for Zn.

The mean concentrations for the metals for the cities were below the CCME guideline except for As in Halifax. Arsenic was elevated in Halifax, Saint John, and Fredericton compared to the other cities while Pb was relatively higher in Toronto. The mean concentrations of As, Cr, Cu, and Pb were higher in the urban park and playground samples compared to regional background surface soil samples as reported by Dodd et al. [15].

3.2. Enrichment Factor and Geoaccumulation Index

Enrichment factors are summarized as individual value plots in Figure 2. One park, each from Halifax and Toronto, showed significant enrichment for As and Pb, respectively.

Moderate enrichment was shown for a few samples for As (Halifax), Pb (Halifax, Saint John, and Toronto), and Cu (Halifax, Fredericton, Saint John, and Toronto).

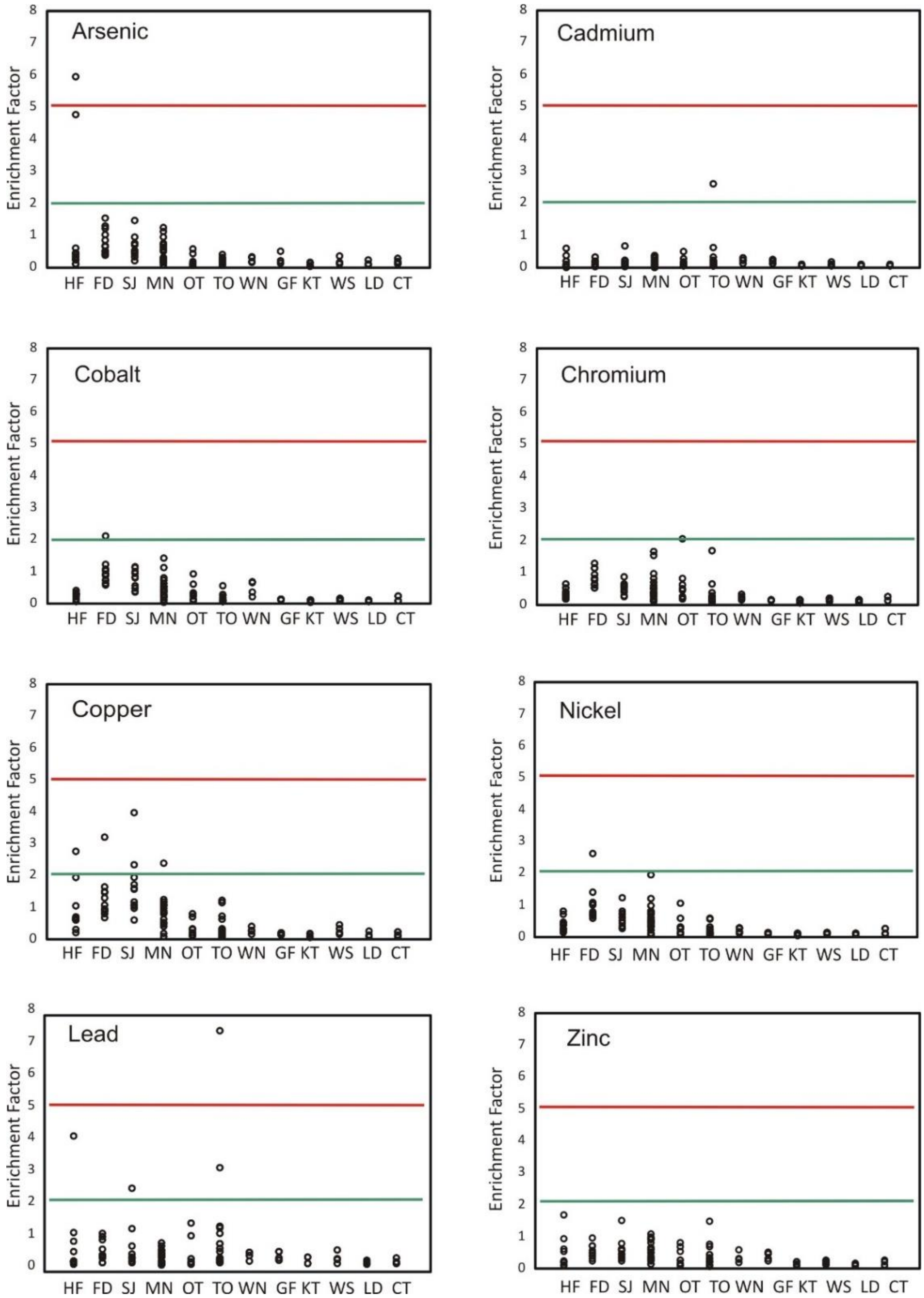

Figure 2. Metal enrichment factor for HF–Halifax, FD—Fredericton, SJ—Saint John, MN—Montreal, OT—Ottawa, TO—Toronto, WN—Windsor, GF—Guelph, KT—Kitchener, WS—Woodstock, LD—London, and CT—Chatham; Green line—minimal enrichment; Red line—moderate enrichment.

The Igeo values (Figure 3) indicated that most of the samples were unpolluted with specific metals based on the classification by Kowalska et al. [18]. However, one sample from Halifax and Toronto was moderately to highly polluted with As or Pb. This observation corroborated the enrichment factor data. Samples from a few parks from various cities were moderately polluted with Cd and Cu while no pollution was associated with the Co, Cr, Ni and Zn.

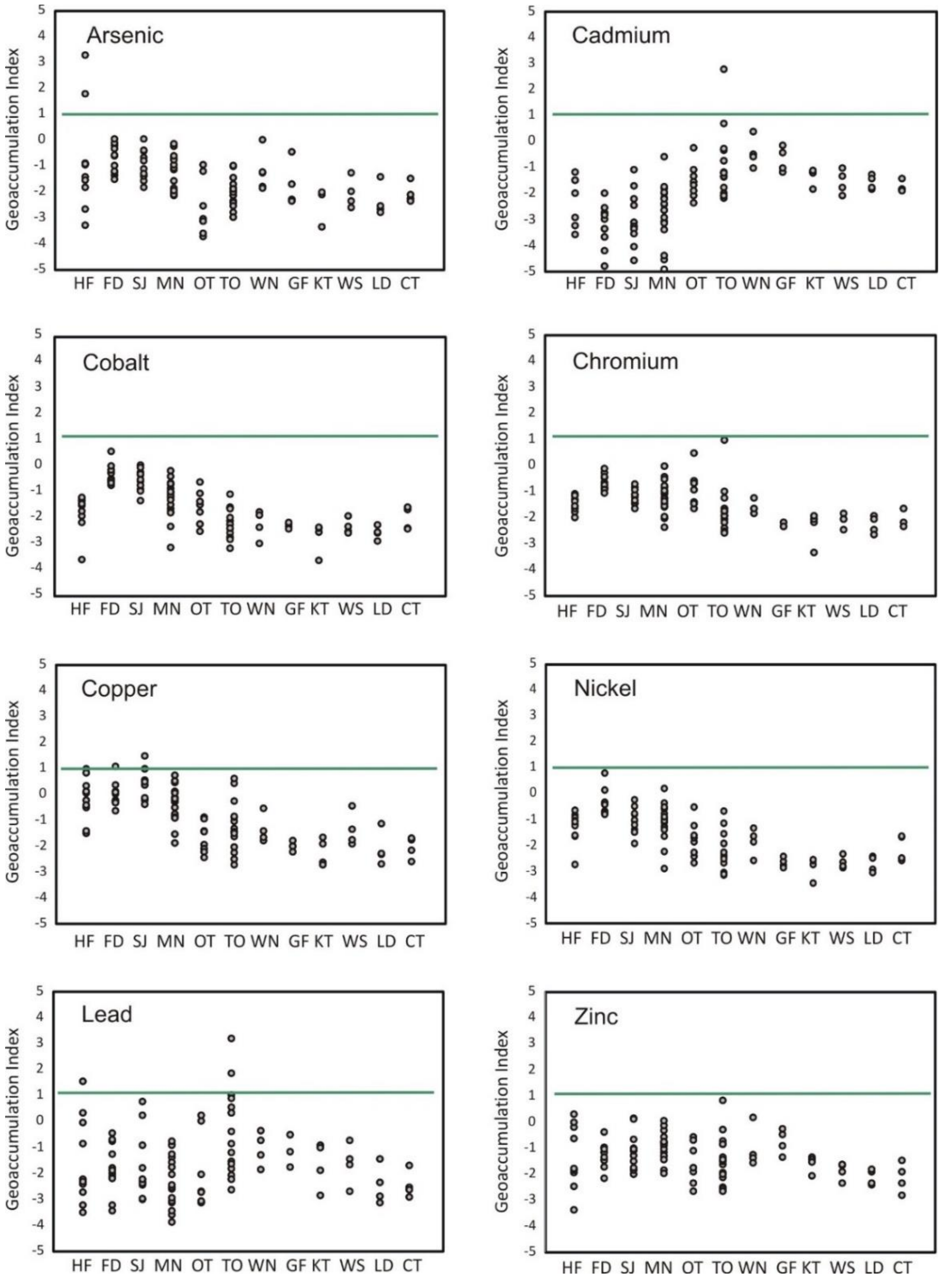

Figure 3. Geoaccumulation index for HF–Halifax, FD—Fredericton, SJ—Saint John, MN—Montreal, OT—Ottawa, TO—Toronto, WN—Windsor, GF—Guelph, KT—Kitchener, WS—Woodstock, LD—London, and CT—Chatham; Green line—moderate pollution.

3.3. Metal Distribution

3.3.1. Arsenic

The mean As concentrations in the cities were below the guideline of 12 mg/kg except for Halifax (mean 36 mg/kg). Elevated As concentrations that exceeded the guidelines were found in three samples, each collected from Halifax and Fredericton and two samples from Saint Johns. The highest concentration of As (218 mg/kg) was detected in a sample obtained from a park in the Waverly Gold District, a region known to have elevated As levels from historical gold mining activities [26]. This sample had very high EF (5.9) and Igeo (3.3), indicating metal enrichment and moderate pollution. The second Halifax sample that exceeded the guideline was from a park in the city center; it had an EF (4.7) and Igeo (1.8) that suggested moderate enrichment and pollution. This sample also had elevated concentrations of Pb and Zn, and the pollution may be attributed to leaching from galvanic fences close to the sampling area [4,6]. All the samples from Fredericton and Saint Johns that exceeded the As guideline also had EF and Igeo values that suggested minimal enrichment and pollution. The elevated levels may be attributed to natural sources in line with previously reported high As in background samples collected from the region [15]. Arsenic concentrations in the samples from the remaining cities were all below the guideline, with the EF and Igeo values (Figures 2 and 3) indicating minimal enrichment and pollution.

3.3.2. Cadmium

Cadmium concentrations were all below the CCME guideline with comparable levels among the cities, except for one location in Toronto. The elevated concentration (4.6 mg/kg) was detected in a sample collected from a park near the airport and a busy transportation corridor. This sample showed moderate Cd enrichment and moderate pollution based on EF (2.6) and Igeo (2.8), respectively. The sample also contained elevated levels of Cr, Cu, Pb, and Zn, which could be associated with aircraft and automobile sources, as suggested by Ajmone-Marsan and Biasioli [4] and Wong et al. [6].

3.3.3. Cobalt

Cobalt concentrations in all the samples were below the CCME guideline with even distribution amongst the cities. Although the mean concentrations were higher than the corresponding regional background [15], the EF (Figure 2) and Igeo (Figure 3) indicated minimal Co enrichment and pollution.

3.3.4. Chromium

Anthropogenic sources of Cr in the urban environment include the burning of fossil fuels, use of wood preservatives, metallurgy, and incineration, leading to their ubiquitous presence in all the samples which were collected in this study. Chromium concentrations ranged from 5.0 to 98 mg/kg, with two samples exceeding the CCME guideline of 64 mg/kg. These included a park in Toronto near the airport and a transportation corridor which also contained elevated levels of Cd, Cu, Pb, and Zn, as discussed above. Miscellaneous refuse was noted at the second location, which could account for the elevated concentrations of Cr and other metals, such as Zn. The levels of enrichment and pollution at both locations were considered minimal based on the EF and Igeo (Figures 2 and 3).

3.3.5. Copper

Copper concentrations in two parks in Toronto and one park each in Saint John and Montreal exceeded the CCME guidelines. The first park in Toronto was near the airport and a busy transportation corridor (discussed above), whereas the second park was situated on former industrial port lands. The park in Montreal is used for road salt deposits and snow dumps in the winter, while the park in Saint John is situated in an industrial area, including a pulp and paper mill, a rock quarry, and a railway yard. The EF and Igeo values indicated moderate enrichment and pollution at these locations, suggesting the elevated levels may be due to the anthropogenic activities associated with the sources indicated above.

3.3.6. Nickel

Except for one sample collected from Fredericton, Ni concentrations were all below the CCME guideline. The sample which exceeded the guideline was retrieved from an amphitheater in the park, and there was no direct evidence to explain the elevated concentration. Based on the EF, this sample showed moderated enrichment (Figure 2), while the Igeo samples (Figure 3) indicated minimal Ni pollution.

3.3.7. Lead

Lead concentrations were relatively higher in Toronto parks (mean 107 mg/kg) compared to the other cities; four out of the fifteen samples collected from Toronto contained lead in excess of the CCME guideline. The Toronto parks with the elevated Pb levels were situated in an industrial area (including metal recycling) and former industrial port lands. One sample, each taken from parks in Saint John and Halifax, which previously had buildings that were demolished, also contained elevated Pb levels, suggesting the contamination may have originated from the former facilities or other associated anthropogenic activities. The EF and Igeo values (Figures 2 and 3) showed moderate pollution and enrichment for the samples that exceeded the CCME guidelines.

3.3.8. Zinc

The concentrations of Zn in most of the soil samples were below the CCME guideline, except for one sample each from Halifax (park situated on a demolished building site), Windsor (a former city dump turned into a park), and Toronto (park located on former port lands), which had zinc at levels that exceeded the guidelines. The EF and Igeo values indicated minimal pollution and enrichment.

3.4. Principal Component Analysis

Principal component analysis was used to explore the inter-relationship between the metals. The result presented in Table 2 indicated Co, Cr, Fe, and Ni were strongly associated with one another within the first component; these metals showed minimal pollution and enrichment and may occur together because of their common origin from natural weathering and atmospheric deposition [3]. Elements such as Cd, Cu, Pb, and Zn, which may be impacted by anthropogenic sources, as discussed in the sections above, were grouped together in the second component, while As, which may be attributed to arsenic-bearing rocks, was unique. Elevated concentrations of As were found in the samples collected in areas where geological investigations have identified gold-bearing metasedimentary rocks (i.e., Meguma Supergroup) with As a major contaminant of concern [26].

Table 2. Component loadings for the principal component analysis of select metals in urban park soils, along with eigenvalues and the percentage of variance accounted for.

	PC1	PC2	Uniqueness
As			0.930
Cd		0.667	0.544
Co	0.944		0.108
Cr	0.757		0.320
Cu		0.746	0.296
Fe	0.875		0.221
Ni	0.941		0.091
Pb		0.783	0.377
Zn		0.783	0.373
Eigenvalue	3.844	1.895	
Proportion variance	0.427	0.211	
Cumulative	0.427	0.638	

Note. Applied rotation method is varimax.

3.5. In Vitro Bioaccessibility

In vitro bioaccessibility values varied among the metals, as depicted in the boxplots in Figure 4 (see Supplementary Material Table S3 for the entire data). Cadmium had the highest bioaccessibility (mean of 74.1%), followed by Pb (60.9% $\pm$ 19.0%), Cu (46.3 $\pm$ 18.1%), Zn (30.0 $\pm$ 13.2%), As (24.4 $\pm$ 13.2%), Cr (24.3 $\pm$ 10.5%), Ni (13.5 $\pm$ 6.8%), and Co (5.1 ± 3.9%). The relatively high bioaccessibility of Cd is consistent with previous observations [27,28] and may be attributed to its occurrence as the highly soluble oxides in the surface soils analyzed. The mean in vitro bioaccessibility values were higher in the urban samples compared to Canadian background samples for As (7 ± 6%), Cu (20 ± 16%), and Pb (63 ± 19%) [15].

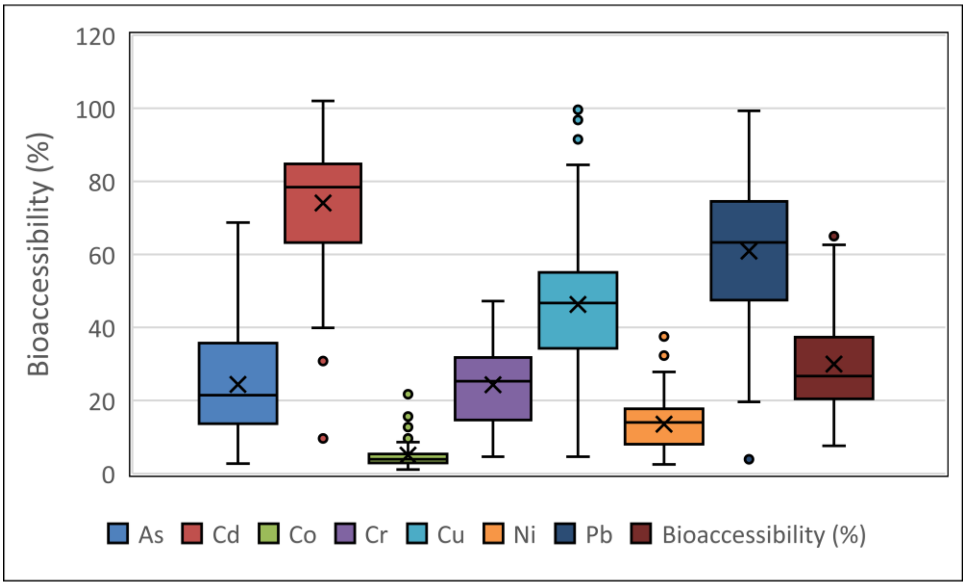

Figure 4. Boxplots of metal bioaccessibility in urban park soils.

Variable metal bioaccessibility among the samples may be due to metal speciation and physicochemical properties. Soil physicochemical properties that affect bioaccessibility include total metal concentration, iron content, pH, and soil organic matter [2,20,29]. The relationships between metal bioaccessibility and pH, LOI, iron, and total metal content were, therefore, explored through ordinary least square regression analyses. The outputs obtained are summarized in Table 3. Soil pH increased As and Zn bioaccessibility, while pH had no significant effect on the bioaccessibility of the other metals. Soil organic carbon had negligible effects on bioaccessibility, whereas increasing Fe concentration decreased bioaccessibility for all the metals except Cd. These observations are consistent with previous observations [2,15,29].

3.6. Human Health Risk Assessment

The non-carcinogenic hazard indices incorporating bioaccessibility for children and adult receptors for all the samples are summarized in Figures 5 and 6, respectively. For adults, unacceptable levels of non-carcinogenic effects (HI > 1) were noted for only 1 out of the 101 sampling locations. Lead was the leading contributor to the elevated human health risk via oral ingestion for this sample, which was collected from a park situated near an industrial area. The number of samples with non-carcinogenic risk for children was much higher, with six sites having HI > 1. As with the risk to adult receptors, Pb was the leading contributor to the non-carcinogenic risk.

The cancer risk for As for adults was greater than 1×10^{-5} at two sites. This represented an unacceptable risk based on the Canadian guidelines, which state that the acceptable risk is one excess cancer death per 100,000 people exposed [14]). The two sites were in Halifax, including a park in the Waverly Gold District, a region known to have elevated As levels from historical gold mining activities [26]. This sample had very high EF (5.9) and Igeo (3.3), indicating metal enrichment and moderate pollution. The second sample was from a park in the city center and had an EF (4.7) and Igeo (1.8), which suggested moderate enrichment and pollution.

Table 3. Correlation coefficients for regression analysis between metal bioaccessibility versus pH, organic matter (OM), iron (FeT), and metal concentration (metal).

		pH	OM	FeT	Metal
As	R	**0.4462**	0.0013	**−0.5986**	−0.1999
	p-value	<0.0001	0.7292	<0.0001	0.052
Cd	R	0.0389	0.1087	**0.3831**	0.0982
	p-value	0.0837	0.3670	0.001	0.4150
Co	R	0.0389	−0.0315	**−0.4706**	**−0.2789**
	p-value	0.7025	0.7659	<0.0001	0.0071
Cr	R	0.1932	0.0007	0.0319	0.1641
	p-value	0.1091	0.9995	0.1390	0.1747
Cu	R	0.0415	0.0802	**−0.2449**	0.0380
	p-value	0.6836	0.4299	0.0127	0.7091
Ni	R	0.0500	0.2629	**−0.3522**	**−0.2591**
	p-value	0.6230	0.0118	0.0006	0.0131
Pb	R	0.1934	0.0427	**−0.5738**	0.1898
	p-value	0.0564	0.6766	0.0000	0.0618
Zn	R	**0.3666**	0.1062	**−0.3466**	**0.3839**
	p-value	0.0003	0.3085	0.0006	0.0001

Note: Values in bold refer to relationships dimmed significant with $p < 0.05$.

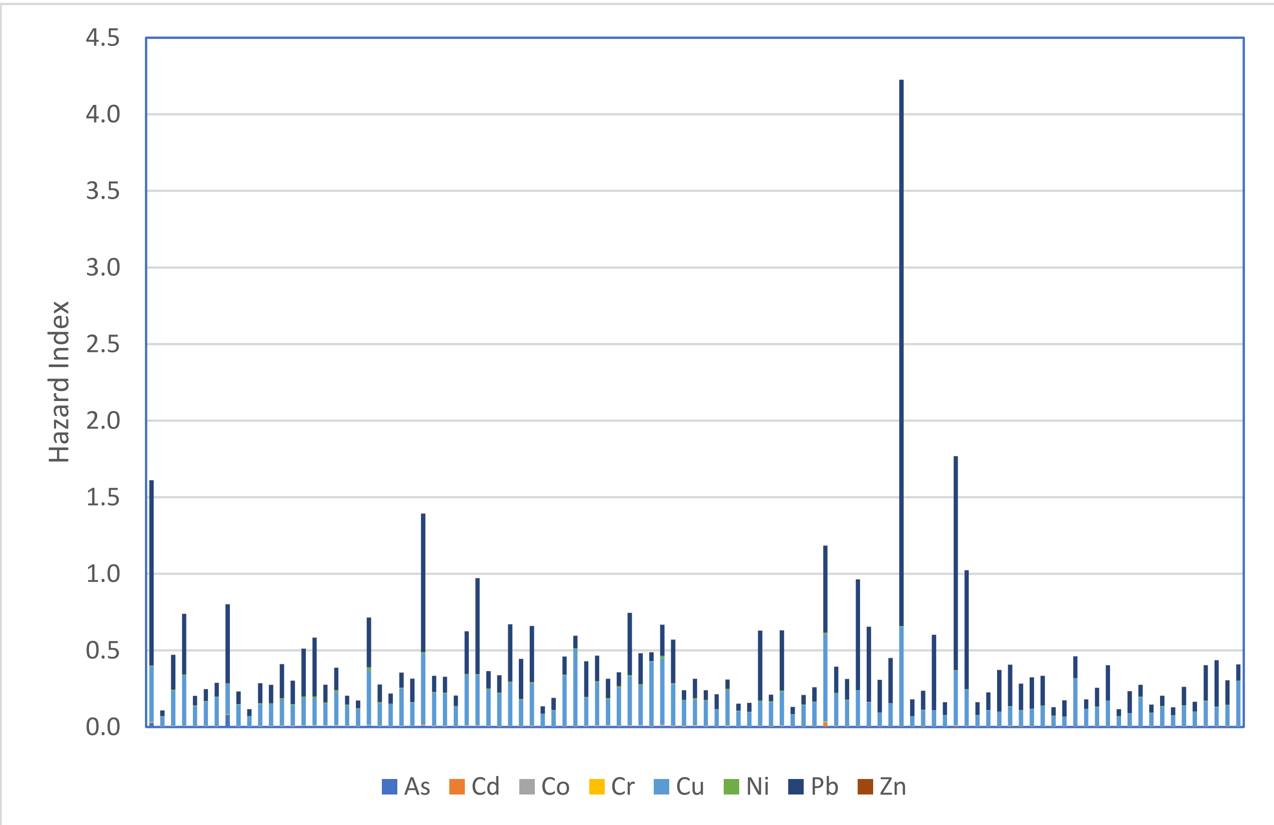

Figure 5. Hazard indices for children.

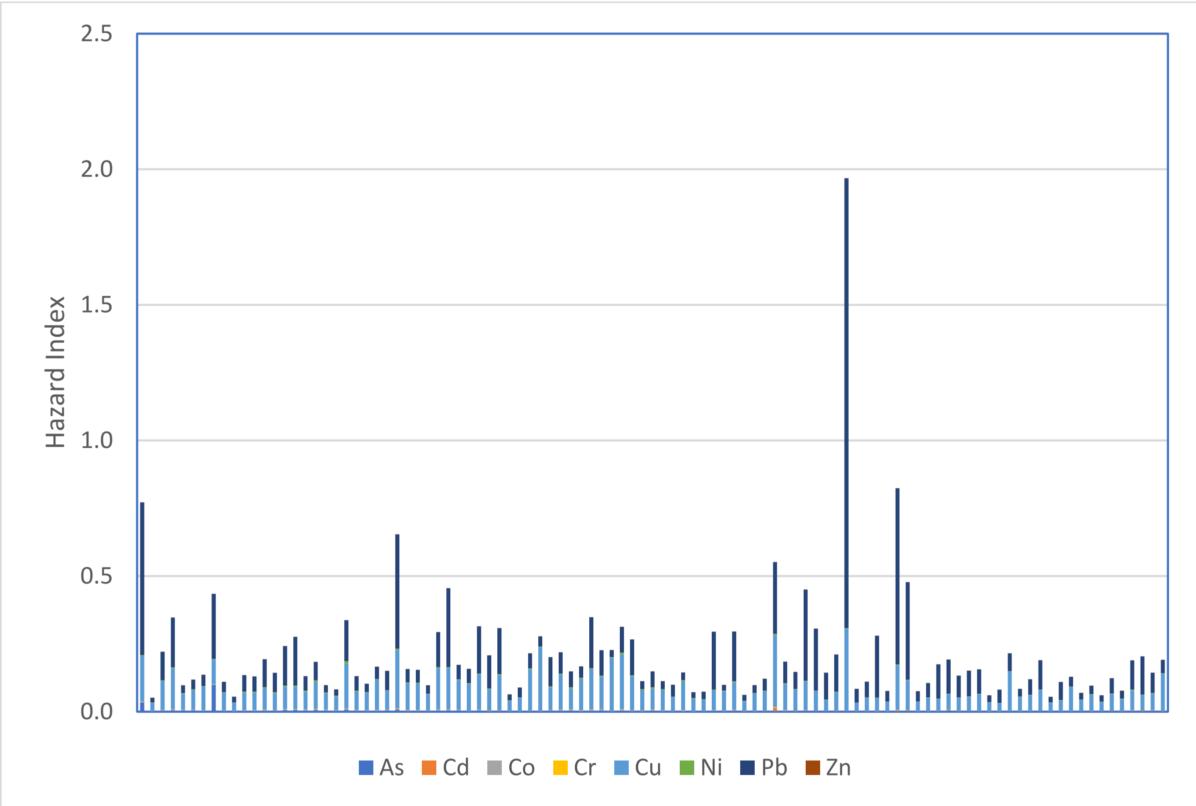

Figure 6. Hazard indices for adults.

4. Conclusions

Metal distribution in surface soils in the parks and playgrounds at the 12 Canadian cities studied reflected the regional natural-occurring differences in metal concentrations and anthropogenic sources, such as proximity to industrial areas (e.g., metal fabrication and recycling facilities), heavy traffic corridors (airport, highways and railway yard) and historical land use (e.g., industrial port land and demolished buildings). Cobalt, Cr, Fe, and Ni showed minimal pollution and enrichment and co-occurred because of their common origin from natural weathering and atmospheric deposition, whereas Cd, Cu, Pb, and Zn concentrations were impacted by anthropogenic sources. Arsenic was unique in that the elevated levels may have been attributed to arsenical-bearing rocks. Metals bioaccessibility values were variable and in the order Cr < Ni < Co < As < Zn < Cu < Pb < Cd. The human health risk associated with incidental soil ingestion for children, incorporating bioaccessibility, indicated unacceptable levels of non-carcinogenic effects for 6 out of the 101 samples analyzed. Lead was the leading contributor to the non-carcinogenic risk. Carcinogenic risk for As was limited to two samples. The importance of personal hygiene in limiting hand-to-mouth contact for children during playtime at these parks and playgrounds is warranted. Additional sampling to delineate the extent of contamination at parks and playgrounds with potential health risks is recommended along with notification of local health authorities.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/soilsystems8040123/s1. The dataset used in this paper are included as follows: Table S1 provides the coordinates for all the sampling locations; Table S2 shows total metal concentrations; and Table S3 gives the in vitro bioaccessibility data.

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