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Oral and inhalation bioaccessibility of metal(loid)s in Chromated Copper Arsenate (CCA)-contaminated soils: assessment of particle size influence

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Abstract

Soil samples adjacent to ten CCA-treated utility poles were collected, sieved into four fractions (<2 mm, 250-90 µm, 90-20 µm and <20 µm), and characterized for their total metal(loid) (As, Cu, Cr, Pb, and Zn) content and physico-chemical properties. Oral bioaccessibility tests were performed using In Vitro Gastrointestinal (IVG) method for fractions 250-90 µm and 90-20 µm. Inhalation bioaccessibility tests were performed in particle size fraction <20 µm using two simulated lung fluids: artificial lysosomal fluid (ALF) and Gamble's solution (GS). The total concentration of metal(loid)s increased with decreasing particle size. Oral As bioaccessibility (%) increased with increasing particle size in 9 out of 10 soils ($p < 0.05$), but oral As bioaccessibility expressed in mg/kg was not significantly different for both particle size. Oral Cu bioaccessibility (% and mg/kg) was not influenced by particle size, but oral Cr bioaccessibility (% and mg/kg) increased when reducing particle size ($p < 0.05$), although Cr bioaccessibility was very low (< 8 %). Oral bioaccessibility (%) of metal(loid)s decreased in the order: Cu > As > Pb > Zn > Cr. Bioaccessibility (%) in simulated lung fluids decreased in the order: Cu > Zn > As > Pb ≈ Cr using ALF, and As > Cu using GS solution. For all elements, inhalation bioaccessibility (% and mg/kg) using ALF was higher than oral bioaccessibility, except for Pb bioaccessibility (mg/kg) in two samples. However, solubility of metal(loid)s in GS presented the lowest values. Copper showed the highest oral and inhalation bioaccessibility (%) and Cr showed the lowest. Moreover, organic matter content and cation exchange capacity in particle size 90-20 µm were negatively correlated with Cu and Pb oral bioaccessibility (%).

Key words: gastro-intestinal bioaccessibility, inhalation bioaccessibility, particle size, metals and metalloids, chromated copper arsenate, contaminated soil.

1. Introduction

Contamination of soils by metal(loid)s is a persistent problem. Lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), and copper (Cu) are listed among the most commonly found metal(loid)s in contaminated soils (Evanko and Dzombak, 1997; Wuana and Okieimen, 2011). Chromated copper arsenate (CCA) is a wood preservative widely used worldwide before the 2000s and sensible to weathering, leaching variable amounts of As, Cu, and Cr in the adjacent soils (Chirenje et al., 2003; Zagury et al., 2003; Zagury et al., 2008; Mohajerani et al., 2018). These metal(loid)s are important in risk assessment studies because As and Cr(VI) are carcinogens, while Cu is a contaminant that, in excess, can be toxic to humans (ATSDR, 2017). Lead and Zn may also be found in soils near CCA-treated utility poles in service located along roads in concentrations that exceed regulatory levels (Gosselin and Zagury, 2020). It is well known that traffic emissions are an important anthropogenic source of Pb, Zn, and Cu in nearby roadside soils (Guney et al., 2010; Luo et al., 2015).

Human exposure to hazardous metal(loid)s in soil can occur via ingestion, inhalation or dermal contact (Madrid et al., 2008) the main pathway being ingestion (WHO, 2010). Children are the most vulnerable, since they might ingest soil accidentally through mouthing dirty hands and objects, eating dropped food, or consuming soil directly (Kissel et al., 1996; Yamamoto et al., 2006). After being ingested or inhaled, not the total amount, but only a portion of the soil-bound contaminant will become bioaccessible i.e., solubilized in the gastrointestinal or lung fluids, and only a portion of the bioaccessible fraction will then reach the systemic circulation and be considered bioavailable (Ruby et al., 1996; Juhasz et al., 2014; Wiseman, 2015; Guney and Zagury, 2016). Therefore, it is important to consider the bioavailable metal concentration instead of using the total metal content in order to avoid an overestimation in risk assessment (Ruby et al., 1996; Rodriguez et al., 1999). Bioavailability can be determined using animal testing (in vivo), but as this type of assay is time consuming, expensive and raises ethical considerations, scientists have developed in vitro bioaccessibility tests that can be used as a surrogate to bioavailability tests, since they present a good correlation with bioavailability tests for some metal(loid)s (Juhasz et al., 2014).

Oral bioaccessibility tests mimic the human digestion processes and measure the amount of contaminant bioaccessible in gastric and gastrointestinal fluids (Ruby et al., 1999; Pouschat and Zagury, 2006). The soil particle size commonly used in incidental ingestion studies is < 250 µm, though some researchers point out that particles adhering to skin would be smaller than this. Duggan et al. (1985) reported that most particles adhering to hands are < 10 µm. Dry soil particles preferentially adhering to hands are < 65 µm according to Kissel et al. (1996), and < 50 µm according to Sheppard and Evenden (1994). A further study indicates that about 90% of soil particles from playgrounds adhering to children's hands was < 100 µm (Ikegami et al., 2014), and others recommend the use of particles < 45 µm in human risk assessment studies (Siciliano et al., 2009). The selection of particle size used in bioaccessibility tests will impact bioaccessibility (expressed as a percentage) and risk calculations (Ljung et al., 2006; Juhasz et al., 2011; Ikegami et al., 2014) because concentrations of metal(loid)s generally increase with decreasing particle size (Duong and Lee, 2011; Dehghani et al., 2018). Moreover, some studies using different size ranges found that oral bioaccessibility is not only size dependent, but is also influenced by numerous soil properties that affect the retention of contaminants (Pouschat and Zagury, 2008; Girouard and Zagury, 2009; Meunier et al., 2011a)

Anthropogenic activity or wind erosion near contaminated soils can cause the suspension of particulate matter (PM) which can be roughly grouped as total suspended particles (TSP) with an aerodynamic diameter (d) of 100 µm or less (James et al., 2012; Neff et al., 2013; Guney et al., 2016). Finer particles in TSP can be subdivided into fractions according to their aerodynamic d: PM_{10} (<10 µm), coarse PM (2.5 µm – 10 µm), fine PM ($PM_{2.5}$, <2.5 µm), and ultra-fine PM ($PM_{0.1}$ <0.1 µm) (de Kok et al., 2006). Because of potential health impacts following PM exposure (Kim et al., 2014), the health hazards caused by inhalation of suspended CCA-contaminated PM should be assessed (Gosselin and Zagury, 2020). Particles smaller than 10 µm can reach the trachea-bronchial region (Kastury et al., 2018). Ideally, the artificial lung fluid used in bioaccessibility tests for PM_{10} should mimic the deep lung interstitial fluid, like Gamble's solution (GS) (Kastury et al., 2017; Gosselin and Zagury, 2020). Particles smaller than 5 µm are presumed to dissolve inside phagolysosomes in conditions more acidic than in GS, making the artificial lysosomal fluid (ALF) a fitting fluid for bioaccessibility test on this particle size (Wiseman, 2015; Gosselin and Zagury, 2020).

The pH, organic carbon content and cation exchange capacity (CEC) of a soil are important properties influencing bioaccessibility (Girouard and Zagury, 2009). For example, an increase in pH increases the number of negative sites for cation adsorption, decreasing the mobility of metals and vice-versa (Harter, 1983). Organic carbon content (TOC) and CEC are parameters favorable for metal adsorption in soil and tend to decrease with increasing particle size (Gunawardana et al., 2014).

Previous work with CCA-contaminated soils has shown that As(V) is the dominant As species in surface soils near CCA-treated wood poles in service (Zagury et al., 2008). Arsenate is also the dominant As species dissolved in oral bioaccessibility tests (Nico et al., 2006; Girouard and Zagury, 2009). Even if Cr is initially in the form of Cr(VI) in CCA, chemical reactions take place during the "fixation" process of the product to the wood, and Cr(VI) is reduced to Cr(III) (Cooper and Ung, 1992). Furthermore, the dominant oxidation states of Cr in CCA treated wood is Cr(III) (Bull et al., 2000; Nico et al., 2004). As(V) and Cr(III) are the less toxic and less mobile forms of these metal(loid)s, nonetheless, oxidation or reduction can take place in-situ once the elements are leached into the soil depending on environmental conditions (such as pH and E_H) and soil composition (Balasoiu et al., 2001; Stewart et al., 2003; Dobran and Zagury 2006).

Regarding the impact of particle size on oral bioaccessibility of metal(loid)s in CCA-contaminated soils, Pouschat and Zagury (2006) found higher As bioaccessibility (%) in coarse-grained soils. However, Girouard and Zagury (2009) couldn't find a trend when comparing As bioaccessibility (%) in different particle sizes, but suggested that As bioaccessibility (mg/kg) increases with decreasing particle size when comparing a very limited set of 3 soil samples. Applying a different oral bioaccessibility assay on mine tailing samples, Meunier et al. (2011a) reported no systematic variation in As (%) bioaccessibility in different particle sizes. Yet, they observed the highest As (mg/kg) bioaccessibility using smaller particle size (<45µm). Very recently, Li et al. (2020) measured As (%) bioaccessibility in four fractions of urban soils and the impact of particle size was not clear. These inconclusive results imply that As bioaccessibility is not only affected by the particle size, but also influenced by the chemical form of arsenic. This being said, results from previous studies suggest a clearer trend for Pb bioaccessibility. For example, Pb presented higher bioaccessibility (%) in larger particles in test realized by Ljung et al. (2006), Madrid et al. (2008) and Ma et al. (2019), analyzing urban soils from Sweden, Spain and Italy, and China respectively.

Due to the high variability of metal(loid)s bioaccessibility when comparing different particle size, there is a need to further evaluate the impact of particle size and the influence of soil properties on the oral bioaccessibility of metal(loid)s in soils. The authors decided to test the 10 field-collected CCA-contaminated soil samples recently used in inhalation bioaccessibility tests (Gosselin and Zagury, 2020) to perform oral bioaccessibility tests. Thus, an evaluation of bioaccessibility of metal(loid)s in CCA-contaminated soils following different exposure pathways can be performed.

Hence, the aim of this study is (1) to investigate the metal(loid) (As, Cu, Cr, Pb, Zn) content in different particle size fractions (2 mm, 250-90 µm, 90-20 µm and <20 µm), (2) to assess physico-chemical characteristics of the soil fractions, (3) to assess the oral bioaccessibility of metal(loid)s (particle size 250-

90 µm and 90-20 µm) and compare it with inhalation bioaccessibility (particle size < 20 µm), and (4) to investigate the influence of soil properties (pH, CEC, TOC) on oral and inhalation bioaccessibility of metal(loid)s.

2. Material and Methods

2.1 Sampling and soil samples preparation

Soil samples were collected near 10 CCA-treated utility poles (S1 to S10) in the Montreal area (QC, Canada), at a maximum distance of 20 cm from the pole and within the first 10 cm of soil surface. Coarse material (> 2 cm) and topsoil vegetation were removed prior to sampling. Soil samples were collected immediately near the CCA-treated wood poles because previous work has shown that metal(loid) concentrations decrease with increasing distance from the poles, approaching background levels within 0.1 m from the pole for Cr, and 0.5 m for Cu and As (Zagury et al., 2003; Pouschat and Zagury 2006; Pouschat and Zagury 2008).

All containers and tools used were washed with phosphate-free detergent, soaked overnight in 10% (v/v) HNO_3, and rinsed three times with deionized water. The soil samples were manually collected using a plastic shovel and placed in zip-lock plastic containers. All samples were air-dried at room temperature for 48h, gently crushed using a mortar, and were sieved (< 2mm) for soil characterization. The soils were then sieved into three fractions: 250-90 µm, 90-20 and < 20 µm using a sieve shaker (Retsch AS-200). A fraction below 10 µm was initially desired for inhalation bioaccessibility tests but inherent limitations of dry sieving prevented it. Furthermore, dry sieving was favored over wet sieving to prevent metal solubilization in water. Other authors reported a similar issue and used PM_{20} (< 20 µm) for inhalation bioaccessibility tests (Kim et al., 2014; Guney et al., 2017; Martin et al., 2018).

This being said, a particle size distribution (PSD) analysis showed that 7 out of 10 studied < 20 µm samples presented a PM_{10} content higher than 50% (Gosselin and Zagury, 2020). Based on this PSD analysis, GS and ALF should be physiologically-relevant extraction fluids (at least in terms of particle size) to assess inhalation bioaccessibility of metals in < 20 µm fraction in the present study.

2.2 Total metal(loid) content

To measure the soil total metal(loid) content, digestion of soils was performed using HNO_3, HF, $HClO_4$, according to standard method 3030-D (Clesceri et al., 1998). Digested samples were filtered (0.45 µm) before analysis. Total As concentrations in the < 2 mm, 250-90 µm 90-20 µm and < 20 µm fraction were determined using ICP-OES (Varian Vista), while Cu, Cr, Pb, and Zn concentrations were measured by atomic absorption spectrophotometry (AAS) (Perkin Elmer A200). Detection limits (DL) for As, Cu, Cr, Pb and Zn were 0.004, 0.3, 0.3, 1, and 0.1 mg/kg, respectively.

2.3 Soil fractions characterization

Soil samples were characterized for pH, cation exchange capacity (CEC), total carbon (TC), and total organic carbon (TOC). Soil pH was measured in a proportion 1:2 (soil : deionized water) using a pH meter (Eutech pH 200 series, probe: Accumet Ag/AgCl) following ASTM D4972-13 (ASTM, 2013). The CEC was determined using the sodium acetate method (pH 8.2) according to the methodology described by Chapman (1965). TC and TOC were assessed using an induction furnace (LECO) (Carter, 1993).

2.4 Bioaccessibility tests

Oral bioaccessibility tests were performed using the In Vitro Gastrointestinal (IVG) method. This method was developed by Rodriguez et al. (1999) and has been validated using in-vivo tests for As and Pb (Schroder et al., 2004; Juhasz et al., 2014; Li et al., 2015). Moreover, the IVG method was chosen among many other methods (Koch et al., 2013) to allow comparison of results with previous oral bioaccessibility studies of metal(loid)s in CCA-contaminated soils (Pouschat and Zagury, 2006; Pouschat and Zagury, 2008; Girouard and Zagury, 2009).

Bioaccessibility of metal(loid)s in gastric (IVG-G) and in gastrointestinal (IVG-GI) phases was measured. The method consists of adding 1 g of soil into 150 ml of gastric solution containing 0.15M NaCl (Anachemia, Lachine, Qc, Canada, ACS Grade), and 1% w/v pepsin (Fisher, laboratory grade, P53-500) in a 250 ml beaker placed in a water bath at 37°C. Gastric solution pH was adjusted and maintained at 1.80 ± 0.05 with environmental-grade HCl during the 1-hour gastric phase. Mixing was performed using individual paddle stirrers at 100 rpm. After 1 h, 20 ml of gastric solution was collected for metal(loid) analysis. The solution was then modified to simulate intestinal solution by adding a saturated $NaHCO_3$ solution to adjust the pH to 5.50 ± 0.05, followed by the addition of porcine bile extract (0.455 g; Sigma-Aldrich, B-8631) and porcine pancreatin (0.0455 g; Sigma-Aldrich, P-1500). After 1 h, 20 ml of intestinal solution was collected. The 20-ml samples were collected using a Luerlock syringe, filtered (0.45 µm), divided in two centrifuge tubes, and stored at 4°C until analysis. One sample was analyzed for total As by ICP-OES, and the other for Cu, Cr, Pb, and Zn content via AAS. In the present study no argon was bubbled during the gastro-intestinal extraction, nevertheless the results of metal(loid)s bioaccessibility in the standard reference material (SRM 2710) were still consistent with previous studies.

Inhalation bioaccessibility results on the fraction < 20µm were obtained from Gosselin and Zagury (2020), who measured inhalation bioaccessibility using two simulated lung fluids (SLFs): artificial lysosomal fluid (ALF, pH= 4.5) and Gamble's solution (GS, pH= 7.4). Briefly, the method consisted in adding 0.4g of PM_{20} sample into 40 ml of SLF in centrifuge tubes, placed on an orbital shaker at 100 rpm in an incubator at 37°C for 24h, and then centrifuged at 10000 x g for 10 minutes. Supernatants were collected, filtered, and stored at 4°C until analysis.

2.5 Quality assurance and quality control

All experiments were conducted in duplicates except for TC and TOC contents in the soil fractions 250-90 and 90-20 µm. All results are presented as average ± standard deviation. For each experiment lot, a blank sample was included for quality control. Blank concentrations were for the most part below detection limits, and half of the value of detection limit was used as blank concentration and subtracted from the metal concentration obtained. It must be noted that Zn contamination (average 0.24 mg/L) was found in some blanks during oral bioaccessibility tests. In this case, blank concentrations were subtracted from the Zn concentrations measured in samples. An internal laboratory standard was used in each batch of AAS analysis and showed a recovery ranging between 98 and 104 % for all metals. For As analysis by ICP-OES, the laboratory standard presented a recovery between 80 and 112%. During all analyses in soil samples, a certified reference material (SRM NIST 2710, National Institute of Standards and Technology) with a particle size < 74 µm, was included in order to evaluate the analytical accuracy. The recovery percentages for total As, Cu, Cr, Pb, and Zn ranged between 88 and 115 % when comparing certified values with the values obtained digesting the standard soil SRM 2710.

The SRM 2710 was also used to determine precision and accuracy of oral bioaccessibility assessment, since it has been used in previous studies using the IVG method. In the gastric phase, the amount of bioaccessible As, Cu, Cr, Pb and Zn measured in SRM 2710 were 32 ± 3.4, 63.5 ± 6.4, 2.8 ± 4.9, 56.4 ± 5.3, and 22.3 ± 1.7%, respectively. For the gastrointestinal phase, the percentage of bioaccessible As, Cu, Cr, Pb and Zn measured were 27.0 ± 3.0, 40.4 ± 0.0, <0.1, 2.6 ± 0.9, 5.0 ± 4.8, respectively. The similarity of oral bioaccessibility values in SRM 2710 found in the present study and in previously published studies using the IVG method (Pouschat and Zagury, 2006; Pouschat and Zagury, 2008; Girouard and Zagury, 2009; Ono et al., 2012; Guney and Zagury, 2013; Koch et al., 2013) indicates a satisfactory reproducibility of the IVG method.

2.6 Statistical analysis

The Wilcoxon rank-test was performed on data to assess the statistical significance of differences between paired groups with level of significance at < 0.05. If a result was below the detection limit, in lieu of a zero value, half of the DL was used for calculation purpose. A non-parametric test was used because the data was not normally distributed, and the sample size was too small to run a parametric test. To assess possible relationships, correlation coefficients were calculated. Correlation was considered significant only if $r^2 > 0.4$ and $p < 0.05$. Statistical treatment of the data was performed using the software XLSTAT and Origin.

3. Results and discussion

3.1. Metal(loid) content in soil fractions

A comparison of As, Cu, Cr, Pb and Zn distribution in the different particle size fractions showed that decreasing particle size resulted in increasing metal concentration (Figure 1). A similar trend has been reported in previous studies (Ljung et al., 2006; Madrid et al., 2008; Juhasz et al., 2011; Meunier et al., 2011a; Kastury et al., 2017). This has been attributed to the higher surface-to-mass in finer particles, increasing the adsorption capacity of smaller fractions. Concentrations of As, Cu, and Cr are presented in Table 1. Concentrations of Pb and Zn are presented in Appendix A (Table A.1). Overall, a broad As contamination was observed. Of all studied soils, only S10 presented an As content below Quebec's regulatory limit for industrial land-use (C criterion, 50 mg/kg) (Beaulieu 2016). Extensive As contamination was observed for S8 (1372 ± 51 mg/kg) and S7 (368 ± 21 mg/kg). Cu content exceeding the C criterion (500 mg/kg) was also observed for S7 and S8. As expected, Cr contamination was relatively lower (Zagury et al., 2003) but soil samples S7 and S8 still contained elevated Cr concentrations (around 500 mg/kg). The observed contamination pattern in the fraction < 2mm (Cu > As > Cr) corroborates previous results regarding levels of contaminants in CCA-contaminated soils near treated poles in service (Cooper et al., 1997; Zagury et al., 2003). The higher metal(loid) content measured in some samples (such as S7 and S8) is not unusual and can be explained by different factors affecting CCA-leaching from wood, such as rainfall, soil humidity, wood species, and age of service (Cooper 1994).

Significantly different concentrations of As and Zn where measured when comparing concentrations in particle sizes used for the ingestion scenario (250-90 and 90-20 µm). As and Zn content in the 90-20 µm particle size fraction were 2.0 and 1.7-fold greater, respectively, than in the 250-90 µm soil fraction (Wilcoxon signed-rank test, $p < 0.05$). Interestingly, the fraction < 2 mm of soil sample S7 contained higher concentrations of all studied metals when compared to the fraction 250-90 µm, but always contained lower concentrations than the fraction 90-20 µm. This can be attributed to the predominance of smaller particles (< 90 µm) in fraction < 2 mm in soil S7.

Comparison of As, Cu, Cr, Pb and Zn between particles 250-90 µm and the fraction < 2 mm revealed no significant difference of the means (Wilcoxon signed-rank test, $p > 0.05$). However, the fraction 90-20 µm presented significantly higher concentrations than the fraction < 2 mm for As (1.9 fold-greater), Cu (1.7 fold-greater), and Cr (2.1 fold-greater) (Wilcoxon signed-rank test, $p < 0.05$). A significant difference (Wilcoxon signed-rank test, $p < 0.05$) in metal(loid)s content was also observed when comparing particles < 20 µm with < 2 mm: As was 4.3-fold greater, Cu was 2.7-fold greater, Cr was 5.2-fold greater, Pb was 1.6-fold greater, and Zn was 2.2-fold greater.

3.2. Physico-chemical properties of soil fractions

The range of pH values across all studied soil fractions was narrow, varying between 6.91 and 8.36 (Table 2). Total carbon content (TC), TOC and CEC values tended to increase with decreasing particle size in the 10 CCA-contaminated soils (Table 2). TOC was variable and ranged between 0.5 and 8 % with higher values observed in smaller fractions of soil S8. The CEC was strongly correlated to the TOC. This correlation was stronger in particle size 90-20 µm ($r^2 = 0.92$, $p < 0.005$) than in the 250-90 µm ($r^2 = 0.78$, $p < 0.005$). Previous studies with CCA-contaminated soils also reported that organic matter content increases CEC (Balasoiu et al., 2001; Pouschat and Zagury, 2006, 2008).

3.3 Bioaccessibility

Because the bioaccessibility expressed as a percentage is directly influenced by the total concentration of metal, it is important to also calculate the bioaccessible (BAC) concentration (mg/kg) in samples. Bioaccessible concentration reveals the amount of metal solubilized in simulated human fluids, while percent bioaccessibility can be useful to compare the solubility behavior of metals. Therefore, in the present study, results are presented in terms of percent bioaccessibility (%) and in terms of bioaccessible concentration (mg/kg). Bioaccessibility results in mg/kg are presented in Appendix A (Tables A.2-A.6). Low recovery values for Cr, Pb and Zn using GS impede the use of these results in the analysis of inhalation bioaccessibility (Gosselin and Zagury, 2020).

Although the oral bioaccessibility was measured in both the gastric and gastrointestinal phases using the IVG method, most attention was given to the gastrointestinal phase (GI), since the GI phase better reflects in vivo conditions (Kelley et al., 2002) and most of metal(loid)s absorption occurs in the epithelium of the intestine (Turner and Ip, 2007). In the present work, studied metals showed a reduction in bioaccessible concentrations from stomach to intestine phase (Wilcoxon signed-rank test, $p < 0.05$) in the order: Zn > Cr > Pb > Cu > As. This decrease is commonly reported in oral bioaccessibility studies, since the lower pH in the gastric phase (1.8) might lead to a larger liberation of contaminants, and an increase of pH in the gastrointestinal phase (5.5) decreases the solubility of metals (Oomen et al., 2002; Goix et al., 2016; Li et al., 2020).

3.3.1. Arsenic bioaccessibility

Oral and inhalation results of As BAC (%) are presented in Table 3. Oral As BAC (%) values (IVG-GI) ranged between 15.7 ± 0.3 and 44.5 ± 0.6 %. Oral As BAC (%) decreases with the decrease of particle size (Wilcoxon signed-rank test, $p < 0.05$). Ljung et al. (2006) also reported a decrease in As BAC (%) when decreasing particle size, from 28.7% in the fraction < 4 mm to 16.1% in the fraction < 50 µm. Reduced oral As BAC (%) in smaller particles could be due to the presence of secondary minerals in this fraction, since finer particles usually contain more clay minerals and oxy-hydroxides that act as strong adsorbent of metal(loid)s (Yu and Li, 2011; Dehghani et al., 2018),

As reported by Pouschat and Zagury (2006) and Girouard and Zagury (2009), the As BAC (%) in CCA-contaminated soils was not correlated with total As concentration ($r^2 < 0.19$) using the IVG method. One important factor that controls As BAC in soils is the amount of Fe oxides, due to the strong affinity As has with Fe oxides (Girouard and Zagury 2009; Li et al., 2015). The Fe oxides are dissolved in the gastric phase because of the low pH (1.8) but in the intestinal phase, the higher pH (5.5) can precipitate the dissolved Fe, adsorbing As in the process. Therefore, the considerable difference between gastric and gastrointestinal As BAC (%) values in the samples S5 90-20 µm (G: 44.2±2.2 %, GI: 29.7±0.7 %) and in S8 90-20 µm (G: 29.1±5.5 %, GI: 15.7±0.3 %), could be explained by the presence of Fe oxides in these samples.

The oral As BAC (mg/kg) in different soil fractions (250-90 µm and 90-20 µm, Table A.2) was strongly correlated to total arsenic concentration (mg/kg) ($r^2 > 0.98$, $p < 0.05$). Even if the average As concentration in particle size 90-20 µm was almost the double of the one measured in fraction 250-90 µm (505 compared to 255 mg/kg), the average oral As BAC (mg/kg) was not significantly different (Wilcoxon signed-rank test, $p > 0.05$) in both fractions (96.8 compared to 88.2 mg/kg). This suggests that the oral As BAC (mg/kg) was not impacted by particle size. Meunier et al. (2011a) compared particles < 45 µm and < 250 µm and reported total As concentrations of 36,000 mg/kg and 17,000 mg/kg, and oral As BAC of 2500 and 1200 mg/kg for the Glycine method, and 2200 to 960 mg/kg for PBET. Hence the average total concentration increased in smaller fractions in a similar way for both studies, however in the present study oral As BAC (mg/kg) using the IVG method did not follow the same trend.

Interestingly, the values of As BAC (mg/kg) in oral tests and inhalation test using GS (Table A.2) were close and strongly correlated with each other ($r^2 > 0.95$, $p < 0.05$). Oral IVG-GI (250-90 µm), IVG-GI (90-20 µm) and inhalation results from GS (< 20 µm) presented average values of 88.2, 96.8 and 103 mg/kg. However, the inhalation As BAC (mg/kg) in ALF (average of 523 mg/kg) was 5-fold greater than in GS (Wilcoxon signed-rank test, $p < 0.05$).

3.3.2. Copper bioaccessibility

Oral Cu BAC (%) values (IVG-GI) ranged from 36.4 ± 3.0 to 59.8 ± 1.5 % (Table 4). Copper bioaccessibility in both particle sizes decreased by 13% on average from the gastric to the gastrointestinal phase (Wilcoxon signed-rank test, $p < 0.05$). No evidence of the impact of particle size on average oral Cu BAC (%) was found when comparing particles of size 250-90 (49.8 ± 6.4 %) with 90-20 µm (49.0 ± 8.4 %) (Wilcoxon signed-rank test, $p > 0.05$). Likewise, Madrid et al. (2008) measured similar values for Cu bioaccessibility in different fractions of soil. Oral Cu BAC (%) was not correlated with total Cu concentration ($r^2 < 0.17$, $p > 0.24$).

Oral Cu BAC (mg/kg) (Table A.3) in different soil fractions (250-90 µm and 90-20 µm) was strongly correlated to total Cu concentration (mg/kg) ($r^2 > 0.94$, $p < 0.005$) but no significant difference in Cu BAC (mg/kg) was observed (Wilcoxon signed-rank test, $p > 0.05$) when comparing the fraction 250-90 µm with the fraction 90-20 µm.

3.3.3. Chromium bioaccessibility

No correlation was found between total Cr concentration and oral Cr BAC (%) (IVG-GI) ($r^2 < 0.11$, $p > 0.36$). Oral Cr BAC (%) ranged between < 0.1 and 8.0 ± 0.1% (Table 5). In a previous study on CCA-contaminated soils using samples < 300 µm, oral Cr BAC (%) values ranged between < 0.3 and 33 (Pouschat and Zagury, 2008).

Differences between mean Cr BAC (%) in particles 250-90 and 90-20 µm were statistically significant (Wilcoxon signed-rank test, $p < 0.05$), showing a higher value in the 90-20 µm particle size fraction. Moreover, the average oral Cr BAC (% and mg/kg) was approximately 4-fold greater in this fraction when compared to the 250-90 µm particle size fraction. Li et al. (2020) likewise applied the IVG method to extract soil samples and observed Cr bioaccessibility increasing when decreasing particle size (250-50 µm: 0.3 %, 50-5 µm: 1.2 %). Overall, oral Cr BAC (%) was the lowest among all metal(loid)s in the present study. Ma et al. (2019) also found that Cr bioaccessibility (0.98 to 3.46 %) was the lowest when analyzing a group of 6 metals. Conversely, inhalation Cr BAC (%) was higher and ranged between 19.6 to 73.0 % when using ALF solution (Table 5).

Resembling As and Cu, oral Cr BAC (mg/kg) in different size fractions (250-90 and 90-20 µm) was correlated to total Cu concentration (mg/kg) ($r^2 = 0.45$, $p < 0.05$ for 250-90 µm and $r^2 = 0.78$, $p < 0.005$ for size 90-20 µm). Oral BAC (mg/kg) ranged between and < 0.3 and 27.7 mg/kg (Table A.4). The fraction 90-20 µm presented an average Cr BAC (mg/kg) 4-fold greater than the fraction 250-90 µm (9.5 and 2.6 mg/kg, respectively) (Wilcoxon signed-rank test, $p < 0.05$), suggesting that oral Cr BAC (expressed in mg/kg) is influenced by particle size. Gastric Cr BAC (mg/kg) was significantly higher (Wilcoxon signed-rank test, $p < 0.05$) than gastrointestinal Cr BAC (mg/kg) in both fractions tested.

3.3.4. Lead bioaccessibility

Oral Pb BAC (%) significantly decreased from gastric to gastrointestinal phase (Wilcoxon signed-rank test, $p < 0.05$) in both fractions (Table A.7). In the G phase, Pb BAC ranged from 4.1 ± 1.2 to 59.1 ± 4.3 % in the 250-90 μm fraction and from 16.6 ± 5.5 to 81.3 ± 14.2 % in the 90-20 μm fraction. In the GI phase, Pb BAC ranged from < 0.9 to 45.4 ± 1.2 % for the 250-90 μm particle size, with a mean value of 15.1 ± 13.9 %. In the particle size 90-20 μm it ranged from < 0.9 to 53.4 ± 7.3 %, with a mean value of 19.1 ± 18.3 % (Table A.7). Considering GI phase, no significant difference was observed in oral Pb BAC (%) between particle size 250-90 and 90-20 μm (Wilcoxon signed-rank test, $p > 0.05$).

Other studies also observed a similar reduction of soil-bound Pb bioaccessibility from gastric to gastrointestinal phase using various physiologically based bioaccessibility tests (Ruby et al., 1996; Schroder et al., 2004; Juhasz et al., 2009; Juhasz et al., 2011). The higher bioaccessibility in the gastric phase could be due to the presence of Fe oxyhydroxides in the soils, which would release associated Pb under very acidic conditions (Smith et al., 2011, Reis et al., 2014).

Inhalation bioaccessibility assessment using ALF yielded Pb BAC (%) ranging from 12.2 to 65.0 %, with an average of 37.8% (Table A.7). Pb was the only element studied that was occasionally more bioaccessible via ingestion than via inhalation. Determination of soil properties specifically affecting Pb solubility such as chloride content, could help explain why S1 and S9 presented higher oral than inhalation (ALF) bioaccessibilities.

Unlike As, Cu, Cr, and Zn, Pb BAC (mg/kg) (Table A.5) was not significantly correlated with total Pb concentration. No significant difference (Wilcoxon signed-rank test, $p > 0.05$) was found between particles 90-20 and 250-90 μm in Pb BAC (mg/kg). The average oral Pb BAC (mg/kg) in soil fraction

90-20 µm was 11.1 ± 10.4 mg/kg whereas in soil fraction 250-90 µm the average Pb BAC was 7.5 ± 6.5 mg/kg.

3.3.5. Zinc bioaccessibility

Zinc BAC (%) decreased significantly from G to GI phase, from 36.0 ± 14.0 to 8.9 ± 8.8 % on average in the fraction 90-20 µm (Wilcoxon signed-rank test, $p < 0.05$) (Table A.8.). In the fraction 250-90 µm a similar trend in decreasing bioaccessibility from the gastric to gastrointestinal phase was observed (from 37.7 ± 23.3 to 6.7 ± 7.3 %) (Wilcoxon signed-rank test, $p < 0.05$). Percentage bioaccessible Zn in oral tests ranged between < 0.1 and 23.7 ± 3.3 %, with an average of 6.7 ± 7.3 % for particle size 250-90 µm and 8.9 ± 8.8 % for particle size 90-20 µm. No significant difference was observed in oral Zn BAC (%) between tested particle sizes (Wilcoxon signed-rank test, $p < 0.05$). Inhalation tests using ALF yielded Zn BAC (%) ranging from 21.5 to 90.9%, with an average of 54.8% (Table A.8.).

Oral Zn BAC (mg/kg) (Table A.6) in different size fractions (250-90 and 90-20 µm) presented a good correlation with total Zn concentration (mg/kg) ($r^2 > 0.46$, $p < 0.05$). Zn BAC in GI phase was below detection limits in 7 out of 20 samples, suggesting that Zn precipitated in the intestinal solution. Turner and Ip (2007) observed the same phenomena using the PBET method. There was no significant difference (Wilcoxon signed-rank test, $p > 0.05$) when comparing oral Zn BAC (mg/kg) in particles sizes 250-90 µm and 90-20 µm.

3.4 Influence of soil properties on bioaccessibility

Considering the narrow pH range in the CCA-contaminated soils collected, it was not deemed appropriate to assess the influence of soil pH on oral bioaccessibility. Organic matter content (TOC) presented a good correlation with total metal content in the particle size < 20 µm for the 5 studied metal(loid)s (As: $r^2 = 0.70$, $p < 0.005$; Cu: $r^2 = 0.44$, $p < 0.05$; Cr: $r^2 = 0.49$, $p < 0.05$; Pb: $r^2 = 0.56$, $p < 0.05$; and Zn: $r^2 = 0.41$,

$p < 0.005$) as well as a good correlation with total metal content in particle size 90-20 µm for 4 out of 5 metal(loid)s (As: $r^2 = 0.66$, $p < 0.005$; Cu: $r^2 = 0.44$, $p < 0.05$; Cr: $r^2 = 0.52$, $p < 0.05$; and Pb: $r^2 = 0.51$, $p < 0.05$). The only element to show a significant correlation between total metal content and TOC in the coarser fraction 250-90 µm was Pb ($r^2 = 0.52$, $p < 0.05$). The CEC was correlated with total metal(loid)s content for As, Cu, and Cr in the fraction 90-20 µm (As: $r^2 = 0.61$, $p < 0.05$; Cu: $r^2 = 0.44$, $p < 0.05$; Cr: $r^2 = 0.47$, $p < 0.05$) and for As, Cr, and Pb in the fraction 250-90 µm (As: $r^2 = 0.48$, $p < 0.05$; Cr: $r^2 = 0.48$, $p < 0.05$; Pb: $r^2 = 0.57$, $p < 0.05$). These results suggest that TOC content and CEC have more influence on CCA components retention by soils in smaller than in larger particle sizes. CEC was not measured in the particle size fraction < 20 µm.

The oral As BAC (mg/kg) in particle size fraction 250-90 µm showed a good correlation with CEC ($r^2 = 0.46$, $p < 0.05$) and not TOC, whereas the As BAC (mg/kg) in particle size 90-20 µm was significantly correlated with CEC ($r^2 = 0.61$, $p < 0.05$) and TOC ($r^2 = 0.64$, $p < 0.05$). It must be noted that As BAC (mg/kg) in inhalation tests using ALF ($r^2 = 0.68$, $p < 0.005$) and GS ($r^2 = 0.67$, $p < 0.005$) were also strongly correlated with TOC. Therefore, an increase of soil organic matter content might entail an increase in As bioaccessibility (mg/kg) when humans are exposed (via ingestion, inhalation or inhalation followed by ingestion) to particles smaller than 90 µm originating from CCA-contaminated soils. It is known that organic matter can act as an electron shuttle (Redman et al., 2002) and contribute to the oxidation of As(III) to a less toxic and more mobile species: As(V) (Meunier et al., 2011b). More specifically, previous work on the influence of organic carbon content on As mobility in CCA-contaminated soils showed that an increase in dissolved organic carbon content promoted both As(V) and As(III) solubilization in soils (Dobran and Zagury, 2006). However, Cr, Cu, Pb, and Zn oral bioaccessibilities (mg/kg) were not significantly correlated to CEC nor TOC.

Oral bioaccessibility expressed as a percentage in the 90-20 µm fraction showed a good negative correlation with CEC and TOC only for Pb and Cu. Lead BAC (%) was correlated with CEC ($r^2 = 0.41$, $p < 0.05$) and TOC ($r^2 = 0.40$, $p < 0.05$). Compared to Pb, Cu BAC (%) presented a stronger negative correlation with CEC ($r^2 = 0.67$, $p < 0.005$) and TOC ($r^2 = 0.80$, $p < 0.005$). Pouschat and Zagury (2008) also found that Cu BAC (%) in the gastrointestinal phase was influenced by CEC ($r^2 = 0.51$, $p < 0.01$) and TOC ($r^2= 0.64$, $p < 0.01$) in CCA-contaminated soils collected near in-service treated utility poles. Organic matter in CCA-contaminated soils has also been shown to potentially reduce Cu mobility (evaluated using chemical extractions) in particles < 75 µm (Balasoiu et al., 2001). Sample S8 strongly illustrates this trend, as the fraction 90-20µm exhibits the highest Cu concentration (2223 ± 53 mg/kg) and TOC (6.1 %) (Tables 1 and 2) but is also the sample that presented the lowest Cu BAC (%) in IVG-GI (36.4 ± 3.0%) (Table 4).

3.5 Inhalation *versus* oral bioaccessibility

Bioaccessibility of studied metal(loid)s using the different synthetic fluids and particle sizes is presented in Fig. 2. The 5 metal(loid)s investigated in order of most to least bioaccessible (mg/kg) using ALF solution were: Cu > As > Zn > Cr > Pb. The order was slightly different when inhalation bioaccessibility was expressed as a percentage (Cu > Zn > As > Pb ≈ Cr). When using GS solution, the inhalation bioaccessibility (mg/kg and %) was: As > Cu. Higher bioaccessibility in ALF compared to GS is in agreement with previous studies (Wiseman, 2015; Goix et al., 2016; Guney et al., 2017; Li et al., 2020) since the lower pH (4.5) in ALF solution enhance metals' solubilization better than in GS solution (pH=7.4). Li et al. (2020) recently found that Cu and Zn were also the most bioaccessible metals in alkaline urban soils using ALF in particle size 5-1 µm (Cu (75.5%) > Zn (40.7%) > Pb (40.5%) > Cr (24.2%) > As (10.8%)).

Metal(loid)s bioaccessible concentration using IVG method showed the following trend: Cu > As > Zn > Pb > Cr and decreased in the order: Cu > As > Pb > Zn > Cr when expressed as a percentage, Previous studies on oral bioaccessibility (using the simplified bioaccessibility extraction test) of metals also reported that Cr was the least soluble metal when compared with Cu, Pb, and Zn in urban garden and playground soils (De Miguel et al., 2012; Izquierdo et al., 2015; Luo et al., 2012). All studied metal(loid)s presented higher inhalation bioaccessibility (mg/kg and %) when extracted in ALF than in gastrointestinal simulated fluids, however, solubility of metal(loid)s in GS presented the lowest values. Mean results of bioaccessibility (mg/kg and %) can be found in Appendix A (Tables A.9 and A.10).

4. Conclusions

Results showed that soils collected near CCA-treated utility poles in service present high concentration of potentially harmful metal(loid)s in all studied fractions. Concentrations of metal(loid)s increased with decreasing soil particle size. Organic matter content played an important role, given that a high TOC content increased the soil total metal content in the fine fraction of soils (90-20 and < 20 µm), although this impact was apparent for Pb only in the coarser fraction (250-90 µm). The bioaccessible fraction (%) was not correlated with total metal concentration for any of the physiologically-based extraction fluids used (IVG, GS and ALF). Average bioaccessibility values (mg/kg and %) in ALF and IVG suggest that metal(loid)s would be more bioavailable if inhaled than ingested. Among the studied metals, Cu presented the highest concentration in different particle sizes except in particles < 20 µm, where As concentrations were slightly higher. Copper was also the most bioaccessible metal (mg/kg and %) using IVG and ALF solutions. This suggests that this metal should be carefully studied in human health risk assessment following exposure to CCA-contaminated soils.

Besides the fact that smaller particles have a higher metal content, they possibly adsorb some metals better than the larger particles, therefore reducing the bioaccessibility in smaller particle size. In fact, oral As bioaccessibility (%) decreased when reducing particle size. However, oral Cr bioaccessibility (mg/kg and %) increased when decreasing particle size and Cu BAC (mg/kg and %) was not influenced by particle size. Therefore, the present study indicates that the influence of particle size fraction on oral bioaccessibility is metal(loid)-dependent.

In the studied soils, TOC content significantly reduced Cu bioaccessibility (%) in both inhalation and ingestion tests whereas organic matter content increased As bioaccessibility (mg/kg) in both inhalation (< 20 µm) and ingestion tests (90-20 µm fraction). These results tend to confirm that particle size is not the only factor controlling metal(loid)s bioaccessibility. Therefore, future research should assess metal(loid)s speciation and mineralogy in addition to physico-chemical properties of soils in all particle size fractions.

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Appendix A. Supplementary data

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Table 3: As bioaccessibility (%, mean ± standard deviation (n=2)) in simulated gastrointestinal solutions (IVG method) and in artificial lung fluids (GS and ALF solutions).

Table 4: Cu bioaccessibility (%, mean ± standard deviation (n=2)) in simulated gastrointestinal solutions (IVG method) and in artificial lung fluids (GS and ALF solutions).

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Figure 1: Boxplot of metal(loid)s concentrations in different particle sizes of soil samples (n=10). A = < 2 mm, B = 250-90 µm, C = 90-20 µm, D = < 20 µm. The outliers are not shown.

Figure 2: Boxplot of bioaccessibility (% and mg/kg) of metal(loid)s in different particle sizes of soil samples (n=10) using different methods. A = IVG-GI (250-90 µm), B = IVG-GI (90-20 µm), C = GS (< 20 µm), D = ALF (< 20 µm). The outliers are not shown in the boxplot of bioaccessibility (mg/kg).

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