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Title

Metal(loid)s inhalation bioaccessibility and oxidative potential of particulate matter from chromated copper arsenate (CCA)-contaminated soils

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Abstract

Field-collected chromated copper arsenate (CCA)-contaminated soils and associated particulate matter (PM) were characterized for their total metal(loid)s content (As, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and physicochemical properties. Copper, Ni, Pb and Zn fractionation (using sequential extraction) and inhalation bioaccessibility (using two lung fluids) of trace elements were assessed in PM samples. In Gamble's solution (GS), low average bioaccessibility (up to 12%) was observed for As, Cu, Mn, and Ni. A strong correlation ($r=0.92$, $p < 0.005$, $n=9$) between the soluble and exchangeable fraction (F1) and bioaccessibility in GS was observed for Cu. Inhalation bioaccessibility in artificial lysosomal fluid (ALF) was higher for Cu (avg. $78.5 \pm 4.2\%$), Mn (avg. $56.8 \pm 12.1\%$), Zn (avg. $54.8 \pm 24.5\%$) and As (avg. $45.4 \pm 18.8\%$). Strong correlations between inhalation bioaccessibility in ALF and the mobile (i.e. F1+F2) metal fraction were observed for all tested metals (i.e. (Cu ($r = 0.95$, $p < 0.005$), Ni ($r = 0.79$, $p < 0.05$), Pb ($r = 0.92$, $p < 0.005$) and Zn ($r = 0.98$, $p < 0.005$)), $n=9$). The oxidative potential (OP) of PM was also assessed using an ascorbate (AA) depletion assay (OP_{AA}). Mobile Cu fractions were deemed to be the main factor

influencing OP_{AA} ((F1 ($r = 0.99$, $p < 0.005$), F2 ($r = 0.97$, $p < 0.005$)), $n=9$) in PM samples. A strong correlation ($r = 0.94$, $p < 0.005$, $n=10$) was also observed between Cu bioaccessibility in GS and OP_{AA} .

Keywords

Inhalation bioaccessibility, Oxidative potential, Particulate matter, Metals and metalloids, Contaminated soils, Chromated copper arsenate.

1. Introduction

The widespread use of chromated copper arsenate (CCA) as a wood preservative during the 20th century led to a considerable ecological burden. Studies in the 1990s warned about the potential leaching of its harmful constituent (CrO_3 , As_2O_5 and CuO) following weathering of treated wood structures (Warner and Solomon, 1990). This assumption was later confirmed in various studies assessing metal content in soils near CCA-treated wood (Stilwell and Gorny, 1997; Chirenje et al., 2003; Zagury et al., 2003; Guney et al., 2010). In 2003, its use was restricted to industrial applications in Canada and the U.S.A. (Zagury et al., 2008). However, existing CCA-treated wood structures still remain in service. Furthermore, CCA impact still lingers today as the disposal of obsolete CCA-treated wood currently poses a global waste management challenge (Janin et al., 2009; Ferrarini et al., 2016; Liu et al., 2018) and recent studies still raise concerns regarding human exposure to CCA-treated wood and contaminated soil (Gress et al., 2015; Ohgami et al., 2015)

The leaching of CCA from treated wood structures leads to soil contamination. Various studies assessed the issue and identified key physicochemical parameters influencing As, Cr and Cu contamination levels in soil. Amongst the most critical ones were soil pH, competing cations (Mg^{2+} , Mn^{2+} and Ca^{2+}) (Tardif et al., 2018), cation exchange capacity (CEC), total carbon (TC) and total organic carbon (TOC) content (Zagury et al., 2003). Arsenic fractionation (i.e. metal partitioning in different soil fractions), using deionized water, ammonium oxalate and hydrochloride hydroxylamine, has also been used to provide information on As mobility in the soil matrix (Girouard and Zagury, 2009).

Despite the extensive literature available on soil contamination by CCA, limited information is available on health risks following exposure to CCA-contaminated soils. The literature is generally focused on soil ingestion as the main exposure pathway (Hemond and Solo-Gabriele, 2004; Pouschat and Zagury, 2006; Girouard and Zagury, 2009; Guney et al., 2010; Deramos King et al.,

2019). However other exposure pathways (i.e. dermal contact and inhalation) should be considered to properly assess human health risks. Particulate matter (PM) can be generated following wind erosion or anthropogenic activity near contaminated soils (James et al., 2012). Considering the well-established health impacts of PM (Kim et al., 2015) as well as carcinogenic risks associated with the inhalation of As (Smith et al., 2009) and Cr(VI) (Gibb et al., 2000), research should be carried out on the possible health hazards produced following inhalation of suspended CCA-contaminated PM.

Significant progress has been made in recent years regarding the assessment of metal inhalation bioaccessibility or lung bioaccessibility. This metric, once validated with *in vivo* data, should enable an estimation of the bioavailability (i.e. fraction of component transferred into the human systemic circulation) by using simulated lung fluids (SLFs) to mimic pulmonary environment conditions. While the inhalation bioaccessibility of metals in airborne PM has previously been studied, little information is currently available on inhalation bioaccessibility of metals in PM originating from soils (Boisa et al., 2014; Witt et al., 2014; Guney et al., 2016; Guney et al., 2017; Zhong and Jiang, 2017).

The most widely used SLFs are Gamble's solution (GS) and artificial lysosomal fluid (ALF) (Wiseman, 2015). GS is a neutral salt solution (pH=7.4) used to mimic extracellular fluid, whereas the more acidic ALF (pH=4.5) simulate conditions encountered during macrophage phagocytosis (Colombo et al., 2008). Given that particle diameter affects PM penetration in the lung, caution should be taken when choosing SLFs for inhalation bioaccessibility testing. It is generally accepted that particles having an aerodynamic diameter of less than 10 μm (PM_{10}) are capable of reaching trachea-bronchial and alveolar regions, making GS the most widely used SLF to study their bioaccessibility (Kastury et al., 2017). Particles with an aerodynamic diameter of less than 5 μm (PM_5) are the most likely to be phagocytosed by alveolar macrophages, making ALF a prime choice to study their bioaccessibility (Wiseman, 2015). But, since the size of alveolar macrophages is

estimated to be 21 μm (Krombach et al., 1997), it is possible for particles larger than 5 μm to be phagocytosed. In addition to particle size and shape, geochemical characteristics of PM should be taken in consideration when assessing inhalation bioaccessibility. For instance, metal fractionation results can be used to correlate specific metal fractions to inhalation bioaccessibility. Previous research demonstrated a significant correlation between exchangeable/soluble Pb in suspended road dust and bioaccessibility in ALF (Witt et al., 2014). But, little to no information is available on metal fractionation influence on inhalation bioaccessibility for other metals and other SLFs (Schaidler et al., 2007; Drysdale et al., 2012).

Oxidative potential (OP) (i.e. the reactive oxygen species (ROS) production capability) is another critical parameter to assess in order to study PM health impacts. Production of ROS in the antioxidant-rich lung fluids can lead to a change in redox conditions in the pulmonary environment (Poschl and Shiraiwa, 2015). This perturbation (i.e. oxidative stress) is associated with various health issues including chronic obstructive pulmonary disease (COPD) (Rahman and Adcock, 2006), asthma (Fitzpatrick et al., 2009; Delfino et al., 2013) and atherosclerosis (Ying et al., 2009). Previous studies correlated transition metals (i.e. Co, Cu, Cr, Fe, Mn, Ni, V and Zn) total content of PM with increased ROS production (Gualtieri et al., 2009; Ghio et al., 2012; Saffari et al., 2014). It was recently suggested that metal oxidation state could also have a significant impact on the ROS generation of PM (Hernández-Pellón et al., 2019). Mudway and co-workers suggested a simplified ascorbate-only assay (OP_{AA}) as a cost-effective OP estimation screening tool (Mudway et al., 2005). In recent years, studies have successfully used this procedure to correlate OP_{AA} with various PM components (Janssen et al., 2014; Yang et al., 2014; Visentin et al., 2016; Calas et al., 2018; Pietrogrande et al., 2018). While the correlation between OP_{AA} and PM total metal content for specific elements (Cu, Fe and Zn) seems significant, conflicting/sparse information can be found on various health relevant metal(loid)s (e.g. As, Mn, Ni, Pb, etc.) (Künzli et al., 2005; Fang et al., 2016; Calas et al., 2018). Our hypothesis is that the OP of PM can be better explained by their trace

element inhalation bioaccessibility. Moreover, to better mimic interactions between PM constituents and lung fluids, GS could be used as a biologically relevant extraction fluid instead of commonly used solvents (i.e. water or phosphate buffer solution).

Therefore, the present study aims (1) to characterize and analyze metal(loid)s content (As, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in 10 field-collected CCA-contaminated soils and associated PM, (2) to assess Cu, Ni, Pb and Zn fractionation in these PM, (3) to assess metal(loid)s inhalation bioaccessibility and OP_{AA} of PM, and (4) to analyze the influence of soil properties and metal fractionation on inhalation bioaccessibility and OP_{AA} of PM.

2. Materials and Methods

2.1 Sampling and sample preparation

Soil samples near 10 CCA-treated utility poles (S1 to S10) were collected in the Montréal area (Québec, Canada). Samples were collected in a 20 cm radius of each pole and up to a 10 cm depth. Coarse material (>2 cm) and topsoil vegetation were removed prior to sampling. Soil was collected using a plastic shovel and stored in zip-lock plastic bags. All containers and tools used were washed with phosphate-free detergent, soaked overnight in 10% (v v⁻¹) HNO₃, and rinsed twice with deionized water.

Soil samples were air dried, gently crushed using a mortar, and were dry sieved to 2 mm and 20 µm (PM₂₀) (P1 to P10) using a sieve shaker (Retsch AS-200). A PM₁₀ fraction was initially desired but inherent limitations of dry sieving prevented it. Moreover, dry sieving was favoured over wet sieving to prevent metal solubilization in water. Sieved samples were stored in HDPE bottles at 4 °C prior analysis.

2.2 Soil characterization

Soil pH was determined according to ASTM D4972-13 (ASTM, 2013). Total carbon (TC) and total organic carbon (TOC) were measured using an induction furnace (LECO) as per (Chapman, 1993) (Carter, 1993). Cation exchange capacity (CEC) was determined using the sodium acetate method (Chapman, 1965).

Soil total metal(loid) content was assessed via acid digestion using HNO₃, HClO₄ and HF (Clesceri et al., 1986). The digested solution was filtered (0.45 µm), diluted to 100 mL with deionized water and stored in HDPE centrifuge tubes. Chromium, Cu, Fe, Mn, Ni, Pb, and Zn concentrations were measured via atomic absorption spectroscopy (AAS) (Perkin-Elmer A200) (Detection limits (DL) in mg kg⁻¹: 0.3, 0.3, 0.6, 0.2, 0.2, 1, and 0.1, respectively). Arsenic content was determined via ICP-OES (Varian Vista) (DL in mg kg⁻¹: 0.004).

2.3 Particulate matter characterization

Since PM₁₀ have the potential to deposit in the deep respiratory tract and alveolar region, and PM₅ are most likely to be phagocytosed by alveolar macrophages, PM₁₀ and PM₅ content of the PM₂₀ was determined. To assess the proportion of these fractions in studied PM₂₀, PM₂₀ samples obtained via dry sieving were subjected to particle size distribution (PSD) analysis (Malvern Mastersizer 3000 with Aero S dispersion unit) in triplicate.

Soluble arsenic was determined using deionized water as per Girouard et al. (2009). PM₂₀ total metal content, TC and TOC content were assessed with the procedure used for soils.

Fractionation of metals (i.e. Cu, Ni, Pb and Zn) was assessed according to (Zagury et al., 1999) based on (Tessier et al., 1979). The sequential extraction procedure (SEP) enabled the determination of five metal fractions: soluble and exchangeable (F1), bound to carbonates (acid soluble) (F2), bound to Fe and Mn oxides (reducible) (F3), bound to organic matter (oxidizable) (F4), and residual (F5). Considering that conventional SEP schemes tend to modify As oxidation state (Huang and Kretzschmar, 2010), this element was not subjected to fractionation. Moreover,

Cr fractionation was determined but is not provided because of non-satisfactory metal recovery percentages (ranging from 41 to 85%) obtained when comparing total digestion values to the sum of all fractions of the SEP.

2.4 Inhalation bioaccessibility

The detailed inhalation bioaccessibility protocol used can be found elsewhere (Guney et al., 2017). Tests were performed using GS and ALF: For each SLF, 0.4 g of PM₂₀ sample was incubated with 40 mL of pre-conditioned lung solution (37 °C) in centrifuge polypropylene tubes and placed on an orbital shaker at 100 rpm in an incubator at 37 °C for 24 h. It must be noted that published S/L ratios and agitation methods used are variable. Their impact on bioaccessibility is not yet fully understood and seems generally sample and metal specific. Please see (Caboche et al., 2011; Guney et al., 2016; Kastury et al., 2018) for a more detailed discussion on this topic. Samples were then centrifuged at 10 000 x g for 10 minutes. Supernatants were collected, filtered using a 0.45 µm PVDF filter syringe and stored at 4 °C until analysis. Supernatants were analyzed via AAS for their Cr, Cu, Fe, Mn, Ni, Pb and Zn content. As content was determined via ICP-OES.

2.5 Oxidative potential

Oxidative potential (OP) was measured by spectrophotometry using the ascorbate-only assay (Mudway et al., 2005; Fang et al., 2016). However, GS was used as an extraction fluid to enable a more accurate depiction of the solubility behaviour of metals in the lung environment. ALF could also have been used but the near neutral pH of GS was preferred in order to prevent AA autoxidation (Buettner, 1988).

Briefly, 0.04 g of PM₂₀ was mixed with 40 mL of preheated (37 °C) GS in a Teflon centrifuge tube. The tube was agitated for 4 hours at 37 °C in an incubator (Fisher Isotemp) using an orbital shaker (100 rpm) and the resulting solution was filtered (0.45 µm) using a Luer lock syringe. An extraction time of 24 hours was originally selected but the higher metal content in the filtrate interfered with

spectroscopic analysis. The filtrate was then cooled down and stored at 20 °C in an HDPE container. The oxidative potential of PM₂₀ samples was assessed using a UV-VIS spectrophotometer (Biochrom Ultrospec 1100 pro) with a quartz cuvette (Hellma Analytics). Filtrates (3 mL) were mixed with 30 µL of a 10 mM ascorbic acid (AA)-deionized water solution directly into a cuvette to obtain a relevant AA concentration of 100 µM (Zielinski et al., 1999). Absorbance (Abs) was measured (λ=265 nm) every 2 minutes for 20 minutes and remaining AA (n_{AA,i}) was determined using eq. (1).

$$n_{AA,i} = \frac{Abs_i * n_{AA,0}}{Abs_0} \quad (1)$$

An AA linear depletion rate (nmol AA min⁻¹) was obtained by plotting AA against time. Depletion rates were considered valid if their coefficient of determination (R²) was higher than 0.95. The mean AA depletion rate of blanks (n=3) was measured and subtracted from sample depletion rates to obtain the oxidative potential (OP_{AA}) of PM₂₀ samples.

2.6 Quality assurance/Quality control

All experiments and analyses, unless otherwise stated, were realized in duplicates. Throughout the article, precision is represented as the standard deviation (SD) of the data. Procedural blanks were added to each experimental set. To verify recovery of trace elements in SLFs during inhalation bioaccessibility extractions, metal solutions (1 mg L⁻¹) were spiked in GS and ALF without soil samples for 24 h. The reference material BGS 102 (Ironstone Soil, d < 40 µm) from British Geological Survey was tested for its total metal content, metal fractionation, inhalation bioaccessibility in GS and ALF and oxidative potential. While this particular reference material presents a coarser granulometry than studied PM samples, it was chosen for comparison with a recent inhalation bioaccessibility study (Guney et al., 2017). SEP metal recovery (%) was assessed by comparing the total digestion value to the sum of all fractions of the SEP.

3. Results and Discussion

3.1 Soil characterization

Complete soil characterization results can be consulted in Appendix A (Table A.1). Soil pH was near neutrality or slightly alkaline (avg. 7.42 ± 0.4) for all study sites. High TC values (i.e. >7%) were observed for samples S1 ($7.2 \pm 0.1\%$), S9 ($7.5 \pm 0.1\%$) and S10 ($7.9 \pm 0.1\%$) but the highest TOC percentages were measured for soils S2 ($2.8 \pm 0.3\%$), S3 ($2.5 \pm 0.3\%$), and S4 ($2.8 \pm 0.3\%$). A broad range of CEC values were observed for studied soils with values spanning from 4.2 to 41.4 meq 100g^{-1} (avg. 20.5 ± 11.8 meq 100g^{-1}). Apart from S1 (6.2 ± 1.4), S9 (8.9 ± 1.0) and S10 (4.2 ± 0.1), with relatively low CEC, all soils presented a CEC higher than 15 meq 100g^{-1} . These values suggest that soil samples, and therefore their associated PM, should efficiently retain cationic metals such as Cu and Zn.

Total metal(loid)s concentrations in CCA-contaminated soils are presented in Appendix A (Table A.2). Values in bold are exceeding Quebec's regulatory limit for industrial land-use (C criterion) (Beaulieu, 2016). Of all studied soils, only S10 presented an As content below the C criterion (50 mg kg^{-1}). Extensive As contamination was observed for S8 ($1372 \pm 51 \text{ mg kg}^{-1}$) (more than 25 times the C criterion) and S7 ($368 \pm 21 \text{ mg kg}^{-1}$). Cu content exceeding the C criterion (500 mg kg^{-1}) was also observed for S7 ($1190 \pm 22 \text{ mg kg}^{-1}$) and S8 ($1046 \pm 18 \text{ mg kg}^{-1}$). As previously reported, Cr contamination was less problematic (Stilwell and Gorny, 1997; Zagury et al., 2003) but soil samples S7 and S8 still contained elevated Cr concentrations (around 500 mg kg^{-1}). The average As, Cr and Cu concentrations of all CCA-contaminated soils were $265 \pm 400 \text{ mg kg}^{-1}$, $165 \pm 182 \text{ mg kg}^{-1}$ and $360 \pm 406 \text{ mg kg}^{-1}$ respectively. This contamination pattern (Cu > As > Cr) corroborates previous results regarding levels of contaminants in CCA-contaminated soils near wood poles in service (Zagury et al., 2003). BGS 102 metal content was also assessed. All values were within $100 \pm 15\%$ of certified values provided by the BGS (Wragg, 2009).

1 **3.2 Particulate matter characterization**

2 Table 1. Physicochemical properties of PM₂₀ samples

PM ₂₀ sample	TC (%)	TOC (%)	PM ₁₀ content (%)	PM ₅ content (%)
P1	9.0 ± 0.1	1.2 ± 7.1	72.3	38.1
P2	7.6 ± 1.4	5.1 ± 3.1	61.8	22.9
P3	6.7 ± 1.5	4.2 ± 1.5	48.8	17.4
P4	4.1 ± 0.5	2.9 ± 0.2	68.6	33.1
P5	8.7 ± 0.3	2.3 ± 0.3	65.3	30.3
P6	6.9 ± 3.0	4.0 ± 0.7	55.4	22.7
P7	7.8 ± 0.5	5.0 ± 2.9	46.4	17.1
P8	12.1 ± 5.3	8.3 ± 1.6	34.1	7.6
P9	9.8 ± 0.1	1.9 ± 0.7	68.3	32.4
P10	6.9 ± 0.0	0.6 ± 3.8	72.2	41.1

3

4 Physicochemical properties of PM₂₀ samples (Table 1) showed that TOC values were
 5 systematically higher in PM samples (avg. 3.5 ± 2.3%) compared to soil samples. P2, P7 and P8
 6 exhibited high TOC values (i.e. >5%). Negative correlations were observed between PM₁₀ ($r = -$
 7 0.92, $p < 0.005$, $n=10$) and PM₅ ($r = -0.96$, $p < 0.005$, $n=10$) content and TOC for studied PM₂₀
 8 samples.

9 The PSD analysis showed that only 3 (P3, P7 and P8) of the 10 studied PM₂₀ samples, presented a
 10 PM₁₀ content below 50%. On average, PM₁₀ and PM₅ represented respectively 59.3 ± 12.8% vol.
 11 and 26.3 ± 10.5% vol. of the studied PM samples. This PSD analysis suggests that GS and ALF are
 12 physiologically-relevant extraction fluids (at least in terms of particle size) to assess inhalation
 13 bioaccessibility of metals in the present study. It should be noted that since total metal

- 14 concentrations in finer fraction are generally higher, bioaccessibility results (expressed as a %)
- 15 obtained using PM_{20} rather than PM_{10} or PM_5 may be overestimated.

Table 2. Total metal(loid)s concentrations of PM₂₀ samples obtained from CCA-contaminated soils

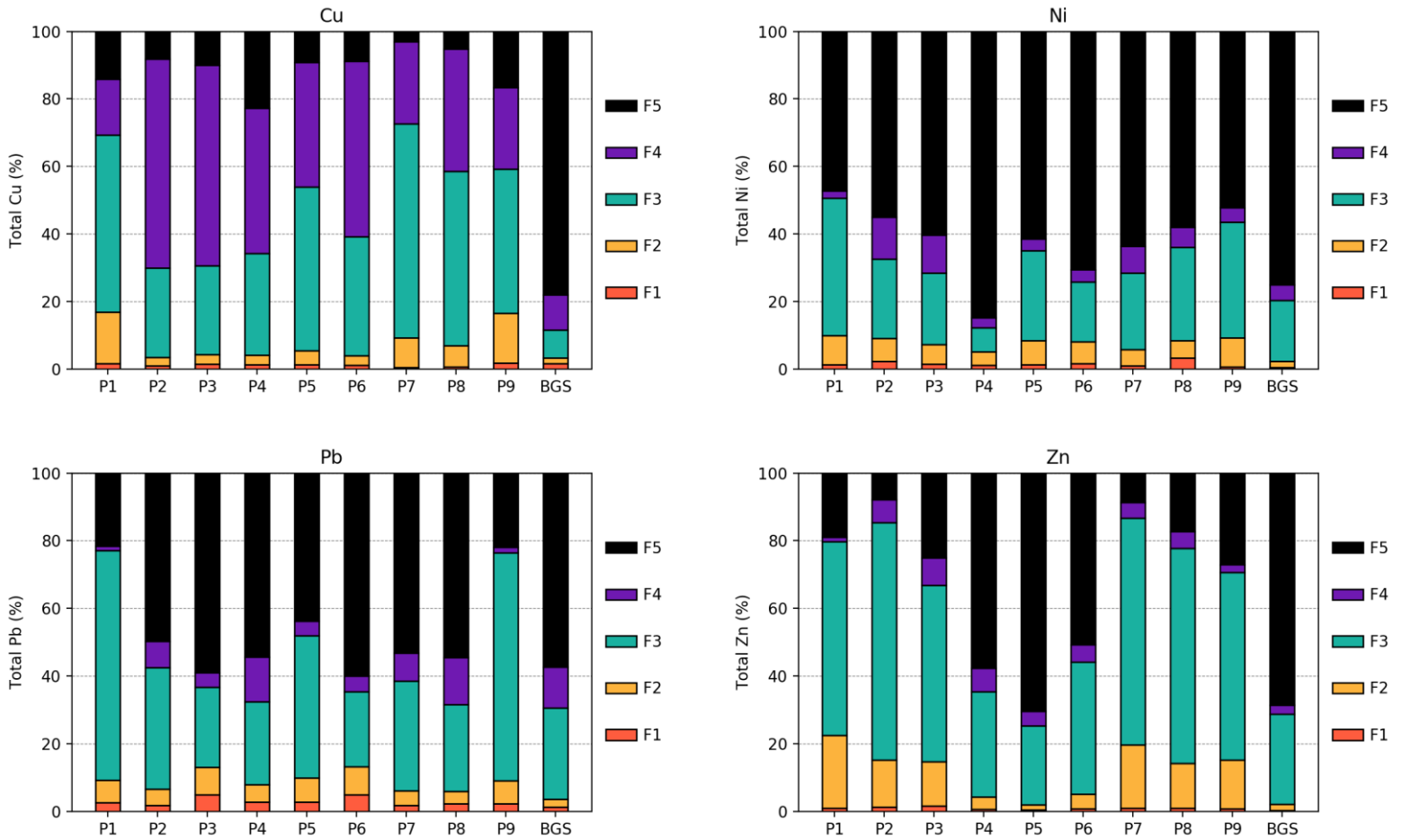
PM ₂₀ sample	As (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Mn (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)
P1	435 ± 3.2	166 ± 1.0	650 ± 28	1.82E+04 ± 9.1E+02	305 ± 1.1	49 ± 0.5	52 ± 2.0	207 ± 1.5
P2	847 ± 106	665 ± 32	454 ± 31	2.98E+04 ± 2.6E+02	594 ± 51	54 ± 3.6	170 ± 7.7	832 ± 26
P3	405 ± 6.2	324 ± 23	402 ± 0.0	3.31E+04 ± 1.3E+03	611 ± 10	53 ± 0.8	47 ± 0.2	259 ± 3.4
P4	167 ± 0.9	228 ± 8.0	188 ± 9.0	3.88E+04 ± 2.0E+03	689 ± 17	44 ± 0.1	89 ± 3.4	205 ± 5.0
P5	340 ± 6.5	121 ± 0.3	448 ± 3.7	2.68E+04 ± 2.4E+03	370 ± 6.6	43 ± 0.1	63 ± 2.1	79 ± 1.1
P6	288 ± 3.0	142 ± 0.5	517 ± 11	2.68E+04 ± 7.0E+02	659 ± 61	41 ± 1.4	49 ± 0.3	160 ± 0.1
P7	2536 ± 89	3815 ± 403	3797 ± 15	3.79E+04 ± 2.4E+02	621 ± 2.7	61 ± 0.4	139 ± 0.8	1058 ± 42
P8	5857 ± 95	2804 ± 94	2906 ± 158	3.79E+04 ± 1.7E+02	534 ± 22	47 ± 1.9	174 ± 2.6	560 ± 0.2
P9	360 ± 4.1	169 ± 2.9	398 ± 4.6	1.73E+04 ± 4.3E+02	384 ± 6.2	50 ± 1.1	65 ± 0.7	131 ± 0.7
P10	59 ± 1.4	65 ± 2.1	148 ± 0.4	1.91E+04 ± 9.6E+02	737 ± 9.3	68 ± 0.6	70 ± 0.4	107 ± 12

18 Total metal(loid)s concentrations in PM₂₀ samples are presented in Table 2. Average metal and
19 metalloid concentrations in PM₂₀ samples were higher than soils for all studied elements. Arsenic
20 ($1129 \pm 1807 \text{ mg kg}^{-1}$), Cu ($991 \pm 1270 \text{ mg kg}^{-1}$) and Cr ($850 \pm 1329 \text{ mg kg}^{-1}$) average
21 concentrations were more than two times higher when compared to their respective soil samples.
22 Soluble As content was also assessed in PM₂₀ and proved to be low for all samples (avg. $0.34 \pm$
23 0.3% , data not shown).

24 An extensive range of contamination levels was observed in PM₂₀ samples, especially regarding
25 As, Cr and Cu. For these elements, P10 presented the lowest values (i.e. $59 \pm 1.4 \text{ mg kg}^{-1}$, 65 ± 2.1
26 mg kg^{-1} and $148 \pm 0.4 \text{ mg kg}^{-1}$, respectively) while P7 showed the highest Cr and Cu content. The
27 highest As contamination was observed in P8 ($5857 \pm 95 \text{ mg kg}^{-1}$). These excessively high levels
28 of As, Cr and Cu contamination in PM₂₀ samples strongly exceed previously reported values for
29 CCA-contaminated soils (Zagury et al., 2003; Pouschat and Zagury, 2006; Girouard and Zagury,
30 2009; Tardif et al., 2018; Deramos King et al., 2019). Such metal(loid)s concentrations in CCA-
31 contaminated PM indicate that even low inhalation bioaccessibility values could entail the
32 solubilisation of health-impacting trace elements doses in the lung environment.

33 Metal fractionation in CCA-contaminated PM₂₀ was determined for Cu, Ni, Pb, and Zn. Even
34 though Ni, Pb, and Zn content (which is not associated with CCA contamination) was low, these
35 metals were studied because of their possible impact on reactive oxygen species production and
36 oxidative potential. An experimental mishap led to the unavailability of metal fractionation for P10.
37 The F1 fraction will be referred as the soluble and exchangeable fraction whereas the (F1+F2)
38 fraction will be referred as the mobile fraction. Metal recovery (i.e. sum of all metal fractions/total
39 metal concentration) of P1 to P9 samples and BGS 102 is presented in Figure A.1. Average
40 recovery was satisfactory (i.e. $100 \pm 20\%$) for all studied elements .

41



42 *Figure 1. Fractionation profiles of metals in PM₂₀ samples obtained from CCA-contaminated soils and BGS 102*

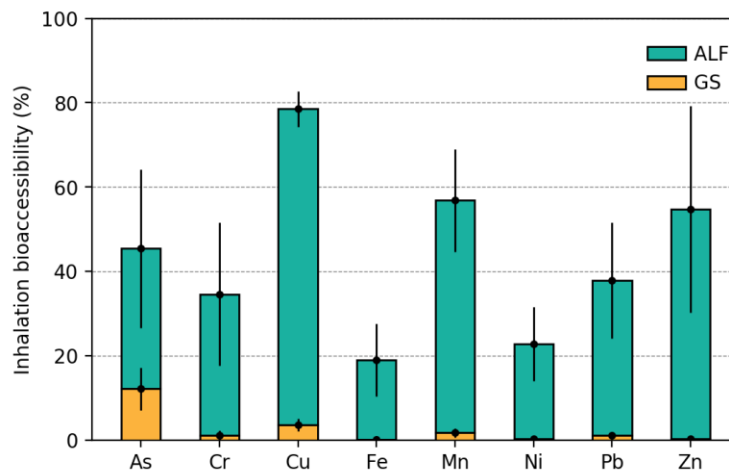
43 At first glance, metal fractionation seems to be metal and sample specific, but a few trends can be
 44 identified. On average, Ni was mostly found in the residual fraction (F5) (avg. $62 \pm 11\%$) and Cu
 45 was the only metal with an important oxidizable fraction (F4) (avg. $39 \pm 16\%$), which suggest a
 46 high affinity of Cu with organic matter. This finding is consistent with previous research on CCA-
 47 contaminated soils (Zagury et al., 2003). Zn was predominantly bound to Fe and Mn oxides (F3
 48 fraction (avg. $51 \pm 16\%$)). Pb exhibited the most important soluble and exchangeable (F1)
 49 (avg. $2.8 \pm 1.2\%$). Copper, Ni, Pb, and Zn fractionation in reference material BGS 102 were also
 50 assessed. Contrary to field-collected samples, all metals were mainly found in the residual fraction
 51 (avg. $70 \pm 9.1\%$). For all samples, metal fractionation values in mg kg^{-1} are presented in Appendix
 52 A (Tables A.3-A.6).

53 **3.3 Inhalation bioaccessibility**

54 **3.3.1 Spiking recovery in SLFs**

55 Spiked trace element solutions (1 mg L^{-1}) were added ($n=3$) to SLFs without PM samples to assess
56 the metal recovery after 24h of extraction (Figure A.2). Satisfactory spiking recovery (i.e. $100 \pm$
57 15%) was observed in ALF for all elements. For GS extractions, satisfactory recovery was obtained
58 for As ($98 \pm 1.1\%$) and Ni ($98 \pm 6.7\%$). Significantly lower, but still acceptable, recovery was noted
59 for Cu ($78 \pm 0.6\%$) and Mn ($74 \pm 7.9\%$). However, low recovery values were obtained for Cr (30
60 $\pm 1.5\%$), Zn ($23 \pm 8.7\%$), Fe ($20 \pm 1.5\%$), and Pb ($2 \pm 1.2\%$). The obtained recovery values for
61 Cu, Ni, Pb, and Zn in GS corroborate previous results (Guney et al., 2017). The low recovery values
62 of Cr, Fe, Pb and Zn should be considered when analyzing inhalation bioaccessibility results. This
63 may hamper the use of GS for the inhalation bioaccessibility assessment of these metals. However,
64 maintaining the pH at 7.4 throughout the experiment might prevent the precipitation of solubilized
65 compounds.

66 **3.3.2 Inhalation bioaccessibility in GS**



67
68 *Figure 2. Metal(loid)s inhalation bioaccessibility in PM₂₀ samples obtained from CCA-contaminated soils (avg. \pm SD)*
69 Considering the aforementioned low recovery of metals when using GS, conclusions cannot be
70 drawn regarding the inhalation bioaccessibility of Cr, Fe, Pb and Zn in PM₂₀ when using GS. Out

71 of the 4 remaining elements (i.e. As, Cu, Mn and Ni), As presented the highest inhalation
72 bioaccessibility in GS ($12 \pm 5.1\%$). A broad range of bioaccessible As values were obtained, with
73 P7 having the lowest ($6.6 \pm 0.3\%$) and P6 the highest ($22.2 \pm 0.2\%$). Cu ($3.6 \pm 1.5\%$) and Mn (1.7
74 $\pm 1.1\%$) both presented low bioaccessibility in GS. All bioaccessible Ni values were below DL
75 when PM₂₀ samples were extracted with GS.

76 The inhalation bioaccessibility of metals and metalloids in BGS 102 using GS was also assessed.
77 For all elements with acceptable recovery, bioaccessibility values were low. Arsenic ($2.3 \pm 0.1\%$)
78 and Cu ($2.2 \pm 2.3\%$) were the most bioaccessible elements followed by Mn ($0.3 \pm 0.0\%$). Nickel
79 concentrations in duplicates were below DL. For each PM₂₀ sample, metals inhalation
80 bioaccessibility values in GS are presented in Appendix A in Tables A.7 (mg kg⁻¹) and A.8 (%).

81 A statistically significant correlation between the soluble and exchangeable fraction (i.e. F1) and
82 bioaccessibility (mg kg⁻¹) in GS was observed for Cu ($r = 0.92$, $p < 0.005$, $n=9$). The near-neutral
83 pH of GS could explain this correlation. This suggests that the amount of Cu found in the F1
84 fraction influences its inhalation bioaccessibility in GS.

85 *3.3.3 Inhalation bioaccessibility in ALF*

86 Trace element inhalation bioaccessibility in PM₂₀ was systemically higher in ALF compared to GS.
87 This has been previously reported by other studies and is generally thought to be caused by ALF's
88 lower pH of 4.5 (Mukhtar and Limbeck, 2013; Guney et al., 2017) and higher/ complexing capacity
89 (Hedberg et al., 2011). This being said, the low recovery values of Cr, Fe, Pb and Zn (without
90 incorporating PM samples) should be considered when analyzing bioaccessibility results obtained
91 using GS. Cu was, by a considerable margin, the most bioaccessible metal in ALF (avg. $78.5 \pm$
92 4.2%). Mn (avg. $56.8 \pm 12.1\%$) and Zn (avg. $54.8 \pm 24.5\%$) also showed a relatively high
93 bioaccessibility in ALF. The broad range of bioaccessibility values in ALF observed for Zn (Fig.
94 2) can be explained by the important inter-sample variation of the mobile (i.e. F1+F2) fraction.

95 Average As bioaccessibility in ALF was slightly lower (avg. $45.4 \pm 18.8\%$) but its known toxicity
96 , carcinogenic nature (Hughes, 2002) and very high total concentration in PM₂₀ samples makes it a
97 major concern regarding the inhalation of CCA-contaminated PM. For each PM₂₀ samples, metals
98 bioaccessibility values in ALF are presented in Appendix A in Tables A.9 (mg kg⁻¹) and A.10 (%).

99 The inhalation bioaccessibility of metals and metalloids in BGS 102 using ALF was consistent with
100 our previously published study for As ($10.8 \pm 0.4\%$), Cu ($26.8 \pm 0.1\%$), Fe ($4.4 \pm 0.2\%$) and Ni
101 ($28.6 \pm 0.1\%$). Higher than previously reported bioaccessibility values were obtained for Mn (74.3
102 $\pm 0.8\%$), Pb ($39.5 \pm 2.8\%$) and Zn ($25.6 \pm 0.5\%$) (Guney et al., 2017).

103 Statistically significant correlations between inhalation bioaccessibility in ALF and the mobile (i.e.
104 F1+F2) metal fraction expressed in mg kg⁻¹ were observed for all metals (i.e. Cu ($r = 0.95$, $p <$
105 0.005), Ni ($r = 0.79$, $p < 0.05$), Pb ($r = 0.92$, $p < 0.005$) and Zn ($r = 0.98$, $p < 0.005$, $n=9$). Witt and
106 co-workers noted a similar correlation for Pb in road dust (Witt et al., 2014). This correlation could
107 be explained by the susceptibility of carbonate-bound metals (i.e. F2) to be solubilized when
108 exposed to acidic environments.

109 ***3.4 Oxidative potential***

110 OP_{AA} was assessed using GS as a physiologically-relevant extraction fluid (Figure 3). Error bars
111 are standard deviation of duplicates except for blank ($n=3$).

112

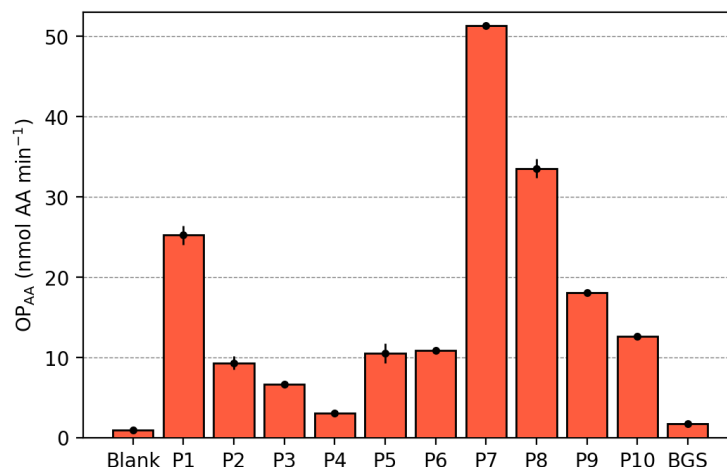


Figure 3. Oxidative potential of PM₂₀ samples obtained from CCA-contaminated soils (avg. ± SD)

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116 PM₂₀ samples obtained from field-collected CCA-contaminated soils induced a statistically
 117 significant depletion of AA (One-way ANOVA, $p < 0.005$). The AA consumption rate of blanks
 118 (0.97 ± 0.1 nmol AA min⁻¹) was about 20 times lower than the average CCA-contaminated PM₂₀
 119 sample (i.e. P1-P10) (avg. 18.1 ± 14.8 nmol AA min⁻¹). A great range of OP_{AA} values can be
 120 observed depending on PM₂₀ samples. P7 (52.3 ± 0.1 nmol AA min⁻¹), P8 (34.4 ± 1.2 nmol AA
 121 min⁻¹) and P1 (26.1 ± 1.2 nmol AA min⁻¹) all induced a significantly higher than average depletion
 122 of AA while P4 (4.0 ± 0.0 nmol AA min⁻¹) and P3 (7.6 ± 0.1 nmol AA min⁻¹) presented significantly
 123 lower values.

124 BGS 102 OP_{AA} was estimated at 1.70 ± 0.2 nmol AA min⁻¹, making it the lowest of all the studied
 125 samples. This result could at first be surprising based on its significant redox-active total metal
 126 loading (Kelly et al., 2007) (Mn (7330 ± 49 mg kg⁻¹), Fe ($1.32E+05 \pm 8E+03$ mg kg⁻¹) and Cr (225
 127 ± 3 mg kg⁻¹)). This being said, the previously highlighted low lability of metals in BGS 102 and
 128 the mineral content of this reference material (Ironstone Soil) could explain this behavior, as non-
 129 soluble metals do not impact OP_{AA}.

130 No significant correlations between TC or TOC with OP_{AA} were observed. Pearson correlations
131 coefficients (r) between individual metal fractions (Total, F1, F2, F1+F2, F3, F4, F5 and inhalation
132 bioaccessibility GS) and OP_{AA} were also calculated. No statistically significant correlations ($p <$
133 0.005) were established for As, Fe, Mn, Ni, Pb, and Zn. However, total Cu ($r = 0.92$, $p < 0.005$,
134 $n=10$), and various Cu fractions presented statistically significant correlations with OP_{AA} with
135 soluble and exchangeable Cu and mobile Cu showing excellent correlation coefficients (F1 Cu (r
136 $= 0.99$, $p < 0.005$, $n=9$), F2 Cu ($r = 0.97$, $p < 0.005$, $n=9$), F1+F2 Cu ($r = 0.97$, $p < 0.005$, $n=9$).
137 Total Cr ($r = 0.88$, $p < 0.005$, $n=10$) also presented a high correlation coefficient with OP_{AA} .
138 Considering the co-occurring nature of Cr and Cu contamination in PM obtained from CCA-
139 contaminated soils, it is difficult to separate the effects of these metals on OP_{AA} . In fact, total Cu
140 concentration is directly correlated with total Cr ($r = 0.99$, $p < 0.005$, $n=10$) in PM_{20} samples.
141 However, taking into account the low spiking recovery of Cr ($30 \pm 1.5\%$) in GS (which was used
142 as the extraction fluid) and the lower Cr bioaccessibility in GS, it is highly probable that Cu was
143 the main factor influencing OP_{AA} of PM obtained from CCA-contaminated soils. Previous studies
144 using ambient PM also highlighted the high sensitivity of the AA assay towards Cu (Janssen et al.,
145 2014; Yang et al., 2014; Calas et al., 2018). Copper is also known to enhance $\cdot OH$ production in
146 the presence of AA (Vidrio et al., 2008). The highly significant correlations observed for F1 and
147 F2 suggest an association between the mobile Cu fractions (F1 and F1+F2) and OP_{AA} . A highly
148 significant correlation between bioaccessible Cu in GS and OP_{AA} ($r = 0.94$, $p < 0.005$, $n=10$) was
149 also observed. This suggests that mobile and bioaccessible Cu fractions should be considered as
150 the main factors influencing OP of PM rather than total Cu content.

151 ***4. Conclusions***

152 This study highlighted possible links between various metal fractions, metal inhalation
153 bioaccessibility and oxidative potential of PM_{20} from CCA-contaminated soils. Even though
154 inherent limitations of dry sieving prevented the obtention of PM_{10} samples, the PSD analysis

155 showed that, on average, PM₁₀ accounted for roughly 60% of studied PM₂₀ samples. A strong
156 correlation between bioaccessibility in ALF and metal mobile fractions was identified for Cu, Ni,
157 Pb and Zn. Copper was the main factor influencing the oxidative potential of particulate matter
158 from CCA-contaminated soils. Its mobile fractions were deemed to play a particularly important
159 role in PM oxidative potential. Significant correlations between Cu bioaccessibility in GS and
160 oxidative potential suggest that these parameters are linked. Nevertheless, obtained results are not
161 enough to conclude on a possible correlation between *in vivo* PM-induced oxidative stress and Cu
162 inhalation bioaccessibility. The use of an *in vitro* cellular OP assay could help verify this
163 assumption in a more biologically-relevant setting. Particulate matter originating from CCA-
164 contaminated soils is considered potentially hazardous to human health in regards of their high As
165 content and significant bioaccessibility in both studied SLF. The elevated Cu content and its
166 apparent role in oxidative processes were also of concern.

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