SCIENCE OF THE TOTAL ENVIRONMENT 407 (2009) 2576–2585

available at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/scitotenv

Arsenic bioaccessibility in CCA-contaminated soils: Influence of soil properties, arsenic fractionation, and particle-size fraction

*Eric Girouard, Gerald J. Zagury**

Department of Civil, Geological and Mining Engineering, École Polytechnique de Montréal, Montreal, Québec, Canada H3C 3A7

ARTICLE DATA

Article history:
Received 28 March 2008
Received in revised form
6 December 2008
Accepted 10 December 2008
Available online 10 February 2009

Keywords:
Arsenic speciation
Oral bioavailability
Bioaccessibility
In vitro
Contaminated soils
Chromated copper arsenate
Soil ingestion
Particle-size

ABSTRACT

Arsenic bioaccessibility in soils near chromated copper arsenate (CCA)-treated structures has recently been reported, and results have shown that soil properties and arsenic fractionation can influence bioaccessibility. Because of the limited data set of published results, additional soil samples and a wider range of soil properties are tested in the present work. The objectives are: (1) to confirm previous results regarding the influence of soil properties on arsenic bioaccessibility in CCA-contaminated soils, (2) to investigate additional soil properties influencing arsenic bioaccessibility, and to identify chemical extractants which can estimate *in vitro* gastrointestinal (IVG) bioaccessibility, (3) to determine arsenic speciation in the intestinal phase of the IVG method and, (4) to assess the influence of two particle-size fractions on arsenic bioaccessibility. Bioaccessible arsenic in eight soils collected near CCA-treated utility poles was assessed using the IVG method. Five out of the eight soils were selected for a detailed characterization. Moreover, these five soils and two certified reference materials were tested by three different metal oxide extraction methods (citrate dithionite (CD), ammonium oxalate (OX), and hydroxylamine hydrochloride (HH)). Additionally, VMINTEQ was used to determine arsenic speciation in the intestinal phase. Finally, two particle-size fractions (<250 μm, <90 μm) were tested to determine their influence on arsenic bioaccessibility. First, arsenic bioaccessibility in the eight study-soils ranged between 17.0±0.4% and 46.9±1.1% (mean value 30.5±3.6%). Using data from 20 CCA-contaminated soil samples, total organic carbon ($r=0.50$, $p<0.05$), clay content ($r=-0.57$, $p<0.01$), sand content ($r=0.48$, $p<0.05$), and water-soluble arsenic ($r=0.66$, $p<0.01$) were correlated with arsenic bioaccessibility. The mean percentage of total arsenic extracted from five selected soils was: HH (71.9±4.1%)>OX (58.0±3.1%)>water-soluble arsenic (2.2±0.5%), while the mean value for arsenic bioaccessibility was 27.3±2.8% ($n=5$). Arsenic extracted by HH ($r=0.85$, $p<0.01$, $n=8$) and OX ($r=0.93$, $p<0.05$, $n=5$), showed a strong correlation with arsenic bioaccessibility. Moreover, dissolved arsenic in the intestinal phase was exclusively under the form of arsenate As(V). Finally, arsenic bioaccessibility (in mg/kg) increased when soil particles <90 μm were used.

* *Corresponding author*. Tel.: +1 514 340 4711x4980; fax: +1 514 340 4477.
E-mail address: gerald.zagury@polymtl.ca (G.J. Zagury).

0048-9697/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2008.12.019

1. Introduction

Natural soil concentrations of arsenic (As) typically range from 0.1 to 40 mg/kg with an average of 5 to 6 mg/kg (WHO, 2001; National Toxicology Program, 2005) and rarely exceed 15 mg/kg in North America (Smith et al., 1998). However, high arsenic concentrations, typically caused by anthropogenic sources, and ranging from 10 to >1000 mg/kg have been observed worldwide (Smith et al., 1998).

Seventy percent of the world arsenic production (WHO, 2001) and ca. 90% of the USA arsenic production is intended for the wood preservation industry (decks, playground equipment, wood poles, etc.) as chromated-copper-arsenate (CCA) (National Toxicology Program, 2005). CCA is an inorganic waterborne wood preservative used to extend the service life of wood, in which arsenic and copper act as the insecticides and fungicides respectively. In North America, the most widely used formulation of CCA is type C, containing (w/w) 47.5% CrO_3, 18.5% CuO and 34% As_2O_5 (Balasoiu et al., 2001). Arsenic in soil and groundwater is a possible threat to humans (Khan et al., 2004), and therefore concerns have been raised over the potential impact of arsenic leachate in soils on human health, particularly children who are most likely to come in contact with soil (Dagan et al., 2006).

In North America, ingestion of drinking water and food is the primary route of exposure to arsenic (Belluck et al., 2003). However, incidental ingestion of As contaminated soil is a significant exposure pathway for children (2 to 6 years old) because of their important hand to mouth activity (Calabrese et al., 1989; Rodriguez et al., 1999; Kwon et al., 2004). In fact, recent studies have shown that incidental ingestion of As-contaminated soil is a major concern (Ljung et al., 2006), and that exposure to As by dermal absorption and inhalation is considered negligible compared to ingestion (Kwon et al., 2004; De Miguel et al., 2007).

Once ingested, the risk for human health is associated with the fraction of arsenic that is available for absorption into systemic circulation (Ruby et al., 1993; Rodriguez et al., 1999). Human oral bioavailability is defined as the fraction of the contaminant that reaches the systemic circulation from the gastrointestinal tract. Bioaccessibility of a contaminant is the fraction that is soluble in the gastrointestinal tract and available for absorption. It is, however, unlikely and impractical that *in vivo* oral bioavailability data would routinely be generated on a site-specific basis. *In vitro* methods are currently recognised as rapid screening tools in assessing relative bioavailability of metals or metalloids at contaminated sites (Ruby, 2004). The *in vitro* gastrointestinal (IVG) method applied on various noncalcinated slags and contaminated soils has been successfully validated for As with *in vivo* tests using juvenile swine (Rodriguez et al., 1999; Basta et al., 2007). Because of the variability of soil properties affecting As retention among soils, As bioaccessibility is expected to vary with sites.

To the knowledge of the authors, only one study has assessed bioaccessibility of As in contaminated soils near CCA-treated wood poles following incidental soil ingestion. Results suggested that As intake from soil ingestion appears negligible compared to the daily intake of inorganic arsenic from water and food ingestion for children (Pouschat and Zagury, 2006). However, this study, performed using a limited data set (12 soils), suggested that As bioaccessibility was systematically higher in coarse-grained soils and in organic soils. Therefore, additional CCA-contaminated soils must be tested to confirm these previous results. Today it is clear that a wider range of soil properties (iron (Fe), manganese (Mn) and aluminium (Al) oxides content, phosphorus content, mineralogy, dissolved organic carbon, etc.) could also influence As bioaccessibility, as reported in numerous studies (Yang et al., 2002; Ruby, 2004; Cave et al., 2007; Juhasz et al., 2007; Sarkar et al., 2007; Wragg et al., 2007). Hence, a strong need exists for further assessment of the influence of soil properties on arsenic bioaccessibility in field-collected CCA-contaminated soils, focusing mostly on arsenic association with metal oxides which has been reported in various studies (Manning and Goldberg, 1997; Manning et al., 2002; Rodriguez et al., 2003; Beak et al., 2006; Palumbo-Roe and Klinck, 2007).

Three extraction methods are typically used to quantify amorphous/crystalline Fe, Mn, Al oxides in soil which can provide an input to estimate As bioaccessibility: hydroxylamine hydrochloride extraction (HH), acid ammonium oxalate extraction (OX) and citrate dithionite extraction (CD). Hydroxylamine hydrochloride is known to dissolve amorphous manganese oxide and iron oxide phases, and to release surficial adsorbed arsenic and some of the arsenic in the mineral matrix (Rodriguez et al., 2003). The extraction capacity of OX is similar to HH (Chao and Zhou, 1983), and has been widely used to dissolve non crystalline forms of iron and aluminum oxides (Carter, 1993). Citrate dithionite extraction dissolves a large proportion of the crystalline iron oxides as well as much of the amorphous materials and the organic complexed iron (Carter, 1993). Citrate dithionite extracted iron oxides (Fe_{CD}) were found to be the most important mineral influencing adsorption of arsenic in soils (Manning and Goldberg, 1997), and arsenic bioaccessibility in contaminated soils has been related to Fe_{CD} (Juhasz et al., 2007).

Another important factor to better understand arsenic bioaccessibility is the knowledge of arsenic speciation in the gastrointestinal tract, especially in the intestinal environment where As absorption across the intestinal membrane occurs. The concern is mainly related to the presence of As(III) because of its higher toxicity compared to that of As(V) (Zagury et al., 2008). Thus, a thermodynamic equilibrium model such as VMINTEQ (Gustafsson, 2006) could be used to model the possible As species present in the intestinal extract from the IVG method.

Particle-size fraction used in *in vitro* methods is generally <250 μm since this fraction adheres more to children's fingers and is thus more available for incidental ingestion (Rodriguez et al., 1999; Yang et al., 2002; Zagury, 2007). A particle-size fraction <250 μm is also used in the standardized *in vitro* extraction protocol published by the Solubility Bioavailability Research Consortium (Kelley et al., 2002). However, some authors report that particles adhering to the skin might be smaller than 250 μm (Duggan et al., 1985; Driver et al., 1989; Kissel et al., 1996; Richardson et al., 2006). Furthermore, previous studies on metal/metalloid oral bioavailability each used a different particle size (<38, <50, <125, <2000 μm): (Hamel et al., 1999; Laird et al., 2007; Ljung et al., 2007; Sarkar et al., 2007; Madrid et al., 2008), while the influence of particle-size on