Speciation, mobilization, and bioaccessibility of arsenic in geogenic soil profile from Hong Kong☆

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ABSTRACT

The behaviour of arsenic (As) from geogenic soil exposed to aerobic conditions is critical to predict the impact of As on the environment, which processes remain unresolved. The current study examined the depth profile of As in geologically derived subsoil cores from Hong Kong and investigated the mobilization, plant availability, and bioaccessibility of As in As-contaminated soil at different depths (0 −45.8 m). Results indicated significant heterogeneity, with high levels of As in three layers of soil reaching up to 505 mg/kg at a depth of 5 m, 404 mg/kg at a depth of 15 m, and 1510 mg/kg at a depth of 27–32 m. Arsenic in porewater samples was <11.5 μg/L in the study site. X-ray absorption spectroscopy (XAS) indicated that main As species in soil was arsenate (As(V)), as adsorbed fraction to Fe oxides (41 −69% on goethite and 0−8% on ferrihydrite) or the mineral form scorodite (30−57%). Sequential extraction procedure demonstrated that 0.5 ± 0.4% of As was exchangeable. Aerobic incubation experiments exhibited that a very small amount (0.14−0.48 mg/kg) of As was desorbed from the soil because of the stable As(V) complex structure on abundant Fe oxides (mainly goethite), where indigenous microbes partly (59 ± 18%) contributed to the release of As comparing with the sterilized control. Furthermore, no As toxicity in the soil was observed with the growth of ryegrass. The bioaccessibility of As was <27% in the surface soil using simplified bioaccessibility extraction test. Our systematic evaluation indicated that As in the geogenic soil profile from Hong Kong is relatively stable exposing to aerobic environment. Nevertheless, children and workers should avoid incidental contact with excavated soil, because high concentration of As was present in the digestive solution (<0.1−268 μg/L).

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1. Introduction

Arsenic (As) contamination has been widely reported in various environmental matrices, including groundwater (Fendorf et al., 2010; Guo et al., 2014; Selim Reza et al., 2010), surface water (Smedley and Kinniburgh, 2002), and soil/sediment (Johnston et al., 2015; Kim et al., 2014). Arsenic contamination of groundwater systems could be caused by Fe (hydr)oxides reductive process induced by microbe or water table change in aquifer-soil-sediments system under anoxic conditions (Fendorf et al., 2010; Smedley and Kinniburgh, 2002), or by the oxidizing process of As-containing sulphide compounds (e.g., orpiment) when exposed to aerobic conditions (Polizzotto et al., 2005).

Recent studies have found high concentrations of As in groundwater in the Pearl River Delta (PRD), with As concentration reaching up to 176 μg/L (Liu et al., 2014; Wang et al., 2012). These high concentrations of As have been caused by microbial reductive process of Fe oxides under reducing conditions (negative Eh, e.g., −126 eV, and high DOC, e.g., 35.8 mg/L) (Wang et al., 2012). The mineral pyrite (FeS_2) found in sediment of the PRD (Wang et al., 2012) and another similar mineral mackinawite (tetragonal FeS) formed during floodplain soil incubation (Burton et al., 2014) play a role in immobilizing As because the iron sulfide compounds can adsorb As under anaerobic conditions and slightly alkaline pH (Niazi and Burton, 2016).

A recent soil survey in the Northeast New Territories of Hong Kong showed high concentrations of As up to 23,400 mg/kg in the

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soil (HK CEDD, 2015). These high levels in the soil may pose a severe risk to the environment. The biogeochemical behaviour of geogenic As in soil exposed to oxygen and the environmental matrix during construction work and soil excavation for urban development remains unclear.

Once soil is excavated for urban development, geogenic As may be released because of the competition to adsorb on Fe oxide sites from various inorganic chemicals, organic compounds, and complex environmental matrices, such as rainwater and plant vegetation (Bergqvist et al., 2014; Cui et al., 2015b; Liu et al., 2016; Youngran et al., 2007). Under high redox levels of 200–500 mV exposed to oxygen, the amount of As released from contaminated soil was low, with arsenate (As(V)) as the major aqueous species (65–98%) (Masscheleyn et al., 1991). When carbon sources including low-molecular-weight organic acids (LMWOAs) such as citrate are present, As(V) can be effectively reduced to arsenite (As(III)) by aerobic As-resistant bacteria harbouring the arsC gene (Corsini et al., 2011; Tian et al., 2015). The reduction from As(V) to As(III) possibly results in high aqueous As because As(III) has a lower affinity than As(V) to Fe (hydr)oxides (Pierce and Moore, 1982; Smedley and Kinniburgh, 2002). Furthermore, As availability can be incresded in As-contaminated soil with vegetation because the root organic exudates facilitate the release of As, which may retard plant growth due to the toxicity of As (Bergqvist et al., 2014; Liu et al., 2016). Excavated soil particles containing As may be incidentally ingested in the human body during construction work, and should be evaluated for As bioaccessibility. Recently, various kinds of polluted soil from mining and smelting sites (Corsini et al., 2011; Kim et al., 2014; Li et al., 2014; Meunier et al., 2010), cattle dip sites using As-based pesticides (Burton et al., 2014; Juhasz et al., 2007; Niazi et al., 2011), and e-waste sites (Cui et al., 2017) have been studied; however, further evaluation is required of the environmental behaviour and mechanism for the release of As from underground geogenic soil.

The above discussed mobilization, plant availability, and bioaccessibility of As is largely determined by As chemical speciation in soil (Foster and Kim, 2014; Kim et al., 2014; Niazi et al., 2011). The general chemical fractions of As in soil can be characterized using a sequential extraction procedure (SEP) (Wenzel et al., 2001) to evaluate the exchangeable and adsorbed species at the macroscopic level. Furthermore, synchrotron-based X-ray absorption spectroscopy (XAS) was also used to in situ characterize the molecular speciation of As in soils, including oxidation states, neighbouring atoms, and local distances (Gräfe et al., 2014; Kelly et al., 2008). The objectives of this study were: (1) to evaluate the potential release and transformation of As; and (2) to elucidate the underlying mechanisms controlling the biogeochemistry of the As in the geogenic soil under aerobic environmental conditions once the soil has been excavated from the subsurface.

2. Materials and methods

2.1. Soil collection

A total of 198 soil samples from 16 soil cores (with a maximum depth at 45.8 m below the surface) were obtained from the Northeast New Territories, Hong Kong, as has been previously reported (HK CEDD, 2015; Li et al., 2017). Hong Kong has humid subtropical weather with an annual average temperature of 23.3 °C and precipitation of 2398.5 mm (Hong Kong Observatory, 2011). The collected soil columns were wrapped using cling film and capped on site, transported to a laboratory, and dismantled in the laboratory as quickly as possible. The sectioned soil samples were passed through a 2-mm sieve, dried at 60 °C until the weights were consistent, ground and mixed homogeneously, and stored in the

dark before being analysed. Parts of the soil columns were transported to the laboratory on ice, and stored at 4 °C until incubation experiments and a spectroscopic analysis could be conducted.

The air-dried samples from different soil columns were divided into three groups according to the total As concentrations of the risk-based remediation goals, including a low level of 21.8 mg-As/kg in urban/rural residential soil, a medium level of 73.5 mg-As/kg in public park soil, and a high level of 196 mg-As/kg in industrial soil (HK EPD, 2007). After homogeneous blending, the soil samples were ground and used in further experiments. The average As concentrations in the three composite soil samples (dry weight) were 55.8 mg/kg (low level), 101 mg/kg (medium level), and 347 mg/kg (high level), respectively (Beiyuan et al., 2017).

2.2. Arsenic mobility and bioavailability in soil

The mobility of the As in soil was measured by aerobic incubation experiments exposed to the environmental matrix at 25 °C in a shaking incubator. The representative soil samples from a depth of 18.9–19.6 m from the collected core-3 (Li et al., 2017) containing 1480 mg-As/kg and 32,100 mg-Fe/kg was used for incubation. The incubation experiments and sampling procedure were performed in triplicate using aseptic techniques. The soil (3 g), which had been stored at 4 °C, was mixed with solutions (40 mL) containing inorganic salts (10 mM KCl, 10 mM $NaNO_3$, or 10 mM Na_2SO_4), organic salts (10 mM sodium acetate or 1 mM sodium salicylate), or synthetic rainwater (Table S1) - conditions that are commonly found in the natural aqueous/soil matrix (Burton et al., 2014; Li and Xu, 2007). Formaldehyde at a concentration of 0.04% was added to the control experiments to inhibit the microbial activities in the soil (Corsini et al., 2011). Because oxygen was being consumed at an unexpected rate, the bottles, which were placed on a sterile bench, were opened to the air every three days. During sampling on 7, 14, and 28 days, suspension samples were collected after the bottles were shaken until the suspension were homogenous, monitored using a pH meter (Model 225 m, Denver Instrument), centrifuged, and filtrated through a 0.2 μm membrane filter. The TOC in the filtrated solution was detected using TOC analyser (SHIMADZU, model: ASI-5000 A). After the aqueous samples were collected, the final centrifuged soil samples were washed three times using a fresh corresponding solution. The remaining solids were freeze-dried under a vacuum for further characterization.

To determine As plant availability, the three kinds of mixed soil samples with different As contamination levels mentioned above were used in the pot experiments. Twelve representative surface soil (<250 μm, 0–0.50 m) samples selected on the basis of the spatial distribution of the sampling cores in the study site (HK CEDD, 2015), which are easily inhaled and ingested by humans, especially children (Juhasz et al., 2007), were evaluated using a simplified bioaccessibility extraction test (SBET) extraction. More detailed information about the pot experiments and the SBET extraction can be found in the supplementary data.

2.3. Sample analysis

The dried soil and plant samples were digested with concentrated HNO_3 and $HClO_4$ on a hot plate (Bergqvist et al., 2014; Li et al., 2004) with the NIST SRM 2711a as a reference for recovery rates for As (105 ± 7%) and Fe (88 ± 3%). Total As and Fe in all of the samples were analysed using ICP-MS (Agilent, 7700 Series) or ICP-OES (Agilent, 700 Series), depending on the concentration. The species of As(III) and As(V) were checked using high-performance liquid chromatography hydride generation atomic fluorescence spectrometry (HPLC-HG-AFS) (Zhang et al., 2013).

Five operationally defined chemical fractions of As in the surface