Fate of arsenic before and after chemical-enhanced washing of an arsenic-containing soil in Hong Kong

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HIGHLIGHTS

- Geogenic As is predominantly present as As^V strongly bound to Fe^{III}-oxides.
- Reductants and alkaline solvents facilitate significant As extraction.
- Yet, residual As displays high leachability, mobility, and bioaccessibility.
- Chemical-enhanced washing is not recommended for geogenic As.

GRAPHICAL ABSTRACT
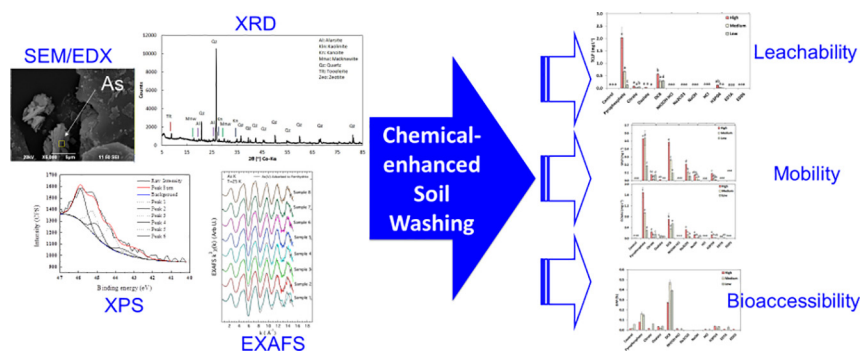
ABSTRACT

This study evaluated the feasibility of 2-h chemical-enhanced washing of As-containing soil resulting from geogenic sources in Hong Kong and the fate of As before and after remediation. The soil morphology and As speciation in soil was elucidated by scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray diffractometer, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy. Integrated analysis of the results suggests that the As (>90%) resides predominantly as arsenate bound to ferric iron oxides, with a minor contribution (<10%) from an As^{III}-sulphide phase. This accounts for the marginal leachability, mobility, and bioaccessibility of geogenic As in the untreated soil despite its high concentration. Among the five types of reagents (organic ligands, reductants, alkaline solvents, inorganic acids, and chelants), only dithionite-citrate-bicarbonate method and alkaline solvents (NaOH and Na_2CO_3) extracted 37–78% and 26–42% of the As by mineral dissolution. However, these extraction methods notably increased the leachability, mobility, and bioaccessibility of remaining As after soil washing, suggesting that a significant proportion of newly released As is prone to re-adsorption onto the soil surface and becomes highly mobile and bioaccessible. While inorganic acids and chelating agents had marginal effects on the fate of remaining As, organic ligands (citrate, oxalate, or pyrophosphate) probably destabilized the bonding of geogenic As and increased its mobility/bioaccessibility despite marginal extraction. The applicability of chemical extraction of geogenic As is questionable regardless of chemical agents, thus proper management of the As-containing soil by containment or physical encapsulation may be considered before land development.

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1. Introduction

Arsenic is toxic and one of the priority pollutants listed by US Environmental Protection Agency. In China, As is one of the major contaminants in soil where over 2.7% the surveyed soil samples exceeded the national standard according to a nationwide land survey conducted in 2014 (Zhao et al., 2015). The anthropogenic sources of As in soils include smelting, mining, coal combustion, use of herbicides/pesticides, use of wood preservatives, and industrial production of steel and glass (Alam et al., 2001). The natural sources for As in soils result from the weathering of primary and secondary As-containing minerals that are associated with sulphur or other ores, such as realgar (α-As_4S_4), arsenopyrite (FeAsS), arsenolite (As_2O_3), and scorodite ($FeAsO_4 \cdot H_2O$) (Smith et al., 1998; Wang and Mulligan, 2006).

Although the As bound with minerals is considered relatively stable, its geochemical behavior depends on the As speciation and redox conditions (Stuckey et al., 2015a). Surface complexes of arsenite are more labile than its oxidized counterpart, arsenate (Kocar et al., 2006; Tufano et al., 2008), whereas As in both exchangeable and amorphous Fe oxides fractions may be available for plant uptake and pose adverse effects on human health (Niazi et al., 2011; Palumbo-Roe et al., 2015). To remove the As from the soil, chemical-enhanced extraction techniques (e.g., soil washing/leaching/flushing and phytoextraction) and immobilization techniques (e.g., stabilization by soil amendments and phytostabilization) are commonly investigated and employed in the field-scale remediation projects (Lestan et al., 2008; Lo et al., 2011; Bolan et al., 2014; Tsang et al., 2014; Beiyuan et al., 2016). Ex-situ soil washing is one of the most suitable technologies because it directly removes contaminants from the soil and minimizes the long-term monitoring requirements. Inorganic acids, alkaline solvents, reductants, organic ligands, salts, chelants, and surfactants are commonly used in the soil washing for extracting metal(loid)s (Dermont et al., 2008; Yan et al., 2010; Voglar and Lestan, 2013; Im et al., 2015).

Proven success of As extraction by chemical-enhanced soil washing has been reported in large-scale applications, such as U.S. Superfund sites (US ACE, 2011), and the latest research studies (Wei et al., 2016: Lee et al., 2017; Wang et al., 2017a). However, after chemical-enhanced washing, the remaining metal(loid)s in the treated soils were destabilized, which resulted in undesirable increase in their mobility and bioaccessibility (Tsang et al., 2013; Beiyuan et al., 2016; Beiyuan et al., 2017a). Kim et al. (2015) showed that As^{III} was re-adsorbed on the newly formed Fe oxides after washing by dithionite, accounting for the enhanced lability of remaining As. Residual lability and change in speciation/distribution of metal(loid)s in the treated soil may arouse environmental concerns, while only a few studies evaluated the fate of remaining As in the treated soils associated with anthropogenic contamination (Tsang et al., 2013; Tsang and Hartley, 2014; Wang et al., 2017b).

Soil minerals play significant roles in affecting the As mobility and bioavailability in soil, especially for the Fe/Mn/Al oxides (Masue-Slowey et al., 2011; Ying et al., 2012; Kim et al., 2014; Lee et al., 2016). To extract As from soil, it is crucial to enhance the dissolution of oxide minerals. Organic ligands, such as pyrophosphate, citrate, and oxalate, can be applied to promote soil mineral dissolution, especially for oxalate that has a mild capacity of reduction (Qiu et al., 2010; Wei et al., 2016). Meanwhile, organic ligands have relatively low impact on the physical, chemical, and biological properties of soil because they can be naturally released by microbes and plants in the rhizosphere. If a high extraction efficiency is needed, chemically aggressive methods using dithionite-citrate-bicarbonate (DCB) or acidified hydroxylamine hydrochloride prove to be effective for dissolving Fe/Mn oxides minerals by reduction (Kim et al., 2015; Beiyuan et al., 2017b). In addition, widely studied synthetic chelants such as EDTA (ethylenediaminetetraacetic acid) and EDDS ([S,S]-ethylenediamine-N,N′-disuccinic acid) can dissolve Fe/Mn-oxides and extract a part of oxide-bound metal(loid)s in soil (Nowack, 2002; Tsang et al., 2009; Yip et al., 2009). Besides, inorganic acids and alkaline

solvents are often employed for As extraction by mineral dissolution and anion exchange in large-scale applications (Jang et al., 2007; Wei et al., 2016). However, nearly all of the studies in the literature were conducted on soils that had been contaminated by anthropogenic sources, such as industrial and agricultural activities. It remains uncertain about the effectiveness of chemical-enhanced washing for soil containing elevated concentrations of arsenic due to geogenic sources as well as the fate of remaining As in the treated soil.

Therefore, this study selected the above five groups of chemical agents for ex-situ washing of As-containing soil resulting from natural geological formations in Hong Kong, China. Besides the extraction efficiency of total As, the treated soil samples were evaluated for the leachability, mobility, and bioaccessibility of remaining As in the soil. The soil morphology and As speciation in soil were also characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS).

2. Materials and methods

2.1. Characterization of geogenic As in soil

Soil samples were collected from Northeast New Territories of Hong Kong, China. Subsamples (every 0.5 m) of 18 boreholes from 0.5 to 35 m below ground surface were analyzed for the concentration of As. The soil columns for individual sample analysis were wrapped using cling film and capped on site, transported to the laboratory on ice, and stored at −20 °C until freeze-drying before microscopic and spectroscopic analysis. According to the risk-based remediation goals (RBRGs) of Hong Kong (HK EPD, 2011), the above samples were divided into three groups based on the As concentrations: high level (i.e., exceeding RBRGs of 196 mg kg^{-1} for industrial land use), medium level (i.e., exceeding RBRGs of 73.5 mg kg^{-1} for public parks), and low level (i.e., exceeding RBRGs of 21.8 mg kg^{-1} for urban/rural residential use), respectively. After grinding, sieving through 2 mm, and homogeneous blending of the individual soil samples into three composite samples for subsequent experiments, the total concentrations of As in the soil samples were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, SPECTROBLUE) after acid digestion by concentrated HNO_3 and $HClO_4$ at a volume ratio of 4:1 (Wong et al., 2002). The three composite samples contained 347, 101, and 55.8 mg kg^{-1} of As, and named as high level (H), medium level (M), and low level (L), respectively. The soil pH values were 4.5 (H), 4.5 (M), and 5.9 (L).

To study the soil characteristics, three individual soil samples (O1, O2, and O3) with high concentrations of As (935, 1366, and 749 mg kg^{-1}) were selected for As speciation analysis. The morphology and elemental mapping of the selected soil samples were studied by SEM-EDX (JEOLJSM-6490), while the crystalline-phase mineralogy of the soil samples were studied by a high resolution powdered XRD (Rigaku SmartLab). The As speciation was investigated by XPS (Kratos AXIS Ultra DLD) equipped with monochromatic Al Kα X-ray. A broad scan was achieved using 50 eV pass energy, while a narrow high resolution scan of As3d was obtained using 20 eV pass energy. The As3d spectra were fitted by a curve-fitting software (XPSPEAK41) and calibrated to the binding energy of C^{1s} at 285 eV. The spectra were fitted by a least-squares procedure with peaks of 20% of the Lorentzian-Gaussian peak shape after subtraction of the Shirley baseline. The sub-peaks were identified by comparison of their binding energies with values collected from literature (NIST, 2012).

The XAS measurements were performed at a beam line of 11-2 at the Stanford Synchrotron Radiation Lightsource, under storage ring conditions of 500 mA current at energy of 3 GeV. The freeze-dried and finely pulverized samples (labelled 1–8) were placed in aluminum holders as pressed powders and held in place using low-density polyamide tape. Energy calibration was done by taking the Au LIII (11,919.0 eV) absorption edge from a standard metal Au foil. The Au Foil spectra were