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Determination of human health risk incorporating experimentally derived site-specific bioaccessibility of arsenic at an old abandoned smelter site

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ABSTRACT

This study was conducted to investigate the contribution of a site-specific bioavailability of arsenic (As) to human health risk at an old abandoned smelter site in Korea. The site was contaminated with As for over 60 years with the same source (As_2O_3 in flue gas), but concentration and *in vitro* bioaccessibility (IVBA) of As differed by operable units (OU), which consequently resulted in difference in estimated risk. Soil samples collected from six OUs showed that *aqua regia*-extractable As concentrations ranged from 9.8 to 52.8 mg/kg (average 34.1 mg/kg) at OUs 1–5, which had been used as rice paddy field and farmland, and a forest region OU 6 showed much higher As concentrations (14.4–169.8 mg/kg, average 85.9 mg/kg). IVBA of As, determined from the ratio of Solubility/Bioavailability Research Consortium (SBRC)-extractable As to *aqua regia*-extractable As had a wide range of values (90th percentile values of 28.2–65.8%). Carcinogenic risk calculated with total soil As concentration was the highest (1.4×10^{-4}) at OU 6 and the risk at the other OUs ranged from 3.8×10^{-5} to 5.7×10^{-5}. In contrast, when site-specific relative bioavailability (*i.e.*, IVBA values) was incorporated, the estimated risk was reduced by 29.5–62.0% and the decrease was the highest at OUs 1 and 5 with the lowest IVBA of 28.2%. The results demonstrate that the chemical forms of As may be different although the source of contamination is similar, and site-specific bioavailability affected by the chemical forms is an important factor in determining human health risk.

1. Introduction

In Korea, we have an old, abandoned smelting site, and arsenic (As) contamination in the vicinity of the site is of a great concern due to its potential adverse human and environmental risk. Arsenic (As) is found in lead (Pb) and copper (Cu) ores in the form of arsenopyrite (FeAsS) and arsenic sulfide (As_2S_3), and it is known that such ores generally contain 2–3% of As (Carapella, 2000). Field investigation of the study site revealed that potential sources of the contamination were arsenic trioxide (As_2O_3) emitted from the smelting stack, dust associated with unattended ores, and field-disposed sludge generated from the smelting process.

The chemical forms and bioavailability of heavy metals, especially As play an important role in determining their toxic effects in soil, rather than the total soil concentration (Kelley et al., 2002; Ruby et al., 1999). Many lines of evidence clearly demonstrate (Bradham et al., 2011; Sarkar et al., 2007; Tang et al., 2007; Wragg et al., 2007; Yang et al., 2002) that chemical forms of As and its bioavailability in soil are closely related to soil properties such as Fe and/or Al content, clay content, and pH, and contamination source, too (Juhasz et al., 2011). According to a broad literature review by U.S. Environmental Protection Agency (USEPA, 2012), relative bioavailability (RBA), reflecting matrix effects, defined as the ratio of absorbed fraction from soil to absorbed fraction from dosing medium used in toxicity studies (Ruby et al., 1999), of As in soils varied greatly depending on As sources and soil properties, ranging from 4.1% to 78%. For this reason, chemical forms and bioavailability of As should be considered to determine a realistic risk for As-contaminated soil (National Research Council, 2003). Thus, it is a crucial step to determine the site-specific RBA of As in contaminated soil for a human health risk assessment.

RBA of heavy metals in soil needs to be determined by *in vivo* testing using surrogate animals, such as swine, monkeys, or mice. Because such tests are expensive and time-consuming, however, many *in vitro* test methods simulating human gastrointestinal

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conditions have been developed to determine *in vitro* bioaccessibility (IVBA) of heavy metals in soil. Among them are the Solubility/Bioavailability Research Consortium (SBRC) method (Kelley et al., 2002), the Physiologically Based Extraction Test (PBET) method (Ruby et al., 1996), and the *In Vitro* Gastrointestinal (IVG) method (Rodriguez et al., 1999). Basically, such methods can be applied to various heavy metals, such as arsenic, lead (Pb), cadmium (Cd), chromium (Cr), and nickel (Ni) (Kelley et al., 2002), and moreover, many studies have demonstrated good linear relationships between RBA and IVBA especially for As and Pb (Basta et al., 2007; Juhasz et al., 2007, 2009b; Rodriguez et al., 1999). In this study, a thorough site investigation was conducted and site-specific IVBA values of As were determined using the SBRC method at the study site, and a site-specific human health risk assessment was performed at an old abandoned smelter site.

2. Materials and methods

2.1. Site characterization

The study site is located in the vicinity of a former smelter, about 180 km southwest of Seoul, Korea. The smelter had been operated from 1936 to 1989 to refine copper and lead ores. The surface soil within the 1.5 km from the smelter stack was found to exceed the Korean soil regulatory level of As (*i.e.*, 25 mg/kg), and thus the Korean Ministry of the Environment (KMOE) purchased the area and evacuated the residents for soil remediation. With permission from the KMOE, in total, six operable units (OUs) were chosen in the purchased area and soil sampling was conducted for this study (Fig. 1). OUs 1–4 were parts of rice paddy fields and OU 5 was farmland, but no cultivation activity is allowed any more at the site. OU 6 is a part of a forest area, still being used as a pine forest therapy park, with trails and a playground. The number of sampling points at each OU was 15–17 and the total number of sampling points was 96. For every 1500 m^2, five soil samples collected at a depth of 15 cm from the surface were combined to make a composite sample for As analysis. The sampling areas were 24,000 m^2 for OU 122,500 m^2 for OU 224,000 m^2 for OU 324,000 m^2 for OU 426,000 m^2 for OU 5, and 24,000 m^2 for OU 6, and the numbers of soil samples were 16, 15, 16, 16, 17, and 16, respectively. The total area investigated for this study was 144,500 m^2, about 12.5% of the whole purchased area (*i.e.*, 1,158,000 m^2).

2.2. Determination of As concentration in soil

To determine total As concentrations in soil samples, the *aqua regia* extraction method (International Standard Organization, 1995), complying with KMOE (2009), was used with slight modifications. Briefly, 3 g of soil was added to 21 mL of HCl and 7 mL HNO_3 in a 100-mL Teflon vessel, and the vessel was slowly heated to 105 °C and maintained for 2 h in a heating block. The digested mixture was then filtered through a 0.45-μm GHP filter for As analysis.

In vitro bioaccessibility (IVBA) of As of each OU soil sample was determined using the SBRC method (Kelley et al., 2002). Briefly, 100 mL of 0.4 M glycine buffer was adjusted to pH 1.5 with concentrated HCl, and 1 g of soil was added to the solution, and the soil solution was shaken at 200 rpm for 1 h at 37 °C. The soil solution was filtered through 0.45-μm GHP filter for As analysis.

Five-step sequential extraction method proposed by Wenzel et al. (2001) was adopted to determine the chemical forms of As in soil. As the first step to extract non-specifically sorbed As fraction, 1 g of soil was shaken with 25 mL of 0.05 M $(NH_4)_2SO_4$ for 1 h at room temperature (fraction 1). The residue was shaken with 25 mL of 0.05 M $NH_4H_2PO_4$ for 16 h at room temperature to extract specifically sorbed fraction (fraction 2). To extract As bound to amorphous Fe oxides (fraction 3), the residue from the second step was shaken with 25 mL of 0.2 M NH_4-oxalate adjusted to pH 3.25 with NH_4OH for 4 h at room temperature in the dark. The fourth step to extract As bound to crystalline Fe oxides (fraction 4), the residue from the former step was extracted with 25 mL of 0.2 M NH_4-oxalate/ascorbic acid adjusted to pH 3.25 with NH_4OH for 30 min at 96 ± 3 °C in the light. The residual fraction of As (fraction 5) was obtained following USEPA method 3052 (USEPA, 1996a). The residue from the fourth step (0.5 g) was with 9 mL of HNO_3, 3 mL of HF, 1 mL of H_2O_2, and 1 mL of H_2O with an aid of microwave (MARS 6, CEM, USA). The sample after each extraction step was centrifuged at 10,000 *g* for 10 min (IEC MULTI-RF, Thermo scientific, USA) and filtered through a 0.45-μm GHP filter for As analysis. The concentrations of As in the extracted solutions were determined by using an inductively coupled plasma-optical emission spectrometer (ICP-730ES, Varian, USA).

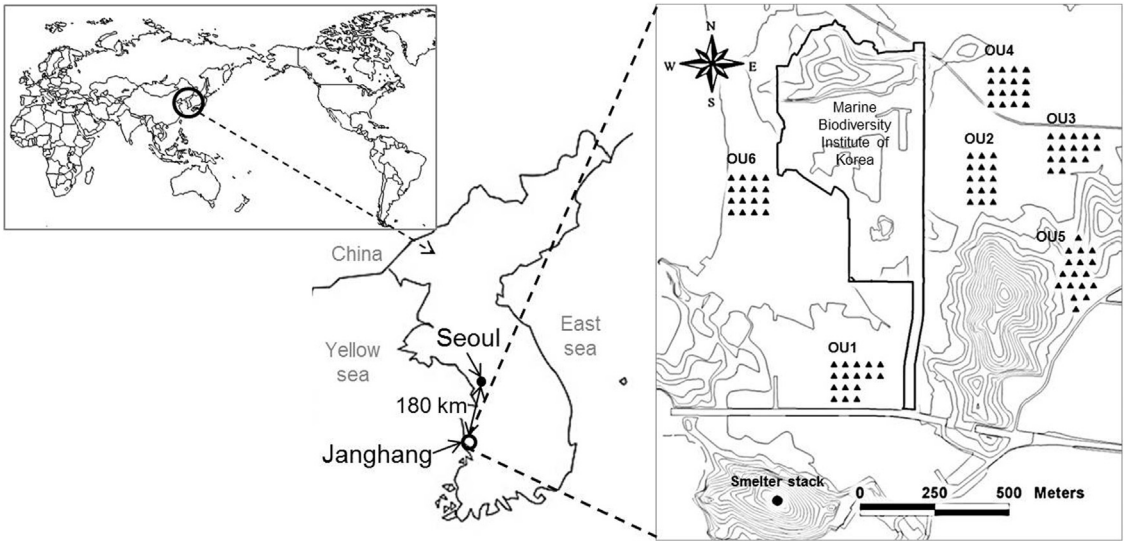

Fig. 1. Soil sampling points (▲) and OUs in the vicinity of the former Janghang smelter located in Korea.