# [Workshop 1] Development of phyto-technology for decreasing heavy metal in food Mechanism and source of arsenic contamination in groundwater in Bangladesh

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Abstract: Naturally occurring contamination of arsenic is of great concern in many Southeast Asian countries especially in Bangladesh. Because of the lack of understanding for the mechanism of As contamination, we have developed two studies through field surveys and laboratory experiments. First topic is focused on the underlying mechanisms controlling large spatial variation of As-contaminated groundwater based on the adsorption reaction. Because adsorption is kinetically first reaction, we hypothesized that groundwater As level for each household well water should controlled by adsorption equilibrium between sediment and water. To verify the hypothesis, we firstly verified adsorption equilibrium using the batch adsorption experiment for the sediment collected from As contaminated region in Bangladesh coupled with solid phase As speciation using X-ray absorption fine structure. The results indicate that dissolved As level is consistent with adsorption equilibrium. We further introduce a new insight to analyze contamination mechanism based on the adsorption equilibrium model. The second topic is the novel approach to identify the ultimate source of As using Sb stable isotope. Although there are enormous numbers of research about arsenic contamination in Bangladesh, the primordial source of arsenic is still unknown. Because arsenic is a monoisotopic element, we cannot discuss this issue using isotope geochemistry of arsenic, which can be a part of the reason why the source of arsenic contamination is unclear. Because of the similar geochemical behavior of As and Sb, we are trying to establish the antimony isotope analysis and verify its applicability to the source analysis of arsenic. Here, two topics: (i) determination method of antimony isotope in natural sample by multicollecter-type ICP-MS, and (ii) verification for the similarity of antimony and arsenic behavior in river water-sediment systems based on a model study around the Ichinokawa antimony mine, is introduced.

Key words: Arsenic, Bangladesh, Groundwater, Adsorption, Source analysis, Antimony isotope

# 1. Introduction

Degradation of groundwater quality has attracted worldwide attention particularly because of increasing dependence on groundwater as a source of water securing for the quality of life. Being different from surface water, remediation of polluted groundwater is quite difficult. In many developing countries, the groundwater problem is particularly serious due to the difficulty to construct the centralized water supply system by economic reasons.

Among various inorganic contaminants, As is recently focused because of its high toxicity and complex geochemical behavior. Arsenic poisoning associating with the consumption of local groundwater and the consequent serious health ailment have been reported from various parts of the world, particularly from Asian countries since late 1980's, e.g. Bangladesh, and West Bengal in India, China, Taiwan, Pakistan, Nepal, Cambodia

and Vietnam (Ravenscroft et al., 2009 and references therein). Despite such a serious situation, the cause of this global pollution is unclear at present due to the lack of any clear sources of As around the polluted region.

The observed health effects of exposure to groundwater As are skin abnormalities and lesions: typically pigmentation changes (e.g., hyperpigmentation) on the upper chest, arms and legs, and keratoses of the palms and soles. Long-term exposure can result in skin cancer and in various types of internal cancer, predominantly cancer of the lung, bladder, and liver (Smith et al., 2000; Karim, 2000; Yu et al., 2003). Yu et al. (2003) predicted that long-term exposure to present As concentrations will result in approximately 1,200,000 cases of hyperpigmentation, 600,000 cases of keratosis, 125,000 cases of skin cancer, and 3000 fatalities per year from internal cancers based on the statistical analysis using the comprehensive dataset of regional distribution of As-contaminated groundwater (BGS and DPHE, 2001) and dose response functions (Mazumder et al., 1998).

It is generally agreed that the As is geogenic, originated from the sediments from the upland Himalayan catchments (e.g., McArthur et al., 2001; Nickson et al., 2000; Harvey et al., 2002). These studies also indicated that the aquifers in Bangladesh do not contain high levels of solid As, and the prevailing of certain chemical condition, which is favorable to mobilize As, is rather important to lead to anomalously high As in groundwater. However, the specific geologic, hydrologic, and geochemical conditions to form As-contaminated groundwater are still unclear.

Because of the lack of understanding for the mechanism of As contamination, we have developed two studies through field surveys in Bangladesh and India, and also laboratory experiments. The objectives of two studies are (i) to clarify the underlying mechanisms controlling large spatial variation of As-contaminated groundwater based on the adsorption reaction, and (ii) to propose the novel approach to identify the ultimate geogenic source of As using Sb stable isotope.

## 2. Mechanism of the As Contamination Based on the Adsorption Equilibrium Approach

In Bangladesh, it is widely recognized that household well waters show a large spatial variation of concentration of As even throughout a small village (van Geen et al., 2003). For example, As concentration in groundwater collected from <30 m of tube-well varied from <1 to  $>1000 \mu$ g/L in the relatively small study area ( $3 \times 3 \text{ km}^2$ ) at Sonargaon, middle east Bangladesh (Itai et al., 2008). This variation creates a difficulty in the design of mitigation strategies. We hypothesized that the concentration of As in each well is controlled by an adsorption–desorption equilibrium between sediment and groundwater. To verify the hypothesis, we have conducted adsorption experiments using the sediment collected from Sonargaon area.

### 2.1. Confirmation of Adsorption Equilibrium by As Speciation and Adsorption Experiment

In order to verify the adsorption equilibrium in the As contaminated aquifer, two factors are focused upon in this study: (i) speciation of As and Fe in the sediment, and (ii) the adsorption properties of As(III) and As(V) to sediment. Sediment core samples were collected from an As-contaminated aquifer at Sonargaon, central eastern Bangladesh. The oxidation states of As and Fe in the sediments determined by X-ray absorption near the edge structure (XANES) showed a distinct redox boundary below 5 m from the ground surface (Fig. 1b), whereas the peak of the concentration of dissolved As is observed below 15 m (Fig. 1a). The apparent distribution coefficient ( $K_d$  =

 $C_{solid}/C_{solution}$ ) of As(V) is always larger than that of As(III) at all the depths (Fig. 1c). A simulated concentrations of As in the groundwater obtained by multiplying the amount of P-extracted As (Fig. 1d) and  $K_d^{-1}$ with considering the oxidation state of As is consistent with the depth profile of As in the groundwater (Fig. 1e). This suggests that the concentration of dissolved As is controlled by an adsorption-desorption equilibrium between sediment and groundwater. Variation in  $K_d$  is primarily controlled by the concentration of Fe oxyhydroxides, whereas surface area is also important for As(III). The discrepancy between the depth of the redox boundary and



the peak of dissolved As is attributed to the difference in the abundance of P-extracted As rather than to a variation of  $K_d$  (Fig. 1f). The adsorption equilibrium model proposed in this study can be applied to the evaluation of the large variation in aqueous As concentration in groundwater from Holocene aquifers.

#### 2.2 A New Insight to Analyze Contamination Mechanism Based on the Adsorption Equilibrium Model

According to the adsorption equilibrium model, only two factors, i.e., concentration of adsorbed As ( $C_s$ ) and apparent distribution coefficient ( $K_d$ ), should be taken into account to explain the dissolved As level in groundwater (Fig. 2). In order to compare the contribution of these factors for the formation of high As groundwater, we determined  $C_s$  and  $K_d$  values of sediment collected from Samta (south-west Bangladesh) as well as the study in Sonargaon. This comparative approach brought us the new insight to analyze the contamination mechanism. Although dissolved As level is similar between two sites, the sediment from Sonargaon is characterized by high  $C_s$  and high  $K_d$ , while the sediment in Samta



Fig. 2: The condition required to form given concentration of dissolved As in groundwater based on the adsorption equilibrium model.

showed low  $C_s$  and low  $K_{d}$ . (Fig. 2) This result indicates that there are different mechanisms to form high As groundwater even if the level of groundwater As is similar.

This finding also gives an important implication for the temporal variation of As in groundwater. Although to investigate the temporal change in As in groundwater is very important to assess the potential chronic effect by As exposure, the trend of temporal change is still controversial despite some monitoring data being available (Cheng et al., 2006 and reference therein). According to the adsorption equilibrium, limited temporal change of dissolved As level is predicted due to the effect of chemical buffering by large amount of adsorbed As.

Simple calculation is conducted to assess the degree of chemical buffering between two sites. In Sonargaon, temporal change in the As level is likely limited due to high  $C_s$  value of sediment (Fig. 3). In Samta, on the other hand, relatively large temporal change is expected because of low buffering capacity derived from  $C_s$  value (Fig. 3). These predictions are consistent with the field observations (Itai et al., 2008; Yokota et al., 2001). Although further study is needed to confirm the causal relation between the degree of temporal change and buffering capacity, our finding gives a potential to predict the future trend of dissolved As level by assessing the  $C_s$  level in sediment.



Fig. 3: Predicted change in the dissolved As concentration in Samta and Sonargaon as a function of  $\Delta K_r$  value.

# 3. Antimony Isotope Study on the Identification of Ultimate Source of As

Although there are enormous numbers of research about arsenic contamination in Bangladesh, the primordial source of arsenic is still unknown. Because arsenic is a monoisotopic element, we cannot discuss this issue using isotope geochemistry of arsenic, which can be a part of the reason why the source of arsenic contamination is unclear. Generally, it is said that chemical property of antimony being congener with arsenic is similar to that of arsenic. Manaka et al. (2007) and Mitsunobu et al. (2006) reported the behaviors of arsenic and antimony in mine drainage water leached from dissolution of sulfide minerals such as realgar (AsS) and stibnite (Sb<sub>2</sub>S<sub>3</sub>) and their behavior in a soil-water system, respectively. According to these reports, antimony shows similar behavior to arsenic under relatively oxidative condition. In addition, antimony has two stable isotopes of mass 121 and 123, which may reflect the source of antimony such as whether antimony originates from sulfide ores or other rocks. Consequently, analysis of antimony isotopes in river water and sediment instead of arsenic may enable us to identify the primordial source of arsenic.

To establish the antimony isotope analysis and its applicability to the source analysis of arsenic, two studies were conducted in 2009. First one is to establish the determination of antimony isotope by multicollecter-type ICP-MS and the method to separate (and enrich) antimony from natural samples from major elements and Sn, the element of which is used as an external standard for the antimony isotope analysis. Second study is to show the validity of the assumption that antimony and arsenic behave similarly in river water-sediment systems. For this aim, we selected a model system in Japan, consisting of Sb-As mine and river systems around the mine. The samples from Himalayas-Ganges River-As contaminated samples from Bangladesh were also recovered in 2008, for which we will apply the antimony isotope analysis, which we have established in the first part of this study.

#### 3.1. Establishment of Antimony Isotope Analysis of Natural Samples

Chemical analysis procedure of antimony isotope in environmental samples is discussed. In order to separate antimony from matrix elements and Sn used as an external standard of isotope analysis, three-step separation consisting of acid digestion + HF-cation exchange + HCl-anion exchange was proposed. The recoveries

of antimony at the first and second experiments are  $102 \pm 1\%$  (n = 3) and  $100 \pm 3\%$  (n = 4), respectively. In all the procedures, high recovery of antimony was achieved. However, it becomes clear that some undesired elements are eluted in column separation such as Fe, Al, Ti, Sn and others. The excess of the amount of sample loading or rinse solution is considered as possible factors. In addition, the experiment using more diluted HF (for example 0.1 N or 0.01 N) is needed. Because HFSEs (Zr, Nb, Hf and Ta) can form stable anionic fluoro-complexes as well as antimony, additional separation of antimony is required if the concentrations of these elements are high in the samples. By anion exchange in HCl medium, the recovery of antimony was generally low even if using various kinds and amounts of the eluant solution. Another method should be developed and connected to acid digestion and HF-cation exchange. Thus, we developed a method suing thiol cotton fiber (TCF) column coupled with elution by HCl. The TCF adsorbs antimony by forming sulfide, which can be eluted using HCl at a certain concentration (e.g., 6 M). To separate antimony from Sn, 3 M of HCl may be appropriate to elute Sn with retention of antimony in the column, which can be eluted subsequently by 6 M HCl.

All of the measurements of the antimony isotope ratio were conducted at Kochi Institute for Core Sample Research using MC-ICP-MS (Thermo Finnigan Neptune; Tanimizu and Ishikawa, 2006). Firstly, the measurement precision was determined by the replicate analysis of antimony standard solution (WAKO and SPEX), which is needed to be corrected by appropriate method (Russel et al., 1978; Russ et al., 1987). The <sup>119</sup>Sn/<sup>117</sup>Sn ratio was used as external standardization for the correction of mass discrimination effect occurring within MC-ICP-MS. As a result of this determination, the measurement precision was 0.4  $\varepsilon$ , which is precise enough to distinguish antimony isotopes of sulfide ores, possible sources of antimony and arsenic, from normal terrestrial materials (Rouxel, 2003).

# 3.2. Studies on the Similarity of the Behaviors of Antimony and Arsenic and Antimony Isotope in a River-Sediment System in Japan

Environmental behaviors of antimony and arsenic in a contaminated river system are mainly discussed in this second study. To use antimony as a tracer of arsenic contamination, the behavior of antimony and arsenic must be the same in environment. Ichinokawa mine, located in Saijo-city (Ehime, Japan) had been one of the largest antimony mines in Japan until 1957. Stibnite (Sb<sub>2</sub>S<sub>3</sub>; antimony trisulfide) was mainly mined, and 16,600 tons of antimony was produced from 1857 to 1900 at the peak productivity of this mine. Although this mine is closed at present, it is expected that antimony and arsenic dissolved from mining waste reach to the downstream, Kamo-river. We collected river waters and stream sediments at respective sites. The concentrations of antimony and arsenic in these samples were measured by ICP-MS. In addition, oxidation-states of antimony and arsenic which control chemical behavior of these elements were determined by HPLC-ICP-MS for river water, and by XAFS for the stream sediment. As a result, it has become clear that chemical behaviors of antimony and arsenic are similar in the contaminated environment originated from sulfide minerals, such as stibnite. Antimony and arsenic in water and sediment are mainly present as pentavalent species, known as thermodynamically stable form in oxic environmet such as in river water (Crecelius et al., 1975). The results of sequential extraction of contaminated river sediment indicated that antimony and arsenic were mainly incorporated in the poorly-crystalline Fe-oxyhydroxide, such as ferrihydrite. Thus, we concluded that As and Sb behave similarly as pentavalent oxyanion and anionic hydroxides  $(Sb(OH)_{6})$ , which adsorb to Fe-oxyhydroxide such as ferrihydrite by the same mechanism by inner-sphere surface complexation (Mitsunobu et al., 2006).

We measured isotope ratios of antimony in environmental samples collected around Ichinokawa-mine by the method presented in the first study. Among them, stibnite, soil water, and river water had different antimony isotope ratios. Because the isotope ratio of stibnite did not differ significantly from non-contaminated background river water, the isotope ratio of stibnite could not be used directly as the data for the source of antimony and arsenic contamination in this case. However, the water samples of Ichinokawa had a high antimony isotope ratio compared to non-contaminated Kamo river (before the confluence with Ichinokawa river), and this high isotope ratio was kept to the downstream of Kamo river after the confluence. The results suggested that we can use this value as a tracer of source of antimony and arsenic contamination.

By the adsorption experiment of ferrihydrite and pentavalent antimony, it was clear that antimony remaining in solution enriched a heavier isotope, and antimony isotope adsorbed to ferrihydrite became lighter. Assuming the simple model of dissolution of antimony from stibnite and of adsorption to ferrihydrite, it is thought that the isotope ratio of river water near the source of antimony was initially close to the isotope ratio of stibnite ( $-0.5 - 1\varepsilon$ ). River water having this value must have reacted with ferrihydrite during the migration of antimony from mine area to Ichinokawa river. As a result of this reaction, the river water may have heavier antimony isotope ratio ( $3.5 - 4.4\varepsilon$ ).

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