

Change in Chemical Species of Arsenic in Groundwater and Surface Water

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Abstract

Groundwater is used for melting snow in several cities in Hokkaido. The mixture of groundwater and melted snow is released to the surrounding rivers. This is an energy-saving system by using higher temperature groundwater. However, if the groundwater contains arsenic (As), the impact of using the groundwater should be evaluated. In this study, the concentrations and chemical species of As in groundwater and surface water in a city were analyzed to evaluate the fate of As-bearing groundwater. The As concentration in groundwater ranged from 23 to 95 µg/L, and the major chemical species of As was dissolved arsenite (As(III)). However, once the groundwater was discharged to the nearby river, the major chemical species of As were changed to suspended one due to the oxidation of ferrous ion coexistent in the groundwater and the subsequent formation of iron precipitate. Thus, the change in chemical species of As is important to evaluate the impact of As on the environment.

Keywords: arsenic, groundwater, chemical species, oxidation

1. Introduction

Arsenic (As) is one of toxic elements, and recently it is well known that naturally occurring As contributes to serious health problems in the world (Acharyya et al., 2000; Akai et al., 2004; Berg et al., 2001; Das et al., 1996; Del Razo et al., 1990; Dowling et al., 2002; Nickson et al., 2002; Smedley and Kinniburgh, 2002; Williams et al., 1996). Groundwater with higher As concentration is used for snow melt in a city. The Quaternary layers of the city lie thick, and the groundwater is rich. In the environmental assessments of the use of the groundwater, the chemical species of As should be evaluated because the toxicity of As depends on its chemical species. Also, evaluating chemical species of As is important to understand the behavior of As in the environment.

In this study, chemical properties, in particular chemical species of As, of groundwater and surface water in the city where groundwater is used for snow melt were investigated by periodic sampling campaigns.

2. Samples and Methods

2.1 Samples

Seven water samples, two groundwater samples (S-1 and S-2) and five surface water samples (TJ, MO, TR, TD, and HA) were taken in the city for analysis. Figure 1 shows the location of sampling points. S-1 and S-2 are groundwater samples. Sample TJ is not affected by groundwater from snow melt pits. The drainage from sampling point of S-1 and the drainage from the other snow melting pits join at the sampling point of HA. The drainage from the sampling point of S-2 and the drainage from the other snow melting pits join at the sampling point of MO. The sampling point of TR is located downstream of the sampling points of TJ and MO.

Groundwater samples were taken once a month from October 2013 to September 2014. Surface water samples were also taken once a month from October 2013 to December 2014.

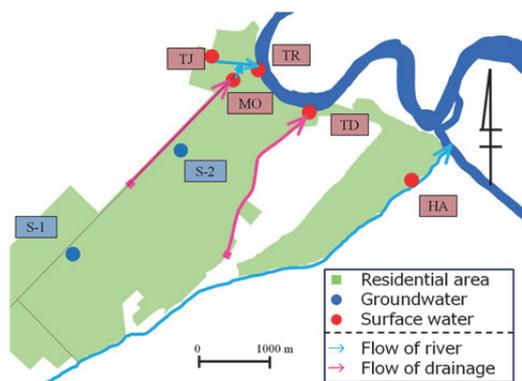


Fig. 1 Location of sampling points

2.2 Analysis of samples

The temperature, pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) of groundwater samples were measured in situ. Only the temperature and EC were measured in situ, and the pH and ORP were measured in the laboratory for surface water samples. Groundwater samples were filtrated with 0.45 μm Millex® membrane filters in situ whereas surface water samples were filtrated with the same filters in the laboratory. This is due to the difference in the redox condition between groundwater and surface water.

Chemical analyses were conducted in the laboratory. Bicarbonate ion (HCO_3^-) concentration was measured by titration with 0.01 mol/L sulfuric acid until pH 4.8. The concentrations of anions (chloride ion (Cl^-), sulfate ion (SO_4^-), and nitrate ion (NO_3^-)) were analyzed by an anion chromatograph (ICS-1000, Dionex Corporation, USA). The concentrations of other elements (sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), and silica (Si)) were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Corporation, Japan). Filtrated samples with 0.45 μm membrane filters were provided for anion analysis. For ICP-AES analysis, 1 or 1.5% hydrochloric acid (HCl) or nitric acid (HNO_3) was added to both original and filtrated samples to dissolve precipitates. For Fe and Si, total and dissolved concentrations were measured. To determine As concentration, hydride generation (HVG-1, Shimadzu Corporation, Japan) attached to ICP-AES was used. Sep-Pak® cartridges (Waters Corporation, USA), were also used to remove As(V) from filtered samples. Thus, As can be divided into three species, dissolved As(III), dissolved total As, and total As including suspended solid. Dissolved As(V) can be calculated by subtracting dissolved As(III) from dissolved total As.

3. Results

3.1 Groundwater

Figure 2 shows changes in the total As concentration of groundwater. The total As concentration changed from 23 to 95 $\mu\text{g/L}$. Figure 3 presents the chemical species of As and Fe of S-2 collected in June 2014. The major species of As was dissolved As(III). The major species of Fe was dissolved Fe. This means that the chemical species of Fe is ferrous ion (Fe^{2+}) by considering the pH range.

The pH of groundwater samples was almost neutral, and the EC was around 20 mS/m. The temperature ranged from 10 to 15 $^\circ\text{C}$, and the Eh was around 150 mV. The major cation was Na of around 20 mg/L. The dissolved Fe concentrations of S-1 and S-2 were around 50 and 20 mg/L, respectively, and the Si concentration was around 20 mg/L.

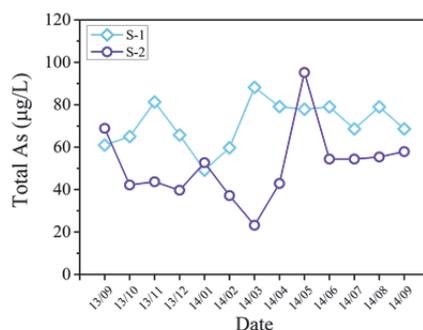


Fig. 2 Changes in total As concentration of groundwater

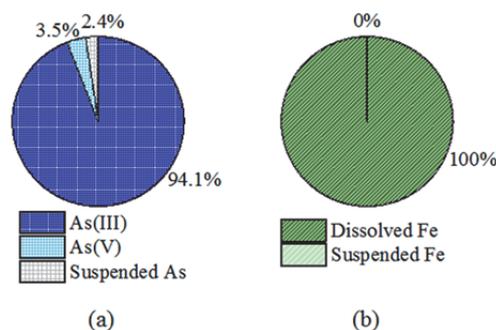


Fig. 3 Chemical species of (a) As and (b) Fe of S-2 collected in June 2014

3.2 Surface water

Figure 4 shows changes in the total As concentration of surface water samples. The total As concentration varied from 2 to 71 $\mu\text{g/L}$. Higher As

concentration was observed in January 2014. Figure 5 presents the major chemical species of As and Fe of HA collected in June 2014. The major species of As and Fe were suspended ones. These results indicate that the higher As concentration is due to the higher suspended solids in surface water.

The pH was almost neutral, and the EC was around 30 mS/m. The Eh varied 200 to 400 mV. The major cations were Na and Ca ranging from 20 to 60 mg/L. The Si concentration was around 10 mg/L.

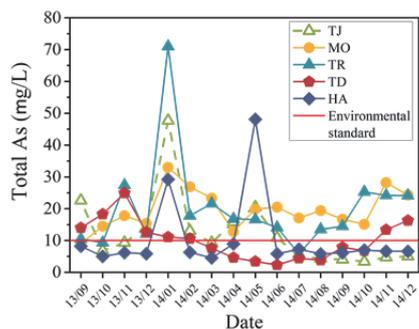


Fig. 4 Changes in total As concentration of surface water

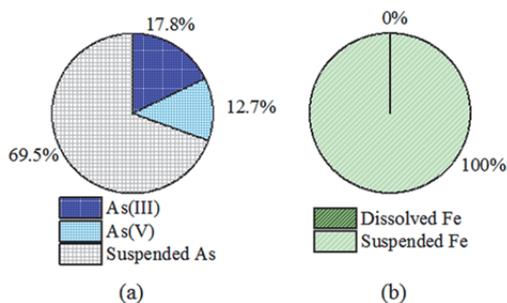


Fig. 5 Chemical species of (a) As and (b) Fe of HA collected in June 2014

4. Discussion

Major chemical species of As in groundwater was dissolved As(III) whereas that in surface water was suspended As. On the other hand, major chemical species of Fe in groundwater was dissolved Fe, that is Fe(II), whereas that in surface water was suspended Fe. These indicate that the dissolved As(III) and dissolved Fe(II) in groundwater were oxidized to dissolved As(V) and Fe(III) once the groundwater flowed into rivers, and that Fe(III) hydroxides were

formed in the river. It is likely that the resultant Fe hydroxides adsorb As or Fe and As coprecipitate because iron hydroxides have a high affinity to As (Tokoro et al., 2001).

Figure 6 shows the relationship between total As concentration and total Fe concentration. There is a positive correlation between total As and total Fe. This relationship implies that Fe plays an important role in As mobility in the aquatic environment.

Environmental assessments of the use of groundwater should be conducted by considering the changes in chemical species of As.

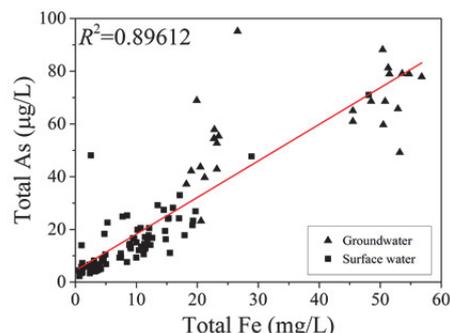


Fig. 6 Total As concentration vs. total Fe concentration

5. Conclusions

The results obtained in this study are as follows:

- (1) The As concentrations in groundwater and surface water ranged 23 to 95 µg/L and 2 to 71 µg/L, respectively.
- (2) The major chemical species of As in groundwater was dissolved As(III) whereas that in surface water was suspended As.
- (3) The major chemical species of Fe in groundwater was dissolved Fe(II) whereas that in surface water was suspended Fe.
- (4) The above results indicate that dissolved As(III) in groundwater is oxidized to dissolved As(V), and then precipitated with Fe hydroxides in surface water.

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