

## ARSENIC RELEASE PROCESSES INTO CONFINED AQUIFERS OF THE SEINO BASINS, NOBI PLAIN, JAPAN

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**ABSTRACT:** To understand the mechanisms of arsenic release from the sediment of the Seino Basins, Nobu Plain, Japan, the present study investigated the characteristics of arsenic dissolution and arsenic phases in the sediments of the G<sub>1</sub> and G<sub>2</sub> aquifers and their upper layers. No significant, direct positive relationship between the total and water-soluble arsenic was found. The results of sequential extraction showed that the main sources of water-soluble arsenic were the non-specifically and weakly bound arsenic phases. In addition, a small portion of the arsenic specifically sorbed on the surface of the sediment was dissolved by water extraction. Multiple regression analyses demonstrated that high pH, total arsenic content, and water-soluble organic carbon (WSOC) content strongly contributed to the enhancement of arsenic release from the specifically bound arsenic fraction. These results suggest that high levels of total and non-specifically bound arsenic are responsible for higher levels of arsenic release. In addition, high pH and WSOC content facilitate arsenic release.

*Keywords: Alluvial Plain, Arsenic Release, Confined Aquifer, Groundwater*

### 1. INTRODUCTION

Arsenic is hazardous to human and animal health. Because of its potential migration into groundwater and subsequent plant uptake, it may also be detrimental to plant growth. High groundwater arsenic concentrations, above the World Health Organization (WHO) standard of 0.01 mg/L, have been observed in many areas of the world, particularly in Asian countries. The Bengal Delta Plain in Bangladesh and West Bengal, India, has been recognized as the most serious case of groundwater arsenic contamination. In this region, serious problems caused by arsenic contamination have risen. It is estimated that in Bangladesh, 20 to 50 million people are at risk from drinking water with a high arsenic concentration [1], and in West Bengal, 180 thousand people were found to have suffered from arsenic poisoning [2]. Therefore, much international and local research has been undertaken to elucidate the mechanisms of arsenic release into groundwater [3]–[5].

Similar to the areas mentioned above, arsenic concentrations exceeding the WHO standard have been found in groundwater from alluvial plains in Japan [6], [7]. One such plain is the Nobu Plain, which is located in central Japan. The Seino Basins that are located in the south-west region of the Nobu Plain have two Pleistocene aquifers: the upper, G<sub>1</sub>, aquifer exists at a depth of 50–80 m and the lower, G<sub>2</sub>, aquifer exists at a depth of 170–200 m. Arsenic concentrations above the WHO standard have been frequently detected in the G<sub>1</sub> aquifer. However, arsenic has not been detected in the G<sub>2</sub> aquifer despite the upper layer of both aquifers (a sedimentary layer

accumulated during the Pleistocene age) containing arsenic-contaminated sediment.

The observation of high arsenic concentrations in such sedimentary aquifers provides impetus for research focused on the sources of arsenic and the mechanisms of arsenic release. In many cases, including the Seino Basins, the minerals that compose the sedimentary layer are considered to be the most probable sources of dissolved arsenic in groundwater [8]. The mechanisms of arsenic release into groundwater have been studied by many researchers, e.g., the oxidation of arsenic-containing sulfide [2], [9] and the dissolution of sorbed iron hydroxide arsenic [10], [11]. In addition, the chemical characteristics of groundwater such as pH [12], phosphate ion concentration [12], bicarbonate ion concentration [13] affect arsenic dissolution.

Arsenic release greatly depends on the site characteristics; therefore, the mechanisms of arsenic release at one site may not be applicable to another. For some alluvial plains in Japan, arsenic release mechanisms have been proposed [7], [14]; however, little information is available on arsenic release at the Seino Basins [8], [15]. In particular, it is not understood why high arsenic concentrations are detected in groundwater from the G<sub>1</sub> aquifer, but not from the G<sub>2</sub> aquifer.

The present study investigated the characteristics of arsenic dissolution and arsenic phases in the sediments of the G<sub>1</sub> and G<sub>2</sub> aquifers and their upper layers, using samples from boring cores. The aim of the study was to elucidate the reasons why arsenic is released into the G<sub>1</sub> aquifer but not the G<sub>2</sub> aquifer.

## 2. MATERIALS AND METHODS

### 2.1 Study Area and Sample Preparation

This study was conducted using sediment samples from boring cores, which were collected from the Seino Basins located at 35° 9' 37" N and 136° 39' 56" E in Kaizu, Gifu prefecture, Japan. The following eight sediment samples were selected for chemical analysis: the Nobi layer at depths of 46 and 52 m, the G<sub>1</sub> aquifer at depths of 60 and 64 m, the Atsuta layer at depths of 167 and 173 m, and the G<sub>2</sub> aquifer at depths of 180 and 184 m. The sediment samples of the Nobi and Atsuta layers were mainly composed of silt and clay; in contrast, those of the G<sub>1</sub> and G<sub>2</sub> aquifers were sand and gravel. The samples were air-dried and passed through a 2- or 0.45-mm sieve prior to analysis.

### 2.2 Water-Soluble and Total Arsenic Contents and Arsenic Phases by Sequential Extraction of Sediment

Total water-soluble arsenic in the sediment samples was extracted using ultra-pure water (1:10 solid/liquid ratio). The inorganic and organic arsenic fractions in the water extraction were determined because arsenic behavior was considered likely to differ markedly between these fractions. The fractions were separated by a permeable membrane with a molecular weight cut off of 1,000 (Spectra/Por 7, SPECTRUM). Arsenic concentrations in the total and organic fractions of the water extraction were measured, and the inorganic arsenic concentration was calculated by difference. The total arsenic content of the sediment sample was determined by acid microwave digestion with 14.5 M HNO<sub>3</sub> and 12 M HCl. Sequential extraction was performed on the sediment sample following the procedure described in Wenzel et al. [16]. A 1.0 g, < 0.425-mm sample was extracted with 25 ml of 0.05 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution (non-specific phase). The sediment remaining after the first extraction procedure was extracted with 25 ml of 0.05 M (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> solution (specific phase). The sediment remaining after the second extraction was further extracted with 25 ml of

0.2 M NH<sub>4</sub>/oxalate buffer at pH 3.25 by shaking for 4 h in the dark (amorphous Fe/Al oxide bound phase). The sediment remaining after the third extraction was extracted with 0.2 M NH<sub>4</sub>/oxalate buffer including 0.1 M ascorbic acid at pH 3.25 in a 95 °C water bath with occasional agitation (crystalline Fe/Al oxide bound phase). The remaining sediment was then digested with 5 ml HNO<sub>3</sub> and 2 ml 30% H<sub>2</sub>O<sub>2</sub> using a microwave oven, and diluted in a 50 ml measuring flask (residual phase). All extracted or digested solutions were passed through a 0.45-μm filter. The arsenic concentrations of the water soluble fraction were measured by inductively coupled plasma mass spectrometry (ICP-MS; 7500cx, Agilent Technologies Inc., USA), and those of the remaining fractions by ICP atomic emission spectrometry (ICP-AES; ULTIMA2, HORIBA Ltd., Japan) equipped with a hydride generator.

### 2.3 Chemical Properties of the Sediment

The pH and water-soluble organic carbon (WSOC) content were determined in the same solution used for water-soluble arsenic, using a pH meter (MM-60R, DKK-TOA Co., Japan) and a total organic carbon (TOC) analyzer (TOC-V<sub>WS</sub> Shimadzu Co. Japan), respectively. The amorphous and crystalline forms of metals in the sediment samples were extracted according to the method of Shuman [17], and the iron, manganese, and aluminum concentrations were measured by ICP-AES.

## 3. RESULTS AND DISCUSSION

### 3.1 Water-Soluble, and Total Arsenic Contents, and Arsenic Phases by Sequential Extraction of Sediment

The highest water-soluble arsenic concentration (0.64 mg/kg) was found in the sediment sample of the Nobi layer at a depth of 52 m. The second highest was found in the sediment sample of the G<sub>1</sub> aquifer at a depth of 64 m (Fig. 1a). In the sediment samples of the G<sub>2</sub> aquifer at depths of 180 and 184 m, a relatively high level of water-soluble arsenic was observed;

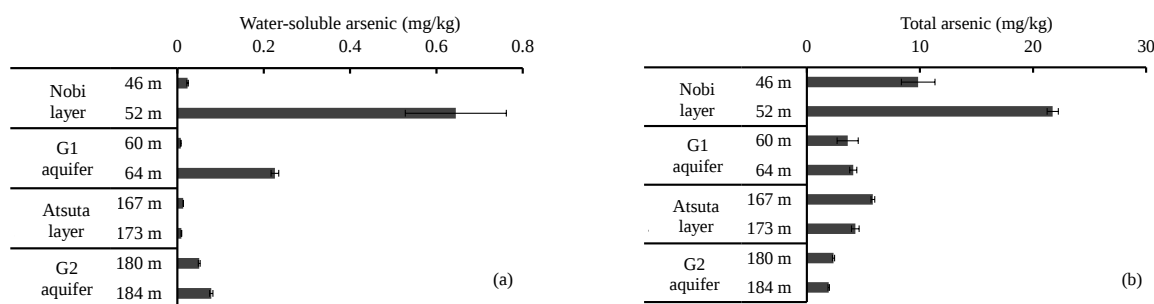


Fig. 1 Water-soluble (a) and total (b) arsenic contents in sediment sample.

however, these values were less than 0.1 mg/kg, the equivalent value of the Japanese environmental standard (converted using the standard value of 0.01 mg/L and the solid/liquid ratio of the water extraction). The total arsenic contents in the sediment samples of the Nobi layer, particularly at a depth of 52 m, were higher than those in the other sediment samples (Fig. 1b). The total arsenic contents in the sediment samples of the G<sub>1</sub> aquifer, the Atsuta layer, and the G<sub>2</sub> aquifer ranged from 1.9 to 5.8 mg/kg. The relationship between the total and water-soluble arsenic contents was investigated, and the result is shown in Fig. 2. When all the samples were included, a significant relationship was found ( $r^2 = 0.716^{**}$ ). However, if the highest concentration sample (open circle in Fig. 2) was excluded, no relationship was found. These results indicate that arsenic release from the sediment was not fully explained by total arsenic content, and that physicochemical characteristics and arsenic phases in the sediment likely controlled arsenic release. The percentage of organic and inorganic arsenic in the water extractions is shown in Fig. 3. The percentage of organic arsenic differed greatly among the sediment samples, ranging from 1 to 68%. In addition, it was not significantly related to the total amount of water-soluble arsenic ( $r^2 = 0.001$ , data not shown). The water-soluble organic arsenic would be easily desorbed from the surface of the sediment because the complexation of arsenic with organic matter enhances its mobility [3], [18], [19]. However, the poor relationship between the total amount of water-soluble arsenic and the percentage of water-soluble organic arsenic suggests a low

contribution of arsenic-organic matter complexation to arsenic release in this study.

Figure 4 shows the arsenic contents of the various fractions in the sequential extraction. The average recovery ratio, which is defined as the ratio of the sum total of each fraction after sequential extraction to the total arsenic content in the sediment sample, was  $88 \pm 13\%$ . In all samples, except those of the Atsuta layer, the dominant fraction in the sequential extraction was the amorphous Fe/Al oxide bound fraction, in which arsenic concentrations ranged from 1.44 to 8.86

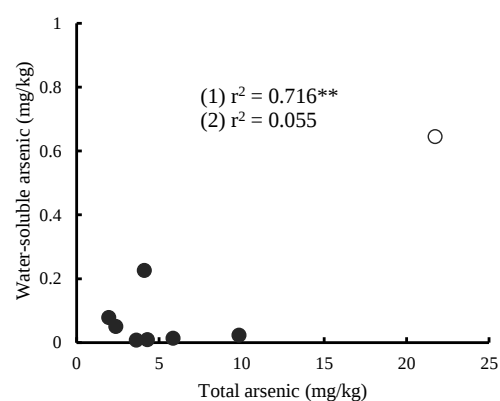


Fig. 2 Relationship between total and water-soluble arsenic contents in sediment sample. A correlation coefficient (1) was evaluated including all the samples. A correlation coefficient (2) was evaluated in the case of removing an open-circled plot.

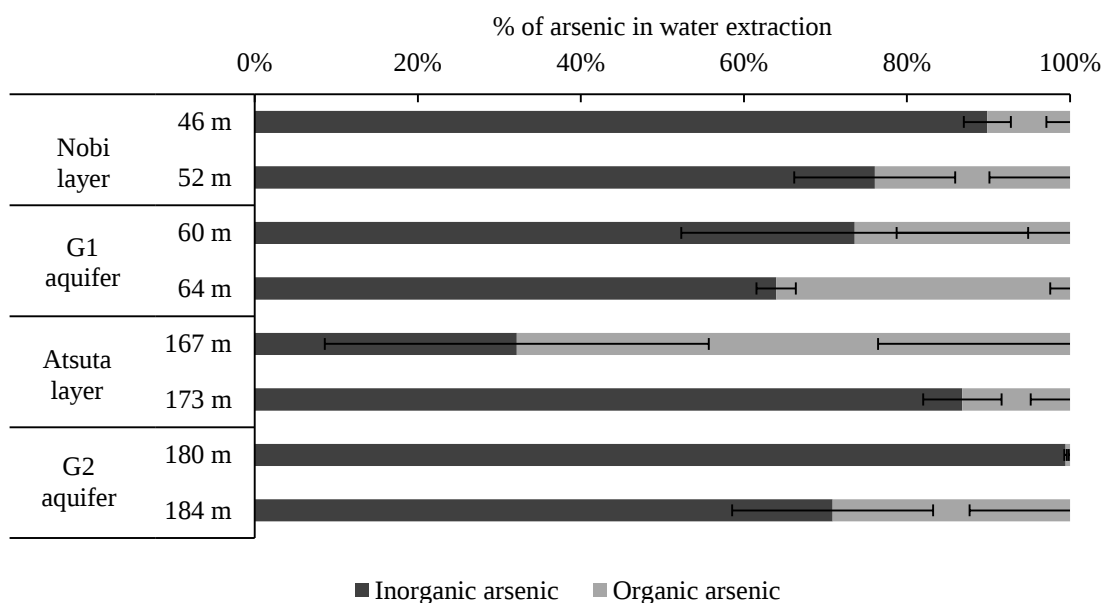


Fig. 3 Percentage of inorganic and organic arsenic fraction in water extraction of sediment sample.

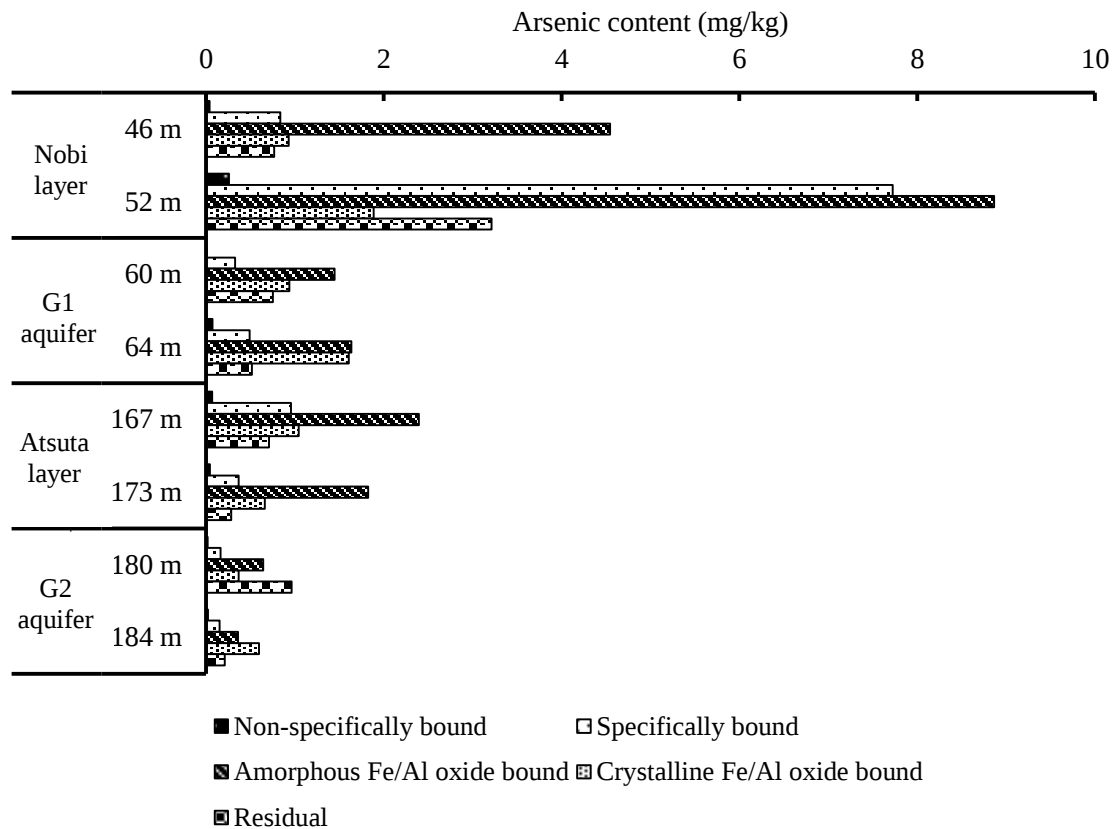


Fig. 4 Sequential extraction of arsenic from sediment sample.

mg/kg. The non-specifically bound fraction, which is the most soluble fraction, showed relatively low arsenic content, 1% or less of the total arsenic content. Figure 5 shows the relationship between the amount of non-specifically bound arsenic and the amount of water-soluble arsenic in the sediment samples. In some samples, which are shown under the broken line, the amount of water-soluble arsenic was lower than the amount of non-specifically bound arsenic, demonstrating that the main sources of water-soluble arsenic were the non-specifically and weakly bound arsenic phases on the surface of the sediment. However, in other sediment samples, shown above the broken line, the amount of water-soluble arsenic was higher than that of the non-specifically bound fraction, indicating that a small amount of arsenic that was specifically sorbed on the surface of the sediment was dissolved during the extraction at the same time as non-specifically sorbed arsenic was released. Specifically sorbed arsenic can be desorbed by changes in chemical properties of the sediment such as pH, redox condition, and dissolved organic carbon (DOC) concentration [3], [12], [19]. Therefore, the chemical properties of such sediments would lead to an enhancement in the release of arsenic from specifically sorbed phases. In the following section, we investigated the relationship between the amount

of water-soluble arsenic and the chemical properties of the sediment samples.

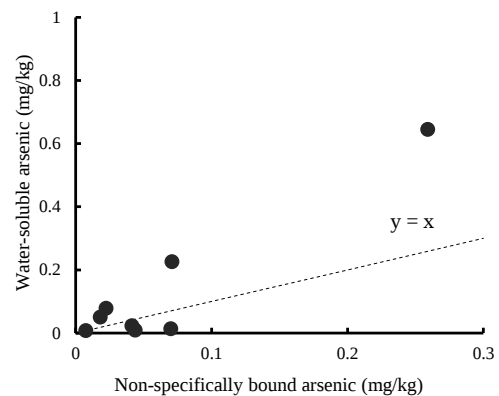


Fig. 5 Relationship between non-specifically bound and water-soluble arsenic contents in sediment sample. A broken line indicates  $y = x$ .

### 3.2 Chemical Characteristics of Sediment Sample

Values of pH in the sediment samples are shown in Table 1. The pH values of the G<sub>2</sub> aquifer at depths of 180 and 184 m were higher than those of the G<sub>1</sub> aquifer at depths of 60 and 64 m, respectively. Similarly, the pH values of the Atsuta layer at depths of 167 and 173 m were higher than those of the Nobi layer at depths of 46 and 52 m, respectively. These results suggest that arsenic would be released more readily from the sediment of the Atsuta layer and the G<sub>2</sub> aquifer compared with the sediment of the Nobi layer and the G<sub>1</sub> aquifer because higher pH induces an increase in the surface net negative charge of sediment, which leads to desorption of oxyanions such as arsenate and arsenite [20]. Figure 6 shows the WSOC contents of the sediment samples. The highest WSOC content of 735 mg/kg was observed in the Nobi layer at a depth of 52 m, and the second highest values were in the Nobi layer at a depth of 46 m and the G<sub>2</sub> aquifer at depths of 180 and 184 m. In the other samples, the WSOC content ranged from 33 to 49 mg/kg. The presence of DOC can enhance arsenic release due to the competition for sorption sites [18], [20]; thus, high WSOC concentrations likely induce arsenic release. The amorphous and crystalline metal contents of the sediments are summarized in Table 2.

Table 1. pH of sediment sample.

|                        | Depth (m) | pH      |
|------------------------|-----------|---------|
| Nobi layer             | 46        | 4.4±0.0 |
|                        | 52        | 6.1±0.2 |
| G <sub>1</sub> aquifer | 60        | 6.3±0.1 |
|                        | 64        | 7.2±0.1 |
| Atsuta layer           | 167       | 5.9±0.0 |
|                        | 173       | 6.4±0.1 |
| G <sub>2</sub> aquifer | 180       | 7.2±0.1 |
|                        | 184       | 8.6±0.7 |

These greatly depended on the metal species and the depth of the sample, particularly for amorphous iron and crystalline aluminum. However, no significant, positive correlations between the amount of water-soluble arsenic and these chemical properties were found (data not shown). Therefore, the multiple regression analysis between water-soluble arsenic content and the chemical characteristics and total arsenic content of the sediment samples was conducted using forward and backward selections for the choice of explanatory variables to identify the most influential chemical properties on the enhancement of arsenic release. The model fitting was evaluated by determining the *t* value of each variable, the coefficient of determination, the *F* value, and Akaike's information criterion (AIC); the parameters obtained from these analyses are listed in Table 3. According to the results of the analyses, sediment pH, total arsenic content, WSOC, amorphous iron, and crystalline aluminum were extracted as the variables. However, the sensitivity (calculated by dividing coefficient by average value of variable), where a higher sensitivity indicates a greater contribution to the model, was not high for all variables. The sediment pH showed the highest sensitivity; second was total arsenic content, and third was WSOC. These results demonstrate that these

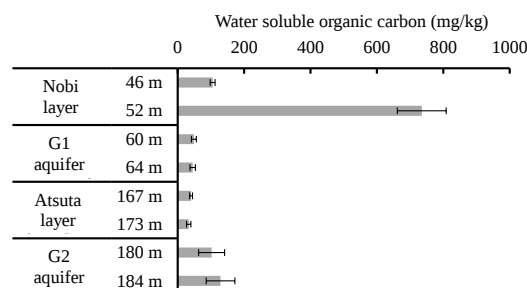


Fig. 6 Water soluble organic carbon in sediment

Table 2. Amorphous and crystalline metal contents of sediment sample (mg/kg).

|                        | Depth (m) | Amorphous  |         |          | Crystalline |        |          |
|------------------------|-----------|------------|---------|----------|-------------|--------|----------|
|                        |           | Fe         | Mn      | Al       | Fe          | Mn     | Al       |
| Nobi layer             | 46        | 7875±740   | 378±37  | 1488±72  | 10552±1335  | 165±19 | 4758±626 |
|                        | 52        | 4648±424   | 100±7   | 1380±38  | 13419±811   | 226±16 | 8576±560 |
| G <sub>1</sub> aquifer | 60        | 2638±163   | 63±8    | 383±40   | 8305±398    | 101±4  | 1907±163 |
|                        | 64        | 1431±120   | 66±23   | 153±124  | 6905±214    | 96±2   | 1046±47  |
| Atsuta layer           | 167       | 4089±569   | 256±97  | 685±44   | 10345±967   | 148±8  | 4160±327 |
|                        | 173       | 8392±556   | 467±31  | 1060±75  | 7945±287    | 161±7  | 2564±171 |
| G <sub>2</sub> aquifer | 180       | 4449±1098  | 374±130 | 443±24   | 5414±285    | 109±6  | 1437±93  |
|                        | 184       | 10099±1955 | 299±97  | 1706±120 | 5473±230    | 103±5  | 1736±140 |

Table 3 Multiple regression analysis between water-soluble arsenic and chemical characteristics in sediment.

|                                       | Coefficient | <i>t</i> value | Sensitivity <sup>1)</sup> |
|---------------------------------------|-------------|----------------|---------------------------|
| Intercept                             | -0.2845     | -2.017         | -                         |
| pH                                    | 0.0492      | 2.771          | $7.56 \times 10^{-3}$     |
| Total arsenic                         | 0.0323      | 3.384          | $4.81 \times 10^{-3}$     |
| WSOC                                  | 0.0005      | 2.541          | $3.23 \times 10^{-6}$     |
| Amorphous iron                        | -0.0001     | -2.488         | $-1.80 \times 10^{-8}$    |
| Crystalline aluminum                  | -0.0001     | -2.205         | $-3.10 \times 10^{-8}$    |
| Coefficient of determination          | 0.9522      |                |                           |
| Adjusted coefficient of determination | 0.9389      |                |                           |
| <i>F</i> value                        | 71.66       |                |                           |
| AIC                                   | -135.96     |                |                           |

1) Coefficient/average

three variables mainly induced the enhancement in release of water-soluble arsenic from the sediment.

As mentioned in the previous section, a portion of the specifically-bound arsenic phase was water-extractable, although the main source of water-soluble arsenic was the non-specifically bound fraction. Samples having a higher level of water-soluble arsenic than non-specifically bound arsenic were found at depths of 52, 64, 180, and 184 m (Figs. 1a and 5). At 52 m, the high total arsenic and WSOC contents would be responsible for the high level of water-soluble arsenic. However, the level of water-soluble arsenic in the sediment sample at 46 m was low, even though the levels of total arsenic and WSOC were high. This can be explained by the low pH of the sediment sample at a depth of 46 m (Table 1), because arsenic sorption on sediment surfaces increases at low pH [20]. The second highest level of water-soluble arsenic was found in the sediment sample at a depth of 64 m, whereas total arsenic and WSOC contents here were comparable to other low-level samples. The pH of the sediment sample at 64 m was 7.2 (Table 1), and this relatively high pH likely led to an enhancement in the level of water-soluble arsenic. The levels of water-soluble arsenic in the sediment samples of the G<sub>2</sub> aquifer at depths of 180 and 184 m were also relatively high, but were lower than the Japanese environmental standard. Despite the high pH and WSOC content potentially enhancing the level of water-soluble arsenic, the low total and non-specifically bound arsenic contents would lead to its suppression, resulting in the preservation of a relatively low level of water-soluble arsenic.

In the Seino Basins, arsenic is detected at levels higher than the Japanese environmental standard in

groundwater from the G<sub>1</sub> aquifer, but is not detected in the G<sub>2</sub> aquifer. As mentioned above, this study demonstrates that non-specifically bound arsenic was the main source of water-soluble arsenic, and chemical characteristics such as pH, WSOC, and total arsenic content in the sediment caused specifically bound arsenic to become water-soluble. Therefore, the results suggest that in the sediment of the Nobi layer and the G<sub>1</sub> aquifer, the high levels of total and non-specifically bound arsenic (as compared with those of the Atsuta layer and the G<sub>2</sub> aquifer, respectively), are responsible for a higher level of arsenic release. In addition, high pH and WSOC content would facilitate the release of arsenic from the specifically bound fraction in the Nobi layer and the G<sub>1</sub> aquifer. This study used only a small number of sediment samples; therefore, in future work, numerous samples should be used to gain a more complete understanding of arsenic release from sediment in the Seino Basins.

#### 4. CONCLUSION

The present study investigated the characteristics of arsenic dissolution and phases in the sediment of the G<sub>1</sub> and G<sub>2</sub> aquifers and their upper layers, the Nobi and Atsuta layers, respectively, in order to understand the mechanism of arsenic release from the sediment in the Seino Basins, Nobi Plain, Japan. A high level of water-soluble arsenic (over 0.1 mg/kg) was found in the sediment samples of the Nobi layer and the G<sub>1</sub> aquifer, but not in those of the Atsuta layer and the G<sub>2</sub> aquifer. No significant, direct positive relationship between total and water-soluble arsenic contents was found. In some sediments, the amount

of water-soluble arsenic was lower than that of the non-specifically bound fraction, demonstrating that the main source of water-soluble arsenic was the non-specifically and weakly bound arsenic phases. However, in other sediments, the amount of water-soluble arsenic was higher than that of the non-specifically bound fraction, indicating that a small portion of the arsenic specifically sorbed on the surface of the sediment was dissolved during the extraction. The results of chemical analyses and multiple regression showed that high pH, total arsenic content, and WSOC content strongly contributed to the enhancement of water-soluble arsenic. These results suggest that in the sediment of the Nobi layer and the G<sub>1</sub> aquifer, the high levels of total and non-specifically bound arsenic would be responsible for the higher level of arsenic release. In addition, high pH and WSOC content would facilitate the release of arsenic from the specifically bound fraction.

## 5. ACKNOWLEDGEMENTS

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## 6. REFERENCES

- [1] Bhattacharya P, Welch AH, Stollenwerk KG, McLaughlin MJ, Bundschuh J, Panullah G, "Arsenic in the environment: Biology and chemistry", *Sci. Total Environ.*, Vol. 379, 2007, pp. 109–120.
- [2] Das D, Samanta G, Mandal BK, Chowdhury TR, Chanda CR, Chowdhury PP, Basu GK, Chakraborti D, "Arsenic in groundwater in six districts of West Bengal, India", *Environ. Geochem. Health*, Vol. 18, 1996, pp. 5–15.
- [3] Anawar HM, Akai J, Komaki K, Terao H, Yoshioka T, Ishizuka T, Safiullah S, Kato K, "Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes", *J. Geochem. Explor.*, Vol. 77, 2003, pp. 109–131.
- [4] Seddique AA, Masuda H, Mitamura M, Shinoda K, Yamanaka T, Itai T, Maruoka T, Uesugi K, Ahmad KM, Biswas DK, "Arsenic release from biotite into a Holocene groundwater aquifer in Bangladesh", *Appl. Geochem.*, Vol. 23, 2008, pp. 2236–2248.
- [5] Polizzotto ML, Harvey CF, Li G, Badruzzaman B, Ali A, Newville M, Sutton S, Fendorf S, "Solid-phases and desorption processes of arsenic within Bangladesh sediments", *Chem. Geol.*, Vol. 228, 2006, pp. 97–111.
- [6] Shimada N, "Geochemical conditions enhancing the solubilization of arsenic into groundwater in Japan", *Appl. Organomet. Chem.*, Vol. 10, 1996, pp. 667–674.
- [7] Kaneko E, "Arsenic concentration in groundwaters in Sendai City", *Chikyukagaku (Geochemistry)*, Vol. 13, 1979, pp. 1–6. (in Japanese with English abstract)
- [8] Nishizawa T, Katoh M, Kitazawa H, Sato T, "Chemical speciation and release of arsenic to groundwater in Seino Basins, Nobi Plain", *J. Japan Society Civil Engineering, Ser. G*, Vol. 68, 2012, pp. 670–679. (in Japanese with English abstract)
- [9] Mandal BK, Chowdhury TR, Samanta G, Mukherjee DP, Chanda CR, Saha KC, Chakraborti D, "Impact of safe water for drinking and cooking on five arsenic-affected families for 2 years in West Bengal, India", *Sci. Total Environ.*, Vol. 218, 1998, pp. 185–201.
- [10] Nickson RT, McArthur JM, Ravenscroft P, Burgess WG, Ahmad KM, "Mechanism of arsenic release to groundwater, Bangladesh and West Bengal", *Appl. Geochem.*, Vol. 15, 2000, pp. 403–413.
- [11] McArthur JM, Ravenscroft P, Safiullah S, Thirlwall MF, "Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh", *Water Res.*, Vol. 37, 2001, pp. 109–117.
- [12] Smedley PL, Kinniburgh DG, "A review of the source, behavior and distribution of arsenic in natural waters", *Appl. Geochem.*, Vol. 17, 2002, pp. 517–568.
- [13] Anawar HM, Akai J, Sakugawa H, "Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater", *Chemosphere*, Vol. 54, 2004, pp. 753–762.
- [14] Masuda H, Ibuki Y, Tonokai K, "Mechanism of natural arsenic pollution of shallow groundwater in the northern part of Osaka prefecture, Japan", *Journal Groundwater Hydrology*, Vol. 41, 1999, pp. 133–146. (in Japanese with English abstract)
- [15] Nishizawa T, Katoh M, Hori A, Sato T, "Mechanisms of arsenic release into groundwater in Seino Basins, Nobi Plain", *J. Japan Society Civil Engineering, Ser. G*, Vol. 68, 2012, pp. III\_507–III\_515. (in Japanese with English abstract)
- [16] Wenzel WW, Kirchbaumer N, Prohaska T, Stinger G, Lombi E, Adriano DC, "Arsenic fractionation in soils using an improved sequential extraction procedure", *Anal. Chim. Acta.*, Vol. 436, 2001, pp. 309–323.
- [17] Shuman LM, "Fractionation method for soil microelements", *Soil Sci.*, Vol. 140, 1985, pp. 11–22.

- [18] Redman AD, Macalady DL, Ahmann D, "Natural organic matter affects arsenic speciation and sorption onto hematite", *Environ. Sci. Technol.*, Vol. 36, 2002, pp. 2889–2896.
- [19] Bauer M, Blodau C, "Mobilization of arsenic by dissolved organic matter from iron oxide, soils and sediments", *Sci. Total Environ.*, Vol. 354, 2006, pp. 179–190.
- [20] Grafe M, Eick MJ, Grossl PR, Saunders AM, "Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon", *J. Environ. Qual.*, Vol. 31, 2002, pp. 1115–1123.

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