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Factors affecting arsenic content of unconsolidated sediments and its mobilization in the Ishikari Plain, Hokkaido, Japan

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ABSTRACT

Arsenic (As) contamination of groundwater is often caused by As leaching from geological formations. This study focused on factors affecting As content in unconsolidated sediments by using three sediment cores in the Ishikari Plain, Hokkaido, Japan. The geochemical properties of the sediments were characterized by the chemical and mineral compositions as well as leaching experiments and sequential extractions of As. The results showed that higher As content of 4-9 mg/kg was observed in peat layers with organic matter content >10 wt%, and that higher As contents deeper than 8 m below the surface were also observed. The deeper sediments were likely to be formed in brackish water conditions due to lower weight ratios of organic carbon content to sulfur content (C/S<10). The results of the leaching experiments showed that As was mobilized at slightly alkaline region. These indicate that the distribution of As depended on the organic content in the sediments and sedimentation condition, and that the mobility of As in the sediment was affected by pH.

Keywords: *Arsenic content, Unconsolidated sediment, Leaching, Sequential extraction, Organic matter, Sedimentation*

1. Introduction

Arsenic (As) is contained in a variety of minerals. In particular, it is dominantly contained in sulfide minerals, such as pyrite, arsenopyrite and realgar (Drahota and Filippi 2009). Thus, the contamination of soils and groundwater by naturally occurring As should be evaluated since As is hazardous to human when taking it through food or water (Cheng et al. 2017; He and Charlet 2013).

Arsenic contamination of soil and groundwater has been found in many regions around the world, such as South Asia (Ahmed et al. 2004; Anawar et al. 2003; Bhattacharya et al. 1997; McArthur et al. 2004; Nickson et al. 1998), Southeast Asia (Berg et al. 2001; Fendorf et al. 2015; Kocar and Fendorf 2012), China and Taiwan (Deng et al. 2011; Jiao and Wang 2014; Yang et al. 2016), and North and South America (McMahon and Chapelle 2008; Smedley et al. 2002). The As concentration in these areas is significantly higher than the WHO guideline (10 µg/L).

There are two different sources of As contamination; one is naturally occurring, and the other is anthropogenic. Many researchers have studied As contamination in soil and groundwater (Nath et al. 2008b; Smedley and Kinniburgh 2002). Naturally occurring As contamination of groundwater has been found in young Quaternary deltaic and alluvial sediments under reducing conditions, and in some areas As was released from soil minerals at oxic and anoxic boundaries (Berg et al. 2008). Recently, the study of source and mobility of As is known to be occurred from: oxidation of As–bearing sulfide minerals (Tabelin et al. 2014a,b), and reductive dissolution of iron oxyhydroxides (FeOOH) (McArthur et al. 2004).

The contamination of As in unconsolidated sediments has been observed in the Ishikari plain of Hokkaido, Japan. This unconsolidated sediment originates from upstream volcanic areas with high content of As (Geological Survey of Japan 2004). However, the details of As distribution of sediments in this area are still unclear because several factors affect the As distribution in the sediments.

The objectives of this study are (1) to elucidate factors affecting As content in unconsolidated sediments in this area, and (2) to understand the characteristics of As leaching from the sediments.

2. Materials and methods

2.1 Study area and sample collection

The study area is located in the Ishikari plain, the western region of Hokkaido, Japan as shown in Fig. 1. This area is known as an alluvial lowland, which covers Neogene-Quaternary volcanic rocks and sediments (Hasegawa et al. 2011). Ishikari River originates from Taisetsu Mountains in central Hokkaido and flows to southwest along the Ishikari Plain. Toyohira River, a tributary of Ishikari River, joins Ishikari River in the

alluvial lowland. Hydrothermally altered areas and mineral deposits, such as Ag, In, Sn, Zn, Pb, are also widely distributed upstream of Toyohira River.

Three boreholes 14 m deep were dug and the undisturbed core sediments were collected at the site near the alluvium. The unconsolidated sediment samples at different layers were selected from the cores of B1, B2 and B3. The profiles of the cores are illustrated in Fig. 2. Each core sample was dried under ambient conditions for one week and crushed the size to less than 2 mm in diameter. Finally, the sample was kept in air-tight containers to minimize oxidation.

2.2 Characterization of sediment sample

The crushed sample was ground by using an agate mortar and pestle, and sieved to less than 0.075 mm for the analysis of mineralogical and chemical compositions. Mineral composition of the samples was identified by using an X-ray diffraction spectrometer, Multiflex (Rigaku Corporation, Japan), while the chemical composition of the samples was measured by X-ray fluorescence spectrometer, Xepos (Rigaku Corporation, Japan). Total organic carbon (TOC) was calculated from the difference between total carbon (TC) and inorganic carbon (IC), and TC and IC were measured by TOC analyzer connected with a solid combustion system SSM-5000A (Shimadzu Corporation, Japan). Loss on ignition (LOI) was also measured by measuring the weight loss in sediment using a muffle furnace FB1300 (Thermo Fisher Scientific Inc., USA).

Sequential extraction procedures used in this study were derived from the methodology based on Marumo et al. (2003) and Tessier et al. (1979). According to the sequential extraction, the As fraction in the sediment can be divided into five phases; exchangeable (weakly adsorbed As), carbonates (bound to carbonate minerals or adsorbed to clays), Fe-Mn oxides, organics and sulfides, and crystalline or residual (mostly silicate minerals). One gram of the sample less than 0.075 mm in diameter was mixed with reagent extractant at each step summarized in Table 1. Total As content was calculated from the data of this sequential extraction.

2.3 Leaching experiments

Leaching experiments were performed under both oxic and reducing conditions. Oxic experiments were conducted at ambient conditions in room temperature. Fifteen grams of a sample with less than 2 mm in diameter were mixed with 150 ml deionized water at 200 rpm for 6 h. For leaching experiments under reducing conditions, the sodium dithionite ($Na_2S_2O_4$) was added in the solvent. Five grams of the sample was mixed with 50 ml of 0.01M $Na_2S_2O_4$ at 200 rpm for 6 h in a 50 ml centrifuge tube to minimize oxidation of $Na_2S_2O_4$. After mixing, temperature, pH, redox potential (ORP) and electrical conductivity (EC) were measured, and then the leachates were filtered by 0.45 µm Millipore sterile filters. The filtrates were stored at 4 ºC for chemical analysis.

2.4 Chemical analysis

Arsenic concentrations of leachates in leaching experiments under oxic conditions and sequential extraction were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) (Shimadzu Corporation, Japan) connected with the hydride vapor generation method whereas As concentrations of leachates under reducing conditions were analyzed by inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Fisher Scientific Inc., USA). Concentrations of heavy metals, such as Fe and Mn, and Si were analyzed using ICP-AES. Cations, such as Na^+, Ca^{2+}, K^+ and Mg^{2+}, and anions, such as Cl^-, NO_3^-, and SO_4^{2-}, were analyzed using ion chromatographs ICS-90 and ICS-100 (Dionex Corporation, USA), respectively. Bicarbonate ion (HCO_3^-) concentration was measured by the titration method with 0.02 N sulfuric acid (H_2SO_4).

2.5 Statistical analysis

Principal component analysis (PCA) was performed using Origin Pro software (OriginLab Corporation, USA). This multivariate statistic method was used to identify the most important factors responsible for the association of As leaching concentration (Guo et al. 2015; Nath et al. 2008b). The calculated factors were normalized by the varimax method. In this study, PCA was applied to investigate leachate samples (15 parameters determined in 25 samples).

3. Results and discussion

3.1 Geological formation, minerals and chemical compositions

The profiles of cores B1, B2, and B3 from the ground surface to a depth of 14 m are shown in Fig. 2. From this figure, the geological unit of the sediments was categorized into sand, silty sand, silt and organic matter. Sediments were divided into two layers, the shallower layers less than 8 m, consisting of organic silt and peat layers, and the deeper layers more than 8 m, consisting mainly of silicate sediments like silt and sand layers.

The XRD data of sediment samples indicated that the most principal minerals were quartz, followed by albite and muscovite as listed in Table 2. Therefore, silicate minerals were main minerals of sediments in this area. However, As-bearing minerals were not detected in this analysis. The XRF data revealed that the major elements contained in the sediments were SiO_2, Al_2O_3, and Fe_2O_3, and that the total content of these major elements were higher than 70% as listed in Table 3. The content of SiO_2 reached over 50% in silty and sandy sediments, and the contents of Al_2O_3 and Fe_2O_3 were also significant. On the other hand, peat and organic silt layers had higher contents of TOC ranging from 1 to 24 wt% and LOI ranging from 2 to 47 wt%. In peat layers, TOC ranged from 18 to 24 wt% and LOI ranged from 36 to 47 wt%.

3.2 Vertical profiles of TOC, sulfur and As

Figures 3a, b and c show the distribution of TOC, sulfur (S) and As contents with depth, respectively. In Fig. 3a, several peaks of TOC were observed in peat layers (TOC > 10%) in B1, B2 and B3. In contrast, TOC content was decreased to less than 1% in silty and sandy layers. In Fig. 3b, higher sulfur content was observed at shallower and deeper layers. In Fig. 3c, higher As content was observed at a depth from 6 to 14 m although As content ranged from 3 to 9 mg/kg.

The ratio of organic carbon content to sulfur content (C/S) was used to distinguish its sedimentary condition, according to Berner and Raiswell (1984). That is, the sediment formed under freshwater conditions is characterized by C/S values >10 whereas that formed under brackish conditions is characterized by C/S<10. Figure 4 shows the weight ratio of C/S. The silt layers deeper than 8 m below the ground surface had C/S<10, indicating that the sediments were formed in brackish water conditions. More abundant sulfur and less total organic matter were obtained in deeper layers. That means that more iron oxyhydroxide is converted to pyrite in deeper layers. In contrast, sediments near the surface were formed in freshwater conditions. As a result, less sulfur is available for reaction with iron (Berner and Raiswell 1983). However, when TOC is high, iron-oxyhydroxide is effectively converted to pyrite.

3.3 Arsenic sequential extraction

The results of As sequential extraction are shown in Fig. 5. The total contents of As in B1 and B3 were generally higher than B2, because organic-rich layers were distributed more widely in B1 and B3. This agrees to the fact that As is concentrated in organic-rich layers. The highest fraction of As in these sediments was associated with the exchangeable one (adsorption), indicating that the majority of As in sediments is easily mobilized under normal environment conditions. The amount of As in the crystalline/residual fraction in silty layers was also significant. However, the organic/sulfide fraction was the main one of As in peat layers and in the sediments deeper than 8 m. These indicated that both organic matter and sulfur affect the total content and organic/sulfide fraction of As in the sediments.

3.4 Effects of organic matter and sulfur on As content

Figure 6 shows the relationship between As content and TOC content. Higher As content was observed in two formations; As content of 3 to 9 mg/kg in peat and organic layers, and As content of 5 to 9 mg/kg in silt and sand layers deeper than 12 m. The As content was ranged from 4 to 6 mg/kg when the TOC content was higher than 10 wt%. However, organic/sulfide fraction of As in peat layers was higher than 1.4 mg/kg. This indicates that As content was affected by organic matter content as pointed out by Anawar et al. (2013).

The As content in silt, silty sand, and sand layers deeper than 12 m below the ground surface was higher compared with that in nonorganic layers shallower than 12 m. The organic/sulfide fraction of As was also higher in deeper layers. These indicate that As content was affected by sedimentary conditions. That is, higher As content of sediments was observed in the layers formed in brackish conditions.

3.5 Relationship between As leaching and sediment

Figures 7a and b show As leaching concentration versus exchangeable fraction of As and SO_4^{2-} leaching concentration in peat, organic silt, silt and sand, respectively. Arsenic released from the sediments was weakly correlated with an exchangeable fraction of As as shown in Fig.7a. This indicates that leaching of As directly corresponded with an exchangeable fraction of As in the sediments. These mean that As may be released from the exchangeable fraction through oxidation of As-bearing sulfide minerals. Several researchers have reported that As leaching concentration was correlated with As content in samples (Igarashi et al. 2007; Nath et al. 2008a; Polizzotto et al. 2008). Furthermore, Fig. 7b shows that As released had a weak correlation with SO_4^{2-} concentration, except samples with SO_4^{2-} leaching concentration higher than 100 mg/L. The other phenomena may occur to restrict As leaching when SO_4^{2-} concentration was higher than 100 mg/L.

The leaching concentration of Fe was changed from 1.5 to 46 mg/L in oxic condition whereas that was changed from 102 to 1,210 mg/L in reducing conditions. On the other hand, the leaching concentration of As ranged from 1 to 41.2 µg/L in oxic conditions whereas that ranged from 56.3 to 204 µg/L in reducing conditions. Both As and Fe leaching concentration dramatically increased by changing from oxic conditions to reducing conditions as shown in Fig. 8. The As leaching is related to Fe leaching by considering a weak correlation between As and Fe concentrations in both conditions for silt and sand samples. These indicate that As was adsorbed on Fe hydroxide/oxide and that both elements were dissolved in reducing conditions. All the data of the leaching experiments are listed in Table 4.

3.6 Effects of pH and silicate on As leaching

The results of leaching experiments showed that pH values increased from 5.1 to 8.8 with depth. Leachates from silty and sandy sediments were slightly alkaline whereas leachates from organic-rich sediments were slightly acidic. The As release as a function of pH is shown in Fig. 9a. The As leaching concentration was higher under weakly alkaline condition (pH>8). Under oxidizing condition, As is less strongly bound to Fe oxide at higher pH than lower pH (Smedley et al. 2002). These may be due to a negative charge of the surface of the sediment under higher pH conditions.

Leaching of Si concentration was correlated with As release as shown in Fig. 9b. This means that colloidal particles containing As were included in the leachates.

3.7 Principal component analysis

For the PCA method, 15 parameters of 25 leachate samples were used to calculate factor loadings as presented in Table 5. The results showed that three factors accounted for 69.8% variance of the geochemical data. Factor 1 with 34% variance had high loadings of Fe, Si, K^+ and pH, which were associated with dissolved Fe and Si. Therefore, in alkaline conditions, factor 1 mainly affects As leaching concentration. Factor 2, with 20.8% of the variance, had high loading on SO_4^{2-}, Ca^{2+} and EC. This factor results from constitute minerals in the sediments. Factor 3, which explained 15.04% of the variance, showed higher loading of Na^+ and Mg^{2+}. These major ions were associated with the formation of sediments in the brackish conditions. These factors can effectively explain As release from the sediments in this site.

4. Conclusion

In this study, two factors affected the distribution of As content in the unconsolidated sediments. The first was organic matter content in the sediments, and the second was the sedimentary condition expressed by C/S. Higher organic matter content of sediments increased the organic fraction of As and higher sulfur content increased the sulfide fraction of As. On the other hand, As release from the exchangeable fraction was significant, because the exchangeable fraction of As was correlated with As leaching, and As mobility was enhanced under higher pH condition. In the reducing condition, both As and Fe were redissolved from the sediments. In addition, As in colloidal particles also affected As leaching. It is found that in this site, major two factors affected the As content in the sediments and its leaching concentrations.

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Table 1 Sequential extraction procedures for As speciation

step	Extractant	Liquid to solid ratio (mL/g)	Extracted phase
1	1 M NaH_2PO_4, pH5, 1 h, 25ºC	20/1	Exchangeable
2	1 M CH_3COONa, pH5, 5 h, 25ºC	20/1	Carbonates
3	0.04 M $NH_2OH.HCl$ in 25% acetic acid, 5 h, 80ºC	20/1	Fe-Mn oxides
4	0.04 M $NH_2OH.HCl$ in 25% acetic acid; $30\%H_2O_2$:0.02M HNO_3, 5 h, 80 ºC	20/1	Sulfides and organics
5	$60\%HNO_3$	20/1	Residual

Table 2 Minerals identified in different lithological units of boreholes B1, B2, and B3

Lithological unit	Minerals identified
Peat layer	Quartz, albite, muscovite
Organic silt layer	Quartz, albite, muscovite, clinochlore
Silt layer	Quartz, albite, muscovite, clinochlore
Sand layer	Quartz, albite, muscovite, clinochlore

Table 3 Chemical compositions of different lithological units

Lithology	Depth (m)	SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	CaO (wt%)	Na_2O (wt%)	As (mg/kg)	S (wt%)	TOC (wt%)	IC (wt%)	LOI (wt%)
B1											
Organic silt	0.55-4.30	49.8	10.1	5	0.5	1.1	5.3	0.15	5.8	<0.01	15.1
Peat	4.30-5.50	33.4	7.6	3.8	0.3	0.4	6	0.04	17.7	<0.01	35.6
Organic silt	5.50-7.90	49.3	11	12.1	0.3	0.5	9	<0.01	2	0.65	9.85
Silt	7.90-10.40	52.5	9.7	5.8	0.5	1.4	6.3	0.16	1	0.07	5.07
Silt	10.40-11.50	56.2	10.1	5.5	0.5	1.4	5.2	0.11	1	0.01	4.73
Silty sand	11.50-13.00	53.8	9.9	6.2	0.8	1.1	8	0.14	0.7	0.01	4.99
Silt	13.00-14.00	53.4	10.9	6.1	0.7	1.1	8.8	0.08	0.8	0.01	5.01
B2											
Silt	0.55-1.80	55.8	10.8	5.2	0.5	1.2	3.5	0.03	0.7	<0.01	4.96
Silt	1.80-2.30	53.8	10.1	5.4	0.5	1.1	5.3	0.04	1.6	0.01	6.35
Silty sand	2.30-3.50	53.3	9.5	6.1	0.8	1.3	5.5	0.02	3.3	0.01	8.67
Organic silt	3.50-5.35	52.2	10.2	5.4	0.5	1.3	5.2	0.05	0.7	0.05	4.62
Peat	5.35-6.80	30.8	6.7	3.3	0.5	0.5	3.4	0.13	19	<0.01	41.4
Organic silt	6.80-7.80	38.6	8.5	4.4	0.5	0.8	4.9	0.12	13.4	<0.01	26.1
Silty sand	7.80-12.20	53.9	9.2	6.1	0.9	1.4	5.6	0.07	0.8	0.05	4.73
Silt	12.20-13.00	54.5	10.5	5.7	0.6	1.3	6.6	0.21	0.9	0.01	4.32
B3											
Organic silt	0.40-0.45	41.6	10.2	5	0.4	0.5	6.2	0.14	7.8	<0.01	16.9
Organic silt	1.45-1.50	56.3	10.7	5	0.3	1.2	4.3	<0.01	1.2	<0.01	4.98
Peat	2.25-2.30	23.9	5.5	3	0.3	0.1	3.7	0.28	23.5	<0.01	47.1
Organic silt	3.25-.3.00	50.6	11.5	4.8	0.4	0.9	3.1	0.06	3	<0.01	8.67
Organic silt	4.75-4.80	53.3	10.4	5.2	0.3	0.9	3.1	0.05	1.9	<0.01	1.86
Organic silt	5.70-5.75	51.3	9.5	5.4	0.3	1.1	8.5	0.07	1.3	<0.01	5.44
Organic silt	6.70-6.75	52.6	9.7	6	0.4	1.1	4.2	0.07	1.2	0.04	4.97
Organic silt	7.65-7.70	53.9	9.6	5.2	0.6	1.6	5.9	0.09	0.9	0.01	4.48
Sand	8.55-8.60	50.8	8	6	0.9	1.3	5.4	0.05	0.4	0.11	4.48
Silt	9.63-9.68	54.9	10.1	5.2	0.5	1.3	4.7	0.07	0.8	0.01	4.05

Table 4 Chemical compositions of leachates

Sample	Depth (m)	Fe mg/L	Al mg/L	Si mg/L	As µg/L	HCO_3^- mg/L	Cl^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	DOC mg/L	pH	EC mS/m	ORP mV
B1																
Organic silt	0.55-4.30	2.2	6.1	16.1	5.7	2.4	16.3	21.2	6.2	4.9	4.1	3.8	18.1	5.22	21.2	242
Peat	4.30-5.50	7.3	21.9	43.7	6.7	20.1	7.5	14.3	14.4	6.1	4.1	0.96	79.3	6.13	13.3	225
Organic silt	5.50-7.90	45.5	63.1	148	14.5	11	10	9.7	11.3	13.5	15.8	1.23	40.8	6.56	9.7	176
Silt	7.90-10.40	14.5	35.7	87	18.8	31.1	11.1	27.8	15.9	15.2	11.4	1.26	22.6	8.61	16.6	149
Silt	10.40-11.50	5.9	4	34.4	3.4	16.5	9	104	20.6	15.1	5.1	2.77	8.8	7.66	33.8	184
Silty sand	11.50-13.00	22.1	46.5	113	10.5	40.3	10.4	58	18.1	18.6	17.2	2.88	17.2	8.62	24	140
Silt	13.00-14.00	26	56.2	133	9.8	26.2	10.7	54.7	16.9	18.9	16.6	2.12	24.2	8.49	22.3	148
B2																
Silt	0.55-1.80	20.1	0.3	71.7	5.4	9.8	8.5	3	3	7.5	13.9	2.24	22.6	6.95	5.8	247
Silt	1.80-2.30	3	6.3	18.1	2.5	3.1	12.8	4.6	3.7	3	3.1	0.73	6.6	5.92	5.5	242
Silty sand	2.30-3.50	4.9	6.8	21.9	2.8	5.5	9.2	16	3.7	2.8	4.1	0.65	7.1	6.79	7.6	221
Organic silt	3.50-5.35	14	31.6	76.1	5	9.8	5.6	14.7	7.8	9.5	8.1	1.11	33.0	7.02	10.8	253
Peat	5.35-6.80	8.6	20.8	46	5.1	22.6	12.5	10.2	14.8	6.5	4.3	0.91	95.4	6.89	16.0	238
Organic silt	6.80-7.80	15.7	35	82.7	7	25	5.7	9.6	12.9	10.2	9.1	1.14	73.4	7.25	10.3	192
Silty sand	7.80-12.20	10.6	20.4	52.4	5	25.6	5.9	40.4	16.4	10.5	8.9	1.05	10.4	7.31	18.2	195
Silt	12.20-13.00	3.5	8.3	20.2	1.6	15.3	2.7	133	23.2	18.7	10.3	6.48	5.3	7.15	36.5	205
B3																
Organic silt	0.40-0.45	2.9	11.4	20.8	2.7	2.4	14.2	28.4	7.6	9	7.4	6.63	32.5	5.41	16.5	337
Organic silt	1.45-1.50	2.1	7.8	16.3	4.3	7.9	5.4	9.9	4.4	2	0.4	0.4	11.0	5.36	4.2	331
Peat	2.25-2.30	1.6	4.4	8.8	1.1	3.1	21.8	40.2	6.9	6.4	3.4	4.05	62.0	5.07	19.6	277
Organic silt	3.25-.3.00	1.6	7.5	13.9	0.8	1.8	5.6	24.1	23.3	3.4	2.6	2.89	17.5	5.02	14.8	253
Organic silt	4.75-4.80	15.4	41.9	88.7	4.9	11	5.1	8.5	11.5	1.8	1	0.95	44.1	6.48	7.7	168
Organic silt	5.70-5.75	7.4	18.4	44.4	6.3	6.1	6.8	61.7	32.2	4.9	1.4	0.98	23.8	6.47	21	173
Organic silt	6.70-6.75	9.5	23	52.6	4.1	14	8.1	36.2	26.1	3.4	1.1	0.78	27.3	7.06	14.3	139
Organic silt	7.65-7.70	5.3	14.8	30.3	9.6	14.6	7.8	42.6	30.3	4.9	1.3	0.6	14.8	7.96	16.1	161
Sand	8.55-8.60	14.7	29.9	68.7	33.2	26.2	8.5	22.3	21.9	4.3	1.5	0.96	16.2	8.53	10.4	128
Silt	9.63-9.68	17.9	49.2	99.6	41.2	44.4	14.9	51.4	40.1	11.2	2.3	1.64	24.5	8.81	26	147

Table 5 Rotated factor loadings of principal components

Variable	Factor 1	Factor 2	Factor 3
As (Concentration)	0.259	-0.141	-0.212
As (Content)	0.251	0.072	0.210
Fe	**0.315**	-0.256	0.288
Si	**0.357**	-0.242	0.198
SO_4^{2-}	0.186	**0.468**	-0.157
NO_3^-	-0.239	0.235	0.158
Na^+	0.237	0.147	**-0.428**
Cl^-	-0.060	0.071	0.194
K^+	**0.333**	0.246	0.261
Mg^{2+}	0.262	0.037	**0.492**
Ca^{2+}	-0.038	**0.463**	0.261
EC	0.185	**0.483**	-0.078
pH	**0.384**	-0.051	-0.177
ORP	**-0.356**	0.084	0.258
DOC	-0.057	-0.177	0.192
Eigenvalue (%)	33.92%	20.83%	15.04%
Cumulative (%)	33.92%	54.74%	69.78%

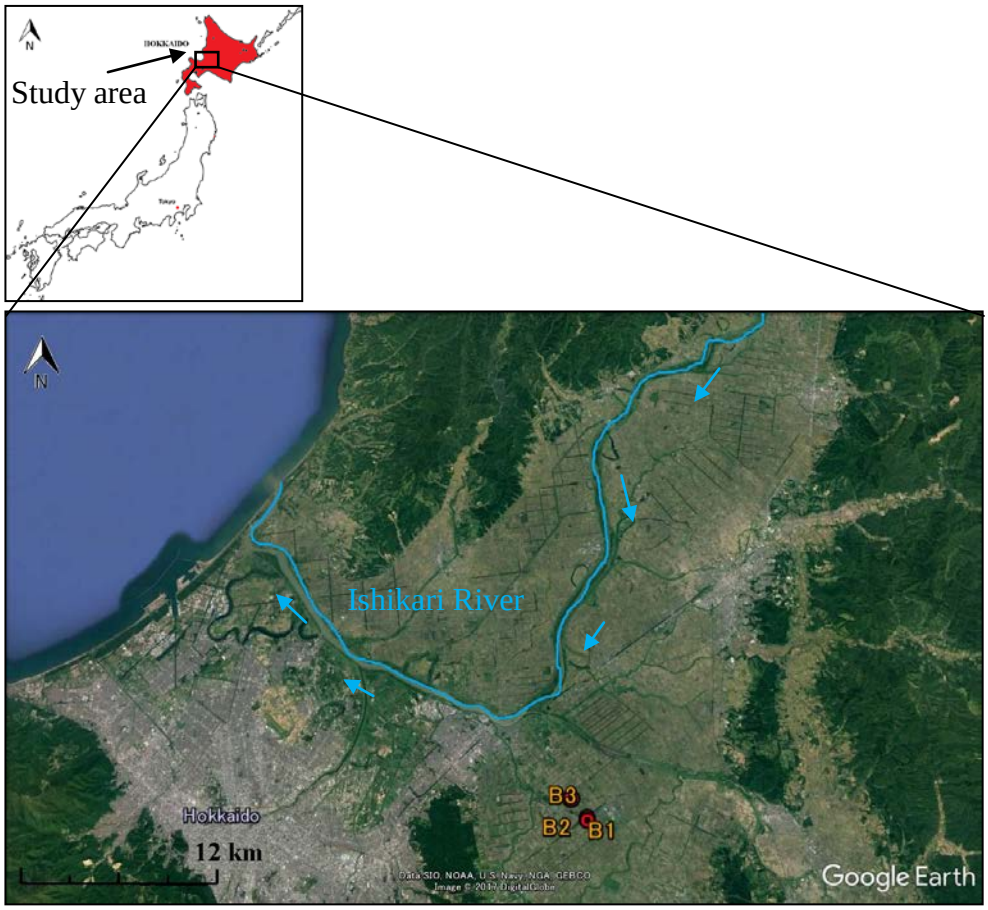

Fig. 1 Loaction of study area (Ishikari plain, Hokkaido, Japan)(●) sampling points and (←) flow direction

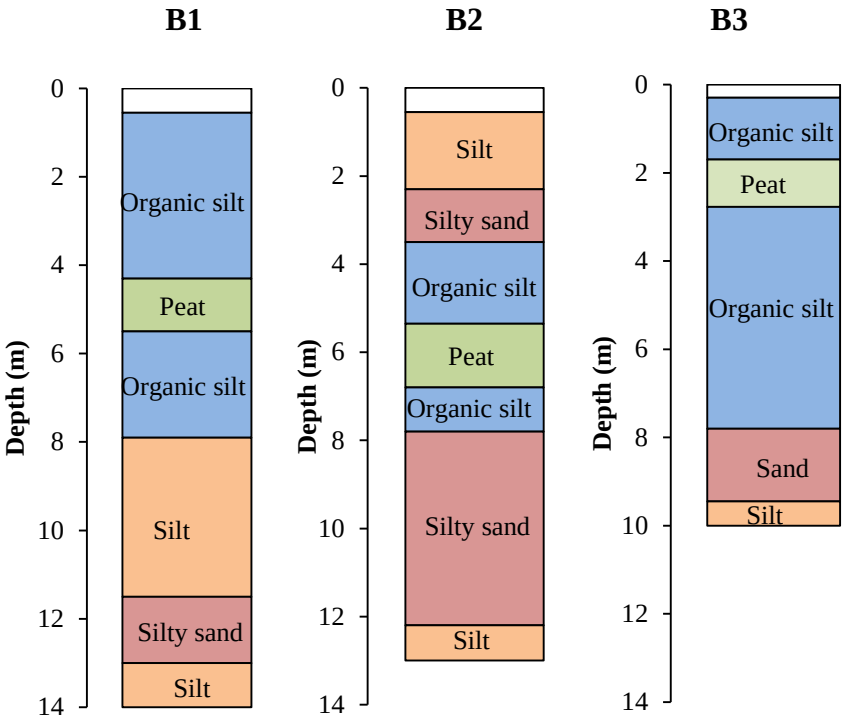

Fig. 2 Geological units of boreholes B1, B2 and B3

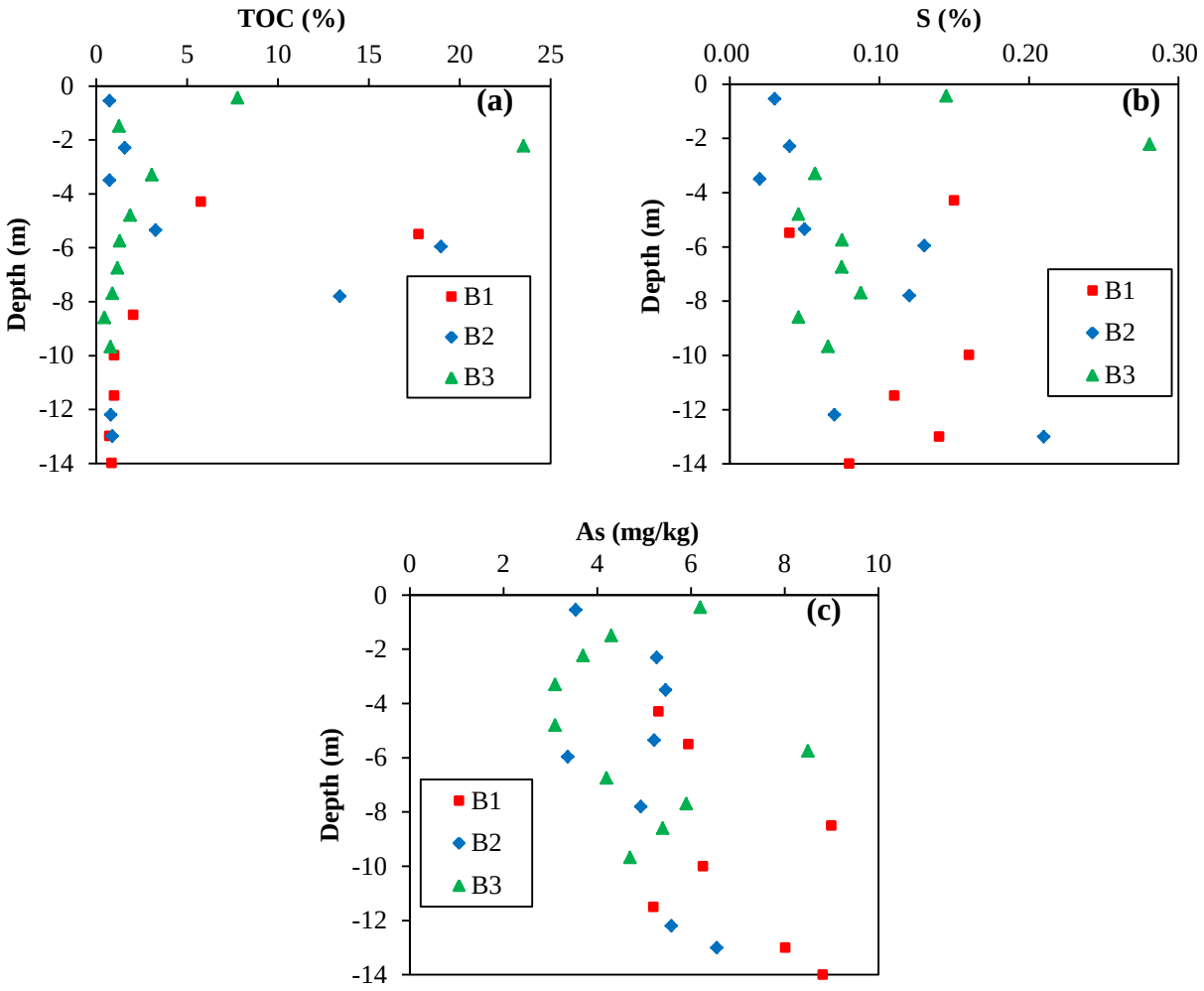

Fig. 3 Distributions of (a) TOC, (b) sulfur and (c) arsenic content in boreholes B1, B2 and B3

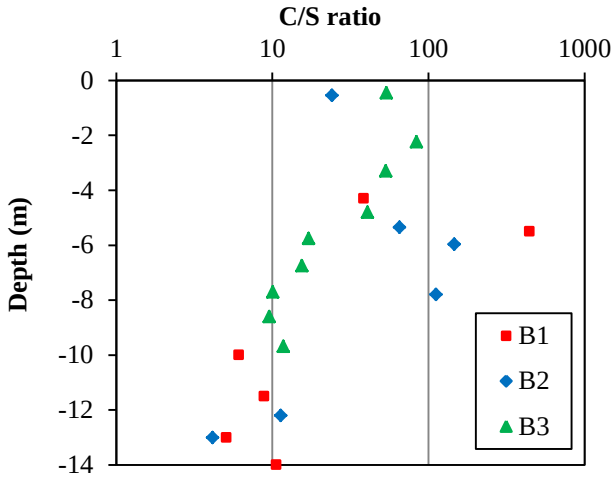

Fig. 4 Vertical profile of C/S

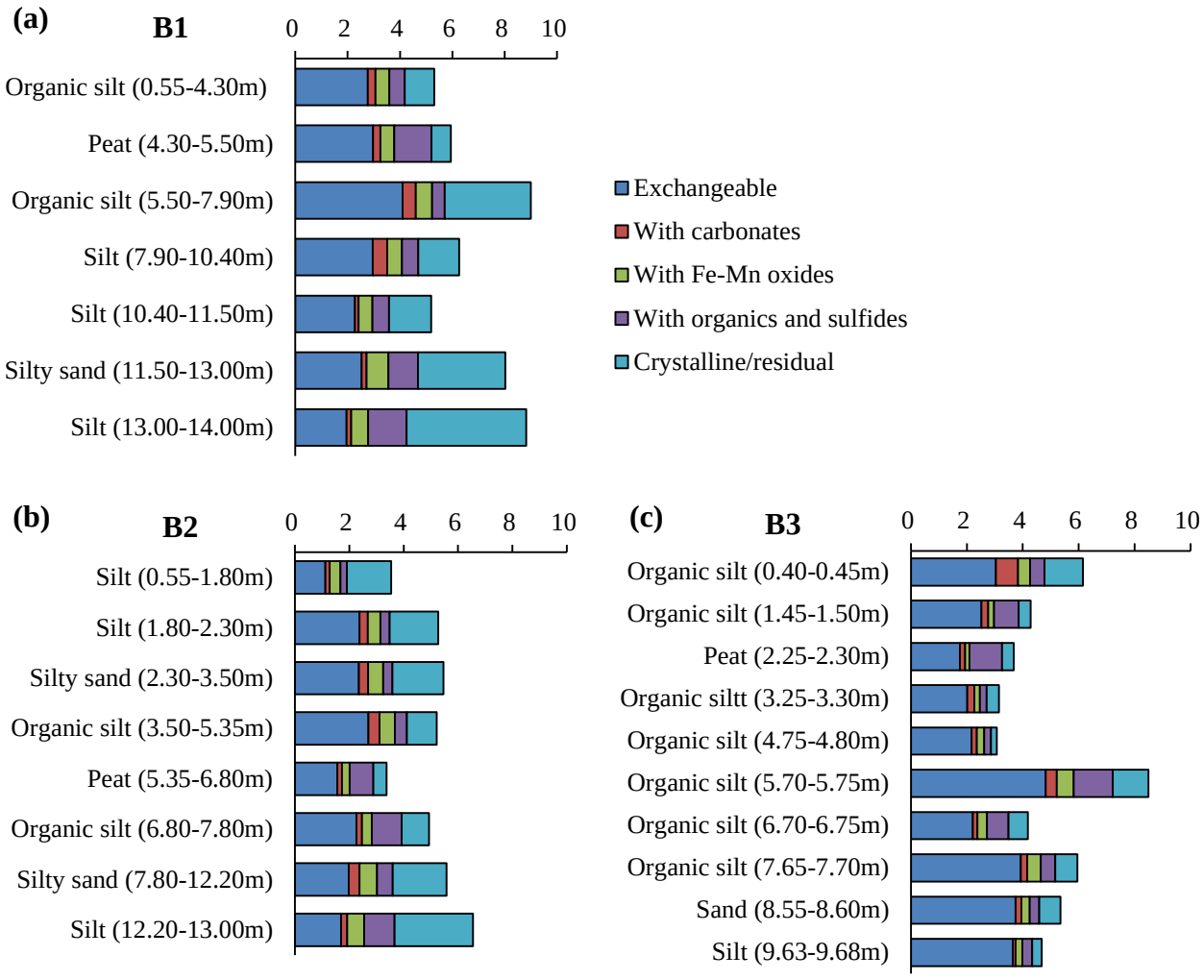

Fig. 5 Solid-phase partitioning of arsenic in boreholes (a) B1, (b) B2 and (c) B3

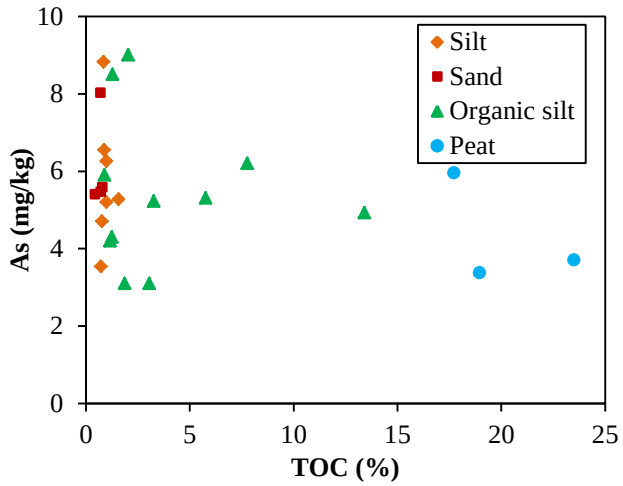

Fig. 6 As content versus TOC content

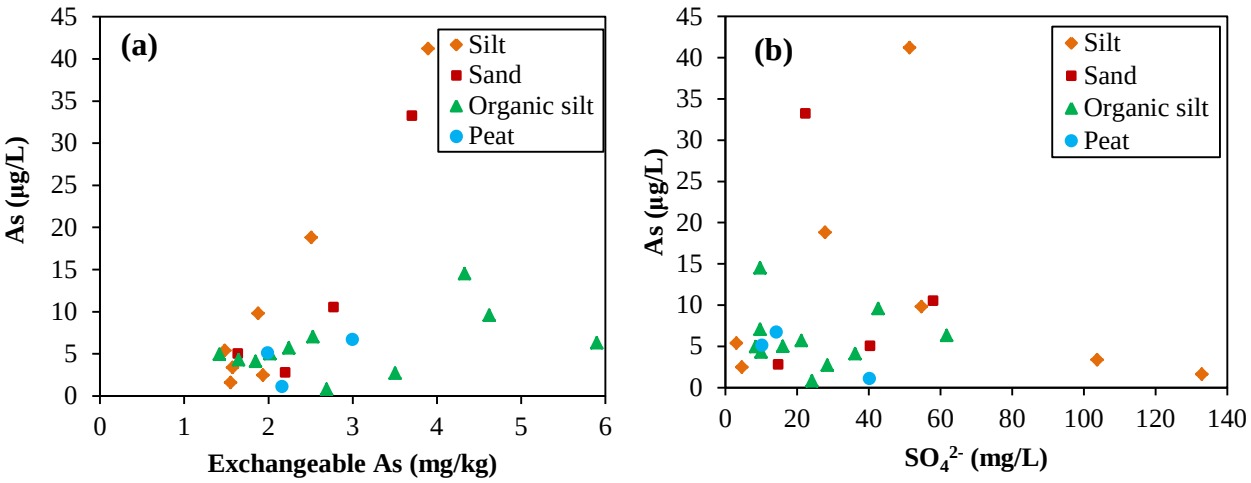

Fig. 7 As leaching concentration versus (a) As content in exchangeable fraction and (b) SO_4^{2-} leaching concentration

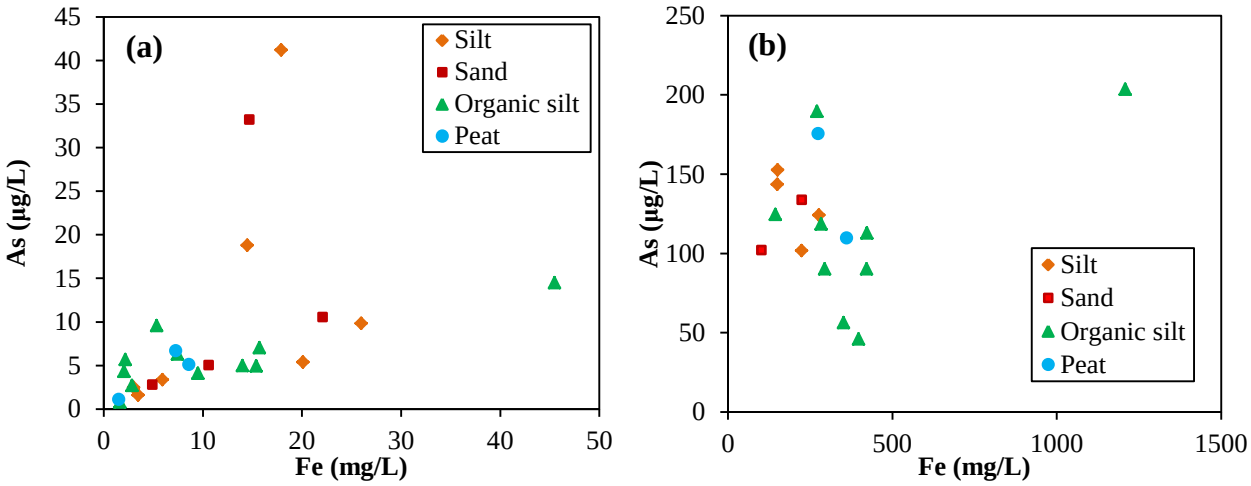

Fig. 8 As leaching concentration versus Fe leaching concentration (a) under oxic condition and (b) under reducing condition

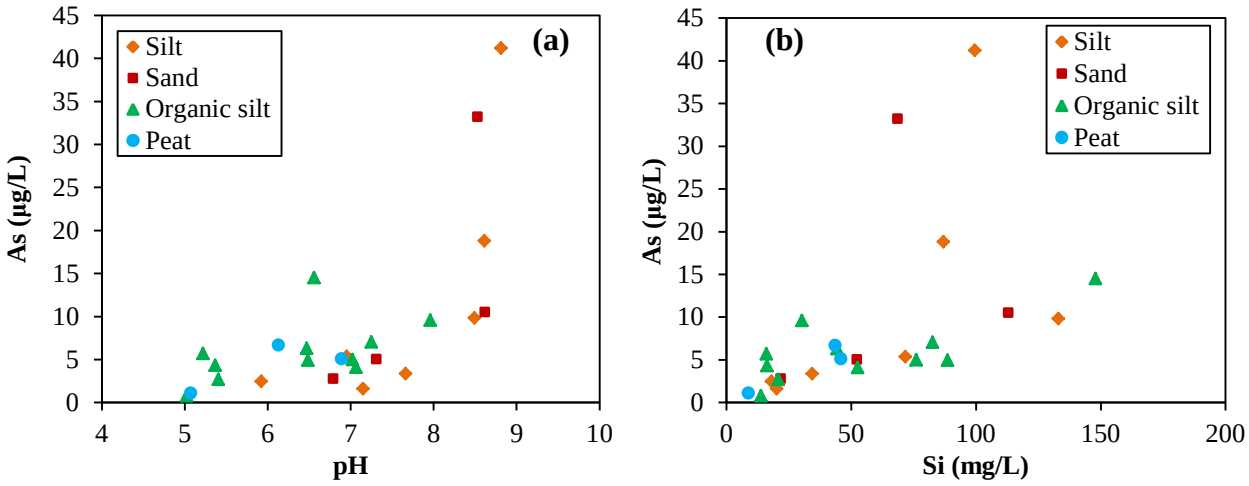

Fig. 9 As leaching concentration versus (a) pH and (b) Si leaching concentration