Factors affecting arsenic content of unconsolidated sediments and its mobilization

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Abstract

Arsenic (As) contamination in groundwater is a serious water resource problem in the world since groundwater is the main water sources as a drinking water in many countries. Arsenic contamination in the environment often results from anthropogenic sources such as mining or pesticide application, but recently the natural sources of As have a potential impact on water quality. The amount of dissolved As is often explained by geochemical reactions, such as dissolution-precipitation, oxidation-reduction, adsorption-desorption, and biological processes. The distribution of As in the subsurface environments is affected by mobilization of As in aquifers. However, geogenic processes related to As in alluvial sediments where groundwater As concentration is high are still unclear. This research targets two objectives: (1) factors affecting As content in areas with high concentration of As in groundwater as case studies of the Ishikari Plain and Mekong Delta, and (2) As release from inorganic and organic sediments in a wide variety of chemical and mineral constituents. The results would help to understand the distribution of As content in an alluvial environment for safe drinking water. This dissertation contains 5 chapters.

Chapter 1 presents introduction, the statement of problems, objectives of this study and outlines of the dissertation. These include the geochemical characteristics of As in the environment and the geochemistry of As contamination in groundwater and sediments.

Chapter 2 describes factors affecting the distribution of As content of unconsolidated sediments in the Ishikari Plain. To understand the mechanisms triggering the enrichment of naturally occurring As, As contents in the sediments were studied. The first factor was organic matter content in the sediments, and the second was the sedimentary condition expressed by the ratio of carbon content to sulfur (S) content. Leaching experiments and sequential extraction were used to explain mobility of As from the sediments. The results showed that higher organic matter content of sediments increased the organic fraction of As and that the higher S 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 concentration, and As mobility was enhanced under higher pH condition. In the reducing condition, both As and iron (Fe) were dissolved from the sediments. In addition, As in colloidal particles also affected As leaching.

Chapter 3 describes the As distribution of unconsolidated sediments in the Mekong Delta. The content of As in the sediments was influenced by Fe, S and organic matter. In this study area, organic-rich sediment concentrated As-bearing sulfide, which enhanced the organic fraction of As. In addition, the higher exchangeable and sulfide fractions of As in the sediment were found in a saline water condition. This demonstrated that the sedimentary condition also affected As distribution and its mobility. Higher As concentration in the leachate was also observed in the layers consisting of finer particle size. This means that As in colloidal particles affected As leaching. These indicate that several factors affected the As content and its mobilization.

In chapter 4, chemical characteristics of sediments affected As content in both areas. By comparing the areas, organic matter content and S content increased As content in sediments. In addition, high As content was observed under saline water conditions. The As leaching in both sites was influenced by the fraction of As in the sediments, pH and colloidal particles.

Finally, conclusion, as well as recommendation of As contamination in shallow alluvial aquifers is discussed in chapter 5.

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Chapter 1
INTRODUCTION

1.1 Geochemistry of arsenic in environments

Arsenic (As) is a metalloid element that is widely distributed in the natural environment, which occurs as more than 200 minerals, including arsenides, sulfides, oxides, arsenite and arsenates (Smedley and Kinniburgh, 2002). Arsenic is commonly found in sulfide-bearing minerals such as arsenopyrite (FeAsS), orpiment (As_2S_3), and realgar (AsS/As_4S_4), which are the most common arsenic sulfide minerals, occurring primarily in geothermal areas. Higher As concentrations, mostly in the range of thousand to ten thousands µg/L, were reported in USA, Mexico, Chile and Japan (Bundschuh and Maity, 2015). The As-bearing minerals easily occur as a minor component in abundant Fe sulfide minerals like pyrite. However, it is not stable when it is exposed to atmosphere, surface water or shallow groundwater. This is because alteration reactions can form simply As oxides or more complex phases of As with oxygen and various metals (Drahota and Filippi, 2009). Arsenic has often been used as an indicator in geochemical prospecting, which is conducted for identifying mineral deposits because it is associated with a wide variety of minerals. For example, As is associated with the deposits of Cd, Pb, Ag, Au, Sb, P, W and Mo (Smedley and Kinniburgh, 2002). Sources of As result from both natural and anthropogenic and the scale of contamination ranges from local to regional. Arsenic is generally derived from erosion of As rich rock or weathering of As-bearing rock from altered igneous rocks and sedimentary rocks (Kocar and Fendorf 2012, Tabelin et al., 2014). Arsenic contents in igneous rocks are generally low. Similarly, content of As in sedimentary rocks is typically in the range 5-10 mg/kg. However, hydrothermally altered rocks contain As more than 100 mg/kg (Smedley and Kinniburgh, 2002; Tabelin et al., 2014; Webster, 1999). Arsenic is commonly presented in igneous, sedimentary, and metamorphic rocks (Table 1-1). High As contents are also found in many oxide minerals and hydrous metal oxides such as iron oxides or hydroxides, manganese oxides, and aluminum oxides.

In nature, As can occur in the environment in several oxidation states: As(-III), As(0), As(III) and As(V). Arsenate ion [As(V)] is most prevalent in oxic conditions whereas arsenite ion [As(III)] is found in anaerobic conditions (Smedley and Kinniburgh, 2002). Both of them can form as inorganic and organic metallic species.

The redox potential (Eh) and pH for aqueous As species are shown in Fig. 1-1 (Brookins, 1998; Yan et al., 2000). Under oxidizing conditions, $H_2AsO_4^-$ is the most stable species between pH 2 and 7 while $HAsO_4^{2-}$ is the most stable species above pH 7. Under reducing condition at pH less than 9.2, arsenic as As(III) is thermodynamically stable and arsenious acid (H_3AsO_3) is usually the

predominant dissolved inorganic arsenic species.

Table 1-1. Arsenic content in rocks (Smedley and Kinniburgh, 2002)

Rock/sediment type	As average content and range (mg/kg)
Igneous rocks	
Ultrabasic rocks (peridotite, dunite, kimberlite etc)	1.5 (0.03–15.8)
Intermediate (andesite, trachyte, latite)	2.7 (0.5–5.8)
Acidic rocks (rhyolite)	4.3 (3.2–5.4)
Volcanic glasses	5.9 (2.2–12.2)
Sedimentary rocks	
Marine shale/mudstone	3–15 (up to 490)
Shale (Mid-Atlantic Ridge)	174 (48–361)
Non-marine shale/mudstone	3.0–12
Sandstone	4.1 (0.6–120)
Limestone/dolomite	2.6 (0.1–20.1)
Metamorphic rocks	
Quartzite	5.5 (2.2–7.6)
Hornfels	5.5 (0.7–11)
Phyllite/slate	18 (0.5–143)
Amphibolite and greenstone	6.3 (0.4–45)

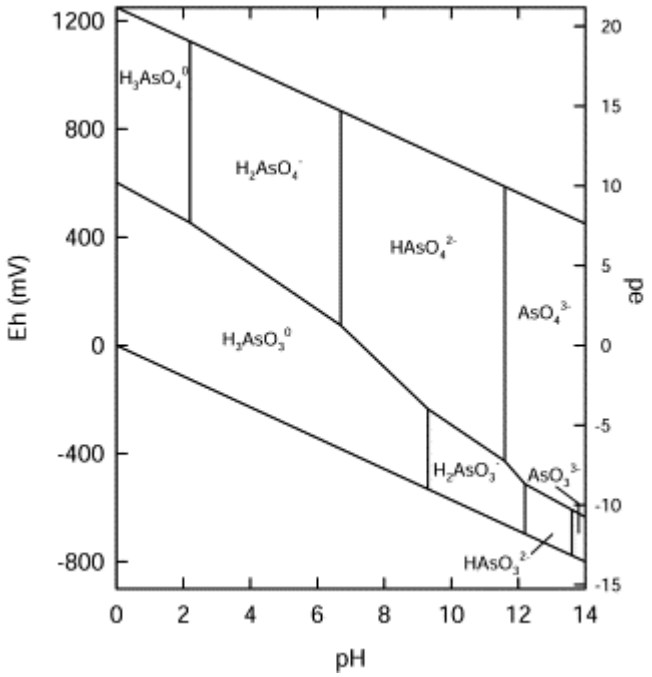

Figure 1-1. Eh-pH diagram of As species for an As–O_2–H_2O system at 25 °C and 1 bar total pressure (Smedley and Kinniburgh, 2002)

1.2 Arsenic content in sediments

The content of As in unconsolidated sediments is not notably different from host rocks in the range 3-10 mg/kg. Arsenic content in the river sediments of the Ganges and Brahmaputra is on average 2-3 mg/kg as shown in Table 1-2 (Smedley and Kinniburgh, 2002). Similar contents have also been found in river sediments where groundwater As contamination is observed in the Mekong Delta (Nguyen and Itoi, 2009). However, content of As in sediments from shallow aquifers was higher than 10 mg/kg in many regions of China (Deng et al., 2011, Yang et al., 2016). The major minerals binding As in sediments are the metal oxides, particularly those of Fe, Al and Mn are present in quantity (Smedley and Kinniburgh, 2002). In addition, clay also adsorbs As because of the oxide-like character of their edges in sediments. To understand the mechanism of As mobilization from sediments to groundwater is important when the groundwater is used for drinking water in areas contaminated by As.

Table 1-2. Arsenic content in sediments (Smedley and Kinniburgh, 2002)

Unconsolidated sediments	As average content and range (mg/kg)
Various	3 (0.6–50)
Alluvial sand (Bangladesh)	2.9 (1.0–6.2)
Alluvial mud/clay (Bangladesh)	6.5 (2.7–14.7)
River bed sediments (Bangladesh)	1.2–5.9
Lake sediments, Lake Superior	2.0 (0.5–8.0)
Lake sediments, British Colombia	5.5 (0.9–44)
Glacial till, British Colombia	9.2 (1.9–170)
World average river sediments	5
Stream and lake silt (Canada)	6 (<1–72)
Loess silts, Argentina	5.4–18

1.3 Arsenic contamination in groundwater

Arsenic has been recognized as toxic and carcinogenic, and the risk depends on its chemical and physical forms, concentration level and time of exposure. Particularly, inorganic As dissolved in drinking water is the most significant. Arsenic poisoning induces cancers of skin, lungs, bladder and kidneys, as reported in China, Taiwan, Bangladesh, India and Vietnam (Bhattacharya et al., 2007; Kuo et al., 2003; 2007; Ng et al., 2003). Unfortunately, As has been detected in groundwater in several countries in the world, with concentration level exceeding the world health organization (WHO) drinking water guideline of 10 μg/L. High As concentrations in groundwater have also been found in

river sediments and alluvial deltaic areas such as in Bangladesh and Bengal Delta, Mekong Delta, and China (Acharyya et al., 2000; Berg et al., 2008; Kim et al., 2011; Nickson et al., 1998). In general, As contamination in the Quaternary and Holocene aquifer of Bengal basin is caused by reduction of iron hydroxides, and bacterial activities generally result in an increase of As concentration in porewater (Acharyya et al., 2000; MacArthur et al., 2004; Nickson et al., 2000). On the other hand, groundwater As from Quaternary loess aquifers in Argentina derived from desorption of As on metal oxide surface under oxidizing conditions and neutral to alkaline pH (Smedley et al., 2002). Naturally-occurring As problems in world groundwater are listed in Table 1-3 (Smedley and Kinniburgh, 2002).

Since As in aquifer often occurs in various chemical forms and geogenic forms, these factors affect the distribution and releasing of As in the aquatic environments. According to the complicated reactions of As, such as (1) adsorption and co-precipitation, (2) desorption and dissolution, and (3) oxidation-reduction, it is important to evaluate the transport of As from minerals in sediment to water phase. However, sources of As and geological conditions of aquifers are related to As concentration in groundwater.

Table 1-3. Naturally-occurring As problems in world groundwater (Smedley and Kinniburgh, 2002)

Country/region	Concentration ranges (μg/L)	Aquifer type
Bangladesh	<0.5–2500	Holocene alluvial/deltaic sediments Abundance of solid organic matter
West Bengal	<10–3200	As Bangladesh
Taiwan	10–1820	Sediments, including black shale
Red River Delta, Vietnam	1–3050	Holocene alluvial/deltaic sediments
Argentina (Chaco-Pampean Plain)	<1–5300 (7500 in some pore waters)	Holocene and earlier loess with rhyolitic volcanic ash
Inner Mongolia (Tumet Plain including Huhhot Basin (HB); Ba Men, Bayingao, Hexi), China	<1–2400	Holocene alluvial and lacustrine sediments
Hungary, Romania (Danube Basin)	<2–176	Quaternary alluvial plain
Mexico (Lagunera)	8–620	Volcanic sediments

1.4 Statement of the problem and the objectives of the study

Arsenic concentration of groundwater in alluvial sediments is a serious global health problem since groundwater is the main sources for drinking water. The natural sources of As recently have potential impacts on water quality. The amount of dissolved As is mostly explained by geochemical reactions, such as dissolution-precipitation, oxidation-reduction, adsorption-desorption, and biologically mediated processes. Although various processes are involved with As release from sediments, e.g., a transition from aerobic to anaerobic conditions, and iron/manganese reduction (Billion et al., 2015; Nickson et al., 2000), the distribution of As in different environments is affected by mobilization of As in aquifers. However, geogenic processes related to As in alluvial sediments where groundwater As concentration is high are still unclear. This research targets two objectives: (1) factors affecting As content in areas with high concentration of As in groundwater as case studies of

the Ishikari Plain and Mekong Delta, and (2) As speciation released from inorganic and organic sediments in a wide variety of chemical and mineral constituents.

1.5 Outline of the dissertation

This dissertation consists of five chapters and the outline is as follows:

Chapter 1 presents introduction, the statement of problems, objectives of the study and outlines of the dissertation. The geochemical characteristics of As in the environment and the geochemistry of As contamination in groundwater was mentioned in this chapter.

Chapter 2 discusses factors affecting As content in alluvial sediments in the Ishikari Plain, Hokkaido, Japan and its mobilization. Leaching experiments and sequential extraction were conducted to explain mobility of As from the sediments. In this area, As content was related with organic and non organic sediments.

Chapter 3 explains factors affecting As content in alluvial sediments in the Mekong Delta, Vietnam and its mobilization. In this region, high As concentration in groundwater was related with high As content in the sediments. Thus, to understand the distribution of As content of sediments could lead to occurrence of As leaching.

Chapter 4 compares of As content in alluvial environments and its mobilization between the Ishikari Plain and the Mekong Delta.

Chapter 5 summarizes sources and occurrence of As in alluvial sediments.

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Chapter 2
ARSENIC CONTENT OF UNCONSOLIDATED SEDIMENTS AND ITS MOBILIZATION IN THE ISHIKARI PLAIN, HOKKAIDO, JAPAN

2.1 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 sources and mobility of As is known to result 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 chapter 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.

2.2 Materials and methods

2.2.1 Study area and sample collection

The study area is located in the Ishikari Plain, the western region of Hokkaido, Japan as shown in Fig. 2-1. 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, and Pb, are also widely distributed upstream of Toyohira River.

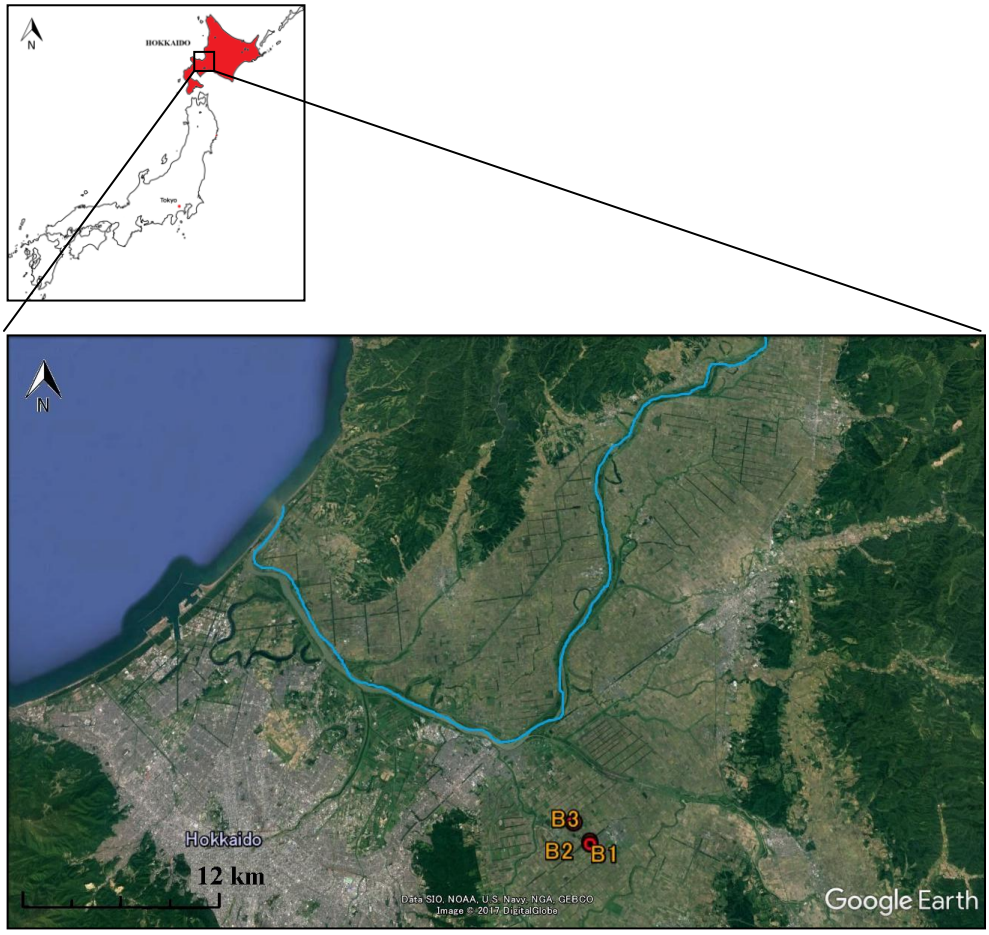

Figure 2-1. Location of study area (Ishikari Plain, Hokkaido, Japan)

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. 2-2. 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.

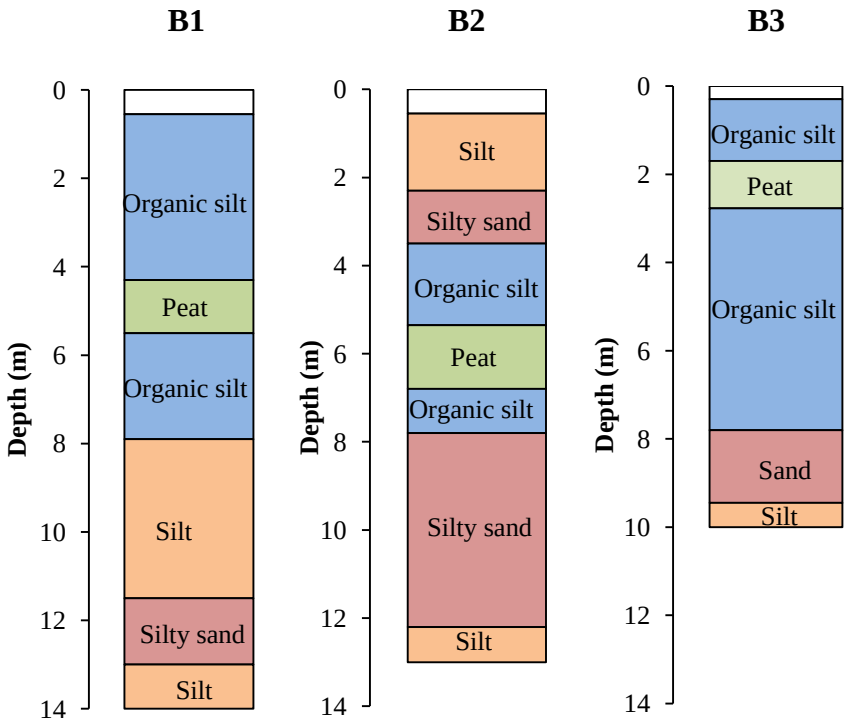

Figure 2-2. Geological units of boreholes B1, B2 and B3

2.2.2 **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 sediments using a muffle furnace FB1300 (Thermo Fisher Scientific Inc., USA).

The sequential extraction of As was carried out to understand the solubility and chemical species of As by the procedure develop by Tessier et al. (1979) and Marumo et al. (2003). The fractions of As were classified into five factions; exchangeable (weakly adsorbed As), carbonates (bound to carbonate minerals or adsorbed to clays), Fe-Mn oxides, organics and sulfides, and crystalline or residual. These extraction processes were started by adding 1 g of a sediment sample into a 50 mL centrifuge tube. By following procedures, As in the sediment was fractionated.

Fraction 1. Exchangeable

The sample was mixed with 20 mL of sodium dihydrogen phosphate (1M NaH_2PO_4 of pH 5 controlled by NaOH) at room temperature for 1 hour. The residue was washed with 10-15 mL of deionized water after the extraction step. The leachate and water used for washing were then combined and diluted to 50 mL for analysis. The same washing and dilution procedures were conducted at the following steps.

Fraction 2. Bound to carbonates

The residue from fraction 1 was mixed with 20 mL of 1 M CH_3COONa adjust to pH 5 with acetic acid (HOAc) at room temperature for 5 hours.

Fraction 3. Bound to Fe-Mn oxides

The residue from fraction 2 was mixed with 20 mL of 0.04 M $NH_2OH.HCl$ in 25% HOAc. This extraction was performed at 80 ºC for 5 hours.

Fraction 4. Bound to organics or sulfides

The residue from fraction 3 was mixed with 20 mL of 0.04 M $NH_2OH.HCl$ in 25% HOAc, 3 mL of 0.02M HNO_3 and 5 mL of 30% H_2O_2 (adjusted to pH 2 with HNO_3). This mixture was heated to 80 ºC for 2 hours, and then 3 mL of 30% H_2O_2 was added. The suspension was heated to 80 ºC for 3 hours with a slow agitation. After cooling, 5 mL 0.02 M HNO_3 was added to the suspension and agitated continuously for 30 min.

Fraction 5. Bound to residual

The residue from fraction 4 was digested with 15 mL of concentrated 60% HNO_3 for 45 min. An additional 5 mL of concentrated 60% HNO_3 was added and the suspension was digested for another 15 min.

2.2.3 **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 were mixed with 50 ml of 0.1M $Na_2S_2O_4$ at 200 rpm for 6 h in a 50 ml centrifuge tube to minimize oxidation of $Na_2S_2O_4$.

The leaching experiments using hydrochloric acid (HCl) solution were performed at ambient conditions at room temperature. Three grams of a sample with less than 2 mm in diameter were mixed with 100 mL of 1 M HCl solution at 200 rpm for 2 h.

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.

2.2.4 **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 with 0.02 N sulfuric acid (H_2SO_4).

2.2.5 **Statistical analysis**

Principal component analysis (PCA) was performed using Origin Pro software (OriginLab Corporation, USA). This multivariate statistical method was used to identify the most important factors responsible for the association of As content and 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 sediments (9 parameters determined in 25 samples) and leaching samples (16 parameters determined in 25 samples).

2.3 Results and discussion

2.3.1 **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. 2-2. From these figures, 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 silicates like silt and sand layers.

Table 2-1. 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

The XRD data of sediment samples indicated that the most principal minerals were quartz, followed by albite and muscovite as listed in Table 2-1. 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 was higher than 70% as listed in Table 2-2. 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%.

Table 2-2. 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

2.3.2 **Vertical profiles of TOC, sulfur and As content**

Figures 2-3(a), (b) and (c) show the distribution of TOC, sulfur (S) and As contents with depth, respectively. In Fig. 2-3(a), 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. 2-3(b), higher S content was observed at shallower and deeper layers. In Fig. 2-3(c), higher As content was observed at a depth from 6 to 14 m although As content ranged from 3 to 9 mg/kg.

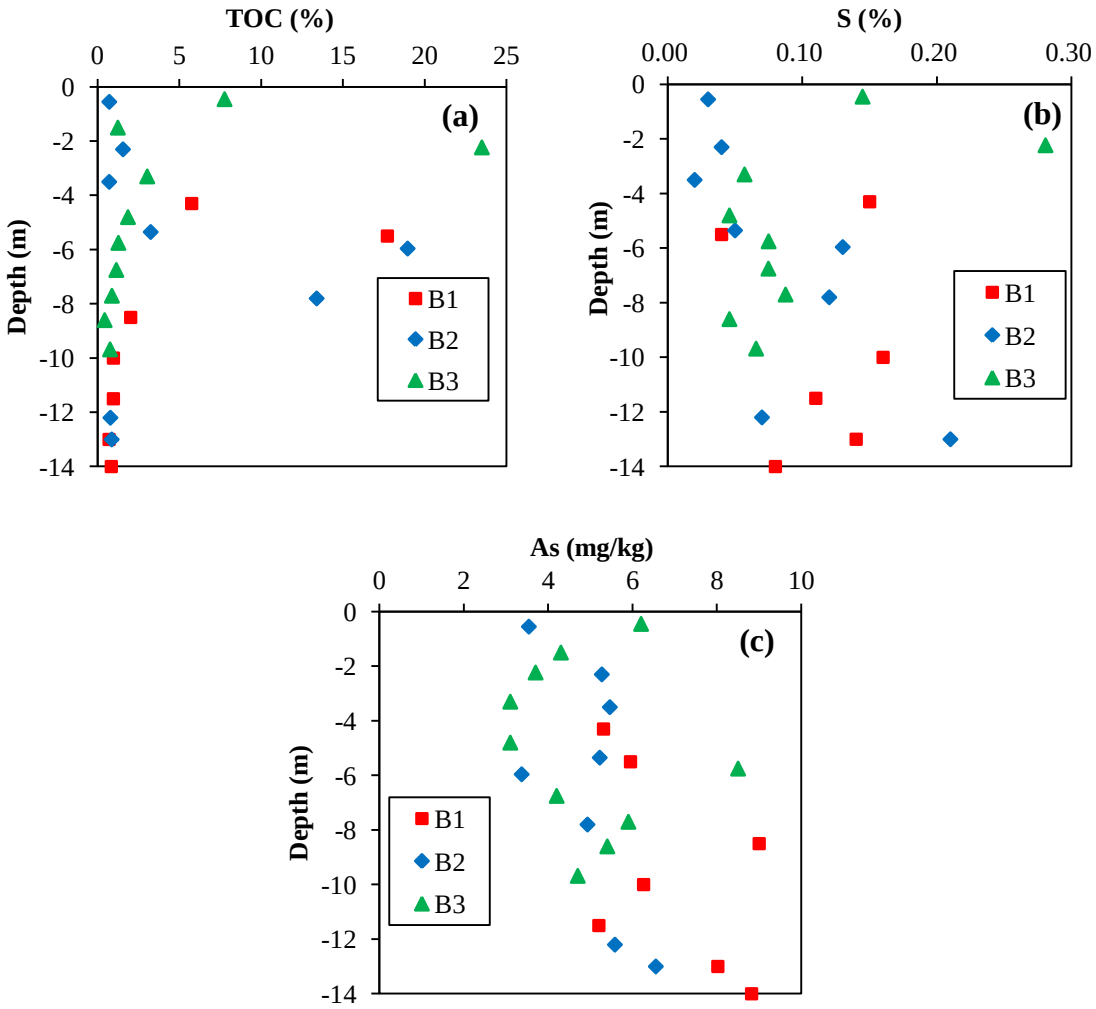

Figure 2-3. Distributions of (a) TOC, (b) S and (c) As content in boreholes B1, B2 and B3

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 saline conditions is characterized by C/S<10. Figure 2-4 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 saline water conditions. More abundant S and less total organic matter were obtained in deeper layers. That means

that more Fe oxyhydroxide is converted to pyrite in deeper layers. In contrast, sediments near the surface were formed in freshwater conditions. As a result, less S is available for reaction with Fe (Berner and Raiswell, 1983). However, when TOC is high, Fe-oxyhydroxide is effectively converted to pyrite.

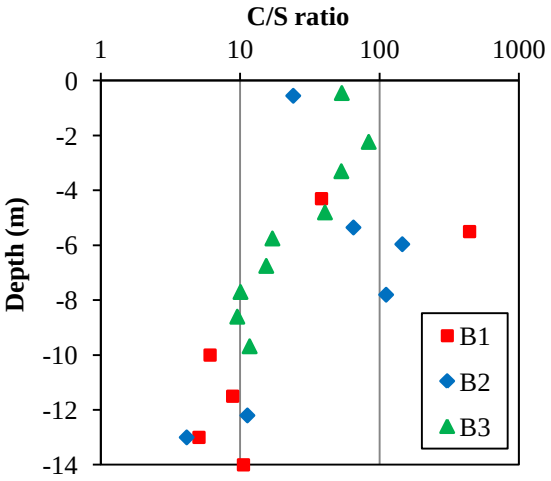

Figure 2-4. Vertical profile of C/S

2.3.3 **Arsenic sequential extraction**

The results of As sequential extraction are shown in Fig. 2-5. 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 indicate that both organic matter and S affect the total content and organic/sulfide fraction of As in the sediments.

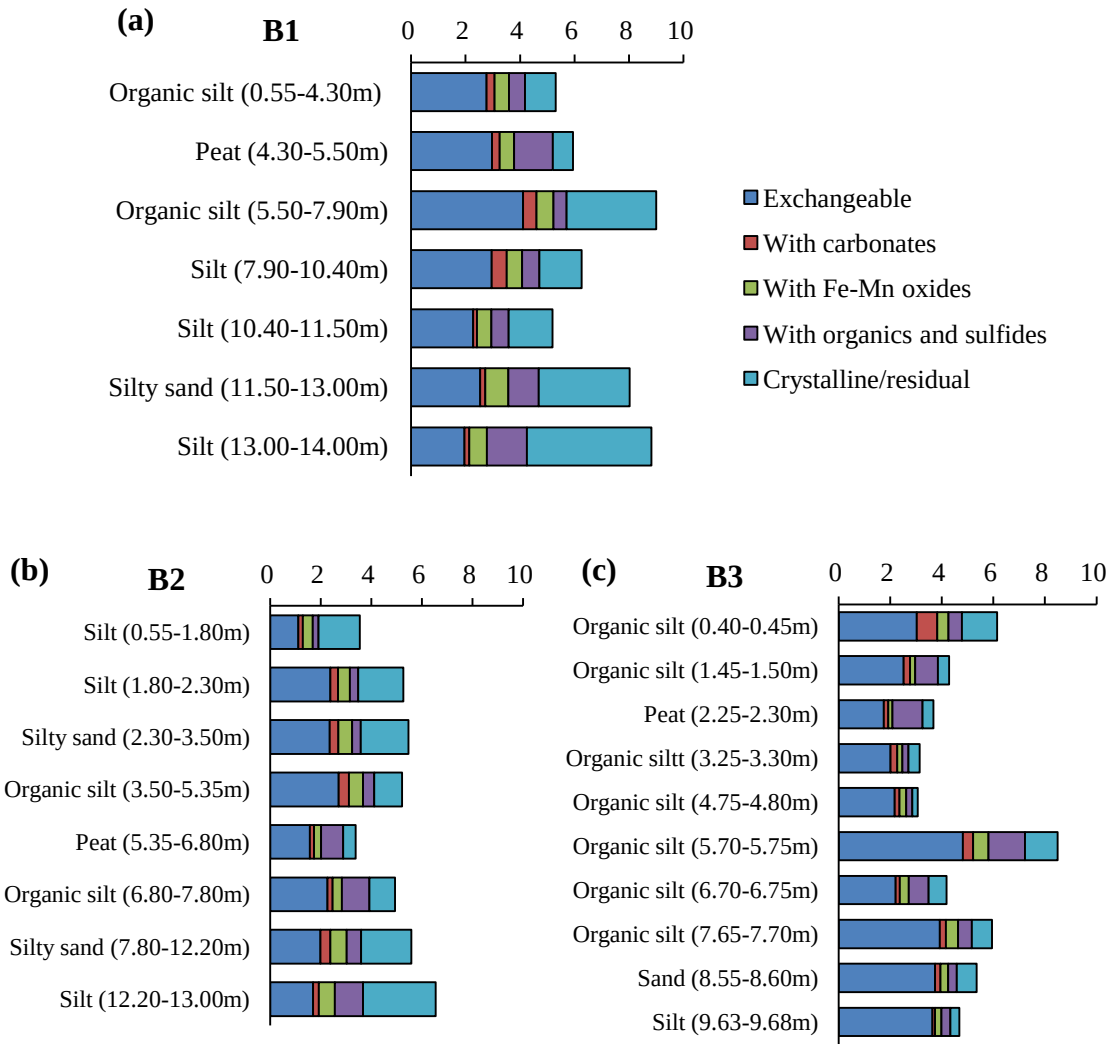

Figure 2-5. Solid-phase partitioning of As in boreholes (a) B1, (b) B2 and (c) B3

2.3.4 **Effects of organic matter and sulfur on As content**

Figure 2-6 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 ranged from 4 to 6 mg/kg when the TOC content was higher than 10 wt%. In addition, 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 saline

conditions.

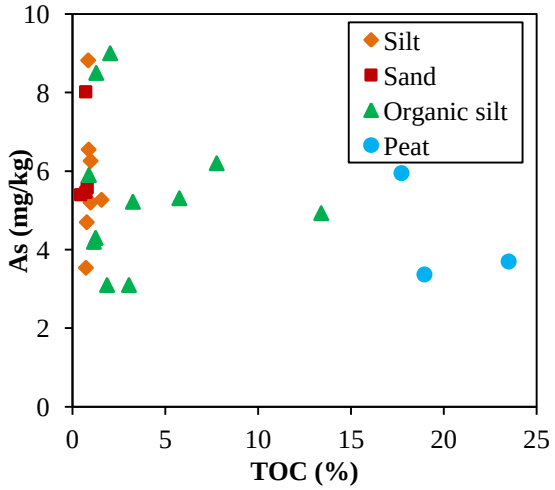

Figure 2-6. As content versus TOC content

2.3.5 **Principal component analysis of sediment samples**

For the PCA method, 9 parameters of 25 sediment samples were used to calculate factor loadings as presented in Table 2-3. The results showed that three factors accounted for 89.24% variance of the geochemical data. Factor 1 had higher loadings of SiO_2, Al_2O_3, S, TOC and LOI with 60.38% variance. Factor 2, with 15.47% of the variance, had higher loading of As, Fe_2O_3 and Na_2O. Factors 3, which explained 13.39% of the variance, showed higher loading of CaO. From the results, As content was affected by many factors.

Table 2-3. Rotated factor loadings of principal components of sediment samples

Variable	**Factor 1**	**Factor 2**	**Factor 3**
As (Content)	0.143	**0.612**	0.460
SiO_2	**0.418**	-0.115	-0.059
Al_2O_3	**0.352**	0.157	-0.338
Fe_2O_3	0.251	**0.591**	0.041
CaO	0.161	-0.276	**0.737**
Na_2O	0.348	**-0.392**	0.193
S	**-0.335**	0.057	0.294
TOC	**-0.425**	0.037	0.012
LOI	**-0.422**	0.063	0.035
Eigenvalue	5.433	1.392	1.205
Explained variance (%)	60.38%	15.47%	13.39%
Cumulative (%)	60.38%	75.85%	89.24%

2.3.6 **Relationship between As leaching and SO_4^{2-} leaching**

Figures 2-7(a) 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. 2-7(a). This indicates that leaching of As directly corresponded to 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. 2-7(b) shows that As released had a weak correlation with SO_4^{2-} leaching 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-} leaching concentration was higher than 100 mg/L.

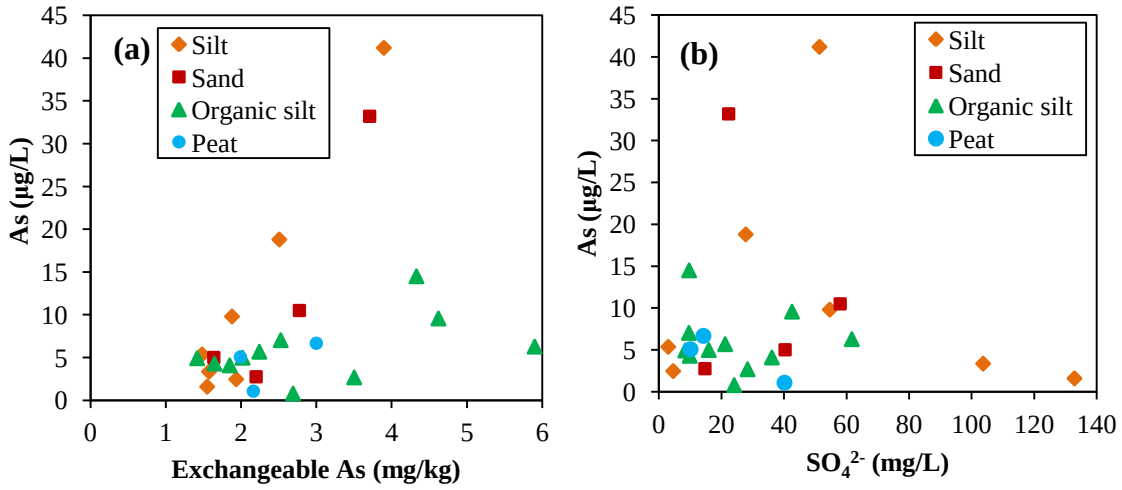

Figure 2-7. As leaching concentration versus (a) As content in exchangeable fraction and (b) SO_4^{2-} leaching concentration

2.3.7 **Relationship between As leaching and Fe leaching**

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, as shown in Fig. 2-8. 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. 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.

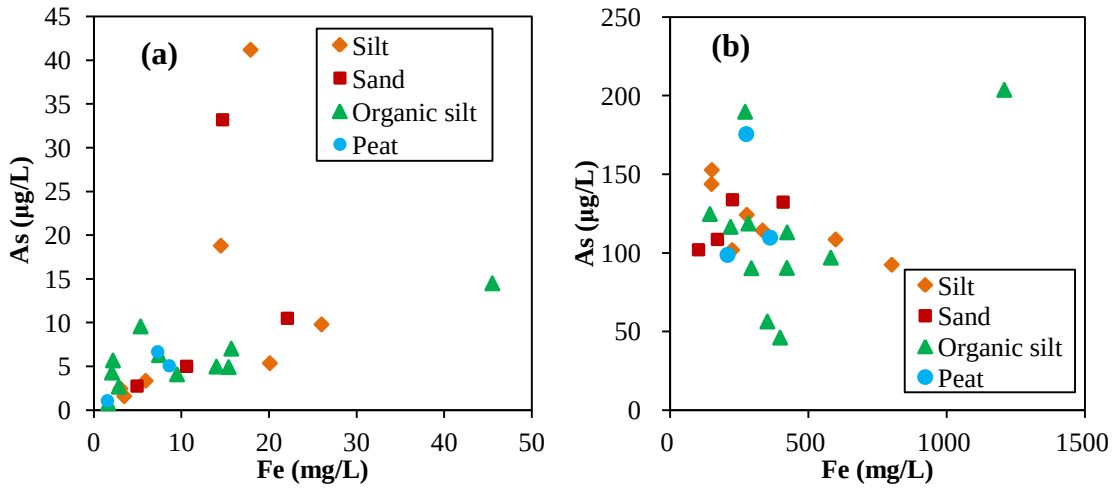

Figure 2-8. As leaching concentration versus Fe leaching concentration (a) under oxic condition and (b) under reducing condition

Figure 2-9(a) shows leaching concentration of As under reductive condition (As red) versus HCl extractable As. The leaching concentration of As ranged from 46 to 203 µg/L under reducing conditions whereas that ranged from 58 to 132 µg/L in HCl extractable As. Figure 2-9(b) shows leaching concentration of Fe under reductive condition (Fe red) versus HCl extractable Fe. The leaching concentration of Fe was changed from 156 to 1040 mg/L in HCl extractable whereas that was changed from 102 to 1210 mg/L in reducing conditions. This means that As is incorporated with not only amorphous Fe but also the other Fe oxyhydroxide.

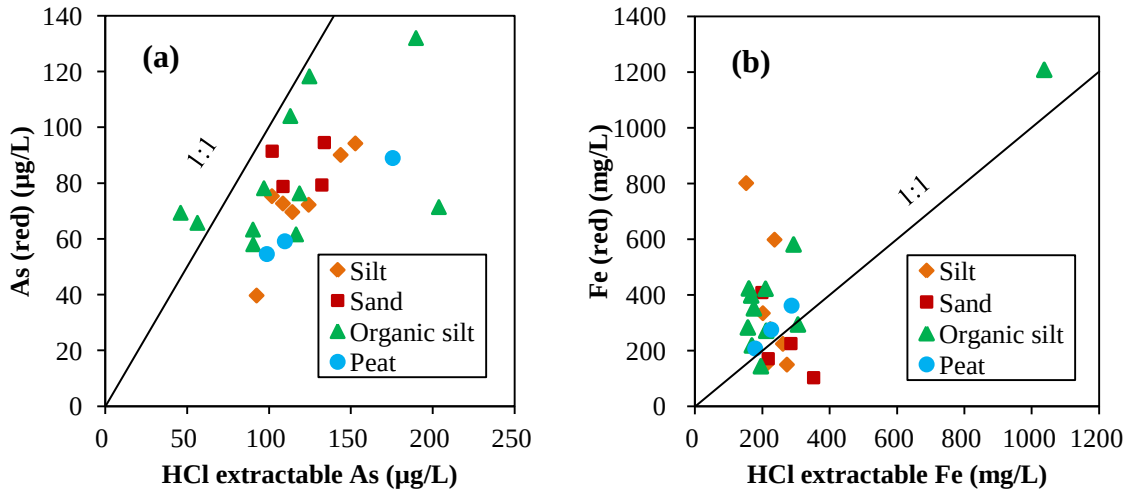

Figure 2-9. The leaching concentration under reducing condition versus HCl extratable (a) As concentration and (b) Fe concentration

2.3.8 **Effects of pH and Si leaching 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. 2-10. The As leaching concentration was higher under weakly alkaline condition (pH>8). Under oxidizing condition, As is less strongly bound to Fe oxyhydroxide 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.

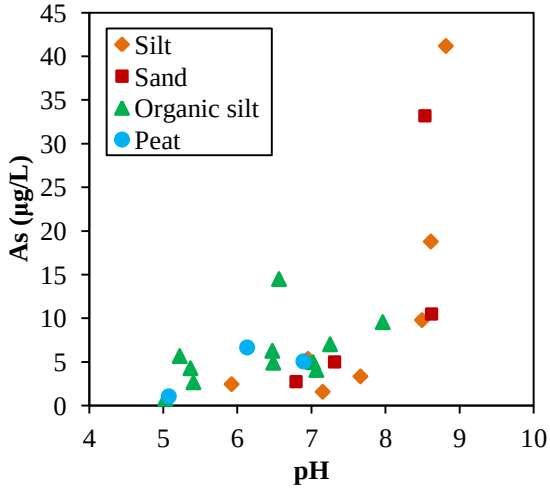

Figure 2-10. As leaching concentration versus pH

Leaching of Si was correlated with As release as shown in Fig. 2-11(a). Furthermore, Fig. 2-11(b) shows turbidity of leaching samples and Si leaching concentration had good correlation. This means that colloidal particles containing As were included in the leachates.

All the data of the leaching experiments under oxic conditions are listed in Table 2-4.

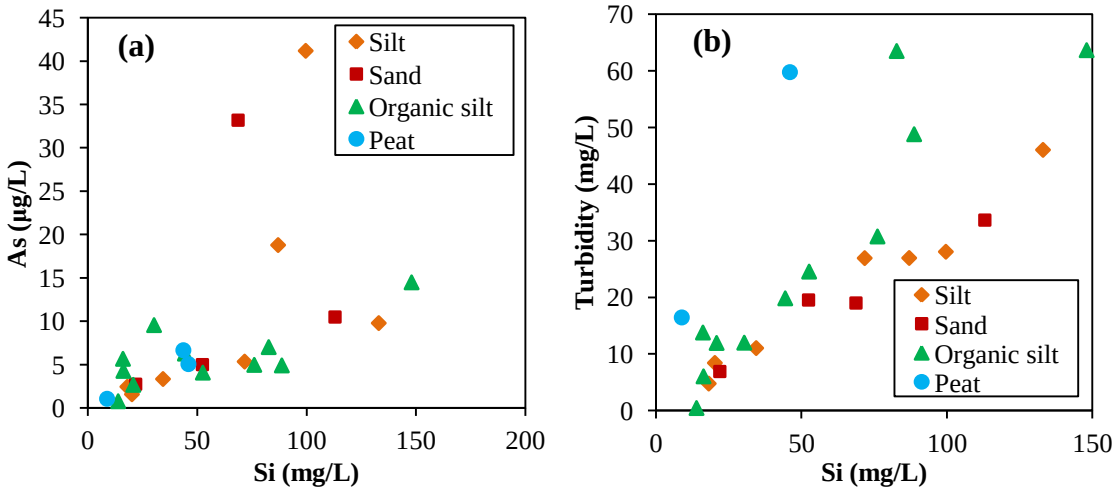

Figure 2-11. Si leaching concentration versus (a) As leaching concentration and (b) turbidity of leaching samples

Table 2-4. Chemical compositions of leachate in leaching experiments under oxic conditions

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

2.3.9 **Principal component analysis of leaching samples**

For the PCA method, 16 parameters of 25 leaching samples were used to calculate factor loadings as presented in Table 2-5. The results showed that three factors accounted for 70.36% variance of the geochemical data. Factor 1 with 36% variance had high loadings of Fe, Al, Si, ORP and pH, which were associated with dissolved Fe, Al and Si. Therefore, in alkaline conditions, factor 1 mainly affects As leaching concentration. Factor 2, with 20.3% 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 14.3% of the variance, showed higher loading of Na^+ and Mg^{2+}. These factors can effectively explain As release from the sediments in this site.

Table 2-5. Rotated factor loadings of principal components of leaching samples

Variable	**Factor 1**	**Factor 2**	**Factor 3**
As (Concentration)	0.254	-0.090	-0.228
As (Content)	0.231	0.102	0.199
Fe	**0.329**	-0.213	0.250
Al	**0.350**	-0.182	0.096
Si	**0.367**	-0.191	0.162
SO_4^{2-}	0.123	**0.495**	-0.132
NO_3^-	-0.231	0.169	0.199
Na^+	0.203	0.195	**-0.418**
Cl^-	-0.052	0.043	0.210
K^+	0.293	0.282	0.257
Mg^{2+}	0.247	0.063	**0.468**
Ca^{2+}	-0.069	**0.426**	0.300
EC	0.129	**0.498**	-0.046
pH	**0.352**	0.028	-0.205
ORP	**-0.334**	0.010	0.281
DOC	-0.021	-0.202	0.191
Eigenvalue	5.721	3.254	2.281
Explained variance (%)	35.76%	20.34%	14.26%
Cumulative (%)	35.76%	56.1%	70.36%

2.4 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 S 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 dissolved from the sediments. In addition, As in colloidal particles also affected As leaching. It is found that in this site, these factors affected the As content in the sediments and its leaching concentrations.

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Chapter 3
ARSENIC CONTENT OF UNCONSOLIDATED SEDIMENTS AND ITS MOBILIZATION IN THE MEKONG DELTA, VIETNAM

3.1 Introduction

Arsenic (As) contamination in groundwater leads to a healthy problem in the Southeast Asian countries, like Vietnam and Cambodia. In this region, groundwater is the main water sources for drinking water, and agricultural activities. The World Health Organization (WHO) recommends 10 µg/L of As as the drinking water guideline. Recent years, high As concentration in Vietnamese and Cambodian groundwater has been studied by several researchers (Agusa et al. 2006; Bang et al. 2010; Berg et al. 2001 and 2008; Nguyen and Itoi 2009; Rowland et al. 2008). Arsenosis has been associated with cancers of skin, lungs, bladder and kidneys, and these were reported in China, Taiwan, Bangladesh, India and Vietnam (Bhattacharya et al. 2007; Kuo et al. 2003; Ng et al. 2003). The approximately 16 million people living in the Mekong Delta in Vietnam and Cambodia are at risk for an elevated level of As in their drinking water (Vengosh et al. 2015).

The Mekong Delta is a vulnerable area for As contamination because this area is a young Quaternary deltaic and alluvial sediments containing As-bearing iron minerals. Arsenic concentration in groundwater related to As content was identified in this area, and higher As concentration is commonly detected in some aquifers. Arsenic contents higher than 10 mg/kg at a depth more than 30 m and close to Mekong River were observed (Bang et al. 2010; Nguyen and Itoi 2009). In the shallowest Holocene-Pleistocene aquifer, As occurrence was described by distance to Mekong River channels and delta front, depth, and location within fault-bounded zones of the region (Gorelick et al. 2014). 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). However, the distribution of As content in geological formations of this area are still unclear because several factors control the As content in alluvial environments.

The objectives of this chapter are (1) to examine factors affecting As content of unconsolidated sediment in the Mekong Delta, Vietnam, and (2) to elucidate As leaching properties using principal component analysis.

3.2 Materials and methods

3.2.1 Study area and core samples

The study area is located in An Giang and Dong Thap Provinces, the Mekong Delta, Vietnam as illustrated in Fig. 3-1. This area is known as groundwater contaminated area by As (Bang et al. 2010; UNICEF 2004).

Six boreholes were drilled along the Bassac River and Tien River (Mekong Rivers). In this study, four cores (PH, PHu, LS and PT) were selected from An Giang Province and other 2 cores (TL and TT) in Dong Thap Province. The description of geological formation of these boreholes is shown in Fig. 3-1 and Table 3-1. Sediment samples were collected from these cores at the different layers and depths as listed in Table 3-2. The core sediment samples were packed in polyethylene bags and then transported to Japan. The samples were dried at room temperature, and then crushed by an agate mortar and sieved through a 2 mm aperture screen. Finally, the samples were kept in air-tight containers to minimize oxidation.

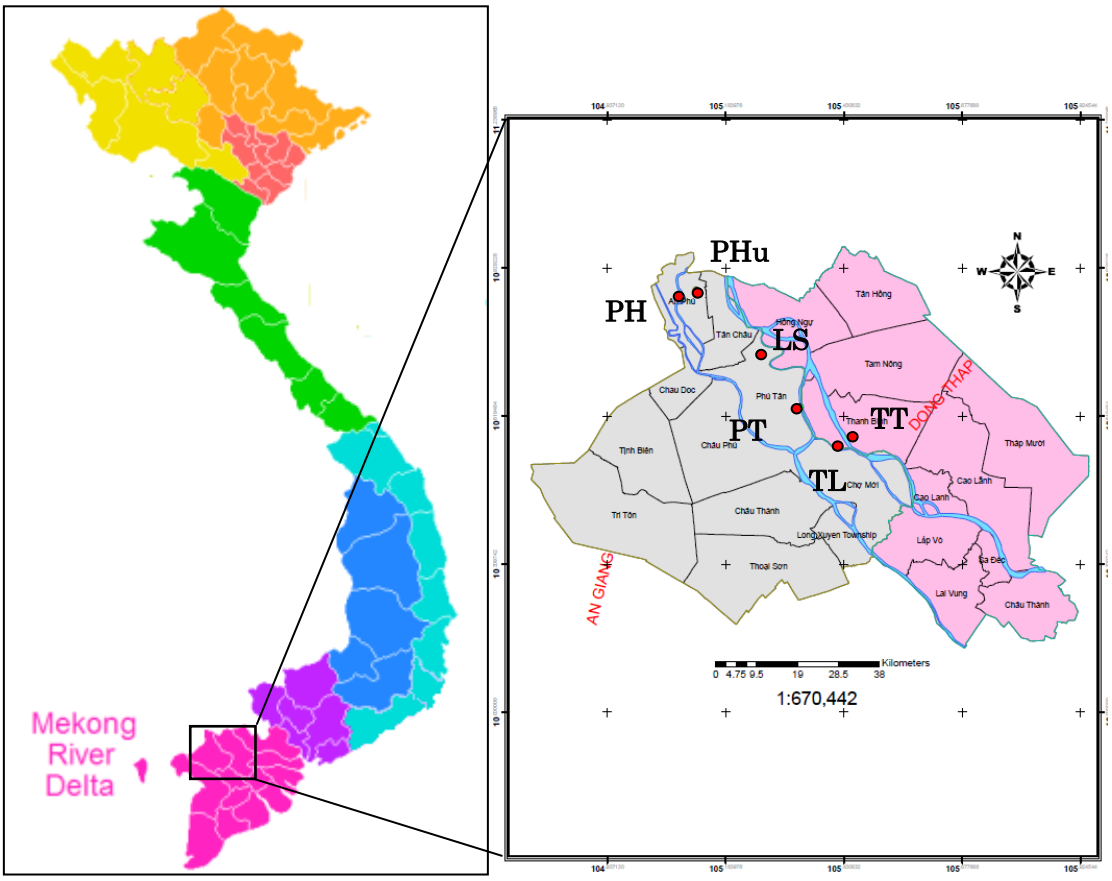


Figure 3-1. Location of the study area (Mekong Delta, Vietnam)

Table 3-1. Description of boreholes

Borehole	Location	Province	Depth (m)	Geological unit
LS	N 10°45'8.93", E 105°15'26.09"	An Giang	0-4.6	Brownish grey clayey silt
			4.6-9.0	Grey fine sand
			9.0-11.6	Brownish grey clayey silt
			11.6-16.5	Grey fine sand
			16.5-21.0	Brownish grey clayey silt
PH	N 10°52'14.5", E 105°05'4.9"	An Giang	0-11.1	Brownish grey clayey silt
			11.1-12.3	Grey fine sand
			12.3-17.2	Brownish grey clayey silt
			17.2-18.6	Grey fine sand
			18.6-20.0	Brownish grey clayey silt
PHu	N 10°52'54.5", E 105°07'16.7"	An Giang	0-4.5	Brownish grey clayey silt
			4.5-6.0	Grey fine sand
			6.0-7.0	Brownish grey clayey silt
			7.0-20.0	Grey fine sand
PT	N 10°38’15", E 105°20'4.6"	An Giang	0-16.0	Dark grey clayey silt
			16.0-19.0	Dark grey fine sand
			19.0-20.0	Black clayey peat
			20.0-24.0	Dark grey fine sand
			24.0-25.0	Black clayey peat
			25.0-32.0	Grey clayey silt
			32.0-36.0	Dark grey fine sand
			36.0-40.0	Dark grey coarse sand
TL	N 10°34'34.5", E 105°26'38"	Dong Thap	0-2.0	Yellow sand
			2.0-9.0	Grey clayey silt
			9.0-14.0	Dark grey fine sand
			14.0-20.0	Dark grey coarse sand
TT	N 10°33’22.8", E 105°27'49.6"	Dong Thap	0-3.0	Grey - yellowish clayey silt
			3.0-5.0	Dark-grey clayey silt
			5.0-21.0	Grey fine sand
			21.0-36.0	Grey medium sand
			36.0-40.0	Grey coarse sand

3.2.2 **Characterization of sediment samples**

The samples were ground in an agate mortar and sieved less than 0.075 mm in diameter for characterization. Mineral constitutes and chemical compositions were analyzed by using X-ray diffraction spectrometer, Multiflex (Rigaku Corporation, Japan) and X-ray fluorescence spectrometer, Xepos (Rigaku Corporation, Japan), respectively. Moreover, a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (SEM-EDX) was used to characterize the crystal morphology of minerals and take element maps on the surface of the samples (SSX-550, Shimadzu Corporation, Japan). Total organic carbon (TOC) was measured using TOC analyzer connected with a solid combustion system SSM-5000A (Shimadzu Corporation, Japan). Loss on ignition (LOI) was measured by the weight loss of the sample by heating 1 g sample inside a muffle furnace FB1300 (Thermo Fisher Scientific Inc., United States).

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 fractions; 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 3-3. Total As content was calculated from the data of this sequential extraction.

Table 3-2. Sediment samples provided for leaching experiments

No.	Sample	Depth (m)	Minerals identified
1	LS1	3.2-3.4	Quartz, pyrite, muscovite, kaolinite
2	LS2	5.8-6.0	Quartz, muscovite, kaolinite
3	LS3	7.7-7.9	Quartz, muscovite, kaolinite
4	LS4	10.6-10.8	Quartz, muscovite, kaolinite
5	LS5	13.7-13.9	Quartz, albite, muscovite
6	LS6	18.7-18.9	Quartz, albite, muscovite
7	PH1	2.8-3.0	Quartz, kaolinite, muscovite
8	PH2	7.2-7.4	Quartz, albite, muscovite
9	PH3	11.6-11.8	Quartz, muscovite
10	PH4	14.7-14.9	Quartz, muscovite, kaolinite
11	PH5	16.2-16.4	Quartz, muscovite
12	PH6	19.1-19.3	Quartz, muscovite, kaolinite
13	PHu1	3.2-3.4	Quartz, muscovite, kaolinite
14	PHu2	6.2-6.4	Quartz, muscovite, kaolinite
15	PHu3	10.7-10.9	Quartz
16	PHu4	16.7-16.9	Quartz
17	PT1	1.2-1.3	Quartz, kaolinite, muscovite
18	PT2	4.2-4.3	Quartz, kaolinite, muscovite
19	PT3	6.4-6.5	Quartz
20	PT4	11.2-11.3	Quartz, kaolinite, muscovite
21	PT5	17.6-17.7	Quartz, albite
22	PT6	19.2-19.3	Quartz, pyrite
23	PT7	21.6-21.7	Quartz
24	PT8	24.5-24.6	Quartz, muscovite
25	PT9	28.3-28.4	Quartz
26	PT10	38.1-38.2	Quartz
27	TL1	3.4-3.5	Quartz, kaolinite, muscovite
28	TL2	9.5-9.6	Quartz
29	TL3	16.5-16.6	Quartz, muscovite, albite
30	TT1	2.5-2.6	Quartz, muscovite
31	TT2	3.4-3.5	Quartz
32	TT3	12.4-12.5	Quartz
33	TT4	25.3-25.4	Quartz, muscovite
34	TT5	37.6-37.8	Quartz

Table 3-3. 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

3.2.3 **Leaching experiments**

Leaching experiments were conducted under both oxic and reducing conditions. The oxic leaching experiments were performed at ambient conditions at room temperature. Fifteen grams of a sample with less than 2 mm in diameter were mixed with 150 mL deionized water in an Erlenmeyer flask at 200 rpm for 6 h. For the leaching experiments under reducing conditions, the sodium dithionite ($Na_2S_2O_4$) was added as a reducing agent. Five grams of the sample were mixed with 50 mL of 0.1 M $Na_2S_2O_4$ solution at 200 rpm for 6 h in a 50 mL centrifuge tube to minimize oxidation of $Na_2S_2O_4$.

After mixing under both conditions, temperature, pH, ORP and EC were measured, and then the leachates were filtered by 0.45 μm Millipore sterile filters. For leaching experiments under reducing conditions, EC was not measured. The filtrates were stored in a refrigerator at 4 ºC for chemical analysis.

The leaching experiments using HCl solution were performed at ambient conditions at room temperature. Three grams of a sample with less than 2 mm in diameter was mixed with 100 mL of 1 M HCl solution at 200 rpm for 2 h. The leachates were filtered by 0.45 μm Millipore sterile filters and then the filtrates were provided for chemical analysis.

3.2.4 **Chemical analysis**

Concentrations of heavy metals, such as Fe and Mn, and Si were analyzed using ICP-AES (Shimadzu Corporation, Japan), and ICP-AES connected with the hydride vapor generation method was used for As concentration analysis. 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 concentration was measured by the titration with 0.02 N H_2SO_4.

3.2.5 **Multivariate statistical analysis**

The statistical software package Origin Pro software (OriginLab Corporation, USA) for windows was utilized for multivariate statistical analyses. This multivariate statistical method was used to identify the most important factors responsible for the association of As content and As leaching concentration (Guo et al. 2015; Jiao and Wang 2014; Nath et al. 2008b). Principal component analysis (PCA) used the eigenvectors of a variance-covariance matrix. Each factor (with high loading of one or more variables) may represent an independent source of variables and the calculated factors were normalized by the varimax method. In this study, PCA was applied for sediment samples (9 parameters of 34 samples) and leaching samples (16 parameters of 34 samples).

3.3 Results and discussion

3.3.1 **Geological units, minerals, and chemical compositions**

The Mekong Delta sediments are mainly composed of Holocene alluvial sediments (depths of 8-40 m) overlying the late Pleistocene sediments (50-80 m). However, The sediments in this area were delivered from an upstream of the Mekong River. The mud content is low, and generally sand is a dominant face. However, the grain size becomes finer seaward, (Gugliotta et al. 2017; Kocar and Fendorf 2012; Nguyen and Itoi 2009). In this area, geological units of 6 boreholes have alternating strata of clayey silt and fine-medium sand, and some clayey peat layers were found with a meter to several meters in thickness. Table 3-2 shows the mineral compositions of sediment samples by XRD analysis. The XRD data reveal that the major minerals in the sediments were quartz, muscovite, and albite, while kaolinite was found in clayey silt. In addition, a trace amount of pyrite was also identified in peat and clayey silt.

The results of XRF analysis in Table 3-4 show that major chemical compositions of sediments were SiO_2, Al_2O_3, and Fe_2O_3 amounting to more than 70 wt% of the total content. The content of SiO_2 reached 70 wt% in sand and decreased in clayey silt. The content of Fe_2O_3 was higher in clayey silt and lower in sand. Higher Al_2O_3 content was observed in clayey silt. The TOC content was higher in clayey silt and peat relative to the dark-grey and brown clayey silt layers with TOC content > 1 wt%. the values of LOI ranged 1-26 wt%. However, the values were significantly high in peat layers. The mineralogical and chemical properties depended on geological formations.

Table 3-4. Chemical compositions of sediment samples

Lithology	SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	CaO (wt%)	Na_2O (wt%)	As (mg/kg)	S (wt%)	TOC (wt%)	LOI (wt%)
LS1	52.9	15.9	4.7	0.2	0.5	16	0.83	1.1	6.2
LS2	58	9.2	4.9	0.5	<0.1	9.8	0.24	1.1	4.1
LS3	52.6	11.1	5.1	0.6	0.2	8.7	0.17	0.9	4.2
LS4	47.9	14.5	7.1	0.6	0.1	15.6	0.1	1.4	7.1
LS5	68.2	6	2.5	0.3	0.3	3.8	0.06	0.2	1.4
LS6	47.6	15.4	7.1	0.5	0.1	12.4	0.11	1.1	6.8
PH1	44.1	13.6	9.6	1.3	<0.1	38.6	<0.01	0.3	5.3
PH2	50.9	11.8	5.4	0.6	0.2	9	0.02	1.0	4.9
PH3	60.5	9.8	4.2	0.4	0.3	6.8	0.01	0.5	2.7
PH4	55.5	11.7	4.8	0.5	0.2	9.3	0.01	0.8	4.2
PH5	51.6	13.8	5.9	0.5	0.2	13	<0.01	1.1	5.8
PH6	48.2	13	6	0.6	0.4	11.4	0.03	1.0	5.8
PHu1	49.3	13.5	6.5	0.9	<0.1	11.6	<0.01	1.0	5.7
PHu2	48.9	14.1	6.8	0.6	<0.1	12	0.1	1.0	5.7
PHu3	71.2	4.4	2.3	0.3	<0.1	4	<0.01	0.04	0.9
PHu4	70.6	3.6	2.1	0.2	0.4	4.9	<0.01	0.02	0.8
PT1	70.8	23.2	4.4	0.3	0.3	9.9	0.03	0.4	4.9
PT2	66.2	24.3	7.5	0.2	0.4	11.8	0.13	0.4	6.8
PT3	72.4	17.1	4.9	0.5	0.8	10.4	1.22	0.1	5
PT4	66.2	22.1	7.2	0.7	0.6	10.5	0.23	0.9	6.8
PT5	86.3	9.6	2.3	0.4	1.1	3.6	0.08	0.2	1.5
PT6	62.9	22.8	7.7	0.7	1.3	35.7	3.9	12.8	26.3
PT7	84	11.6	2	0.5	1.6	3.2	0.06	0.2	1.9
PT8	64.9	25.4	4.5	0.4	0.9	25.9	0.54	6.6	16.2
PT9	67.7	21.6	7.4	0.4	0.8	8.6	0.02	0.2	5.1
PT10	90	7.3	2	0.3	1	2.6	0.02	0.1	1.1
TL1	71.5	19.1	5.8	0.9	0.7	14.8	0.03	0.8	4.7
TL2	81.6	12.5	3.5	0.5	1.2	5.8	<0.01	0.1	1.8
TL3	91.5	6.7	1.8	0.2	0.8	6.2	<0.01	0.04	0.8
TT1	68.4	21.8	4.8	0.8	0.8	7.5	<0.01	0.1	5.3
TT2	75.8	17.8	3.8	0.4	0.8	12.6	0.08	0.7	3.7
TT3	89.4	8.3	1.8	0.3	1	3.4	<0.01	0.1	1.1
TT4	90.2	7.7	1.7	0.2	1	2.8	<0.01	0.1	1.1
TT5	84.2	9.5	4.6	0.3	0.9	9.8	0.02	0.1	1.7

3.3.2 **Effects of Fe, organic matter, and sulfur on As content**

Figure 3-2 shows the vertical distribution of As content in the sediments. The total As content of the sediment samples ranged from 2.8 to 38.6 mg/kg with a mean of about 9.8 mg/kg of all samples. These are within the typical range for sediments of a previous study (Bang et al. 2010). Higher As content was observed in boreholes PT, PH and LS compared to the other boreholes. The three boreholes were located in a river meander of An Giang area between Mekong River and Bassac River. Higher As content was found in clayey silt layers and decreased in sand layers. Particularly, As content higher than 25 mg/kg was observed in clayey silt (PH1) and peat (PT6 and PT8).

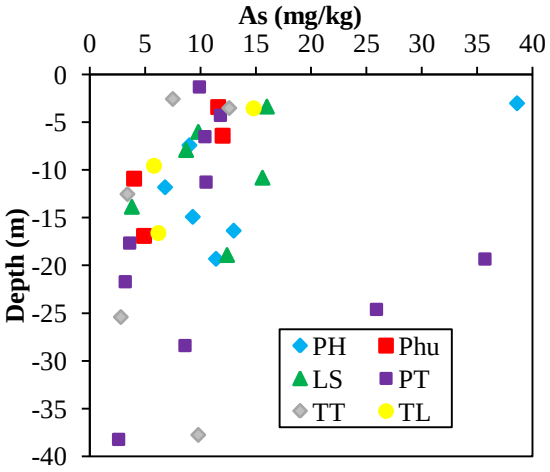


Figure 3-2. As content with depth

Figure 3-3 shows the relationship between As content and Fe_2O_3, S or TOC content. Arsenic content had a good correlation with Fe_2O_3 content as illustrated in Fig. 3-3 (a). The clayey silt layers contained higher Fe_2O_3 than sand layers. Higher As content in peat, clayey silt, and sand coresponeded to higher Fe_2O_3 content, indicating that As coexists with Fe. This suggests an association between As and Fe-oxyhydroxide. This was confirmed by results of SEM-EDX observation as shown in Fig. 3-4. The As-bearing mineral associated with Fe-Ti oxides was found in sample TT2.

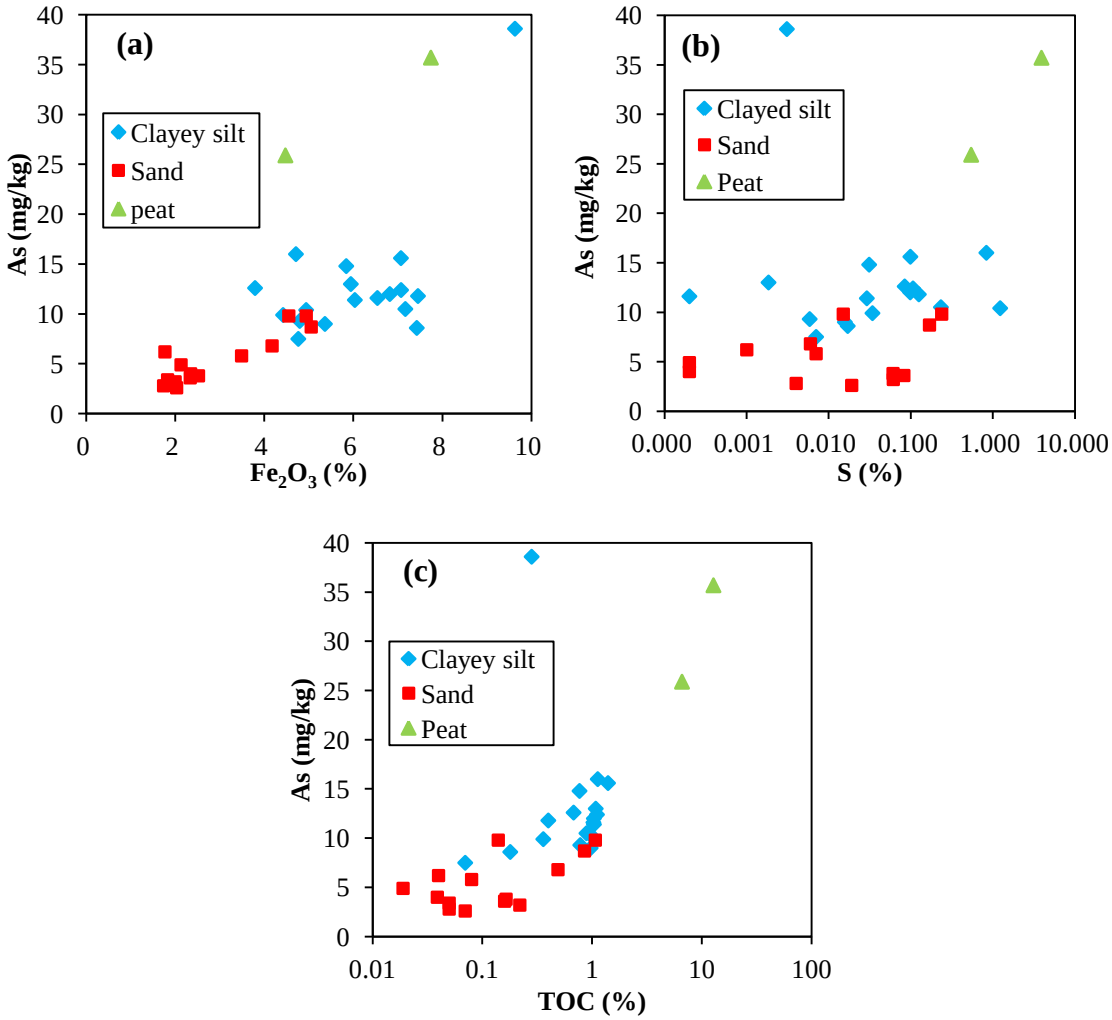


Figure 3-3. As content versus (a) Fe_2O_3, (b) S, and (c) TOC contents

The S content was weakly correlated with As content. Higher As content was found in peat and clayey silt compared with sand in Fig. 3-3 (b). Figures 3-5 and 6 show framboidal pyrite containing As in peat (PT8) and clayey silt (TT2), indicating that pyrite is responsible to As content. In particular, framboidal pyrite is often found in coastal, marine and estuarine sediments, where pore water contains high concentration of S (Wilkin and Barnes 1997).

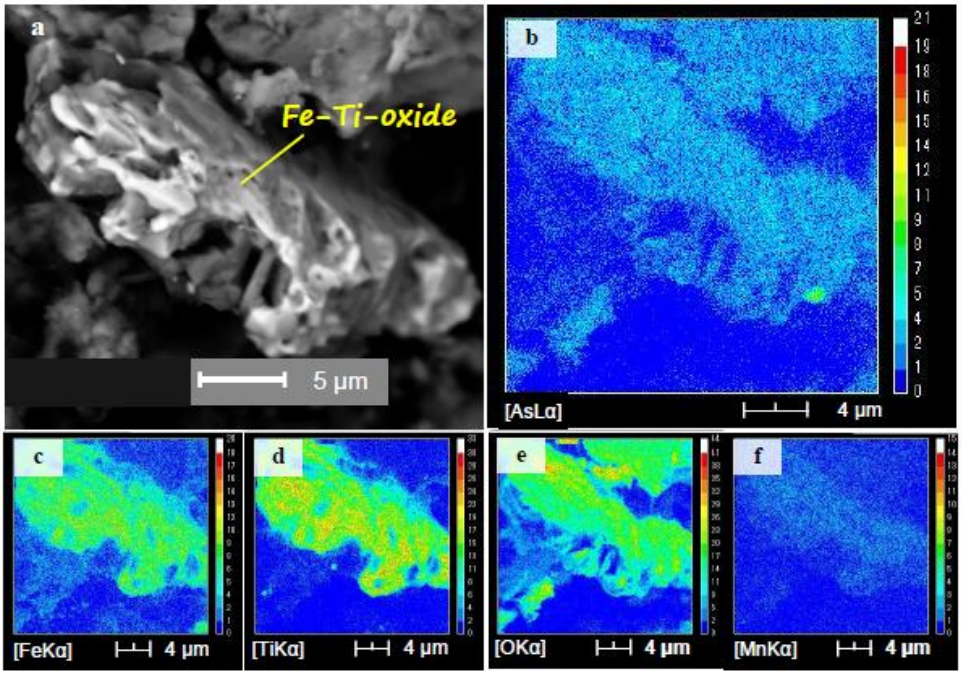


Figure 3-4. SEM-EDS observation of TT2 (a) SEM of Fe-Ti oxides, and its element maps of As (b), Fe (c), Ti (d), O (e), and Mn (f)

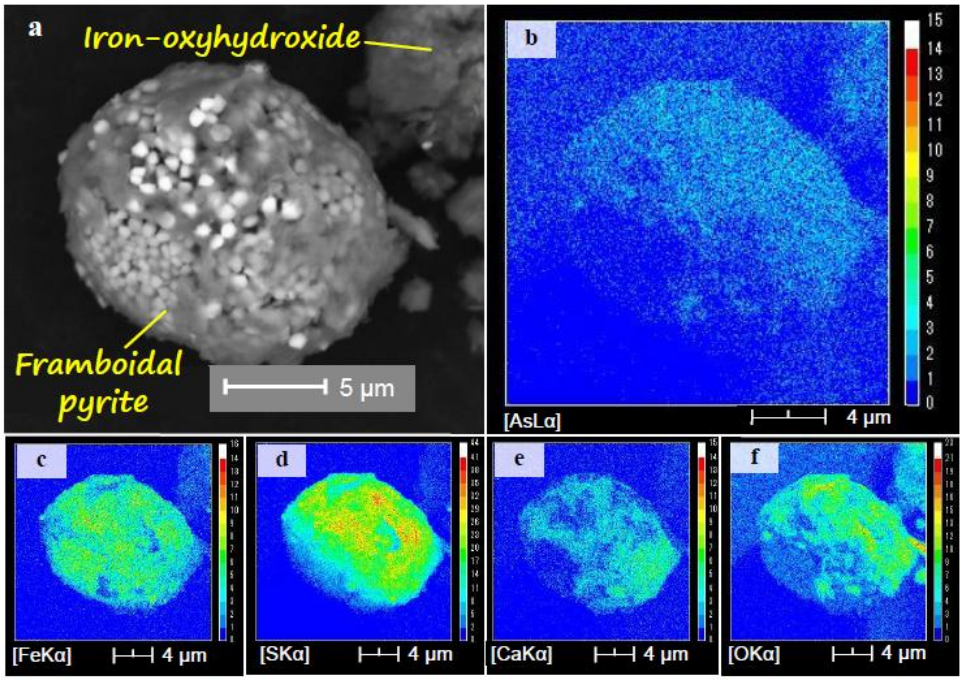


Figure 3-5. SEM-EDS observation of TT2 (a) SEM of slightly oxidized framboidal pyrite, and its element maps of As (b), Fe (c), S (d), Ca (e), and O (f)

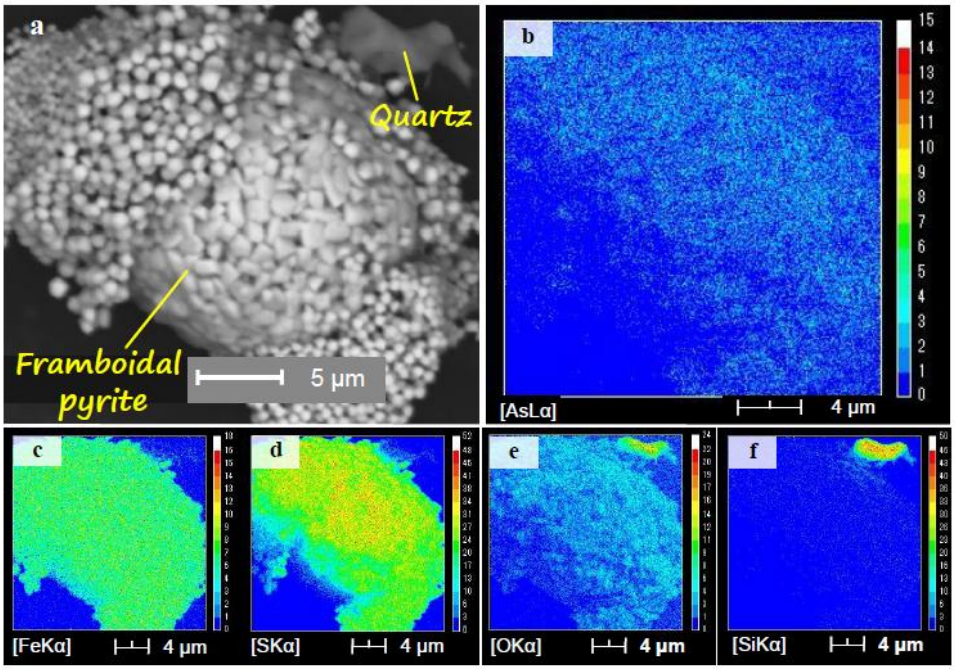


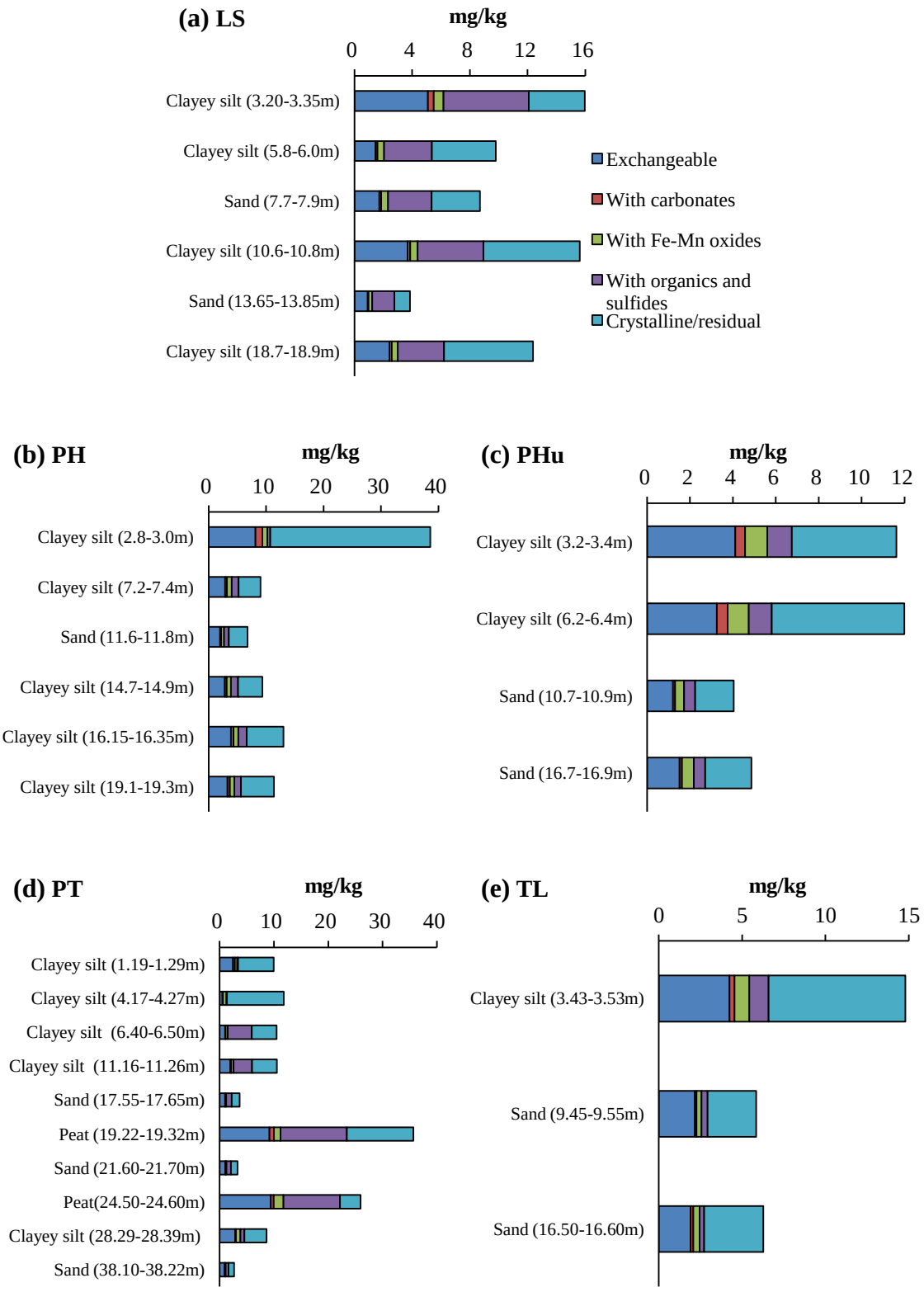
Figure 3-6. SEM-EDS observation of PT8 (a) SEM of slightly oxidized framboidal pyrite and its element maps of As (b), Fe (c), S (d), O (e), and Si (f)

Figure 3-3 (c) shows that As content had a positive correlation with TOC content. This means that As content in sediments increased with TOC content. The clayey silt contained higher TOC than the sand. The TOC of clayey silt was higher than 0.1 wt%, whereas that of peat was higher than 10 wt%. The previously research stated that the pyrite is likely to be formed upon deposition/formation of peat in the past estuarine environment, and that the present geochemical conditions represent a stable host of As under the reducing aquifer condition (Fendrof et al. 2015). This agreed with our results. Pyrite was also identified in the peat sample as shown in Fig. 3-6, and the As content of higher organic samples (PT6 and PT8) was higher than 25 mg/kg. These results mean that organic matter may be the site of high rates of sulfide production by sulfate reducing bacteria and the consequent precipitation of iron monosulfides (Wilkin and Barnes 1997).

3.3.3 **Effects of geology and sedimentation condition on As content and fraction**

Figure 3-7 shows vertical profiles of solid phase partitioning of As. Two major fractions were observed irrespective of depth; one was an exchangeable fraction ranging from 10 to 40 % of the total As content of samples, and the other was a residual fraction ranging from 20 to 70 %. Significant As content was also observed for the organic/sulfide fraction (5-40 %). The higher organic/sulfide fraction of As was found in peat and clayey silt samples, indicating that part of As was associated with the oxidizable phase. The remaining was carbonates (2-7 %) and with Fe-Mn oxides (2-13 %). The As content higher than 25 mg/kg was observed at shallow clayey silt with higher exchangeable fraction

of borehole PH, and at peat with higher organic/sulfide fraction of borehole PT. These results agreed with those of Gustafsson and Tin (1994).



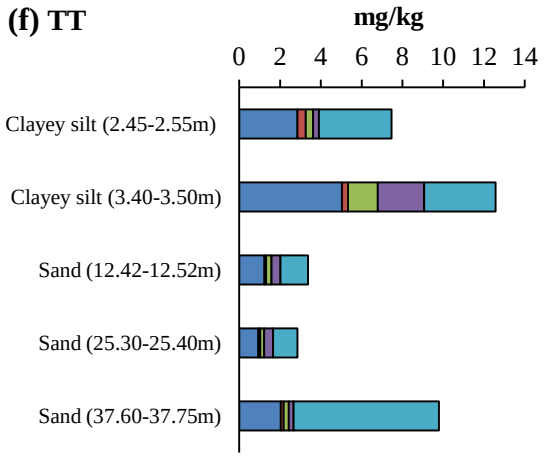


Figure 3-7. Solid-phase partitioning of As in boreholes (a) LS, (b) PH, (c) PHu, (d) PT, (e) TL and (f) TT

Sulfur and organic carbon contents in modern and ancient sediments have been used to characterize sedimentary environments by several researchers (Berner and Raiswell, 1984; Sampei et al., 1997). The ratio of organic carbon content to sulfur content (C/S) (wt%/wt%) was used to distinguish its sedimentary condition. According to their researches, the sediment formed under freshwater conditions is characterized by C/S values >10 whereas that formed under saline conditions is characterized by C/S<10. Figure 3-8 shows the vertical distribution of C/S. One-third of sediment samples (clayey silt and sand) had C/S<10, indicating that the sediments were formed in saline water conditions. As a result, more S is available for reaction with Fe (Berner and Raiswell 1983). The higher As content of the sediments was observed in the layers formed in saline conditions (LS, PT). When TOC is high even under saline conditions, Fe-oxyhydroxide is effectively converted to pyrite. That is why the higher organic/sulfide fraction of As was observed in LS and PT samples as shown in Figs. 3-7 (a) and (d). These indicate that As content was affected by sedimentary conditions. These conditions are common processes in marine sediments of deltaic environments (Lin and Morse 1991; Emeis et al, 1991). However, the sedimentary condition depended on location of boreholes in this area.

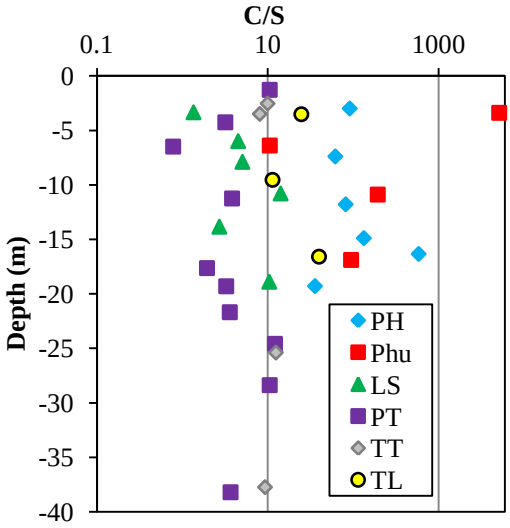


Figure 3-8. Vertical profile of C/S

3.3.4 **Principal component analysis of sediment samples**

For the PCA method, 9 parameters of 34 sediment samples were used to calculate factor loadings as presented in Table 3-5. The results showed that two factors accounted for 77.34% variance of the geochemical data. Factor 1 mainly affected As content of sediment with 51.13% variance with higher loadings of Fe_2O_3, Al_2O_3, TOC and LOI. The content of As is associated with organic matter, Fe, and Al in the sediments. Factor 2, with 26.21% of the variance, had higher loading on S, SiO_2 and Na_2O which was associated with the formation of sediments in the saline conditions and sandy layers. As a result, the content of Fe, Al, Si, S and organic matter, in addition particle size, affected distribution of As content.

Table 3-5. Rotated factor loadings of principal components of sediment samples

Variable	**Factor 1**	**Factor 2**
As (Content)	**0.417**	-0.022
SiO_2	-0.281	**0.461**
Al_2O_3	**0.319**	0.066
Fe_2O_3	**0.373**	-0.301
CaO	0.276	-0.270
Na_2O	-0.052	**0.566**
S	0.324	**0.376**
TOC	**0.368**	0.332
LOI	**0.428**	0.210
Eigenvalue	4.601	2.359
Explained variance (%)	51.13%	26.21%
Cumulative (%)	51.13%	77.34%

3.3.5 **Effects of leaching conditions on As release**

The leaching concentration of As ranged from 0.1 to 50 μg/L in oxic conditions (Table 3-6) whereas that ranged from 35 to 577 μg/L in reducing conditions. The leaching concentration of Fe was changed from 0.2 to 138 mg/L in oxic conditions whereas that was changed from 99 to 1,200 mg/L in reducing conditions. Both As and Fe leaching concentrations dramatically increased by changing from oxic conditions to reducing conditions as shown in Figs. 3-9(a) and (b). The As leaching is likely to be related to Fe leaching by considering weak correlations between As and Fe in both conditions except peat samples. These indicate that As was adsorbed on Fe hydroxide/oxide and that both elements were dissolved in reducing conditions.

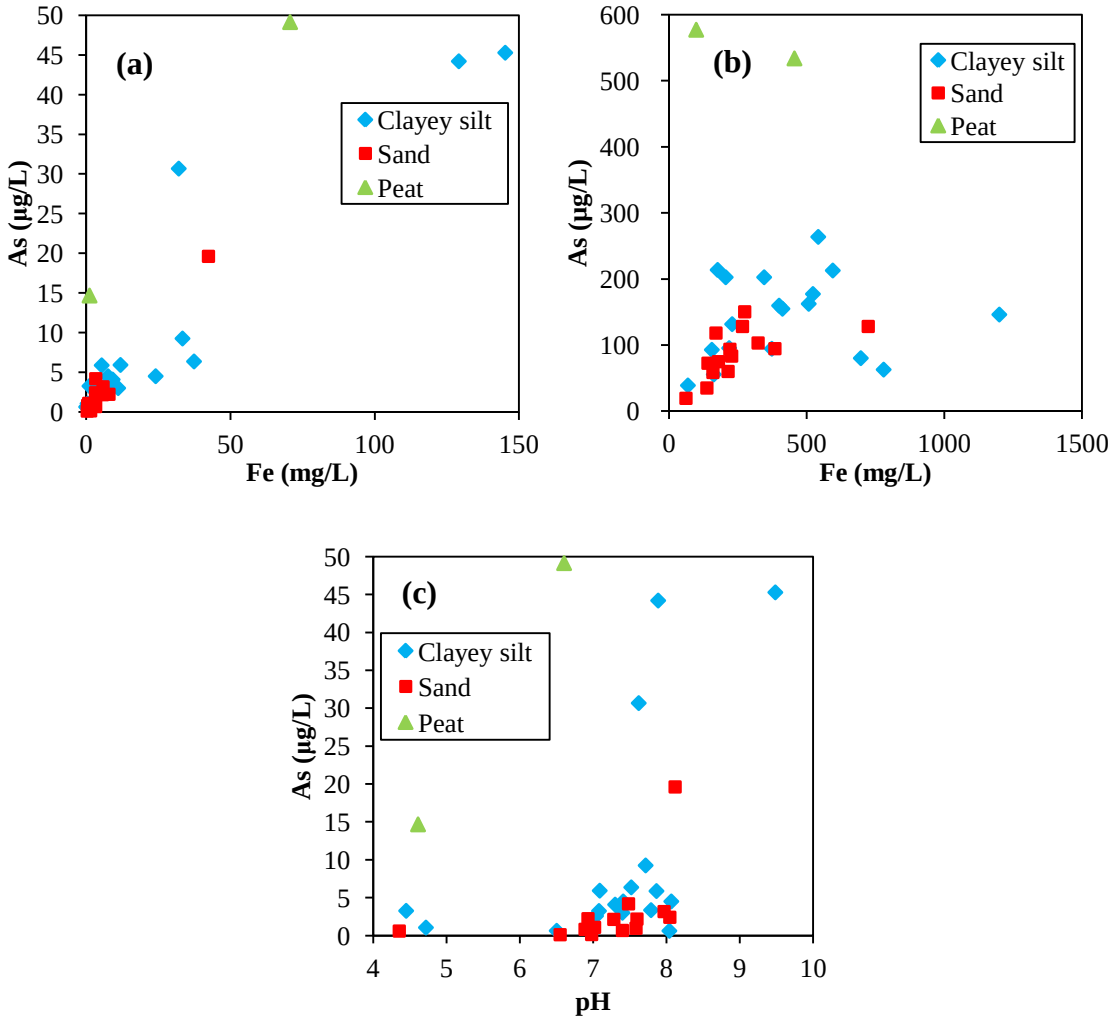


Figure 3-9. As leaching concentration versus (a) Fe leaching concentration under oxic conditions, (b) Fe leaching concentration under reducing conditions and (c) pH under oxic conditions

Although the pH values of the leachates in oxic conditions ranged from 4.5 to 9.5, slightly acidic pH of the leachates was observed from pyrite-bearing sediments in Fig. 3-9(c). The As leaching concentration was higher under weakly alkaline condition (pH>7.5) except peat. Under the oxic condition, As is less strongly bound to Fe oxide at higher pH than lower pH. Thus, at neutral pH under oxic conditions, As is effectively immobilized by sorption or co-precipitation with Fe oxide, whereas at higher pH the negative charge of the sediment surface releases As (Smedley and Kinniburgh, 2002).

Arsenic leaching concentration was in a good correlation with Si leaching concentration as shown in Fig. 3-10(a) since the filtrates were not transparent. In addition, Fig. 3-10(b) shows turbidity of leaching samples and Si leaching concentration had positive correlation. This means that colloidal particles containing As is partly responsible to the mobility of As.

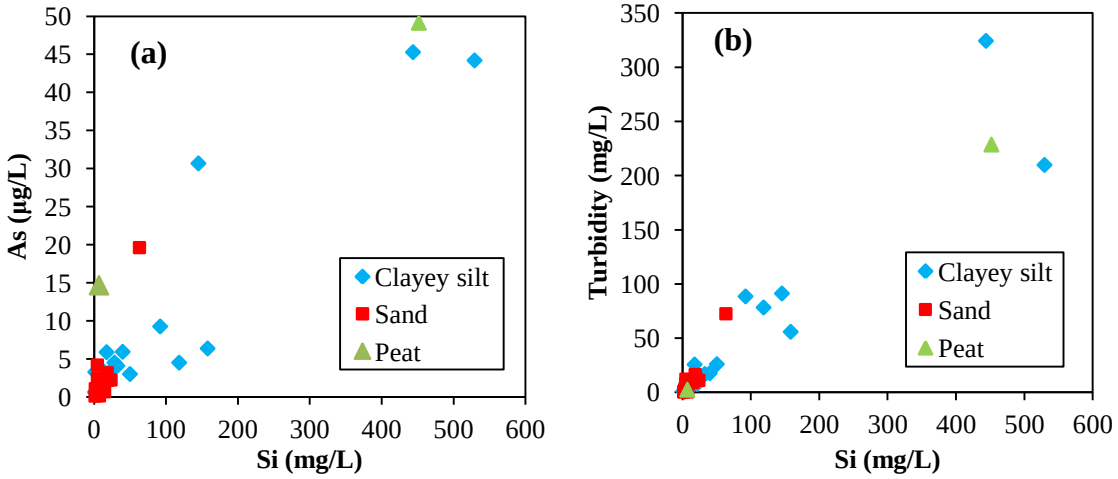


Figure 3-10. Si leaching concentration versus (a) As leaching concentration under oxic conditions and (b) turbidity of leaching samples

Figure 3-11(a) shows leaching concentration of As under reductive condition (As red) versus HCl extractable As. The leaching concentration of As ranged from 35 to 577 µg/L under reducing conditions whereas that ranged from 8 to 211 µg/L in HCl extractable As. Figure 3-11(b) shows leaching concentration of Fe under reductive condition (Fe red) versus HCl extractable Fe. The leaching concentration of Fe was changed from 7 to 661 mg/L in HCl extractable whereas that was changed from 99 to 1,200 mg/L in reducing conditions. This means that As is incorporated with not only amorphous Fe but also the other Fe oxyhydroxide.

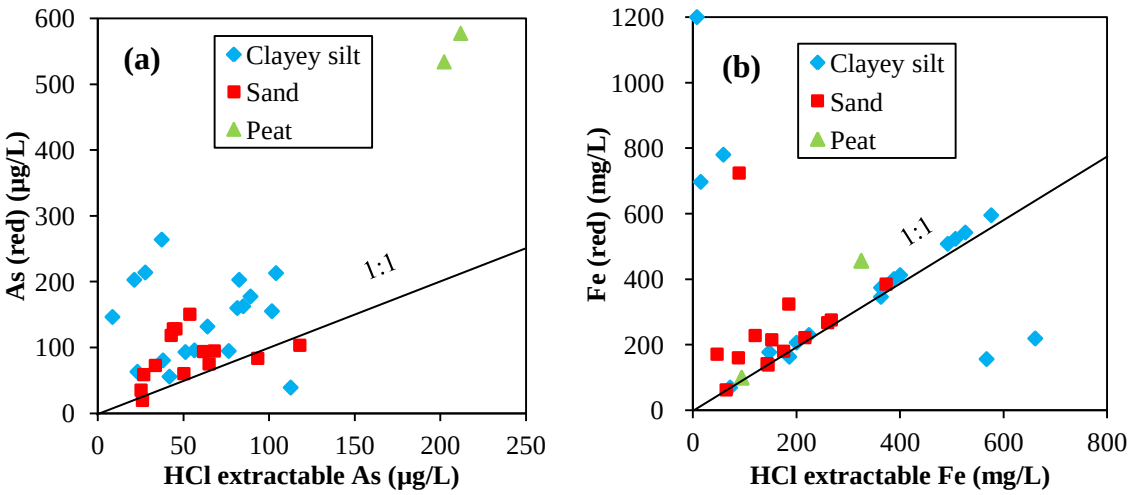


Figure 3-11. The leaching concentration under reducing condition versus HCl extratable (a) As concentration and (b) Fe concentration

3.3.6 **Effects of sulfate and organic matter on As release**

Arsenic leaching concentration increased with sulfate (SO_4^{2-}) leaching concentration, except some samples in boreholes PT and TT with As leaching concentration higher than 15 µg/L, as shown in Fig. 3-12 (a). These leaching properties of As are due to oxidation of As-bearing pyrite, resulting in higher SO_4^{2-} concentration (Tabelin et al. 2014). When the sediments are formed, sulfate-reducing bacteria are active. The produced sulfide is precipitated with Fe and As (Jin et al. 2004).

Dissolve organic carbon (DOC) concentration was correlated with As leaching concentration for clayey silt and peat, as demonstrated in Fig. 3-12 (b). This indicates that DOC is responsible for As release (Bauer and Blodau 2006).

All the data of the leaching experiments under oxic conditions are listed in Table 3-6.

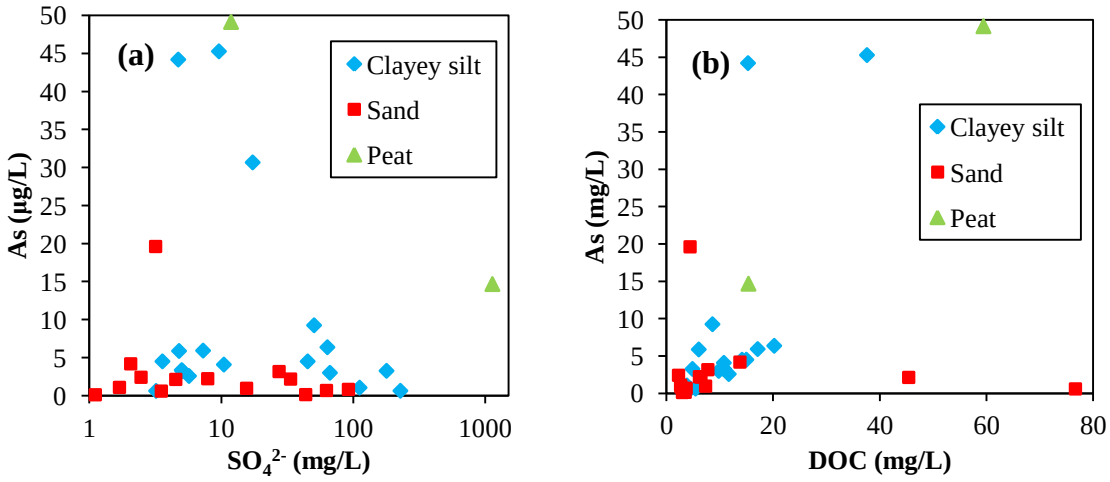


Figure 3-12. As leaching concentration versus (a) SO_4^{2-} leaching concentration and (b) DOC leaching concentration

Table 3-6. Chemistry of leachate in leaching experiments under oxic conditions

Sample	pH	EC (mS/m)	ORP (mV)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Fe (mg/L)	Al (mg/L)	Si (mg/L)	As (μg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	HCO_3^- (mg/L)	DOC (mg/L)
LS1	4.5	37.5	300	3.8	3.7	11.8	48.1	1.1	1.3	1.7	3.3	179	2.7	0	4.9
LS2	6.9	23.3	166	3.9	4.1	12.9	21.0	0.5	1.8	3.9	0.8	91.9	2.7	14.6	2.7
LS3	7.4	21.3	159	5.0	8.2	11.8	14.5	3.3	9.8	14.7	0.7	62.7	11.4	17.7	3.7
LS4	7.4	21.1	147	12.9	8.8	15.2	6.2	11.1	33.5	50.0	3.0	66.6	6.7	20.7	9.8
LS5	7	11.9	160	1.7	2.3	7.4	9.0	1.6	4.5	7.5	0.1	43.6	1.7	6.7	3.5
LS6	7.5	28.2	126	41.4	18.3	12.1	2.3	38.8	10.9	158	6.4	63.7	20.9	28.7	20.2
PH1	8	12.7	154	3.4	0.7	5.1	16.7	0.2	0.4	2.4	0.6	3.2	1.6	72.5	4.5
PH2	7.4	6.8	173	2.5	3.3	1.6	3.0	7.6	24.0	28.4	4.5	3.6	4.1	22.6	15.0
PH3	6.9	4.8	189	1.6	2.6	2.6	4.6	7.9	18.9	23.6	2.2	7.9	4.3	8.5	6.2
PH4	7	5.1	200	4.5	2.6	1.9	3.4	6.3	17.0	21.1	3.2	5.1	3.4	14.6	10.8
PH5	7	6.1	190	10.0	3.8	2.2	1.9	11.9	28.9	39.8	5.9	7.3	2.0	14.0	17.1
PH6	7.3	9.8	187	10.1	3.5	3.8	6.2	9.2	23.1	32.4	4.1	10.5	12.7	19.5	10.7
PHu1	7.8	11.6	173	5.8	3.2	2.6	12.4	3.9	10.6	13.4	3.4	5.0	3.9	60.3	10.5
PHu2	7	7.4	194	5.0	2.4	1.5	3.2	5.0	11.8	15.7	2.6	5.7	7.8	13.4	11.7
PHu3	7	2.2	174	1.3	0.9	0.4	1.9	0.9	0.7	1.8	1.1	1.7	2.2	9.8	2.6
PHu4	6.6	1.4	185	1.0	0.6	0.2	1.0	0.4	0.3	1.4	0.1	1.1	1.6	5.5	3.0
PT1	7.7	23.9	146	30.6	10.9	8.0	8.1	34.8	66.5	92.1	9.3	50.5	30.1	18.0	6.0
PT2	4.7	29.9	322	17.0	2.2	11.7	16.6	0.5	1.1	4.3	1.1	112	14.5	1.46	1.4
PT3	6.5	54.7	155	15.5	4.3	31.7	42.6	<0.1	0.2	2.6	0.7	228	6.3	9.74	3.0
PT4	8.1	22.9	119	22.0	14.1	13.5	7.9	26.0	74.4	118	4.5	42.9	1.3	39.0	13.0

PT5	7.6	13.0	130	7.5	6.1	4.7	6.7	5.7	12.0	18.8	2.2	33.5	8.0	11.2	4.0
PT6	4.6	217	255	128	22.4	149	125	1.1	0.2	6.9	14.7	1134	57.4	0	15.4
PT7	8.0	12.6	122	8.7	5.6	3.9	6.5	5.8	12.2	18.3	3.2	27.4	9.9	15.6	5.2
PT8	6.6	56.1	158	84.0	42.5	21.3	6.6	65.1	301	424	49.1	119	62.3	13.2	59.1
PT9	7.9	14.5	91	27.9	42.6	22.2	5.5	121.3	343	491	44.2	4.7	18.0	36.1	15.0
PT10	7.6	7.9	132	5.2	2.9	2.1	4.0	1.8	1.9	4.0	1.0	15.5	7.7	9.74	4.8
TL1	7.9	8.3	95	4.6	2.8	2.2	8.9	5.4	11.4	17.5	6.1	4.8	7.7	34.1	6.0
TL2	8.0	3.0	88	0.9	1.5	0.7	3.4	3.2	2.6	4.7	2.6	2.5	1.1	17.1	2.2
TL3	7.5	2.8	151	1.3	1.7	0.8	2.8	3.3	2.4	4.6	4.4	2.1	2.5	14.1	13.8
TT1	9.5	23.5	50	49.5	40.4	23.2	9.4	138	290	411	45.9	9.6	9.2	132	37.5
TT2	7.6	9.3	116	18.3	12.8	6.7	4.9	33.4	100	145	31.2	17.3	9.2	17.1	25.4
TT3	7.3	14.4	159	19.3	2.4	1.0	1.2	3.3	3.2	5.8	2.4	4.5	36.9	8.28	45.4
TT4	4.4	15.5	170	18.6	2.0	0.6	0.9	0.7	0.8	2.8	0.8	3.5	39.4	0	76.7
TT5	8.1	13.5	95	19.2	5.4	2.9	1.1	42.8	40.1	63.4	20.0	3.2	31.0	15.6	4.4

3.3.7 **Principal component analysis of leaching samples**

For the PCA method, 16 parameters of 34 leaching samples were used to calculate factor loadings as presented in Table 3-7. The results showed that three factors accounted for 78.5% variance of the geochemical data. Factor 1 mainly affected As leaching concentration with 35% variance with higher loadings of Na^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}. These major ions are associated with the formation of the sediments in the saline conditions. Factor 2, with 33% of the variance, had higher loading of Fe, Al, As, Si and ORP, which was associated with dissolved Fe and Si. Factors 3, which explained 10.64% of the variance, showed higher loading of DOC, alkalinity, and pH. By focusing on As release, Fe, Al, Si, and SO_4^{2-} concentrations affected As mobility.

Table 3-7. Rotated factor loadings of principal components of leaching samples

Variable	**Factor 1**	**Factor 2**	**Factor 3**
As (concentration)	0.203	**0.353**	-0.037
As (content)	0.274	-0.048	0.228
Fe	0.123	**0.395**	0.055
Al	0.157	**0.387**	-0.049
Si	0.160	**0.386**	-0.044
SO_4^{2-}	**0.343**	-0.201	0.205
Na^+	**0.402**	0.073	0.008
Cl^-	**0.320**	0.052	-0.330
K^+	0.290	-0.112	0.172
Mg^{2+}	**0.348**	-0.180	0.233
Ca^{2+}	**0.329**	-0.204	0.219
EC	0.245	0.051	-0.199
pH	-0.176	0.278	**0.408**
ORP	0.103	**-0.306**	-0.231
DOC	0.145	0.172	**-0.492**
Alkalinity	-0.006	0.285	**0.393**
Eigenvalue	5.494	5.124	1.509
Explained variance (%)	34.93%	32.92%	10.64%
Total Cumulative (%)	34.93%	67.85%	78.5%

3.4 Conclusion

Arsenic in the unconsolidated sediments in the Mekong Delta was influenced by behaviors of Fe, S and organic matter. Based on the results of this chapter, As was concentrated in organic-rich layers

and layers with high contents of Fe and S. The As corresponded to organic/sulfide fraction. In addition, colloidal particles containing As contributed to leaching concentration of As significantly. These mean that several factors affected the As content and its mobilization.

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Chapter 4
COMPARISON OF ARSENIC CONTENT OF UNCONSOLIDATED SEDIMENTS AND ITS MOBILIZATION IN THE ISHIKARI PLAIN, HOKKAIDO, JAPAN AND THE MEKONG DELTA, VIETNAM

4.1 Introduction

The distribution of As content in alluvial aquifers is different depending on sedimentary environments. Several researchers reported sources and mechanisms of As concentration in alluvial aquifers (McArthur et al., 2000; Nath et al., 2008a, b; Nickson et al., 2000; Nguyen and Itoi, 2009). The hydrochemical conditions affect mobilization of As in alluvial sediments under varied climatic and geological conditions. However, few studies have been compared about As geochemistry in different regions (Jing et al., 2012; Mukherjee et al., 2009).

This chapter compares factors affecting As content and its release of unconsolidated sediments in the Ishikari Plain and Mekong Delta. Both sites have different climate and geological formations. The main objectives of this chapter are (1) to compare As content of unconsolidated sediments in the Ishikari Plain and Mekong Delta, and (2) to compare As mobilization of unconsolidated sediments in the two areas.

4.2 Materials and methods

The materials and methods used in this chapter were described in the previous chapters. The sampling and measurements of groundwater samples are described below.

4.2.1 Groundwater sample

Groundwater samples were collected from 6 boreholes by an electrical pump or a bailer. First three samples were from the Ishikari Plain (B1, B2, and B3) and three were from the Mekong Delta (PH, LS, and PHu). The groundwater samples were taken after enough volume of pumping for achieving stable quality of the groundwater. Redox potential (ORP), pH, and temperature were recorded on site. Then the samples were collected in polypropylene bottles. Each sample was filtered by 0.45 μm membrane filters and the aliquot was acidified with 1% HNO_3. Anions and alkalinity were determined using non-acidic samples.

4.3 Results and discussion

4.3.1 Factors affecting the distribution of As content

By comparing the content of As of the Ishikari Plain (Chapter 2) with that of Mekong Delta (Chapter 3), there are differences and similarities. This is due to the different factors, such as particle size, organic matter, and sedimentation conditions.

The content of As was negatively correlated with SiO_2 content in the Mekong Delta in Fig. 4-1(a). Since coarser particles contained higher SiO_2, As content increased with a smaller particle size. However, As content was not dramatically changed with SiO_2 content in the Ishikari Plain.

Figure 4-1(b) shows that TOC content had a weak correlation with As content of the sediments in the Mekong Delta. Organic/sulfide fraction of As was higher in organic rich sediments. However, the As content of the Ishikari Plain was in the range of 3 to 9 mg/kg. This means that not only TOC but also S content affects As content. In particular, the As content of peat formed in saline conditions (PT) was higher than 25 mg/kg.

The relationship between As content and Fe_2O_3 content is shown in Fig. 4-1(c). The As content increased with Fe_2O_3 content of sediments in both the Ishikari Plain and Mekong Delta. However, the range of Fe content was 2.1 to 9.6 wt% in the Mekong Delta whereas that was 3 to 12.1wt% in the Ishikari Plain. The As content had a good correlation with Fe_2O_3 content in both areas. However, As content in the Ishikari Plain was lower than in the Mekong Delta, maybe due to the difference in sedimentation conditions.

Figure 4-1(d) shows the relationship between As content and S content, which had a weakly positive correlation in the Mekong Delta. This results from weathering of sulfide minerals by considering higher S content in the Mekong Delta. Arsenic-bearing pyrite was also observed in the sediments formed under saline conditions. As a result, the content of S affects As content.

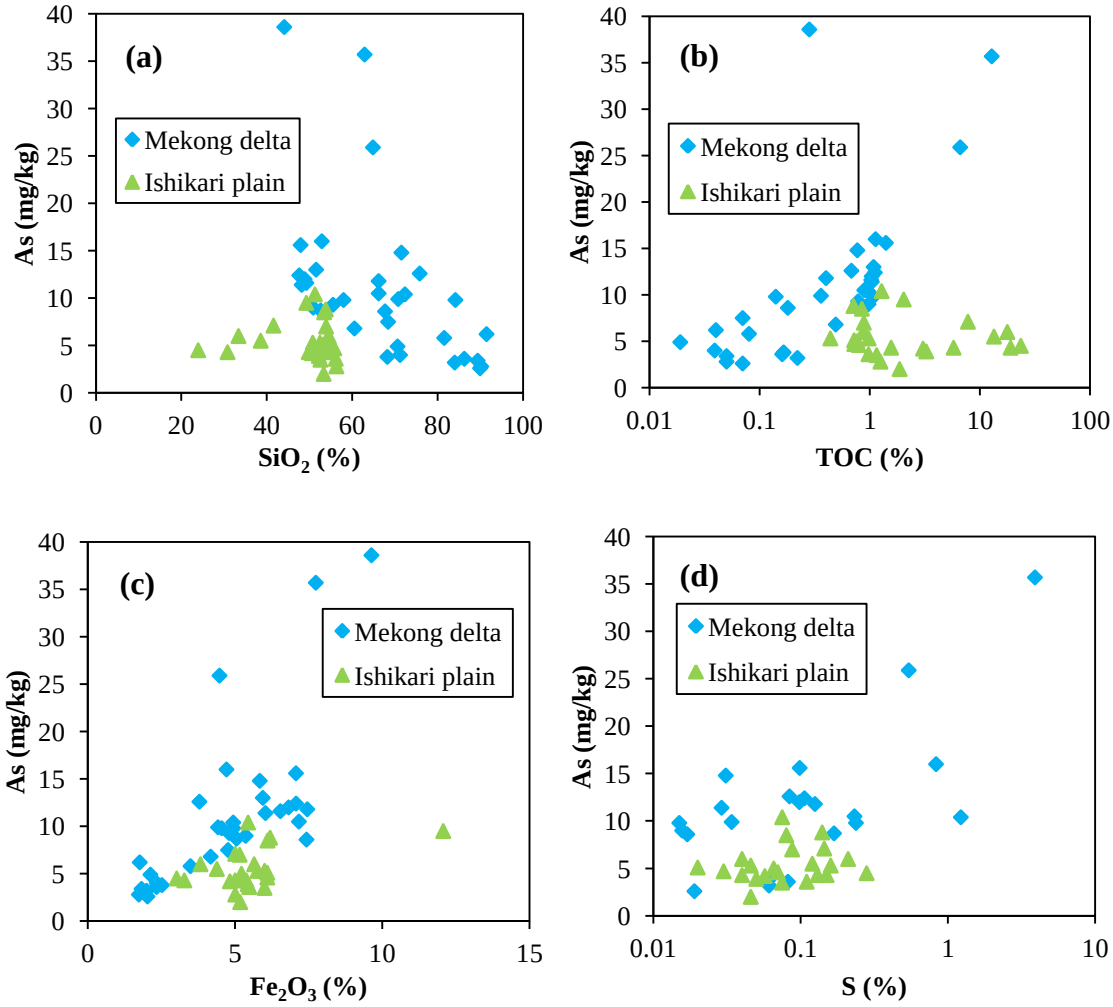

Figure 4-1. As content versus (a) SiO_2, (b) TOC, (c) Fe_2O_3, and (d) S contents of sediments in the Ishikari Plain and Mekong Delta

4.3.2 **Geochemistry of groundwater**

The geochemistry of groundwater in the study areas is shown in Table 4-1 and the distribution of major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and anions (Cl^{-}, HCO_3^{-} and SO_4^{2-}) in groundwater samples in the two areas were shown in the piper diagram (Fig. 4-2).

In the Ishikari Plain, the type of groundwater was mainly Na-K-HCO_3 and was near neutral (pH 6.7-7.0). Arsenic concentration in groundwater samples ranged 3 to 44 µg/L and As (V) was dominant in the Ishikari Plain. High HCO_3^{-} and DOC concentrations affected dissolved As concentration and As species in the groundwater of the Ishikari Plain.

In the Mekong Delta, the groundwater type was Ca-Cl-SO_4 and was weakly acidic to neutral (pH

5.6-7.1). Arsenic concentration in groundwater was 5.1 to 340 μg/L and As (III) was dominant in this area. Concentration of As(III) in groundwater was influenced by the sulfate reductive process in the area.

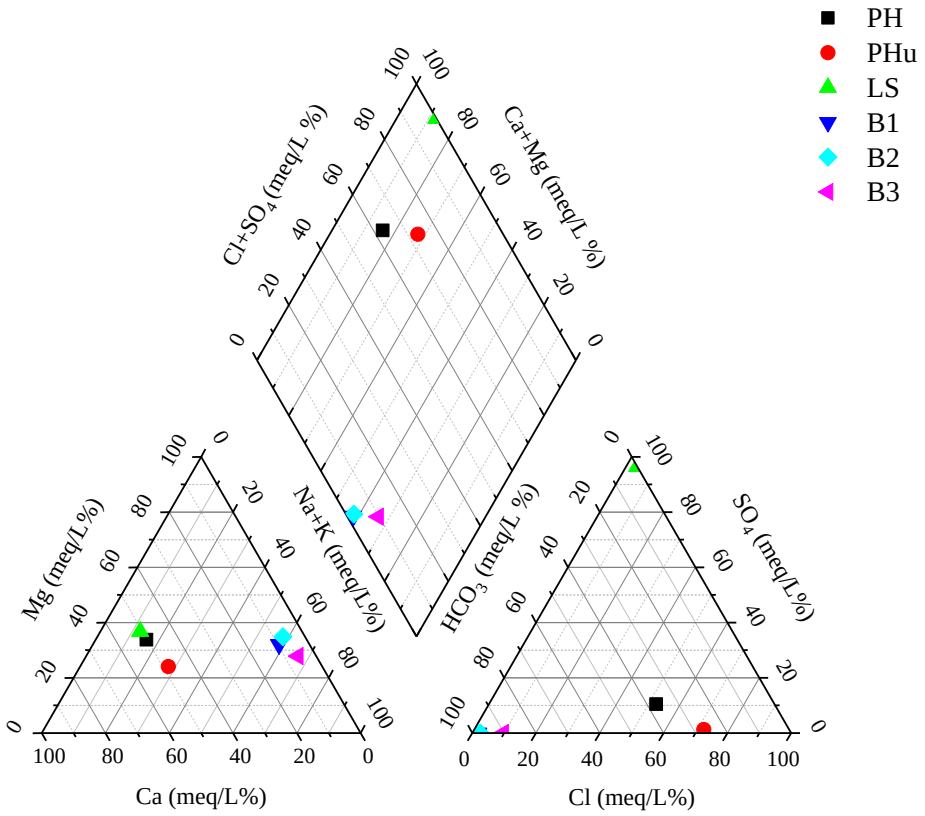

Figure 4-2. Piper diagram of groundwaters

Saturation indices (*SI*s) of representative minerals in groundwater were calculated by PHREEQC (Parkhurst et al., 1999) as shown in Table 4-2. There were no As-bearing minerals in this table, meaning that As is precipitated with amorphous Fe.

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Table 4-1. Geochemistry of groundwater

Borehole	pH	ORP (mV)	T (^oC)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Fe (mg/L)	Al (mg/L)	Si (mg/L)	As (μg/L)	As(III) (μg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	DOC (mg/L)
B1	7.03	130	13.6	343.3	35.1	92.5	45.25	89.7	14.8	22.3	9.64	1.59	15.6	-	1401.3	48.8
B2	6.71	96	15.6	329.6	27.56	98.1	32.22	22.7	2.44	27	2.99	-	20.9	-	1398.1	49.4
B3	6.86	118	15.3	460.8	23.87	92.6	31.4	394	83.9	25.5	44	5.31	95.4	-	1520.1	83.4
PH01	6.92	-112	28.1	26.1	0.77	29.7	72.8	0.22	0.69	10.6	8.93	8.4	59.8	16.1	72.6	6.24
PHu01	7.06	10	30.7	37.9	4.42	18.6	61.4	6.3	0.63	11.5	340	220	94.7	2.28	60.4	16
LS02	5.58	30	28.5	38.7	7.35	67.1	152	129	2.25	23.1	5.13	8.74	27.3	1030	0	6.08

(-) less than detection limit

Table 4-2. Saturation indices of minerals

Location	Sample	$Fe(OH)_3$	Goethite (FeOOH)	Hematite (Fe_2O_3)	Calcite	SiO_2
Ishikari Plain	B2	3.6	9.15	20.26	-0.41	-0.52
	B1	5.13	10.6	23.15	-0.01	-0.39
	B3	2.89	8.42	18.8	-0.25	-0.06
Mekong Delta	PH	3.29	9.29	20.6	-1.48	-1.07
	PHu	3.18	9.27	20.57	-0.93	-1.05
	LS	3.07	9.08	20.19	-	-0.73

4.3.3 **Condition lead to As mobilization from sediment**

Figure 4-3(a) shows the relationship between As content and As leaching concentration of sediments in the Ishikari Plain and Mekong Delta. Arsenic leaching concentration roughly increased with As content. However, some sediment samples with higher As content did not release As due to the other factors.

Figure 4-3(b) shows the relationship between As leaching concentration and pH. This figure shows that As leaching concentration increased with pH and that As leaching concentration was higher in alkaline conditions in both areas. For peat, As leaching concentration was high in acidic conditions.

The relationship between Si leaching concentration and As leaching concentration is shown in Fig. 4-3(c). Arsenic leaching concentration increased with Si leaching concentration. This means that colloidal particles contained As. Meng et al. (2000) and Luxton et al. (2008) reported that Si concentration significantly decreased As adsorption on ferric hydroxide and goethite when Si concentration was higher than 1 mg/L and the pH was greater than 5. This agrees with our data.

The relationship between As leaching concentration and SO_4^{2-} leaching concentration is shown in Fig. 4-3(d). Arsenic leaching concentration increased with SO_4^{2-} leaching concentration in two areas. These leaching properties of As are due to oxidation of As-bearing sulfide minerals.

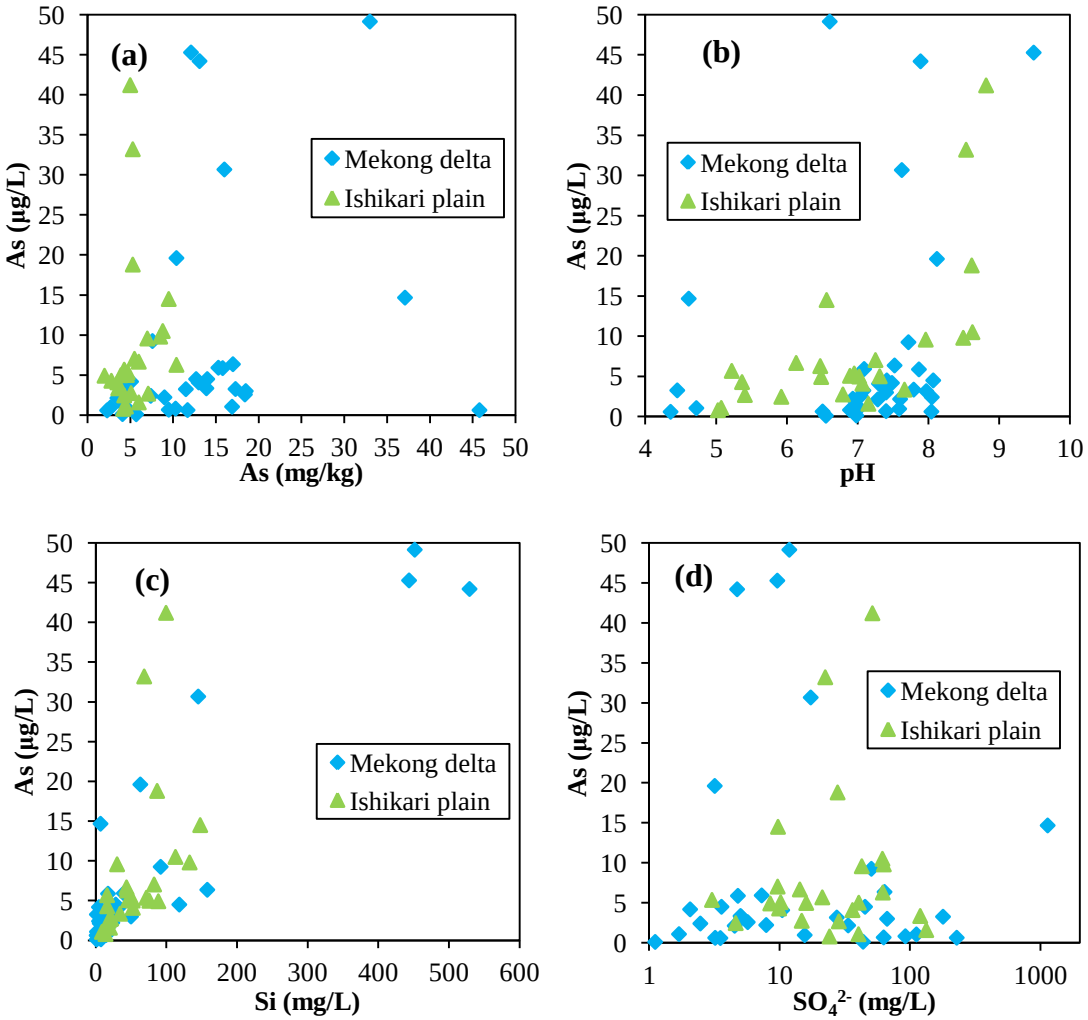

Figure 4-3. As leaching concentration versus (a) As content, (b) pH, (c) Si leaching concentration, and (d) SO_4^{2-} leaching concentration in the Ishikari Plain and Mekong Delta

4.4 Conclusion

Chemical characteristics of sediments affected As content in the Ishikari Plain and Mekong Delta. By comparing the two areas, several factors affect As content in aquifer sediments. Organic matter and S content increased As content, in particular organic/sulfide fractions of As in sediments. The leaching of As in both sites was influenced by sedimentary condition, pH and colloidal particles.

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Chapter 5
CONCLUSION

5.1 General conclusion

This dissertation consists of five chapters. Chapter 1 presents introduction, the problem and objectives of this study. These include the geochemistry of As in the environment and the As contamination in groundwater and sediments. Arsenic contamination in the environment results from anthropogenic sources and natural sources, but recently the natural sources of As have a potential impact on water quality. The amount of dissolved As is often explained by geochemical reactions, such as dissolution-precipitation, oxidation-reduction, adsorption-desorption, and biological processes. The distribution of As content in different environments affects mobilization of As in aquifers. However, geogenic process related to As in alluvial sediments where groundwater As concentration is high are still unclear.

Chapter 2 describes factors affecting the distribution of As content of unconsolidated sediments in the Ishikari Plain. To understand the mechanisms triggering the enrichment of naturally occurring As, As contents in the sediments were studied. The first factor was organic matter content in the sediments, and the second was the sedimentary condition expressed by the ratio of carbon content to S content. Leaching experiments and sequential extraction were used to explain mobility of As from the sediments. The results showed that higher organic matter content of sediments increased the organic fraction of As and that the higher S 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 concentration, and As mobility was enhanced under higher pH condition. In the reducing condition, both As and Fe were dissolved from the sediments. In addition, As in colloidal particles also affected As leaching.

Chapter 3 describes the unconsolidated sediments in the Mekong Delta. The content of As in the sediments was influenced by Fe, S and organic matter. In this study area, organic-rich sediment concentrated As-bearing sulfide, which enhanced the organic fraction of As. In addition, the higher exchangeable and sulfide fractions of As in the sediment were found in a saline water condition. This demonstrated that the sedimentation condition also affected As distribution and its mobility. Higher As concentration in the leachate was also observed in the layers consisting of finer particle size. This means that As in colloidal particles affected As leaching. These indicate that several factors affected the As content and its mobilization.

In chapter 4, higher As concentration is often found in shallow aquifers in the alluvial

environment of the Ishikari Plain, Japan and Mekong Delta, Vietnam. Chemical characteristics of sediments affected As content in both areas. By comparing the areas, several factors affected As content in aquifer sediments. The organic matter, S increased As content in organic/sulfide fractions of As of the sediments. The As leaching in both sites was influenced by sedimentary condition, pH and colloidal particles.

Finally, by considering the results and conclusion obtained in this dissertation, As contamination is characterized by the content of As of shallow alluvial sediments in the Ishikari Plain and Mekong Delta. In addition, As content and leaching concentration were affected by the geological formation and geochemical reaction of the alluvial environments. The organic matter and S contents were important factors for As reactions affecting its speciation and mobility.

5.2 Recommendation

This study enhanced understanding of the As characteristics of sediments in the Ishikari Plain and Mekong Delta by conducting mineralogical and chemical analyses, and sequential extraction. The study showed that redox condition significantly enhanced the release of As to groundwater via the leaching experiments. The results of this study may help to understand As occurrence in sediments as well as its mobilization from sediments to groundwater for water quality management. Thus, this research could serve as a background for selection of safe drinking water. In order to get better understanding of As release processes, it is recommended that further researches be conducted as follows:

The age of the sediments of the alluvial aquifers may be effective in predicting groundwater As concentration, because the details of the sedimentation conditions in alluvial aquifer in both areas are not clear. The complex distribution of older and younger sediments in the two areas may lead to understanding the distribution of As.

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For the past ten years after I graduated my bachelor degree, I wanted to be a lecturer and transfer knowledge to a new generation. In my country, we need to develop human resources for economic growth. However, high education and new methodologies need more education instructors to produce new engineers and scientists. Thus, I would like to continue in a doctoral course and deliver that knowledge to students in my hometown.

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