

**GEOCHEMICAL STUDY OF ARSENIC
BEHAVIOR IN AQUIFER OF THE
MEKONG DELTA, VIETNAM**



By

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**GEOCHEMICAL STUDY OF ARSENIC
BEHAVIOR IN AQUIFER OF THE
MEKONG DELTA, VIETNAM**

A dissertation submitted in partial fulfillment of the requirements for the
Degree of Doctor of Engineering in Kyushu University

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ABSTRACT

Arsenic (As), a toxic metalloid, is often found at high concentration in groundwaters because it is soluble and it sorbs weakly under reducing conditions. Naturally occurring arsenic can be mobilized from aquifer materials by induced reducing condition, as observed in the Mekong Delta, Vietnam.

The Mekong Delta is characterized by the Holocene sediments mainly composed of alluvial unconformably overlying the Late Pleistocene sediments. The burial of sediments rich in organic matter leads the sediment formations to reduced conditions. Moreover, the inherently abundance of acid sulfate soil and pyrite in the Mekong Delta, along with low pH are favorable conditions for the release of arsenic. Arsenic concentrations in sediments in the Mekong Delta range from 4 to 45 mg/kg. Where concentration of arsenic and iron are high, the sediments are yellowish brown to reddish brown implying a presence of iron oxides/hydroxides. Results of adsorption experiments on core sample indicated that maximum adsorption capacity of arsenite (As(III)) at pH 7.5 and arsenate (As(V)) at pH 5 are 2.57 mg/g and 6.58 mg/g, respectively. Moreover, more than 0.77 mg/g and 2.1 mg/g (74%) of the As(III) and As(V), respectively, was adsorbed on core sample within 1h. More than 0.85 mg/g (82%) and 2.2 mg/g (88%) of As(III) and As(V) adsorbed after 3h of reaction time.

Groundwater samples collected from tube wells at different depths (20 to 440 m) in the Mekong Delta indicate that groundwaters are of sodium bicarbonate and chloride type. The high Na^+ and Cl^- concentrations and high EC values of samples near coastal areas are due to differences in degree of mixing ratio

between fresh groundwater and seawater. ORP values of the groundwater range from -260 mV to 124 mV. Generally, chemical analyses result indicate that groundwater in this area is under reducing condition because of negative values of ORP and presence of reduced components such as NH_4^+ , Mn^{2+} and Fe^{2+} , except Cao Lanh (CL) and Hong Ngu-Tan Hong (HN-TH), which have positive ORP values. In groundwater arsenic concentrations range from 1 $\mu\text{g/l}$ to 741 $\mu\text{g/l}$. Arsenic concentrations exceeding 100 $\mu\text{g/L}$ are detected at shallow depths around 25 m, whereas arsenic concentrations more than 10 $\mu\text{g/L}$ are not found at deeper level (> 100 m depths) except for sample Binh Minh (BM2). From the correlation between Fe and As concentrations, the release mechanism of arsenic is as follows: dissolution of $\text{Fe}(\text{OH})_3$ and desorption of arsenic under reducing condition, oxidative decomposition of FeS_2 containing arsenic, or desorption of arsenic from $\text{Fe}(\text{OH})_3$ due to decrease in pH under oxidizing condition.

Sequential extraction (SE) method was employed to evaluate chemical speciation of arsenic in soil in (1) Mekong Delta, Vietnam and (2) Sasaguri town, Kasuya Province, Fukuoka Prefecture, Japan. Soil samples (1 m depth) in the Mekong Delta were collected at Tan Chau (TC), An Phong (AP), Tan My (TM) and Lai Vung (LV). Among these area arsenic concentrations in groundwater in TC, AP and LV were relatively high while arsenic concentrations in TM were low. However, TM soil is affected by acid sulfate soil which relatively low pH (3.46). Surface soil samples (0 - 10 cm depth) in Sasaguri (N4b) were collected in area where is geologically covered by metamorphic rocks such as schist, being rich in magnesium and iron. The arsenic in fraction, which was presumably associated with amorphous and poorly crystalline Fe-Mn hydroxides and extracted by strong

reducing agents $(\text{NH}_4)_2\text{C}_2\text{O}_4$ was the largest one, comprising about 73% of total arsenic for the N4b, TC, AP, LV soil and 50% for TM soil. The percentage of arsenic in the residual fraction was from 15 to 23%. The small amount of extracted arsenic in residual fraction was probably retained by silicate and Al silicate. In contrast, large dissolution of Al (74%) but slight release of Fe and Mn in residual fraction indicated that the HF-soluble aluminum silicate minerals. The mobile fractions of arsenic made up 1.5 - 2.9% and 7.2% of total arsenic for soils in the Mekong Delta and in Sasaguri, respectively. Sulfide fraction did not contribute to arsenic retention in the soils except TM sample (up to 30%).

Laboratory column experiments were conducted to examine the mobility of arsenic from soil in the presence of Fe hydroxide under controlling redox conditions. The soil column was made by packing mixture of Sasaguri soil and Fe hydroxide coprecipitated with arsenic. In order to control the redox conditions, tap water and ascorbate solution was supplied with a specified time interval. In the experiment, supplying of sodium ascorbate solution strongly affected redox potential in the soil column. A significant decrease in ORP from -143 mV to -229 mV (Period I) and from -25 mV to -135 mV (Period III) was observed. The concentration of arsenic and iron significantly increased when ascorbate solution was supplied. ORP values started decreasing after 7 hrs whereas arsenic and iron concentrations increased gradually up to 70 hrs. After reaching the maximum value (71.2 mg/L), As concentrations again decreased and ORP increased. Like arsenic, dissolved iron increased up to 4154 mg/L after a few hours and then the concentrations decreased. However, neither arsenic nor iron was detected when column was fully in oxidizing condition. Results column experiments indicated a

strong dependence of redox potential on both As and Fe concentrations. Under moderately oxidizing conditions, arsenic mainly associated with adsorption or co-precipitated onto Fe hydroxides. Upon reduction, arsenic concentrations increased significantly and reached maximum. Under highly reduced conditions, arsenic solubility seemed to be controlled by the dissolution of Fe hydroxides

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Chapter One

INTRODUCTION

1.1 General introduction

Incidence of arsenic (As) has become a particular interest in recent years due to the discovery of high arsenic concentration in groundwater used for domestic supplies in South Asia (Nickson et al., 1998; Chowdhury et al., 1999; Acharyya, 2004; McArthur et al., 2004). High arsenic concentrations have also been reported in Taiwan, China (Smedley and Kinniburgh, 2002), Mexico (Rodriguez et al., 2004) and Argentina (Farias et al., 2003). Although groundwater contamination by arsenic is commonly due to natural sources, anthropogenic arsenic pollution is also a very important issue. Exposure to arsenic from mining and industrial sources has been reported in Japan, Australia, Spain, Ghana, Canada, and United States (Bottomley, 1984; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002; Garcia-Sanchez and Alvarez-Ayuso, 2003). In addition, the effects of high arsenic concentrations on human health have been announced for centuries. At low concentrations, arsenic is a suspected carcinogen, reportedly responsible for lung, bladder, and skin cancers (Nriagu, 2002). Arsenic may also cause neurological damage to those who drink water contaminated with slightly higher than 0.1 mg/L, while higher concentrations (9 to 10 mg/L) of arsenic in drinking water have resulted in severe gastrointestinal disorders, impairment of bone marrow function and neurological abnormalities (Korte and Fernando, 1991). This global crisis has increased the urgency of understanding the geochemistry of arsenic.

Arsenic tends to be predominantly present in the solid phase of natural systems and concentrated in many types of mineral deposits. Arsenic is relatively mobile at high pH (> 8.5) in oxic waters or under circum-neutral (pH 6.5 - 7.5) in strongly reducing condition (Bottomley, 1984; Smedley and Kinniburgh, 2002).

The mechanisms of arsenic release under reduced subsurface conditions have been elucidated and postulated, however, they vary significantly both time and space. Reductive dissolution of iron oxyhydroxide minerals, with which arsenic is often coprecipitated or sorbed, may release a significant amount of arsenic to the aqueous phase (Nickson et al., 2000; Bose et al., 2002; Dowling et al., 2002; Acharyya, 2004; McArthur et al., 2001; McArthur et al., 2004). Desorption arsenic from iron oxides and oxyhydroxides has shown to release arsenic (Korte and Fernando, 1991).

Arsenic is often found in association with sulfide mineral phases. Under anoxic subsurface conditions, sulfide minerals influence arsenic concentration. Oxidation of sulfide minerals can lead to release of sorbed and incorporated arsenic species, and is the primary mechanism involved in arsenic release at acid rock-drainage and acid mine sites (Evangelou and Zhang, 1995).

In general, arsenic release to groundwater is affected by geochemical conditions of subsurface. If conditions become more oxic and iron oxyhydroxides are formed, arsenic can be adsorbed and/or coprecipitated, and dissolved arsenic concentration will decrease (Pierce and Moore, 1982; McArthur et al., 2001; Dowling et al., 2002). However, if conditions become more reducing, adsorbed and/or coprecipitated arsenic will be released from these minerals and dissolved arsenic concentration will increase (Kirk et al., 2004; McArthur et al., 2004).

Whether geogenic or anthropogenic, mobility of arsenic in subsurface is influenced by combination of the dissolved species present, minerals in aquifer, microbial activity, and especially geochemical parameter such as Eh and pH.

In this study, groundwaters and core samples of one borehole were collected from the Mekong Delta, Vietnam to analyze chemical composition as well as arsenic concentrations. This dissertation aims to elucidate the source of arsenic and the mechanism of arsenic release to aquifers in the Mekong Delta through chemical analysis and soil column experiments. Adsorption experiments were carried out to understand adsorption capacity of arsenic on core sample. In addition, chemical characteristics of soils collected in the Mekong Delta and in Fukuoka Prefecture, Japan were examined by sequential extraction method (SE). Results of arsenic fractionation in soil and its relationship with distribution of arsenic in the Mekong Delta were explained. The effects of redox potential on arsenic release were examined by the soil column experiments.

1.2 Motivation

As mentioned above, arsenic is present as severely natural groundwater contaminant in many countries in the world. A large number of wells contained high arsenic concentration have been detected in the Red River and the Mekong Delta, Vietnam (Berg et al., 2001, Stanger et al., 2005, Agusa et al., 2006). Public media have also expressed their concern that arsenic contamination in groundwater may become key environmental problems.

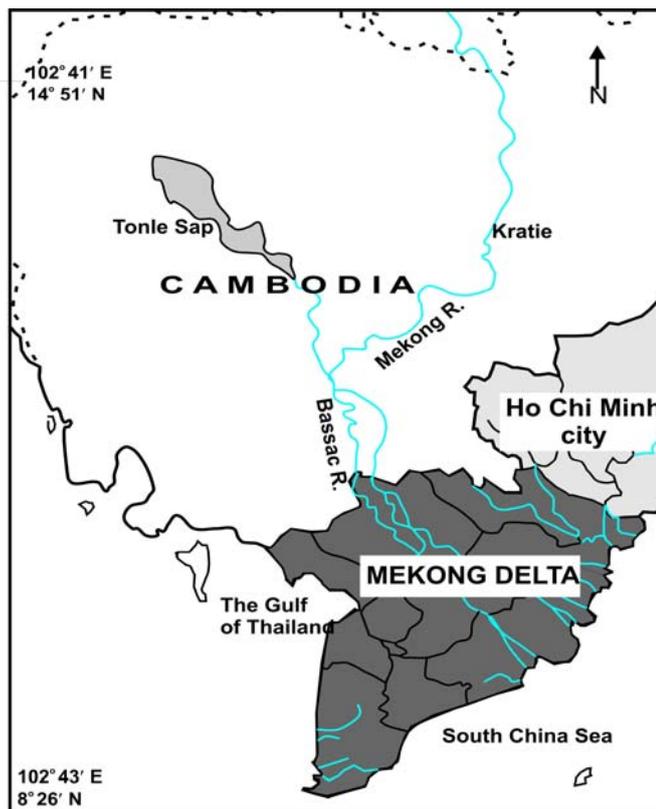


Fig. 1.1 Location map of the Mekong Delta.

Figure 1.1 shows location of the Mekong Delta. This delta is densely populated (around 17 million people) and with favorable conditions for agriculture. Aquifers in the Mekong Delta are formed in continental sedimentary deposits, and developed in a wide Quaternary plain.

Moreover, approximately 1.8 million hectares of the

Mekong Delta are covered with acid sulphate soils (ASS). These soils are characterized by pyrite deposits at relatively shallow depth. When these pyrites oxidize, they produce sulphuric acid (Akira, 2006). Soil pH in acid sulfate areas may drop to values below pH 2.0, and toxic polyvalent cations (metals) are dissolved from the soil minerals under these conditions. Recently, Stanger et al. (2005) reported on arsenic contamination in areas along the Lower Mekong River including the Mekong Delta in Vietnam proposed possible processes that cause a high concentration of arsenic. Although some studies have been conducted on arsenic problem in the Mekong Delta, sources of arsenic and release mechanism of arsenic to groundwater remain enigmatic even at present.

1.3 Objectives of the study

The objectives of this research are to understand source and mechanism of arsenic release in aquifers of the Mekong Delta. In order to achieve the objectives, field survey for groundwater sampling and its chemical analysis are essential works. Furthermore, geological and geochemical studies on soils, aquifer sediment are also important. These data provide evidences of relationship between distribution of arsenic in groundwater and arsenic species in soils, sedimentary rocks in the Mekong Delta. On the basis of interpretation of the field data, hypotheses of arsenic contamination are proposed.

Laboratory experiments are conducted to elucidate hypotheses. Chemical characterization of the soil samples is performed by sequential extraction method to determine the chemical species of arsenic and iron. Core samples of one borehole are examined by adsorption experiments for arsenic adsorption capacity. Soil column experiments are carried out to investigate behaviors and transport of arsenic under controlled oxidation/reducing conditions in the presence of iron (hydro)oxides.

In addition, soil in Sasaguri Town, Fukuoka Prefecture, Japan is collected and examined for physical, chemical characteristics as well as sequential extraction for a comparative studies with the soil in the Mekong Delta.

1.4 Outline of dissertation

This dissertation consists of seven chapters. **Chapter One** presents general introduction, motivation, objectives and outlines of the dissertation.

Chapter Two reviewed the geochemical characteristics of arsenic in environment. Arsenic is a naturally occurring element that is present in lithosphere, hydrosphere, atmosphere and biosphere. Weathered arsenic compounds may be retained or sorbed in the solid phase (soils and sediments) or dissolved in the liquid phase and subsequently transported. The most important process controlling arsenic mobility in aquatic system is its tendency to adsorb on soils or sediments. In oxic water, amorphous iron oxyhydroxides and aluminum hydroxides sorb a large amount of arsenate. Arsenate has adsorption maxima around pH 4 with decreasing amount in sorption with increasing pH. In addition, changes in redox potential are another process, which can affect the mobility of arsenic in the natural environment. Inorganic arsenic will either be oxidized or reduced depending on the redox status of the water or sediment.

Field survey for groundwater in the Mekong Delta, Vietnam, was presented in **Chapter Three**. Groundwater samples were collected and analyzed in laboratory for water chemistry, arsenic concentrations and its species. Core samples of the borehole LK204 were analyzed for total arsenic and mineral constituents. Piper diagram plotted for 47 groundwater samples indicated that groundwater is of a typical sodium bicarbonate and chloride type. Total arsenic concentrations range from 1 to 741 $\mu\text{g/L}$. Arsenic concentrations higher than 100 $\mu\text{g/L}$ are found at around 25 m depth. The groundwater in the delta is under reducing conditions because of negative values of ORP and presence of reducing components such as NH_4^+ , and Fe^{2+} . For core samples, total arsenic contents range from 4 to 45 mg/kg. Iron hydroxide minerals such as goethite and hematite were identified by XRD analyses. The results indicated that Fe oxyhydroxides are the

principal As-carrier phase. It was concluded that reductive dissolution of iron hydroxides induce high arsenic concentration in groundwater and sulfide-bearing minerals such as pyrite can be a source for arsenic in a oxidizing environment.

Chapter Four discussed arsenic speciation using sequential extraction (SE) method. Soil samples in the Mekong Delta and in Sasaguri, Fukuoka Prefecture were collected and analyzed arsenic speciation. The results showed that characteristics of soils in Sasaguri are similar to those in the Mekong Delta. The principal minerals present in the soils are quartz, iron hydroxides or oxides and clay minerals. Sulfate species and jarosite have been found in Tan My (TM) soil in the Mekong Delta. The results of the speciation analysis show that more than 70% of arsenic is associated with Fe oxyhydroxides in Sasaguri and the Mekong Delta soil (Tan Chau, An Phong, and Lai Vung). This suggests that the hydroxides of Fe are important minerals for arsenic adsorption or coprecipitation in these samples. On the other hand, pyrite was detected in TM soil and 30% of arsenic is bound to pyrite fraction. This causes relatively high arsenic concentration for oxic groundwater samples.

Adsorption of arsenic on core sample was written in **Chapter Five**. It is observed that maximum uptake of As(V) occurred under acid conditions and decreased with increasing pH. Amount of adsorbed arsenite (0.32 - 2.5 mg/g) and adsorbed arsenate (0.5 - 10 mg/g) increased with an increase of initial arsenic concentrations. The maximum adsorption capacities were identified 2.57 mg/g and 6.58 mg/g for As(III) for As(V). In the adsorption kinetics experiments, more than 0.85 mg/g (82%) and 2.2 mg/g (88%) of As(III) and As(V) were adsorbed after 3h of reaction time. A rather short time to reach equilibrium state implied

that film diffusion along with chemical adsorption was the essential mechanism of rate controlling and played a major role in the arsenic uptake.

Chapter Six investigated chemical reactions and behavior of arsenic and iron in oxidation/reducing conditions. Repeat oxidation-reducing conditions in soil column experiments were realized by changing influent from ascorbate solution to tap water. The results indicated that feeding ascorbate solution led to reducing condition throughout the soil column. There is an apparent relationship between As, Fe and ORP values such that arsenic was detected only under condition of negative ORP values. Arsenic and iron concentrations reached the highest concentration then started decreasing which corresponds to an increase in ORP values. The release of arsenic from Fe oxyhydroxide was delayed compared to that of Fe. This implies that during rapid dissolution of Fe oxyhydroxide caused high iron concentrations in the pore water stimulate the transformation of Fe oxyhydroxide to more stable crystalline forms whose surface area and the number of adsorption sites for arsenic becomes small to contain all the arsenic.

Finally, conclusions and recommendations are given in **Chapter Seven**.

Chapter Two

CHEMISTRY OF ARSENIC

2.1 Introduction

The most abundant arsenic mineral is arsenopyrite, FeAsS . It is believed that arsenopyrite, together with the other dominant arsenic-sulfide minerals realgar (AsS) and orpiment (As_2S_3) are formed under high temperature conditions in the earth's crust. Besides, common rock-forming minerals such as pyrite also contain high content of arsenic (more than 100 mg/kg) (Smedley and Kinniburgh, 2002). During the formation of pyrite, it is likely that some of soluble arsenic will be included. Pyrite is not stable in aerobic condition and is oxidized to Fe oxides accompanied by a release of SO_4 and associated arsenic. High arsenic concentrations are also found in many oxide minerals and hydrous metal oxides such as iron oxides or hydroxides, manganese oxides and aluminum oxides.

Partitioning of arsenic to the surface of sediment minerals such as adsorption and precipitation influences mobility of arsenic in aquatic systems. Adsorption of arsenate (As(V)) to hydrous Fe oxides is particularly strong even at very low arsenic concentrations in solution. In contrast, at higher arsenite (As(III)) concentrations, the sorption of arsenite increases continuously with an increase in concentration of ferrous iron. Adsorption to hydrous Al and Mn oxides may also be important if these oxides are present in quantity. Arsenic may also be adsorbed to the edges of clay minerals and on the surface of calcite.

Chemical reactions lead to the oxidation of arsenic in sedimentary minerals to As(III) and As(V). Those reactions also influence the transport of As(III) and As(V). It is possible for arsenic to become dissolved or mobilized under redox conditions and then transported through aquifers or surface water systems to other locations where it may be adsorbed. There is considerable evidence that high arsenic groundwaters can be associated with reducing conditions, particularly, in alluvial and deltaic environments (Smedley and Kinniburgh, 2002). One of the principal causes of high arsenic in groundwaters is reductive dissolution of hydrous Fe oxides and/or the release of adsorbed arsenic.

In general, arsenic occurs in various chemical forms and their chemical forms are the results of chemical and biological transformations in the aquatic environment. Therefore, understanding of the geochemical reactions such as (1) adsorption (including sorption isotherm) and precipitation, (2) dissolution and coprecipitation and (3) redox reactions are important to evaluate the transport of arsenic from minerals in sediment to water phase.

2.2 Geochemistry of arsenic in the environment

Arsenic, a metalloid occurs naturally, is a component of more than 245 minerals (Mandal and Suzuki, 2002). In nature, arsenic can exist in any one of four different oxidation states: As(-III), As(0)-metallic arsenic, As(III) and As(V) as both inorganic and organic metallic species (Ferguson and Gavis, 1972; Boyle and Jonasson, 1973; Wang and Mulligan, 2005). Metallic state is not common for the element in certain types of mineral deposits. The As(-III) is present in the gaseous compound as AsH_3 (arsine) that may occur under limited natural

conditions. Arsenate ion [As(V)] is most prevalent in oxic conditions whereas arsenite ion [As(III)] is found in anaerobic conditions.

Arsenic is found as trace element and minor quantities in common sulfides and in a great variety of amount in secondary oxidation products, particularly in sulfate and phosphates, etc. The principal carrier of arsenic in rocks and in many types of mineral deposits is pyrite: FeS₂. A generalized geochemical cycle of arsenic is shown in Figure 2.1.

2.2.1. Mineralogy

Arsenic has often been used as an indicator element when geochemical prospecting is conducted for identifying mineral deposits because it is associated with a wide variety of minerals. Arsenic is associated with the deposits of Cd, Cu, Fe, Hg, Ni, Pb, Se, Sn and Zn.

Arsenic is commonly presented in igneous, sedimentary, and metamorphic rocks (Table 2.1). Wang and Mulligan (2005) represented that the source of arsenic is also found in volcanic rocks, specifically their weathered products and ash, hydrothermal ore deposits, and is associated with geothermal waters and fossil fuels including coal and petroleum (Korte and Fernando, 1991; Smedley and Kinniburgh, 2002). Among sedimentary rocks, shales and argillites contain higher concentration of arsenic compared with the other sedimentary rocks (Boyle and Jonasson, 1973; Garcia-Sanchez and Alvarez-Ayuso, 2003). Iron-rich rocks show wide variation in their arsenic content. The sulfide facies of iron formations are commonly rich in the mineral, mainly in pyrite. The iron oxides, however, are frequently reported to have high contents, up to 2000 mg/kg, evidently as a result

of the strong adsorption and absorption of arsenate by hydrous iron oxides and sulfide (Boyle and Jonasson, 1973; Webster, 1999).

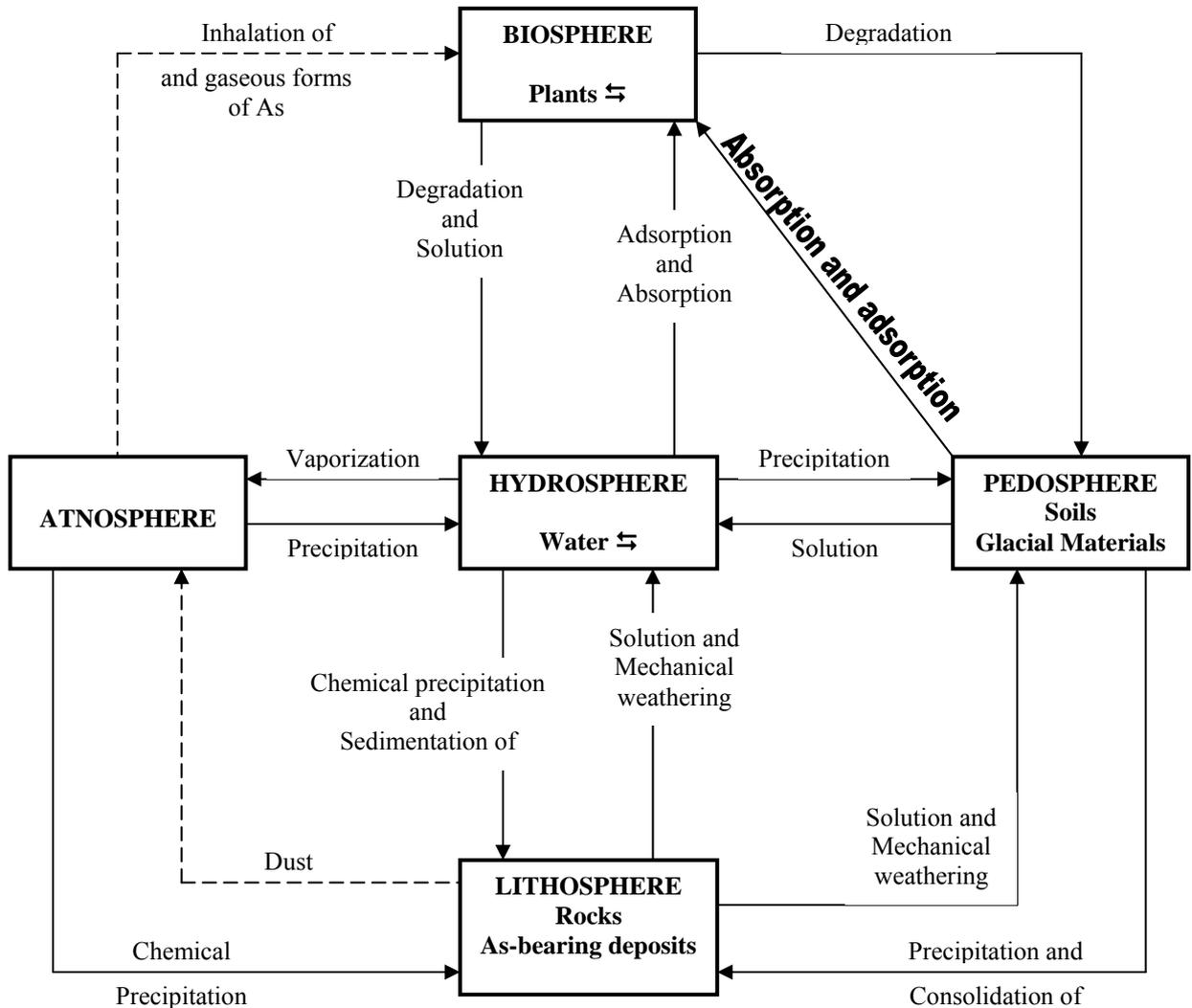


Fig. 2.1 Generalized geochemical cycle of arsenic (Boyle and Jonasson, 1973).

Arsenic occurs naturally in a wide range of minerals in several forms of inorganic compounds. The most common of arsenic minerals is arsenopyrite, FeAsS (Webster, 1999; Mandal and Suzuki, 2002; Garcia-Sanchez and Alvarez-Ayuso, 2003), which is a ubiquitous component of many sulfidic ore deposits, and can be associated with gold mine tailings (Savage et al., 2000; Wang and

Mulligan, 2005). Sulfide oxidation from pyrite due to mining can cause acid mine drainage and can potentially mobilize the associated arsenic. Other common arsenic sulfides include realgar (AsS), orpiment (As₂S₃), which occur in hydrothermal veins and show brilliant colour, depositing from hot springs in Yellowstone (USA), Waiotapu (New Zealand), and Beppu (Japan) geothermal systems (Webster, 1999).

Table 2.1 Arsenic contents of various terrestrial materials (Boyle and Jonasson, 1973; Mandal and Suzuki, 2002).

Rock type		Concentration (mg/kg)
Igneous	Acidic Extrusive (Rhyolite) Intrusive (Granite)	3.2 – 5.4 0.18 - 15
	Intermediate Extrusive (Latite, Andesite, Trachyte) Intrusive (Diorite, Granodiorite, Syenite)	0.5 – 5.8 0.09 – 13.4
	Basic Extrusive (Basalt) Intrusive (Gabbro)	0.18 – 113 0.06 - 28
	Ultrabasic (Peridotite, Dunite, Pyroxenite)	0.3 – 15.8
Sedimentary	Recent sediments Muds Clays Stream, river, and lake	3.2 – 60 4.0 – 20 5.0 – 4000 (mineralized area)
	Marine Shale/claystone (nearshore/offshore) Carbonate (Limestone, dolomite, etc.) Sandstone, arkose, and conglomerate	3.0 – 490 0.1 – 20.1 0.6 - 120
	Iron formations and iron-rich sediments Gypsum and anhydrite	1 - 2900 0.1 – 10
Metamorphic	Quartzite	2.2 – 7.6
	Slate/Phyllite	0.5 – 143
	Schist/Gneiss	0.0 – 18.5
	Amphibolite and greenstone	0.4 - 45

According to Grosz et al. (2004), the distributions of arsenic in sediments and soils are mostly controlled by the bedrock characteristics. The global average arsenic content of uncontaminated soils and sediment are 5 – 6 mg/kg (range from 0.1 to 40 mg/kg) and 5 – 15 mg/kg, respectively (Mandal and Suzuki, 2002) while Wang and Mulligan (2005) reported the naturally occurring arsenic concentrations in soil in Canada range from 4.8 to 13.6 mg/kg.

In addition, Farias et al. (2003) concluded that high arsenic concentrations associated with soils developed in loess or loessic sediment zones and transported volcanic material sites in Argentina. The A-horizon of some soils is markedly enriched in arsenic compared with other horizons, but it is usual to find enrichments of arsenic in the B-horizons of most normal soils (Boyle and Dass, 1967). Strong adsorption of arsenic by hydrous iron oxides results in enrichment of arsenic in the B-horizon. On the other hand, acid sulphate soils generated by oxidation of pyrite in sulfide-rich terrains are relatively rich in arsenic. An average of 5 mg/kg arsenic in soils from Alberta, Canada, was reported by Dudas (1984) whereas arsenic ranges from 8 to 45 mg/kg were found in acid sulphate soils derived from the weathering of pyrite-rich shales (Dudas, 1984; Benett and Dudas, 2003; Wang and Mulligan, 2005). Acid sulfate soils also lead to contamination of soil and surface water in the Mekong Delta, Vietnam (Minh et al., 1997; 2002). Gustafsson and Tin (1994) indicated the soils are slightly rich in arsenic (from 6 to 41 mg/kg). Moreover, the solubility of arsenic varied considerably within the soil profiles due to drainage and was much influenced by redox conditions. Arsenic contents in uncontaminated and contaminated soils in different countries are summarized in Table 2.2.

Table 2.2 Arsenic contents in uncontaminated and contaminated soils in different countries (Mandal and Suzuki, 2002).

Country	Types of soil/sediment	Range (mg/kg)	Mean (mg/kg)
Bangladesh	Sediments	9.0 - 28	22.1
Argentina	All types	0.8 – 22	5
China	All types	0.01 – 626	11.2
France	All types	0.1 – 5	2
Germany	Berlin region	2.5 – 4.6	3.5
Italy	All types	1.8 – 60	20
Japan	All types	0.4 – 70	11
	Paddy	1.2 – 38.2	9
Mexico	All types	2- 40	14
South Africa	-	3.2 – 3.7	3
Switzerland	-	2 - 2.4	2.2
United States	Various states	1.0 – 20	7.5
	Tiller	1.6 - 72	7.5

2.2.2. Aqueous phase speciation of arsenic

Arsenic is found at low concentration (0.001 – 0.002 mg/L) in natural water such as stream, rain, river and lake waters whereas groundwaters tend to have higher concentrations of arsenic (Table 2.3). Boyle and Jonasson (1973) reported arsenic concentration in groundwater near arseniferous deposits show significantly high values as well as in hot spring and cold springs in active volcanic terrains. For example, water of thermal area in New Zealand shows high value up to 8.5 mg/L (Webster, 1999). Boyle et al. (1998) reported that high arsenic concentration in groundwater up to 0.58 mg/L from an area of sulfide mineralization in Bowen Island, British Columbia, Canada.

Table 2.3 Arsenic contents of natural waters (Boyle and Jonasson, 1973).

Water type	Range ($\mu\text{g/L}$)	Mean ($\mu\text{g/L}$)
Rainwater and snow	0.01 – 13.9	1.44
Stream, river, lake waters	0.25 – 22,400	3.08
Normal groundwaters	0.01 – 800	17.9
Groundwaters and mine waters near sulfide deposits	3 – 400,000	-
Oilfield and other saline waters	10 – 243,000	-
Hot springs	0.2 – 40,000	2,090
Cold carbonated waters in volcanic terrains	120 – 37,500	22,200
Spring waters depositing travertine	30 – 500	307
Thermal waters associated with epithermal mineral deposits	50 – 200	117
Ocean and seawater	0.0056 – 11.24	2.57

On the other hand, high arsenic concentrations in water in the vicinity of gold mine are also found. Azcue and Nriagu (1995) found arsenic concentration in the Moira River, Ontario, Canada increased from 0.0007 (upstream) to 0.023 mg/L (downstream) due to influences by tailings from gold mines. Near Yellowknife in Canada, arsenic concentrations in lake waters range from 0.7 to 5.5 mg/L (Wagermann et al., 1978) while the surface water in Kam Lake, Yellowknife contained as high as 1570 mg/L of arsenic.

In aquatic system, arsenic has a complex and interesting chemistry with oxidation-reduction, ligand exchange, precipitation, and adsorption reactions (Ferguson and Gavis, 1972; Cullen and Reimer, 1989; Akai et al., 2004). Chemical characteristics of arsenic are different from many of the common heavy metals. For instance, the majority of the organic arsenic compounds are less toxic than inorganic arsenic compounds. Whilst having many chemical similarities to phosphorous (P), the soil chemistry of arsenic is more diverse because it can exist

in more than one oxidation states, and can form bonds with sulfur (S) and carbon (C) more readily than P (Mucci et al., 2000). Both As and P commonly form oxyanions (arsenate, AsO_4^{3-} , and phosphate, PO_4^{3-}) in the +5 oxidation state in soils. However, phosphate is stable over a wider range of Eh and pH than arsenate (Ferguson and Gavis, 1972). Arsenic is also found in soil in the +3 oxidation states (arsenite, AsO_3^{3-}) (Sadiq et al., 1983; Mucci et al., 2000; Ryu et al., 2002).

Based on thermodynamic data (Robie et al., 1978; Dove and Rimstidt, 1985; Ryu et al., 2002), Eh-pH diagram for arsenic related to predominant soluble species and the solids is shown in Fig. 2.2 (Ferguson and Gavis, 1972; Ryu et al., 2002; Smedley and Kinniburgh, 2002; Appelo and Postma, 2005). As(III) and As(V) are usually the main soluble species in water. Relative proportions of As(V) and As(III), however, vary depending on changes in the pH, Eh and microbial activities (Agett and Brien, 1985; Lumsdon et al., 2001; Ryu et al., 2002).

In oxidizing fresh and marine waters of circum-neutral pH, inorganic arsenic is mainly present as As(V) as deprotonated species of arsenic acid (H_2AsO_4^- , HAsO_4^{2-}) but As(III) remains in significant amounts (about 10% of total As) (Seyler and Martin, 1989). 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. In reducing waters of near-neutral pH, such as hot springs and groundwater, arsenic as As(III) is thermodynamically stable and arsenious acid (H_3AsO_3) is usually the predominant dissolved inorganic arsenic species. As(V), however, is still present. Diamond (1995) found total arsenic in the anoxic pore water of sediment collected at Moire Lake to be composed of approximately 70% arsenite, 20% arsenate and

10% organoarsenicals. Therefore, arsenic reaches to thermodynamically equilibrium state either in oxic or anoxic system. On the other hand, Dobran and Zagury (2006) reported that As(III) is more prevalent and more toxic than As(V) in groundwater as well as in soils.

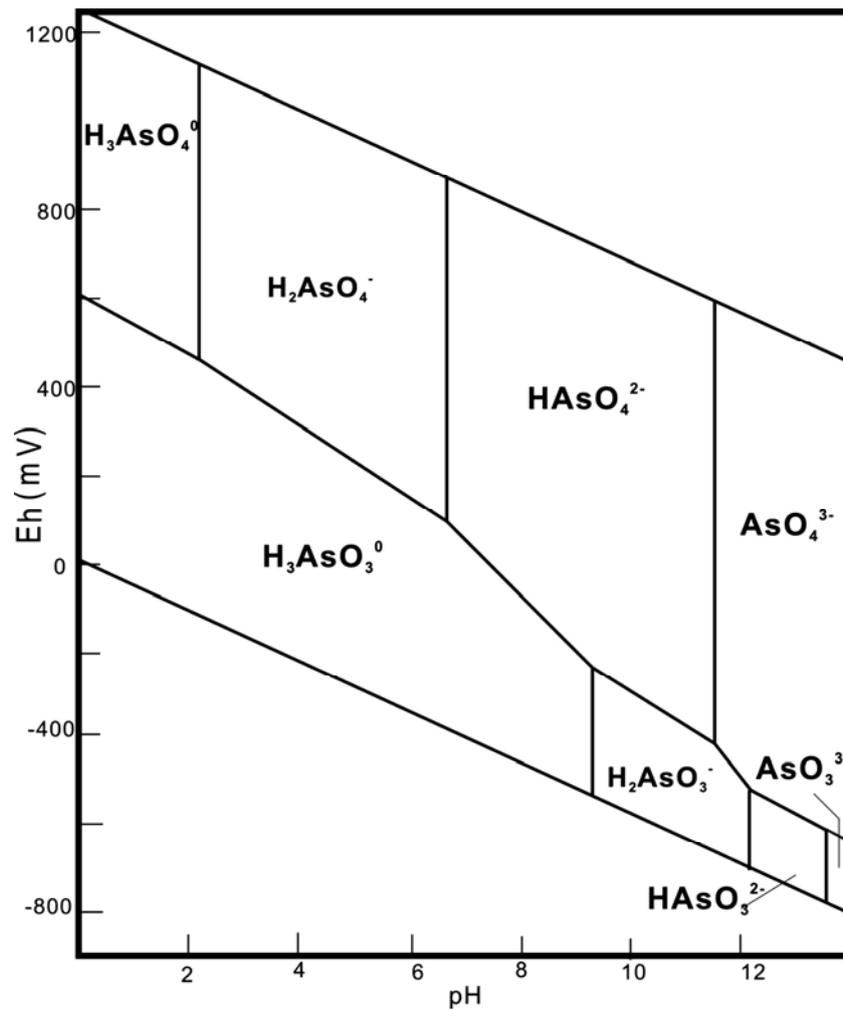


Fig. 2.2 Eh-pH stability diagram of dissolved arsenic species. Boundaries indicate equal activities of both species. Modified from Ferguson and Gavis (1972) and Smedley and Kinniburgh (2002).

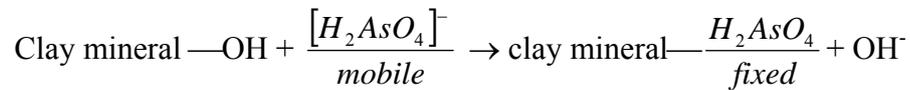
2.3 Factors controlling aqueous concentration of arsenic

2.3.1 Adsorption and coprecipitation

Adsorption and coprecipitation are probably the most important processes that determine concentration of dissolved arsenic in the oxic freshwater environments. The impacts of these processes in transport of the contaminant are important aspects for the removal of many arsenic species in groundwater system. Geochemically, arsenic may form insoluble precipitates in the presence of calcium, sulfur, iron and aluminum in the natural waters. However, these reactions tend to be markedly slow that arsenic is more likely to adsorb onto the surface of existing precipitates. Since adsorption and coprecipitation are difficult to distinguish, both processes will be referred to as sorption. According to Fendorf et al. (1997) and Jain et al. (1999), ligand exchange is the main sorption mechanism by which arsenic is complexed with surface hydroxyl groups and oxyhydroxides, clay minerals, organic matters and amorphous silicates.

In oxic waters, amorphous iron oxyhydroxides, aluminum hydroxides and manganese oxides tend to concentrate arsenic probably because the negative arsenate anions are strongly attractive by the positive iron colloids (gels) (Boyle and Jonasson, 1973; Pierce and Moore, 1982; Aggett and O'Brien, 1985; Seyler and Martin, 1989). Azcue and Nriagu (1995) reported a linear correlation of dissolved arsenic, iron and manganese in pore waters of sediments in Moira Lake. It is demonstrated by Mucci et al. (2000) that fixation of arsenate ion probably also takes place by adsorption on clay minerals and by anion exchange with these

minerals. Then under slightly acid conditions, the replacement of an OH⁻ ion in the clay mineral complex by soluble arsenate ion may occur:



Iron oxides efficiently scavenge arsenic from pore waters and reduce its toxicity by oxidation to arsenate. Arsenate adsorption onto iron oxides is enhanced at acid pH, similarly to other oxyanions (Lumsdon et al., 2001). Iron oxides play an important role in the sorption of arsenic because of their high point of zero charge (PZC) (Jain et al., 1999). A value of PZC of iron oxides ranges from 8.5 to 9.3 for Fe(OH)₃ and α-FeOOH, respectively (Appelo and Postma, 2005). Below these PZC, surface-hydroxyls (S-OH) become protonate and form very reactive acid sites which complex arsenic by ligand exchange. Arsenate displays the highest adsorption around pH 4 with decreasing sorption with increasing pH (Raven et al., 1998).

For arsenite, there is a maximum range of sorption at pH 4.0 - 9.2 with a decrease in sorption with increasing pH (Pierce and Moore, 1982; Raven et al., 1998; Fuller et al., 1993; Appelo and Postma, 2005). The decrease of arsenate and arsenite sorptions at high pH (above the PZC of iron oxides) is because the iron oxides surface becomes increasingly negative charge. The adsorption of arsenic to iron (hydro)oxides is extremely rapid. Typically, the adsorption rate is in the order of hours indicating that a specific adsorption between the arsenic species and the adsorbent occurs.

The main conclusions regarding the sorptive characteristics of arsenic are:

(1) arsenic sorption was related to amorphous aluminum oxides and iron oxide

content in soil; (2) sorption behavior was dependent on the oxidation state of the arsenic species and (3) the mobility of arsenite was significantly greater than that of arsenate.

2.3.2 Dissolution and precipitation

Another important geochemical process controlling the dissolved concentration of arsenic in the aquatic environment is dissolution and precipitation.

Most arsenic minerals are either sulfides (arsenite) or metal arsenates. Organic arsenical solids are too unstable to exist in natural waters (Ferguson and Gavis, 1972). Moore et al. (1988) concluded that diagenetic sulfides were important sinks for arsenic in reduced and sulfidic environments. However, they also pointed out that although the formation of authigenic sulfides can store vast amount of arsenic, they may also be a potential source of secondary contamination of unstable sulfides if moved into oxidizing environments.

Orpiment (As_2S_3) is one of the most common arsenite sulfides formed under anoxic conditions. At low pH and Eh and in the presence of sulfides, orpiment may control solubility of dissolved arsenic. However, in the presence of other elements (e.g. Fe^{2+}), sulfide activity may be limited and arsenic sulfide may not reach saturation (Cherry et al., 1979). Redox conditions also affect on the solubility of metal arsenates such as $\text{Fe}_3(\text{AsO}_4)_2$ and $\text{Ca}_3(\text{AsO}_4)_2$. For instance, under oxidized conditions, $\text{Fe}_3(\text{AsO}_4)_2$ is more stable than all arsenite minerals

and in more reduced conditions, sulfides of arsenite (AsS , As_2S_3 , and As_2S_2) were the most stable arsenic minerals.

2.3.3 Redox reactions

In groundwater, the concentrations of O_2 , Fe^{2+} , SO_4^{2-} , H_2S and CH_4 , are controlled by reduction and oxidation conditions. Redox reactions also control the mobility of arsenic in the natural environment. Depending on the redox status of the water or sediment, inorganic arsenic will either be oxidized or reduced. An Eh-pH diagram (Fig. 2.2) presents the stability of dissolved arsenic species in either oxygenated or reduced environment. Arsenate is thermodynamically stable species where high Eh values are found at neutral pH while arsenite is stable in reducing conditions.

The conversion from arsenite to arsenate and vice versa in the environment can be chemically or biologically mediated. Appelo and Postma (2005) also reported that the electron transfer in redox reactions is often significantly slow and may only proceed at significant rates when mediated by bacterial catalysis. In the study by Tamaki and Frankenberger (1992), the authors found that bacterial plays an important role in the oxidation of arsenite to arsenate presumably as a detoxification mechanism. In contrast, bacterial and marine phytoplankton can reduce arsenate. It has been suggested that arsenate metabolically reduced to arsenite that is further methylated.

The kinetic of oxidation of arsenite to arsenate with oxygen is markedly low at neutral pH (Lemmon et al., 1983). In the study of sorption of arsenite and

arsenate on amorphous iron oxyhydroxides, Pierce and Moore (1982) found that the conversion of arsenite to arsenate occurs over a week in basic solutions. Furthermore, laboratory and field studies presented that arsenite is metastable in the presence of oxygen and will not be oxidized to arsenate for days to months, even in the presence of iron oxides (Cherry et al., 1979; Mucci et al., 2000). Oscarson et al. (1980) reported that Mn and Fe oxides, present on the surface of organic and mineral compounds may be the primary component responsible for catalyzing the oxidation of arsenite through electron transfer mechanism. Although both Fe and Mn oxides can oxidize arsenite to arsenate, it is thought that Mn oxides are primarily responsible for the oxidation (Oscarson et al. 1980; Mucci et al., 2000).

Masscheleyn et al. (1991) reported that the influence of pH and redox potential on the oxidation state of arsenic markedly affected its solubility. At high redox levels, arsenic mobility is low. Under alkaline or reducing condition, the reduction of arsenate to arsenite results in mobilization of arsenic. Under moderately reduced conditions (OPR = 0 – 100 mV), arsenic solubility was controlled by reductive dissolution of iron oxyhydroxides (Masscheleyn et al., 1991).

2.4 Sorption isotherms

Many investigators described the adsorption of arsenic by using either the Langmuir equation or the Freundlich equation. The Langmuir equation is based on four assumptions (Sparks, 1995): 1) Only monolayer coverage is permitted; 2)

Adsorption is reversible; 3) There is no lateral movement of molecules on the surface and 4) The adsorption energy is the same for all sites and independent of surface coverage and there is no interaction between adsorbate molecules.

The Langmuir equation can be expressed as:

$$s = \frac{Kbc}{(1 + Kc)} \quad (2.1)$$

where s is the amount of adsorption (μg of As/kg of sample), c is the equilibrium concentration of the adsorptive, b is the maximum amount of adsorptive that can be adsorbed (monolayer coverage), and K is the constant related to the binding strength. While it is useful to calculate maximum sorption (b) values for different substrates and qualitatively compare them, the calculation of binding is questionable (Sparks, 1995).

On the other hand, the Freundlich equation can be expressed as:

$$s = K_d c^{1/n} \quad (2.2)$$

where K_d is the distribution coefficient and $1/n$ is the correction factor. One of the major disadvantages of the Freundlich equation is that it does not predict an adsorption maximum (Sparks, 1995). The K_d term implies that the energy of adsorption on a homogeneous surface is independent of surface coverage.

2.5 Summary

Arsenic concentration can reach to appreciably high levels in water and soil because of the underlying geology or geothermal activity. In the aquatic environment, arsenic concentrations can also be high in some estuaries and in

waters near heavy industrial or mining and mineral-processing areas. Arsenic is widely distributed in surface freshwaters, and background concentrations in rivers and lakes are generally $< 2 \mu\text{g/L}$ except in areas with volcanic rock and sulfide mineral deposits. Background concentrations in soil and sediment tend to range from 0.1 to 40 mg/kg, with a mean value of 5 - 15 mg/kg. Naturally, elevated levels of arsenic in soils may be associated with geological substrata such as sulfide ores.

Arsenic toxicity is affected by pH, Eh, organic matter content, adsorption to solid matrices, and the presence of other substances. Despite the ease with which total arsenic concentrations can be determined, the environmental behaviors of arsenic are dependent on the chemical properties, mobility and transformation of individual arsenic compounds. Studying the sorptive characteristics of individual arsenic species onto material and effect of redox reactions are important in order to understand arsenic transport in a particular aquatic system. Iron oxides are probably the most important adsorbents in sandy aquifers because of their greater abundance and the strong binding affinity. Nevertheless, aluminum oxides can be expected to play a significant role when present in quantity. On the other hand, clay minerals also adsorb arsenic because of the oxide-like character of their edges.

Redox reactions play an important role in determining the mobility of arsenic in the environment. Not only do redox reactions convert arsenic from less reactive species to more reactive species and vice versa, they also influence the stability of the sorbent to which the arsenic is bound. As the surrounding environmental conditions are altered, the availability and species composition of

arsenic are also altered. For example, at high redox levels, arsenic mobility is low. Under alkaline or reducing condition, the reduction of arsenate to arsenite occurs. Under moderately reduced conditions (OPR = 0 – 100 mV), arsenic solubility was controlled by reductive dissolution of iron oxyhydroxides.

Chapter Three

GROUNDWATER CHEMISTRY RELATED TO ARSENIC

3.1 Introduction

Arsenic is a serious natural inorganic contaminant in groundwater. Long-term ingestion of inorganic arsenic causes cancer, degenerative effects on circulatory system, and neurotoxic effects. Arsenic is present as a groundwater contaminant in many Asian countries such as Bangladesh, Vietnam, Taiwan and China (Nickson et al., 1998; Chowdhury et al., 1999; Berg et al., 2001; Acharyya, 2004; McArthur et al., 2004; Stanger et al., 2005; Agusa et al., 2006). The Bengal delta region is particularly affected as an estimated 35 million people have been drinking arsenic-rich water for the past 20-30 years (Smedley and Kinniburgh, 2002). Chronic levels of 50 $\mu\text{g/L}$ can cause health problems after 10-15 years of exposure. The development of symptoms of chronic arsenic poisoning (arsenicosis) is strongly dependent on exposure time and the resulting accumulation in the body.

In Vietnam, a large number of wells have been suffered from high arsenic concentrations in the Red River Delta and Mekong Delta (Berg et al., 2001; Stanger et al., 2005; Agusa et al., 2006). In the Red River Delta, groundwater arsenic concentrations vary in the range from 1 to 3050 $\mu\text{g/L}$ (average 159 $\mu\text{g/L}$)

(Berg et al., 2001) while arsenic concentrations in the Mekong Delta range from 1 to 1610 $\mu\text{g/L}$ (average 212 $\mu\text{g/L}$) (Stanger et al., 2005; Berg et al., 2007). In the Mekong Delta, drinking water supplies are mainly dependent on groundwater resources. The groundwaters are normally under strongly reducing condition with high concentrations of iron, manganese, and ammonium in some areas. Recently, Stanger et al. (2005) reported on arsenic contamination in the areas along the Lower Mekong River, including the Mekong Delta in Vietnam, and proposed possible processes that cause a high concentration of arsenic. A reconnaissance study of arsenic levels in hair conducted in 2004 in two villages in the Mekong Delta for the first time revealed that people in Southern Vietnam are exposed to high levels of arsenic (Berg et al., 2007). Since the daily use of groundwater as drinking water has become popular in the Mekong Delta only during the last 10 - 15 years, it is expected that victims suffering from chronic arsenic poisoning will also be identified in the near future in Southern Vietnam. However, neither sources of arsenic nor release mechanism of arsenic to groundwater have been studied in detail.

In this chapter, the water chemistry and arsenic levels in groundwater of the Mekong Delta are presented. The main geochemical triggers leading to groundwater contamination are evaluated using analytical data of 47 groundwater samples and 25 core samples from the borehole LK204. Arsenic contents and mineral constituents in the core samples were identified by XRF and XRD, respectively in order to examine relationship between arsenic in groundwater and core samples. In addition to the chemical characteristics of groundwater and core samples in this region, the geology of the Mekong Delta is summarized.

3.2 Characteristics of the study area

The study area is located along Tien River and Hau River systems (Fig. 3.1). To northeastern of Tien River, Dong Thap-Cao Lanh is a low-lying marshy plain, which contains potential aluminous soil. Along the two rivers, there are high alluvial bank and natural dikes.

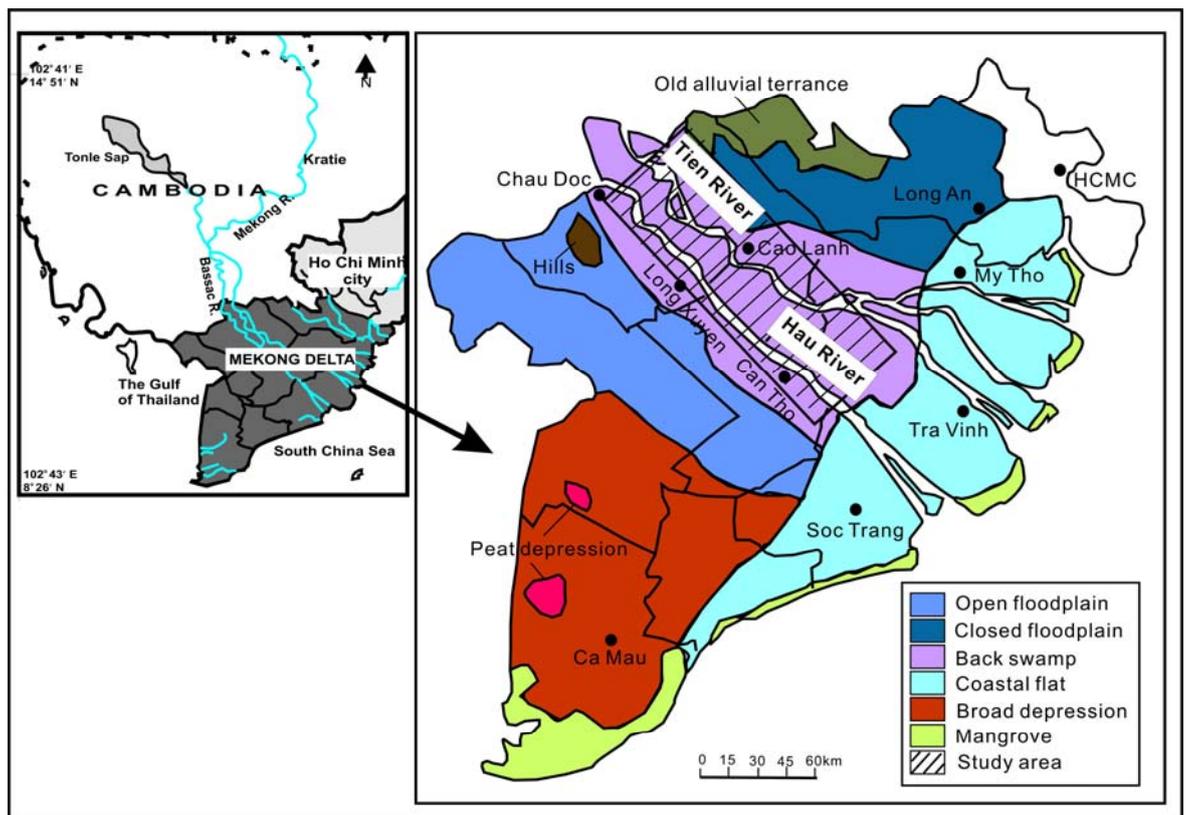


Fig. 3.1 Location map of the study area.

3.2.1. Topography of the Mekong Delta

Most of the region in the Mekong Delta has very low landform with the range of 0 - 4 m above sea level (a.s.l.) and the delta is very vulnerable to flood from upper area and tidewater from lower sea (Fig. 3.1). It is cited that the delta

plain show two parts: the upper delta plain dominated by fluvial process, and the lower delta plain characterized by a well-developed beach-ridge system and mainly influenced by marine process (Nguyen et al. 2000). Geomorphologic features of the upper delta plain are mainly described depending on location of the study area and its surrounding (Nguyen 1993). In the northern bank of the Tien River, swamp deposits with elevation of about 0.5 - 1 m a.s.l. occupy large area of Dong Thap province (Cao Lanh). Late Pleistocene terraces of 5 - 6 m a.s.l. to the north (Tan Hong) while closed floodplain deposits to the northeast (Fig. 3.1). This alluvial plain is deep prolonged inundation during seasonal floods as well as covered by acid sulphate soil. Central area is predominant of fluvial deposits such as channel, bank and flood basin. Bank deposits consisting of natural levees deposits occur along the channels with elevation of 3 - 3.5 m a.s.l. in the northwestern. A broad flood basin with an elevation of 2.5 m a.s.l. in which some lowlands of back swamp deposits are located. Hills of older rocks occupies in the northwest of this area.

3.2.2. Geological settings of the Mekong Delta

According to Molnar and Tapponier (1975), the Lower Mekong basin (including Laos, Thailand, Cambodia and Vietnam) were covered by an inland sea during the upper Mesozoic Era, where thick sandstones and evaporates were deposited. In the Quaternary period, it has been most important in forming the present topography, river courses, and major soil groups. The Pleistocene epoch is characterized by climatic fluctuations with humid stages between dry periods. The dry periods probably coincided with glaciations at higher latitudes and they were

responsible for major erosion in the Lower Mekong basin (Molnar and Tapponier, 1975). The Holocene epoch, starting about 10,000 years ago, began with rapid rise of sea level.

Geologically, the Mekong Delta in Vietnam is occupied by Holocene sediments mainly composed of alluvial unconformably overlying the Late Pleistocene sediments. Figure 3.2 presents geological map of the Mekong Delta together with locations of groundwater samples collected for chemical analysis (Section 3.2). Figure 3.3 shows cross section of geology along A-D line and A'-E' line in Fig. 3.2. The Late Pleistocene deposits or basement strata are mainly composed of stiff, slightly oxidized, yellowish gray stiff silt, fine-medium sand bearing scattered quartz pebbles and laterites (Fig. 3.2). The Holocene deposits covered the Late Pleistocene sediments were incised with river silts and coastal sand dunes up to 30 m thick (Stanger et al., 2005). It is stated that during the Late Pleistocene low-stand setting, the delta was developed with sedimentation transported from the upper region. Medium grain-size sand and gravel beds of the Pleistocene were deposited and covered the delta in upland terraces in the west and north (Fig. 3.1). In the Early-Mid Holocene, sea level continued to rise and caused transgression, most area in the Mekong Delta was inundated and where tidal mangrove grew up. The delta, therefore, was divided into two parts: the upper delta plain dominated by fluvial processes, and the lower delta plain characterized by a well-developed beach-ridge system and mainly influenced by marine processes (Nguyen et al., 2000).

3.2.3 Hydrogeological conditions

The Mekong alluvial plain is composed of four interconnected aquifer systems. The Holocene aquifer variably extends down to 31 m and 39 m depths below the surface in the east and central area, respectively. The aquifer is composed of silty clay, sandy silt, clayey silt and fine-grained sands with occasional intercalations of clay lenses. These clay lenses restrict entry of air to the aquifers. In contrast, the sediments of the Pleistocene aquifer (40 - 110 m) are dominantly of coarse-grained sand, pebble, grits, and gravel. All the aquifers are interconnected due to the spatial variation of grain sizes in the sediments. The Lower Pleistocene and Neocene aquifers (>110 m) were partly occupied by clay lenses and lenses of fresh water, respectively, are seldom exploited.

3.3 Sampling and analysis

3.3.1 Groundwater samples

To understand the distribution of the arsenic concentration in the Mekong Delta, groundwaters were collected at 13 locations: Cao Lanh (CL), Lai Vung (LV), An Phong (AP), Tan My (TM), Hong Ngu (HN), Tan Hong (TH), Chau Phu (CP), Tan Chau (TC), Can Dang (CD), Long Xuyen (LX), Binh Minh (BM), Mang Thit (MT) and Tieu Can (TC). The groundwater samples were collected in March (●) and September (A) 2006. Locations of groundwater samples are shown in Fig. 3.2. Wells deeper than 100 m are mostly tube wells that are cased to a depth of the aquifer whereas shallow wells for local use in CL, HN and TH are not cased. Forty seven (47) groundwater samples are classified into 8 groups as CL, LV, AP, TM, HN-TH, CP-TC, CD-LX, BM-MT by the proximity of their locations. In most locations, wells of different depths present within 10 m in radius. Field measurements of pH, EC, temperature and oxidation-redox potential (ORP) were measured immediately after continuous pumping of groundwater from the wells for about 10 min. Samples for the chemical analysis of As, Fe and Mn were filtered with 0.45 μm membrane filters, acidified with adding 1 mL of 12 M HCl and preserved in 100 mL polypropylene bottles. Other 250 mL samples were used to analyze major ions.

The pH, EC and ORP were measured onsite using a HORIBA D-54 meter. ORP was measured using a platinum (Pt) combination ORP electrode. Prior to the measurement, accuracy of the equipment was checked by ORP standard solution (89.0 mV at 25°C). Total alkalinity as HCO_3^- was measured by titration with 0.1 M

HCl using methyl orange and bromocresol green indicators in the laboratory. Concentrations of F^- , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , K^+ , Ca^+ and Mg^{2+} ions were determined with ion chromatography (Dionex ICS-90). Dissolved Mn and Fe were detected by inductively coupled plasma – atomic emission spectrometry (ICP-AES) (Vista-MPX). Inorganic arsenic was volatilized as arsine with sodium borohydride-hydrochloric acid solution using hydride generation equipment then analyzed with the HG-AAS (SOLAAR S4 with detection limit $1\mu g/l$). As(III) and As(V) were determined separately by a combination of the AsH_3 generation-AAS, separation of As(III) and As(V) by liquid chromatography-ICP-AES.

3.3.2 Core samples

In addition to the groundwater samples, core samples of the borehole LK 204 (265 m depth) near Chau Phu (Fig. 3.2) were collected over 10 m intervals. The major elements (Na, K, Mg, Ca, P, Fe, Mn, Al, S and total As) are identified using wavelength-dispersive XRF (Rigaku RIX 3100). Core samples were ground by vibration mill in order to make pellets and determine the loss on ignition (LOI). X-ray diffraction (XRD-Rigaku RINT 2100) was used to identify constituent minerals in the core samples.

3.4 Results of analysis and data interpretation

3.4.1 Water chemistry

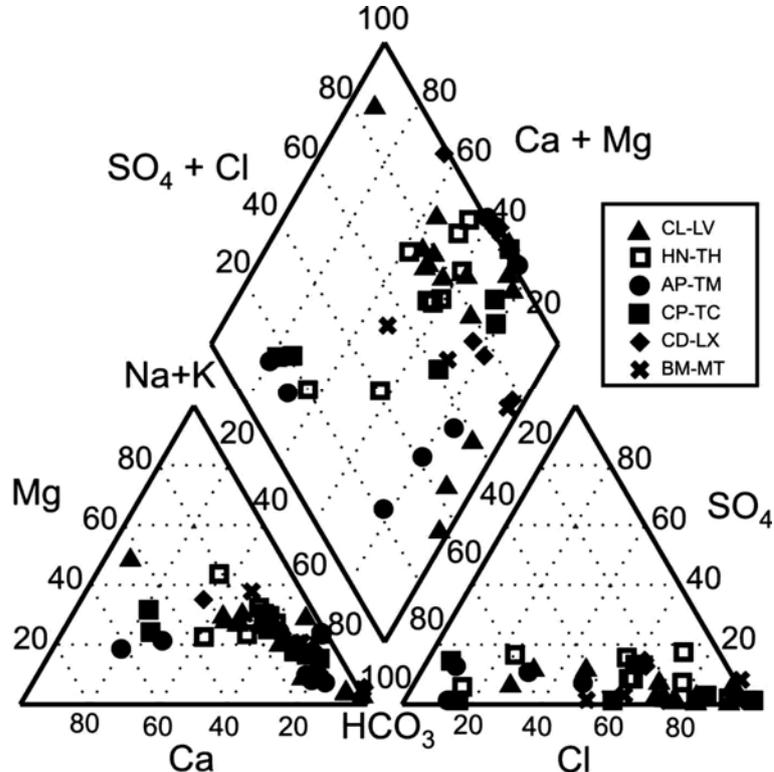


Fig. 3.4 Chemical composition plotted on Piper diagram.

▲ Cao Lanh-Lai Vung; ◻ Hong Ngu-Tan Hong; ● An Phong-Tan My; ■ Chau Phu-Tan Chau; ◆ Can Dang-Long Xuyen; ✕ Binh Minh-Mang Thit

Chemical compositions including arsenic concentration for the groundwaters are summarized in Table 3.1. Figure 3.4 shows the Piper diagram plotted for 47 groundwater samples, indicating that groundwater is of a typical sodium bicarbonate and chloride type. The pH is in the range from 5.77 to 9.38. EC values in groundwater are from 377 to 22600 $\mu\text{S}/\text{cm}$. The major ions such as Na^+ , Cl^- and HCO_3^- have concentration ranges of 21 to 4187 mg/L, 17 to 8280 mg/L and 10 to 697 mg/L, respectively (Table 3.1). The difference in the Na^+ and Cl^- concentrations and the high EC values is probably due to different mixing ratio between groundwater and seawater. High sodium and chloride concentrations are

found in samples near coastal area (MT) and in Pleistocene aquifer (LX, CD, CP, AP3, AP4).

3.4.2 Arsenic concentration and its speciation in groundwater

Figure 3.5 shows distribution of arsenic concentrations corresponding to location of groundwater samples in Fig. 3.2. Total dissolved arsenic concentrations range from 1 to 741 $\mu\text{g/L}$ (Table 3.1).

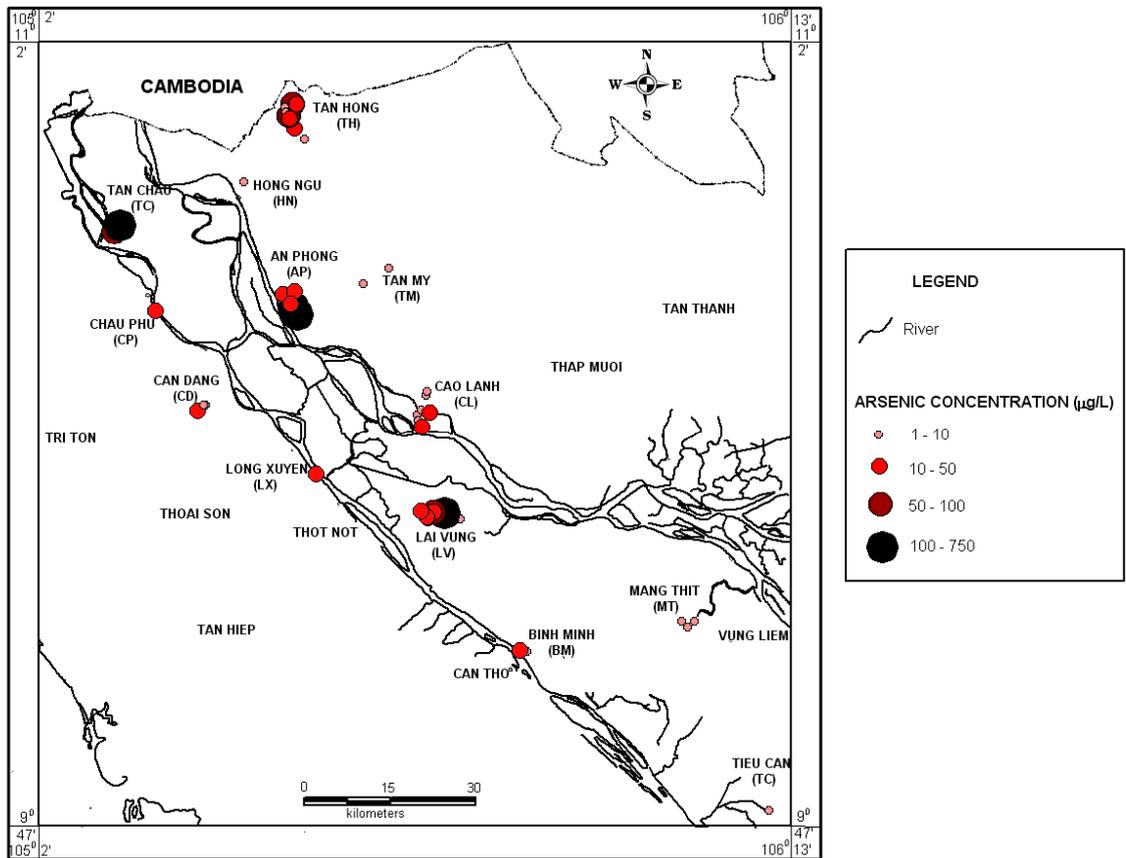


Fig. 3.5 Distribution of arsenic in groundwater.

In most locations, wells of different depths present within 10 m in radius. Thus, the chemical analyses are plotted at the depth of the well bottom. Figure 3.6

shows vertical profiles with concentrations of As, Fe, NH_4^+ and SO_4^{2-} . In this figure, groundwater samples are divided into two groups based on ORP values: 1) CL, HN-TH positive ORP values are predominant, and 2) LV, AP-TM, TC-CP, and CD-LX ORP values are negative. In general, as CL and HN-TH samples have positive ORP values, and Fe concentrations should be low because of precipitation of ferric hydroxide if organic ligand is absent. Moreover, arsenic concentrations of these samples are lower than $55 \mu\text{g/L}$. The results indicate that arsenic concentrations varied with depth. For example, arsenic concentrations higher than $100 \mu\text{g/L}$ are detected at around 25 m depth. In Table 3.1, relatively high arsenic concentrations from 10 to $50 \mu\text{g/L}$ are not found in the level deeper than 100 m except sample BM2. In Fig. 3.6, the depths where maximum arsenic concentration of AP, LV, CP and TC appeared coincide with that of total Fe concentrations. These facts indicate that the dissolution and fixation of arsenic occurs simultaneously with dissolution and precipitation of Fe controlled by the change in redox condition with depth.

Arsenic in aqueous solution is ordinary present as arsenious acid (H_3AsO_3 , As(III)) or arsenic acid (H_2AsO_4 , As(V)). The toxicity of As(III) is stronger than that of As(V). Therefore, the speciation of arsenic is important in environmental chemistry. In this study, differential analysis of As(III) and As(V) for several groundwater samples was conducted. The results are present in Table 3.1. On the other hand, the speciation is also possible thermodynamically by plotting samples on the Eh-pH diagram for arsenic as shown in Fig. 3.7.

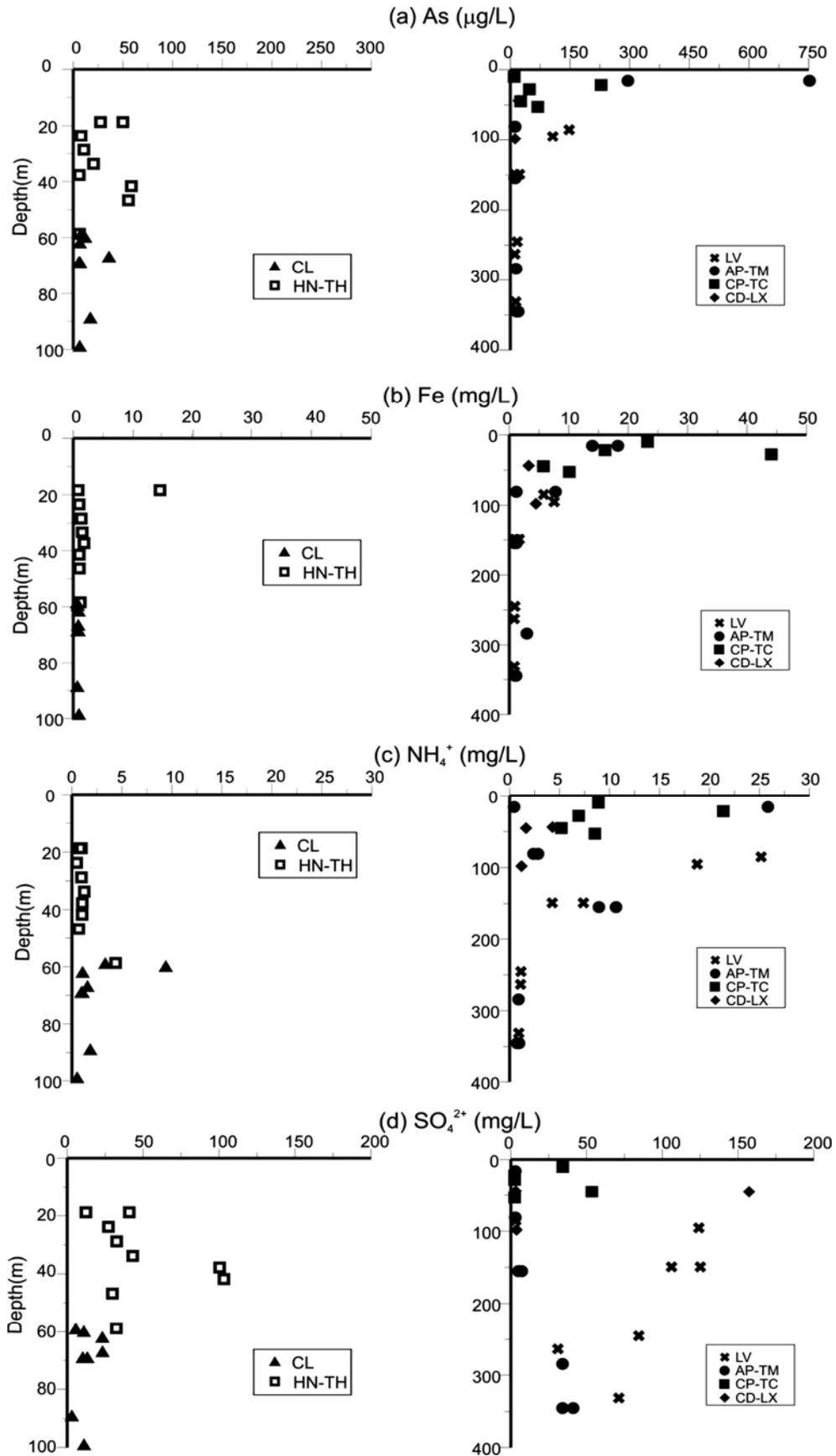


Fig. 3.6: Concentration profiles of: (a) As; (b) total Fe (c) NH_4^+ and (d) SO_4^{2-} vs. depth.

Although a part of samples (a part of TH, CL, LV, CD and TieuCan samples) are plotted on the stability field for As(V) which is present under oxidizing condition, most of the samples are plotted on the stability field of As(III) which is present under reducing condition.

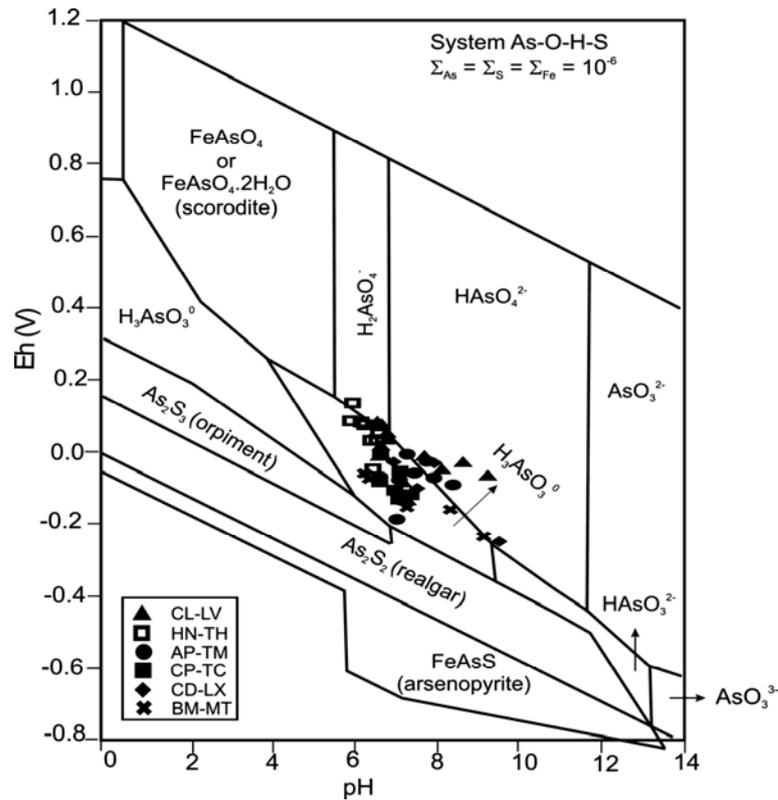


Fig. 3.7: Groundwater Eh-pH data plotted on an arsenic speciation diagram at 25°C, constructed by Ferguson and Gavis (1972); Peters and Blum (2003).

3.4.3 Characterization of the redox condition and behavior of iron in groundwater

ORP values of the groundwater range from -260 mV to 124 mV (Table 3.1). In general, chemical analysis results indicate that groundwater in this area is under reducing conditions because of negative values of ORP and presence of reducing

components such as NH_4^+ , and Fe^{2+} , except CL, and HN-TH which have positive ORP values (Table 3.1, Fig. 3.6).

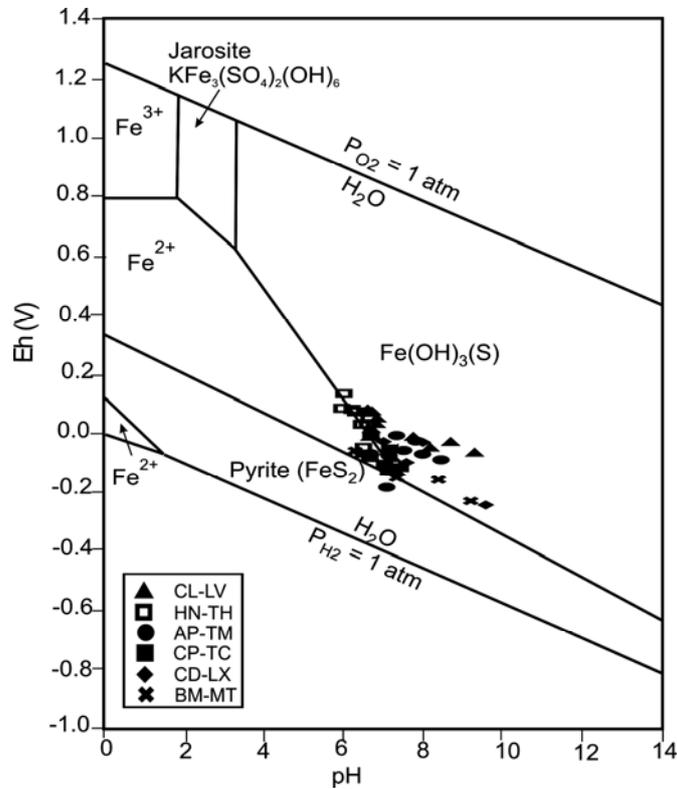


Fig. 3.8: Eh-pH diagram for iron species (after Deutsch, 1997).

Under oxidizing condition hydrous Fe(III) oxide such as $\text{Fe}(\text{OH})_3$ can remove both arsenious and arsenic acids from solution. Oppositely, when the $\text{Fe}(\text{OH})_3$ dissolves under reducing condition, arsenic is released into solution. Consequently, iron can affect the behavior of arsenic in natural water depending on the redox condition. In order to confirm the precipitation-dissolution conditions for Fe, values of Eh and pH of groundwaters are plotted on the stability diagram of Fe in Fig. 3.8. The results show that most of the samples are plotted in the stability field of Fe^{2+} (dissolved state) or $\text{Fe}(\text{OH})_3$ (precipitated solid state).

Higher concentration of Fe is expected in the groundwater samples plotted in the stability field of Fe^{2+} . In Figure 3.8, the most important point is that many samples are located near and on the boundary between Fe^{2+} and $\text{Fe}(\text{OH})_3$, indicating that Fe^{2+} is easily oxidized to precipitate $\text{Fe}(\text{OH})_3$. On the other hand, $\text{Fe}(\text{OH})_3$ can be dissolved to form Fe^{2+} by only slight change in redox condition. Samples in TM are plotted in the field of pyrite. In this area, pyrite may be present because of the occurrence of ASS in TM.

The SO_4^{2-} presents in a number of samples (average 53 mg/L, maximum 773 mg/L). Local sources of SO_4^{2-} can be gypsum, oxidation of pyrite, mixing of fresh water with seawater and also fertilizers. SO_4^{2-} concentrations in HN-TH are up to 40 mg/L except two samples of about 100 mg/L. High SO_4^{2-} concentration may be caused by both oxidation of pyrite and dissolution of gypsum because aquifer in this area formed in Moc Hoa Formation which consists of pebble in the lower part and clay, silty clay and sandy silt containing gypsum in the upper part. Unlike HN-TH, sources of SO_4^{2-} in LX, LV, BM-MT samples are results of interaction between groundwater and marine deposits or mixing of fresh water and seawater. The salinity in the Mekong Delta significantly increases from north to south. Therefore, groundwaters in MT and Tieu Can with high Na^+ , Cl^- , and SO_4^{2-} are affected by seawater intrusion. The behavior of SO_4^{2-} is quite complicated and some sources are considered. However, there is no correlation between ORP values and SO_4^{2-} concentrations (Table 3.1 and Fig. 3.6).

3.4.4 Arsenic contents of core samples

Table 3.2 summarizes major constituents and mineral compositions for core samples obtained by XRF and XRD analyses. Total arsenic contents in the core samples range from 4 to 45 mg/kg. XRF analysis shows appreciable Fe contents in the cores as 13.61 wt % (30 m depth), 13.61 wt %, 12.62 wt % (133.7 m depth), 8.33 wt % (155 m depth) and 18.98 wt % (194 m depths). Quartz, clay minerals and iron hydroxide minerals such as goethite and hematite are major mineral constituents. High total arsenic concentration and iron occur where goethite and/or hematite are present at depths of 20 - 40 m (37 mg/kg), 155 m (16 mg/kg) and 194 m (45 mg/kg) (Table 3.2).

There is no appearance of arsenopyrite while pyrite is identified at depths of 115.5 m, 127.5 m, 209 m, 252.5 m and 265 m. However, arsenic contents in these samples are low (from 4 to 15 mg/kg). Figure 3.9 shows relationship among contents of total arsenic with Fe and Mn oxides. This figure indicates positive correlation of arsenic with Fe and Mn oxides of the core samples. High concentrations of Fe and Mn oxides exist at depths where peaks of total arsenic occur (Table 3.2, Fig. 3.9). These results suggest that hydrous ferric oxide with arsenic are present or Fe-oxides are the principal arsenic -carrier phase.

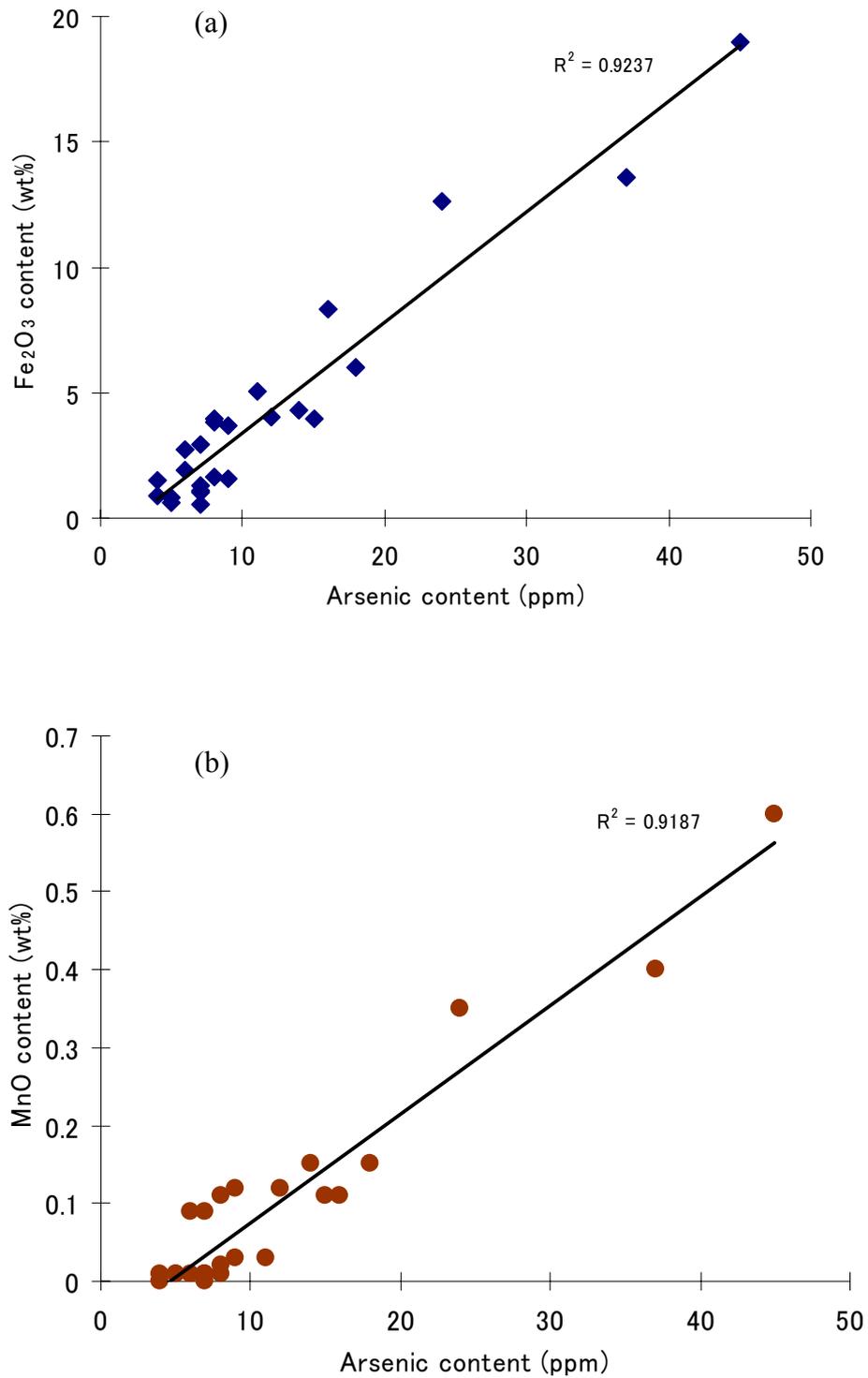


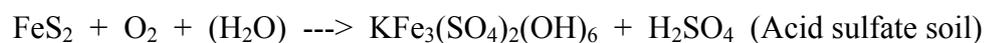
Fig. 3.9: Relationship between contents of As and (a) Fe_2O_3 ; (b) MnO in core samples.

3.5 Source and release mechanism of arsenic in aquifers of the Mekong Delta

3.5.1 Source of arsenic

The Mekong Delta in southern Vietnam was developed by sediments transported from the 'palaeo-Mekong' rivers. In general, natural arsenic originates from arsenious shales of the Upper Mekong basin (Stanger et al., 2005).

The whole present Mekong Delta was submerged due to sea expansion about five to six thousand years ago, and the Mekong Delta was the bottom of the sea. In this era, sediment rich in Fe (iron) from the upper Mekong River and SO₄ from seawater were combined each other, and then ultimately, pyrite was generated under reducing condition. Soil containing pyrite are called "potential acid sulfate soil", which characterize soils of majority of the Mekong Delta. During evolution of transgression, pyrite is in oxygen-deficient condition at the sea bottom. After that, the sea regression caused oxidation of pyrite by the chemical reaction (Akira, 2006):



The areas whose top soil layer has undergone such chemical reaction are defined as acid sulfate soil groups. Figure 3.10 shows distribution of soil in the Mekong Delta and indicates that groundwater samples at HN-TH and TM located within an area of ASS. In the western Mekong Delta, Brinkman et al. (1993) found that sulfidic materials are of two kinds (1) the older ones and (2) the younger ones. In the north west of this area, the older ones which have high

contents of pyrite and finely distributed organic matter was presented at several meters depth. The younger ones are the most extensive. They are generally found less than 1.5 - 3 m depth and have low organic matter contents with pyrite mostly found in root remnants. On the other hand, in the northeastern Mekong Delta, soils are characterized by a grayish brown sulfuric horizon with yellow brown goethite and pale yellow mottles jarosite in the vicinity of Hong Ngu (HN) and Tan My (TM) (Fig. 3.10). However, soils in Long An have a sulfuric horizon without jarosite or goethite mottles (Husson et al., 2000a). Husson et al. (2000a) also concluded that the sulfuric horizon with jarosite mottles had a pH 2.8 - 3.0, high sulfates, and Eh varied from 590 to 670 mV.

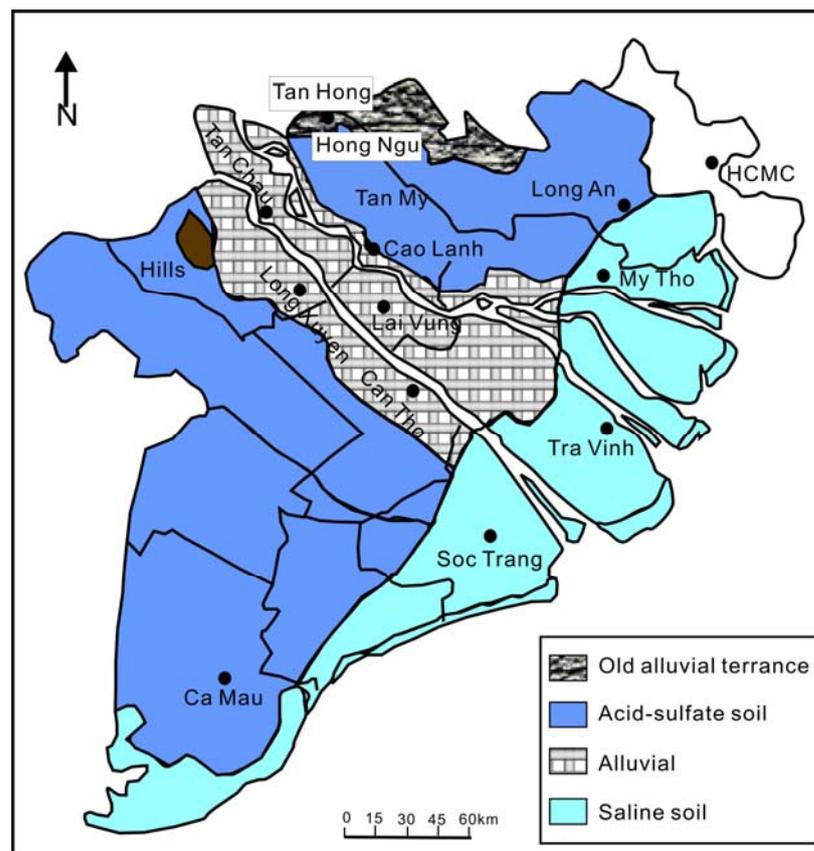


Fig. 3.10: *Distribution of soils in the Mekong Delta (Akira, 2006).*

In agreement with these findings by Brinkman et al. (1993) and Husson et al. (2000, (a)), pyrite was identified in the core samples of LK204 (Table 3.2) while jarosite and chalcopyrite was identified in soil samples in Tan My (Table 4.2) by XRD. Moreover, ORP values of groundwater samples in CL, HN-TN were positive. Therefore, arsenic release in pyrite can be source that cause relatively high arsenic concentrations in groundwater in these areas (HN-TN).

Contamination of Al and SO_4^{2-} of surface water affected by ASS in the Mekong Delta were investigated by Minh et al. (1997). In particular, Gustafsson and Tin (1994) reported the enrichment of arsenic (6 - 41 mg/kg) in ASS due to the uptake of arsenic by sulfides. If these sulfides containing arsenic encounter oxidizing condition, they are decomposed to ferric ions and sulfate ions, but ferric ions are rapidly hydrolyzed to form hydrous ferric oxide. Under this condition, arsenic is present as As(V) and easily adsorbed by the hydrous ferric oxide. It also indicated that the solubility of arsenic considerably varies within the soil profiles and is much influenced by the redox conditions (Gustafsson and Tin, 1994). Most of the arsenic in the B-horizons was present as insoluble Fe-arsenate complexes. Besides, Stanger et al. (2005) explained that at least there is coupling processes of arsenious pyrite oxidation and release of adsorbed As through the process of reductive dissolution of FeOOH. Therefore, it is reasonably concluded that there are two different arsenic sources in the aquifers at the Mekong Delta, that is, pyrite including arsenic and hydrous ferric oxide adsorbing arsenic.

3.5.2 Redox potential of soil during flooded period

It was reported that finely disseminated sulfide is widely dispersed within arsenic and organic-rich sediments, and these near-surface sediments or soil are subject to cycles of oxidation (non-flooded period) and reduction (flooded period). Annually occurred flooding in the Mekong Delta or naturally inundated of swampland may contribute to enhance reducing condition in the aquifers (Fig. 3.1). The Mekong Delta annually suffers from flood for long period by changing its water level. Recorded data during the last 45 years, there were 10 serious flood events (water level at Tan Chau hydrological station > 4.5 m a.s.l.) during the years of 1961, 1966, 1978, 1984, 1991, 1994, 1996, 2000, 2001 and 2002. Three of these (1961, 1966, and 2000) have been considered as the historical flood events (water level at Tan Chau hydrological station > 4.5 m a.s.l.) (Mekong River Commission, MRC, 2007).

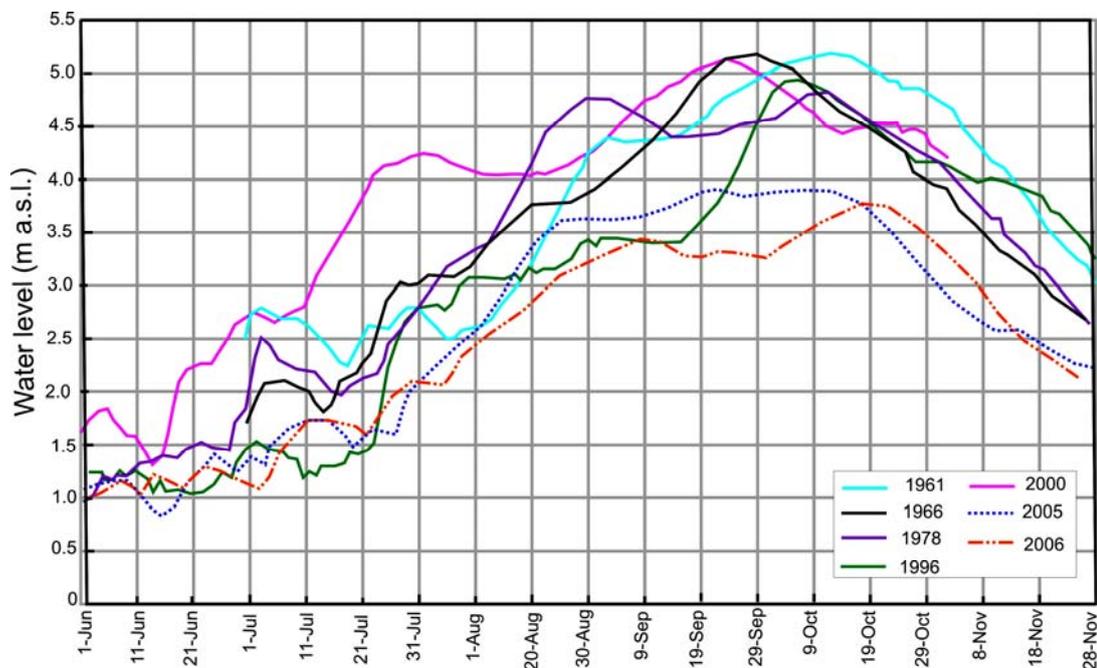


Fig. 3.11: Water level at Tan Chau hydrological station during rainy season (Mekong River Commission, MRC, 2007).

Figure 3.11 shows water level from June to December at Tan Chau hydrological station (Fig. 3.5) in the years when serious flood occurred seriously. Flood with water level from 3.5 m and 4.5 m is considered as ‘normal’ flood. Above 4.5 m, however, it becomes a ‘serious’ flood. Above 5 m, it is considered as a ‘dreadful’ flood (Mekong River Commission, MRC, 2007). The flood in the Mekong Delta occurs during the rainy season, from May to December, and its peak is in September or October. This means during the flood season, majority areas in the Mekong Delta are inundated.

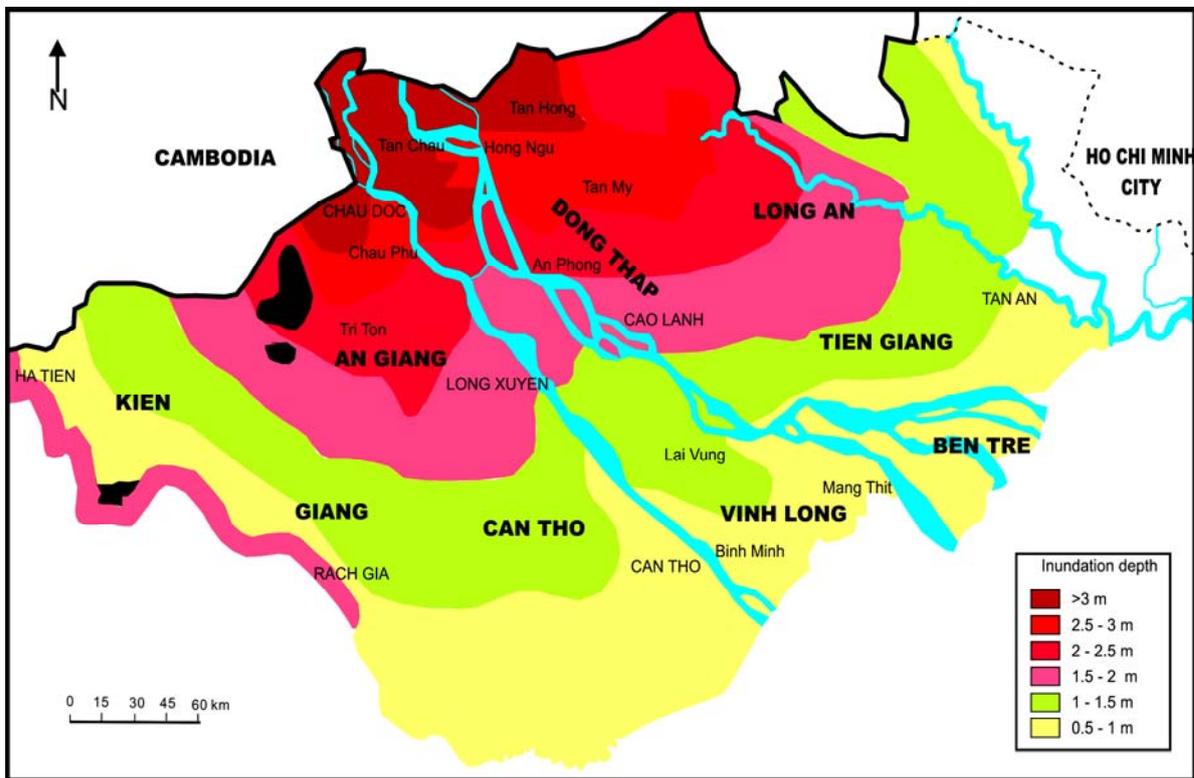


Figure 3.12: *Inundation depth in the Mekong Delta (Mekong River Commission, MRC, 2007).*

Figure 3.12 presents the distribution of inundation depths in the Mekong Delta. The flood can be divided into four inundation zones: very deep inundation

area (> 3 m); deep inundation area (2 - 3 m), average inundation area (1 - 2 m) and little inundation area (< 1 m). Dong Thap and An Giang provinces are classified as deep inundation areas while other provinces are considered as average or mildly inundated ones (Mekong River Commission, MRC, 2007).

Husson et al. (2000b) studied changes of surface waters such as river and canal waters and soil characteristics during flood. The authors explained that redox potential of soil is governed by the relative soil/water table level. Natural drainage causes water recession below the soil surfaces, and increases the rate of fall in groundwater level. Figure 3.13, based on 1995 data, Husson et al. (2000b) showed that in the north-east of the Mekong Delta soils experienced alternating redox conditions that can be distinguished into three different stages:

- On high topographic positions, higher than 1 m a.s.l. (Cao Lanh, An Phong, Tan My, Hong Ngu and Tan Hong), a period of complete submersion and, as a consequence of reduction, lasts from middle of August to middle of January on average. This period is followed by a short period (middle of January to middle of February) during which tidal movements lead to alternating reduction and oxidation. Then a long period of deep oxidation starts from the beginning of the rainy season in April to May. From that time, alternating periods of oxidation and reduction will last until complete submersion by floodwater in August.

- At intermediate elevation (0.75 - 1 m a.s.l.), the same four periods can be identified. However, the time of each period is different (Fig. 3.13).

- At low topographic locations (Long An), complete submersion by flood lasts for a long period, usually starting at the end of June, and ending in the beginning of February. In contrast, the period when the surface is exposed to atmosphere is extremely short. This period is limited from the end of April or the beginning of May as flood lead to alternating oxidation and reduction.

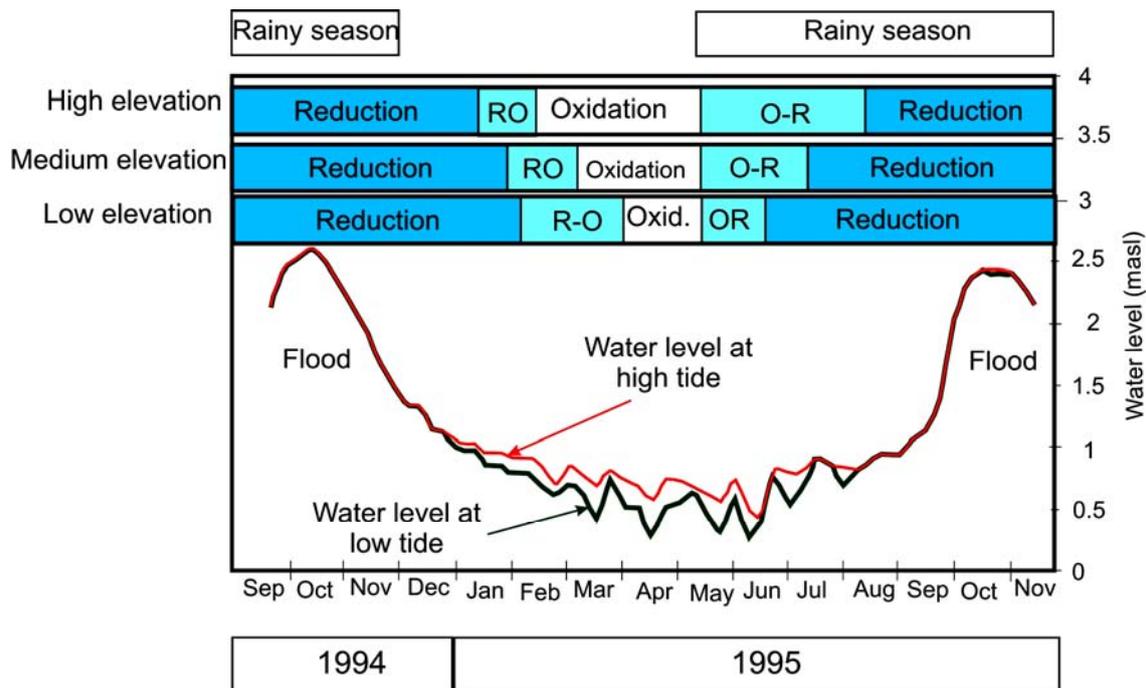


Fig. 3.13: Changes in redox potential of soil in relation to surface water level, 1994-1995.

3.5.3 Release mechanism of arsenic in aquifers

In the Mekong Delta, a sequence of reduction reactions occurs when soils and sediments become anaerobic due to annual flood. The processes causing changes in iron redox chemistry are important since they can affect the mobility of arsenic. One of the principal causes of high arsenic concentrations in

groundwaters is reductive dissolution of hydrous Fe oxides and/or release of adsorbed arsenic.

This sequence begins with the consumption of O₂ because of decomposition of organic matter. Next, NO₃⁻ decreases by reduction to NO₂⁻, the gas N₂ and finally reduction of N₂ to NH₄⁺. Insoluble hydrous Fe oxides are reduced to Fe²⁺. These processes are followed by SO₄²⁻ reduction to S²⁻. Arsenate reduction occurs after Fe(III) reduction but before SO₄²⁻ reduction (Smedley and Kinniburgh, 2002).

In Table 3.1 and Fig. 3.6, the groundwater samples can be divided into two groups based on the redox condition: with negative ORP values (under reducing condition) and with positive ORP values (under oxidizing condition). The redox condition of groundwater samples is different depending on depth in the same area or depending on locality. For example, in LV, the water is under reducing condition regardless to depth. The samples at 60 - 61 m are under reducing condition, however, those from deeper than 63 m are under oxidizing condition. On the other hand, in TH, all the samples are under oxidizing condition in the range of 20 - 48 m depth. For many groundwater samples with negative ORP values with high arsenic > 50 µg/L (e.g. LV5, LV7, AP1, AP5, TC2, TC3, CP1, CP2, LX and BM2), the Fe concentration are relatively high (5.1 – 43.4 mg/L), NO₃⁻ (< 0.1 mg/L) and pH values (≥ 7). This suggests that arsenic is released into groundwater by reductive dissolution of hydrous ferric oxides or hydrous manganese oxide that adsorbed arsenic under reducing condition in the aquifer. Under this condition, arsenic is present as As(III) than As(V). While, for groundwater samples with positive ORP values and with relatively high arsenic concentration (e.g. CL3, TH3, TH4, TH5 and TH8), the Fe, NH₄⁺ concentrations

and pH values are low, suggesting that arsenic may be released by decomposition of pyrite including arsenic due to oxidation Fe^{2+} and S_2^{2-} . The Fe^{3+} ions hydrolyze rapidly to precipitate $\text{Fe}(\text{OH})_3$ and S_2^{2-} ions are oxidized to SO_4^{2-} ions. The arsenic may be present as As(V).

3.6 Summary

Groundwater samples collected from wells in the Mekong Delta were chemically analyzed for major ions, arsenic and iron for understanding geochemical conditions in the aquifers. Core samples of borehole LK204 were also analyzed with XRF and XRD for vertical profiles of As, Fe together with iron hydroxides. Chemical analyses indicate that groundwaters are of a sodium bicarbonate and chloride type. High arsenic concentrations ($> 100 \mu\text{g/L}$) were detected generally shallow aquifer of less than 50 m depth, of Holocene age and comprise sands, silts, and clays. The aquifer sediments were capped by a layer of clay or silt, which effectively restricts entry of air to the aquifers. On the other hand, samples from deep wells (> 150 m depth) generally showed low arsenic concentrations. Groundwaters were classified into two groups based on ORP values: 1) samples with positive ORP values and low As and Fe concentrations and 2) samples with negative ORP values and high As and Fe concentrations. XRD analysis showed that quartz, clay minerals and iron hydroxide minerals such as goethite and hematite are major mineral constituents. High contents of As and Fe occurred where goethite and/or hematite present implies that Fe hydroxides are the principal arsenic-carrier phase. In contrast, arsenic contents were low at depth

where pyrite was identified. There is evidence from analyzed data that reductive dissolution of iron hydroxides is a controlling mechanism that causes high arsenic concentrations in reduced groundwater samples; negative ORP values, high concentrations of NH_4^+ , total Mn and Fe. Low arsenic concentrations, however, in oxidized groundwater samples of CL and HN-TH are the results of oxidative decomposition of sulfide-bearing minerals such as pyrite.

Table 3.1 Chemical composition of groundwater. Concentrations in mg/L except as noted.

Location	ID	Depth (m)	Temp (°C)	pH	EC (mS/cm)	ORP mV	Fe	Mn	As µg/l	A(III) µg/l	As(V) µg/l	HCO ₃ ⁻	F ⁻	Cl ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Lai Vung	LV 1	154	30.2	7.03	4.77	-94	0.85	n.d.	1.0	n.a.	n.a.	88	n.d.	1515	122.0	832	3.80	15.9	134	34
	LV 2	268	30.6	9.12	0.93	-76	0.02	0.01	1.0	n.a.	n.a.	403	0.62	94	28.0	228	0.63	1.6	3	3
	LV 3	336	37.1	7.99	1.18	-58	0.04	n.d.	2.4	n.a.	n.a.	442	0.52	138	68.2	262	0.45	2.1	5	15
	LV4	250	34.2	7.56	1.50	-21	0.11	0.02	5.7	n.a.	n.a.	392	0.45	246	81.4	316	0.67	3.0	7	17
	LV5	90	29.9	7.10	5.41	-143	7.0	0.57	136.5	65.5	71.0	382	0.11	1110	0.2	537	24.70	11.0	89	124
	LV 6	154	31.2	8.51	4.85	-39	0.21	0.10	11.5	n.a.	n.a.	124	n.d.	1513	103.0	832	6.92	15.5	143	30
	LV7	100	29.4	7.14	4.04	-144	6.74	0.42	95.3	63.8	31.5	527	0.22	894	121.0	462	18.30	9.8	119	141
Cao Lanh	CL1	61	29.4	6.45	1.76	-21	0.51	4.66	7.7	n.a.	n.a.	222	0.48	385	8.3	149	8.98	6.2	50	86
	CL2	63	29.5	6.40	2.53	73	0.25	6.33	2.3	n.a.	n.a.	199	0.40	656	20.5	21	0.66	4.4	93	145
	CL3	68	28.9	6.46	2.08	62	0.30	4.24	31.8	10.2	21.6	167	0.22	523	20.6	189	1.15	4.7	69	111
	CL4	60	28.0	6.53	2.20	-20	0.5	1.89	3.4	n.a.	n.a.	260	0.43	530	3.0	242	2.93	2.5	55	15
	CL5	90	30.1	6.49	4.33	6	0.5	4.92	13.0	n.a.	n.a.	163	0.37	1239	0.4	663	1.43	4.2	39	121
	CL6	70	29.4	6.62	1.73	23	0.15	1.60	1.4	n.a.	n.a.	197	0.69	392	7.6	168	0.66	2.1	49	78
	CL7	100	29.7	6.64	1.46	42	0.3	2.07	2.3	n.a.	n.a.	193	0.57	317	8.4	142	0.12	2.4	43	64
	CL8	70	29.5	6.51	1.22	66	0.25	5.27	2.6	n.a.	n.a.	175	0.47	264	10.6	113	0.54	4.0	38	47
An Phong	AP 1	21	28.9	7.13	0.58	-19	23.2	0.01	741.0	674.3	66.7	324	n.d.	25	n.d.	31	n.d.	4.5	12	50
	AP 2	86	29.7	6.46	6.87	-81	0.41	0.47	1.4	n.a.	n.a.	20	n.d.	2556	n.d.	997	1.94	13.3	199	215
	AP 3	160	29.4	7.79	14.7	-83	0.04	0.85	1.0	n.a.	n.a.	35	n.d.	4611	4.3	2600	8.49	78.2	411	111
	AP 4	289	28.9	7.62	1.08	-38	2.18	0.28	3.5	n.a.	n.a.	316	4.85	189	31.2	207	0.45	3.2	8	23
	AP 5	25	29.0	6.88	0.66	-198	17.5	0.42	284.5	256.1	28.4	354	0.11	28	n.d.	33	25.40	3.9	17	103
	AP 6	76	29.2	7.05	7.29	-134	8.0	2.76	1.3	n.a.	n.a.	56	n.d.	2437	n.d.	883	2.40	13.6	202	238
	AP 7	140	28.9	8.26	14.9	-103	0.42	0.60	1.4	n.a.	n.a.	57	n.d.	4798	2.0	2567	10.20	84.3	423	105
Tan My	TM 1	350	34.9	6.94	0.52	-89	0.21	0.01	8.8	n.a.	n.a.	279	0.32	17	31.2	99	0.50	4.1	6	17
	TM 2	350	33.7	7.31	0.82	-70	0.37	0.01	5.1	n.a.	n.a.	309	0.24	90	38.2	153	0.30	3.7	7	24

n.d.: not detected

n.a.: not analyzed

Table 3.1 Chemical composition of groundwater. Concentrations in mg/L except as noted (cont.)

Location	ID	Depth	Temp	pH	EC	ORP	Fe	Mn	As	A(III)	As(V)	HCO ₃ ⁻	F ⁻	Cl ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Hong Ngu	HN 1	60	29.6	6.41	8.07	38	0.42	2.74	1.4	n.a.	n.a.	362	0.37	2677	29.2	963	3.89	6.3	216	404
Tan Hong	TH 1	39	29.2	6.46	1.89	-19	1.04	1.31	1.1	n.a.	n.a.	291	0.36	354	97.2	236	0.56	4.0	52	66
	TH 2	20	29.1	6.27	0.67	-59	13.8	2.93	45.0	n.a.	n.a.	100	0.29	109	37.7	71	0.48	2.1	20	59
	TH 3	43	29.8	5.77	1.58	124	0.25	1.11	53.5	16.0	37.5	99	0.12	327	100	163	0.54	7.4	53	49
	TH 4	48	29.6	6.07	0.75	63	0.56	0.91	50.6	n.a.	n.a.	153	0.20	163	26.6	89	0.21	4.6	26	25
	TH 5	20	29.2	6.37	0.38	22	0.5	1.93	22.5	n.a.	n.a.	211	0.35	20	9.2	30	0.31	4.3	21	19
	TH 6	25	29.8	5.98	0.67	71	0.81	0.47	2.9	n.a.	n.a.	132	0.22	149	24.0	80	n.d.	3.6	22	20
	TH 7	30	30.0	5.72	1.05	74	1.27	0.92	5.8	n.a.	n.a.	111	0.21	273	29.4	121	0.48	8.0	29	28
	TH 8	35	29.2	6.22	0.60	20	1.33	0.70	15.5	n.a.	n.a.	205	0.24	45	40.0	79	0.76	6.3	21	23
Tan Chau	TC 1	15	30.8	6.48	0.47	-94	2.6	0.16	1.4	n.a.	n.a.	244	n.d.	11	31.8	26	8.50	1.5	13	49
	TC 2	27	29.6	6.85	0.55	-118	15.5	0.28	219.0	192.7	26.3	302	n.d.	31	n.d.	22	21.00	2.2	18	48
	TC 3	58	29.5	7.25	1.85	-130	9.44	0.09	59.7	n.a.	n.a.	416	n.d.	354	n.d.	291	8.15	14.0	42	47
Chau Phu	CP 1	50	29.0	6.98	6.05	-65	5.08	0.5	16.7	n.a.	n.a.	478	0.15	1886	51	1108	4.80	6.3	122	144
	CP 2	33	28.9	6.95	4.55	-142	43.4	n.d.	38.8	35.7	3.1	441	n.d.	1300	n.d.	845	6.53	6.0	80	75
Can Dang	CD 1	49	29.2	7.78	4.42	-42	2.41	0.05	9.1	n.a.	n.a.	697	0.44	1136	n.d.	790	3.80	13.5	99	81
	CD 2	103	29.0	6.78	2.55	-40	3.62	0.05	1.0	n.a.	n.a.	44	n.d.	769	0.5	190	0.70	7.5	101	157
Long Xuyen	LX	50	28.5	7.36	2.92	-112	4.78	n.d.	12.7	n.a.	n.a.	434	1.65	620	154.0	549	1.15	8.5	35	65
Binh Minh	BM 1	115	29.5	8.19	2.35	-171	0.41	0.89	1.0	n.a.	n.a.	507	n.d.	495	20.0	409	0.76	10.4	61	55
	BM 2	190	31.7	7.12	1.69	-165	28.1	0.02	16.9	n.a.	n.a.	486	n.d.	302	1.7	186	11.37	10.5	79	59
	BM 3	310	31.0	9.01	2.67	-246	n.d.	0.05	1.0	n.a.	n.a.	419	0.62	534	144.0	619	1.24	5.5	13	5
Mang Thit	MT 1	85	30.0	6.07	16.6	-71	12.3	0.01	1.0	n.a.	n.a.	14	n.d.	5442	17.6	2584	11.27	23.6	446	548
	MT 2	161	30.4	6.19	22.6	-86	13.5	1.05	1.0	n.a.	n.a.	65	n.d.	7640	773.0	4187	12.23	40.4	620	614
Tieu Can	TC	440	30.7	9.38	3.86	-260	n.d.	0.01	1.0	n.a.	n.a.	567	0.91	814	241.0	927	1.85	14.0	23	2

n.d.: not detected
n.a.: not analyzed

Table 3.2 Concentration of major elements and sulfur (%) and arsenic (ppm) in core samples with depths.

Depth	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	As	Minerals
(m)	%	%	%	%	%	%	%	%	%	%	ppm	
30	54.62	27.70	13.61	0.40	1.31	0.21	0.34	2.31	0.03	0.111	37	Quartz, Smectite, Illite, Feldspar, Goethite, Hematite
51.5	63.81	18.04	4.00	0.12	1.48	0.51	0.24	1.47	0.03	0.011	12	Quartz, Smectite, Illite
57.2	70.22	14.16	3.99	0.02	1.27	0.49	0.22	0.97	0.03	0.016	8	Quartz, Smectite, Illite, Kaolinite, Feldspar, Goethite
82.5	88.97	4.29	1.11	0.01	0.52	1.16	0.24	1.16	0.03	0.028	7	Quartz, Illite, Kaolinite, Feldspar, Hematite
90	79.80	8.23	3.85	0.11	1.07	0.32	0.44	2.14	0.04	0.023	8	Quartz, Smectite, Illite, Kaolinite, Feldspar
98.2	82.94	7.59	2.71	0.09	0.97	0.22	0.45	1.65	0.04	0.015	6	Quartz, Smectite, Illite, Feldspar, Hematite.
101	73.43	11.00	6.04	0.15	1.01	0.87	0.37	1.52	0.44	0.249	18	Quartz, Smectite, Illite, Kaolinite, Feldspar, Goethite
103	64.75	17.63	4.27	0.15	1.41	0.38	0.21	2.01	0.06	0.024	14	Quartz, Illite, Kaolinite, Feldspar, Goethite
109	87.51	4.62	2.96	0.09	0.55	0.22	0.38	1.44	0.04	0.031	7	Quartz, Smectite, Kaolinite, Feldspar, Hematite
115.5	85.19	5.40	3.66	0.12	0.70	0.24	0.43	1.49	0.05	0.054	9	Quartz, Illite, Kaolinite, Feldspar, Goethite, Pyrite.
127.5	76.25	10.48	3.93	0.11	1.31	0.32	0.42	1.70	0.08	0.106	15	Quartz, Illite, Feldspar, Goethite, Hematite, Pyrite
133.7	57.65	10.43	12.62	0.35	1.60	0.90	0.35	1.54	0.17	0.100	24	Quartz, Illite, Feldspar, Hematite
137	86.94	6.06	1.56	0.03	0.73	0.18	0.43	1.49	0.05	0.039	9	Quartz, Illite, Kaolinite, Feldspar, Goethite
143	92.14	2.88	5.08	0.03	0.42	0.14	0.23	0.80	0.03	0.047	11	Quartz, Illite, Kaolinite, Feldspar, Hematite
155	66.64	14.38	8.33	0.11	0.96	0.28	0.25	1.41	0.08	0.022	16	Quartz, Smectite, Illite, Kaolinite, Feldspar, Goethite
166.5	81.89	9.54	1.63	0.01	0.71	0.19	0.22	0.91	0.02	0.016	8	Quartz, Illite, Feldspar, Goethite, Hematite
182	80.15	10.56	1.94	0.01	0.67	0.25	0.14	0.19	0.02	0.012	6	Quartz, Illite, Hematite
194	54.70	33.78	18.98	0.60	1.06	0.34	0.36	1.36	0.07	0.008	45	Quartz, Illite, Feldspar, Goethite
203	69.69	19.84	1.04	0	0.34	0.08	0.19	2.19	0.02	0.006	7	Quartz, Illite, Kaolinite, Hematite
209	56.99	29.41	1.53	0	0.40	0.13	0.19	1.49	0.02	0.007	4	Quartz, Illite, Kaolinite, Feldspar, Pyrite
215.5	84.33	9.07	0.62	0.01	0.31	0.06	0.17	2.09	0.01	0.006	5	Quartz, Illite, Hematite
225.5	74.79	14.17	1.31	0.01	0.43	0.19	0.53	3.69	0.01	0.010	7	Quartz, Smectite, Illite, Feldspar, Hematite
245	79.14	10.96	0.57	0.01	0.31	0.11	0.50	5.37	0.01	0.006	7	Quartz, Feldspar, Hematite
252.5	76.87	12.87	0.85	0.01	0.40	0.11	0.33	4.48	0.01	0.010	5	Quartz, Feldspar, Hematite, Pyrite
265	73.07	13.61	0.87	0.01	0.36	0.09	0.27	3.01	0.01	0.011	4	Quartz, Feldspar, Hematite, Pyrite.

Chapter Four

ARSENIC FRACTIONATION IN SOILS BY SEQUENTIAL EXTRACTION METHOD

4.1. Introduction

Minerals, metals and metalloids as arsenic are present in soils in various forms with varying bioavailability, toxicity and mobility. The toxicity and mobility of metals or metalloids depend strongly on their specific chemical forms and on their binding state (precipitated with primary or secondary minerals, complexed by organic ligand, and so on). Indeed, changes in environmental conditions, such as acidification and changes in the redox potential conditions or increases in organic ligand concentrations can cause trace-element mobilization from the solid to the liquid phase that resulted in the contamination of surrounding waters.

Important factors affecting arsenic chemistry and therefore its mobility in soils are soil solution chemistry, pH, redox conditions, soil mineral composition, arsenic-bearing phase, and adsorption and/or desorption. The soil constituents related to arsenic mobility are oxide/hydroxides of Fe, Mn and Al (Raven et al., 1998), clay minerals (Manning and Goldberg, 1997) and organic matter. The chemical associations of arsenic with various soil solid phases affect its mobility and toxicity. Therefore, speciation of arsenic bearing solid phases in soils is important to understand the mechanism of arsenic. Arsenic fractionation in

different solid phases in soil can be examined by a selective sequential extraction (SE) technique with reagents of increasing dissolution strength. Ideally, each reagent should be targeting a specific solid phase associated with arsenic. The selective SE results will aid in understanding the persistence of arsenic in the subsurface and the role of various soil solids in the arsenic retention.

Soil samples in the Mekong Delta, Vietnam and in Fukuoka Prefecture, Japan were collected and conducted for SE to examine arsenic is associated to which chemical components in order to compare their properties. These results may imply appropriate explanation for source and released mechanism of arsenic from soil to groundwater.

4.2. Soil sampling and characterization

4.2.1 Soil sampling

Soil samples were collected in two sites: (1) Sasaguri Town, Kasuya Province, Fukuoka Prefecture, Japan and (2) the Mekong Delta, Vietnam. Locations of soil samples in Fukuoka and the Mekong Delta are shown in Figs 4.1a and 4.1b, respectively. Surface soil samples (0 – 10 cm depth) (N4b) were collected in Sasaguri where covered by metamorphic rocks such as schist being rich in magnesium and iron. Soil samples (1 m depth) from the Mekong Delta were collected at Tan Chau (TC), An Phong (AP), Tan My (TM) and Lai Vung (LV). Among these samples, TM was collected in the area where acid sulfate soil covers the surface.

The soil samples were brought into the laboratory, air-dried, disaggregated by manual crushing. Then the samples were sieved retaining the < 2 mm fraction and stored in airtight polyethylene bags until use for chemical analysis. Soil pH was measured in 1:1 soil: water suspension after 1h of equilibration using a Pt combination pH electrode (HORIBA D-54).

4.2.2 Analysis method for total arsenic

Arsenic was analyzed by HG-AAS after digestion with strong acids and 2 mL of KMnO_4 solution (2%) as follow:

- 1) 1.0 g of sample was placed in a Teflon beaker (60 mL).
- 2) 3 mL of 0.1 M HCl, 5mL of conc. HNO_3 , 25 mL conc. HF and 2 mL KMnO_4 solution (2%) were added.
- 3) The solution was heated about 150 – 180°C on a hot plate for 2 days. If necessary, the KMnO_4 solution (2%) was added to maintain indicator color.
- 4) Then evaporate the solution at about 250°C until nearly dry.
- 5) The residue was dissolved with 5 mL of 6 M HCl and made up to 50 mL with deionized water.
- 6) The digest was filter through 0.45 μm membrane filter to analyze for total arsenic.

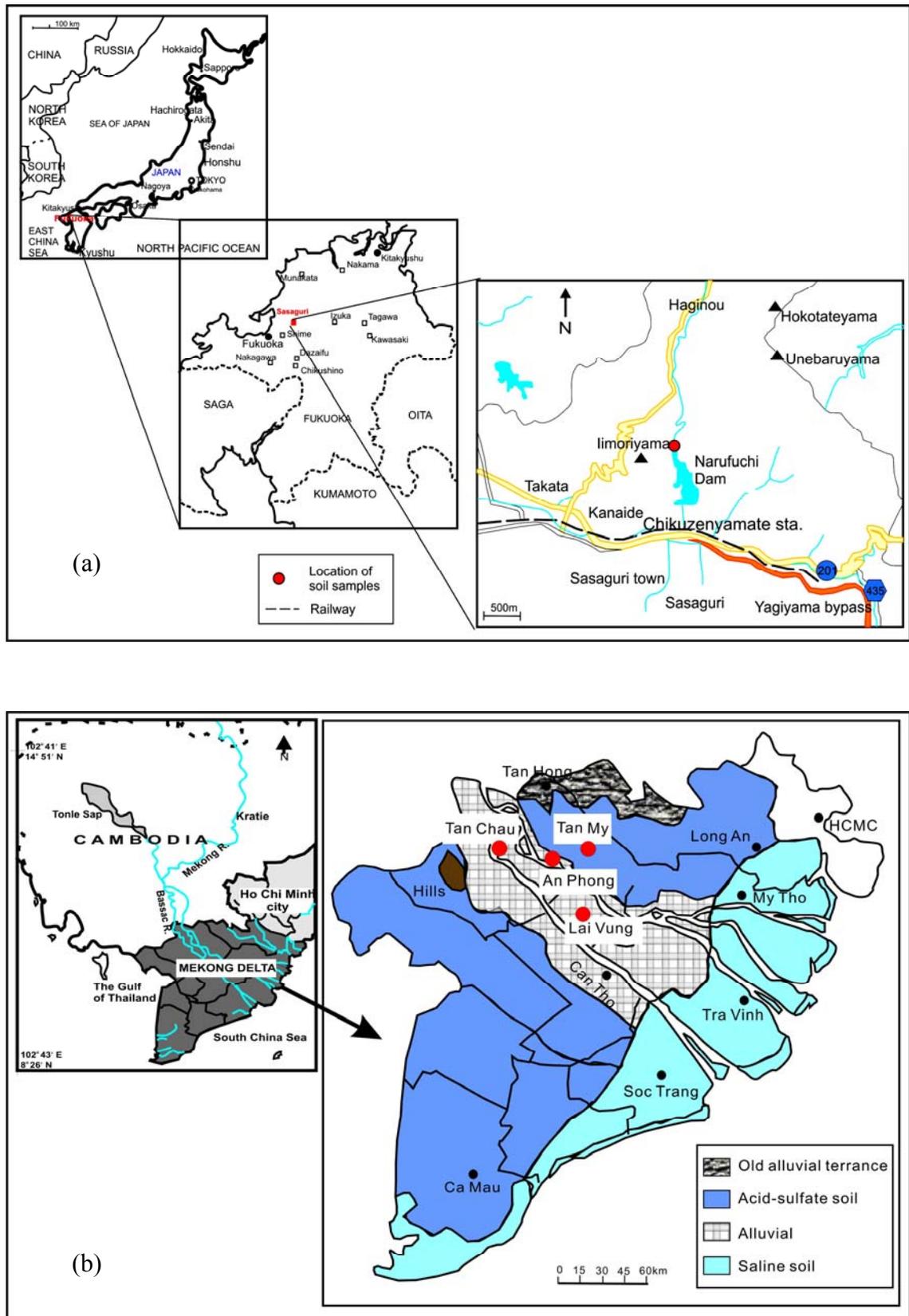


Fig. 4.1 Location maps of soil samples in: (a) Fukuoka Prefecture, Japan; (b) the Mekong Delta, Vietnam.

Concentrations of Fe, Al and Mn were determined by ICP-AES after the same decomposition method above. Table 4.1 shows the results of concentration of Fe, Al, Mn and total As. It is observed that characteristics of soils in Sasaguri are similar to those of soils in the Mekong Delta which Fe and As concentrations range from 170 to 210 g/kg and from 23 to 35 mg/kg, respectively (Table 4.1). Concentrations of Al and Mn, however, in the Sasaguri soils are higher than those in the Mekong Delta (Table 4.1)

Table 4.1 *Properties of soils in Sasaguri and the Mekong Delta.*

Soil properties		Sasaguri	Mekong Delta			
		N4b	TC	AP	TM	LV
pH		7.3	7.2	7.1	3.46	6.7
Elemental content (g/kg soil)	Al	189	118	130	145	95
	Fe	210	190	180	170	189
	Mn	65	0.68	0.77	0.560	1.1
	As	0.027	0.023	0.026	0.029	0.035

4.2.3 Mineralogical composition

Mineralogy was determined by XRD (Rigaku RINT 2100) analysis. The mineral species of soils are given in Table 4.2. Mineral composition of each sample was obtained using X-ray diffraction method (XRD-Rigaku RINT 2100). Sasaguri soil consists mainly of quartz and iron hydroxides or oxides. Clay minerals are the second most abundant and minor quantities of carbonate minerals (trace). Comparing to Sasaguri soil, quartz is also the most abundant mineral followed by iron hydroxides or oxides (abundance) and clay minerals (less abundance) for the soils of the Mekong Delta. Carbonate minerals present in trace quantities. Moreover, small quantities of sulfide minerals as jarosite and

chalcopyrite (moderate) and sulfate as gypsum (trace) were identified in the Tan My soil (TM). These minerals are secondary in origin; i.e. they are weathering products. The presence of these minerals implies that this sample was affected by acid sulfate soil formed by oxidation of pyrite (Fig. 4.1b), and sulfate formation (Table 4.1). On the basis of XRD results, it is suggested that principal minerals of the Sasaguri soil and the soil of the Mekong Delta (TC, AP and LV) are similar, except sample of Tan My (TM).

Table 4.2 Mineralogy of soil samples by XRD analysis.

Mineral constituents		Sasaguri	Mekong Delta			
		N4b	TC	AP	TM	LV
Silicate minerals	Quartz - SiO ₂	⊙	⊙	⊙	⊙	⊙
	Pyrophyllite - Al ₂ Si ₄ O ₁₀ (OH) ₂	-	○	○	△	△
Iron hydroxides minerals	Goethite (FeOOH)	○	○	○	-	○
	Magnetite - Fe ₃ O ₄	○	○	○	○	○
Clay minerals	Smectite/Chlorite	△	x	-	x	x
	Illite	-	-	x	x	△
	Kaolinite/ Halloysite - Al ₂ Si ₂ O ₅ (OH) ₄ . n H ₂ O	△	-	x	-	x
	Albite - NaAlSi ₃ O ₈	△	-	-	-	-
Sulfide minerals	Jarosite - KFe ₃ (SO ₄) ₂ (OH) ₆	-	-	-	△	-
	Chalcopyrite - CuFeS ₂	-	-	-	x	-
Sulfate minerals	Gypsum - CaSO ₄ ·2H ₂ O	-	-	-	△	-
Carbonate minerals	Rhodochrosite - MnCO ₃	x	x	-	-	x
	Calcite - CaCO ₃	x	-	-	-	-
	Dolomite - (Ca, Mg)(CO ₃) ₂	x	-	-	-	-

⊙ : more abundance; ○ : abundance; △ : moderate; x : trace; - : not identified

4.3. Sequential extraction (SE) method

4.3.1 SE: an overview

Chemical speciation analysis in soils and sediments is defined by the Community Bureau of Reference (BCR) of the European Community (Ure et al., 1993) as: *the process of identification and quantification of the different defined species, forms or phases in which an element occurs in the material*. Chemical speciation can be subdivided into three classes: (i) functionally defined species (e.g. plant available species) where the species are defined by their role, (ii) operationally defined species, characterized by the procedure of isolation and identification (e.g. acid ammonium oxalate extractable fraction), and (iii) specific chemical compounds or oxidation states (e.g. methyl-mercury, AsH₃, etc). However, according to the recent recommendations of the International Union for Pure and Applied Chemistry (IUPAC) (Templeton et al., 2000), the former two speciation classes are referred to as fractionation, which is the process of classification of an analytes from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties. These methods are based on the rational use of a series of chosen reagent to solubilise successively different mineralogical fractions retaining a larger part of trace elements. However, these developed SE schemes reflect complexity of the problems: lack of uniformity in the procedure, lack of selectivity of the reagents used, lack of quality control, results highly depend on the procedure used, and so on. Despite these problems, this widely used technique can provide crucial information about

the ecotoxicological characteristics (reactivity, bioavailability, toxicity) of contaminants.

The extraction scheme for trace elements developed by Tessier et al. (1979) are the most accepted and popular ones. The scheme proposed by Tessier et al. (1979) includes five fractions:

- (i) Exchangeable. The sediment was extracted with 1 M MgCl_2 , pH 7.0, with continuous agitation.
- (ii) Bound to Carbonates. The residue from (i) was extracted with 1 M CH_3COONa , adjusted to pH 5.0 with CH_3COOH at room temperature.
- (iii) Bound to Fe-Mn oxides. The residue from (ii) extracted with 0.04 M $\text{NH}_2\text{OH.HCl}$ in 25% (v/v) CH_3COONa . Then experiment was performed at $96 \pm 3^\circ\text{C}$ with occasional agitation.
- (iv) Bound to organic matter. For the residue from (iii), 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3 were added. The mixture was heated to $85 \pm 2^\circ\text{C}$ for 2 h with occasional agitation. A second 3 mL of 30% H_2O_2 was then added and the mixture was again heated for 3 h with the same temperature.
- (v) Residual. The residue from (iv) was decomposed with mixture strong acid according to the method described above for total arsenic analysis.

Application of these SE schemes on metalloid like arsenic that are prevailing in anionic form in soils, however, in this study SE schemes has been modified as followed. Applied SE schemes and procedure is described in detail in the next section (Section 4.3.2).

- (i) Exchangeable.
- (ii) Bound to Carbonates.
- (iii) Bound to sulfide phase (mostly pyrite).
- (iv) Bound to amorphous and poorly crystalline Fe-Mn hydroxides.
- (v) Residual.

4.3.2 Applied SE schemes and procedure

Flowchart of the applied SE procedure in this study is shown in Fig. 4.2.

a. Exchangeable fraction

Metals extracted in this operation would include weakly sorbed metal species, particularly those retained on the soil surface by relatively weak electrostatic interactions and those that can be released by ion-exchange processes.

Extraction with 1 M $\text{CH}_3\text{COONH}_4$ was used in this step instead of 1 M MgCl_2 . The MgCl_2 reagent was not used because Gleyzes et al. (2001) showed that Mg^{2+} cannot be exchanged efficiently with the anionic species and the chloride ion has low anion exchange power. Moreover, $\text{CH}_3\text{COONH}_4$ favors the exchange and reduces re-adsorption or precipitation of the extracted metals as arsenic (Gleyzes et al., 2001).

This extraction step consisted of weighing 1 g of soils into 50 mL centrifugation tubes and adding 25 mL of 1 M $\text{CH}_3\text{COONH}_4$ at pH of 7 (Fig. 4.2). The reaction was allowed to continue for 1 h at room temperature with a shaker. After shaking, the mixture was centrifuged for 20 min at 4500 rpm. The supernatant was decanted and filtered through 0.45 μm membrane filters. Then

rinsing the remaining residue with 10 mL deionized water and rinsate was discarded before the next extraction reagent is added. It was recommended by Keon et al. (2001) to wash extractant after each step in order to remove any potentially readsorbed As.

b. Carbonate fraction

The metal fraction recovered in this step indicates the presence of arsenic as co-precipitate with carbonate minerals. According to Tack and Verloo (1995), large proportions of total Mn are frequently found in the acetic acid/sodium acetate extracts. The Mn extracted with this reagent can be derived from the dissolution of Mg carbonates as Mn^{2+} can substitute for Mg^{2+} in carbonate minerals. The dissolution rate of carbonates depends on parameters related to the samples such as the grain size, the initial content and nature of carbonates, and the sample size.

The procedure described by Tessier et al. (1979) was used because of low carbonate content in the soil samples.

The residue from (a) was extracted with 25 mL of using 1 M CH_3COONa adjusted to pH 5.0 with CH_3COOH . The experiment was allowed to continue for 4 h at room temperature (Fig. 4.2). After shaking the procedure of centrifugation, filter and collection the supernatant as well as rinsing the remaining residue for the next step are the same as fraction (a).

c. Sulfide fraction (mostly pyrite)

Trace elements and arsenic may be incorporated in many forms of organic matter. Under oxidizing conditions, organic materials tend to degraded, leading to the release of sorbed metals or arsenic. So, oxidizing reagents such as hydrogen peroxide (H_2O_2) is frequently used in fractionation studies in order to extract the fraction associated with organic mater. Nevertheless, H_2O_2 is used in dilute HNO_3 solution in order to prevent metals being consumed by the formation of Fe hydroxides in higher pH ranges. The oxidation process is promoted by heating for several hours. Under these conditions, H_2O_2 can not fully decomposed organic matter but sulfides are partially dissolved (Tessier et al., 1979). Moreover, Wenzel et al. (2001) did extraction of arsenic in soil but the results showed no relation to soil organic matter. In this study, therefore, extraction of arsenic bounded to sulfide fraction (mostly pyrite) is considered because of presence of pyrite in the soil. In this step, 25 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3 was added and the mixture was extracted at 35°C for 3 hours.

For the residue from (b), 25 mL of 30% H_2O_2 adjusted to pH 2.0 with HNO_3 was added. The mixture was extracted at 35°C for 3 h (Fig. 4.2). After extraction the procedure of centrifugation, filter and collection the supernatant as well as rinsing the remaining residue for the next step are the same as fraction (a).

d. Fraction bound to amorphous and poorly crystalline Fe and Mn hydroxides

The use of a 0.1 mol/L hydroxylamine solution prepared in 0.01 mol/L HNO_3 (pH 2) can selectively dissolve Mn oxides in 30 min while minimizing iron extraction (<5%) (Chao and Zhou, 1983). Simultaneous extraction of Mn-Fe oxides can be achieved by 0.02 mol/L or 0.04 mol/L hydroxylamine solution

prepared in 25% v/v acetic acid, at high temperature (96–100°C). However, this protocol was considered insufficient for iron extraction (Arunachalam et al., 1996), particularly in the case of materials with a high Fe content (Gleyzes et al., 2002). Greubel et al. (1988) found that the $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction dissolved completely amorphous iron hydroxides so all arsenic adsorbed on it was released. However, in a mixture of amorphous and crystalline iron oxides (goethite and/or hematite), this reagent appeared to be ineffective in releasing arsenic from the solid phases. It was concluded that the amorphous iron oxides were totally dissolved, and the released arsenic were re-adsorbed by the crystalline iron hydroxides (goethite or hematite).

In this study, 0.2 M NH_4 -oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, acidified pH 3.25 with oxalic acid solution at ambient temperature in the dark were used. In these conditions, this reagent appears to be effective for amorphous iron phases with a low degree of crystallinity. As oxalate action is light sensitive, the UV catalysis is effective to promote the decomposition of crystallized iron oxides (Shuman, 1982). Moreover, given excess concentration of oxalate present during extraction, re-adsorption of arsenic is minimized (Wenzel et al., 2001).

The residue from (c) was extracted with 25 mL of 0.2 M NH_4 -oxalate acidified pH 3.25 with oxalic acid solution. The experiment was allowed to shake for 4 h at room temperature in the dark (Fig. 4.2). After shaking the procedure of centrifugation, filter and collection the supernatant as well as rinsing the remaining residue for the next step are the same as fraction (a).

e. Residual fraction

Primary and secondary minerals contain metals in the crystalline lattice constitute the bulk of this fraction. Its destruction is achieved by digestion with strong acids such as HF, HClO₄, HCl and HNO₃. In this fraction, KMnO₄ (2%) solution was added in order to prevent arsenic vaporizing during evaporation.

The residue from (d) was decomposed with a mixture of strong acid 3 ml of HCl, 5 mL of conc. HNO₃, 25 mL of conc. HF and 2 mL of KMnO₄ solution (2%). The solution was heated about 150 – 180°C on a hot plate for 2 days (Fig. 4.2). If necessary, the KMnO₄ solution (2%) was added to maintain indicator color. Then evaporate the solution at about 250°C until nearly dry. Finally, the residue was dissolved with 5 mL of 6 M HCl and made up to 50 mL with deionized water.

All the filtrates collected were acidified with HCl prior to analysis of As with HG-AAS and Fe, Al, Mn with ICP-AES. The SE was repeated three times for the same samples. All results of SE analysis can be seen in Appendices.

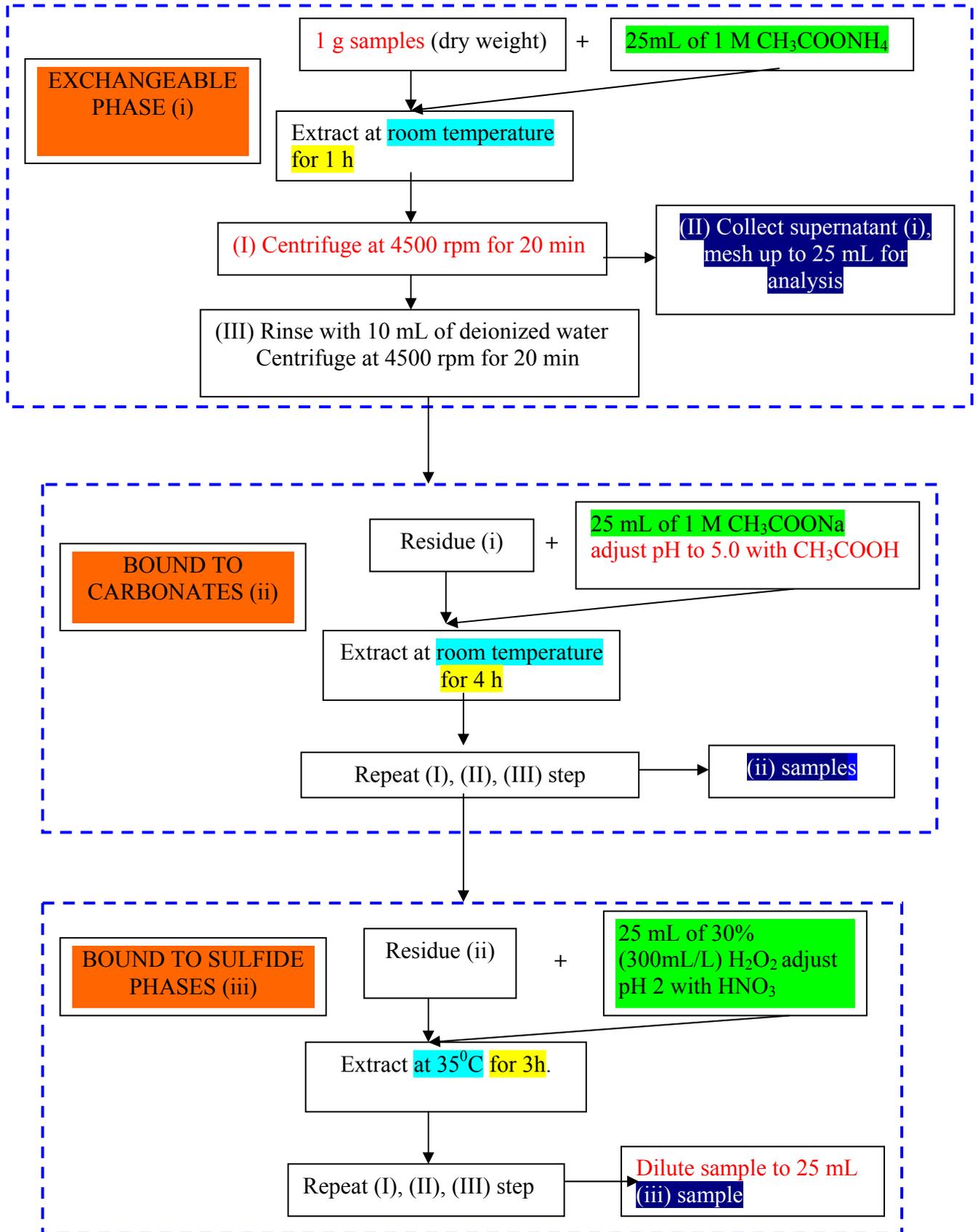


Fig. 4.2 (a) Flowchart of applied SE method for the first three fractions

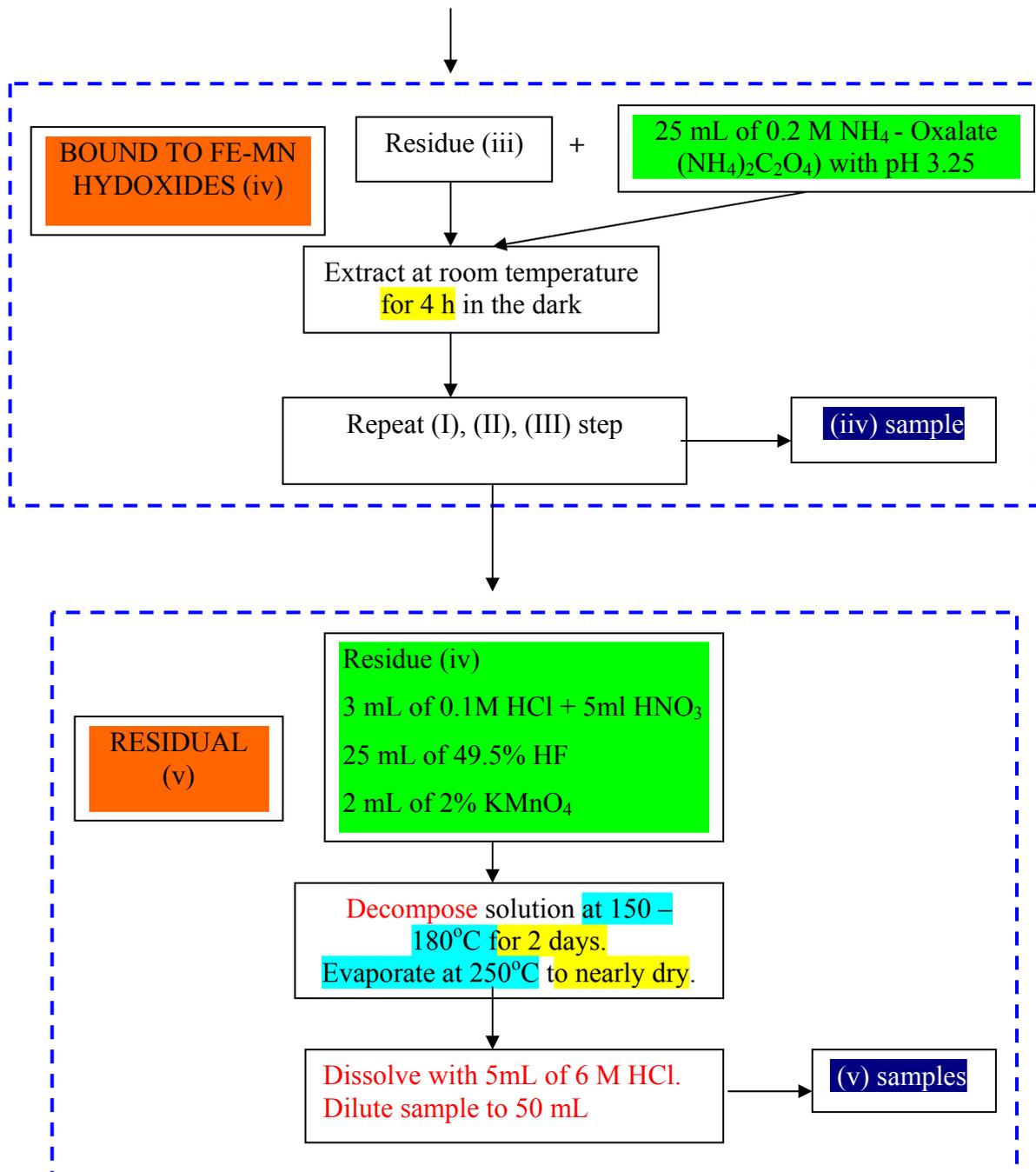


Fig. 4.2 (b) Flowchart of applied SE method for the last two fractions

4.4. Chemical speciation of arsenic in soils and distribution of arsenic in groundwater in the Mekong Delta

4.4.1 Fractionation of arsenic in soils

Fractionation studies were conducted to investigate the potential mobility of arsenic in the soil samples. Table 4.3 shows the As, Fe, Mn and Al contents among the five fraction of SE.

Regarding to Sasaguri soil, 1.86 mg/kg of total As is extracted as exchangeable fraction while 2.09 mg/kg and 0.9 mg/kg of total As for carbonate and sulfide fractions, respectively. Highest arsenic is identified as 15.47 mg/kg from Fe-Mn hydroxides and 5.65 mg/kg for residual fractions. Likely As, Fe (138,600 mg/kg) and Mn (39,519 mg/kg) show the highest contents for Fe-Mn hydroxides, following by residual, carbonate, sulfide and exchangeable fractions. On the other hand, highest content of Al is present for residual fraction (135,500 mg/kg).

For soils in the Mekong Delta, arsenic (14.12 - 24.07 mg/kg) is predominantly associated with the Fe-Mn hydroxides compared to exchange (0.36 - 1.0 mg/kg), carbonate (0.94 - 1.29 mg/kg), sulfide (0.19 - 8.34 mg/kg) and residual fractions (4.19 - 7.37 mg/kg). Along with arsenic contents, about 102,000 - 132,000 mg/kg and 369 -707 mg/kg of the Fe and Mn, respectively, were extracted from the Fe-Mn hydroxides fraction (Table 4.3). In contrast, the majority of extracted Al is associated with the residual (about 20,000 - 90,000

mg/kg). Figure 4.3 shows the percentages of As, Fe, Mn and Al contents to the total amount of element extracted for each extraction step.

Table 4.3 Arsenic and other elements fractionation in soils.

Elements	Fractions	Sasaguri	Mekong Delta			
		N4b	TC	AP	TM	LV
As (mg/kg)	Exchangeable	1.86	0.64	0.36	0.62	1.00
	HCO ₃ fraction	2.09	0.94	1.29	1.08	1.13
	Sulfide fraction	0.90	0.21	0.19	8.34	0.41
	Fe-Mn hydroxides	15.47	15.94	17.58	14.12	24.07
	Residual phases	5.68	4.55	5.19	4.19	7.37
	Total	26.00	22.00	25.00	28.00	34.00
Fe (g/kg)	Exchangeable	5.12	3.00	2.47	2.50	3.78
	HCO ₃ fraction	5.27	5.76	8.40	4.04	7.34
	Sulfide fraction	7.05	2.52	1.96	39.59	2.50
	Fe-Mn hydroxides	138.60	130.30	121.30	102.50	131.50
	Residual phases	48.08	37.62	38.97	13.75	38.83
	Total	204.00	179.00	173.00	162.00	184.00
Mn (mg/kg)	Exchangeable	1555	14.99	9.88	7.8	21.6
	HCO ₃ fraction	4927	62.13	29.29	20.4	115.0
	Sulfide fraction	1953	9.40	8.57	5.8	10.5
	Fe-Mn hydroxides	39519	416.00	506.00	369.0	707.0
	Residual phases	13952	111.90	146.80	103.9	193.0
	Total	61906	614.00	700.00	507.0	1047.0
Al (g/kg)	Exchangeable	5.1	2.7	2.0	1.8	2.2
	HCO ₃ fraction	9.8	11.2	5.6	3.6	7.5
	Sulfide fraction	4.2	1.7	1.7	20.2	0.9
	Fe-Mn hydroxides	31.0	74.9	21.2	28.0	15.6
	Residual phases	135.3	20.2	89.6	78.5	59.5
	Total	185.0	111.0	120.0	132.0	86.0

Exchangeable arsenic fraction, supposedly the most potentially mobile fraction, consists of 1.44 - 2.9% and 7.2% of total As for the soil in the Mekong Delta and in Sasaguri, respectively. The arsenic retention in this fraction was mainly because of an anion exchange (Cl⁻ for arsenic oxyanions) mechanism.

This fraction is important since they are considered the most available to biota and most easily leached to groundwater (Lombi et al., 2000). On the other hand, for carbonate fraction extracted by CH_3COONa , total arsenic concentrations range from 4.3 to 8.04% for all soils. Arsenic bound to this fraction of Sasaguri soil (8.04%) is higher than those of the Mekong Delta soils (3.3 – 5.2%) because carbonate minerals were found in Sasaguri soil. Fraction 3 as sulfide fraction does not contribute to arsenic retention in all of the soil samples excluding TM soil (up to 30%) (Fig. 4.3). Due to the presence of pyrite minerals in TM soil (Table 4.2), arsenic is adsorbed on the mineral structure of the secondary Fe hydroxides as jarosite. Therefore, relatively significant amount of arsenic and Fe were extracted by this fraction.

Fe-associated minerals played an important role in As retention. The percentage of As in Fraction 4, which is presumably associated with amorphous and poorly crystalline Fe-Mn hydroxides is the largest one, comprising about 73% of total As for the Sasaguri soil (N4b), TC, AP, LV soil and 50% for TM soil in the Mekong Delta (Fig. 4.3). The percentages of arsenic in the residual fraction range from 15 to 23%. Arsenic in this fraction is probably retained by silicate and Al silicate.

There is significant percentage of Fe dissolved (up to 73%) by this reducing extraction reagents, which result in a high percentage of arsenic released. The primary sources of Fe extracted by NH_4 -oxalate are considered to be Fe oxides.

Most Mn is also released in this step though Mn oxides were not detected in these soils. This suggests that Mn oxides are not a major sink of arsenic in these soils and Mn oxides may catalyze redox transformations of arsenic in soils, e.g.

the oxidation of As(III) to As(V) (Lombi et al., 2000). In contrast, large amount of Al (75%) with slight release of Fe and Mn (Table. 4.3, Fig. 4.3) during extraction of residual fraction indicate that residual is mostly the HF-soluble aluminum silicate minerals.

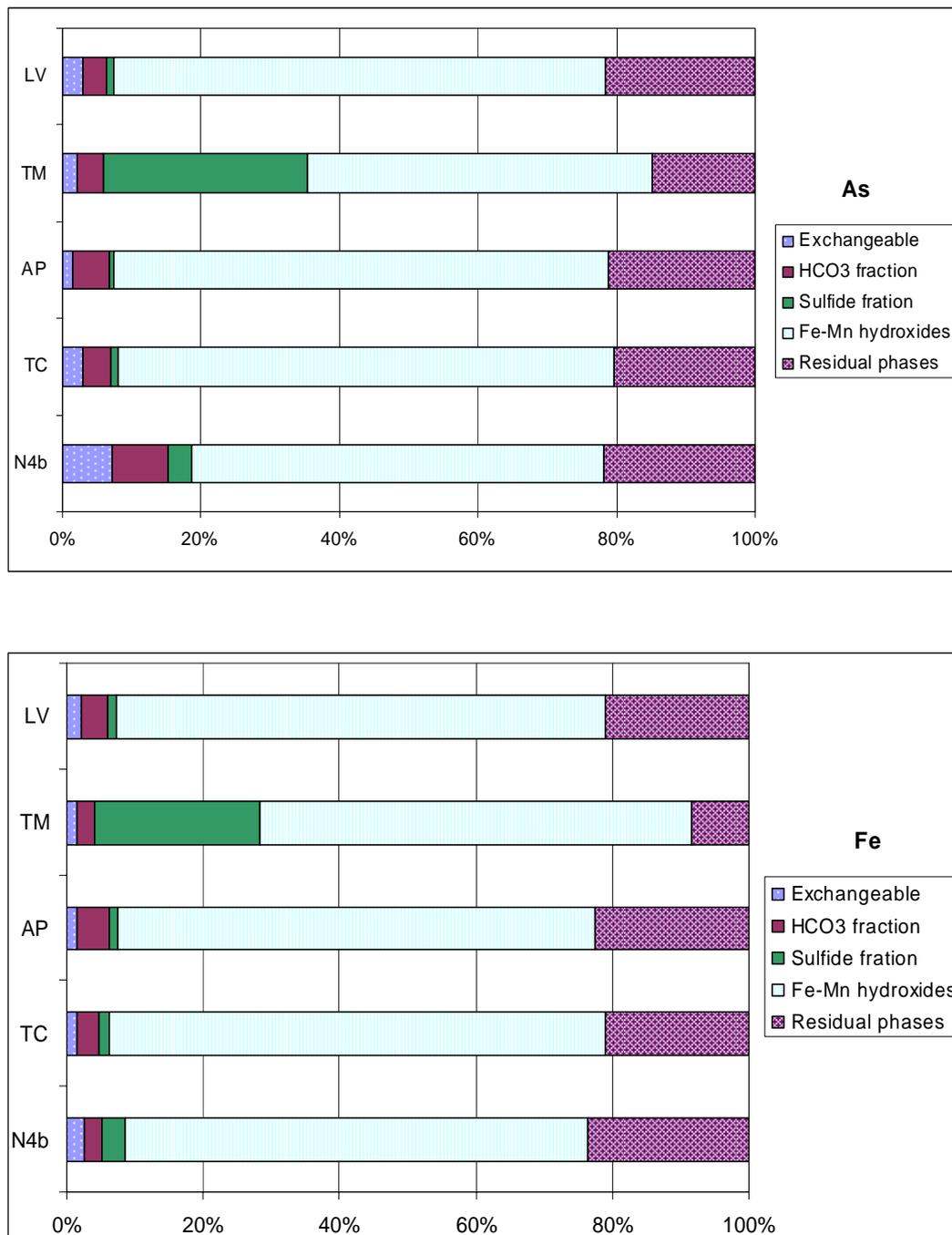


Fig. 4.3 (a): Percentages of As and Fe extracted by SE method.

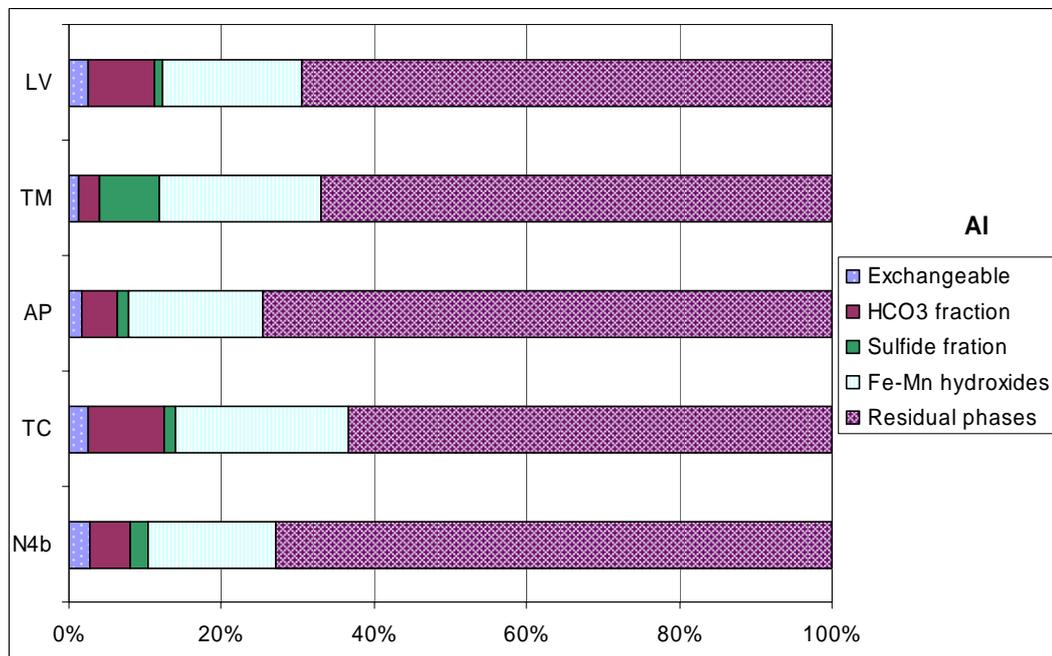
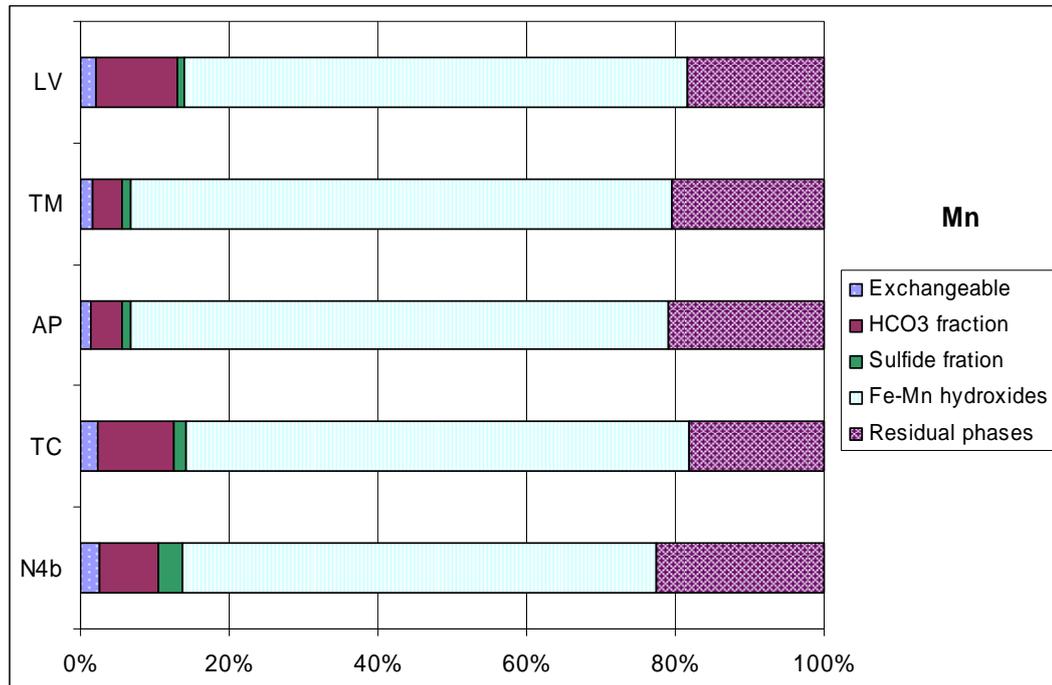


Fig. 4.3 (b): Percentages of Mn and Al extracted by SE method.

4.4.2 Chemical speciation and distribution of arsenic in groundwater

From the viewpoint of groundwater chemistry, reductive dissolution of iron hydroxides and release of arsenic are predominant mechanism that control high arsenic concentrations in reduced groundwater. The results of the speciation analysis showed that more than 70 wt% of arsenic is associated with Fe hydroxides in TC, AP and LV soils. This suggests that the Fe hydroxides are important minerals for arsenic adsorption or coprecipitation in these samples. Stability of this adsorbed arsenic can be affected by abiotic reactions (oxidation, reduction, precipitation, and dissolution) and biotic (microbial activities) (Sanders et al., 1994). If redox conditions remain oxidizing, the Fe hydroxides will remain stable. Upon burial, however, reduction of Fe hydroxides can cause the release of adsorbed or coprecipitated arsenic.

On the other hand, oxidizing decomposition of sulfide-bearing minerals such as pyrite can be a source for arsenic in oxidized groundwater samples. Dissolved arsenic can also be co-precipitated with pyrite (Sanders et al., 1994). Moreover, pyrite was identified in TM soil and 30 wt% of arsenic is bound to pyrite fraction. From this result, it can be said that in reduced environments, sulfides control the distribution of arsenic in aquifer. Physical disturbance of the soil by seasonal changes or agricultural activities may cause an oxidizing environment where the sulfides undergo oxidation, thus releasing arsenic.

4.5. Summary

Arsenic fractionation was conducted with sequential extraction (SE) method.

In general, soils from Sasaguri and the Mekong Delta show similarity both in arsenic fraction as well as mineralogy. Total arsenic determined by decomposition showed in a range from 23 mg/kg to 35 mg/kg for the soils of Sasaguri and the Mekong Delta. Mineralogical composition of the soils (Sasaguri soil, Tan Chau, An Phong and Lai Vung) indicated that quartz is the most abundant mineral followed by iron hydroxides as goethite and hematite. Different from the other soils, Tan My soil was acidic with pH 3.46 and contained sulfide minerals as small quantities and abundant iron hydroxides.

The analysis with sequential extraction method showed the majority of arsenic is mainly associated with amorphous and poorly crystalline Fe hydroxides (60 wt% and 73 wt% of the total As) followed by residual (about 22 wt%, except TM soil). These findings are consistent with XRD results providing evidence for presence of Fe hydroxides whereas primary minerals containing arsenic are generally scarce and limited to arsenopyrite or pyrite for N4b, TC, AP and LV soils. Arsenic is typically less extractable by ammonium acetate as exchangeable fraction and sodium acetate as carbonate fraction. Exchangeable carbonate fractions may represent ecologically important forms of arsenic that can be mobilized more easily than arsenic associated with iron hydroxides. Carbonate fraction only played a minor role in arsenic retention. On the other hand, sulfide fraction distributed minor role in release arsenic from Tan My soil. It is implied that pyrite can be a source for arsenic in oxidized groundwaters.

Chapter Five

ARSENIC ADSORPTION CAPACITY OF CORE OF BOREHOLE LK204 IN THE MEKONG DELTA

5.1. Introduction

Adsorption characteristics has been the focus in many studies regarding the mobility of arsenic in soils (Ladeira and Ciminelli, 2004; Jiang et al., 2005). The oxidation state and speciation of arsenic has caused variability in the degree of adsorption to particular minerals. Arsenite has been shown repeatedly to be typically less likely to adsorb to particles consisting of minerals such as iron oxyhydroxides and clays when compared to arsenate under different conditions (Frost and Griffin, 1977). Many works have been devoted to study of arsenic adsorption on iron oxides (Pierce and Moore, 1982; Fuller et al., 1993; Fendorf et al., 1997; Waltham and Eick, 2002), aluminum oxides (Anderson et al., 1975), manganese oxides and clay minerals (Frost and Griffin, 1977). Frost and Griffin (1977) found a pH dependence on adsorption characteristics of arsenite and arsenate on montmorillonite and kaolinite. Among the various adsorbents, Fe oxides were identified to have high adsorption capacity for arsenic (Hsia et al., 1992; Fuller et al., 1993). Typically, more arsenate adsorbs to these minerals when compared to arsenite.

Results of adsorption experiments are analyzed and frequently expressed by adsorption isotherm equations either by the Freundlich or the Langmuir equations. The Langmuir equation often provides the better fit to metal or metalloids adsorption data. This equation also enables to estimate the maximum adsorption capacity (Davis and Kent, 1990; Appelo and Postma, 2005).

In this study, core samples at 30 m depth of borehole LK204 were used to investigate arsenic adsorption capacity. This sample is fine sand which contains pale yellow iron staining. The mineralogical compositions of the core sample indicated that they are rich in Fe minerals by the presence of goethite and hematite. Arsenic concentration in this core was analyzed in Chapter Three, and is 37 mg/kg. Moreover, high arsenic and iron concentrations in groundwaters were also found at shallow depth (more or less 50 m depth). Therefore, adsorption experiments for core sample at this depth (30 m depth) is preferable to understand whether this core sample has high adsorption capacity on arsenic. Regarding to adsorption experiments, Langmuir equation was employed to calculate maximum adsorption capacity. On the other hand, the influences of various chemical parameters on arsenic adsorption were examined namely for pH, initial arsenic concentration and contact time.

5.2. Characterization of core samples

Figure 5.1 shows location map of the borehole LK204. Core samples were collected from the borehole LK 204 near Chau Doc. The composition and distribution of mineral species of the core samples were identified using

wavelength-dispersive XRF (Rigaku RIX 3100) and XRD (Rigaku RINT 2100) and presented in Table 3.2.

Location of borehole LK204 is occupied by back swamp and meander channel deposits of Hau River. When back swamp area is artificially drained, it yields fine-grained soil, rich in organic matter. The sediments deposited in the late Holocene and Recent deltaic.

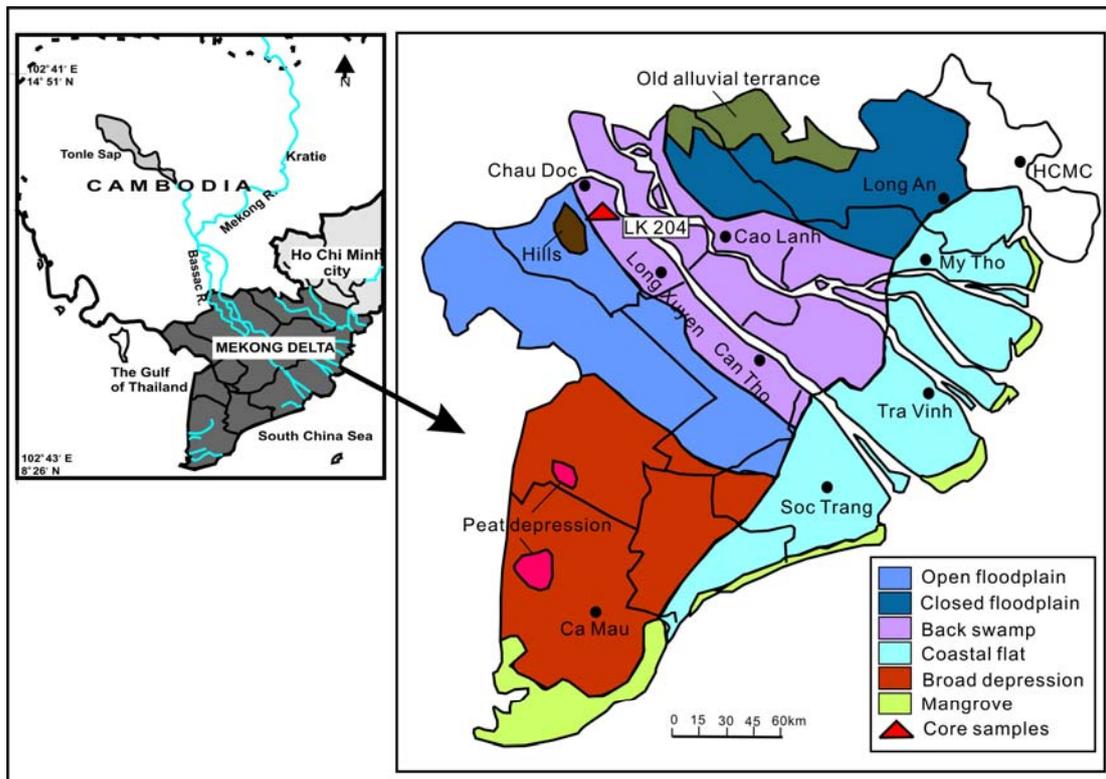


Fig. 5.1 Location map of borehole LK204 in the Mekong Delta.

Figure 5.2 represents lithology of the borehole LK204. The constituents from surface to downward are silty clay, clay with occasional intercalatery with silty sand, fine sand and minor medium sand. Siltone and sandstone are present at the bottom. Moreover, clay and fine sand with iron staining occupy from the surface to 50 m depth (Fig. 5.2). The sandy litho-facies is dominantly channel fill

and the finer muddy litho-facies is over-bank levee deposit formed during floods. Clay in the surface possibly represent a reducing, marshy environment. On the other hand, the aquifer sediments are capped by a layer of clay or silt (of variable thickness) which effectively restricts entry of air to the aquifers.

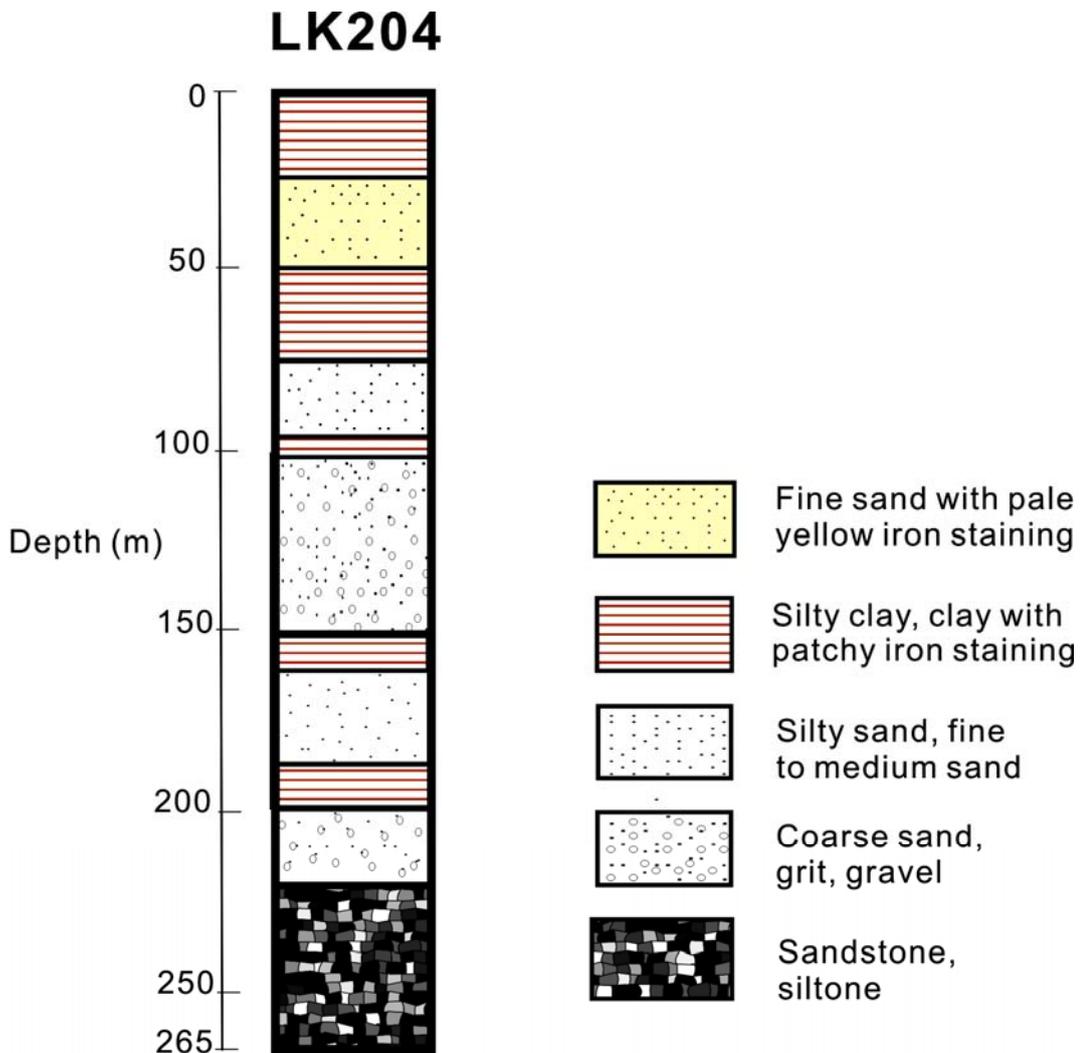


Fig. 5.2 *Lithology of borehole LK204.*

The principal minerals present in the core sample are quartz, iron hydroxides or oxides and clay minerals (Table 3.2). Their relative abundances present in the order of quartz, clay minerals, iron hydroxides or oxides. XRD pattern for the iron

oxyhydroxides/oxides such as goethite and hematite is shown in Fig. 5.3. XRD pattern which consists of a plot of intensities (count per second) versus a detector angle 2θ (degree). Peaks correspond to the d-spacings of the strongest lines of minerals. XRD pattern shows the presence of goethite, hematite and quartz as the predominant crystalline phases (Fig. 5.3). Total As in core sample was evaluated to be 37 mg/kg (Table 3.2). Small amount of sulfur such as 0.111% was determined by XRF but there is no sulfide mineral detected by XRD.

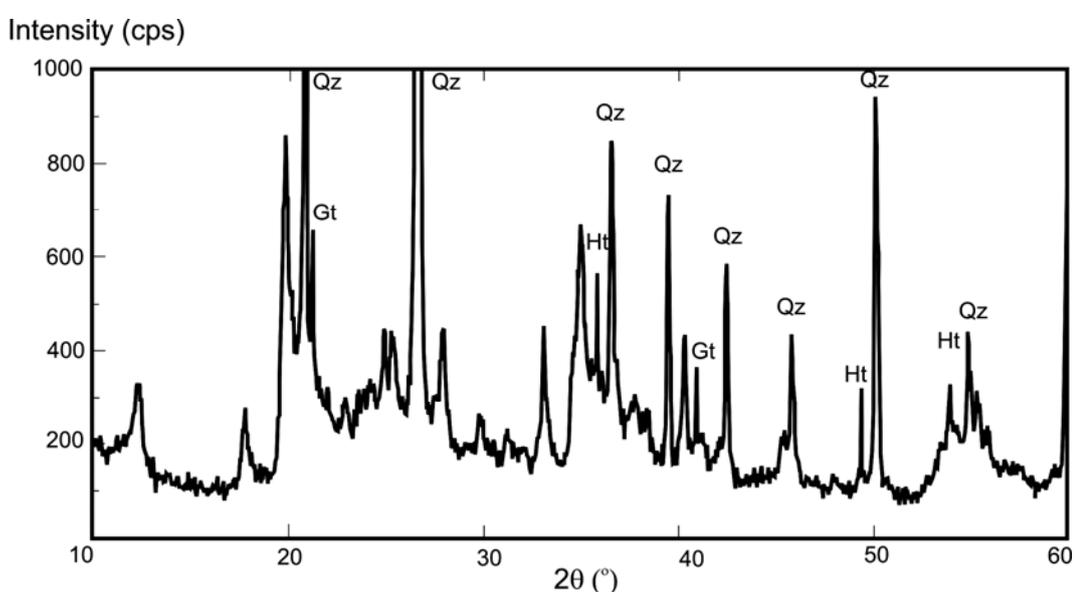


Fig. 5.3 XRD pattern of core sample at 30 m depth. Qz (quartz), Gt (goethite) and Ht (hematite).

5.3. Experiments and analysis methods

5.3.1. Reagents and stock solutions

Two kinds of 1000 mg/L arsenic stock solutions for As(V) and As(III) were prepared by dissolving disodium hydrogenarsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, purity 99%) and sodium metaarsenite (NaAsO_2 , purity >90%)

with distilled water, respectively. Then arsenic solutions with specified concentrations were prepared by diluting the stock solutions with distilled water. Solutions of 0.1 M HCl and 0.1 M NaOH solutions were used for pH adjustment.

5.3.2. Preparation for core sample

The core sample was air dried, disaggregated by manual crushing. Then the sample was sieved retaining the < 2 mm fraction and stored in airtight polyethylene bag until use for adsorption experiments.

5.3.3 Batch experiments

a. Effect of pH

Experiments were performed with pH ranges from 3 to 9 with initial arsenic concentration of 0.4 mmol/L.

The experiments were conducted using 100 mL conical flasks. The reaction mixture consisted of 40 mL of 0.4 mmol/L As(III) or As(V) solution and 2 g of the core sample. pH of reaction mixtures was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution. A magnetic stirrer was used to agitate the solutions before purging with N₂ for 30 min. The mixtures were shaken for 24h with a laboratory shaker at room temperature (25°C). The supernatant was filtered through 0.45 µm membrane filter for arsenic analyses. Then the pH of the supernatant was measured. Five (5) mL of filtrates was stored in a polyethylene bottles, acidified with 12M HCl and kept in refrigerator before analyses for arsenic.

b. Effect of initial arsenic concentrations

experiments on adsorption isotherms were carried out with varying initial concentrations of arsenic solution from 0.1 to 0.8 mmol/L with fixed at pH 7.5 and pH 5 for As(III) and As(V), respectively, by adding 0.1 M HCl or 0.1 M NaOH solutions.

The experiments were conducted using 100 ml conical flasks; a magnetic stirrer was used to agitate the solutions before purging with N₂ for 30 min. The reaction mixture consisted of 40 mL As(III) or As(V) solution of known concentration and 2 g of the core sample. The mixtures were shaken for 24h with a laboratory shaker at room temperature (25°C). The supernatant was filtered through 0.45 µm membrane filter for arsenic analyses. Then the pH of the supernatant was measured. Five (5) mL of filtrates was stored in a polyethylene bottles, acidified by 12M HCl and kept in refrigerator before analyses for arsenic.

c. Effect of reaction time

The effect of reaction time was studied with 0.4 mmol/L As(III) or As(V) solution.

This experiment was conducted using 300 mL conical flasks containing mixture of 10 g core sample and 200 mL of 0.4 mmol/L of arsenic solutions. pH was kept at 7.5 by adding 0.1 M HCl or 0.1 M NaOH solutions. The mixtures were shaken for 24h with a laboratory shaker at room temperature (25°C). Five (5) mL of supernatant was taken after 1, 3, 6, 9, 12 and 24 hours. These supernatant were filtered through 0.45 µm membrane filter, acidified by 12M HCl and kept in

refrigerator before analyses for arsenic. After sampling, the mixture solution was purged by N₂ for 15min.

5.3.4 Arsenic analyses

Arsenic concentration of the filtrates was determined by hydride generation atomic adsorption spectrometry (HG-AAS, SOLAAR S4 with detection limit 1 µg/L).

5.4. Adsorption of arsenite (As(III)) and arsenate (As(V)) on core sample

5.4.1 Effect of pH

The results of pH effect on arsenic adsorption are shown in Fig. 5.4. Under acidic conditions ($3 < \text{pH} < 5$), 0.65 - 0.91 mg/g (62 - 87%) of As(III) is adsorbed whereas more than 0.84 - 1 mg/g (81 - 96%) for neutral pH values ($6 < \text{pH} < 8$) (Fig. 5.4a). The adsorption maximum at pH 7 can be explained by the difference between the energy released upon adsorption, and the energy required to dissociate the acid is at a maximum (Pierce and Moore, 1982). It is recognized that arsenous acid (H_3AsO_3) has the first pK at 9.2 and the anion, H_2AsO_3^- , can coordinate the surface metal atom of the adsorbent. Then the adsorption of the anion provides sufficiently large energy of adsorption to dissociate the acid.

In contrast, amount of adsorbed As(V) is more than 2.4 mg/g (96%) and remains constant in the pH range from 3 to 6, then decreases to 2.1 mg/g (81%) at

higher pH values (Fig. 5.4b). It is apparent that maximum adsorption of As(V) on soil is observed from pH 3 to 4. In this pH range, surface of the sample has a positive charge that would attract H_2AsO_4^- .

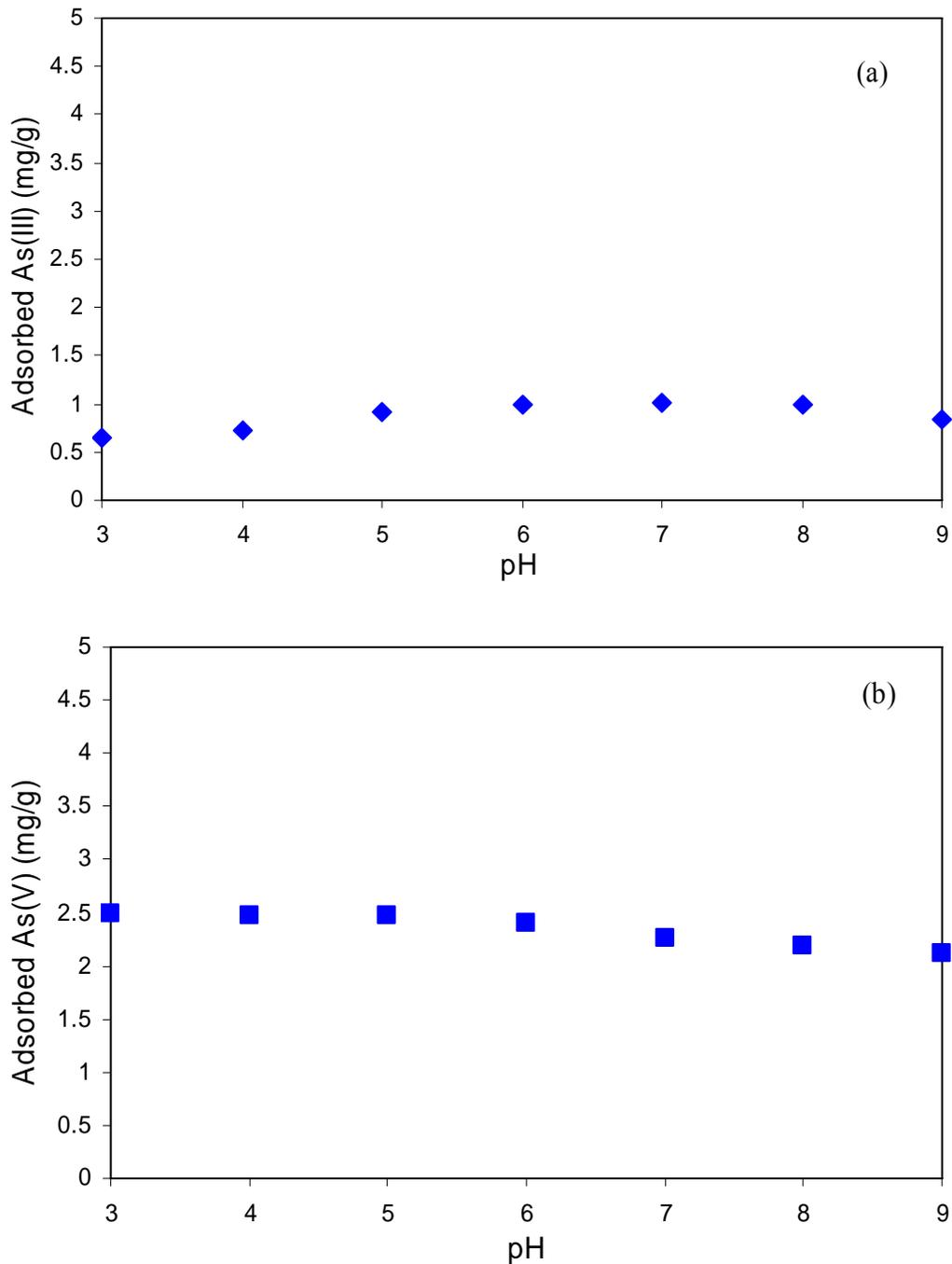


Fig. 5.4 Effect of pH on adsorption of (a) As(III) and (b) As(V) on core sample.

The arsenic acid (H_3AsO_4) has three pK values of 3.6, 7.3, and 12.5. H_2AsO_4^- and HAsO_4^{2-} are the predominant anions in the pH range studied. Therefore, it would have strong effects on the surface charge than the singly charged anion of arsenous acid. Decrease in adsorption amount of As(V) at higher pH is elucidated by the fact that the surface has a negative charge at higher pH range and would tend to repulse the HAsO_4^{2-} ion into solution. In the experiment pH of mixtures shifted slightly towards higher pH. This may be attributed to the adsorption reactions of As(V) releases OH groups from sorbent (Lakshmiathirai, et al., 2006).

5.4.2 Effect of initial arsenic concentrations

Solutions of different arsenic concentrations (0.1 - 0.8 mmol/L) were used to study the effects of initial arsenic concentrations. Figures 5.5 (a) and (b) show the relationship between adsorbed amount and equilibrium As(III) and As(V) concentrations, respectively. Vertical axis represents amount of adsorbed arsenic on the core sample while horizontal axis is equilibrium concentrations of arsenic that correspond to initial arsenic concentration from 0.1 to 0.8 mmol/L. On the other hand, solid lines indicate trend of data follows power equation calculated by EXCEL. The amount of adsorbed arsenite and adsorbed arsenate increases with an increase of initial arsenic concentrations or equilibrium concentrations (Fig. 5.5a, Fig. 5.5b). However, the amount of adsorbed arsenate finally reaches saturation point in spite of different initial concentrations (Fig. 5.5b).

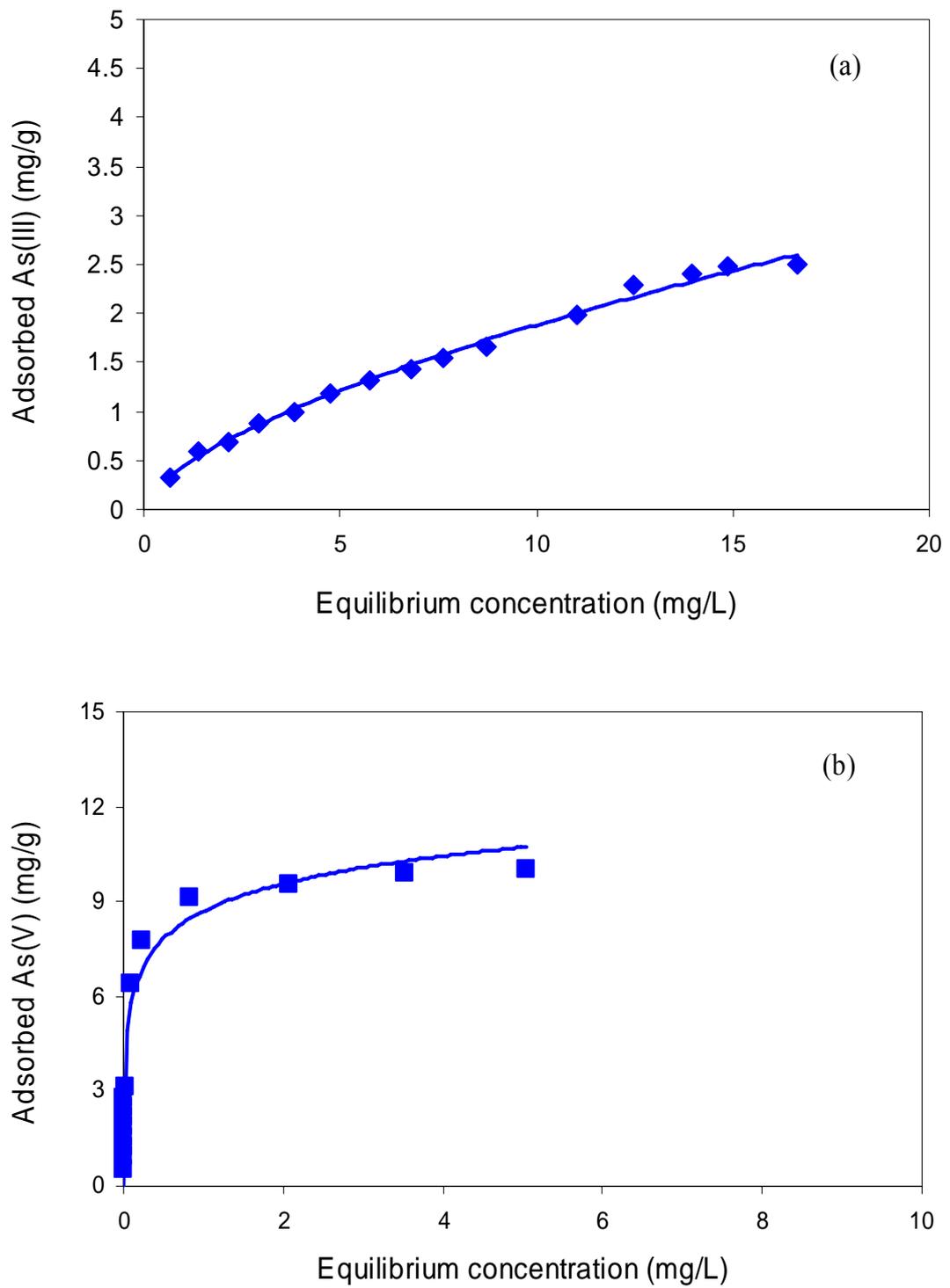


Fig. 5.5 Arsenite (a) and arsenate (b) adsorption isotherm as a function of initial arsenic concentrations.

This is due to the fact that by increasing concentration of arsenate in solution, the availability of arsenate ion at the interfaces of the core sample increases, thus enhancing the amount of adsorption. Nevertheless, adsorption sites on material surface eventually occupied, and then the adsorbed amount reaches to the upper limit resulting in a saturated adsorption. Figure 5.5 also reveals the affinity of the sorbents to the As(V) by the steep slope in the range of low arsenic concentration (Fig. 5.5b). Conversely, As(III) shows a relatively smooth slope, which may elucidate a relatively less affinity (Fig. 5.5a). This implies that core sample has low capacity for arsenite adsorption.

The adsorption data was analyzed with the Langmuir isotherm to estimate the maximum arsenic uptake at different initial arsenic concentrations. The maximum adsorption capacity (b) and adsorption coefficient (K) can be calculated using the Langmuir's equation as:

$$\frac{1}{s} = \frac{1}{Kb} \frac{1}{c} + \frac{1}{b} \quad (5.1)$$

where s is the amount of arsenic adsorbed per unit weight of sample (mg/g), c is the equilibrium concentration (mg/L), b is the adsorption capacity (mg/g), and K is the Langmuir coefficient (L/g). A plot of $1/s$ against $1/c$ provides a straight line with a slope of $1/Kb$ and an intercept of $1/b$. Figures 5.6a and 5.6b show that the Langmuir model can well represent for As(III) and As(V) data on the basis of correlation coefficients ($R^2 \approx 1$). The values of constants are determined by the least squares method, and are summarized in Table 5.1 with the coefficients of correlation.

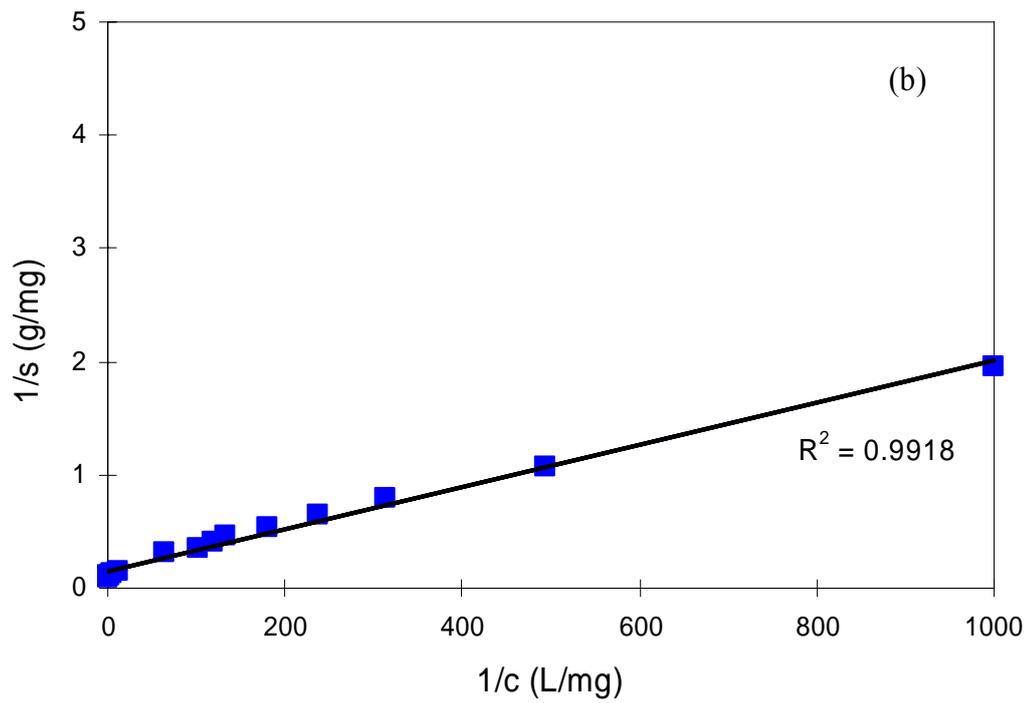
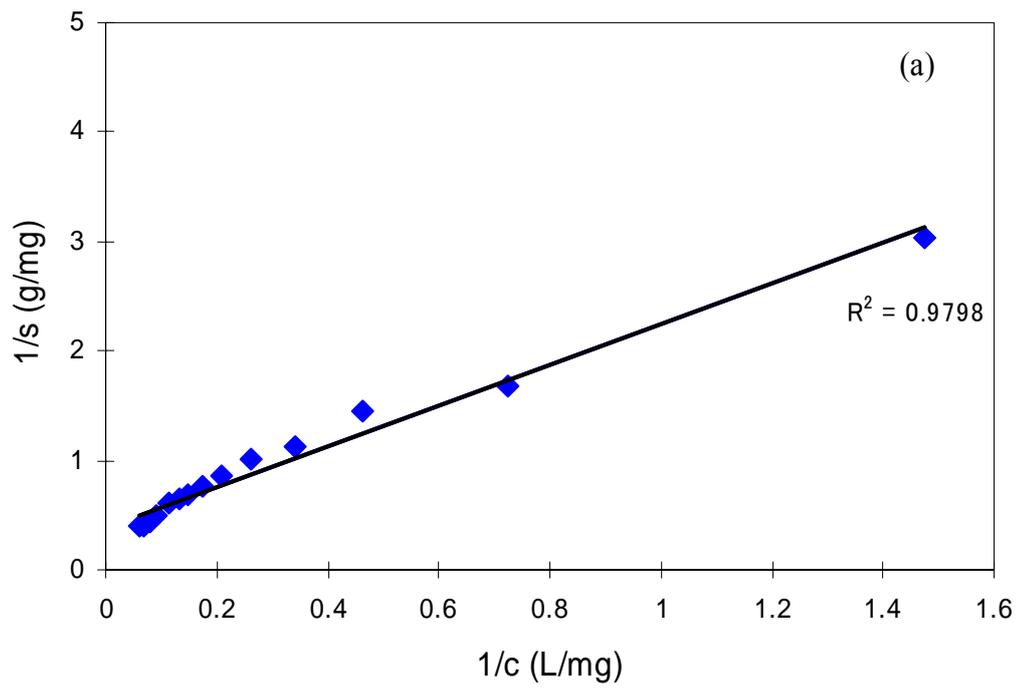


Fig. 5.6 Langmuir adsorption isotherm plots. (a) As(III); (b) As(V).

The maximum adsorption capacities, b , were calculated as 2.57 mg/g and 6.58 mg/g for As(III) for As(V) (Table 5.1, Fig. 5.6). The results indicate that the adsorption capacity of As(V) is three times as high as that of As(III). This means As(V) has higher adsorption capacity on core sample than that of As(III).

Table 5.1 Langmuir coefficients for adsorption isotherm.

	Langmuir coefficients		R^2
	b (mg/g)	K (l/g)	
As(III)	2.567	0.21	0.980
As(V)	6.578	84.4	0.992

5.4.3 Effect of reaction time

Figure 5.7 demonstrates the relationship between adsorption of arsenic and reaction time. Amount of adsorbed arsenic quickly increases within 1h and then it remains stable from 9h to 24h. It is clear that for As(III) (Fig. 5.7a), adsorbed amount increases from 0.77 to 0.98 mg/g within 9h. Then time required for maximum adsorption of As(III) can be defined to be 9h. However, amount of adsorbed As(V) (Fig. 5.7b) is considerably higher than that of As(III). For examples, after 1h of reaction, As(III) and As(V) adsorption amounts are more than 0.77 mg/g and 2.1 mg/g, respectively. A maximum adsorption amount can be defined for values after 24 hours of reaction as they have stabilized, and they are of 1.0 mg/g for As(III) and 2.4 mg/g for As(V).

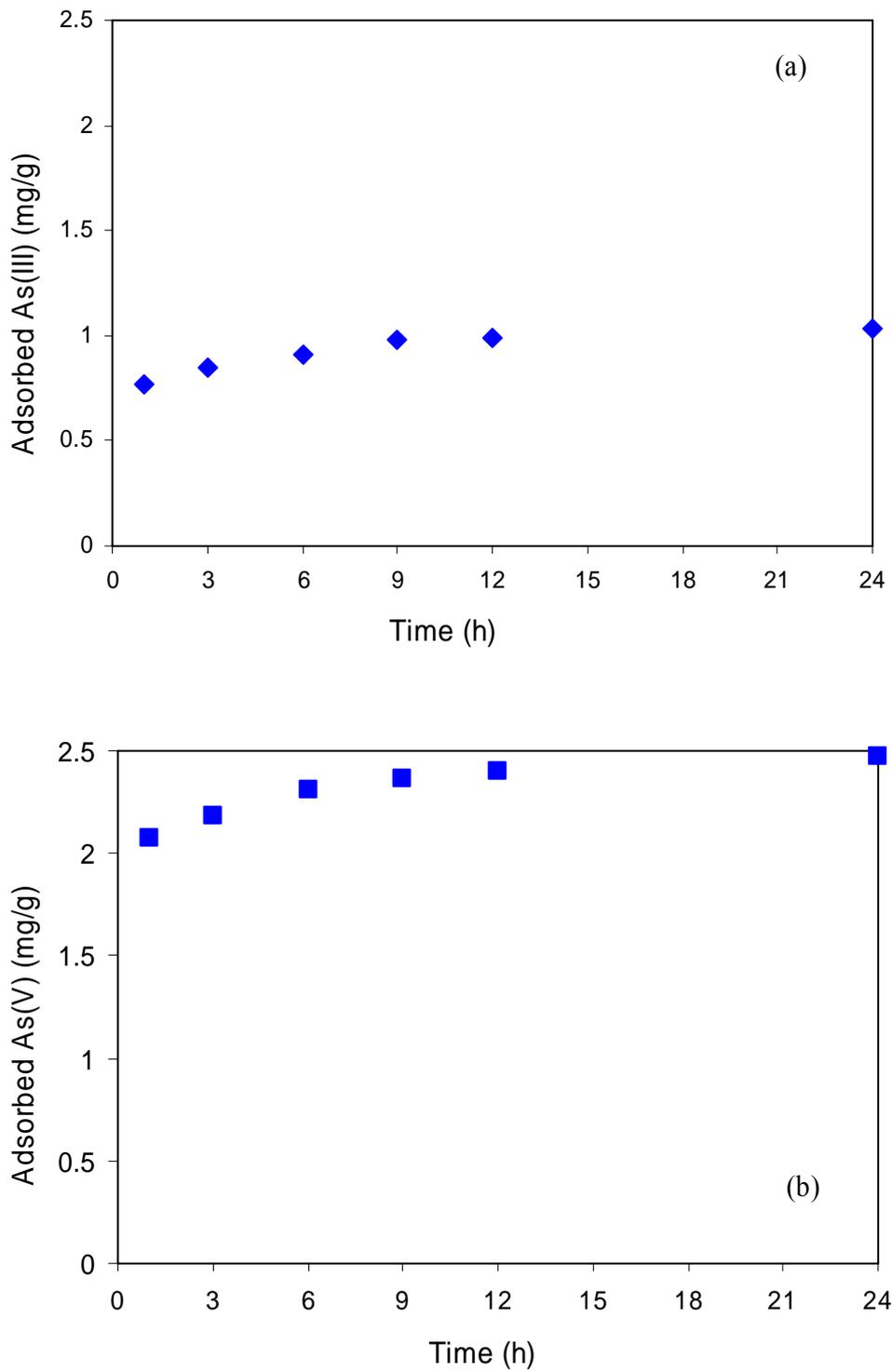


Fig. 5.7: Effect of reaction time on arsenic adsorption. (a) As(III); (b) As(V).

Davis and Kent (1990) stated that sorption of inorganic ions on mineral surfaces is a two-step process consisting of a short period of rapid initial uptake of adsorbate followed by slower processes. The fast step that takes minutes to hours in order to reach equilibrium indicates a diffusion controlled adsorption reaction and formation of a chemical bond between the arsenic species and the adsorbent. The slow step presents surface precipitation, microspore diffusion and formation of aggregates via coagulation. This process can take weeks to months to attain equilibrium. The arsenic adsorption data in the current study were examined to elucidate adsorption kinetics. They are evaluated using the expression (Lalvani et al., 1998; Kundu and Gupta, 2005):

$$R_{ad} = at^B \quad (5.2)$$

Equation (5.2) can be expressed as a linear function by taking both sides for logarithms as follows

$$\ln R_{ad} = B \ln t + \ln a \quad (5.3)$$

where R_{ad} and t are the amount of As adsorbed (mg/g) and the reaction time (h), respectively. Plot of $\ln R_{ad}$ versus $\ln t$ is shown in Fig. 5.7 for As(III) and As(V).

Table 5.2 Constants a and B for adsorption kinetics.

Arsenic species	Constants			Correlation coefficients (R^2)	
	$R_{ad} = at^B$		$R_{ad} = at^{0.5}$	$R_{ad} = at^B$	$R_{ad} = at^{0.5}$
	a	B	a		
As(III)	74.11	0.0975	11.4 – 43.8	0.9817	0.9483
As(V)	82.97	0.0579	25.5 – 123.1	0.9914	0.8417

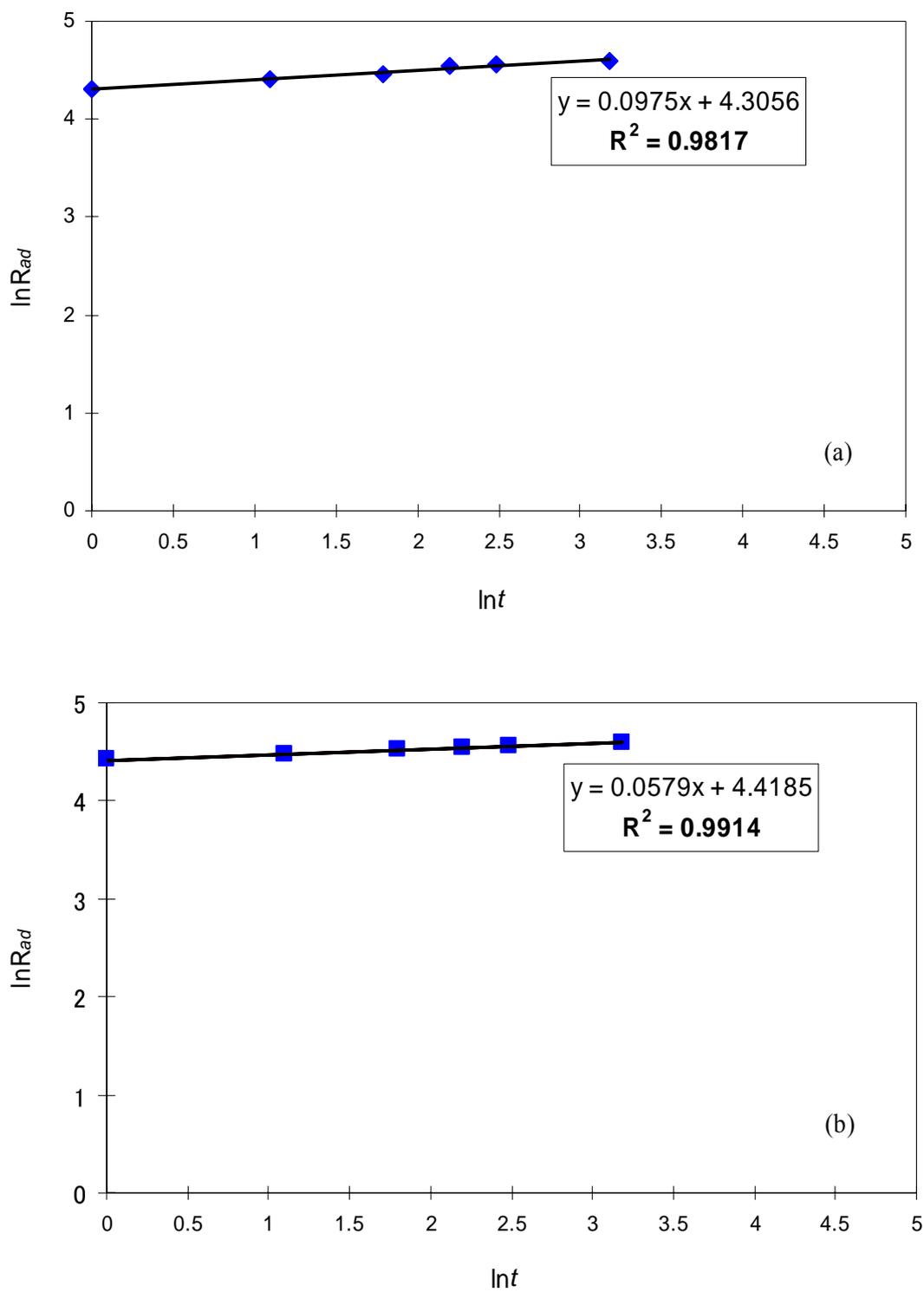


Fig. 5.8: Plot of $\ln R_{ad}$ and $\ln t$ for (a) As(III); (b) As(V).

The values of constants a and B are given in Table 5.2. The data of As(V) with correlation coefficient $R^2 = 0.9914$ show better fit with Eq. (5.2) than that of As(III) with $R^2 = 0.9817$. A near straight-line fit was observed for arsenic indicating that adsorption kinetics may be diffusion-controlling reactions such as film diffusion or pore-diffusion. Low values of constant B (Table 5.2) implies that film diffusion as arsenic migrates from solution to solid surface appears to be rate-controlling step. According to Raven et al. (1998), pore diffusion can be expressed with a function of the square root of time ($t^{0.5}$) in Eq. (5.2). Adsorption data were plotted using this function to confirm whether pore diffusion is rate-controlling process for arsenic adsorption on core samples. Results of correlation coefficients of the function are also shown in Table 5.2. The results indicate that As(III) show relatively good fit to the function of the square root of time ($t^{0.5}$) with higher correlation coefficient compared to As(V). However, it can conclude that adsorption data can be better fit to the Eq (5.2). This means film diffusion is a rate controlling mechanism for arsenic adsorption. Moreover, Poots et al. (1978) represented that the presence of a deviation from the origin of plotting between $\ln R_{ad}$ and $\ln t$ as shown in Fig. 5.8 confirm the phenomena to be film diffusion.

5.5. Summary

The mineralogical compositions of the core sample indicated that core sample is rich in arsenic contents and Fe minerals by the presence of goethite and hematite. The adsorption process of As(III) was favored by increasing to pH 7 and attained maximum adsorption while adsorption of As(V) decreases at higher pH values (pH > 6). The lower adsorption amount of As(V) in high pH ranges is

attributable to an increased repulsion between more negatively charged As(V) species and negatively charged surface sites. Adsorption kinetics experiments indicate that film diffusion along with chemical adsorption was the essential rate controlling mechanism and played a major role in the arsenic uptake.

Maximum adsorption capacity of As(III) at pH 7.5 and As (V) at pH 5 are 2.57 mg/g and 6.58 mg/g, respectively, estimated by Langmuir equation. This result implied that As(V) is more adsorbed on core sample than As(III). In other words, low adsorption capacity of As(III) can induce the transport of As(III) in groundwater. It is postulated that source of arsenic is provided by sediments from upper region of the Mekong Delta. There is transport of sediment as well as adsorption and release of arsenic. While released As(V) can be re-adsorbed by core sample or iron hydroxides, As(III) can follow groundwater flow because of its less adsorption capacity.

Chapter Six

EFFECTS OF REDOX POTENTIAL ON ARSENIC TRANSPORT IN SOIL COLUMN EXPERIMENTS

6.1. Introduction

The transport of arsenic from soil to groundwater is dependent on soil–water interaction in the subsoil environment. Oxidation/reduction state in soil layers is a controlling chemical factor for arsenic transport. According to Signes-Pastor et al. (2007), redox conditions of soil layers vary widely from approximately +500 mV (surface soils) to approximately –300 mV (strongly reducing conditions). Iron oxides, clays minerals, and organic matters in soil will adsorb or desorb arsenic when the ionic composition and/or Eh–pH changes (Gambrell et al., 1980). Iron oxides existing as nodules and concretions are excellent scavengers for arsenic and are affected by sediment Eh and pH changes (Feijtel et al., 1988). Burial, flooding, transport of organic matter or other reducing agents into soil can initiate reduction conditions and subsequently lead to dissolution of ferric (hydro)oxides (Stumm et al., 1992). The reductive dissolution of iron (hydro)oxides can release ferrous iron into the pore water and lead to the precipitation of secondary minerals.

Arsenic is subject to chemically and/or microbiologically mediated oxidation–reduction reactions in soils and natural waters (Masscheleyn et al., 1991). Arsenic mobility in the environment is dependent on its interactions with heavy metal oxides such as iron (hydro)oxides. The binding of arsenic to different solid phase iron (hydro)oxides via the formation of thermodynamically stable inner-sphere complexes is well documented in literatures (Fendorf et al., 1997; Raven et al., 1998). Among the arsenic species, As(V) binds more strongly with the oxides of Fe and Mn, as compared to the As(III) species. However, the binding mechanisms are dependent on the pH and redox potential of the environment. With decreasing pH, arsenic mobility tends to increase due to mineral dissolution, and increased surface potential. On the other hand, an increase in pH can result in desorption of arsenic due to the lower stability of metal oxide arsenic complexes (Masscheleyn et al., 1991; Raven et al., 1998). In a reducing environment, reductive dissolution of arsenic containing iron oxides and hydroxides can also result in increased concentrations of dissolved arsenic (Nickson et al., 2000; Meng et al., 2001).

A wide variety of column experiments, which address the role of pH and complexation, are reported in the literature but very few have focused on the effect of changes in the redox potential on contaminant release (Chatain and Sanchez, 2005). However, many factors can significantly affect the oxidation–reduction status of soils such as periodic inundation, fluctuating groundwater levels, excess organic matter and deterioration of soil physical properties (Barcelona et al., 1991). The effect of reducing conditions, however, can be substantial. Contaminant release can be affected by either direct reduction or

indirect effects such as precipitation of metal sulfides (e.g., CuS, FeS₂, MnS, ZnS) or dissolution of hydrous aluminum, iron and manganese oxides, releasing adsorbed or co-precipitated metals (Stumm et al., 1992; Chuan, et al., 1996; Davranche and Bollinger, 2000). Therefore, evaluation on mobility of contaminants such as arsenic using experimentally controlled reducing conditions will contribute to a better understanding of geochemical and biological oxidation/reduction processes that affect contaminant transport in the subsurface environment.

In the laboratory, reducing conditions may be realized by biological methods or the use of chemical reducing agents. Biological methods may require several weeks to realize reducing condition and are largely dependent upon the characteristics of the microorganisms and nutrients present in the soil. In contrast, the use of chemical agents can easily control reducing condition with a specified degree of the condition. Davranche and Bollinger (2000) used chemical reducing agent such as sodium ascorbate to characterize the potential mobility of inorganic contaminants in soils under various pH and redox environments. The objectives of experiment in this study were to evaluate (i) the ability of chemical reducing agents to produce different redox environments and (ii) the impact of oxidizing/reducing conditions on the mobility of arsenic from soil in the presence of Fe oxyhydroxide.

6.2. Experimental

6.2.1 Production of synthetic Fe hydroxide coprecipitated with arsenic

All used reagents were of reagent grade. Water used was double-deionized water ($< 0.05 \mu\text{S}/\text{cm}$). All glassware and plasticware were cleaned by soaked in 0.12 M HCl and at least twice rinses with deionized water.

Stock solutions of 1 M FeCl_3 and 1 M $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ were prepared in 0.01 M HCl within 24h of use. Fe hydroxide coprecipitated with arsenic was prepared in the laboratory. A solution containing 475 mL of 1 M FeCl_3 , 15 mL of 1 M $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and 10 mL of 3 M NaCl was placed in a 1L beaker and then adjusted pH to 6.5 by adding 5 M NaOH solution while stirring the mixture with a magnetic stirrer (Fig. 6.1). Suspensions showed that more than 95% arsenic coprecipitated with Fe hydroxide within 2h. Therefore, suspension was allowed to stabilize for 2h, during which time pH was adjusted to maintain a value of 6.5. Then the suspension was filtered and filtered solid was washed with distilled and deionized water to remove dissolved salts. Fe hydroxide coprecipitated with arsenic was air-dried and stored in dark before use (Fig. 6.1). Digestion the Fe hydroxide coprecipitated with arsenic with HCl and ICP-AES analysis indicated the As, Fe content of the coprecipitate was 28 mg/g and 580 mg/g coprecipitate, respectively (As : Fe = 1 : 20).

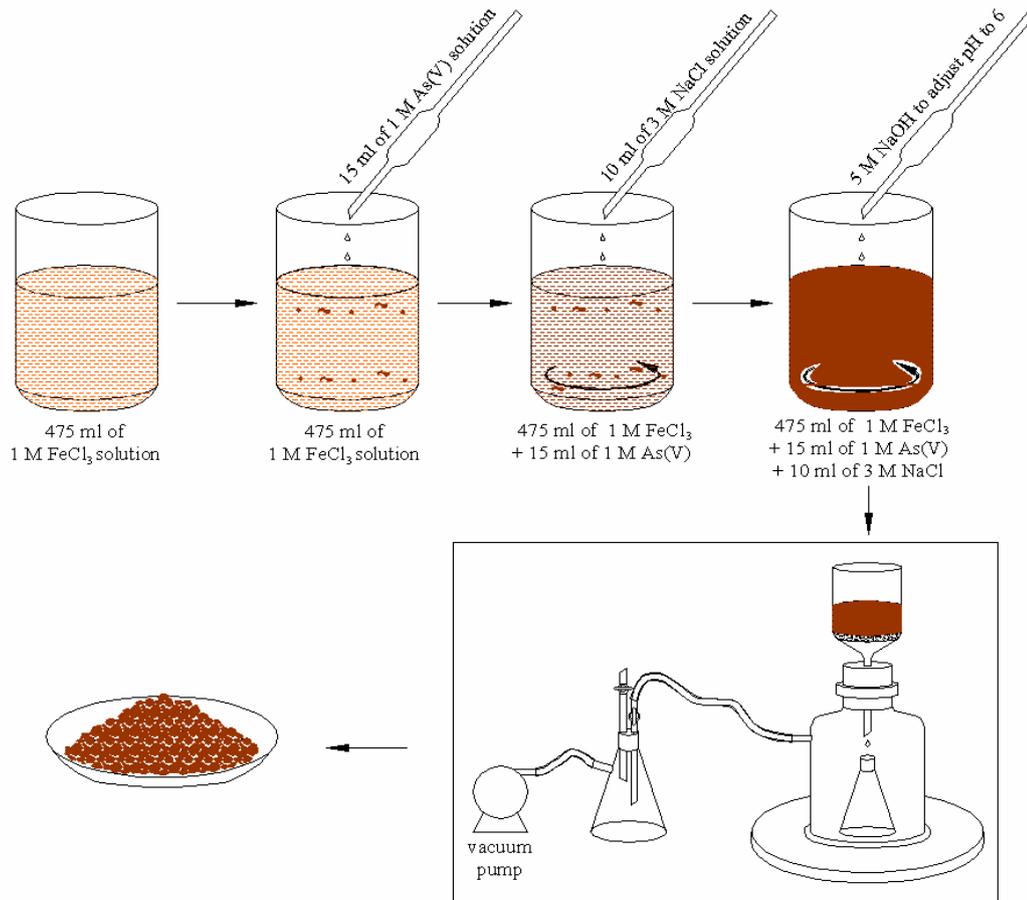


Fig. 6.1 Production of Fe hydroxide coprecipitated with arsenic.

6.2.2 Set up soil column experiment

The apparatus consists of cylindrical cell, storage tank of solution, pump, over flow tank and manometers. Speciation of the soil column is shown in Table 6.1. The soil column was made by packing of Sasaguri soil (Table 4.1 and Table 4.2) and coprecipitate in the cell. The soil column experiments were performed two times by changing concentrations of ascorbate solution and constituent of soil column; Run 1 and Run 2:

- Run 1: 1 M of ascorbate solution was used. The column was packed with mixture of Sasaguri soil and coprecipitate.

- Run 2: 0.1 M of ascorbate solution was used. The column consists of two layers: Sasaguri soil and coprecipitate. Coprecipitate was overlain of the Sasaguri soil as source of arsenic. A schematic diagram of the experimental set up for the Run 1 and 2 are shown in Fig. 6.2a and Fig. 6.2b.

Table 6.1 *Speciation of the soil column.*

Height	35 cm
Diameter	8 cm
Surface area	50.26 cm ²
Volume	1709 cm ³
Porosity	43 %
Flow rate	1.0 mL/min
Hydraulic Conductivity	0.12 cm/min

The cell is 50 cm long and 8 cm in diameter. Filter paper was placed at the bottom of the column to avoid soil particle flowing out. The cell was set in a vertical position, and tap water was first supplied from the bottom to fill pore space of the soil column. After the column was filled with the tap water, then the solution was fed from the top of the column under the constant head difference between the inlet and outlet of the column. The flow rate was kept constant at 1.0 mL/min during the experiment. The flow rate was determined such that residence time in the column allows observation for transformation of redox potential in the effluents. The experiment was conducted at room temperature.

a. Preparation for soil column of Run 1

Sasaguri soil, which mixed with Fe hydroxides coprecipitated with

arsenic, was packed in the cell of 35 cm long with 5 cm layers of ceramic beads of 2 mm diameter both top and bottom of the soil column (Fig. 6.2a).

b. Preparation for soil column of Run 2

Soil column for Run 2 was separated into three layers: (1) 5 cm layers of ceramic beads of 2 mm diameter both top and bottom of the soil column, (2) 3 cm layer of Fe hydroxides coprecipitated with arsenic as second layer, and (3) 32 cm layer of Sasaguri soil (Fig. 6.2b).

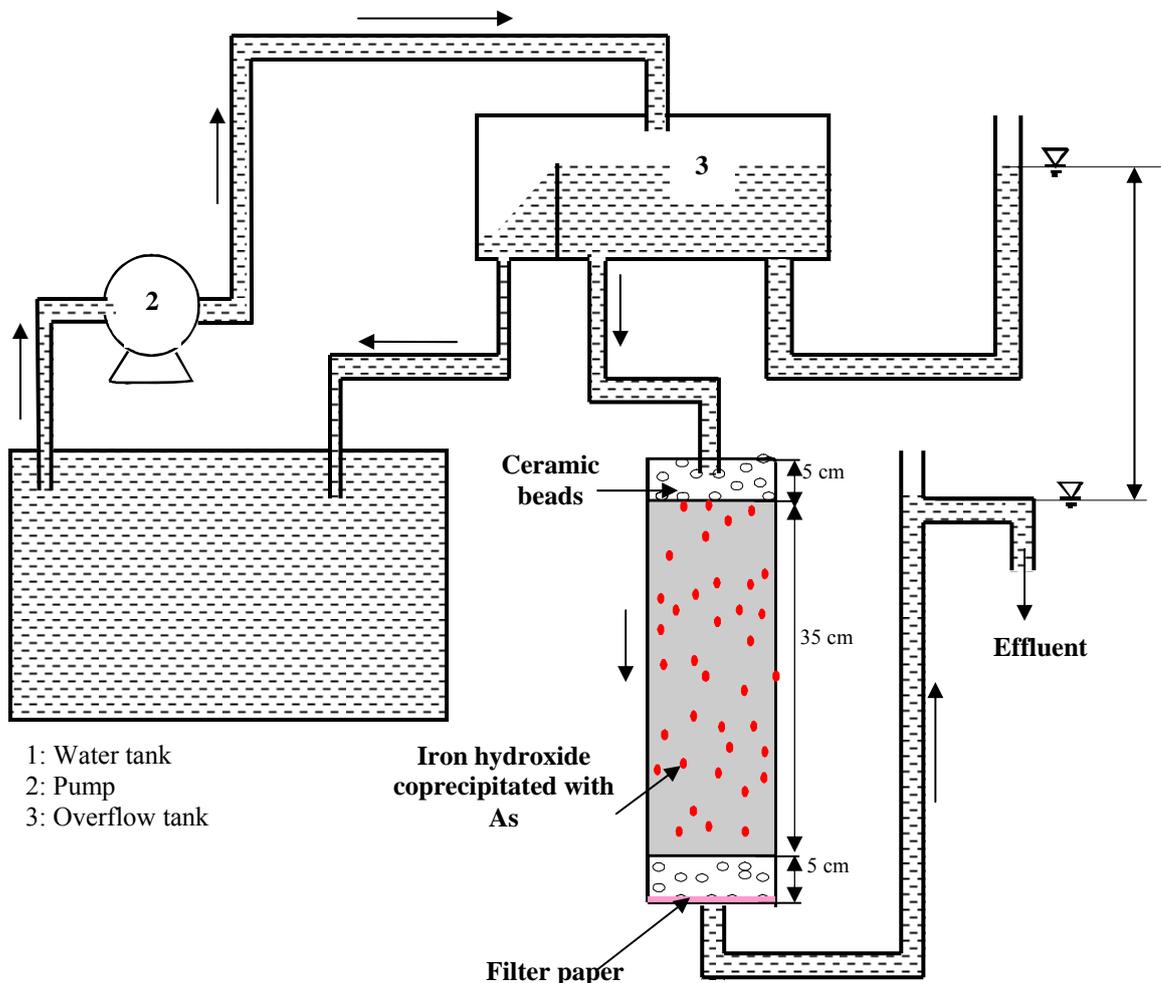


Fig. 6.2 (a) Schematic diagram of the soil column experimental apparatus for Run 1

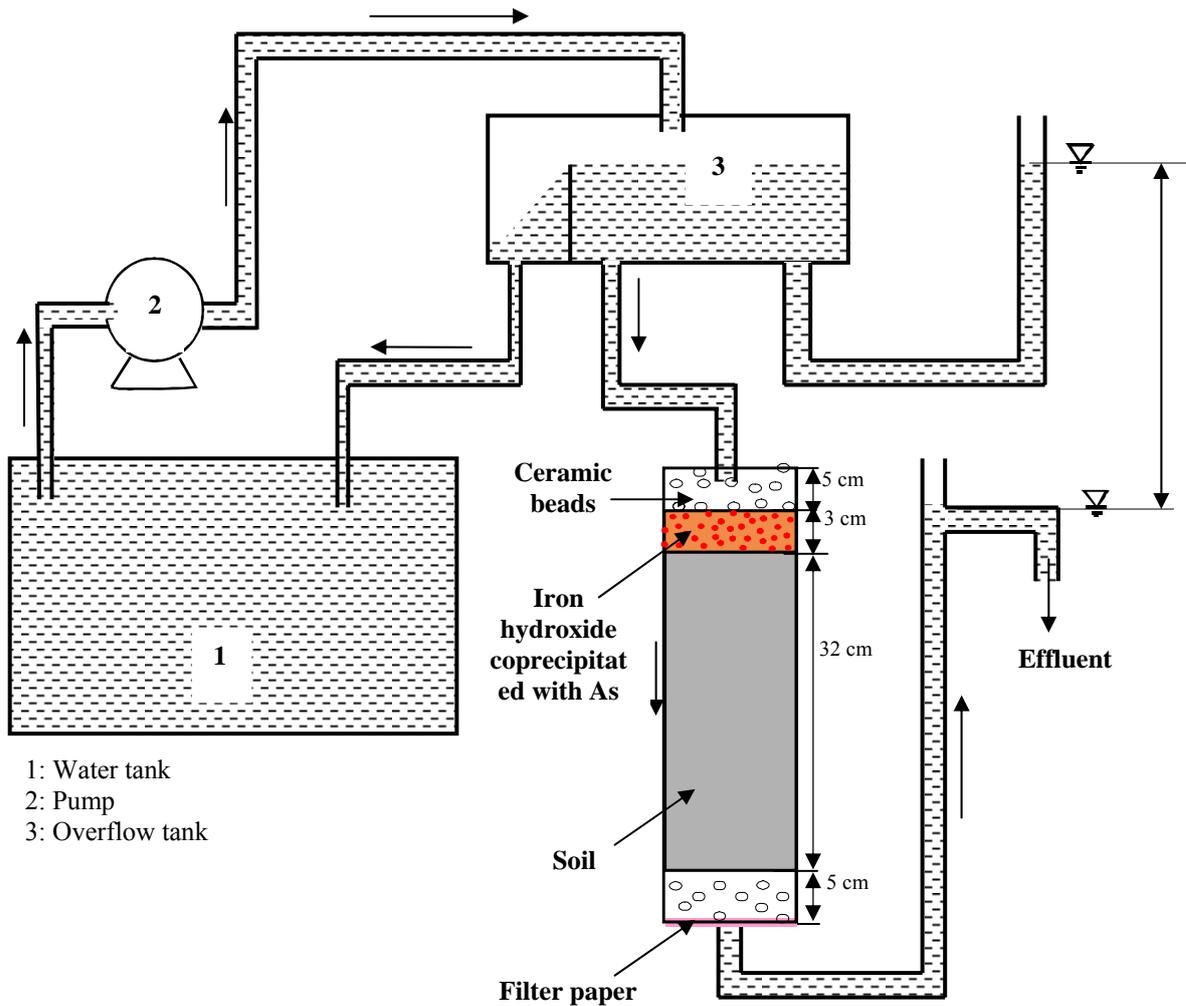


Fig. 6.2 (b) Schematic diagram of the soil column experimental apparatus for Run 2

The main characteristics of the Sasaguri soil are summarized in Table 6.2. The experiment was conducted under controlled redox and pH conditions by alternately supplying sodium ascorbate solution and tap water to provide reducing and oxidizing conditions in the column, respectively. The main characteristics of the influents are such that tap water has pH 6.25 and ORP values of 157 mV whereas ascorbate solution has pH 6.25 and ORP values are -186 mV and -136 mV for 1 M and 0.1 M ascorbate solution, respectively. Effluents were collected every 2-3 hours and filtered through 0.45 μm membrane filters for the chemical

analyses. pH and redox potential were measured upon collection of effluent by a glass electrode and platinum (Pt) combination electrode, respectively. Total concentrations of As and Fe were analyzed by inductive couple plasma and atomic emission spectrometry (ICP-AES).

Table 6.2 *Properties of the soil.*

Parameter	Sasaguri soil
Total carbon	1.58 wt%
pH	7.3
Ca	1.2 wt%
Fe	21 wt%
Mn	0.65 wt%
Total As	27 mg/kg

6.3. Arsenic solubility as effects of redox potential

6.3.1 Effect of ascorbate solution on redox potential

a. Run 1

Repeated oxidation-reducing conditions in the soil column were conducted by successive supply of influent from ascorbate solution, tap water and ascorbate solution. Figure 6.3 presents changes in pH and ORP values of the effluents with time. The results are divided into three periods of column operation demarcated by different influent compositions. For Period I and III, sodium ascorbate solution was supplied for reducing conditions in the column. Period II represents that tap water was supplied for oxidizing condition. Firstly, ascorbate solution was fed for 45 hours. Influent, then, was changed to tap water and fed until 143 hours followed by another supply of ascorbate solution until 203 hours.

Redox values remain negative and the same for 35 hours after the influent changed to tap water then rapidly increase with time. Redox values turn to positive at about 95 hours since the start of the experiment. This implies that oxidizing condition is eventually formed in the column after changing the influent to tap water. ORP value then gradually increases and reaches to the maximum values, +135 mV, at about 142 hours. Influent was changed to ascorbate solution at 143 hours to repeat redox condition in the column. ORP values start decrease soon after the influent changed from tap water to ascorbate solution, and shows continuous decrease down to -135 mV at about 203 hours. This implies that feeding sodium ascorbate solution leads to reducing condition throughout the column. A significant decrease in ORP from -143 mV to -229 mV (Period I) and from +135 mV to -135 mV (Period III) is observed. The largest change in ORP is observed from negative to positive values when the influent was changed from ascorbate solution to tap water. Redox potential of the column gradually changes from strongly-moderately reducing condition (-213 mV to -37 mV) to moderately oxidizing condition (-6 mV to +101 mV) in Period II. During experiment, pH gradually increases from 6.5 to 7.94.

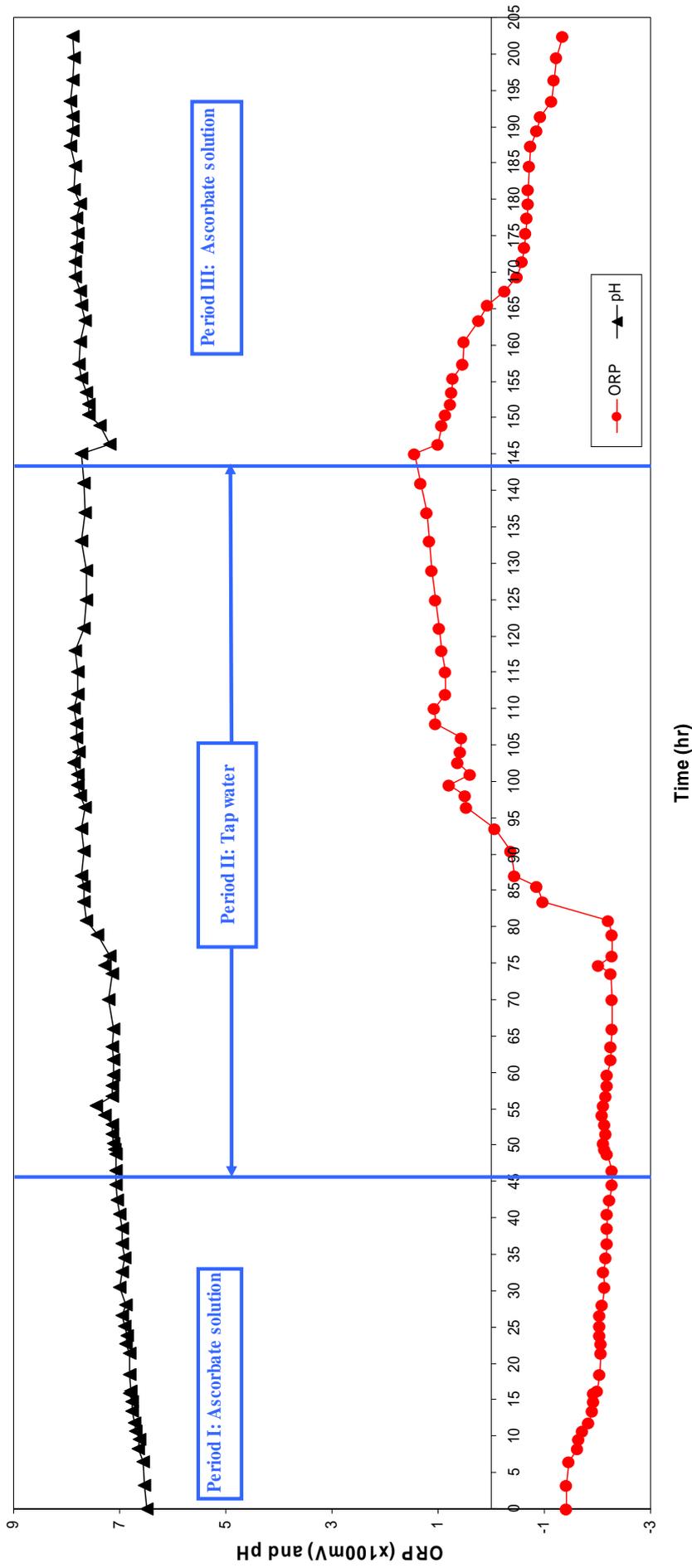


Fig. 6.3 Changes of ORP, pH of effluents for Run 1 with time.

b. Run 2

Figure 6.4 depicts changes in pH and ORP values of the effluents for Run 2 with time. The results are indicated for two periods of column operation demarcated by different influent compositions. For Period I, sodium ascorbate solution was supplied for reducing conditions in the column. Period II represents that tap water was supplied for oxidizing condition. Firstly, ascorbate solution was fed for 65 hours. Influent was, then, changed to tap water and fed until 165 hours.

Redox values are positive until 27 hours then rapidly decrease with time. The presence of positive redox values was resulted from interrupted supplying of ascorbate solution from 5 to 15 hours. ORP values start decrease from -1 mV at about 30 hours to -192 mV and keep stable from 55 hours to 90 hours. ORP values start increasing and reach +2 mV at 135 hours. The increase of redox values implies that oxidizing condition is eventually formed in the column after changing the influent to tap water. Redox potential of the column gradually changes from strongly-moderately reducing condition (-192 mV to -25 mV) to moderately oxidizing condition (+2 mV to +139 mV) in Period II. During the experiment, pH gradually increases from 6.5 to 7.83.

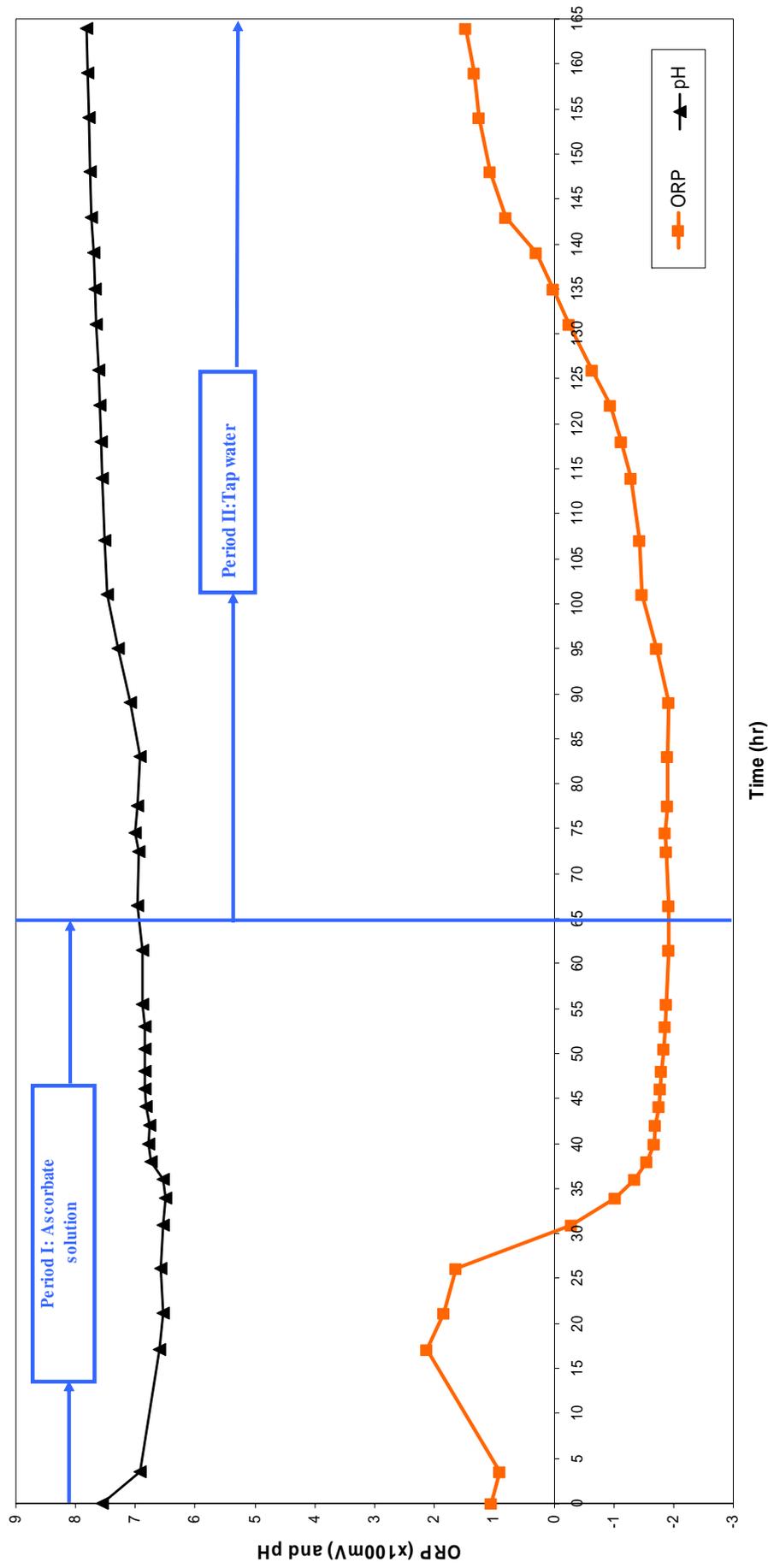


Fig. 6.4 Changes of ORP, pH of effluents for Run 2 with time.

6.3.2 Effects of redox potential

a. Run 1

The influence of redox potential on released As and Fe is determined by soil column experiments. Concentrations of arsenic and iron with ORP values of the effluents for the first experiment are shown in Fig. 6.5(a) and (b). There is an apparent relationship between As and ORP values such that arsenic is detected only under condition of negative ORP values. The arsenic concentrations seem to be correlated to the magnitude of ORP values. From Fig 6.5(a), ORP values starts decreasing after 7 hours of commencement of supplying influent whereas arsenic concentrations increase gradually up to 70 hours. For arsenic concentration, it reaches the highest value of 71.2 mg/L at 70 hours, then start decreasing which corresponds to an increase in ORP values.

On the other hand, dissolved Fe concentrations increase with time in Period I and reach the highest ones of 4154 mg/L at about 20 hours. Then its concentrations start decreasing whereas ORP values remain negative (Fig. 6.5b). It can be said that both As and Fe start decreasing once they reach the maximum values, but iron concentrations start decreasing much faster than those of As. At the beginning of period II, reducing condition remains in the column and As concentrations still increase. However, neither As nor Fe are detected when column is completely in oxidizing condition (Fig. 6.5). For addition of sodium ascorbate in Period III that yield significant decrease in the ORP again, the increases in As and Fe concentrations seem to be indicative of a reductive dissolution of iron hydroxides. The release of Fe accompanies by a simultaneous release of precipitated As.

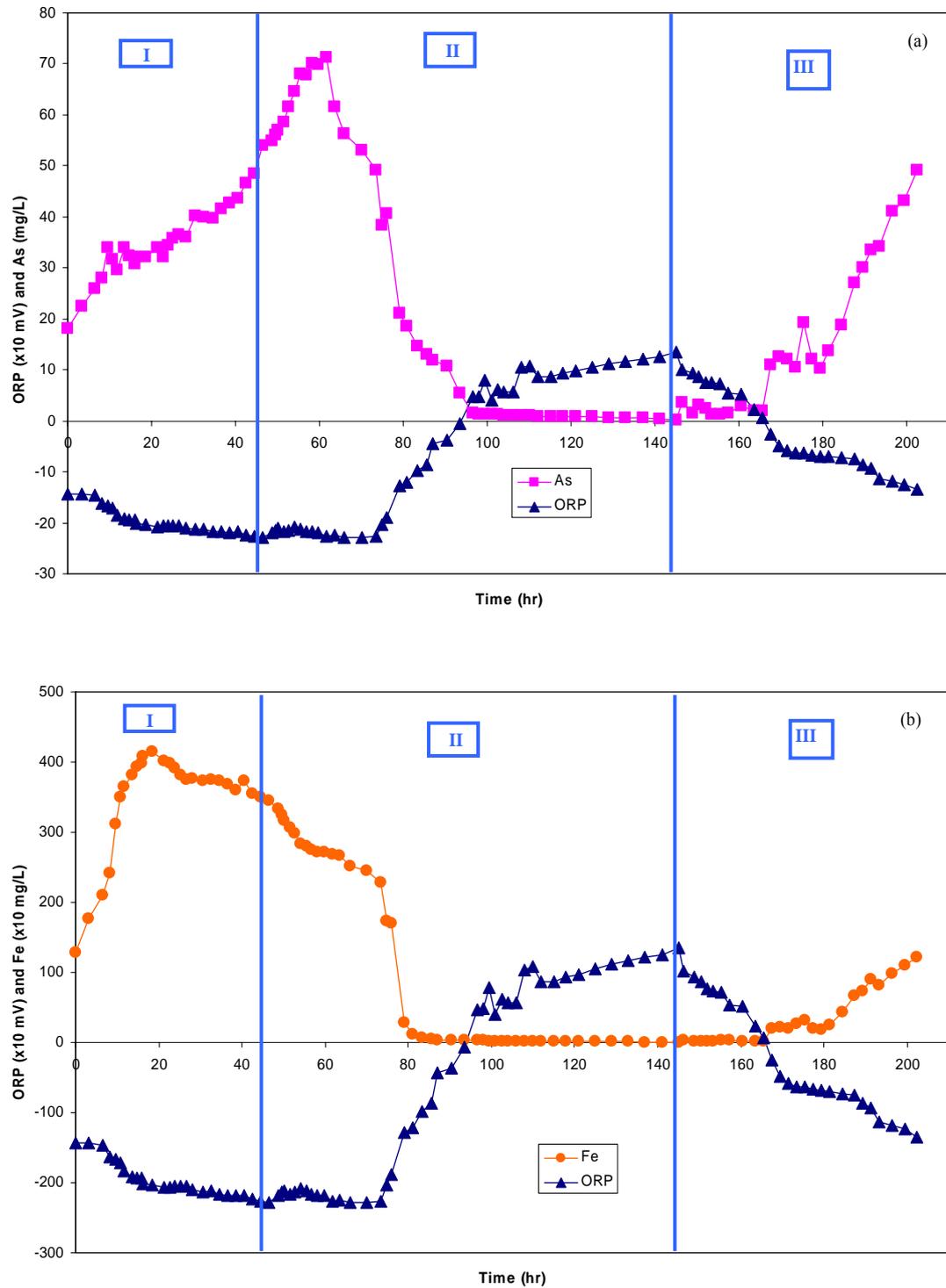


Fig. 6.5 Relationship of ORP with concentrations of (a) As and (b) Fe for Run 1.

b. Run 2

Concentrations of As and Fe with ORP values of the effluents for the second experiment are shown in Fig. 6.6(a) and (b). From Fig 6.6(a), ORP values starts decreasing after 30 hours of commencement of supplying influent whereas As concentrations increase gradually up to 75 hours. Arsenic concentration is lower than 0.1 $\mu\text{g/L}$ when ORP values are positive. Then the concentration starts increasing ($> 50 \mu\text{g/L}$) after ORP values decreases to negative values. Finally, it reaches the highest value of 290 $\mu\text{g/L}$ at 75 hours, then start decreasing which corresponds to an increase in ORP values.

On the other hand, dissolved Fe concentrations increase with time in Period I (after 30 hours) and reach the highest ones of 60 mg/L at about 67 hours. Its concentrations gradually decrease to 47 mg/L until 83 hours whereas ORP values continue decreasing and remain negative. Then Fe concentrations quickly decrease down to 12 mg/L at about 100 hours with increase of ORP values (Fig. 6.6b). Finally, when oxidizing conditions is formed in the column (positive ORP values), As and Fe concentrations are lower than 1 $\mu\text{g/L}$ and 1 mg/L , respectively (Fig. 6.6).

On the basis of results from the soil column experiments, it can be said that:

1) Feeding sodium ascorbate solution led to reducing condition throughout the column. However, ORP values in Period I of Run 1 are higher than these of the Run 2. This can be explained by lower concentration of ascorbate solution used in the Run 2.

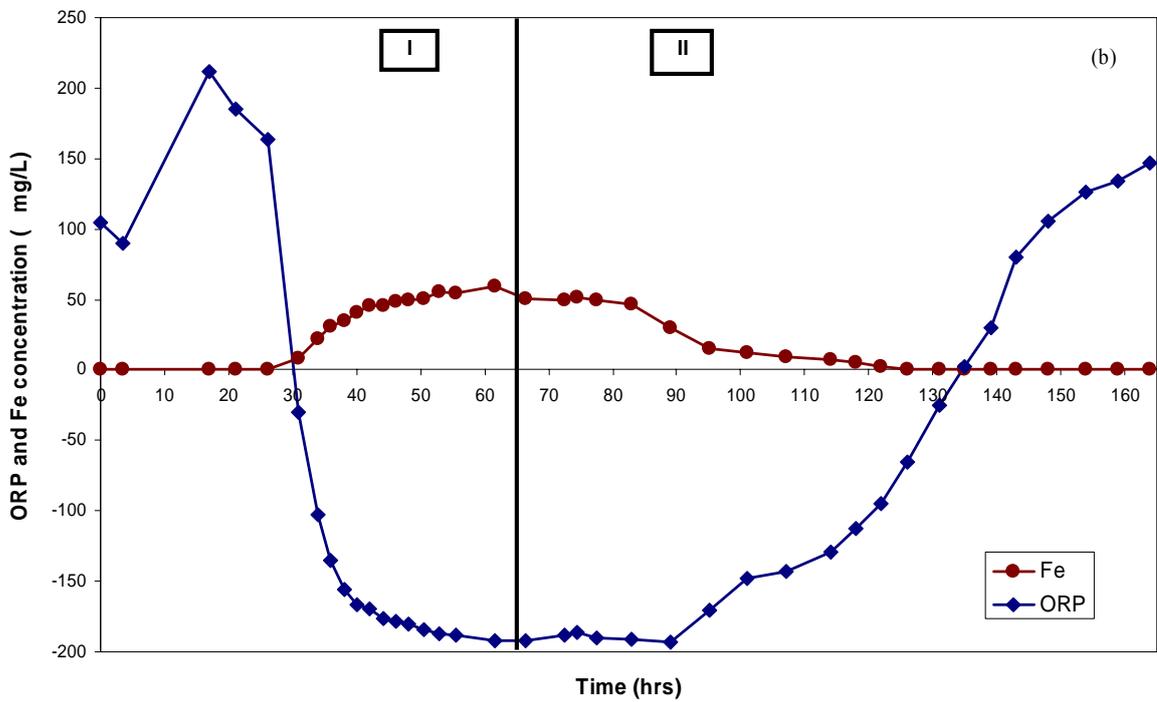
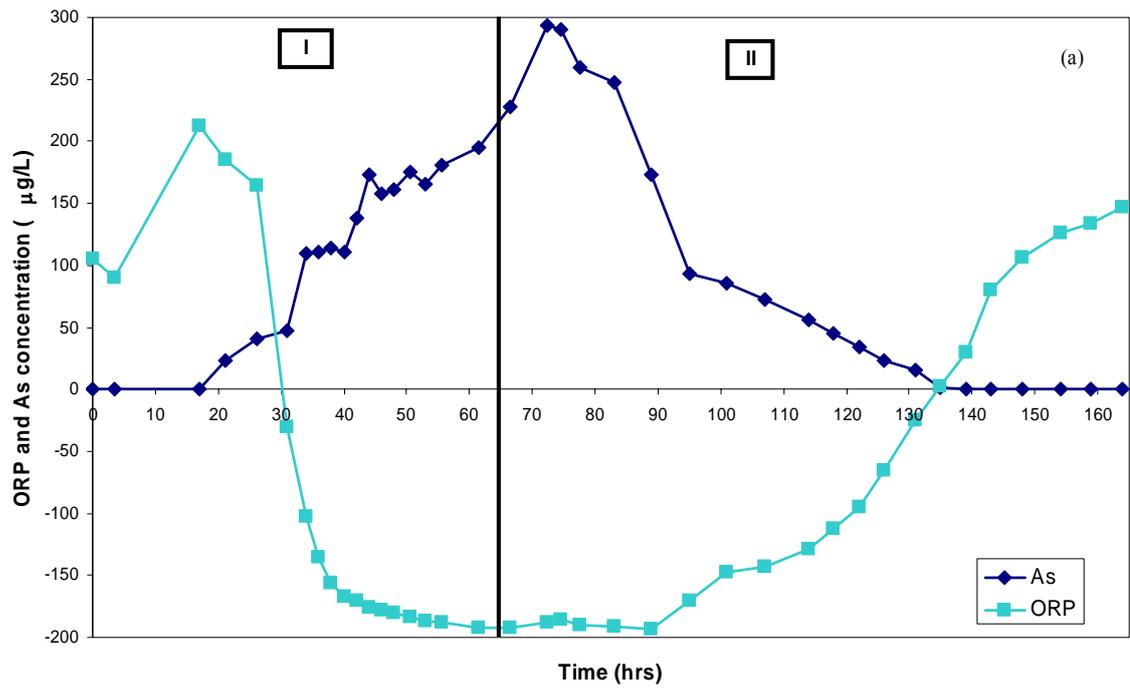


Fig. 6.6 Relationship of ORP with concentrations of (a) As and (b) Fe for Run 2.

2) Both As and Fe concentrations start decreasing once they reach the maximum values although their maximum values are different. Like ORP values, As and Fe concentrations of effluents for Run 2 are also lower than these of Run 1. These may be resulted from differences of both ascorbate solution and amount of Fe hydroxides coprecipitated with arsenic.

3) For Fe concentrations of Run 1, it starts increasing faster and higher than that of Run 2 but Fe concentrations decrease much faster than these of As in both Run 1 and Run 2. At the beginning of Period II, reducing condition remains in the column and arsenic concentrations still increase.

4) Finally, neither As nor Fe were detected when column is completely in oxidizing condition (Figs. 6.5, 6.6). The increase in As and Fe concentrations seem to be indicative of a reductive dissolution of iron hydroxides. The release of iron accompanies by a simultaneous release of precipitated arsenic.

6.3.3 Release of arsenic during reductive dissolution of Fe hydroxide

The release of arsenic during reductive dissolution of Fe hydroxide was investigated using sodium ascorbate solution in pH 6.5 - 8. Figure 6.7 shows pictures of soil column for Run 1 taken at different elapsed time of the experiment. Increases in Fe concentrations of the effluents correspond to a change in color of the soil column from orange to black (Fig. 6.7 (a)). For example, changes in color of the soil column reach 3 cm and 24 cm depth after 4h and 18h, respectively (Fig. 6.7b, c). After 29h, there was little visible change (Fig. 6.7d).



(a)



(b)



(c)



(d)

Fig. 6.7 Pictures of the soil column for Run 1 during experiment for different elapsed time. (a) Starting point; (b) 4h; (c) 18h and (d) 29h.

Results of Fe concentrations from the column imply reductive dissolution of Fe hydroxide occurs, following by transport of dissolved Fe and precipitation of secondary Fe minerals.

Reductive dissolution of Fe hydroxide occurs with an increase in total aqueous Fe and As. However, the release of arsenic from Fe hydroxide is significantly delayed compared to the release of Fe (Fig. 6.5 (a), (b)). Apparently, the dissolution of the Fe hydroxide led to an increase in arsenic concentrations. The explanation is that partial dissolution of Fe hydroxide as the redox potential decreases may change concentrations of Fe and As. Calculation of arsenic concentrations in the effluents indicated that only small amount of arsenic is recovered (0.01% and 4% of the total As for Run 2 and Run 1, respectively). The very low recovery suggests that a fraction of initial arsenic has effectively adsorbed to the soil and/or remain Fe hydroxide. It is suggested that during rapid reductive dissolution of Fe hydroxide elevated dissolved Fe concentrations in the pore water stimulate the transformation of Fe hydroxide to more stable crystalline forms whose surface area and the number of sites for As being adsorbed become small to contain all the As.

6.4. Summary

Characterization of the soil by XRD analyses indicated the predominant presence of iron hydroxides either in crystalline form of goethite and hematite or in the amorphous form of Fe hydroxides with adsorbed and/or contained arsenic. Synthetic Fe hydroxides coprecipitated with arsenic were prepared to pack in soil

column. The soil column experiment was conducted twice as Run 1 which Sasaguri soil and coprecipitate were mixed and Run 2 which Sasaguri soil and coprecipitate were divided into two layers. Results of column experiments conducted under controlling pH and redox conditions indicated a strong dependence of redox potential on both concentrations of As and Fe in the effluents of the column. The As and Fe concentrations seemed to be correlated to the magnitude of negative ORP values. When the column was in moderately oxidizing conditions judged from ORP values of effluents, As and Fe concentrations were very low and arsenic adsorbed or co-precipitated onto iron hydroxides. Upon reduction, arsenic concentration increased significantly and reached maximum value. When the column was in highly reduced conditions, arsenic solubility seems to be controlled by the dissolution of Fe hydroxides.

Chapter Seven

CONCLUSIONS AND RECOMMENDATIONS

7.1 General conclusions

The main conclusions derived from this study are summarized as follows:

1) Field survey for groundwater and core samples indicated interesting results for arsenic contaminant in the Mekong Delta. For core samples, high As and Fe contents occurred at depth where iron hydroxides as goethite and hematite were present. For groundwater samples with negative ORP values and As concentrations higher than 50 $\mu\text{g/L}$, the Fe, NH_4^+ and Mn concentration is relatively high, suggesting that adsorbed As is released into groundwater by dissolution of hydrous ferric oxides under reducing condition. For groundwater samples with positive ORP values and relatively high As concentrations (up to 55 $\mu\text{g/L}$), the Fe and NH_4^+ concentrations are low, suggesting that As may be released by oxidative decomposition of pyrite including As.

2) XRD analyses for soils in Sasaguri and the Mekong Delta (Tan Chau, An Phong and Lai Vung) indicated the abundance of iron hydroxides as goethite and hematite whereas small quantities of sulfide minerals were present in Tan My soil. From results of sequential extraction method for arsenic fractionation, it is concluded that majority of arsenic in the soils of Sasaguri and the Mekong Delta (Tan Chau, An Phong and Lai Vung) is

associated with amorphous and poorly crystalline Fe hydroxides (60-70 wt% total As) followed with residuals. Different from other soils, about 30 wt% of total arsenic bound to sulfide fraction in Tan My soil.

3) The experiments of arsenic adsorption were conducted to investigate adsorption capacity of arsenic adsorption on core sample at 30 m depth of the borehole LK204. It was elucidated that adsorption capacity of As(V) is three times as high as that of As(III). This result also implied that adsorption of arsenic on Fe hydroxide in core sample is another primary source of arsenic in groundwater.

4) The results of soil column experiment indicated a strong dependence of redox potential on both concentrations of As and Fe in the effluents. The As and Fe concentrations seemed to be correlated to the magnitude of negative ORP values. The As and Fe concentrations increased due to dissolution of Fe hydroxides.

7.2 Conclusions on source and release mechanism of arsenic in aquifers of the Mekong Delta

7.2.1 General discussions on source and cycling of arsenic

Two dominant sources of arsenic of the Mekong Delta aquifer in Vietnam were revealed: arsenic in sulfide minerals (greater than 30 wt% of the total solid phase arsenic). A second source consists of arsenic adsorbed on Fe(III)

hydroxides. Then reductive dissolution of Fe (III) (hydro)oxides and concomitant release of arsenic is mechanism for the cause of high arsenic concentrations in the aquifer.

Some of the arsenic bearing sulfide minerals appears detrital, having been transported from source rock, deposited, and buried without complete oxidation. Pyrite has been detected in core samples of the aquifer as well as in soil samples. Due to monsoonal activity and dry-season irrigation, surface soils we examined have undergone at least two major reduction–oxidation cycles each year (and possibly more based on irrigation and crop cycling). Both solid-phase arsenic and iron become more reduced with depth in the soils. Important depositional sources of arsenic include arsenic associated with Fe (hydro)oxides and detrital sulfide minerals. The presence of arsenic -bearing sulfide grains was confirmed by the sequential extractions method that applied to near-surface soil in Tan My.

Arsenic-bearing sulfide grains in soils would yield a source of arsenic during oxic cycles, which would then be subject to reductive dissolution during flooding events (Fig. 7.1). Upon oxidation, Fe(III) (hydro)oxides would be formed; arsenic in the sulfide matrix would undergo a solid phase transformation and be adsorbed to and coprecipitated with ferric (hydro)oxides. Arsenic released from Fe(III) minerals, both those newly formed and those deposited, during subsequent reducing periods (flood events where flood waters carry high, labile dissolved organic carbon) could be re-sequestered into authigenic sulfide minerals. However, because sulfur would be partially removed via sulfate transport following oxidation, only a portion of the original arsenic could be re-precipitated in sulfidic form; additionally, competition from other ions, such as Fe^{2+} , could limit

sequestration of arsenic by sulfide production. Early diagenetic framboidal pyrite in the sediments (Nickson et al. 2000) and remaining detrital sulfides could be reoxidized during the dry season and thus continue the arsenic cycle.

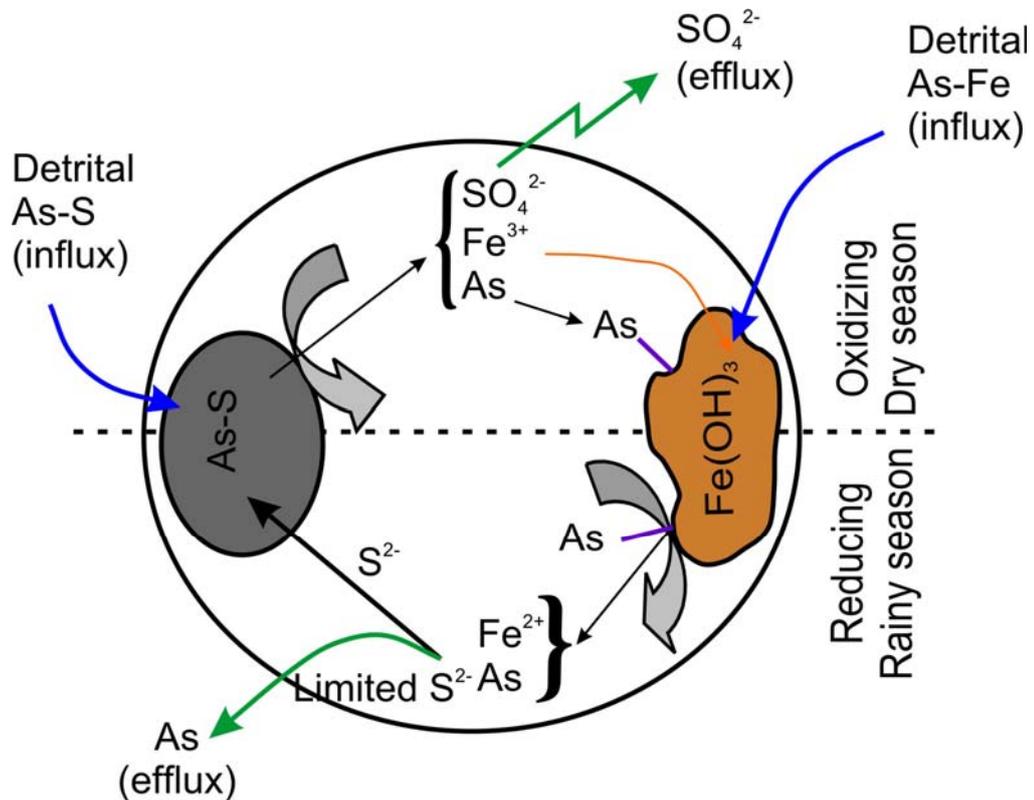


Fig. 7.1 Proposed cycling and transport of arsenic. At the surface, detrital sulfides are oxidized forming ferric hydroxides, which are then subject to reductive dissolution during reducing periods.

7.2.2 Conclusions on release mechanism of arsenic in aquifers

It is evident that the distribution of arsenic in the groundwater is governed by a complex interaction of different factors, among which microbial mediated redox process, adsorption/desorption and precipitation are the most important. Based on the above results and taking into account the redox chemistry of arsenic,

the following mechanism can be suggested to explain the distribution of arsenic in the groundwater in the Mekong Delta:

- 1) Natural arsenic originates from the Upper Mekong basin. The Mekong Delta was supplied by the sediment containing arsenic. Arsenic bearing “primary minerals” (such as pyrite and other sulfides) were secondary formed in the Mekong Delta. These pyrites were rapidly oxidized and arsenic (mainly As(V) species) were coprecipitated or adsorbed on the particulate matter, or the surface of grains coated with Fe oxyhydroxides.
- 2) After that, sediments were buried and induced strong reducing environment in the alluvial aquifers.
- 3) An oxidation stage may have occurred during low sea level during Late Pleistocene, during which the As-bearing sulfides were oxidized to Fe hydroxide, retaining adsorbed arsenic.
- 4) At a later stage, during the subsequent transgression and sea level rise, swamp, marshy and peat deposits rich in organic matter were formed above the deep aquifer that developed during the Late Pleistocene. Moreover, salinity and SO₄-rich seawater mixed into groundwaters.
- 5) The arsenic in groundwater was released and its concentration was increased due to changes of redox conditions. In the early stage, organic matter degraded (slightly reducing condition), then reduction of Mn oxides occurred. In the presence of Fe hydroxide, arsenic can be re-adsorbed. With gradual decrease in magnitude of redox state, reduction of As(V) to

As(III) occurred. In modest – strong redox state, Fe hydroxides dissolved, reduction of Fe(III) to Fe(II) occurred and release arsenic.

7.3 Recommendations

This research has enhanced understanding of the characteristics of groundwater related to arsenic, soil and core samples in the Mekong Delta by employed chemical analysis, sequential extraction method and adsorption capacity of arsenic. The research has also shown that redox potential significantly enhances the release of arsenic to groundwater via the soil column experiments. These results may elucidate the arsenic behaviors in aquifer of the Mekong Delta. Nevertheless, due to limitation in terms of time and resources, the research raises many unanswered questions. In order to gain a better overall understanding of arsenic release processes, it is recommended that further research be conducted regarding:

- 1) Carry out characterization on much more core samples in the Mekong Delta. Core samples in other areas should be collected and analyzed. This will enhance the understanding of the mineralogical constituents, the potential of the Mekong Delta sediments to bind to the various arsenic species as well as arsenic sorption.
- 2) Analysis of the arsenic species released from the soil column. When arsenic releases from the soil column, it would be useful to determine which species present in effluents. This will aid in the understanding whether

reduction of arsenate to arsenite followed by desorption occurred in the soil column.

3) In addition, numerical simulation for geochemical reactions leads for the better understanding of column experiments.

4) The involvement of microorganisms on mobilization of arsenic should be considered in this study because microorganisms can also affect the kinetics of important arsenic reactions affecting speciation and mobility.

5) Evaluation of precipitation of different sulfidic minerals will be very useful for understanding potential mobilization implications for arsenic, iron and sulfur. Varying pH, redox conditions and constituent concentration could confirm thermodynamic conditions.

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APPENDICES

RESULTS OF SEQUENTIAL EXTRACTION FOR SASAGURI SOIL, FUKUOKA

	Fractions	N4b			
		1st exp.	2nd exp.	3rd exp.	Average
As (mg/kg)	Exchangeable	1.72	1.95	1.92	1.86
	HCO ₃ fraction	2.26	2.02	1.99	2.09
	Sulfide fraction	0.85	0.98	0.87	0.9
	Fe-Mn hydroxides	14.64	16.46	15.31	15.47
	Residual phases	5.26	6.08	5.71	5.68
	Total	24.73	27.49	25.80	26
Fe (g/kg)	Exchangeable	4.69	5.46	5.21	5.12
	HCO ₃ fraction	5.2	4.58	6.02	5.27
	Sulfide fraction	7.24	7.74	6.18	7.05
	Fe-Mn hydroxides	140.8	137.3	137.71	138.6
	Residual phases	48.06	45.83	50.36	48.08
	Total	205.97	200.91	205.48	204
Mn (mg/kg)	Exchangeable	1474	1664	1527	1555
	HCO ₃ fraction	5087	4789	4904	4927
	Sulfide fraction	2026	1879	1954	1953
	Fe-Mn hydroxides	40875	38062	39621	39519
	Residual phases	14509	14874	12471	13952
	Total	63972	61268	60477	61906
Al (g/kg)	Exchangeable	4.85	5.43	5.1	5.13
	HCO ₃ fraction	9.91	8.86	10.6	9.79
	Sulfide fraction	3.35	4.31	4.91	4.19
	Fe-Mn hydroxides	29.23	30.06	33.68	30.99
	Residual phases	137.2	137.1	131.6	135.3
	Total	184.55	185.79	185.88	185

**RESULTS OF SEQUENTIAL EXTRACTION FOR SOIL IN
TAN CHAU, MEKONG DELTA**

	Fractions	TC			
		1st exp.	2nd exp.	3rd exp.	Average
As (mg/kg)	Exchangeable	0.6	0.72	0.61	0.64
	HCO ₃ fraction	0.89	1	0.92	0.94
	Sulfide fraction	0.22	0.2	0.21	0.21
	Fe-Mn hydroxides	15	16.92	15.90	15.94
	Residual phases	4.12	4.78	4.74	4.55
	Total	20.84	23.62	22.39	22
Fe (g/kg)	Exchangeable	3.24	2.02	3.14	3
	HCO ₃ fraction	5.73	5.94	5.61	5.76
	Sulfide fraction	2.02	1.66	3.87	2.52
	Fe-Mn hydroxides	127.8	134.9	128.3	130.3
	Residual phases	36.44	36.1	40.33	37.62
	Total	175.25	180.63	181.27	179
Mn (mg/kg)	Exchangeable	16.09	13.78	15.1	14.99
	HCO ₃ fraction	65.69	59.41	61.3	62.13
	Sulfide fraction	6.37	5.73	16.1	9.40
	Fe-Mn hydroxides	439	408	400	416
	Residual phases	112.7	105.4	117.7	111.9
	Total	640	593	610	614
Al (g/kg)	Exchangeable	2.74	2.61	2.73	2.7
	HCO ₃ fraction	11.2	11.26	11.09	11.18
	Sulfide fraction	1.09	1.09	2.91	1.7
	Fe-Mn hydroxides	74.87	77.39	72.37	74.88
	Residual phases	19.22	19.97	21.29	20.16
	Total	109.12	112.31	110.39	111

**RESULTS OF SEQUENTIAL EXTRACTION FOR SOIL IN AN
PHONG, MEKONG DELTA**

	Fractions	AP			
		1st exp.	2nd exp.	3rd exp.	Average
As (mg/kg)	Exchangeable	0.37	0.36	0.35	0.36
	HCO ₃ fraction	1.35	1.22	1.3	1.29
	Sulfide fraction	0.21	0.19	0.19	0.19
	Fe-Mn hydroxides	18.6	16.37	17.76	17.58
	Residual phases	5.95	4.34	5.28	5.19
	Total	26.47	22.47	25	25
Fe (g/kg)	Exchangeable	2.27	2.52	2.6	2.47
	HCO ₃ fraction	8.64	8.39	8.17	8.4
	Sulfide fraction	1.87	2.35	1.66	1.96
	Fe-Mn hydroxides	118	123.81	122	121.3
	Residual phases	39.83	38.11	38.96	38.97
	Total	171	175.18	173.51	173
Mn (mg/kg)	Exchangeable	8.94	10.34	10.37	9.88
	HCO ₃ fraction	27.08	32.43	28.37	29.29
	Sulfide fraction	6.60	13.28	5.84	8.57
	Fe-Mn hydroxides	533	498	486	506
	Residual phases	150.6	135.5	154.4	146.8
	Total	726	690	685	700
Al (g/kg)	Exchangeable	1.88	2.36	1.67	1.97
	HCO ₃ fraction	5.54	5.73	5.67	5.65
	Sulfide fraction	1.06	2.52	1.59	1.73
	Fe-Mn hydroxides	23.43	20.6	19.66	21.23
	Residual phases	90.77	94.85	83.24	89.62
	Total	122.68	126.06	111.83	120

**RESULTS OF SEQUENTIAL EXTRACTION FOR SOIL IN
TAN MY, MEKONG DELTA**

	Fractions	TM			
		1st exp.	2nd exp.	3rd exp.	Average
As (mg/kg)	Exchangeable	0.54	0.8	0.54	0.62
	HCO ₃ fraction	1.03	1.09	1.1	1.08
	Sulfide fraction	8.8	8.39	7.82	8.34
	Fe-Mn hydroxides	14.37	14.37	13.61	14.12
	Residual phases	4.85	3.57	4.15	4.19
	Total	29.59	28.22	27.22	28
Fe (g/kg)	Exchangeable	2.78	3.04	1.66	2.50
	HCO ₃ fraction	5.45	3.17	3.5	4.04
	Sulfide fraction	38.21	40.98	39.58	39.59
	Fe-Mn hydroxides	95.77	104.9	106.8	102.5
	Residual phases	14.34	12.85	14.07	13.75
	Total	156.55	164.98	165.64	162
Mn (mg/kg)	Exchangeable	8.65	7.74	6.99	7.8
	HCO ₃ fraction	24.08	18.26	18.78	20.4
	Sulfide fraction	6.35	4.33	6.66	5.78
	Fe-Mn hydroxides	384	354	369	369
	Residual phases	109.9	101.6	100.3	103.9
	Total	533	486	501	507
Al (g/kg)	Exchangeable	1.36	1.65	2.4	1.8
	HCO ₃ fraction	3.21	3.30	4.28	3.60
	Sulfide fraction	20.23	20.36	20.07	20.22
	Fe-Mn hydroxides	28.71	28.56	26.86	28.04
	Residual phases	80.59	77.01	77.88	78.49
	Total	134.10	130.87	131.48	132

**RESULTS OF SEQUENTIAL EXTRACTION FOR SOIL IN
LAI VUNG, MEKONG DELTA**

	Fractions	LV			
		1st exp.	2nd exp.	3rd exp.	Average
As (mg/kg)	Exchangeable	1.03	0.95	1	1
	HCO ₃ fraction	1.28	1.11	1	1.13
	Sulfide fraction	0.37	0.44	0.42	0.41
	Fe-Mn hydroxides	26.51	23.35	22.37	24.07
	Residual phases	6.98	7.87	7.27	7.37
	Total	36.17	34	32.06	34
Fe (g/kg)	Exchangeable	4.25	3.42	3.68	3.78
	HCO ₃ fraction	6.79	7.82	7.42	7.34
	Sulfide fraction	2.25	2.6	2.64	2.5
	Fe-Mn hydroxides	136.5	130.8	127.2	131.5
	Residual phases	33.75	41.35	41.38	38.83
	Total	183.56	185.95	182.35	184
Mn (mg/kg)	Exchangeable	23.44	19.06	22.23	21.58
	HCO ₃ fraction	112.4	126	106.8	115
	Sulfide fraction	10.09	10.88	10.63	10.53
	Fe-Mn hydroxides	696	753	672	707
	Residual phases	177.4	208.8	193	193
	Total	1020	1118	1005	1047
Al (g/kg)	Exchangeable	2.38	1.81	2.36	2.18
	HCO ₃ fraction	7.53	6.87	7.97	7.46
	Sulfide fraction	1.05	0.97	0.76	0.93
	Fe-Mn hydroxides	15.85	15.44	15.49	15.59
	Residual phases	60.54	59.72	58.16	59.47
	Total	87.36	84.81	84.74	86