



# Effect of sulfidogenesis cycling on the biogeochemical process in arsenic-enriched aquifers in the Lanyang Plain of Taiwan: Evidence from a sulfur isotope study



Yu-Hsuan Kao<sup>a,b</sup>, Chen-Wuing Liu<sup>a,\*</sup>, Pei-Ling Wang<sup>c</sup>, Chung-Min Liao<sup>a</sup>

<sup>a</sup> Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei 106, Taiwan, ROC

<sup>b</sup> Center for Weather Climate and Disaster Research, National Taiwan University, Taipei 106, Taiwan, ROC

<sup>c</sup> Institute of Oceanography, National Taiwan University, Taipei 106, Taiwan, ROC

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## SUMMARY

This study evaluated the biogeochemical interactions between arsenic (As) and sulfur (S) in groundwater to understand the natural and anthropogenic influences of S redox processes on As mobilization in the Lanyang Plain, Taiwan.  $\text{Cl}^-$  and the sulfate isotopic composition ( $\delta^{34}\text{S}_{\text{SO}_4}$ ) were selected as conservative tracers. River water and saline seawater were considered as end members in the binary mixing model. Thirty-two groundwater samples were divided into four types of groundwater (I, pyrite-oxidation; II, iron- and sulfate-reducing; III, sulfate-reducing; and IV, anthropogenic and others). The binary mixing model coupled with discriminant analysis was applied to yield a classification with 97% correctness, indicating that the DO/ORP values and  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\text{Fe}^{2+}$  concentrations are effective redox-sensitive indicators. Type I groundwater is mostly located in a mountainous recharge area where pyrite oxidation is the major geochemical process. A high  $^{18}\text{O}$  enrichment factor ( $\epsilon_{\text{SO}_4-\text{H}_2\text{O}}$ ) and high  $^{34}\text{S}$  enrichment factor ( $\epsilon_{\text{S}_{\text{FeS}_2-\text{SO}_4}}$ ) indicate that disproportionation and dissimilatory sulfate reduction are both involved in Type II and Type III groundwater. The process of bacterial sulfate reduction may coprecipitate and sequester As, a mechanism that is unlikely to occur in Type II groundwater. The presence of high As and  $\text{Fe}^{2+}$  concentrations and enriched  $\delta^{34}\text{S}_{\text{SO}_4}$  in Type II groundwater suggest that biogeochemical reactions occurred under anaerobic conditions. The reductive dissolution of As-bearing Fe oxyhydroxides together with microbial disproportionation of sulfur explains the substantial correlations among the high As concentration and enriched  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\text{Fe}^{2+}$  concentrations in the iron- and sulfate-reducing zone (Type II). The As concentration in Type III groundwater (sulfate-reducing) is lower than that in Type II groundwater because of bacterial sulfate reduction and coprecipitation with As. Furthermore, the dissolution of sulfate minerals is not the major source of aqueous  $\text{SO}_4$ , based on the sulfur isotopic composition of solid-phase sulfate ( $\delta^{34}\text{S}_{\text{sulfate mineral}}$ ). Finally, the anthropogenic influence of fertilizers with wide S isotopic ranges is proposed as the plausible sulfate budget in Type IV groundwater. The results of this study suggest that the As release into groundwater involves the reductive dissolution of As-bearing Fe-hydroxides, bacterial sulfate reduction, and microbial disproportionation in the Lanyang Plain.

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## 1. Introduction

Arsenic (As)-enriched groundwater represents over 90% of the sources of drinking water in the Lanyang Plain, Taiwan. Residents have used high-As artesian well water for more than 50 years (Chiou et al., 1997). Many symptoms associated with the ingestion of well water containing As have been observed (Chiou et al., 1997; Yang et al., 2003). Approximately 80% of wells exhibit As concentrations above 10  $\mu\text{g/L}$  (Agricultural Engineering Research Center,

2012); the major species of As is arsenite, and the As(III)/As(V) concentration ratio is approximately 2.61 (Agricultural Engineering Research Center, 2007). A substantial dose-dependent relationship exists between the As concentration in groundwater and increased risks of cerebrovascular disease, urinary cancer, and adverse pregnancy outcomes (Chiou et al., 1997, 2001; Yang et al., 2003).

Geochemical processes involving redox reactions, mineral dissolution, precipitation, and desorption substantially influence As mobilization in groundwater systems. An investigation of the geochemical characteristics of groundwater in the Lanyang Plain indicated that As release was associated with the dissolution of Fe-oxides, mineralization of organic carbon, and oxidation of pyrite

\* Corresponding author. Tel.: +886 2 2362 6480; fax: +886 2 2363 9557.

E-mail address: [cwliu@ntu.edu.tw](mailto:cwliu@ntu.edu.tw) (C.-W. Liu).

(Chen, 2001; Shih, 2003; Lee et al., 2007; Lewis et al., 2007). Lewis et al. (2007) suggested that the sources of As contained sulfide deposits, and found that cinnabar was present in slate chimneys in the hydrothermal activity area in the middle of the Lanyang plain. Lee et al. (2007) indicated that the major sinks of As are Fe minerals and As-bearing sulfides, which are mostly deposited in groundwater aquitards.

Researchers have recently focused on assessing the effects of the oxidation and reduction of sulfur compounds on As release and retention (Lipfert et al., 2007; Xie et al., 2009; Kocar et al., 2008; Kao et al., 2011). Bacterial sulfate reduction, which is ubiquitous in environmental systems including hydrothermal systems (Böttcher et al., 1999) and hypersaline soda lakes (Stam et al., 2010), followed by abiotic and biotic reduction of As(III)-bearing iron oxides were reported to be responsible for the spatial heterogeneity of As in aquifers (Burnol and Charlet, 2010). Studies have shown that As is preferentially released into groundwater in an anoxic environment where sulfate reduction occurs (Hosono et al., 2011). Sulfidogenesis occurring in proximity to Fe hydroxides changes the As partitioning and results in the formation of As-containing Fe sulfides (Xie et al., 2014). The sulfur and oxygen isotopic compositions of aqueous sulfate are frequently determined to understand the sulfur cycling in hydrothermal systems, isolated saline aquifers, fractured bedrocks, and sulfate-reducing aquatic environments (Sidle, 2002; Zheng et al., 2004; Mukherjee and Fryar, 2008; Lewis et al., 2007). The heavy  $^{34}\text{S}$  and  $^{18}\text{O}$  isotopic compositions of residual sulfate can be used to examine the occurrence of bacterial sulfate reduction (Kaplan and Rittenberg, 1964; Fritz et al., 1989) or secondary sources of sulfur.

Moreover, the origin of sulfate in groundwater is diverse. Sulfate may be derived naturally during the dissolution of gypsum or oxidation of sulfide.  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\delta^{18}\text{O}_{[\text{SO}_4]}$  have been used as tracers of (1) various natural sources of sulfate (modern seawater, dissolution of sulfate minerals, and soil sulfates) (Clark and Fritz, 1997; Krouse and Mayer, 2000), (2) manmade sulfates (sewage, agrochemicals, detergents and sulfates of industrial origin) (Torssander et al., 2006; Brenot et al., 2007; Otero et al., 2008), and (3) sulfur redox processes (oxidation of sulfide and reduction of sulfate) (Seiler et al., 2011; Kao et al., 2011, 2013). To determine the influence of sulfur cycling and sulfate sources on As mobility in groundwater, the sulfur and oxygen isotope compositions of aqueous and solid sulfates were analyzed, and the associated reactions were inferred.

A portion of the salinized groundwater in the Lanyang Plain originated from the vertical infiltration of salt water from fish ponds and seawater intrusion (Chiang, 1994; Peng et al., 1995); thus, geochemical interactions between sulfur cycling and As enrichment may have occurred. Newly formed sulfide, resulting from the reduction of sulfate, may reduce As concentrations by either coprecipitation or adsorption, or both (Schreiber et al., 2000; Smedley et al., 2003). Moreover, sulfide reacts spontaneously with arsenic to form thioarsenates (Stauder et al., 2005) through arsenite disproportionation, which affects As mobility (Planer-Friedrich et al., 2007; Suess and Planer-Friedrich, 2012; Couture et al., 2013).

Furthermore, the reoxidation of As-bearing sulfides may subsequently increase the release of As into groundwater. Determinations of the sulfur isotopic compositions, multivariate statistical analyses, and geochemical simulations were performed to evaluate the geochemical characteristics of the Lanyang Plain. The isotopic compositions (aqueous compositions of  $\delta^{34}\text{S}_{[\text{SO}_4]}$ ,  $\delta^{18}\text{O}_{[\text{SO}_4]}$ , and  $\delta^{18}\text{O}_{[\text{H}_2\text{O}]}$ , and solid compositions of  $\delta^{34}\text{S}_{[\text{FeS}_2]}$  and  $\delta^{34}\text{S}_{[\text{sulfate minerals}]}$ ) were used to illustrate the probable biogeochemical processes related to the sources of sulfate, as well as the relationship between sulfur cycling and As mobility.

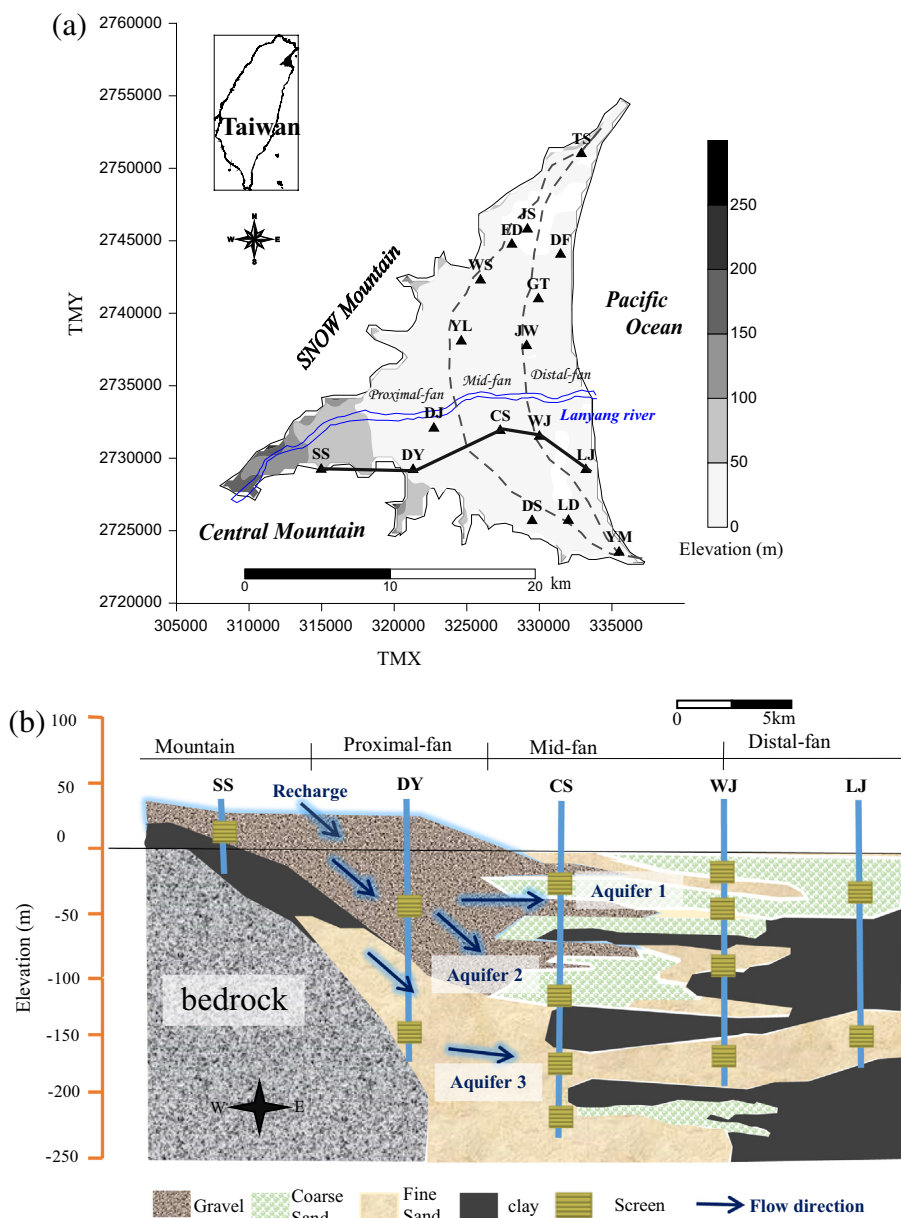
## 2. Material and method

### 2.1. Study area

The Lanyang Plain is located in the northeastern part of Taiwan; it is a basin plain drained by the Lanyang River (Fig. 1a). The groundwater catchment of this region is surrounded by the Taiwan Strait to the west, Central Mountain to the southeast, and Snow Mountain to the northeast. The plain is broadly partitioned into proximal-fan, mid-fan, and distal-fan areas. The west part of the plain is near the mountains and comprises the main groundwater natural recharge area. Groundwater flows from west to east (Peng et al., 1995). According to the stratigraphic correlation of the Lanyang Plain, the sequence boundary of the basement was formed with weathered and unintegrated surfaces approximately 18,000 years ago. The bedrock of the north bank of the Lanyang River is characterized by a sedimentary terrain of Eocene to Oligocene origin, whereas the bedrock of the south bank is characterized by a sedimentary terrain of Miocene origin. The sediments mainly consist of silty sand, silty clay, slate, metamorphic sandstone, schist, and shale. The cementing minerals between sandy grains are quartz, calcite, and clay minerals (Chen, 2000). According to the hydrogeological stratigraphy and depths of observation wells in the Lanyang Plain (Taiwan Central Geological Survey, <http://hydro.moeaegs.gov.tw/>), three aquifers were approximately identified: Aquifer 1, with depths of 18.9–56.7 m; Aquifer 2, with depths of 70.6–139 m; and Aquifer 3, with depths of 157.9–233 m, from top to bottom (Fig. 1b). Aquifer 1 in the second interval corresponds to the Holocene, and the deposits in Aquifers 2 and 3 are classified as Pleistocene to Holocene sands and silt mixed with the muddy sediments of the marine sequence (Chen, 2000). Lee (2008) used a scanning electron microscope and energy dispersive spectrometer and reported that magnetite, hematite, titanite, rutile, ilmenite pyroxene, epidote, amphiboles, hornblende, and garnet were major minerals, and pyrite, zircons, apatite, sillimanite/kyanite/andalu site, and xenotime were minor minerals.

### 2.2. Groundwater sampling and chemical analyses

Thirty-two groundwater samples were collected from 17 hydrological stations, including 16 shallow groundwater samples (Aquifer 1) and 16 deep groundwater samples (Aquifers 2 and 3) (Fig. 1). Temperature (T), dissolved oxygen (DO), redox potential (Eh), pH, and electrical conductivity (EC) were measured in situ. The remaining 14 physicochemical parameters of groundwater including alkalinity (Alk, mg/L as  $\text{CaCO}_3$ ),  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HS}^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , As, Fe, Mn, and total organic carbon (TOC) were analyzed in the laboratory. The field sampling method followed the NIEA (National Institute of Environmental Analysis, NIEA) code W103.52B established by the Taiwan Environmental Protection Administration. At least three wellbore volumes of groundwater were purged before taking samples. Water samples were collected only after pH and EC stabilized and when the fluctuations of pH and relative EC were less than 0.1% and 5%, respectively. Samples were then kept in ice boxes and delivered to the laboratory within 24 h. Alkalinity was analyzed using the Gran titration method. Sulfide was determined through spectrophotometry by using turbidimetric methods. Unacidified parameters ( $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ ) and acidified parameters ( $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) were measured using ion chromatography (DIONEX ICS-900). The acidified parameters of Fe and Mn were measured using inductively coupled plasma and atomic emission spectrometry (Varian, VISTA-MPX). Ferrous ( $\text{Fe}^{2+}$ ) concentrations of the samples were measured colorimetrically by using the ferrozine method (Gibbs 1976) and determined by adding 1.5 mL of ferrozine solution to



**Fig. 1.** (a) Study area of the Lanyang Plain (The TMX and TMY are based on Taiwan Datum 1997 (TWD97). The triangle symbols and line represent the samplings sites and stratigraphic profile, respectively. (b) Typical hydrogeological profile of aquifers (modified by Lee (2008)).

digest 200  $\mu\text{L}$  of the sample (1 g of ferrozine to 1 L of 50 mM HEPES buffer) with a measuring absorbance of 562 nm. The lower detection limit was 0.05 mg/L; variances of duplicate measurements were less than 3%; recoveries of check and spike samples were between 90% and 110%.

The analytical method for As(III) and As(V) was followed closely from our previous study (Huang et al., 2003). After pumping, all groundwater samples were filtered through a 0.2  $\mu\text{m}$  pore membrane syringe filter to prevent microbial activity and remove suspended particles. In this study, we used 1 mL of 8.7 M acetic acid for the preservation of As species per 100 mL of groundwater sample. All samples were stored at 4  $^{\circ}\text{C}$  and kept in the dark before analysis within 2 weeks. Concentrations of As species were analyzed using a high performance liquid chromatograph (Hitachi 7110) connected to a hydride generation (FIAS 400 Perkin-Elmer) and atomic absorption spectroscopy (Perkin-Elmer AA100). The detection limits of As(III) and As(V) were 0.4 and 0.3  $\mu\text{g/L}$ , respectively. Samples were spiked with As species to determine the

recovery rate in the laboratory procedure, which yielded As(III) and As(V) recovery rates of  $100.7 \pm 3.8\%$  and  $97.2 \pm 4.0\%$ , respectively. The coefficient of variation was used to test the reliability and was less than 5% in all experiments. For sulfides, the lower detection limit was 0.03 mg/L; variances of duplicate measurements were less than 10%; recoveries of check and spike samples were between 85% and 115%. For all parameters (except As and Fe speciation and sulfides), a total of 10 samples comprising blank, spiked, duplicate, and check samples (standard solution from Merck) were sequentially measured (Lenore et al., 1998). The variance of duplicate measurements was less than 3%; the recoveries of the check and spiked samples were between 90% and 110%.

### 2.3. Analysis of sulfur isotopes

The isotopic compositions of  $\delta^{34}\text{S}_{[\text{SO}_4]}$ ,  $\delta^{18}\text{O}_{[\text{SO}_4]}$ , and  $\delta^{18}\text{O}_{[\text{H}_2\text{O}]}$  in groundwater and that of  $\delta^{34}\text{S}_{[\text{FeS}_2]}$  in sediment were analyzed. All

groundwater samples were immediately filtered through a 0.45- $\mu\text{m}$  membrane after sampling. Groundwater samples that were high in  $\text{SO}_4^{2-}$  (>20 mg/L) were acidified with HCl, and 0.5 M  $\text{BaCl}_2$  was then added to obtain  $\text{BaSO}_4$  as a precipitate. Groundwater samples that were low in  $\text{SO}_4^{2-}$  (<20 mg/L) were passed through an anion-exchange resin (Bio Rad AG1X8 200–400 mesh in chloride form) bed column with a flow rate of 500–1000 mL/h. Subsequently, 2 mL of 1 M NaCl was added to each sample for reextraction, and 0.5 M  $\text{BaCl}_2$  was added to the reextracted solution to obtain  $\text{BaSO}_4$ , with a recovery of 80–90%. Precipitated  $\text{BaSO}_4$  was recovered by centrifugation, carefully washed, and dried prior to isotope analysis.  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\delta^{18}\text{O}_{[\text{SO}_4]}$  were analyzed in the isotope laboratory of the University of Arizona. Sulfur isotope ratios were reported in per mil (‰) as the conventional delta-notation ( $\delta$ ), with  $^{34}\text{S}/^{32}\text{S}$  and  $^{18}\text{O}/^{16}\text{O}$  scaled to the Vienna Canyon Diablo Troilite and VSMOW NIST standards, respectively. The precisions ( $1\sigma$ ) of  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\delta^{18}\text{O}_{[\text{SO}_4]}$  from the samples were  $\pm 0.15\text{‰}$  and  $\pm 0.3\text{‰}$ , respectively.

Twelve sediment samples were collected. Sulfur isotope analysis of the sulfide minerals ( $\delta^{34}\text{S}_{[\text{FeS}_2]}$ ) was performed by reducing the inorganic sulfur by using the diffusion method (Hsieh and Shieh, 1997). Before analyzing the sulfur isotopes from the sediment samples, acid-volatile sulfide (AVS; FeS), chrome-reducible sulfide (CRS;  $\text{FeS}_2\text{-S}$ ), and elemental sulfur (ES;  $\text{S}^0$ ) were determined using chemical sequential extraction methods. In brief, AVS, CRS, and ES were sequentially separated with 6 M HCl (18 h), acidic Cr (II) (48 h), and N,N-dimethylformamide (24 h), respectively, under pure  $\text{N}_2$  at ambient temperature ( $25 \pm 3^\circ\text{C}$ ). The liberated  $\text{H}_2\text{S}$  was then passively trapped in an alkaline Zn solution, which was in a small beaker containing 15 mL of a 3% alkaline zinc (Zn) acetate solution in a bottle. However, the undetected AVS and ES in sediment samples S2 and S5 may have been caused by the unstable formation or lack of mackinawite (FeS) and elemental sulfur in the natural environment.  $\delta^{34}\text{S}_{[\text{FeS}_2]}$  was analyzed using ZnS powder on the Thermo Scientific Delta PlusXL in the isotope laboratory of the University of Arizona. In addition, a similar  $\text{BaSO}_4$  precipitation method was applied for collecting sulfate minerals. Sediment samples were soaked overnight and then filtered. The filtrates were collected for sulfur isotope analysis of the sulfate minerals. Sodium hydroxide was added into each sample, and supersaturated 0.5 M  $\text{BaCl}_2$  was used to precipitate  $\text{BaSO}_4$ .

#### 2.4. Chemical speciation and saturation index

The geochemical program PHREEQC based on the database WATEQ4F.dat was used to calculate the distribution of the aqueous species (Parkhurst, 1995; Parkhurst and Appelo, 1999). This program is based on an ion-associated theory of aqueous solutions and is designed to perform numerous aqueous geochemical calculations. PHREEQC can handle problems of environmental pollutants by employing the saturation index (SI), and has been used to determine solids that might precipitate or dissolve. The SI is defined as the logarithm of the ratio of the ion activity product (IAP) of the component ion of the solid in solution to the solubility product ( $K_{\text{sp}}$ ) of the solid ( $\text{SI} = \log(\text{IAP}/K_{\text{sp}})$ ) (Nordstrom and Alpers, 1999). In this study, 17 geochemical parameters of groundwater samples, including pH, pe, DO, Alkalinity,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HS}^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , TOC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , Fe, Mn, and As concentrations, were considered to calculate the equilibrium speciation and SI.

#### 2.5. Binary mixing model and discriminant analysis

Chloride is the most conservative of dissolved constituents in groundwater (Hendry et al., 2000), which makes it a suitable tracer in groundwater mixing models (Buschmann and Berg, 2009). The

$\text{Cl}^-$  content in seawater is generally higher than that in fresh water. If seawater and river water are considered as two end-member components with different  $\text{Cl}^-$  compositions, a binary mixture model can be used to calculate the  $\text{Cl}^-$  concentrations in groundwater because the resulting mixtures vary systematically depending on the relative abundance of the end-members.

The  $\text{Cl}^-$  concentration was used as a reference to estimate the  $\delta^{34}\text{S}_{[\text{SO}_4]}$  in groundwater. In a simple mixing model,  $\delta^{34}\text{S}_{[\text{SO}_4]}$  (Est.  $\delta^{34}\text{S}_{[\text{SO}_4]}$ ) behaved as a  $\text{Cl}^-$  conservative tracer, which had the same migration rates in specific sulfate sources. River water has a  $\text{Cl}^-$  concentration of 5.8 mg/L (Lanyang River), whereas the  $\text{Cl}^-$  concentration in seawater is 19,500 mg/L (Stumm and Morgan, 1981). The  $\text{Cl}^-$  concentration in groundwater from the Lanyang Plain resulted from the mixing of river water and seawater, and can be calculated using Eq. (1) (Schreiber and Mitch, 2006), as follows:

$$[\text{Cl}^-]_{\text{actual}} = X \times [\text{Cl}^-]_{\text{river}} + (1 - X) \times [\text{Cl}^-]_{\text{sea}} \quad (1)$$

where the fractions of river water and seawater are  $X$  and  $1 - X$ , respectively. Based on Eq. (1), the Est.  $\delta^{34}\text{S}_{[\text{SO}_4]}$  can be computed using Eq. (2), as follows:

$$\text{Est. } \delta^{34}\text{S}_{[\text{SO}_4]} = X \times [\delta^{34}\text{S}_{[\text{SO}_4]}]_{\text{river}} + (1 - X) \times [\delta^{34}\text{S}_{[\text{SO}_4]}]_{\text{sea}} \quad (2)$$

where the average  $\delta^{34}\text{S}_{[\text{SO}_4]}$  in river water and seawater is 1.47‰ and 20.1‰, respectively. The  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values in the Lanyang River (1.47‰) were similar to those in the Tanshui River (3–5‰; Hosono et al., 2011) and Yuanyang Lake (1.9–3.0‰; Chen, 2008). The actual and estimated  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values were then compared. Anthropogenic  $\text{SO}_4^{2-}$  inputs were not considered.

The redox reaction and various sulfur complexation or precipitation processes were not considered in the Est.  $\delta^{34}\text{S}_{[\text{SO}_4]}$ . Hence, the actual  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and Est.  $\delta^{34}\text{S}_{[\text{SO}_4]}$  may be different. To illustrate the distinct behavior of the actual  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and Est.  $\delta^{34}\text{S}_{[\text{SO}_4]}$ , four groups are depicted in Fig. 2.

In this study, discriminant analysis (DA), a multivariate method, was applied to delineate the redox zones in the As-enriched groundwater aquifer. DA was performed on the data matrix by using SPSS Version 12 in the standard mode (SPSS Inc., 1998). These representative parameters and levels were evaluated for each group, with reference to the classification correctness (hit ratio) of DA. The detailed principle of DA methods was performed by Lee et al. (2007). Most classifications of redox zones in groundwater aquifers have been mainly performed using redox sensitivity parameters such as dissolved oxygen, nitrate, dissolved Fe, and sulfide (Berner, 1981; Bjerg et al., 1995). In this study, we integrated the binary mixing model with DA to determine the various sulfur redox processes that may affect the sulfur isotopic composition of sulfate. Groundwater samples were initially classified into the following four types: I, pyrite-oxidation; II, iron- and sulfate-reducing; III, sulfate-reducing; and IV, anthropogenic and others. The classification criteria of the measured parameters of each groundwater sample (DO, Eh, pH, EC, Alk,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , As, Fe, Mn,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{As}^{3+}$ ,  $\text{As}^{5+}$ , TOC, and sulfur isotopes ( $\delta^{18}\text{O}_{[\text{SO}_4]}$  and  $\delta^{34}\text{S}_{[\text{SO}_4]}$ )) were determined using the results of the binary mixing model coupled with DA. Subsequently, the effectiveness of sulfur as a redox indicator and the criteria determined using DA was demonstrated. Most classifications of redox zones in groundwater aquifers were performed according to the concentration of dissolved oxygen (Berner, 1981; Bjerg et al., 1995; Christensen et al., 2000; Chen and Liu, 2003; Lee et al., 2007). Secondary indicators, such as nitrate, dissolved Fe, and sulfate, were then chosen as an assistant parameter. To demonstrate the effective redox indicator and the criteria determined using DA, this study selected three other classification criteria (dissolved oxygen,

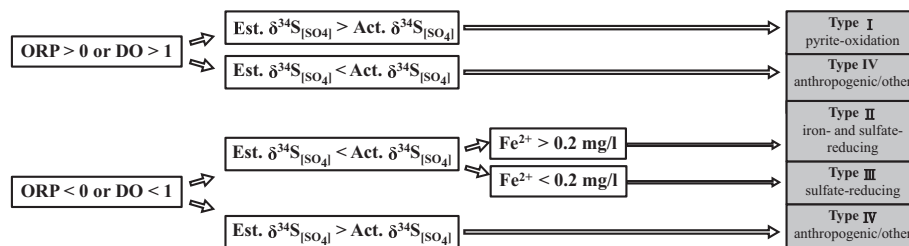


Fig. 2. Flow chart of the four redox zones grouped according to redox-sensitive indicator (ORP, DO, Act.  $^{34}\text{S}_{[\text{SO}_4]}$ , Est.  $^{34}\text{S}_{[\text{SO}_4]}$  and  $\text{Fe}^{2+}$ ).

dissolved Fe, and sulfur isotope compositions) proposed by Bjerg et al. (1995), Christensen et al. (2000), Chen and Liu (2003), Lee et al. (2007) and Buschmann and Berg (2009) for comparison.

### 3. Results and discussion

#### 3.1. Geochemical characteristics of redox zonation

The  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values of the groundwater of the Lanyang Plain widely ranged from  $-7.5\text{‰}$  to  $+60.5\text{‰}$ . The wide distributions of the  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values suggested varied redox conditions in the groundwater or a mix of diverse sulfate sources. Following the binary mixing model classification of four redox zones (Fig. 2), all groundwater samples were classified into one of the four types. In oxidized conditions where Est.  $\delta^{34}\text{S}_{[\text{SO}_4]} > \text{Act. } \delta^{34}\text{S}_{[\text{SO}_4]}$  (Type I), the lighter Act.  $\delta^{34}\text{S}_{[\text{SO}_4]}$  may be attributed to pyrite oxidation because the fractionation of sulfur isotopes is limited under pyrite oxidation conditions ( $-5\text{‰}$  to  $5\text{‰}$ ) (Toran and Harris, 1989; Van Stempvoort and Krouse, 1994). In reducing conditions where Est.  $\delta^{34}\text{S}_{[\text{SO}_4]} < \text{Act. } \delta^{34}\text{S}_{[\text{SO}_4]}$ , the heavier  $\delta^{34}\text{S}_{[\text{SO}_4]}$  may be affected by bacterial sulfate reduction (Andersson et al., 1992; Robertson and Schiff, 1994). The fractionation of  $^{34}\text{S}$  through bacterial sulfate reduction is more apparent than that through sulfide oxidation, resulting in heavier  $^{34}\text{S}$  isotopic compositions of residual sulfate ( $>49\text{‰}$ ; Canfield and Thamdrup, 1994). Furthermore, the reducing groups were split further; the wells where Est.  $\delta^{34}\text{S}_{[\text{SO}_4]} < \text{Act. } \delta^{34}\text{S}_{[\text{SO}_4]}$  were classified into iron- and sulfate-reducing (Type II) and sulfate-reducing (Type III) types if  $\text{SO}_4^{2-}$  was still measurable, which is a prerequisite for sulfate reduction (Kirk et al., 2004) (Fig. 2). Moreover, the wells where Est.  $\delta^{34}\text{S}_{[\text{SO}_4]} < \text{Act. } \delta^{34}\text{S}_{[\text{SO}_4]}$  were classified as Type II if the Fe concentration was  $>0.2$  mg/L, and Type III if Fe was  $<0.2$  mg/L (Buschmann and Berg, 2009). However, additional sulfate sources were not considered in these three types (Types I–III) and were attributed to other natural sources or anthropogenic sources (Type IV). These additional sulfate sources may include sulfate-rich manmade materials such as fertilizers or detergents and natural sources such as dissolved gypsum, anhydrite, or evaporates (Clark and Fritz, 1997; Vitòria et al., 2004; Hosono et al., 2011).

Samples were regarded as nonenriched  $^{34}\text{S}_{[\text{SO}_4]}$  and low  $\text{Fe}^{2+}$  with a low As content (Type I), enriched  $^{34}\text{S}_{[\text{SO}_4]}$  and high  $\text{Fe}^{2+}$  with a high As content (Type II), enriched  $^{34}\text{S}_{[\text{SO}_4]}$  and low  $\text{Fe}^{2+}$  with a moderate As content (Type III), and nonenriched  $^{34}\text{S}_{[\text{SO}_4]}$  with low  $\text{Fe}^{2+}$  and a low As content (Type IV) (Fig. 3). Type I is distributed in the proximal-fan area, in contrast to Types II and III, which are mostly located in the mid- and distal-fan areas of the redox zones of aquifers in the Lanyang Plain, indicating that the reduction potential increased from the proximal-fan (west) to the distal-fan (east) (Lee et al., 2007). Table 1 shows that the average As concentration in Type I groundwater samples (0.0003 mg/L) was lower than those in Type II (0.18 mg/L) and Type III (0.03 mg/L) groundwater samples. The high As concentration, low Eh value, and low

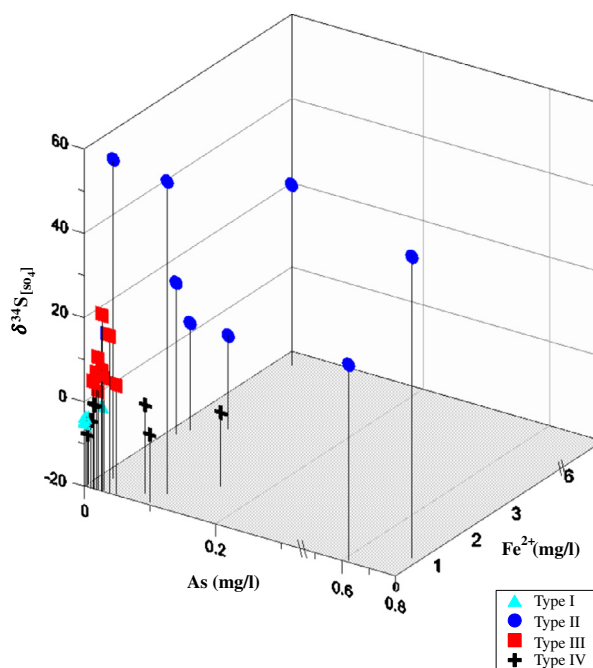


Fig. 3. Distribution of  $\delta^{34}\text{S}_{[\text{SO}_4]}$ ,  $\delta^{18}\text{O}_{[\text{SO}_4]}$  and As concentration of four types groundwater of the Lanyang Plain.

DO and  $\text{NO}_3^-$  concentrations in Type II and Type III groundwater explains their reductive conditions. Moreover, the high  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values associated with a low  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio and low Eh (Table 1) indicate that bacterial sulfate reduction may be involved in Type II and Type III groundwater samples (Andersson et al., 1992; Böttcher et al., 1999). By contrast,  $\text{SO}_4^{2-}/\text{Cl}^-$ , Eh, and DO values in Type I groundwater samples (Table 1) differed from those of Type II and Type III groundwater samples. According to the scatter plots of  $\delta^{18}\text{O}_{[\text{SO}_4]}$  versus  $\delta^{34}\text{S}_{[\text{SO}_4]}$  of Type I groundwater (Fig. 4a), oxidation of sulfide caused the low  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and high Eh value (Fig. 4b). Furthermore, all Type I groundwater samples originated in the proximal-fan area, a groundwater recharge region.

According to the results of the binary mixing model classification (Fig. 2), Est.  $\delta^{34}\text{S}_{[\text{SO}_4]} > \text{Act. } \delta^{34}\text{S}_{[\text{SO}_4]}$  values indicated that the reduced  $\delta^{34}\text{S}_{[\text{SO}_4]}$  value may have been caused by the dissolution of pyrite under oxidized conditions. However, low  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values were possibly caused by (1) the dissolution of  $^{16}\text{O}$ -enriched sulfate minerals (Taylor and Wheeler, 1994), (2) oxidation of  $^{16}\text{O}$ -enriched sulfate-bearing manmade sulfides such as chemical fertilizers and detergents (Krouse and Mayer, 2000), and (3) sulfide oxidation (Toran and Harris, 1989; Van Stempvoort and Krouse, 1994).

The considerably high concentrations of TOC (7.86 mg/L),  $\text{Fe}^{2+}$  (3.47 mg/L), and As (0.18 mg/L) corresponded to the high  $\delta^{34}\text{S}_{[\text{SO}_4]}$  levels (28.18‰) in Type II groundwater (Table 1; Fig. 4c, d, and f), which may enhance the reductive dissolution of Fe-oxides in a reducing environment (Lee et al., 2007; Liu et al.,

**Table 1**  
Chemical and isotopic composition (‰) of groundwater in Type I–Type IV regions of the Lanyang Plain.

| Samples   | Type I               |         | Type II              |         | Type III             |         | Type IV              |         |
|---|----------------------|---------|----------------------|---------|----------------------|---------|----------------------|---------|
|   | Minimum<br>(Average) | Maximum | Minimum<br>(Average) | Maximum | Minimum<br>(Average) | Maximum | Minimum<br>(Average) | Maximum |
| <i>Chemical composition</i>                       |                      |         |                      |         |                      |         |                      |         |
| DO (mg/L)   | 0.18<br>(1.69)       | 4.54    | 0.16<br>(0.63)       | 1.39    | 0.17<br>(0.56)       | 0.86    | 0.11<br>(0.40)       | 0.83    |
| Eh (mV)   | −125<br>(−47.98)     | 70      | −255<br>(−186)       | −97     | −269<br>(−200.56)    | −163    | −229<br>(−198.86)    | −141    |
| pH  | 6.65<br>(7.16)       | 7.46    | 7.06<br>(7.52)       | 8.06    | 7.51<br>(8.11)       | 8.36    | 6.80<br>(7.82)       | 8.51    |
| EC (μS/cm)  | 195<br>(383.29)      | 578     | 168<br>(2016.56)     | 107.00  | 133<br>(580.89)      | 1220    | 0<br>(811.7)         | 4000    |
| Cl <sup>−</sup> (mg/L)                            | 1<br>(2.43)          | 3.50    | 0.65<br>(1014.48)    | 7440    | 0.65<br>(24.62)      | 159     | 0.65<br>(18.6)       | 62.0    |
| SO <sub>4</sub> <sup>2−</sup> (mg/L)              | 51.60<br>(68.21)     | 90.20   | 3.40<br>(113.69)     | 958     | 4.00<br>(14.2)       | 39.50   | 1.15<br>(11.86)      | 20.9    |
| NO <sub>3</sub> <sup>−</sup> (mg/L)               | 0<br>(0.14)          | 0.34    | 0.02<br>(0.074)      | 0.18    | 0.02<br>(0.15)       | 0.02    | 0.02<br>(0.99)       | 0.29    |
| NH <sub>4</sub> <sup>+</sup> (mg/L)               | 0.01<br>(0.07)       | 0.14    | 0.31<br>(3.66)       | 10.70   | 0.04<br>(1.71)       | 4.86    | 0.10<br>(4.50)       | 20.20   |
| HS <sup>−</sup> (mg/L)                            | 0.01<br>(0.02)       | 0.02    | 0.01<br>(0.17)       | 0.02    | 0.02<br>(0.02)       | 0.02    | 0.01<br>(0.03)       | 0.09    |
| TOC (mg/L)  | 0.10<br>(0.19)       | 0.50    | 0.10<br>(7.86)       | 42.80   | 0.10<br>(2.04)       | 8       | 0.10<br>(13.76)      | 77.4    |
| Fe (mg/L)   | 0.02<br>(0.35)       | 0.78    | 0.21<br>(4.14)       | 19.50   | 0.07<br>(0.28)       | 0.53    | 0.05<br>(1.05)       | 4.31    |
| Mn (mg/L)   | 0.02<br>(0.37)       | 0.90    | 0.03<br>(0.16)       | 0.78    | 0.02<br>(0.94)       | 0.23    | 0.02<br>(0.11)       | 0.26    |
| Ca (mg/L)   | 27.50<br>(54.47)     | 73.20   | 4.57<br>(33.7)       | 144     | 2.21<br>(17.16)      | 45.50   | 4.78<br>(16.17)      | 26.9    |
| Mg (mg/L)   | 11.10<br>(19.16)     | 24.80   | 4.47<br>(48.84)      | 364     | 1.39<br>(8.10)       | 20.40   | 3.05<br>(7.58)       | 20.2    |
| Na (mg/L)   | 8.57<br>(14.47)      | 20.40   | 18.70<br>(694.1)     | 4270    | 10.70<br>(140.78)    | 320     | 16.30<br>(95.9)      | 283     |
| K (mg/L)  | 1.00<br>(1.52)       | 2.06    | 0.93<br>(30.37)      | 158     | 1.96<br>(14.45)      | 41.30   | 2.41<br>(14.32)      | 38.30   |
| Alkalinity  | 111<br>(226.86)      | 281     | 112<br>(389.78)      | 820     | 76.30<br>(444.9)     | 845     | 106<br>(365.86)      | 1100    |
| As (mg/L)   | 0<br>(0.00)          | 0       | 0<br>(0.18)          | 0.77    | 0.01<br>(0.03)       | 0.05    | 0.01<br>(0.05)       | 0.10    |
| SO <sub>4</sub> <sup>2−</sup> /Cl <sup>−</sup>    | 14.74<br>(34.34)     | 90.20   | 0.01<br>(2.37)       | 5.54    | 0.20<br>(7.98)       | 26.33   | 0.05<br>(1.81)       | 6.62    |
| Fe <sup>2+</sup>                                  | 0.00<br>(0.12)       | 0.39    | 0.20<br>(3.47)       | 14.26   | 0.00<br>(0.01)       | 0.03    | 0.00<br>(0.20)       | 1.03    |
| As <sup>3+</sup>                                  | 0.00<br>(0.55)       | 1.59    | 0.48<br>(176.48)     | 834.02  | 5.96<br>(24.46)      | 39.79   | 0.00<br>(44.8)       | 107.54  |
| <i>Isotopic composition</i>                       |                      |         |                      |         |                      |         |                      |         |
| δ <sup>18</sup> O <sub>[SO<sub>4</sub>]</sub> (‰) | −0.50<br>(2.29)      | 5.26    | 9.60<br>(15.53)      | 18.86   | 1.19<br>(13.1)       | 16.01   | −9.29<br>(4.29)      | 17.77   |
| δ <sup>34</sup> S <sub>[SO<sub>4</sub>]</sub> (‰) | −5.00<br>(−3.87)     | −3.12   | 2.36<br>(28.18)      | 60.54   | 3.56<br>(9.92)       | 21.92   | −7.54<br>(−2.40)     | 0.99    |
| δ <sup>18</sup> O <sub>[H<sub>2</sub>O]</sub> (‰) | −7.09<br>(−6.78)     | −6.52   | −6.57<br>(−4.95)     | −0.58   | −6.96<br>(−6.13)     | −4.87   | −6.72<br>(−6.00)     | −5.15   |
| δD <sub>[H<sub>2</sub>O]</sub> (‰)                | −42.59<br>(−39.34)   | −35.17  | −36.55<br>(−25.06)   | −1.35   | −40.75<br>(−6.06)    | −21.28  | −44.2<br>(−32.5)     | −23.43  |

2003; Baedecker and Back, 1979). Arsenic pollution in groundwater is affected by the high aqueous alkalinity and TOC in south-western Taiwan (Liu et al., 2003). The redox conditions control the dissolution and precipitation of As-bearing minerals, which release As into groundwater. The mineralization of OM progressively promotes the dissolution of calcite, increases alkalinity, and causes the reduction of arsenate to arsenite (Masscheleyn et al., 1991; Nickson et al., 2000). Hence, a high aqueous As<sup>3+</sup> concentration was observed in Type II groundwater. Moreover, the presence of Fe<sup>2+</sup> typically corresponds to dissolved As, Fe<sup>2+</sup>, and TOC in Type II groundwater, which is consistent with the mechanism of the reductive dissolution of Fe-oxyhydroxides through the respiration of OM in reducing conditions (Nickson et al., 2000). The binary mixing model classification (Fig. 2) revealed that the Est. δ<sup>34</sup>S<sub>[SO<sub>4</sub>]</sub> was lower than the Act. δ<sup>34</sup>S<sub>[SO<sub>4</sub>]</sub>. High Act. δ<sup>34</sup>S<sub>[SO<sub>4</sub>]</sub>

values were caused by substantial bacterial sulfate reduction accompanied by the reductive dissolution of FeOOH. Hence, Type II groundwater was classified as an iron- and sulfate-reducing type.

The scatter plots of the Eh value and SO<sub>4</sub><sup>2−</sup>/Cl<sup>−</sup> ratios versus enriched δ<sup>34</sup>S<sub>[SO<sub>4</sub>]</sub> in Type III groundwater were similar to those of the Type II groundwater (Fig. 4b and e), suggesting that bacterial sulfate reducing conditions were also the primary characteristics of those two groundwater types (Habicht and Canfield, 2001; Xie et al., 2013). Several field studies of marine sediments, lake sediments, and groundwater aquifers have reported that bacterial Fe reduction may occur simultaneously and continuously, with SO<sub>4</sub><sup>2−</sup> reduction occurring as long as the FeOOH in solids is bioavailable (Postma and Jakobsen, 1996; Washington et al., 2004). Although aqueous Fe<sup>2+</sup> concentrations increase in iron-reducing zones because of the dissolution of Fe (hydr)oxides, they decrease in

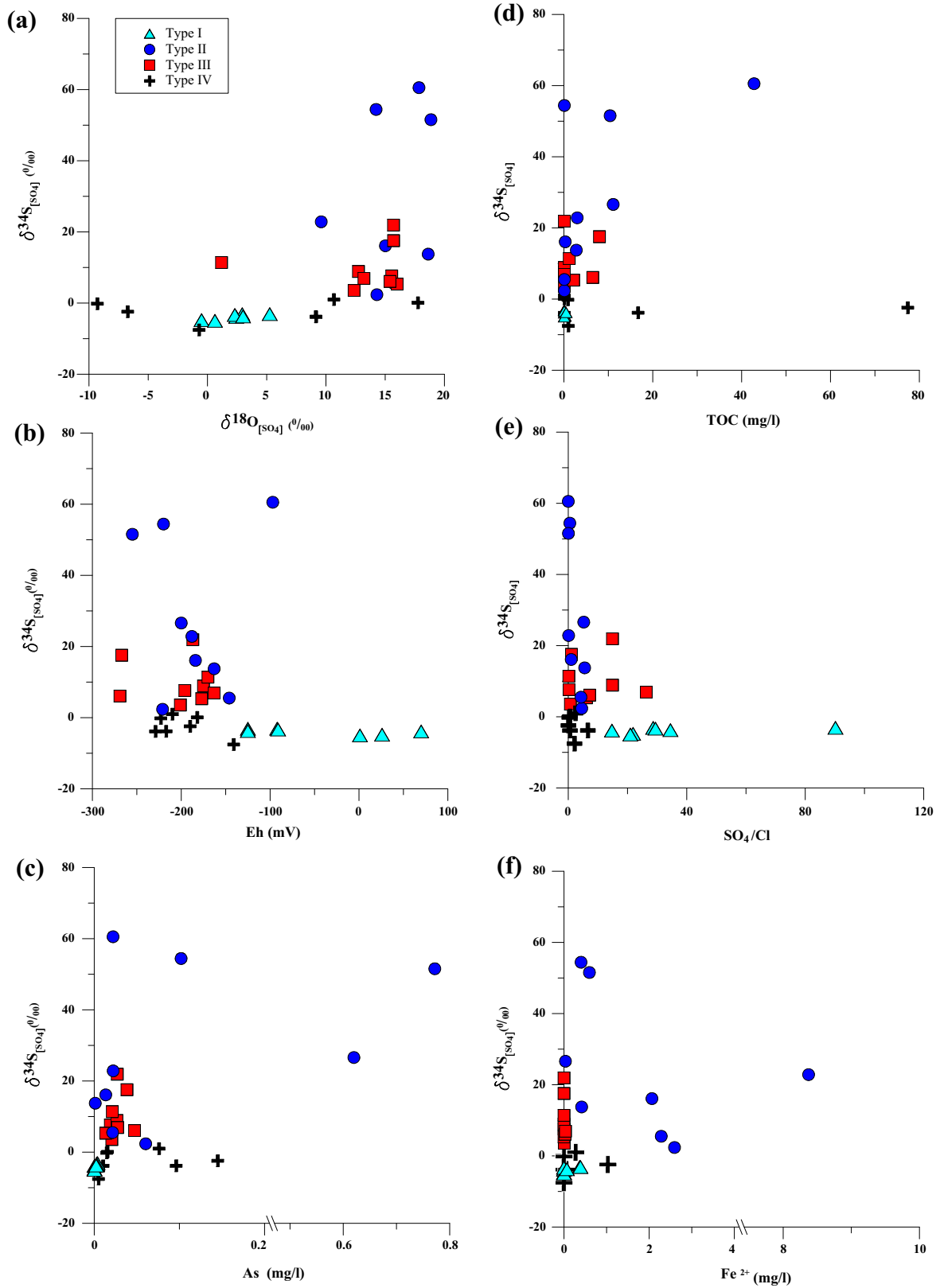


Fig. 4. Scatter plot of  $\delta^{34}\text{S}_{\text{SO}_4}$  and chemical parameters in four type groundwater samples of the Lanyang Plain.

sulfate-reducing zones, most probably because of the precipitation of FeS (Wolthers et al., 2005; Lowers et al., 2007). In sulfate-reducing zones (Type III), As concentrations exhibit lower levels than in Type II groundwater, either because of sorption to evolving

amorphous FeS (Wolthers et al., 2003) or the precipitation of amorphous As sulfide phases (Kober et al., 2005). Only three well samples belonged to Type IV groundwater, in which natural or anthropogenic  $\text{SO}_4^{2-}$  sources predominate.

The SI values of sulfide minerals, iron minerals, and carbon minerals were undersaturated (except for pyrite and orpiment) in the four types of groundwater from the Langyang Plain. Low correlations between the  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and SI values of various minerals ( $R^2 < 0.2$ ) indicated that multiple geochemical processes occurred. The reduction of Fe-oxides caused by organic matter is crucial for evaluating the water chemistry of enriched  $\text{Fe}^{2+}$  in reducing conditions (Heron and Christensen, 1995; Jakobsen and Postma, 1999; Tuccillo et al., 1999); therefore, the increase in enriched  $^{34}\text{S}$  may be caused by sulfate-reducing bacteria. Hence, Type II groundwater samples exhibited substantial negative SI values of iron minerals (e.g., ferrihydrite) and high  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values (Fig. 5a). The SI values of iron minerals (such as hematite ( $\text{Fe}_2\text{O}_3$ ), goethite ( $\text{FeOOH}$ ), and magnetite ( $\text{Fe}_3\text{O}_4$ )) are positive (see the Supplementary material, Appendix A). These minerals are commonly found in groundwater aquifers of the Lanyang Plain (Chen, 2000). Reductive dissolution of iron oxides mineral may increase the  $\text{Fe}(\text{II})$  concentration. The SI values of sulfide minerals such as pyrite and orpiment were positive, indicating that iron and sulfate reduction may proceed concurrently when the available iron oxides have a low solubility (Postma and Jakobsen, 1996) (Fig. 5b and c). Moreover, the negative SI values of FeS and low  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values in Type I groundwater indicated that the dissolution of FeS occurred under oxidized conditions (Fig. 5d). By contrast, the SI values of FeS in Type II and Type III groundwater were mildly undersaturated, which may have been caused by the precipitation of FeS under sulfate-reducing conditions (Fig. 5d). The SI values of calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) were mostly negative in Type I groundwater, and were mostly oversaturated in Type II and Type III groundwater (Fig. 5e and f). These results indicated that calcite and dolomite dissolved in Type I groundwater, whereas carbonate minerals formed gradually in Type II and Type III groundwater. Furthermore, slight oversaturation of calcite and dolomite and dissolution of gypsum–anhydrite in Type III may be expected under near equilibrium conditions of dedolomitization (see the Supplementary material, Supplementary material, Appendix A). The process of dedolomitization consists of dolomite dissolution and concurrent precipitation of calcite caused by the dissolution of gypsum–anhydrite (Back et al., 1983; Plummer et al., 1990). When oxygenated rainwater infiltrates Type I groundwater, it reacts with sediments, producing  $\text{NO}_3^-$ -N and possibly  $\text{SO}_4^{2-}$ , which are then transported by groundwater and reduced by reducing matter in the aquifer (e.g., organic compounds or Fe-bearing minerals). Both  $\text{Mg}^{2+}$  and sulfate are major components of seawater, and the negative SI values of magnesite ( $\text{MgCO}_3$ ) and sulfate minerals (gypsum and anhydrite; see Supplementary material, Appendix A) suggest that both minerals tend to dissolve in groundwater.

### 3.2. Geologic and anthropogenic effects on sulfur cycling

The probable sources of aqueous sulfate in the four types of groundwater in the Lanyang Plain are manmade sulfate-bearing materials (Krouse and Mayer, 2000), modern marine sediments (Clark and Fritz, 1997), and water from the Lanyang River (Fig. 6). The source of aqueous sulfate in Type I groundwater in the Lanyang Plain is the dissolution of  $^{34}\text{S}$ -depleted terrestrial evaporates from the proximal-fan area (Fig. 6). However, the  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values of Type I groundwater were higher than those of the solid-phase sulfate minerals (Table 2), indicating that the major sources of aqueous sulfate are not from terrestrial evaporates. Moreover, the  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\delta^{18}\text{O}_{[\text{SO}_4]}$  values of Type I shallow groundwater samples were similar to those of water from the Lanyang River, because Type I shallow groundwater samples were obtained from the unconfined aquifer corresponding to recharge areas, where river water can easily infiltrate. The  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and

$\delta^{18}\text{O}_{[\text{SO}_4]}$  values of Type I deep groundwater samples exhibited low  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values. According to the binary mixing model, the dissolution of pyrite under oxidized conditions resulted in low  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values and high Eh values, which are considered as the major sulfur redox processes in Type I deep groundwater (Fig. 7).

The distribution of Types II and III groundwater samples mostly corresponded to the paleomarine sulfate minerals and terrestrial evaporates area (Fig. 6). The dissolution of paleomarine sulfate minerals, formed during seawater transgression, may be the sulfate source. Specifically, the composition of the salinized groundwater sample from well DF01 ( $\text{Cl}^-$ , 7440 mg/L; Ca, 144 mg/L;  $\text{Na}^+$ , 4270 mg/L; and EC, 10 700  $\mu\text{S}/\text{cm}$ ) was close to that of modern seawater (Fig. 6). The infiltration of brackish water from fish ponds was a crucial source for salinizing the groundwater (Lee et al., 2007; Nath et al., 2008). Moreover, several Type II groundwater samples exhibited high  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values and were collected outside of the paleomarine sulfate minerals area, which was affected by substantial bacterial reduction of sulfate minerals (Fritz et al., 1989). Although the salinized groundwater of the Lanyang Plain is not more serious than other salinized groundwater in Taiwan, the highest  $\delta^{34}\text{S}_{[\text{SO}_4]}$  value (60.5‰) detected in the groundwater samples of well CT02 exhibited high  $\text{Cl}^-$  (1500 mg/L),  $\text{Na}^+$  (1250 mg/L), and EC values (5131  $\mu\text{S}/\text{cm}$ ), moderate As concentrations (0.012 mg/L), and a low  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio (0.01) (Fig. 6). The groundwater of well CT02 may be affected by perched brackish groundwater, as well as by the underused sulfate pool from paleoseawater intrusion (Mukherjee and Fryar, 2008).  $^{14}\text{C}$  and  $^3\text{H}$  (radiotritium isotope) dating revealed that substantial bacterial sulfate reduction of paleoseawater may result in the coprecipitation of sulfide and As (Peng et al., 1995; Zheng et al., 2004).

Enriched  $\delta^{18}\text{O}_{[\text{SO}_4]}$  in Type II, Type III, and Type IV groundwater suggests that complex biogeochemical reactions or an external source of  $^{18}\text{O}$  were involved in sulfate formation. Previous studies have reported that high  $^{18}\text{O}$ -enriched sulfate may be caused by the dissolution of sulfate-bearing manmade materials such as chemical fertilizers and detergents (Krouse and Mayer, 2000; Vitòria et al., 2004). Although the sulfate isotopic compositions of Type II and III groundwater samples were in the range of chemical fertilizers and detergents, groundwater samples were obtained mostly from deep aquifers (Table 2). Thus, the infiltration of surface water containing sulfate-bearing manmade materials is unlikely. However, Type IV groundwater samples were mostly obtained from shallow aquifers, and their sulfate isotopic compositions were close to the range of chemical fertilizers (except for groundwater from the TS01, LJ02, and ED01 wells; Fig. 6). Hence, the sulfate in Type IV groundwater samples can be attributed to anthropogenic sources (Fig. 7), whereas the other three wells may have been affected by natural sources such as terrestrial evaporates (Fig. 6).

The correlations among the As contents, sediment material, and geological ages of the core samples observed in Bangladesh are similar to those found in the coastal aquifer of the Lanyang Plain (Lee, 2008). The core sediments of Type II and Type III samples were formed by the alternating invasion and retreat of seawater, with interlayered marine and nonmarine sequences. The high As content in the marine formation with a high clay content may be attributed to the bioaccumulation and biotransformation of As in sea organisms, which are then accrued and deposited in the formation (Francesconi and Edmonds, 1997; Francesconi et al., 1998). Most clayey layers consist of small particles with a large surface area, which may have a high adsorption capacity for As (Smith et al., 1991; Lee, 2008). According to the result of  $^{14}\text{C}$  dating (Central Geological Survey, <http://www.moecgs.gov.tw/main.jsp>), the geologic ages of the Type II and Type III core samples can be grouped into  $8113 \pm 73$  to  $9620 \pm 80$  and  $2126 \pm 49$  to  $11,960 \pm 70$  years ago in the Lanyang Plain (Table 2), respectively,



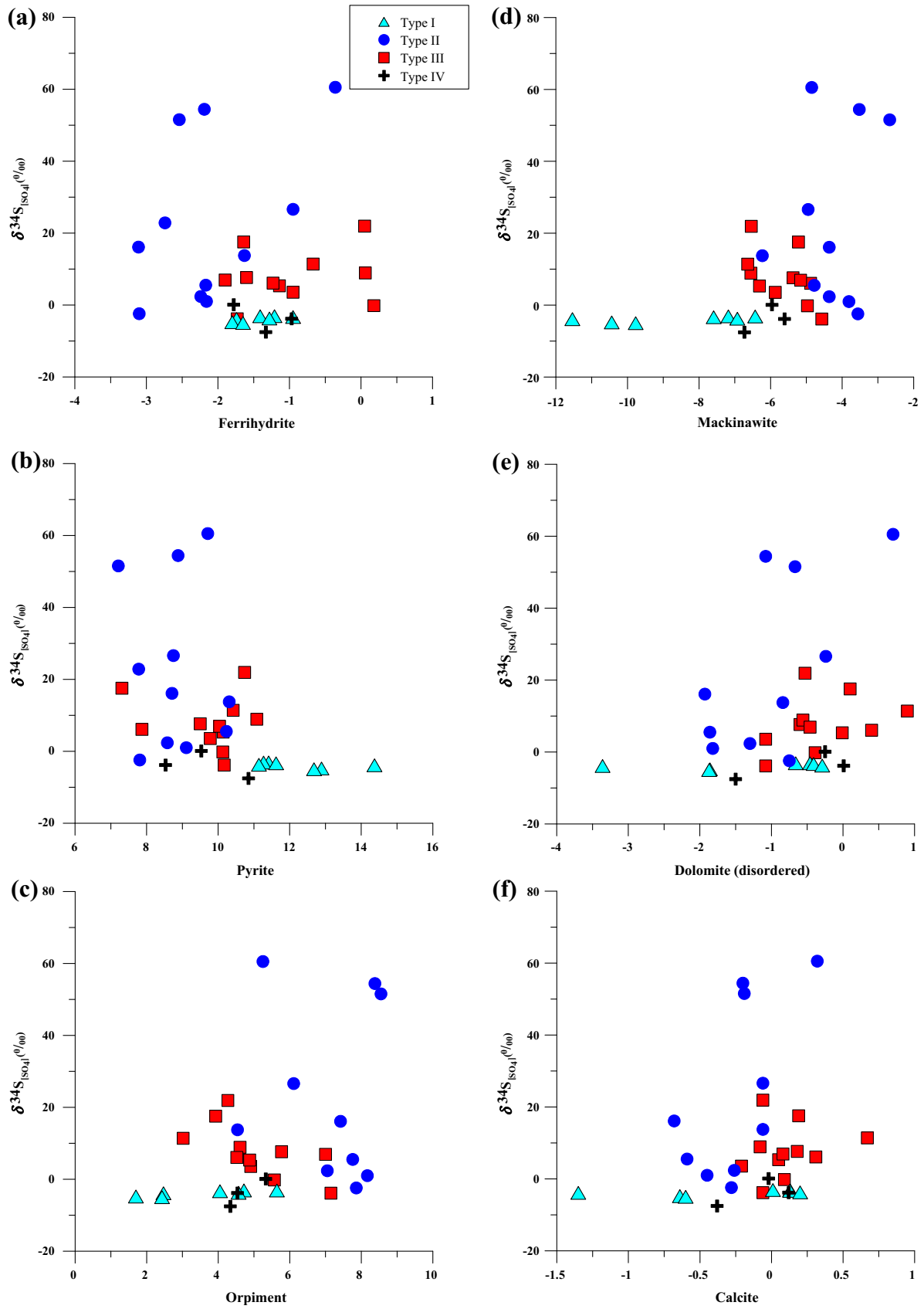
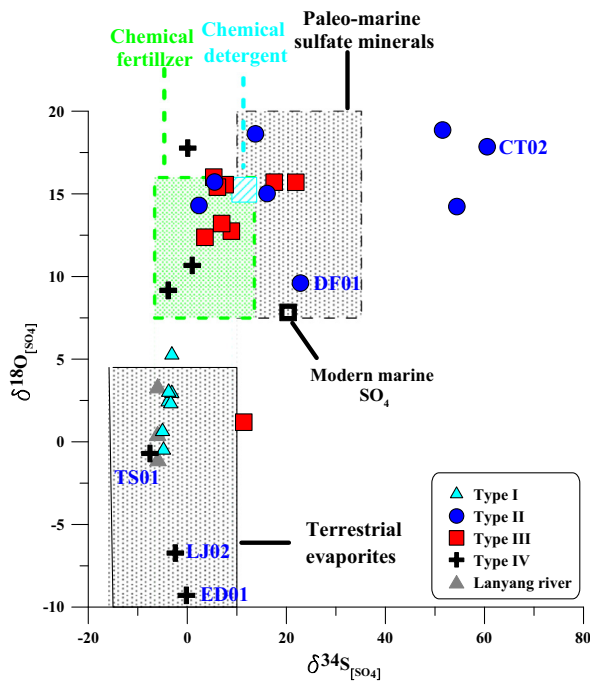


Fig. 5. Scatter plots of  $\delta^{34}\text{S}_{\text{SO}_4}$  (‰) and SI values of minerals in the Lanyang Plain.



**Fig. 6.** Scatter plot of  $\delta^{18}\text{O}_{[\text{SO}_4]}$  and  $\delta^{34}\text{S}_{[\text{SO}_4]}$  in four type groundwater/river samples of the Lanyang Plain. The reference data of isotopic compositional ranges of sulfate are from sulfate-bearing manmade material (Krouse and Mayer, 2000) terrestrial evaporates and paleo-marine sulfate mineral (Clark and Fritz, 1997).

corresponding to the Holocene transgression. Lee (2008) demonstrated the moderate correlation between the As and Fe contents in the core samples of the marine sequence ( $R^2 = 0.37$ ) and the high As contents in marine formations. Elevated As concentrations in groundwater in the mid- and distal-fan areas are responsible for the reductive dissolution of As-bearing Fe oxides, a process associated with the mineralization of organic carbon in a reducing environment. (Lee, 2008; Chen, 2001). High  $^{18}\text{O}$  enrichment factors in Type II and Type III groundwater samples were mainly contributed by microbial disproportionation reactions and bacterial sulfate reduction under anaerobic conditions (Kao et al., 2011). Hence, anaerobic bacterial disproportionation of sulfide may have occurred in this discharge area of the coastal aquifer during the Holocene transgression.

### 3.3. Effects of sulfate/sulfide cycling on As enrichment

The binary mixing model combined with DA yielded a correct (97.1%) classification (Fig. 2). The correctness of the classification in this study was compared with that of Bjerg et al. (1995) and Christensen et al. (2000) (79.5%), Chen and Liu (2003) (71.8%), and Lee et al. (2007) (92.3%), indicating that the estimated  $\delta^{34}\text{S}_{[\text{SO}_4]}/\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\text{Fe}^{2+}$  concentrations were effective redox indicators for spatially delineating the redox zones (Table 3). The high  $\text{SO}_4^{2-}/\text{Cl}^-$ , Eh, and DO values and the low  $\delta^{34}\text{S}_{[\text{FeS}_2]}$  and  $\epsilon^{34}\text{S}_{[\text{FeS}_2-\text{SO}_4]}$  values ( $-3.1\text{‰}$  and  $-0.75\text{‰}$ , respectively) implied that the Type I sediment samples were under oxidizing conditions. Because biotic and abiotic oxidized dissolution of sulfide cannot fractionate S

**Table 2**  
Sulfur and oxygen isotopic compositions (‰) in groundwater/sediment of the Lanyang Plain.

| No.    | Type | Depth (m) | Date       | Aqueous phase                         |                                       |  | Solid phase                            |  |  | Enrichment factor         |                           | $^{14}\text{C}$ dating (yr) <sup>c</sup> |
|--------|------|-----------|------------|---------------------------------------|---------------------------------------|--|--|--|--|---------------------------|---------------------------|--|
|        |      |           |            | $\delta^{18}\text{O}_{[\text{SO}_4]}$ | $\delta^{34}\text{S}_{[\text{SO}_4]}$ | $\delta^{18}\text{O}_{[\text{H}_2\text{O}]}$ | $\delta^{34}\text{S}_{[\text{FeS}_2]}$ | $\delta^{34}\text{S}_{[\text{sulfate}]}$ | $\delta^{18}\text{O}_{[\text{sulfate}]}$ | $\epsilon^{34}\text{S}^a$ | $\epsilon^{18}\text{O}^b$ |  |
| DT01-2 | I    | 50        | 2010/7/28  | 2.42                                  | -3.89                                 | -6.95  | -3.14                                  | -15.80                                   | -  | -0.75                     | 9.37                      | 8113 ± 73                                |
| DY02   | I    | 148       | 2008/10/29 | -0.50                                 | -4.80                                 | -6.52  | -                                      | -  | -  | -                         | 6.02                      | -  |
| DY02-2 | I    | 148       | 2010/7/28  | 0.63                                  | -5.00                                 | -6.69  | -                                      | -  | -  | -                         | 7.32                      | 9620 ± 80                                |
| DJ01   | I    | 34        | 2008/10/29 | 5.26                                  | -3.12                                 | -6.77  | -                                      | -  | -  | -                         | 12.03                     | 2126 ± 49                                |
| DJ01-2 | I    | 34        | 2010/7/28  | 2.94                                  | -3.14                                 | -7.09  | -                                      | -12.21                                   | -  | -                         | 10.03                     | 3400 ± 70                                |
| DJ02   | I    | 111       | 2008/10/29 | 2.31                                  | -3.35                                 | -6.67  | -                                      | -  | -  | -                         | 8.98                      | 6030 ± 30                                |
| DJ02-2 | I    | 111       | 2010/7/28  | 3.00                                  | -3.77                                 | -6.74  | -                                      | -  | -  | -                         | 9.74                      | -  |
| YL01   | II   | 27.5      | 2010/7/26  | 14.23                                 | 54.42                                 | -5.92  | -                                      | -  | -  | -                         | 20.15                     | -  |
| LD03   | II   | 109       | 2010/7/27  | 18.86                                 | 51.54                                 | -5.58  | -                                      | -  | -  | -                         | 24.45                     | -  |
| WS01   | II   | 60.5      | 2010/7/26  | 15.02                                 | 16.10                                 | -5.69  | -                                      | -  | -  | -                         | 20.71                     | 6110 ± 40                                |
| WS02   | II   | 147       | 2010/7/26  | 14.30                                 | 2.36                                  | -6.08  | -                                      | -  | -  | -                         | 20.38                     | 8113 ± 73                                |
| GT02-2 | II   | 109       | 2008/10/28 | 17.85                                 | 60.54                                 | -0.58  | -10.30                                 | -  | -  | 70.84                     | 18.43                     | -  |
| WJ04   | II   | 164       | 2010/7/28  | -                                     | 26.60                                 | -6.51  | 14.00                                  | 12.75                                    | -23.35                                   | 12.60                     | -                         | 5576 ± 40                                |
| CS01   | II   | 30        | 2010/7/27  | 15.72                                 | 5.51                                  | -5.92  | -                                      | -  | -  | -                         | 21.64                     | 9440 ± 70                                |
| CS03   | II   | 186       | 2010/7/27  | 18.63                                 | 13.75                                 | -6.57  | -                                      | -  | -  | -                         | 25.20                     | 11900 ± 70                               |
| DF01   | II   | 24.5      | 2009/7/1   | 9.60                                  | 22.84                                 | -1.74  | -                                      | -  | -  | -                         | 11.34                     | 11960 ± 40                               |
| LJ01   | III  | 25        | 2010/7/27  | 12.38                                 | 3.56                                  | -4.87  | -7.60                                  | -  | -  | 11.16                     | 17.24                     | 2800 ± 70                                |
| LD01   | III  | 25        | 2010/7/27  | 15.55                                 | 7.63                                  | -5.36  | -                                      | -  | -  | -                         | 20.91                     | 7750 ± 40                                |
| LD02   | III  | 69        | 2010/7/27  | 15.71                                 | 17.54                                 | -5.33  | -                                      | -  | -  | -                         | 21.04                     | 9090 ± 270                               |
| JW01   | III  | 63        | 2010/7/28  | 16.01                                 | 5.33                                  | -6.44  | -2.90                                  | -7.30                                    | 0.04                                     | 8.23                      | 22.45                     | -  |
| JW02   | III  | 118       | 2010/7/28  | 15.70                                 | 21.92                                 | -6.62  | -1.80                                  | 11.18                                    | 12.28                                    | 23.72                     | 22.32                     | -  |
| JW03   | III  | 168       | 2010/7/28  | 12.74                                 | 8.89                                  | -6.68  | -2.70                                  | -4.23                                    | -1.07                                    | 11.59                     | 19.43                     | -  |
| WJ03   | III  | 73        | 2010/7/28  | 15.41                                 | 6.08                                  | -6.68  | 0.10                                   | 1.26                                     | -1.44                                    | 5.98                      | 22.09                     | -  |
| CS02   | III  | 115       | 2010/7/27  | 13.21                                 | 6.93                                  | -6.96  | -7.20                                  | -  | -  | 14.13                     | 20.16                     | -  |
| JS01   | III  | 32        | 2009/7/1   | 1.19                                  | 11.39                                 | -6.27  | -                                      | -  | -  | -                         | 7.45                      | -  |
| ED01   | IV   | 32        | 2009/7/1   | -9.29                                 | -0.19                                 | -6.32  | -                                      | -  | -  | -                         | -2.97                     | -  |
| GT01   | IV   | 37        | 2010/7/26  | 17.77                                 | 0.08                                  | -6.38  | -                                      | -  | -  | -                         | 24.14                     | -  |
| WJ01   | IV   | 9         | 2010/7/28  | 9.16                                  | -3.84                                 | -6.72  | -5.40                                  | -6.71                                    | -1.50                                    | 1.56                      | 15.88                     | -  |
| TS01   | IV   | 13        | 2009/7/1   | -0.70                                 | -7.54                                 | -5.65  | -                                      | -  | -  | -                         | 4.95                      | -  |
| DS01   | IV   | 38.5      | 2010/7/27  | 10.67                                 | 0.99                                  | -5.34  | -                                      | -  | -  | -                         | 16.02                     | -  |
| DS02   | IV   | 77        | 2010/7/27  | 9.16                                  | -3.86                                 | -5.15  | -                                      | -  | -  | -                         | 14.31                     | -  |
| LJ02   | IV   | 164       | 2009/7/1   | -6.73                                 | -2.43                                 | -6.45  | -13.27                                 | -  | -  | 10.84                     | -0.28                     | 10510 ± 60                               |

<sup>a</sup> The enrichment factor of  $\epsilon^{34}\text{S}_{[\text{FeS}_2-\text{SO}_4]}$  as  $\delta^{34}\text{S}$  of pyrite minus  $\delta^{34}\text{S}$  of sulfate.

<sup>b</sup> The enrichment factor of  $\epsilon^{18}\text{O}_{[\text{SO}_4-\text{H}_2\text{O}]}$  as  $\delta^{18}\text{O}$  of sulfate minus  $\delta^{18}\text{O}$  of  $\text{H}_2\text{O}$ .

<sup>c</sup> The data source of  $^{14}\text{C}$  dating is from Central Geological Survey <http://www.moeacgs.gov.tw/main.jsp>.

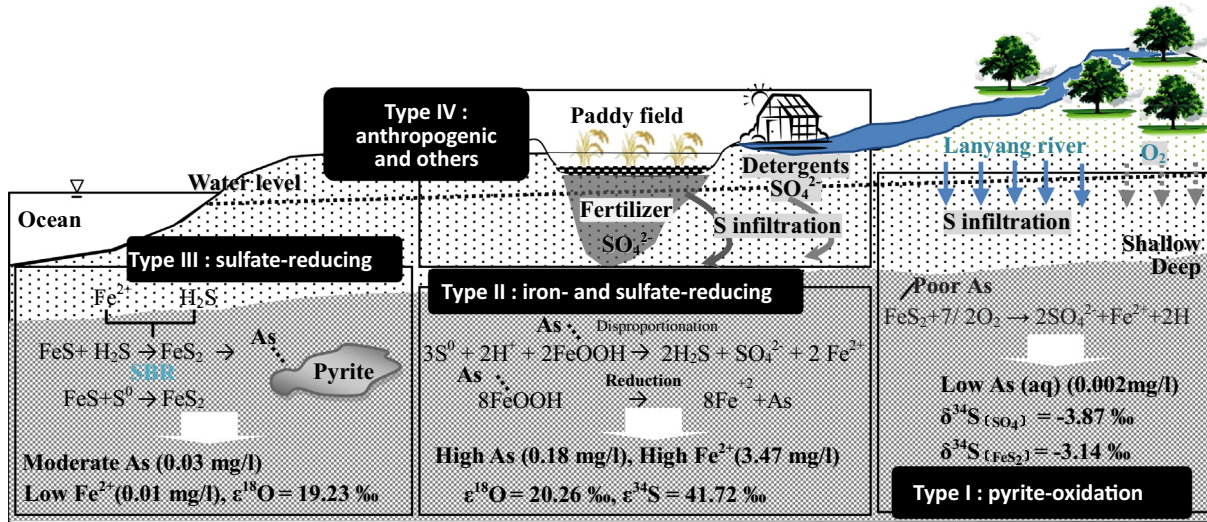
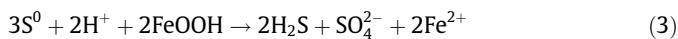


Fig. 7. Conceptual diagram of sulfidogenesis cycling on the As redox processes in the Lanyang Plain. (SRB: sulfate reducing bacteria).

isotopes (Nakai and Jensen, 1964; Taylor et al., 1984), Type I ground-water samples may have experienced sulfide oxidation. However, the  $\delta^{34}\text{S}_{[\text{SO}_4]}$  values of Type I groundwater were higher than those of solid-phase sulfate minerals (Table 2), indicating that sulfate minerals are minor sources of aqueous  $\text{SO}_4$ . The major sulfur redox process in Type I samples was pyrite oxidation, which agreed with the result of the binary mixing model (Fig. 2). Fig. 7 shows that sediment containing a low As concentration promotes the oxidation of As-containing pyrite and maintains low groundwater As levels in the proximal-fan area of the Lanyang Plain (Lee, 2008).

By contrast, the  $\delta^{34}\text{S}_{[\text{FeS}_2]}$  and  $\epsilon^{34}\text{S}_{[\text{FeS}_2-\text{SO}_4]}$  values ranged from  $-15.8\text{‰}$  to  $14.0\text{‰}$  and  $-0.75\text{‰}$  to  $70.8\text{‰}$  in Type II and Type III samples, respectively (Table 2). Depletions of  $^{34}\text{S}$  mostly exceeded  $45\text{‰}$ , indicating that bacterial disproportionation was involved in the Type II and Type III groundwater samples (Canfield and Thamdrup, 1994; Habicht and Canfield, 2001). However, Rudnicki et al. (2001), Wortmann et al. (2001), and Habicht and Canfield (2001) suggested that sulfur isotope fractionation up to  $70\text{‰}$  may also be directly caused by dissimilatory sulfate reduction. Therefore, the isotope compositions of  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\delta^{18}\text{O}_{[\text{SO}_4]}$  coupled with the As and Fe concentrations should be considered to differentiate these two processes.

The enriched  $\delta^{34}\text{S}_{[\text{SO}_4]}$  together with the high As and high  $\text{Fe}^{2+}$  levels in Type II groundwater from the Lanyang Plain suggests that other biogeochemical reactions may occur under anaerobic conditions. The relative enrichment of the  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\delta^{18}\text{O}_{[\text{SO}_4]}$  content in Type II and Type III groundwater (Fig. 4a) is caused by disproportionation processes (Böttcher et al., 2001) or bacterial sulfate reduction (Fritz et al., 1989), or both. However, the process of bacterial sulfate reduction may coprecipitate or sequester As, lowering As concentrations, as observed in the Type II groundwater (Zheng et al., 2004). Eq. (3) accounts for the  $\delta^{18}\text{O}_{[\text{SO}_4]}$  enrichment and for As and Fe mobility in the anaerobic bacterial disproportionation processes (Böttcher et al., 2001; Kao et al., 2011).



The high fractionation factor of  $\epsilon^{18}\text{O}_{[\text{SO}_4-\text{H}_2\text{O}]}$  in Type II groundwater (avg.  $20.0\text{‰}$ ; Table 2) indicate that anaerobic bacterial disproportionation in the presence of  $\text{MnO}_2$ ,  $\text{FeOOH}$ , and  $\text{FeCO}_3$  may

result in the reductive dissolution of Mn and Fe oxides and enrichment of  $^{18}\text{O}$  in the sulfate (Böttcher et al., 2001; Böttcher and Thamdrup, 2001; Lipfert et al., 2007), increasing the groundwater As and  $\text{Fe}^{2+}$  levels (Eq. (3)). Moreover, arsenite is the primary species in Type II groundwater ( $[\text{As(III)}] > [\text{As(V)}]$  in 96% of groundwater samples). Therefore, Fe-oxides act as a crucial electron acceptor in the As-enriched sediment of the Lanyang Plain, causing the coupled adsorption of As on the surface of Fe-oxides and their reductive dissolution into groundwater (Lyngkilde and Christensen, 1992; Heron and Christensen, 1995; Chen, 2001; Lee et al., 2007). Seiler et al. (2011) suggested that high  $\epsilon^{18}\text{O}$  values (up to  $20\text{‰}$ ) probably result from sulfur cycling caused by bacterial sulfate reduction and abiotic oxidation of  $\text{H}_2\text{S}$  to  $\text{S}^0$  by Mn oxides, followed by bacterial disproportionation of  $\text{S}^0$ . Therefore, the high  $\epsilon^{18}\text{O}_{[\text{SO}_4-\text{H}_2\text{O}]}$  and high  $\epsilon^{34}\text{S}_{[\text{SO}_4-\text{FeS}_2]}$  values in Type II groundwater samples indicated that the reductive dissolution of As-bearing Fe oxyhydroxides together with the microbial disproportionation of sulfur explain the substantial correlation among the high As concentration, high  $\text{Fe}^{2+}$ , and enriched  $\delta^{18}\text{O}_{[\text{SO}_4]}$ , which conform to the proposed iron- and sulfate-reducing processes (Fig. 7). Furthermore, the reduction of As enriched-amorphous Fe(III) hydroxides with the minor microbial reduction of  $\text{SO}_4^{2-}$  under the moderate reducing condition may result in the observed positive correlation between  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\text{Fe}^{2+}$  concentrations in Type II (Xie et al., 2013; Fig. 4f) and high  $\text{Fe}^{2+}$  concentrations (Fig. 7).

The relative enrichment of the  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\delta^{18}\text{O}_{[\text{SO}_4]}$  content in Type III groundwater is similar to that in Type II groundwater (Fig. 4a), which may be caused by either disproportionation processes or bacterial sulfate reduction. The high  $\epsilon^{18}\text{O}_{[\text{SO}_4-\text{H}_2\text{O}]}$  values, low As, and low  $\text{Fe}^{2+}$  contents in Type III groundwater samples indicate that the disproportionation reaction (Eq. (3)), followed by the reactions represented by Eqs. (4) and (5), generate pyrite (Wilkin and Barnes, 1996; Böttcher et al., 2001). By contrast, the reduction of crystalline Fe(III) hydroxides and  $\text{SO}_4^{2-}$  in a strongly sulfate-reducing environment can preferentially produce Fe sulfide and pyrite precipitation (Matsunaga et al., 1993; Xie et al., 2013) and result in a negative correlation between  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\text{Fe}^{2+}$  concentrations in Type III groundwater (Fig. 4f). Hence, the bacterial sulfate reduction and disproportionation reaction generated Fe sulfide and/or pyrite, which coprecipitates with As, producing Type III groundwater. Arsenic-sulfide phases indicate the existence of sulfate-reducing conditions, which result in low As and low  $\text{Fe}^{2+}$  contents in Type III groundwater (Fig. 7).

**Table 3**  
The comparison of the classification accuracies of redox zonation by various DA models.

|   | Type I   | Type III   | Type IV  | Accuracy (%) |
|---|--|--|--|--------------|
| Bjerg et al. (1995) and Christensen et al. (2000) | DO $\geq 1$ mg/L   | DO < 1 mg/L  |  |              |
| Chen and Liu (2003)                               | DO $\geq 0.5$ mg/L and NO <sub>3</sub> <sup>-</sup> $\geq 0.5$ mg/L  | NO <sub>3</sub> <sup>-</sup> $\geq 0.2$ mg/L<br>DO < 0.5 mg/L and NO <sub>3</sub> <sup>-</sup> < 0.5 mg/L  | HS <sup>-</sup> $\geq 0.1$ mg/L<br>DO, NO <sub>3</sub> <sup>-</sup> < 0.5 mg/L and HS <sup>-</sup> $\geq 0.03$ mg/L  | 79.5         |
| Lee et al. (2007)                                 | DO $\geq 1$ mg/L or NO <sub>3</sub> <sup>-</sup> $\geq 0.5$ mg/L<br>↑ oxidizing  | 0.3 mg/L $\leq$ DO < 1 mg/L or NO <sub>3</sub> <sup>-</sup> < 0.35 mg/L<br>↑ transition  | DO < 0.3 mg/L or HS <sup>-</sup> $\geq 0.07$ mg/L<br>↑ reducing  | 71.8         |
| Buschmann and Berg, 2009                          | Est. SO <sub>4</sub> <sup>a</sup> $\leq$ Act. <sup>b</sup> SO <sub>4</sub> and Fe <sup>2+</sup> > 0.2 mg/L<br>↑ iron-reducing            | Est. SO <sub>4</sub> $\geq$ Act. SO <sub>4</sub> and SO <sub>4</sub> > 0<br>↑ sulfate-reducing   | Est. SO <sub>4</sub> $\leq$ Act. SO <sub>4</sub> and Fe <sup>2+</sup> < 0.2 mg/L<br>↑ neither Fe nor S-reducing  | 92.3         |
| Current study (Lanyang)                           | ORP > 0 or DO > 1 mg/L and Est. $\delta^{34}\text{S}_{[\text{SO}_4]}$ > Act. $\delta^{34}\text{S}_{[\text{SO}_4]}$<br>↑ pyrite-oxidation | ORP < 0 or DO < 1 mg/L and Est. $\delta^{34}\text{S}_{[\text{SO}_4]}$ < Act. $\delta^{34}\text{S}_{[\text{SO}_4]}$ and Fe <sup>2+</sup> > 0.2 mg/L<br>↑ iron- and sulfate-reducing | ORP < 0 or DO < 1 mg/L and Est. $\delta^{34}\text{S}_{[\text{SO}_4]}$ < Act. $\delta^{34}\text{S}_{[\text{SO}_4]}$ and Fe <sup>2+</sup> < 0.2 mg/L<br>↑ sulfate-reducing | 97.1         |

<sup>a</sup> The Cl<sup>-</sup> concentration from seawater/river was used as reference for the estimation of sulfate concentration (Est. SO<sub>4</sub>) that was expected in the groundwater.

<sup>b</sup> The measured value.

<sup>c</sup> The Cl<sup>-</sup> concentration from seawater/river was used as reference for the estimation of  $\delta^{34}\text{S}_{[\text{SO}_4]}$  (Est.  $\delta^{34}\text{S}_{[\text{SO}_4]}$ ) that was expected in the groundwater.

## 4. Conclusion

This study investigated the effects of sulfate/sulfide cycling on As mobility in the groundwater of the Lanyang Plain by using sulfur isotopic compositions, multivariate statistical analyses, and geochemical simulations. The high correctness of the classification (97.1%) by using DA coupled with a binary mixing model suggests that the DO/ORP values,  $\delta^{34}\text{S}_{[\text{SO}_4]}$ , and Fe<sup>2+</sup> concentrations are effective redox-sensitive indicators for delineating redox zones. The low values 2.29‰, -3.9‰, -3.1‰ and -0.75‰ of  $\delta^{18}\text{O}_{[\text{SO}_4]}$ ,  $\delta^{34}\text{S}_{[\text{SO}_4]}$ ,  $\delta^{34}\text{S}_{[\text{FeS}_2]}$ , and  $\epsilon^{34}\text{S}_{[\text{FeS}_2-\text{SO}_4]}$ , respectively, in Type I groundwater implied that pyrite oxidation may be caused by the oxidizing conditions in the mountainous recharge area. However, the oxidation of poor As-containing pyrite resulted in low groundwater As levels in Type I groundwater. The high fractionation factor of  $\epsilon^{18}\text{O}_{[\text{SO}_4-\text{H}_2\text{O}]}$  in Type II groundwater (avg. 20.0‰) indicated that the reductive dissolution of Fe-oxyhydroxides, together with bacterial disproportionation reactions and bacterial sulfate reduction, is responsible for the high As and high Fe<sup>2+</sup> concentrations in Type II groundwater (iron- and sulfate-reducing). Additionally, the SI values of iron minerals (such as ferrihydrite, hematite, and goethite), were slightly negative in Type II groundwater, suggesting that Fe-oxides were dissolved as well. The high  $\epsilon^{18}\text{O}_{[\text{SO}_4-\text{H}_2\text{O}]}$  values (avg. 19.2‰), low As, and low Fe<sup>2+</sup> contents in Type III groundwater samples revealed that the reduction of crystalline Fe(III) hydroxides and SO<sub>4</sub><sup>2-</sup> in a strongly sulfate-reducing environment can preferentially produce Fe sulfide and/or pyrite precipitation and result in a negative correlation between  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and Fe<sup>2+</sup> concentrations. Moreover, the range of  $\delta^{34}\text{S}_{[\text{SO}_4]}$  and  $\delta^{18}\text{O}_{[\text{SO}_4]}$  from sulfate-bearing manmade materials such as fertilizers was similar to that in Type IV groundwater samples, which were thus affected by anthropogenic sulfate sources, whereas a few wells may have been affected by natural sulfate sources such as dissolved gypsum. However, the correlation between As and anthropogenic sulfate is not clear. This study successfully used sulfur isotopes and the binary mixing model to evaluate the effects of sulfate/sulfide cycling on As enrichment. Pyrite oxidation, bacterial sulfate reduction, and elemental sulfur disproportionation were identified as the major biogeochemical processes of sulfur cycling in As-enriched groundwater in the Lanyang Plain.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhydrol.2015.06.033>.

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