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Hydrogeochemical and mineralogical investigations of arsenic- and humic substance-enriched aquifers

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SUMMARY

This study investigated the hydrogeochemical and mineralogical characteristics of arsenic-contaminated and humic-substance-enriched aquifers in the Chianan Plain, Taiwan, which is an endemic area for blackfoot disease (BFD). Factorial analysis (FA) was used to evaluate the hydrochemical characteristics of 83 groundwater samples in the Chianan Plain, and 462 geological core samples obtained from 9 drilling wells were collected to analyze their arsenic and iron contents. The major mineral phases and chemical components were determined using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy and energy dispersive spectrometry (SEM–EDS). Partition of arsenic among various hosting solids in sediments was determined by sequential extraction. The results of FA showed that the hydrochemical characteristics of the groundwater samples could be grouped by 4 factors: salinization, arsenic, sulfide, and iron. Arsenic was positively correlated with alkalinity, dissolved organic/inorganic carbon, and fluorescence intensity [humic acids, (HAs)]. As(V) has a higher chelating affinity with HAs than does As(III), resulting in higher As(V) concentrations distributed throughout the reducing environment. High levels and correlations of As and HAs may cause BFD in the Chianan Plain. No correlation was found between the measured and calculated redox potentials of the various redox couples. The As(III)/As(V) was under a chemical non-equilibrium condition. The vertical distribution of the sedimentary As (solid phase) typically increased with depth, but the aqueous As concentrations were higher in the second aquifer (depth of 80–120 m). Arsenic content (solid phase) was higher in the clay/silt sediments and marine formations. The major minerals identified by XPS and SEM–EDS were goethite, hematite, magnetite, pyrite, and siderite, agreeing with the SI values calculated by PHREEQC. Arsenic content was strongly correlated with sulfur (weight%; $R^2 = 0.76$, $p < 0.05$), but was weakly correlated with iron (weight%). However, a moderate correlation ($R^2 = 0.44$–0.75; $p < 0.001$) between $As_{(s)}$ and $Fe_{(s)}$ in the sediments was found in the transitions in the marine and non-marine formations, especially in the fine grains. The chelation of humic complex, competition for sorption sites of organic carbon, reduction dissolution of Fe oxides are mainly responsible for the groundwater As mobility in the Chianan Plain, especially for the marine sequence.

1. Introduction

Naturally occurring As in the groundwater of sedimentary aquifers is a worldwide problem (Bhattacharya et al., 2002; Smedley and Kinniburgh, 2002). In the sedimentary aquifers in the Chianan Plain in Southwest Taiwan, the high arsenic concentrations in groundwater are a paramount environmental health concern that causes blackfoot disease (BFD). Blackfoot disease is a peripheral vascular disease that was first reported between 1910 and 1920 (Kao and Kao, 1954). Outbreaks of BFD increased dramatically in the 1950s when local villagers drilled deep artesian wells for drinking water. Blackfoot disease is associated with the ingestion of deep well water that contains high amounts of arsenic (Tseng et al., 1961). Previous studies have proposed that fluorescent compounds known as humic acids (HAs) cause BFD (Lu et al., 1975; Lu, 1990). The carbon–metal bonds between HAs and As are thought to be responsible for causing BFD. The monomers of HAs and As may not cause BFD (Reza et al., 2011). However, the geochemical and mineralogical characteristics of the groundwater and sediment in the Chianan Plain have not been comprehensively studied.

Several studies have recently investigated the hydrogeochemical characteristics of As in the Chianan Plain (Wang et al., 2007; Chen and Liu, 2007; Nath et al., 2008, 2011; Lu et al., 2011; Reza et al., 2011). Wang et al. (2007) determined that salinization and As enrichment are the 2 chief hydrogeochemical characteristics of the Chianan Plain. Chen and Liu (2007) found that the As-rich groundwater in the Chianan Plain is under strongly reducing

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conditions with low Eh (<−110 mV; Ag/AgCl reference electrode) and low SO_4^{2-} (<2 ppm). The reductive dissolution of As-rich Fe (hydr)oxides has been proposed as being the chief source of As in groundwater, and the content of SO_4^{2-}, humic substances, and residence times of the water cause variations in the dissolved As in the Chianan coastal area. Nath et al. (2008) indicated that As concentrations and mobility in Chianan Plain aquifers are influenced by several biogeochemical processes, including (1) chemical and redox changes associated with sea water intrusion; (2) bacterial Fe(III)- and Mn(IV)- reduction; (3) biomineralization of Fe carbonate and sulfide minerals; and (4) hydrolysis and weathering of the silicate minerals in metamorphic rock. Furthermore, there may be a link between the mud from volcanic activity (the exhumation of fluids from the deep crust) and As enrichment in the Chianan Plain (Lewis et al., 2007; Nath et al., 2008). Lu et al. (2011) assessed the spatial variations in groundwater quality in BFD-endemic areas and found that 76% of the groundwater samples had As amounts exceeding 10 μg/L. The primary geochemical process in this area pertains to the reducing dissolution of As-bearing Fe/Mn oxyhydroxides. Reza et al. (2011) indicated that these high levels of As and humic substances may play a critical role in causing the prevalence of BFD in the Chianan Plain.

Over the past decade, the Water Resources Agency of the Ministry of Economic Affairs has established a Groundwater Monitoring Network (GMN) program, and 33 hydrological stations and 100 monitoring wells with depths ranging from 4 to 289 m have been established in the Chianan Plain (Taiwan Sugar Company, 2003). The hydrogeochemical measurements were funded by the Water Resources Agency of the Ministry of Economic Affairs, Groundwater Monitoring Network program, and conduct by National Taiwan University and Agricultural Engineering Research Center jointly. This study investigates the hydrogeochemical and mineralogical characteristics of arsenic-enriched and humic-substance-enriched aquifers in the Chianan Plain, Taiwan. This study analyzed groundwater samples from GMN monitoring wells. Arsenic and iron contents and the mineralogical characteristics of core samples from 9 drilling wells were evaluated. Aqueous chemical speciation and mineral saturation calculations were performed using PHREEQC. The sources, distribution, and geochemical and mineralogical characteristics of As in humic substance-enriched groundwater and sediments in the Chianan Plain were assessed. In addition, the relationship between the arsenic species and humic substances were elucidated.

2. Materials and methods

2.1. Hydrogeological setting of the study area

Taiwan is a relatively young and active mountainous island that was formed by the collision of the Philippine Sea plate and the continental margin of the Eurasian plate (Teng, 1987). The backbone of Taiwan (Central Range of Taiwan) is chiefly composed of Tertiary sedimentary rocks consisting of metamorphosed rocks. The Chianan Plain in Southwest Taiwan is primarily a coastal alluvial-deltaic plain formed during the Quaternary. The plain extends 40 km from east to west and 60 km from north to south and is enclosed by the Taiwan Strait to the west and the Central Mountains to the east. Furthermore, it is located between Pachang River to the north and Ernjen River to the south, and the plain covers an area of 2100 km^2 (Fig. 1a). Fast erosion of surface water upstream and a sharp change of river gradient have caused thick clay-rich muddy sediments to be deposited in the upper plain and have led to poor hydraulic properties in the aquifers. Regional geological studies revealed that the sedimentation rate since the Pliocene has been very high. Alluvial deposits of clay, silt and fine-grained sand have

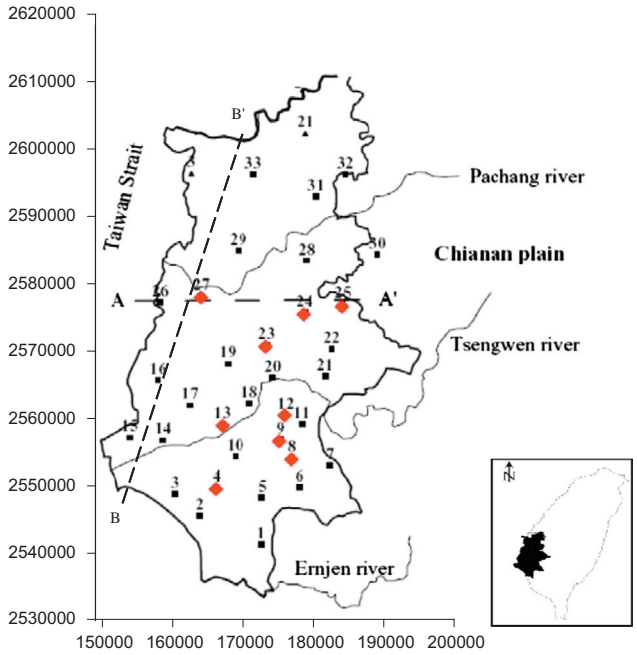

Fig. 1a. Study areas of the Chianan Plain. The solid squares (■) and solid diamonds (♦) represent the hydrological stations and sampling sediment core drilling wells in the Chianan Plain, respectively. Wells 29–33 in the upper part of the Chinan Plain belong to the Choushui River alluvial fan.

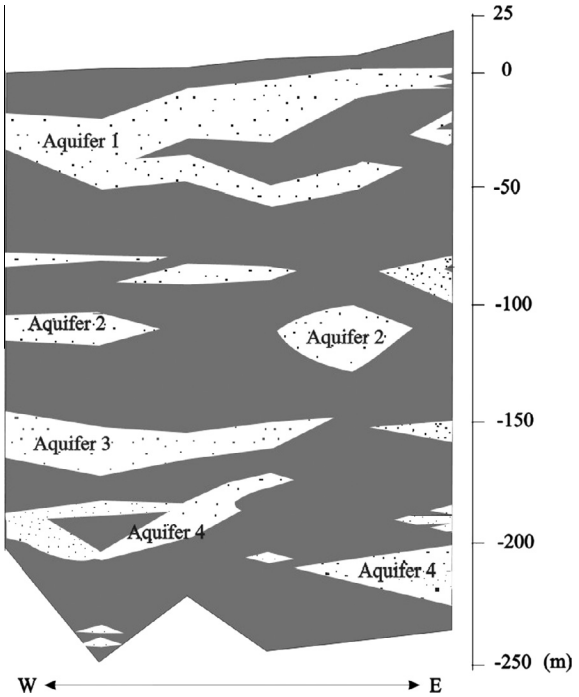

Fig. 1b. Hydrogeological profile along A–A′ denoted in (a) in the Chianan Plain.

extensively covered the coastal plain (Wu, 1999). The hydrogeological profiles of the Chianan Plain exhibit no obvious layer structure (Wang et al., 2007; Nath et al., 2008). Four aquifers are in the plain. Aquifer 1 has a depth of 0–80 m, Aquifer 2 is 80–120 m, Aquifer 3 is 120–210 m, and Aquifer 4 is located at depths beyond 210 m (Fig. 1b; Wang et al., 2007). The uppermost 100-m layer was deposited in the last 10,000 years. These sediments were deposited in mixed alluvial and delta environments, such as fluvial flood