



Multivariate statistical analyses on the enrichment of arsenic with different oxidation states in the Quaternary sediments of the Pearl River Delta, China



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ABSTRACT

Core sediments of boreholes from a Quaternary aquifer–aquitard system of the Pearl River Delta (PRD), China, were collected for the geochemical, particle size and X-ray absorption near-edge spectroscopy analyses. Multivariate statistical techniques of Pearson's correlation analysis and R-mode factor analysis were applied to the geochemical data (TOC, SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, V, Cu, Ni, Cr, Ba, Zn, Sr, Y, Zr and Pb), particle size (ϕ) and solid arsenic contents with different oxidation states (As(–1), As(III) and As(V)) of the bulk sediments. The results demonstrated that the existence and contents of As(III) and As(V) were dominantly directly related to the terrestrial detrital sources. As(III) showed significant correlation with Fe₂O₃, but correlation between As(V) and Fe₂O₃ was insignificant. Aqueous arsenic mainly existed in the form of As(III) as indicated by Eh–pH diagram. As(III) was speculated to exist on amorphous iron oxide. Therefore, this suggested that arsenic in groundwater had the same oxidation state with arsenic adsorbed on amorphous iron oxide. This conclusion was consistent with the previous conclusion that iron oxyhydroxide reduction was an important mechanism to mobilize arsenic in the aquifer–aquitard system. Significant correlations between oxidation forms of arsenic (As(III) and As(V)) and trace elements V, Cu and Ni suggested similar enrichment behaviors among them. Sedimentary organic matter was not correlated with any oxidation states of solid arsenic. Factor analysis indicated that good hydrodynamic conditions of the fluvial dominated sedimentary environment seemed to favor the enrichment of As(III) and As(V). Reduced form of arsenic in the sediments most likely existed in authigenic pyrite in the sediments.

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1. Introduction

Processes of arsenic mobility within Quaternary sediments are the subject of intense academic debate, as a number of large Quaternary aquifers have been identified with elevated arsenic in groundwater (Smedley and Kinniburgh, 2002; Rahman et al., 2005; Guo et al., 2011; Rowland et al., 2011). Previous studies postulated various processes of arsenic mobilization, including oxidation processes (Das et al., 1996; Armienta et al., 1997; Peters et al., 1999; Schreiber et al., 2000), reduction processes (Nickson et al., 1998; McArthur et al., 2001; Ahmed et al., 2004; Islam et al., 2004), and ionic competition processes (Kim et al., 2000; Lee et al., 2005) etc.. Mechanisms of arsenic mobility vary with specific hydrogeochemical conditions and forms of solid arsenic in sediments. Although solid arsenic was found to exist in different phases of sediments hosting elevated arsenic in groundwater (Akai et al., 2004; Reza et al., 2010; Wang et al., 2012), there have been relatively less

studies concerning partitioning of arsenic with different oxidation states in various phases of sediments. An understanding of the speciation of arsenic and contents of different forms of arsenic could help in the testing of various postulated models of arsenic mobility, and evaluating the potential contribution of various As-bearing phases in the sediments to aqueous arsenic. This understanding is important because the environmental impact and mobility of arsenic in the sediments are controlled by not only the total content of arsenic, but also the contents of arsenic of different forms (Ciardelli et al., 2008; Kocar et al., 2008; Chakraborty et al., 2011; Ying et al., 2012). It should be noted that variation in oxidation state of arsenic in soils and sediments were studied previously (Rowland et al., 2005; Cances et al., 2008; Wang et al., 2013).

The X-ray absorption near-edge spectroscopy (XANES) is applicable to solid-phase samples with minor or no pre-treatments and gives chemical identity empirically by comparing sample spectra to known compounds. XANES has been widely used to study various As-bearing materials with solid arsenic varying from several hundred to several thousand mg/kg (e.g. Marcus et al., 2004; Endo et al., 2008). However, its application to Quaternary sediments receives relatively much less attention but is also very important as elevated arsenic concentrations have often been found in groundwater in Quaternary aquifers with only

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average arsenic content in sediments (e.g. Berg et al., 2008; Datta et al., 2009; Ahmed et al., 2010). Arsenic in bulk samples of Quaternary sediments has been found to exist in the form of a mixture of arsenate and arsenite, and reduced arsenic has been found to be the dominant form in the bulk sediments in some cases (Lowers et al., 2007; Polizzotto et al., 2008). The coexistence of different oxidation states of arsenic in the bulk sediments could be attributed to the complex hydrogeological and geochemical conditions of the Quaternary sediments. This work aimed to investigate the relationships between geochemical environment and the enrichments of arsenic with different oxidation states, by adopting multivariate statistical analyses on the geochemical parameters, particle size, and XANES data of arsenic of bulk sediments.

The Pearl River Delta (PRD), China was chosen as the study area. Geochemistry and oxidation states of arsenic of sediments from the Quaternary aquifer–aquitard system of the PRD were well documented in previous studies (Wang et al., 2012, 2013). This work focused on analyses of data from cores of two boreholes MZ4 and SD1 of the aquifer–aquitard system. The sediments had solid arsenic content ranging from 11 to 40 mg/kg, which is not high compared to Quaternary sediments of other regions, as will be discussed later, but hosted elevated aqueous arsenic in the basal aquifer (161 and 38 $\mu\text{g/L}$, respectively). As geochemical conditions are complicated and there are many geochemical parameters, multivariate statistical studies, would be a useful tool to identify relationships between geochemical environment and the enrichments of arsenic with different oxidation states.

2. Site background

The PRD is located in the coastal areas of the South China Sea (Fig. 1A). The bedrocks below the Quaternary sediments consist of sand–shale, sandstone, carbonatite, limestone, granite, dolomite and gneiss etc., and they were formed during the Cambrian to Tertiary periods (Long, 1997). These rocks outcrop around and occasionally inside the PRD. Late Quaternary stratigraphic units in the PRD receiving basin are generally composed of four sequences: older marine and terrestrial units (M2 and T2) and younger marine and terrestrial units (M1 and T1) (Zong et al., 2009) (Fig. 1B). The old terrestrial unit (T2) is mainly composed of sand and gravel and widely distributed in paleo-valleys prior to the last transgression in the late Pleistocene; the old marine unit (M2) was formed during the interglacial period started from about 130 ka before present and mainly composed of silt and clay (Yim, 1994; Yim et al., 2002; Zong et al., 2009). The upper part of M2 was largely weathered due to the low sea level during the last glacial period, and formed a layer of weathered clay in most areas of the plain. Meanwhile, a younger terrestrial unit of alluvial sediments, mainly composed of sand, was laid down along paleo-river channels. Both the weathered clay and alluvial sediments are considered as the younger terrestrial unit (T1). After 8.2 calibrated ka before present (cal. ka BP), rapid rise of sea level resulted in large-scale Holocene transgression, and formed a layer of younger marine sediment (M1) (Zong et al., 2009). The calibrated radiocarbon ages measured on sedimentary organic matter were collected from various studies of the PRD (Huang et al., 1982; Li et al., 1991; Zong et al., 2009) and provided in Fig. 1B.

Regionally, the water level elevations vary from less than 0.5 m near the sea to over 4 m in the inland area, and regional groundwater flow is towards east or southeast to the sea (Wang et al., 2013). As the overall hydraulic gradient is small, the regional groundwater flow is quite slow in the confined basal aquifer. Vertically, marine sequences of M1 and M2 are aquitards, and the terrestrial unit T2 of sand and gravel is the basal aquifer. Water levels from the piezometer site of MZ4 show a downward vertical flow (Jiao et al., 2010). The vertical groundwater velocities at different depth of the aquitards are estimated to range from 0.39×10^{-3} to 1.84×10^{-3} m/yr, indicating very slow vertical flow within the aquitard (Wang, 2011).

3. Methods

Core samples from two boreholes SD1 and MZ4 were selected for detailed geochemical, particle size and oxidation states of solid arsenic studies. Borehole MZ4 was located very close to the coastline. SD1 was located about 48 km away from MZ4 (Fig. 1A).

Total organic carbon (TOC) in sediments was analyzed on ThermoQuest Italia S.P.A. EA 1110 at State Key Laboratory of Marine Geology, Tongji University. 1 M HCl was used to remove inorganic carbon before determination. The contents of major elements (K_2O , CaO, Na_2O , MgO, Al_2O_3 , Fe_2O_3 , MnO and TiO_2) in sediments were determined on wavelength-dispersive X-ray fluorescence spectrometer (WD-XRF) in the Department of Earth Sciences, the University of Hong Kong. Sediment samples and lithium borate (1:7 ratios) were used to prepare glass beads. Total contents of various trace elements (As, V, Cu, Ni, Cr, Ba, Zn, Sr, Y, Zr and Pb) in bulk sediment were determined using the powder press method on WD-XRF. Standard curves were prepared on the basis of Chinese, American and Japanese rock standards. Standard reference materials of aqueous sediment GBW07311 (GSD-11) and rock powder GBW07104 (GSR-2) were used for experiment quality control. Particle size of sediments was analyzed on a laser diffraction particle size analyzer (LS 13320) in the Department of Earth Sciences, the University of Hong Kong. Particle size results were reported in the Krumbein ϕ (ϕ) scale (Krumbein and Sloss, 1963). Eh and pH of the groundwater in the basal aquifer were analyzed in-situ by YSI 6-Series Multiparameter Water Quality Sondes (6920 V2) (YSI, 2006). Geochemist's Workbench software (Bethke, 1996) was used to draw the Eh–pH diagram. Arsenic K-edge XANES technique was used to determine oxidation states of solid arsenic, technique details were recorded in (Wang et al., 2013). Least-squares fitting of bulk XANES spectra of samples were used to quantitatively estimate the amount of each arsenic oxidation states.

Multivariate statistical techniques can help to organize and simplify datasets to provide meaningful insight or useful information that could not be available at first glance. In this study, multivariate statistical analyses were employed to examine the relationship among solid arsenic with different oxidation states (As(–1), As(III) and As(V)) and sediment geochemical constituents in 16 selected sediment samples at different depths from two cores SD1 and MZ4. All the data were standardized by converting them into their standard scores (Davis, 2002) before analysis, so that each variable was weighted equally in the statistical analyses.

The statistical software package SPSS 16.0 for windows was utilized for multivariate statistical analyses. The techniques used included Pearson's correlation analysis and R-mode factor analysis (Laaksoharju et al., 1999; Chen et al., 2007). The original matrix consisted of 26 columns indicating the forms of solid arsenic and geochemical components in the bulk sediments and 16 rows describing the individual samples of the two sedimentary cores of SD1 and MZ4.

4. Results and discussion

4.1. Arsenic enrichment in the sediments

Arsenic contents in sediments ranged from 11 to 40 mg/kg, with an average value of approximately 21 mg/kg. The highest solid arsenic concentrations (40 and 30 mg/kg, respectively) of boreholes SD1 and MZ4 were found within 5 m from the ground surface. These arsenic contents were similar to, or slightly higher than those in sediments in other coastal aquifer–aquitard systems (Wang et al., 2012), and were typical for Quaternary sediments hosting elevated arsenic in groundwater ($>10 \mu\text{g/L}$). For example, results of regional lake sediment surveys conducted in central British Columbia showed that solid arsenic contents ranged from 0.9 to 44 mg/kg (Cook et al., 1995); Solid arsenic ranged from 6 to 35 mg/kg in sediments of silt, clays and peat of the Meghna River Delta, Bangladesh (Bibi et al., 2008); Sediment-bound arsenic of the Hanoi area, Vietnam, varied from 1.3 to 22 mg/kg (Berg et al., 2008).

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