

Speciation and Seasonal Variations of Dissolved Inorganic Arsenic in Jiaozhou Bay, North China

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Abstract The distributions and biogeochemical cycles of arsenic in the aquatic environment have captured the interest of geochemists due to arsenic's multiple chemical forms, the toxicity of certain arsenic species and large anthropogenic input. Seasonal variations in the dissolved inorganic arsenic concentration and speciation in Jiaozhou Bay, which is located on the west coast of the Yellow Sea in northern China, are presented here. Three cruises were carried out in Jiaozhou Bay under varying tidal regimes, one at neap tide and one at spring tide in August and one at spring tide in October of 2001. In addition to the transect surveys, the main sources of dissolved inorganic arsenate and arsenite in Jiaozhou Bay, including riverine input from five major tributary rivers, atmospheric dry and wet depositions, and groundwater and wastewater input, were collected in different seasons to estimate arsenic transport through different sources. The mean concentrations of total

dissolved inorganic arsenic (TDIAs, As (V+III)) in Jiaozhou Bay were statistically comparable between summer and autumn, with higher concentrations at the northwest and northeast parts of the bay, reflecting human activities. The As (III)/TDIAs ratio ranged between 0.045 and 0.68, with an average of 0.16, implying that arsenate was the dominating species in Jiaozhou Bay. A preliminary box model was established to estimate the water-mass balance and arsenic budgets for Jiaozhou Bay, which demonstrated that river inputs and atmospheric depositions were the main sources of arsenic into Jiaozhou Bay. The concentrations of dissolved inorganic arsenic in Jiaozhou Bay have decreased in the last two decades. Compared with other areas in the world, the concentration of arsenic in Jiaozhou Bay remains at the natural level and this region can be characterized as a less disturbed area.

Keywords Arsenic · Speciation · Jiaozhou Bay · Seasonal variation

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1 Introduction

All the metalloid elements can exist in multiple chemical forms in seawater, including different oxidation states and organic compounds. Arsenic is of great concern in terrestrial as well as aquatic environments because of the high toxicity of this element to ecosystems at certain concentration levels (Kim and Nriagu 2000; Cai et al. 2002). Inorganic

arsenic species in water mainly exist in the pentavalent state as arsenate (As (V)) and in the trivalent state as arsenite (As (III)). Previous studies of arsenic biogeochemistry have demonstrated that arsenate is the most stable arsenic species in oxic waters, whereas arsenite is also present in natural waters mediated by biological production or photochemical processes (Neff 1997).

Arsenic in the aquatic environment is usually derived from natural (volcanism, weathering) and anthropogenic sources and is released as a by-product of mining, metal refining processes, burning of fossil fuels, preserving of woods, and agricultural use (herbicides, pesticides, fungicides) (Cullen and Reimer 1989; Nriagu 1994). Average As concentrations in open seawater usually show little variation and typically range between 14 and 25 nmol/l (Cutter et al. 2001; Ellwood and Maher 2002). As a member of Group V in the Periodic Table, the behavior of arsenic is similar to that of phosphate and shows nutrient-like depth profiles in the ocean, indicating uptake by phytoplankton and regeneration from degradation of organic detritus (Andreae 1979; Sanders 1979; Middelburg et al. 1988; Sanders and Riedel 1993; Santosa et al. 1994, 1996, 1997; Cutter and Cutter 1998; Cutter and Measures 1999; Cutter et al. 2001). The As content in riverine and estuarine waters are more variable as a result of varying bedrock lithology and river inputs, but are usually low, at typically less than $2 \mu\text{g l}^{-1}$ for river water and $4 \mu\text{g l}^{-1}$ for estuarine water under natural conditions (Smedley and Kinniburgh 2002). Relatively high concentrations of As can occur in some areas as a result of inputs from geothermal sources or high As groundwater and as an effect of industrial and mining effluent (e.g., Tamar, Schelde, Loire Estuaries) (Smedley and Kinniburgh 2002).

Jiaozhou Bay (JZB) is located at the west coast of the Yellow Sea ($35^{\circ}58'–36^{\circ}18'N$, $120^{\circ}04'–120^{\circ}23'E$), and is connected with the Yellow Sea through a narrow channel (~ 2.5 km, Fig. 1). The bay is surrounded by the city of Qingdao (population 7×10^6), and has a surface area of about 390 km^2 and an average water depth of about 7 m. There are more than 10 small rivers that enter JZB, but with limited river discharge. The Daguhe is the largest river, located on the west coast, with an annual mean discharge of about $7.2 \times 10^8 \text{ m}^3$ (1952–1979) (Editorial Board of *Annals of Bays in China* 1993), accounting for 84% of the total riverine discharge into JZB (Marine Environ-

mental Monitoring Center 1992). In recent decades, the total amount of freshwater discharge from rivers into JZB decreased considerably, according to the data from the State Oceanic Administration of China and the Qingdao Aquiculture Bureau (SOA and QAB 1998). With the recent rapid economical and social development, most of the rivers entering the bay have become discharge trenches for industrial and living wastes from Qingdao (Fan and Zhou 1999). The average rainfall is 775.6 mm, with 58% occurring in the summer and 23% in the winter (Shen 2001). Tides induce strong turbulent mixing in JZB, resulting in nearly well mixed vertical profiles of temperature and salinity. The stratification is weak even in the summer when land-source (e.g., river) input reaches its maximum (Weng et al. 1992; Liu et al. 2004).

In this paper, we present the data for total dissolved inorganic arsenic (TDIAs, As (III+V)) and arsenite in the water column of JZB. Additionally, observations were carried out in the rivers around Jiaozhou Bay in the dry and flood seasons, together with data from waste discharge, groundwater and atmospheric depositions. The impact of anthropogenic activity on the environment of JZB and the biogeochemical behavior of arsenic in the continental shelf were studied.

2 Materials and Methods

2.1 Sample Collection

Field observations were carried out in Jiaozhou Bay on August 13 and 14 (grid 1, G1, neap tide), August 21 and 22 (grid 2, G2, spring tide), and October 20 and 21 of 2001 (grid 4, G4, spring tide) using small fishing boats (Fig. 1). In each of the cruises, about 14 grid stations were occupied, with CTD and ADCP profiles at each station. Water samples were collected with 5-l Niskin bottles based on the CTD profiles. Only surface waters were collected when water depths were shallower than 3 m. After collection, samples were filtered immediately through pre-cleaned and pre-weighed $0.45 \mu\text{m}$ pore-size acetate cellulose filters, and the filtrates for arsenic measurement were frozen at -20°C . Filtrates for the nutrients were poisoned with saturated HgCl_2 (ca. 1.5×10^{-3} v/v). After filtration, the filters were washed by 5 ml Milli-Q water, dried at 45°C and weighed again to determine suspended particulate matter (SPM).

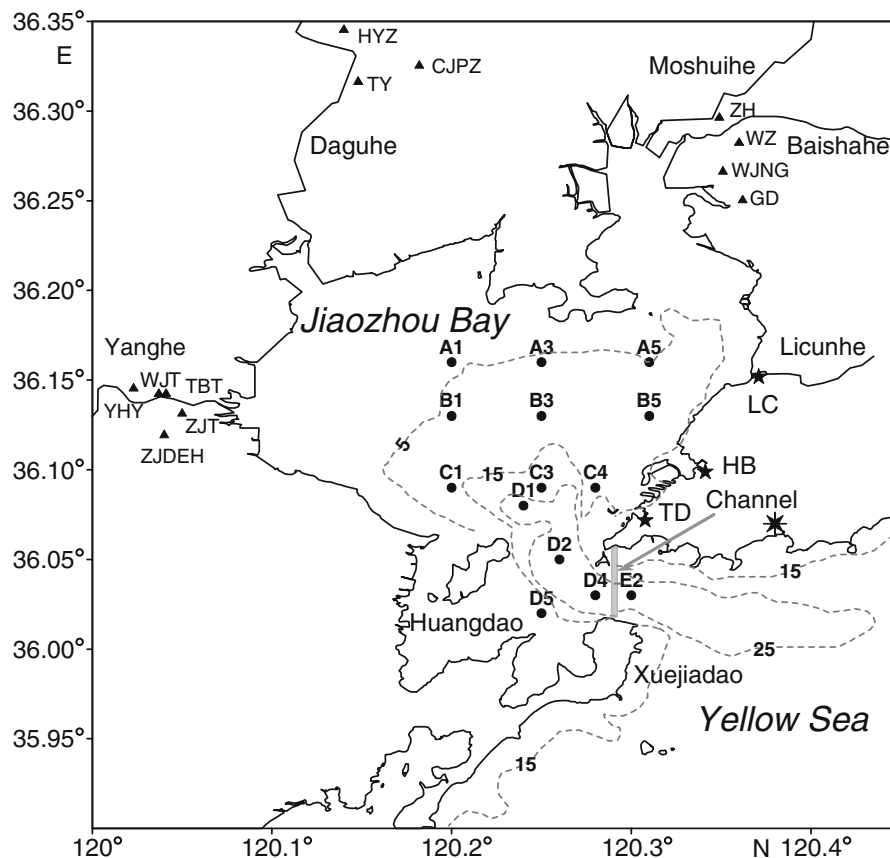


Fig. 1 Map of Jiaozhou Bay, which shows grid stations (•), Haibohe (HB), Tuandao (TD) and Licun (LC) wastewater disposal plants (★), underground water stations nearby the bay (▲), rainwater and aerosol stations on Fulong Hill (✱), and the major rivers surrounding the Bay: Daguhe, Yanghe, Moshuihe, Baishahe and Licunhe

The river water sampling was undertaken in March–April (dry season) and August (flood season) of both 2002 and 2004. Water samples were collected using 2-l polyethylene bottles attached to a fiberglass reinforced fishing pole. Wastewater samples were collected in April and November of 2004 at the discharge exits of the Haibohe and Tuandao sewage treatment plants. Groundwater samples were collected from 12 wells along the coastline of Jiaozhou Bay in December 2003 and July 2004. The wells were located in three main regions including the Daguhe, Yanghe and Baishahe watersheds, with depths varying from about 4 to 20 m (Fig. 1). Aerosol and rain samples were collected at the meteorological station on Fulong Hill from December 2003 to August 2004. Rainwater was sampled using Plexiglas collectors of 400 cm² in surface area with a porous polyethylene funnel cover. The rain collectors were opened to the atmosphere immediately prior to

each collection, and were closed afterwards and the rain collector was replaced. Rainwater samples were filtered in the laboratory right after the rainfall, and only those with rainfall higher than 10 mm were frozen at –20°C for the measurement of arsenic. Unfortunately, five rainfall samples were missed in the summer. Aerosol samples which were collected onto 0.45 μm nuclear pore membrane were soaked in 10 ml Milli-Q water for 50 min by ultrasonic, and the solutions were filtered and analyzed for the dissolvable arsenic in the aerosol particles.

Sediment samples were collected by a box corer at 18 stations in Jiaozhou Bay in December 2004. Overlying waters were removed and the top 1–2 cm of sediments were collected. The pore waters were extracted by centrifugation at 4,000 rpm for 15 min and filtered through 0.45 μm pore size acetate cellulose filters. The filtrates were stored frozen until analysis.

2.2 Analytical Methods

Concentrations of dissolved arsenic were measured using a Hydride Generation-Atomic Fluorescence Spectrometry (HG-AFS). Arsenite generation was performed by hydride generation at pH 5.3–5.5 buffered by sodium citrate-HCl solution, which did not allow arsenate to be reduced to arsenite. Arsenite generation by the reduction of potassium borohydride was thus limited to the As (III) initially present in the sample. Total dissolved inorganic arsenic (TDIAs, As (III+V)) was determined by hydride generation at an acidity of 1 M HCl, after reduction into arsenite by thiourea-Vc mixed solution. The concentration of arsenate was calculated from the difference of TDIAs and As (III) (Li 2003). The detection limit for TDIAs and As (III) by HG-AFS were 0.11 nM and 0.02 nM, respectively. The precision of HG-AFS measurement for TDIAs was 6.8% at 1.6 nM, while it was 3.1% at 1.3 nM for As (III). The precision and accuracy of inorganic arsenic analysis was monitored daily by national standard samples. The recovery of the measurement was 98–104%. In order to test the robustness of the proposed method for the measurement of TDIAs, inter-calibration experiments were performed by our laboratory (OUC) and the University of Brussels (VUB) with the international standard sample NASS-4 and North Sea samples (Fig. 2). The certified value of As in NASS-4 is $1.26 \pm 0.09 \mu\text{g l}^{-1}$, and the result from our method was $1.28 \pm 0.04 \mu\text{g l}^{-1}$. The difference between our method and the certified value is within 2%, which can ensure the quality of our HG-AFS method. As for the inter-calibration samples from the North Sea, our average results were statistically higher than those of VUB.

3 Results

3.1 Hydrographic Properties

Salinity and SPM distributions for the cruises carried out in 2001 in Jiaozhou Bay have been discussed elsewhere, and are only briefly introduced here (Table 1; Liu et al. 2004, 2005). Typhoon Taozhi passed over Jiaozhou Bay on August 1st, 2001, and brought as much as ~120 mm precipitation within 9 days, which accounted for nearly 1/6 of the annual mean rainfall (Editorial Board of Annals of Bays in

China 1993). Salinity in the cruises G1 and G2 of August was about ~28 PSS, 3 PSS lower than the long-term average of ~31.3 PSS (Yang and Wu 1999) following the heavy rainfall events before the investigation. Salinity increased to ~30 PSS with the decreasing river water discharge and exchange between the bay and offshore waters in late August; 2 months later, it had increased to ~31 PSS in the G4 cruise. The salinity was lower in the northwest following the freshwater discharge from the Daguhe and Yanghe rivers, and increased gradually to the channel.

In the summer, SPM concentrations were higher in the northern than the southern parts following the high run-off of freshwater, and were higher during the spring tide (August 21–22) than during the neap tide (August 13–14) (Table 1). The SPM contents were higher in the bottom than the surface waters in all cruises. The SPM concentration in the bottom water of Jiaozhou Bay was higher than in the Yellow Sea during the neap tide, while it was similar during the spring tide (Yang et al. 2004; Liu et al. 2005). The SPM content in autumn increased by 1.5–2 folds relative to August and was higher in the bay mouth than in the inner bay, showing a strong tidal mixing influence.

3.2 Distribution of Total Dissolved Inorganic Arsenic and Arsenite in Jiaozhou Bay

The average concentrations and standard deviation of arsenic species during the G1, G2 and G4 cruises are summarized in Table 1. Figure 3 gives the distribution of TDIAs, As (III) and the ratio of As (III)/TDIAs during the G1 and G4 cruises, respectively. The concentrations of TDIAs were higher in the northern

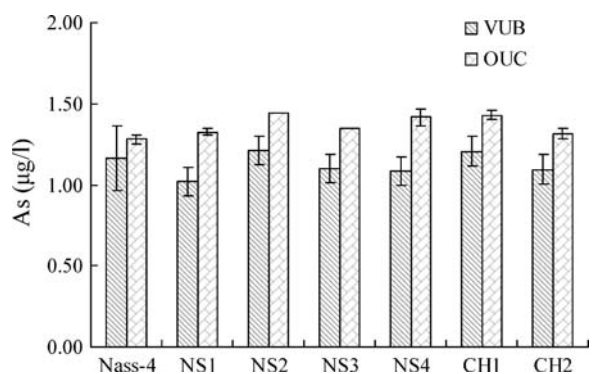


Fig. 2 Comparison of international reference material and the inter-calibration with North Sea samples between the laboratories of Vrije Universiteit Brussel (VUB) and the Ocean University of China (OUC)

Table 1 Salinity, concentration of SPM (mg l^{-1}), TDIAAs and As(III) (nM) in Jiaozhou Bay in August 13–14 neap (G1), August 21–22 spring (G2) and October 20–21 spring (G4)

Cruise	Depth	SPM	Salinity	TDIAAs	As (III)	As (III)/TDIAAs
G1	Surface	14.3±5.1	26.6±1.5	16.0±3.2	2.2±0.9	0.14±0.03
	Bottom	17.8±5.0	29.3±1.4	15.5±1.7	1.9±0.5	0.12±0.02
G2	Surface	19.7±7.4	28.8±1.3	18.4±4.1	2.4±1.0	0.14±0.07
	Bottom	29.9±8.0	29.9±0.6	15.6±3.4	6.2±3.3	0.39±0.17
G4	Surface	22.5±7.1	31.5±0.4	17.2±3.9	1.8±0.5	0.11±0.02
	Bottom	29.6±7.6	31.8±0.4	16.0±2.5	1.7±0.3	0.11±0.02
Yellow Sea				16.2±3.0	1.0±0.3	0.08±0.02
East China Sea				16.9±3.3	0.5±0.2	0.03±0.01

Average and standard deviations (\pm) are shown. The concentrations of TDIAAs and As (III) in the coastal area of the Yellow Sea and East China Sea (unpublished data) are shown for comparison.

part of Jiaozhou Bay than in the southern part during both the summer and autumn cruises, especially in the northwest, following the discharge from rivers, i.e., the Daguhe and Yanghe in the west, and the Baishahe, Moshuihe and Licunhe in the northeast (Fig. 3). The TDIAAs concentrations in rivers were 0.2 to 2.6 times the concentrations in the seawater of Jiaozhou Bay, which will be discussed later (Table 2). The TDIAAs concentrations near the channel were lower than in the inner bay due to the dilution of the Yellow Sea, and were vertically homogeneous in both the summer and autumn. The mean concentrations of TDIAAs between the summer and autumn were statistically comparable at the confidence level of 0.05 (Morgan 1991).

The concentrations of As (III) during the G1 and G2 cruises were higher in the north, especially in the northwest, and were similar to the distribution of TDIAAs but with lower concentrations (Fig. 3). The distribution of As (III) in the autumn was different from the summer. In the autumn, the freshwater discharges decreased, and the As (III) concentration was higher near the channel than in the inner bay. As (III) showed vertically well mixed profiles and similar concentrations during the G1 and G4 cruises, but had abnormally higher concentrations during the G2 cruise, especially in the near-bottom waters. Since the Typhoon Taozhi caused heavy precipitation right before the G2 cruise, arsenic was brought into Jiaozhou Bay by the freshwater discharge, especially in the northwest part of the bay that receives the discharges from the Daguhe and Yanghe rivers. The As(III)/TDIAAs ratio ranged from 0.045 to 0.68 in Jiaozhou Bay, with higher ratios appearing in the summer than in the autumn, especially in the bottom

waters of G2, which shed light on the effect of freshwater input on arsenic levels.

3.3 Arsenic in Jiaozhou Bay

3.3.1 Riverine Input

Table 2 gives the concentrations of TDIAAs and As (III) in the dry and flood seasons of both 2002 and 2004 in the main streams emptying into JZB. Figure 3 shows the average concentrations of TDIAAs, As (III) and the ratio of As (III)/TDIAAs in the dry and flood seasons, respectively. The concentrations of TDIAAs and As (III) varied considerably, depending on the specific streams (e.g., the Yanghe, Daguhe for TDIAAs; and the Yanghe, Daguhe and Moshuihe for As (III)) and specific observations, with a weighted mean concentration of 16.8 nM. The concentrations of TDIAAs in the main streams were comparable to that in JZB, except for the Daguhe and Licunhe rivers (Fig. 4a). The concentrations of As (III) in the main stream were relatively higher than in JZB, especially in the Moshuihe and Licunhe (Fig. 4b). The average As (III) to TDIAAs ratios in the rivers ranged from 13 to 76%, with an extremely high percentage of 98% in the Moshuihe in March 2002 (Fig. 4c). This variation shows the existence of non-point pollution by industrial and domestic activities in the drainage basin of Jiaozhou Bay (e.g., the Licunhe, Zhang et al. 2003). For example, the Moshuihe is heavily polluted and has a black color and a foul smell. Domestic wastewater is drained into the Licunhe, and its drainage area is the most contaminated of the Jiaozhou Bay region (Zhang et al. 2003).

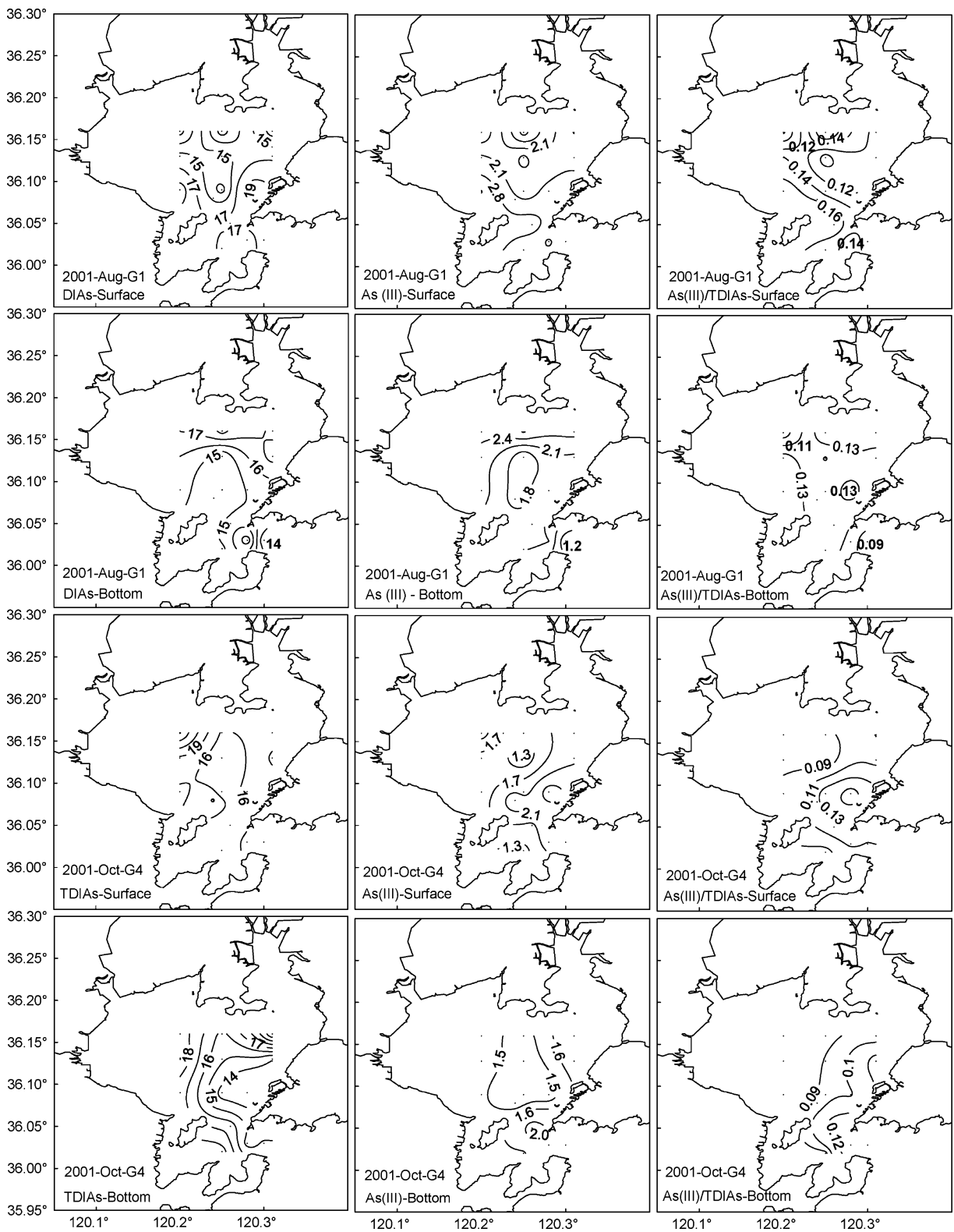


Fig. 3 Horizontal distributions of total dissolved inorganic arsenic (TDIAs), arsenite (As(III)) and As(III)/TDIAs ratio in Jiaozhou Bay. To reduce the number of figures, cruises of August 13–14 neap and October 20–21 spring were selected as examples

Table 2 Concentrations of TDIAAs and As (III) (nM) in major rivers

River	Mar-02		Aug-02		Apr-04		Aug-04	
	TDIAAs	As (III)	TDIAAs	As (III)	TDIAAs	As (III)	TDIAAs	As (III)
Yanghe	4.9	0.6	18.3	8.1	8.2	2.7	9.1	2.3
Daguhe	4.8	0.7	43.3	5.3	3.0	0.6	21.0	1.3
Moshuihe	10.6	10.4	12.1	9.3	14.4	7.8	14.1	3.6
Baishahe	15.3	5.2	15.6	2.9	3.9	0.5	7.0	3.4
Licunhe	26.3	7.2	29.1	4.3	11.9	4.5	20.3	4.9

The riverine input fluxes of TDIAAs into Jiaozhou Bay can be estimated by annual freshwater discharges and average TDIAAs concentrations, ranging from $(0.2 \pm 0.1) \times 10^3$ to $(9.6 \pm 10.0) \times 10^3$ mol yr⁻¹ (Table 3). The total TDIAAs flux into Jiaozhou Bay from streams is $(11.1 \pm 10.0) \times 10^3$ mol yr⁻¹, mainly from the Daguhe (ca. 86% of total riverine input).

3.3.2 Atmospheric Deposition

Figure 5a gives the concentrations of As (V) and As (III) in the rainwater samples that were collected on Fulong Hill from December 2003 to August 2004. The concentrations of TDIAAs were higher in the winter and in the early spring than in the summer because of the infrequent rainfall and emissions from fuel combustion (Waldman et al. 1991; Niragu and Pacyna 1998), and showed a poor relationship with the rainfall. The arsenic emission flux into the atmosphere by coal combustion in the power plants of China was estimated to be 195.0 ton yr⁻¹ (Luo et al. 2004). The concentrations of As (III) in the rainwater were 4.7 ± 0.6 nM in the winter and 2.2 ± 1.8 nM in the summer, and the levels were higher in rainwater than in seawater during the winter. The As (III)/TDIAAs ratio ranged from 0–48 %, with an average of 18 %, and decreased with the increase of rainfall (Fig. 8b). It has been proven that ferric iron can be reduced to Fe (II) during the transport of aerosol (Zhuang et al. 1992, 2003). A similar photochemical reaction may exist for arsenic, which may explain the existence of As (III) in the rainwater. The geometric average of TDIAAs in the rainwater was 18.5 nM, and the annual transport flux can be estimated to be 5.6×10^3 mol yr⁻¹ by the product of annual rainfall and average concentrations, with an uncertainty of 40% according to the variation of annual rainfall during the last 100 years (Dai et al. 2004).

The annual aerosol transport from mainland Asia to the North Pacific is about 480×10^{12} g yr⁻¹ (Duce et al. 1991), and the atmospheric deposition flux of As should be included in budgetary work (Zhang et al. 2002). Leaching experiments were carried out in Milli-Q water to estimate the average dissolvable As from aerosols (Fig. 6). The soluble inorganic As ranged from 0.6 to 12.5 $\mu\text{g g}^{-1}$ of aerosol particles, with an average of 4.4 ± 2.8 $\mu\text{g g}^{-1}$ and high solubility in the autumn and winter. The abundance of arsenic in the crust ranges from 1.8 $\mu\text{g g}^{-1}$ dry wt. (Taylor 1964), 5.7 ± 4.2 $\mu\text{g g}^{-1}$ in remote aerosols of the Russian Arctic (Shevchenko et al. 2003), 10.62 ± 9.78 $\mu\text{g g}^{-1}$ in the dusts of Xi'an, which covers a large part of the Loess Plateau of China (Han et al. 2006), 78.2 ± 12.8 $\mu\text{g g}^{-1}$ in urban aerosols of southern Taiwan (Tsai et al. 2003) to 120 $\mu\text{g g}^{-1}$ in one sandstorm (PM2.5) in Beijing (Sun et al. 2004), showing the effects of anthropogenic disturbance. The abundance of arsenic in the aerosols that were collected in the Yellow Sea during the cruise was 165 ± 46 $\mu\text{g g}^{-1}$ (Moon et al. 2002). The arsenic contents in the aerosols were concentrated by the anthropogenic activities if compared with the average crust content and remote aerosol. An average of 120 ± 46 $\mu\text{g g}^{-1}$ based on the last three abundances that were affected by anthropogenic activities was adopted to calculate the solubility of As in Jiaozhou Bay, and gave a result of $3.7 \pm 2.2\%$.

The annual dry deposition flux of arsenic to the Yellow Sea was estimated to be 0.98 mg m⁻² yr⁻¹ (Yang et al. 1994) and 0.56 mg m⁻² yr⁻¹ (Moon et al. 2002) by model calculation and aerosol samples collected in the Yellow Sea, respectively. The average flux of 0.77 mg m⁻² yr⁻¹ and average solubility of 3.7% were used to estimate the contribution of As from dry deposition into Jiaozhou Bay, giving a value of 0.15×10^3 mol yr⁻¹ with an uncertainty of 60% based on the range of As solubility in the aerosol samples. Total

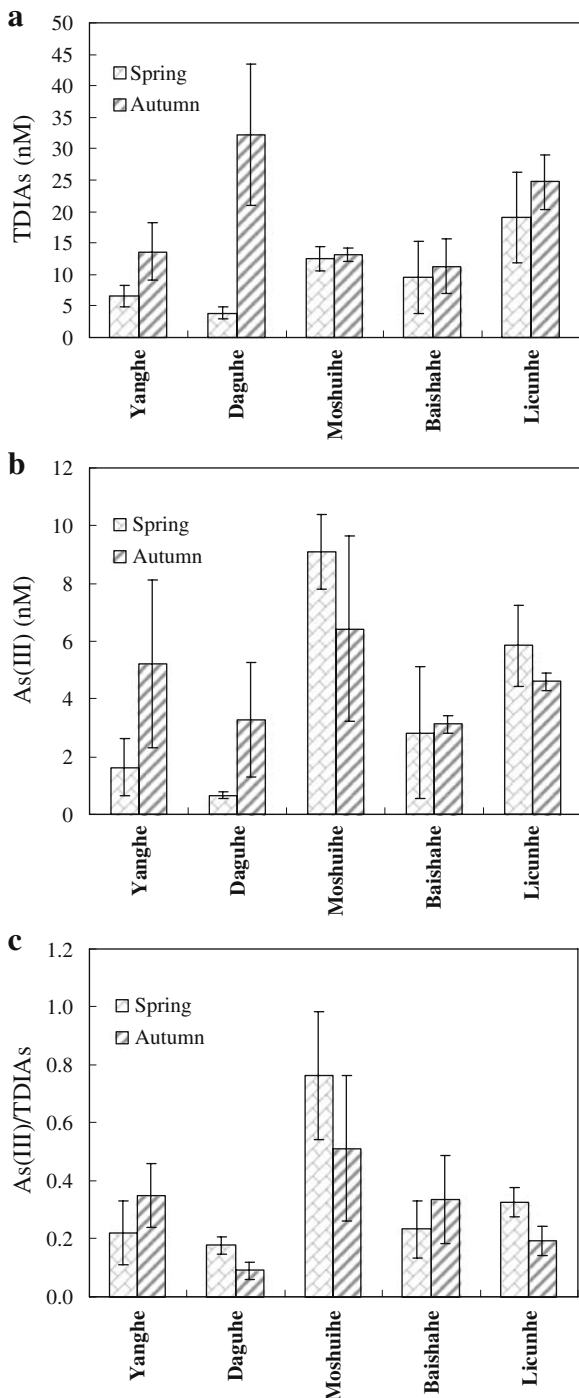


Fig. 4 Average concentrations of **a** TDIAAs, **b** As (III) and **c** As (III)/TDIAAs ratio in the major rivers emptying into Jiaozhou Bay in spring and autumn

atmospheric input of As into Jiaozhou Bay is 5.75×10^3 mol yr⁻¹, which is nearly half of the input from the rivers, with an obviously seasonal and sporadic character.

3.3.3 Groundwater and Wastewater Discharge

Table 4 gives the concentrations of TDIAAs and As (III) in the groundwater of the Baishaha, Daguhe and Yanghe drainage basins, respectively. The concentrations of TDIAAs and As(III) varied considerably, showing highly spatial and temporal variations (Table 4). The TDIAAs contents were lower or similar to the concentrations of seawater in nearly 88% of groundwaters, except for 30 nM in CJPZ of the Daguhe drainage basin and 43 nM in TBT of the Yanghe drainage basin. The concentrations of TDIAAs in the groundwater were lower than the maximum contaminant level (MCL) of $10 \mu\text{g l}^{-1}$ for arsenic in drinking water according to the World Health Organization (WHO 1993). The arsenic concentrations in groundwater may range up to several hundred milligrams per liter, most notably in Bangladesh and West Bengal, where two thirds of the population are at risk of serious health effects due to high concentrations of arsenic in the drinking water which mainly comes from the shallow alluvial and deltaic aquifers. (Bhattacharya et al. 2002; Manzurul et al. 2003; Ahmeda et al. 2004).

The concentrations of As (III) were quite low, except for abnormally high concentrations of 15.4 nM at CJPZ in July 2004 in which As (III) constituted 50% of TDIAAs. According to batch experiments, As (III) could be removed by aquifer materials through the mechanisms of oxidation and/or adsorption depending on the concentration of As (III), as well as the Mn:Fe ratio of the aquifer material (Amirbahman et al. 2006). On the other hand, arsenate can be reduced to arsenite under low Eh conditions (Carbonell-Barrachina et al. 1999), which can explain the extremely high concentration of 15.4 nM As (III) at CJPZ. The concentrations of nitrate in the groundwater of JZB are relatively high due to the lixiviation of fertilizers since the drainage basin is an intensively fertilized agricultural region (Zhu et al. 2005). The ratio of reductive (NH_4^+) to oxidized (NO_3^-) nitrogen species in the groundwater shows the nutrient regeneration occurs by a denitrification process. The high As (III)/TDIAAs ratio of 0.5 appearing in CJPZ corresponds with a high $\text{NH}_4^+/\text{NO}_3^-$ ratio of 2.6, while the average ratio of $\text{NH}_4^+/\text{NO}_3^-$ for other groundwater is only 0.6 (Liu G. Q. et al., in the same special issue).

Annual TDIAAs discharge from groundwater into Jiaozhou Bay can be estimated from the mean concentration in each drainage basin and submarine

Table 3 The mean concentration of TDIAAs in the main streams and annual TDIAAs discharge from rivers emptying into Jiaozhou Bay

River	Yanghe	Daguhe	Moshuihe	Baishahe	Licunhe
Mean concentrations (nM)	10.1±5.7	18.0±18.7	12.8±1.8	10.4±5.9	21.9±7.6
Water discharge (m ³ /s) ^a	1.78	17.0	0.923	0.90	0.34
TDIAAs Discharge (10 ³ mol yr ⁻¹)	0.6±0.3	9.6±10.0	0.4±0.1	0.3±0.2	0.2±0.1

^a Data are from Liu and Wang 1992, in which water discharge in Daguhe has been calibrated based on water discharge after the main dam was constructed in the 1960s (Liu et al. 2005).

Fig. 5 Dissolved arsenic in the rainwater. **a** Concentrations of TDIAAs and As (III) in the rainwater; **b** the relationship between concentrations of TDIAAs and rainfall

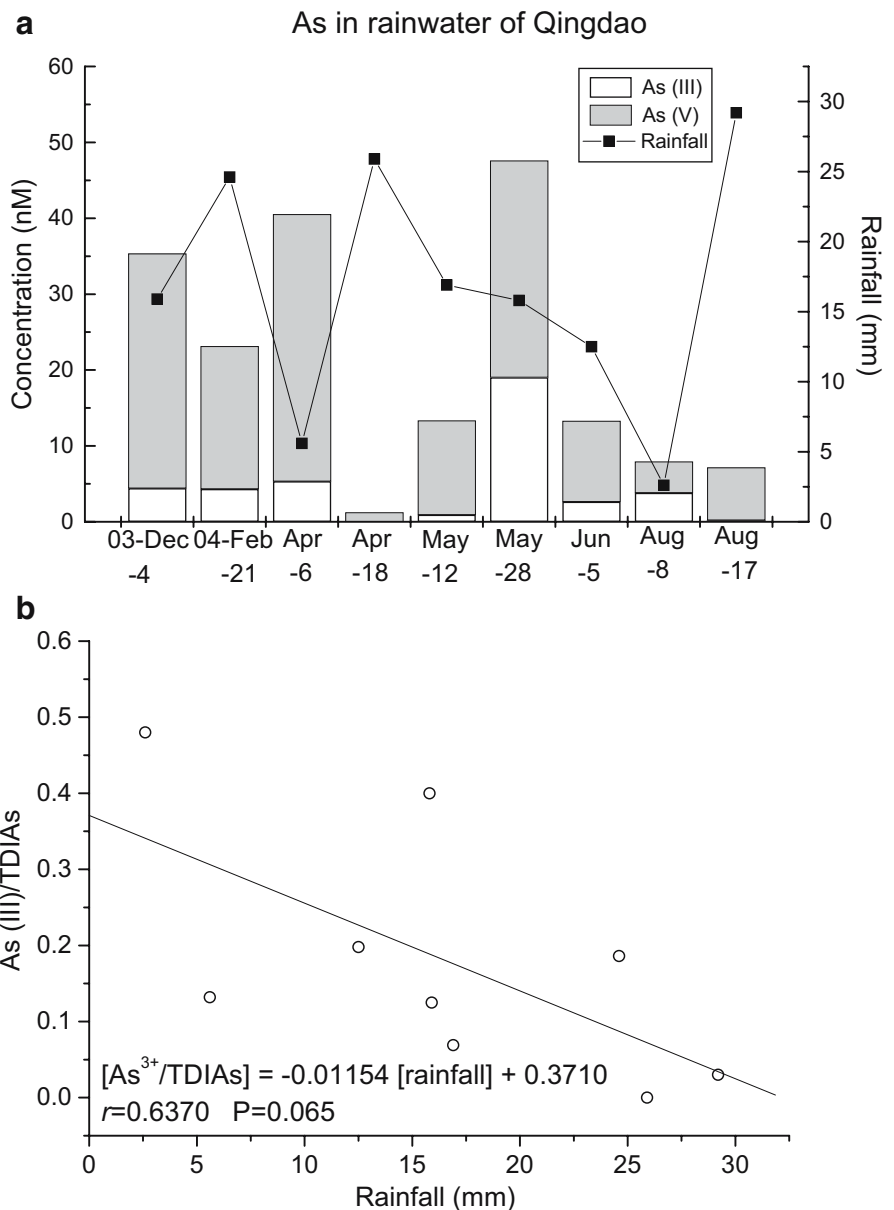
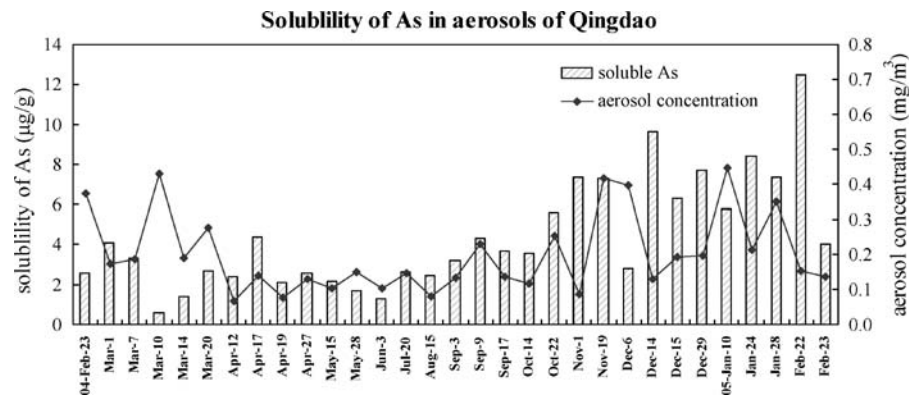


Fig. 6 Soluble inorganic arsenic in aerosols collected near Jiaozhou Bay



groundwater discharge estimated by model calculation, with the value of $6.81 \pm 9.2 \text{ mol yr}^{-1}$ (Zhu et al. 2005, private communication). These discharges are moderately lower than the river input and the atmospheric deposition. Two factors should be considered for this situation. First, the concentrations of TDIA in the groundwater are relatively low. Second, the water discharge from the groundwater to Jiaozhou Bay has decreased very much since the construction of embankments, especially in the Daguhe drainage basin, where the water discharge decreased from $2,000 \text{ m}^3 \text{ d}^{-1}$ to $<1,000 \text{ m}^3 \text{ d}^{-1}$ in the last few years.

There are three wastewater treatment plants (Haibohe, Licunhe and Tuandao) that discharge directly into Jiaozhou Bay, with wastewater discharges of 7.54×10^4 ,

5.01×10^4 and $5.96 \times 10^4 \text{ m}^3 \text{ d}^{-1}$, respectively. TDIA and As (III) were only measured for the wastewater from Haibohe (15.6 nM for TDIA and 14.8 nM for As (III)) and Tuandao (13.8 for TDIA and 11.1 nM for As (III)). It was assumed that the concentrations at the Licunhe wastewater treatment plant were comparable to those at Tuandao, since they use a similar treatment technique. As the wastewater treatment technique mainly depends on bacterial reduction, the content of As (III) in TDIA ranged from 73.6 to 97.5%. TDIA discharge from the wastewater was estimated to be $1.0 \times 10^3 \text{ mol yr}^{-1}$. The extent of wastewater discharge follows the TDIA fluxes from rivers and atmospheric deposition, and is higher than the groundwater input.

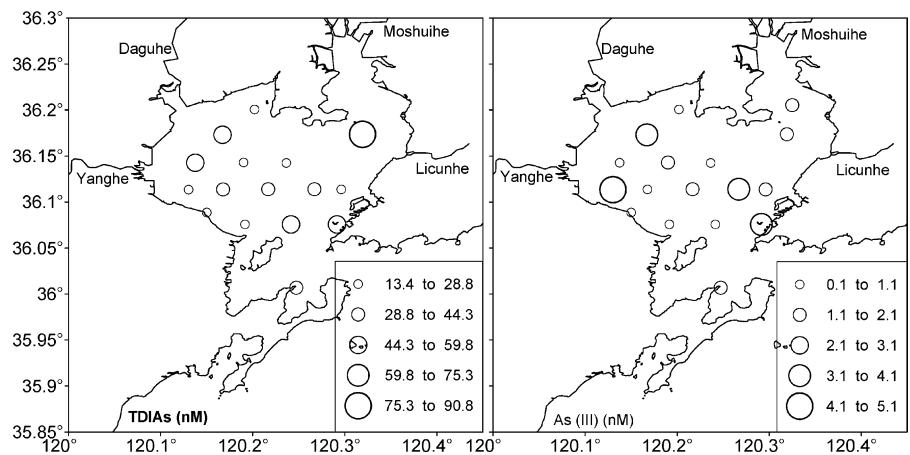
Table 4 The concentration of TDIA and As (III) and annual discharge in the groundwaters around Jiaozhou Bay

Drainage basin	Station	TDIA (nM)		As (III) (nM)		Average TDIA (nM)	Water discharge ($\text{m}^3 \text{ yr}^{-1}$) ^a	Flux (mol yr^{-1})
		Dec 2003	July 2004	Dec 2003	July 2004			
Baishahe	ZH	BDL	1.0	BDL	BDL	2.3±4.2	2.18×10^6 ^b	5.0±9.2
	WJNG	11.3	6.0	3.35	5.42			
	WS	0.25	BDL	BDL	BDL			
Daguhe	GD	BDL	BDL	BDL	BDL	12.4±14.1	800	0.010±0.011
	TY	7.5	6.7	0.078	0.29			
	CJPZ	29.4	30.8	0.51	15.4			
Yanghe	HYZ	0.08	BDL	0.02	BDL	13.2±22.3	1.39×10^5	1.8±3.1
	ZJT	18.6	13.0	1.60	0.38			
	WJT	6.3	6.9	3.22	3.5			
	ZJDEH	BDL	1.3	BDL	0.33			
	YHY	BDL	0.6	BDL	BDL			
TBT	11.0	74.2	8.6	5.4				

^a Data of groundwater discharges were provided by Dr. Liu Guan Qun of the College of Environmental Science and Engineering of the Ocean University of China

^b Zhu et al. 2005

Fig. 7 Horizontal distributions of TDIAAs and As (III) in the pore water of Jiaozhou Bay



3.3.4 Arsenic in the Pore Water

Figure 7 gives the distributions of TDIAAs and As (III) in pore water in December 2004. The concentrations ranged from 13.3 to 93.8 nM for TDIAAs and from 0.1 to 5.1 nM for As (III), with averages of 32.5 nM and 1.7 nM, respectively. The As (III)/TDIAAs ratio ranged from 0 to 0.27, with an average of 0.06. The concentrations of TDIAAs in the pore water were up to 5.5 folds higher than in the seawater except for two stations, with higher concentrations in the coastal area, especially in the northeast and northwest part of Jiaozhou Bay following the freshwater run-off. The distribution profile of TDIAAs shows the effect of anthropogenic inputs, especially near the Licunhe estuary, which was proven to be heavily polluted. The concentrations of As (III) in the pore water were nearly the same as the concentrations in seawater at most stations, except for the Daguhe and Yanghe

estuaries and the area near the Tuandao sewage treatment plant. In these areas, the concentrations were nearly 2 folds higher than the seawater As (III) concentration. The ratios of As (III)/TDIAAs in pore water were lower than in seawater, which implied that the As (III) in the pore water was easily removed by adsorption and/or oxidation (Chaillou et al. 2003).

4 Discussion

4.1 Arsenic Regime in Jiaozhou Bay

The concentrations of TDIAAs and As (III) show high levels in the north, especially the northeast and northwest parts of the bay, for the following reasons. First, the east and west shore are densely populated with various kinds of industrial waste discharge and aquaculture and show the effect of anthropogenic input (Li 1988); second, the tidal current moves mainly back and forth in a north-south direction, which is closely related to the geomorphology and structure of residual tidal currents. The residence time near the channel is less than 10 days, but in the western part of the bay, it is more than 100 days, based on calculations (Liu et al. 2004).

Three cruises carried out in JZB during the summer and autumn and during the spring and neap tides show similar distribution profiles and similar concentrations of TDIAAs, even with the strong perturbation and heavy rainfall from the typhoon that passed through JZB 12 days before the first cruise. This is quite different from the distribution of aluminum, which mainly comes from lithogenic sources. The

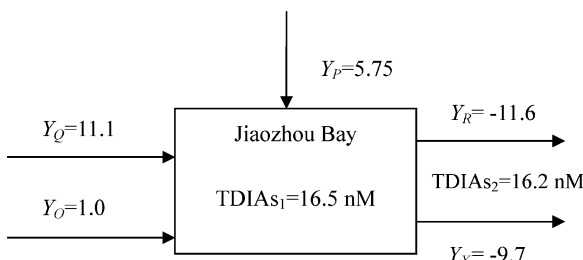


Fig. 8 Arsenic budget (10^3 mol yr^{-1}) in Jiaozhou Bay. In the figure, positive values indicate transports into Jiaozhou Bay; negative values indicate export of TDIAAs from Jiaozhou Bay. (P =Atmospheric deposition; Q =riverine input; O =wastewater transportation; X =exchange between Jiaozhou Bay (1) and the Yellow Sea (2); R =net transport from Jiaozhou Bay to the Yellow Sea)

Table 5 Comparison of TDIAAs and As (III) concentrations in this study with other regions (nM), in which averages are given in parentheses

Region	Period	TDIAAs	As (III)	Reference
Jiaozhou Bay	8–10/2001	7.7–28.3 (16.4)	1.0–12.6 (2.7)	This study
	2–8/1991	5–60 (19)	0–42 (5)	Xiao et al. 1996
	10/1980	13.3–34.7 (23.2)		Zhang 1982
		16.4–21.4 (18.2)	4.7–16.0 (8.9)	Li et al. 1981
Bohai Bay, China	8/1980, 1981	13.3–60.1 (25.4)		Li et al. 1984
Laizhou Bay, China	5,8/2002	11.1–143.4 (53.8±4.5)		Ma et al. 2003
Xiamen Harbor, China	8/1988	(16.3±2.7)		Li et al. 2002
	8/2000	34–58 (during typhoon)		
Biscayne Bay, USA	1993	(9.2)	(0.4)	Valette-Silver et al. 1999
Charleston Harbor, South Carolina	9/1998–9/1999	14.8–25.6 (19.6)	0.4–1.9 (1.1)	Riedel and Valette-Silver 2002
Chesapeake Bay, USA	7/1983	0.94–1.18	0.36–1.0	Sanders 1985
Darwin Harbor, Australia	2/1997, 3/1998, 2/2000	13.3–18.0 (15.5)		Munksgaard and Parry 2001
Huanghe drainage	8/1985	19.2–31.5 (26.8)		Zhang 1996
Huanghe Estuary	5/1985, 1986	3.8–28.8		Zhang 1996
	8/1985, 1986	17.8–38.8		
Changjiang	1986	(10.6)		Elbaz-Poulichet et al. 1990; Zhang et al. 1990
Changjiang Estuary	8/2002–5/2003	3.8–29.7 (18.8)	0.05–6.8 (1.79)	Cheng et al. 2006
Pearl River Estuary	11/1992	26.7–36.0 (30.7)		Zhang et al. 1995
Rhône Estuary, France	3/1984, 7/1987, 7/1988	14.7–50.7 (29.4)		Seyler and Martin 1990
Gironde Estuary, France	5/1994, 1995	14.2–20.2 (17.5)	0.2–3.9 (1.8)	Michel et al. 1997
Lena, Russia	9/1989	(2)		Martin et al. 1993
North Atlantic (surface)	8–9/1993	(15.7±1.3)	(0.45±0.21)	Cutter and Cutter 1998
Western Atlantic	5–6/1996	8.0–23.0 (16.3±2.1)	0.1–2.0	Cutter et al. 2001
Eastern Atlantic	3–5/1990	(12.9±1.8) surface		Cutter and Cutter 1995
		(20.9±0.5) bottom		
North Pacific		(24.2±0.4)	0–4.0	Andreae 1979
Central North Sea	8/1988	9.73–14.80 (11.39)		Millward et al. 1996
	9/1989	11.20–17.07 (13.1)		

distribution of aluminum also showed high levels in the northeast and northwest coasts during the summer due to freshwater input, but Al content decreased with the decline of freshwater input in the autumn (Xie et al. 2007). The relatively stable concentration of TDIAAs in Jiaozhou Bay shows that there are other sources besides freshwater runoff.

The average concentration of TDIAAs in Jiaozhou Bay is similar to concentrations in the Yellow Sea and East China Sea. The average As (III)/TDIAAs in Jiaozhou Bay is 0.16 ± 0.12 , which is higher than in the Yellow Sea or the East China Sea (Table 1). This implies that the anthropogenic input of arsenic in the drainage areas around Jiaozhou Bay contains larger

portions of As (III); particularly, abnormally high concentrations appeared at the bottom water during the G2 cruise when freshwater runoff was increased due to heavy rainfall.

4.2 Arsenic Budget

Based on the discussion above, annual TDIAAs discharged from major rivers, the atmosphere and wastewater treatment plants emptying into Jiaozhou Bay were calculated as $(11.1 \pm 10.0) \times 10^3 \text{ mol yr}^{-1}$, $5.75 \times 10^3 \text{ mol yr}^{-1}$ and $1.0 \times 10^3 \text{ mol yr}^{-1}$, respectively.

A steady-state box model based on the LOICZ Biogeochemical Modelling Guidelines was used to

construct a TDIA budget for Jiaozhou Bay from non-conservative distributions of TDIA and water budgets, which in turn are constrained by the salt balance under a steady-state assumption (Gordon et al. 1996). The model starts by calculating the water and salt budgets and then estimates the mass balance of arsenic in Jiaozhou Bay, including the exchange with the Yellow Sea. The water and salt budgets in Jiaozhou Bay have been calculated elsewhere, and are only briefly introduced here (Liu et al. 2005). Freshwater inputs from river discharge (V_O) and precipitation (V_P) are 768×10^6 and 248×10^6 $\text{m}^3 \text{yr}^{-1}$, respectively, reduced by evaporation (V_E), which is 371×10^6 $\text{m}^3 \text{yr}^{-1}$ (Liu Guan Qun, personal communication). Wastewater discharge (V_O) into Jiaozhou Bay is 67.5×10^6 $\text{m}^3 \text{yr}^{-1}$. From the water mass balance, the net water exchange (V_R) is from Jiaozhou Bay to the Yellow Sea with a residual flow of 712.5×10^6 $\text{m}^3 \text{yr}^{-1}$. Taking salinity as 0 PSS for freshwater and wastewater input, and as 31.3 PSS and 32 PSS for Jiaozhou Bay and the Yellow Sea (Yang and Wu 1999; Lin et al. 2005), respectively, the water exchange flow from the Yellow Sea to Jiaozhou Bay (V_X) is 32216×10^6 $\text{m}^3 \text{yr}^{-1}$ based on the salt balance in the bay.

The mean concentration of TDIA is 16.5 ± 3.3 nM in Jiaozhou Bay based on this study, while it is 16.2 ± 3.0 nM in the Yellow Sea based on the results of four cruises from September of 2000 to September 2003 (unpublished data). Figure 7 shows the arsenic budget based on the water budget and TDIA concentration in each source, in which the atmospheric deposition (P), the riverine input (Q), the wastewater transport (O), the exchange (X) between the Yellow Sea (2) and Jiaozhou Bay (1), and net transport (R) from Jiaozhou Bay to the Yellow Sea are shown. As shown in Fig. 7, the TDIA mainly came from riverine input, which accounted for 62% of the total input, followed by atmospheric deposition (32%) and wastewater transport (6%). The net transport (R) of TDIA from Jiaozhou Bay to the Yellow Sea is comparable with the exchange via circulation. However, there is a net imbalance between the inputs and outputs of dissolved TDIA. The arsenic budgets in Jiaozhou Bay are only rough results, depending on the accuracy of the freshwater flux, residual and mixing fluxes between Jiaozhou Bay and the Yellow Sea. If these flux estimates are valid, this imbalance suggests that there are net internal sources of dissolved TDIA entering into Jiaozhou Bay, with a value of 3.4×10^3 mol yr^{-1} .

These internal sources of dissolved TDIA in Jiaozhou Bay might include regeneration from particulate arsenic during the deposition of particles and resuspension of sediments, and diffusion from the pore water at the sediment-water interface, which can be proven by the high concentrations of TDIA in the pore water. The detailed flux at the sediment-water interface could not be considered in this study due to the absence of data for the core profile.

4.3 Comparison with other Areas in the World

The distribution of arsenic in Jiaozhou Bay has been a concern since the 1980s due to its toxicity and anthropogenic inputs (Li et al. 1981; Zhang 1982; Xiao et al. 1996). The concentrations of TDIA and As (III) in JZB have decreased in the last two decades (21% for TDIA and 70% for As (III) between the 1980s and 2000s), perhaps for the following reasons (Fig. 9, Table 5). People have begun to recognize the toxicity and environmental effect of arsenic and started to control the use of pesticides containing arsenic in recent years. Wastewater treatment plants have been established in the polluted drainage areas around JZB recently, and the treatment efficiency for arsenic is acceptable according to our results. However, the information of TDIA and As (III) concentrations in the main streams around Jiaozhou Bay has been very limited for the last few decades, and does not explain the decreasing trend of TDIA in Jiaozhou Bay. This should be studied further.

Table 5 tabulates the TDIA and As (III) from some of the world's rivers, estuaries, coastal bays and the open ocean. Concentrations of TDIA and arsenite in

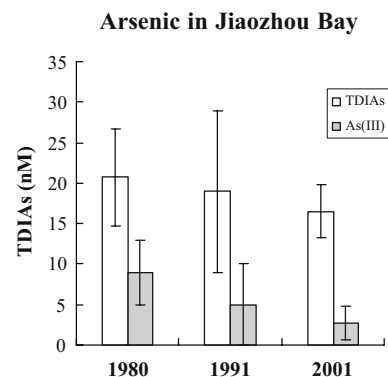


Fig. 9 Historical changes of TDIA in Jiaozhou Bay in the last 2 decades

Jiaozhou Bay are comparable to those reported in open oceans, including the Yellow Sea, East China Sea, the Atlantic and Pacific Oceans, the North Sea, and the coastal waters of America and Australia. However, the concentrations of TDIAAs in Jiaozhou Bay are lower than in some coastal bays, such as Bohai Bay, Laizhou Bay and Xiamen Harbor in China, which were proven to be seriously polluted by anthropogenic activities.

Comparing the rivers emptying into Jiaozhou Bay with other rivers in the world (Table 5), the Huanghe drainage basin and its estuary, the Pearl River estuary in China, the Rhône estuary in France and the main streams around Jiaozhou Bay had higher levels than those from pristine (Lena) and/or less disturbed riverine systems (Changjiang and Gironde). The high levels of As in the Huanghe are controlled by natural weathering and lithology and have not changed significantly since the 1940s (Zhang 1996). However, the high levels of As in the estuaries of the Pearl River and the Rhône River are caused by heavy anthropogenic disturbance (Zhang et al. 1995; Seyler and Martin 1990). The concentrations of arsenic in the main streams of Jiaozhou Bay showed high variations during the observations of both 2002 and 2004; most of the time, the concentrations were comparable to those in seawater, except for a few abnormally high concentrations. These variations indicated the presence of non-point anthropogenic input into Jiaozhou Bay.

5 Conclusion

Relatively low concentrations of dissolved inorganic arsenic were observed in Jiaozhou Bay compared to other locations with anthropogenic activities. Concentrations of total dissolved inorganic arsenic (TDIAAs, As (V+III)) were higher in the north than in the south of Jiaozhou Bay following freshwater discharges, and had statistically comparable concentrations between summer and autumn. The mean concentration of TDIAAs in this study was comparable to concentrations reported in the 1990s, but with relatively lower concentrations in the coastal region. A simple budget for TDIAAs in Jiaozhou Bay was estimated in this study. Examination of the data demonstrates that the major processes controlling the As geochemistry in Jiaozhou Bay are riverine input, atmospheric deposition, and exchange between Jiaozhou Bay and the

Yellow Sea; the contributions from groundwater and sewage input are negligible.

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