



## Arsenic content and fractionation in the surface sediments of the Guangzhou section of the Pearl River in Southern China

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### ABSTRACT

The Guangzhou section of the Pearl River (GSPR) has been seriously affected by long-term intensive industrial and urban activities. The objectives of this study were to determine the total As (TAs) content and the forms of that As in order to investigate the geochemical relationships between As forms and sediment mineral phases of the surface sediments of the GSPR. Fifteen samples of surface sediment were collected and analyzed for TAs as well as As chemical forms. Results indicated that TAs in the sediment samples averaged 24.6 mg kg<sup>-1</sup> and ranged from 16.7 to 33.4 mg kg<sup>-1</sup>. These values are generally higher than the probable effect level of 17.0 mg kg<sup>-1</sup>. The As was mostly associated with iron oxides (53.5%), followed by association with the residual fraction (36.2%). Amor-Fe bound As and Cry-Fe bound As quantities were positively correlated to the Amor-Fe and Cry-Fe quantities, respectively. In addition, organic matter (OM), clay and Sum-Fe contents were positively correlated to TAs in the sediment fractions. The molar ratios of iron oxide-bound As to iron content approached the maximum molar ratios of As to Fe for natural hematite, magnetite, and goethite. Adverse effects caused by As will likely frequently occur at these high levels of As contamination. Thus, it is necessary to remediate the sediment of the GSPR to reduce the potential risks of As contamination.

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## 1. Introduction

Arsenic buildup in the environment is of increasing concern due to its high toxicity and increasingly widespread occurrence [1,2]. It is ubiquitous in nature and elevated levels have resulted from both natural and anthropogenic sources [2,3]. Whereas As removal from naturally occurring groundwater and wastewater has been intensively studied [4], the geochemistry of As contamination in sediment has not been well studied. In general, low levels

*Abbreviations:* OM, organic matter; TAs, total As; Amor-Fe, amorphous and crystalline Fe oxide/oxyhydroxides; Amor-Al, amorphous and crystalline Al oxide/oxyhydroxides; Cry-Fe, well-crystallized Fe oxide/oxyhydroxides; Cry-Al, well-crystallized Al oxide/oxyhydroxides; Sum-Fe, sum of Amor-Fe and Cry-Fe; Sum-Al, sum of Amor-Al and Cry-Al.

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of As are typically reported in most sediment. However, elevated concentrations have been observed in sediments contaminated by anthropogenic activity [5]. The average content of As is 5 mg kg<sup>-1</sup> in world river sediments [6], while the average content in contaminated areas can be as high as 200 mg kg<sup>-1</sup> [5]. Although sediment has been widely recognized as the main sink for anthropogenic trace metallic and metalloid elements such as As [7], high concentrations of As in sediment are of potential concern, as this As might leach into pore or surface waters through desorption or dissolution. Therefore, it is critical to understand As geochemistry in sediment to protect aquatic environments.

In order to estimate the mobility, bioavailability, and toxicity of As in sediment, it is necessary to determine the chemical forms of As that are associated with different phases of the sediment in addition to the total As accumulation. Sequential chemical extraction can provide a valuable tool to distinguish among trace element fractions of different solubility related to mineralogical phases [8]. Thus, sequential selective extraction procedures are

generally applied to estimate As fractions in soils and sediments [9–11]. However, it is well known that an extractant cannot remove all of a targeted solid-phase component without affecting other soil compounds. In addition, redistribution and readsorption during the sequential extraction procedure can also occur, thus further complicating analysis. Despite these shortcomings, which are common to many other chemical extraction procedures, this technique still furnishes useful information regarding As binding, mobility, and availability. In addition, As species in the sediment can be transformed when the sediment is exposed to changing environmental conditions such as pH, redox potential, mineral composition and organic matter (OM) [7].

The Pearl River is the largest river system in Southern China. It has an average water flow of  $11,070 \text{ m}^3 \text{ s}^{-1}$  and flows through the central region of the city of Guangzhou City, one of the most densely populated industrial cities in China (Fig. 1). The climate of Guangzhou City is characterized with high annual rainfall of 1600–2300 mm. There has been rapid economic development in Guangzhou City since the 1970s. This rapid industrialization and urbanization might lead to an excessive release of pollutants, such as heavy metals, into the river sediment. It was found that the concentrations of Zn, Cu, Cd and Pb in the sediments of the Guangzhou Section of the Pear River (GSPR) were higher than those in the sediments of the Pearl River estuary [12]. Generally, the untreated effluents from industrial and municipal activities, the upstream runoff from mining sites and agricultural land, and the deposition of air pollutants all contribute to the increase of As levels in sediment. Therefore, we investigated the content and chemical forms of As in the sediment of the GSPR.

The major objectives of this study were to characterize the contamination and chemical forms of As in the surface sediments of the GSPR and to investigate the geochemical relationships between the As chemical forms and the sediment mineral phases. This study also provides initial prescriptions for the cleanup, dredging and management of the sediment around the GSPR.

## 2. Materials and methods

### 2.1. Sediment sampling

In the present study, 15 surface sediment samples (between 0 and 15 cm depth from the surface) were collected in the main river of the GSPR in March 2007 (Fig. 1) using cable operated sediment samplers (Van Veen grabs, Eijkelpamp) from a boat. At each site, samples from three different locations were taken, mixed together, and then transferred to acid-washed dark-colored polyethylene bags. Then they were taken to the laboratory immediately after collection. In laboratory, sediment samples were freeze-dried (FD-1A, China), slightly crushed, passed through a 2 mm sieve and stored at  $4^\circ\text{C}$  in glass bottles before analysis.

### 2.2. Analytical methods

The amount of sediment OM was determined by the potassium dichromate dilution heat colorimetric method [13]. Particle size analysis was performed by an LS 230 laser diffraction particle analyzer (Beckman Coulter) and the percentages of clay ( $<4 \mu\text{m}$ ), silt ( $4\text{--}63 \mu\text{m}$ ) and sand ( $63\text{--}2000 \mu\text{m}$ ) were calculated. The pH value

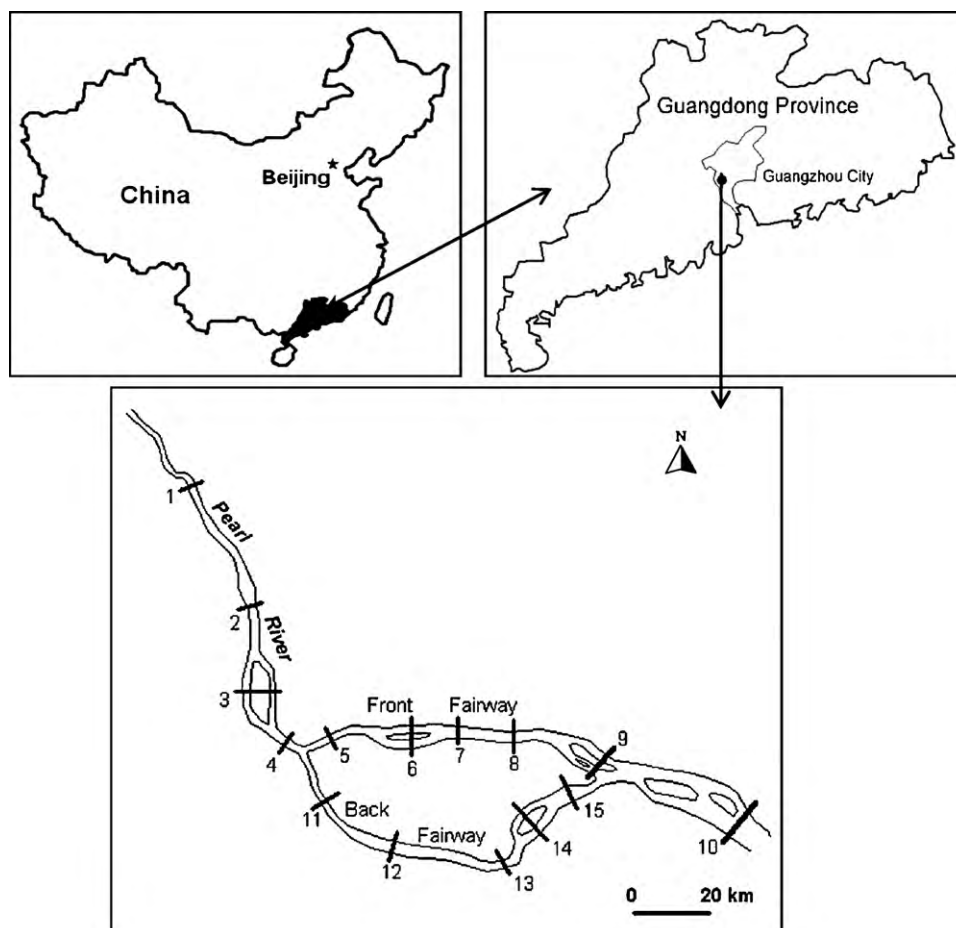


Fig. 1. Schematic graph of the sampling sites in the Guangzhou section of the Pearl River.

**Table 1**  
Steps in the selective sequential extraction procedure.

Step	Fraction	Extractant	Experimental conditions
1	Non-specifically sorbed As	0.05 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	4 h shaking (20 °C)
2	Specifically sorbed As	0.05 M NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	24 h shaking (20 °C)
3	Al oxides/oxyhydroxides associated As	0.5M NH <sub>4</sub> F (pH 7.0)	1 h shaking (20 °C)
4	Amorphous and poorly crystalline Fe oxide/oxyhydroxides bound As	0.2 M NH <sub>4</sub> -oxalate (pH 3.25)	4 h shaking in the dark (20 °C)
5	Well-crystalline Fe oxide/oxyhydroxides bound As	wash step: 0.2 M NH <sub>4</sub> -oxalate	10 min shaking (20 °C)
		0.2 M NH <sub>4</sub> -oxalate + 0.1 M ascorbic acid (pH 3.25)	30 min shaking in water bath at 96 °C
		wash step: 0.2 M NH <sub>4</sub> -oxalate	10 min shaking (20 °C)
6	Residual	HNO <sub>3</sub> -H <sub>2</sub> O <sub>2</sub>	Microwave digestion

of the sediment samples was analyzed in a 1:10 solid:liquid ratio suspension using a combination pH electrode (Orion, USA).

Another aliquot of sediment sample was digested with aqua regia (1% KMnO<sub>4</sub>) and 1% oxalic acid. The As concentration in the supernatant was measured by hydride generation atomic fluorescence spectroscopy (HG-AFS) (HG-AFS230, Beijing Haiguang Instruments, Inc., China). The accuracy of the total As (TAs) measurements was checked by conducting an analysis of a certified reference material (BCR-CRM 277b). The error was less than 9%.

Taking into account the anionic behavior of As in the sediment samples, the six-step sequential extraction procedure modified from Wenzel et al. and Lombi et al. [10,14] was performed using one gram of dry sediment. The extraction procedures were designed to separate specific environmental compartments of As and other trace metals in the sediment samples (Table 1). Non-specifically sorbed As (F1), specifically sorbed As (F2), Al oxide/oxyhydroxides associated As (F3), amorphous and poorly crystalline Fe oxide/oxyhydroxides bound As (F4) and well crystalline Fe oxide/oxyhydroxides bound As (F5) were sequentially and selectively extracted by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>, NH<sub>4</sub>F, NH<sub>4</sub>-oxalate and NH<sub>4</sub>-oxalate/ascorbic acid solutions, respectively (Table 1). Residual As (F6) was determined by the difference between the TAs content and the sum of the reactive fractions described above. The suspensions in each step were centrifuged at 10,000 rpm for 10 min at room temperature using a Xiang Yi centrifuge. The supernatants were filtered through a 0.45 μm membrane and analyzed for As by Hydride Generation Atomic Absorption Spectrometric (HGAFS) method. Amor-Fe (Al) and Cry-Fe (Al) were extracted in steps four and five, respectively, of the As

sequential extraction and measured by ICP-OES (IRIS Instrepid II, Thermo Electron). All reagents were of analytical grade. The precision of the sequential extraction method was calculated as the variation coefficients (CV) of three replicates from two sediment samples. Average CVs of As were 7.2%, 5.8%, 6.4%, 6.5% and 5.9% for F1, F2, F3, F4 and F5, respectively.

### 3. Results and discussion

#### 3.1. General properties of the sediments

A selection of general physical and chemical characteristics of the sediment samples are shown in Table 2. The pH values of the sediments were in the range of 7.45–8.32, displaying an alkaline character. The amount of OM in the sediments ranged from 1.86% to 7.02%. Higher OM content was observed at sites 4, 5 and 7. These sites are located in the central region of Guangzhou City, and thus, it is likely that their sediments are mainly polluted by the local industrial activities and the municipal wastewater. The sediments of the GSPR generally contained higher clay and silt particles than other sediments, e.g., the sediments of the Yangtze River generally contained sand particles of 50–90% and clay particles of <10% [15]. The sediment contents of Amor-Fe, Amor-Al, Cry-Fe, and Cry-Al existed in the ranges of 1.6–4.1, 0.8–2.3, 7.9–14.1, and 1.0–3.2 g kg<sup>-1</sup>, respectively. The Amor-Fe content was obviously lower than the content of Cry-Fe. The sediment contents of Amor-Al and Cry-Al were both lower than those of Amor-Fe and Cry-Fe. Very high Fe content in the sediment at site 10 might be caused by solid waste from local industries.

**Table 2**  
Properties of the surface sediments of the Guangzhou section of the Pearl River.

Sites	pH	OM (%)	Amorphous		Crystalline		Particle size distribution (%)		
			Fe (g kg <sup>-1</sup> )	Al (g kg <sup>-1</sup> )	Fe (g kg <sup>-1</sup> )	Al (g kg <sup>-1</sup> )	Clay (<4 μm)	Silt (4–63 μm)	Sand (63–2000 μm)
1	7.55	2.79	1.7	2.3	7.9	1.9	17.25	39.45	35.94
2	8.03	4.72	3.1	2.1	9.8	1.9	24.92	32.18	35.86
3	7.89	4.02	3.5	1.1	10.6	1.1	22.43	42.23	29.56
4	8.32	5.62	3.2	1.1	12.5	1.0	29.64	40.29	27.09
5	8.16	7.02	3.9	1.7	12.9	2.9	25.48	42.23	27.58
6	7.72	4.06	3.5	0.8	11.9	1.9	23.42	35.55	34.98
7	7.96	6.05	3.0	1.2	9.5	2.3	26.25	40.69	28.28
8	8.02	2.32	2.6	1.2	11.3	1.3	20.57	34.85	40.64
9	7.45	4.03	3.1	2.1	11.5	3.0	21.95	36.88	40.78
10	8.18	5.02	4.1	1.5	14.1	2.1	26.28	32.56	42.65
11	7.89	3.04	2.3	1.3	9.4	2.5	22.46	36.79	34.25
12	8.05	2.05	2.0	2.2	12.6	2.4	20.18	32.18	45.82
13	7.94	2.14	2.2	1.8	9.6	2.1	16.87	42.65	35.68
14	7.88	1.86	1.6	0.9	9.0	1.9	14.68	38.47	44.24
15	8.13	3.24	2.5	1.6	12.8	3.2	17.54	33.51	46.84
Ave.	7.94	3.87	2.82	1.53	11.03	2.10	21.99	37.37	36.68
Std.	0.23	1.58	0.77	0.49	1.78	0.65	4.19	3.80	6.65
CV%	2.9	40.8	27.3	32.1	16.1	31.1	19.0	10.2	18.1
Max.	8.32	7.02	4.10	2.30	14.10	3.20	29.64	42.65	46.84
Min.	7.45	1.86	1.60	0.80	7.90	1.00	14.68	32.18	27.09

**Table 3**

The basic statistical parameters of various As chemical forms in the surface sediments of the Guangzhou section of the Pearl River.

Sites	As concentrations (mg kg <sup>-1</sup> )							As proportions (%)					
	F1	F2	F3	F4	F5	F6	TAs	F1	F2	F3	F4	F5	F6
1	0.29	0.70	0.09	4.12	3.82	7.63	16.65	1.74	4.20	0.54	24.74	22.94	45.83
2	0.87	2.05	0.21	8.35	5.02	8.06	24.56	3.54	8.35	0.87	34.00	20.44	32.81
3	0.64	1.14	0.38	8.78	5.25	7.23	23.42	2.73	4.87	1.64	37.49	22.42	30.85
4	1.21	1.82	0.17	13.75	7.51	8.96	33.42	3.62	5.45	0.52	41.14	22.47	26.80
5	0.74	1.21	0.37	12.27	6.16	9.10	29.85	2.48	4.05	1.25	41.11	20.64	30.48
6	1.05	1.97	0.63	9.97	5.75	8.14	27.51	3.82	7.16	2.29	36.24	20.90	29.59
7	0.52	1.45	0.42	8.84	4.58	10.61	26.42	1.97	5.49	1.60	33.46	17.34	40.15
8	0.51	1.86	0.28	7.72	5.44	8.87	24.68	2.07	7.54	1.13	31.28	22.04	35.94
9	0.78	1.78	0.68	7.49	4.21	12.38	27.32	2.86	6.52	2.49	27.42	15.41	45.31
10	0.72	1.25	0.61	10.84	6.52	10.60	30.54	2.36	4.09	2.01	35.49	21.35	34.70
11	0.51	1.05	0.25	6.58	4.25	9.90	22.54	2.26	4.66	1.11	29.19	18.86	43.92
12	0.62	1.48	0.18	5.97	6.05	7.27	21.57	2.87	6.86	0.83	27.68	28.05	33.70
13	0.43	2.09	0.14	6.25	3.68	6.65	19.24	2.23	10.86	0.73	32.48	19.13	34.56
14	0.48	1.18	0.22	4.68	4.48	7.58	18.62	2.58	6.34	1.18	25.13	24.06	40.71
15	0.38	2.18	0.25	5.02	5.83	8.18	21.84	1.74	9.98	1.14	22.99	26.69	37.45
Ave.	0.65	1.55	0.33	8.04	5.24	8.74	24.55	2.59	6.43	1.29	31.99	21.52	36.19
Sta.	0.25	0.45	0.19	2.79	1.09	1.56	4.70	0.66	2.09	0.61	5.75	3.27	5.91
CV%	38.8	29.1	57.3	34.7	20.7	17.9	19.2	25.4	32.6	47.0	18.0	15.2	16.3
Max.	1.21	2.18	0.68	13.75	7.51	12.38	33.42	3.82	10.86	2.49	41.14	28.05	45.83
Min.	0.29	0.70	0.09	4.12	3.68	6.65	16.65	1.74	4.05	0.52	22.99	15.41	26.80

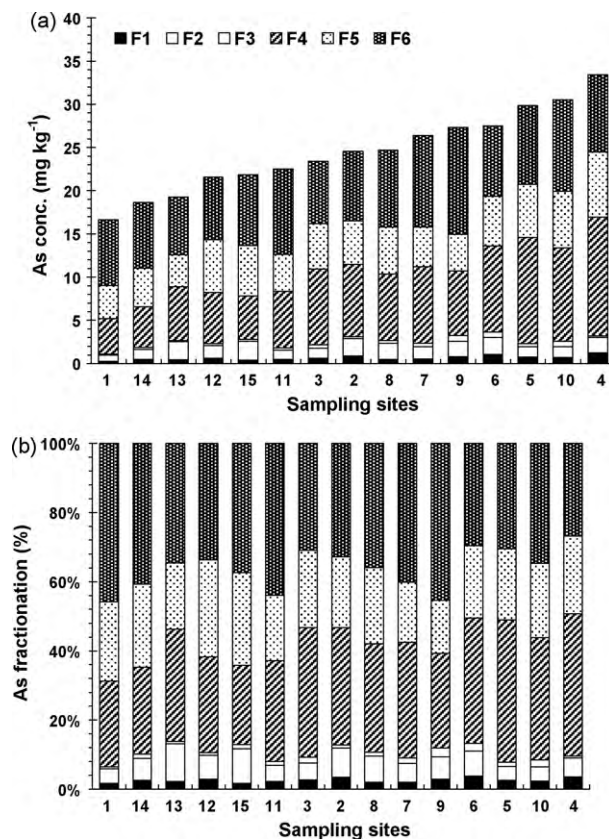
### 3.2. Total As in the surface sediments of the GSPR

TAs in the sediment ranged from 16.65 mg kg<sup>-1</sup> at site 1 to 33.42 mg kg<sup>-1</sup> at site 4 with a mean value of 24.55 mg kg<sup>-1</sup> (Table 3). The highest concentrations of As was found at site 4. There are industrial zones around site 4 and a large number of industrial wastewater and municipal wastewater from Foshan City also flows through this site. These industrial influences may be large contributors to the contamination at site 4. On the other hand, the lowest content of As was found at site 1. Site 1 is located in the source region of the drinking water for Guangzhou City, so little wastewater is discharged around this site. The background content of As in the soils of the Guangdong province is 8.9 mg kg<sup>-1</sup> [16]. The mean content of As in worldwide river sediments is 5 mg kg<sup>-1</sup> [6]. Hence, the surface sediments of the GSPR contained much higher As than worldwide river sediments and the Guangdong province soils. In addition, Huang et al. [17] reported that the sediments of the Pearl River estuaries contained 21.1 mg kg<sup>-1</sup> of As. This value is only slightly lower than the mean content of As in the surface sediments of the GSPR. On the other hand, the As content in the GSPR sediments was lower than that for the well-known contaminated sediments. For example, the sediments of the Le An River and Huangpu River in China contained 41 and 81 mg kg<sup>-1</sup> of As, respectively [18,19]. The sediments of the Huangpu River were contaminated by the wastewater from the Shanghai economic zone, whereas the sediments of the Le An River were heavily contaminated by mining activity. Anthropogenic sources of As include pesticides, herbicide and fertilizer production, glass and ceramic manufacturing industries, petroleum refining, and smelting of As-bearing ores [3]. Since the 1970s, there has been rapid economic development in the cities of Guangzhou and Foshan. This rapid industrialization and urbanization has led to the excessive release of pollutants including As into the river sediments. Industries such as glass and ceramic manufacturing, paper and semiconductors production, smelting, printed circuit board manufacturing and automobile manufacturing developed very quickly and have most likely led to an increase in the As content in the surface sediments of the GSPR.

### 3.3. Chemical forms of As in the surface sediments of the GSPR

The As content in the F1, F2, F3, F4, F5 and F6 fractions ranged from 0.29 to 1.21, 0.70 to 2.18, 0.09 to 0.68, 4.12 to 13.75, 3.68

to 7.51 and 6.65 to 12.38 mg kg<sup>-1</sup>, respectively; the average contents of the sediment fractions were 0.65, 1.55, 0.33, 8.04, 5.24, and 8.74 mg kg<sup>-1</sup>, respectively; these fractions had TAs contents of 2.6%, 6.4%, 1.3%, 32.0%, 21.5% and 36.2%, respectively (Table 3, Fig. 2). The rank order of the average As content in each fraction was F6 > F4 > F5 > F2 > F1 > F3. In addition, the sum of fractions F4, F5 and F6 comprised more than 90% of the TAs content. Iron oxide-bound As comprised over 53% of the TAs. Devesa-Rey et al. observed a



**Fig. 2.** Absolute partition patterns (a) and relative partition patterns (b) of As among sediment fractions in the main river sediments of the Guangzhou section of the Pearl River.



similar distribution of As in the sediments of Anllóns River in north-west Spain (3.4%, 2.7%, 1.4%, 20.7%, 13.6% and 58.2% of As in the F1, F2, F3, F4, F5 and F6, respectively) when they extracted As using the same procedure [20]. In another study, As fractions in the lake, canal, and river sediments were determined with the Community Bureau of Reference (BCR, now Standards, Measurements and Testing Programme SM&T) sequential extraction method and yielded ranges of 3.7–8.3%, 46.4–51.9%, 11.7–16.5%, and 23.9–31.3% in the acid soluble fraction, the reducible fraction, the oxidizable fraction, and the residual fraction, respectively [11]. The reducible fraction in this study is similar to the iron oxide-bound As in our study, thus the As content in the reducible fraction is roughly equal to that of the iron oxide-bound As. The concentration of iron oxide-bound As in the sediments of the GSPR generally increased as the TAs concentration increased, whereas other phases did not show a similar correlation (Fig. 2). Therefore, it is likely that anthropogenic As may first bind to Fe oxides and oxyhydroxides in the sediment.

The residual phase As that is mostly associated with sediment organic matter and primary minerals represented a large proportion of TAs in the sediments of the GSPR. The residual phase As is relatively stable compared to the pH and redox sensitive Fe, Mn, or Al oxide and oxyhydroxide-bound As. This phase is thus not expected to be a significant source of As in the water column system. Therefore, the relatively high content of As in the residual fraction might be beneficial from an environmental risk perspective [21]. The major minerals that bound As in the sediment fractions were metal oxides. Particularly, iron oxides were major binders due to their greater abundance, specific surface area, and stronger binding affinity [22–25]. The binding of As with iron oxides occurred either via co-precipitation, which allowed for the incorporation of As into the mineral or amorphous phase structures, via adsorption onto surface sites [26] or via penetration into the lattice [27]. Therefore, the geochemistry of As in the sediment is closely coupled to the biogeochemical cycling of iron oxide/oxyhydroxides. The main retention mechanism of As in the sediment of the GSPR might be co-precipitation with Fe as indicated by the higher proportion of amorphous Fe oxides-bound As. A secondary mechanism of As retention is likely via penetration into the crystalline Fe oxides.

#### 4. Relationships between As and mineral phases in the sediments of GSPR

Regressions of the As content in fraction F3 vs. Sum-Al, the As content in fraction F4 vs. Amor-Fe, the As content in fraction F5 vs. Cry-Fe, and the As content in fraction F6 vs. organic matter are shown in Fig. 3 and reveal that the As content in the fraction F4, F5 and F6 were positively correlated to the Amor-Fe, Cry-Fe and

organic matter content in the sediments of the GSPR, respectively. The As content in the fraction F3 was not correlated to the content of Sum-Al. In addition, TAs content was positively correlated to the content of Sum-Fe, clay and OM contents but was not correlated to the content of Sum-Al in the sediment fractions (Fig. 4).

##### 4.1. As and clay contents

The size of the particles in the sediment has a pronounced role in controlling the distribution and mobility of As in the sediment. Because fine-grained sediments possess greater surface areas, they adsorb large amounts of As onto their surfaces. In addition, Fe oxide colloids were found as fine particles within the clay particles. Previous research determined positive correlations between the amount of As and the amount of clay in sediments [28]. In general, soils with higher clay contents retain more As than soils with lower clay contents [28]. On the contrary, As has a shorter residence time in sandy soils, especially under alkaline conditions [29]. Therefore, studies of arsenate and arsenite removal from water by oxides and clay minerals have been performed [4].

##### 4.2. As and organic matter

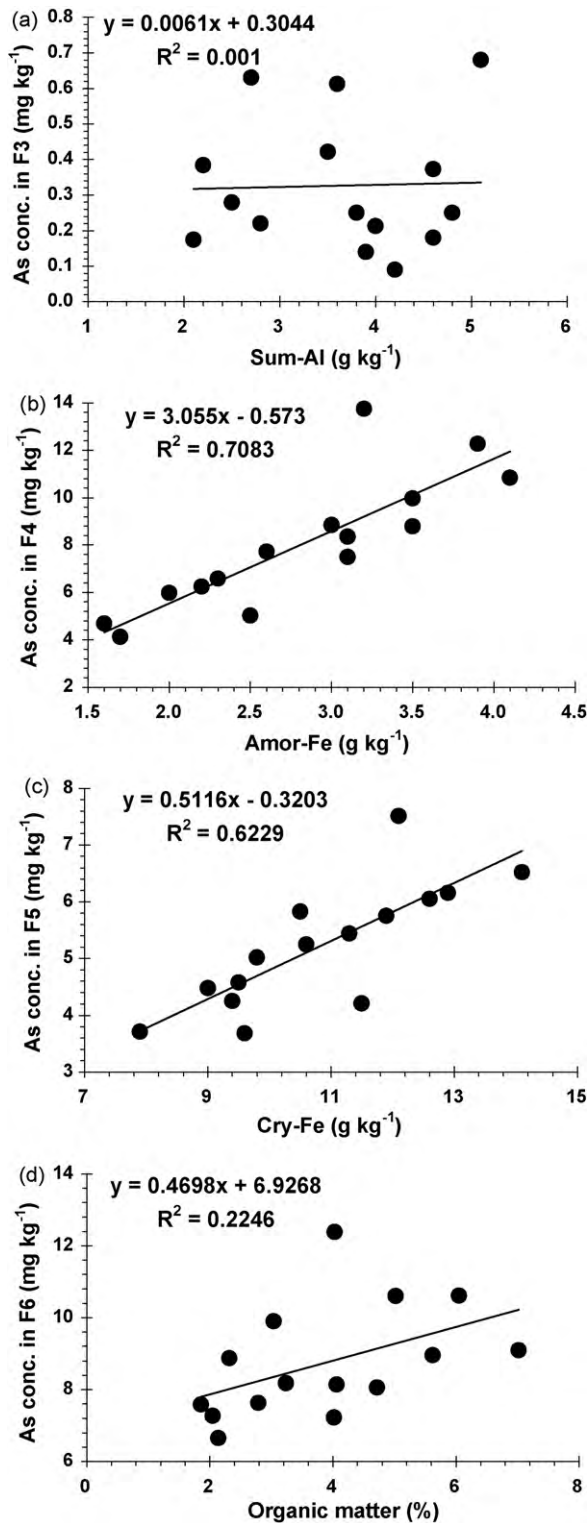
Sediment and soil organic matter, especially humic substances, are known to be adsorbents for As [30]. The occurrence of higher concentrations of As with increasing organic matter contents is possibly caused by the formation of organo-As complexes [30]. Saada et al. [31] reported that As adsorption onto humic acids occurs through positively charged amine groups. In the present study, positive correlations of organic matter vs. TAs and residual As (F6) suggest that organic matter plays a significant role in controlling As transport in the sediments of the GSPR. Moreover, OM-bound As had a high stability in the sediment because most of it cannot be exchanged by phosphate anions (Fig. 4).

##### 4.3. As and Fe/Al oxyhydroxides

Fe and Al oxides and hydroxides are the natural As-binding phases. The presence of these metals is strongly correlated to the fine-grained sediment fraction, as is true for As. Hence, Fe and Al oxides have been often used as sorbents to remove As from water and wastewater [4]. Generally, the correlation coefficients of As vs. Fe were higher than those of As vs. Al (Table 4). In addition, As was negatively correlated to Al in the sediments of the Western North Sea [32] and the GSPR. The regression slopes of As vs. Fe generally ranged from 1.90 to 15.4, whereas the slope for the sediments of the GSPR was 17.16. It should be noted that the Fe

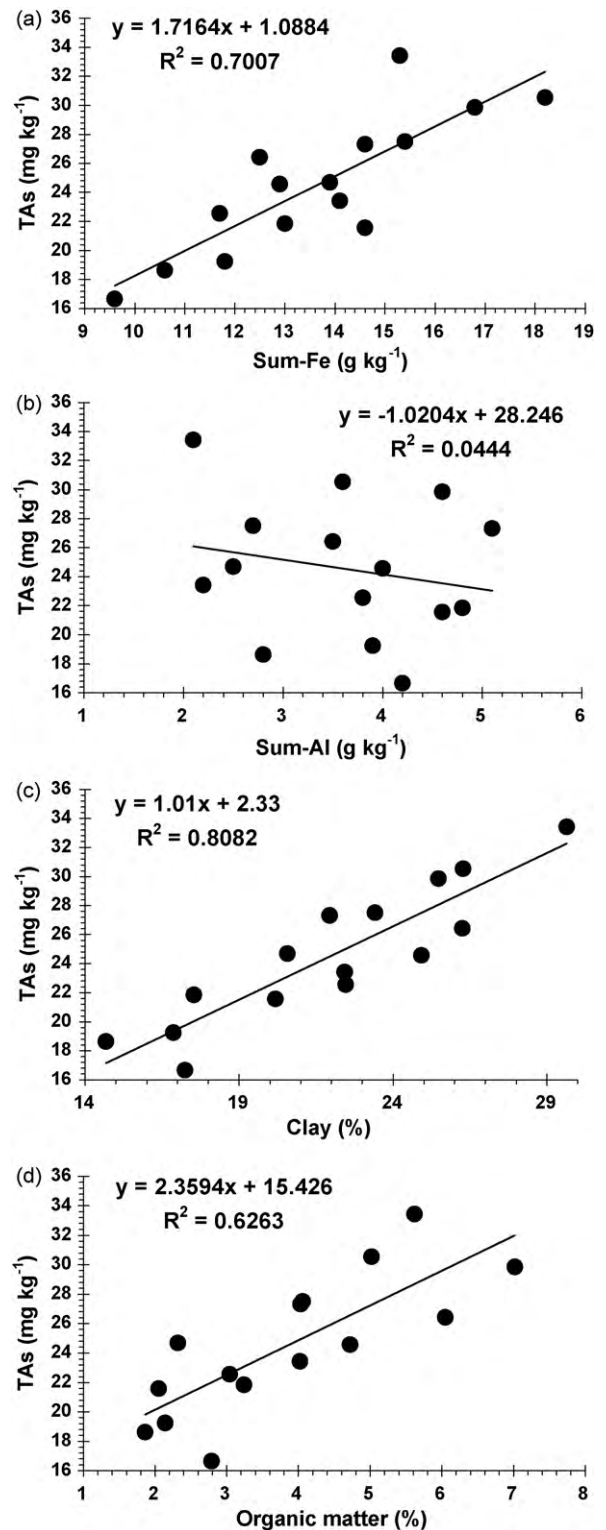
**Table 4**  
Regression equations of As vs. Fe or Al in units of  $\text{mg kg}^{-1}$  in the sediment at various sites.

Site	Regression equation	$R^2$	$n$	Reference
East and Gulf of Mexico	$[\text{As}] = 3.25 \times 10^{-4}[\text{Fe}] + 0.59$	0.680	360	[34]
	$[\text{As}] = 1.68 \times 10^{-4}[\text{Al}] - 0.54$	0.520	360	[34]
Southern California coastal shelf	$[\text{As}] = 1.90 \times 10^{-4}[\text{Fe}] + 1.49$	0.750	110	[35]
Gulf of Mexico	$[\text{As}] = 0.91 \times 10^{-4}[\text{Al}] + 1.19$	0.830	103	[36]
Humber	$[\text{As}] = 8.09 \times 10^{-4}[\text{Fe}] + 6.81$	0.747	16	[32]
	$[\text{As}] = 5.32 \times 10^{-4}[\text{Al}] + 9.00$	0.750	16	[32]
Western North Sea	$[\text{As}] = 15.40 \times 10^{-4}[\text{Fe}] - 4.12$	0.541	195	[32]
	$[\text{As}] = -1.19 \times 10^{-4}[\text{Al}] + 16.78$	0.003	195	[32]
Dogger Bank	$[\text{As}] = 7.31 \times 10^{-4}[\text{Fe}] - 0.06$	0.406	258	[32]
	$[\text{As}] = 6.09 \times 10^{-4}[\text{Al}] - 3.23$	0.203	258	[32]
Dexing area	$[\text{As}] = 2.16 \times 10^{-4}[\text{Al}] + 2.42$	0.317	326	[37]
GSPR	$[\text{As}] = 17.16 \times 10^{-4}[\text{Fe}] + 1.09$	0.701	15	This study
	$[\text{As}] = -10.20 \times 10^{-4}[\text{Al}] + 28.25$	0.044	15	This study



**Fig. 3.** Correlations between As chemical forms and content of mineral phases in the sediments of the Guangzhou section of the Pearl River: (a) the As content in fraction F3 vs. Sum-Al content, (b) the As content in fraction F4 vs. Amor-Fe content, (c) the As content in fraction F5 vs. Cry-Fe content, and (d) the As content in fraction F6 vs. organic matter content.

content was not total content in the sediments of the GSPR and that this might lead to the observed steeper slope. Nevertheless, steep regression slopes of As vs. Fe were usually associated with high anthropogenic input of As into sediments. In addition, the molar ratio of As to Fe in sediments can further show the anthropogenic



**Fig. 4.** Correlations between TAs and the contents of sum-Fe, sum-Al, clay, and OM in the surface sediments of the Guangzhou section of the Pearl River: (a) TAs content vs. sum-Fe, (b) TAs content vs. sum-Al, (c) TAs vs. clay, and (d) TAs vs. OM.

input of As into the sediments. The average molar ratios of the As content in fraction F4 to Amor-Fe content and the As content in fraction F5 to Cry-Fe content in the sediments of the GSPR were  $2.11 \times 10^{-3}$  and  $3.54 \times 10^{-4}$ , respectively, indicating that Amor-Fe can sorb more As. Further, The average molar ratio of Sum-As to Sum-Fe was  $1.32 \times 10^{-3}$ . These molar ratios are in the range

of  $3.80 \times 10^{-5}$  to  $2.12 \times 10^{-2}$  that has recently been reported for lacustrine sediments by Belzile and Tessier [33]. The maximal molar ratios of As to Fe for natural hematite, magnetite, and goethite were  $2.83 \times 10^{-4}$ ,  $2.21 \times 10^{-4}$ , and  $4.45 \times 10^{-4}$  for As(III), respectively; while the ratios were  $8.82 \times 10^{-4}$ ,  $2.71 \times 10^{-4}$ , and  $5.34 \times 10^{-4}$  for As(V) [24]. Therefore, iron oxides in the sediment of the GSPR might be saturated by As. However, synthesized Schwermannite had a maximum molar ratio of  $2.0 \times 10^{-2}$  [25], 10 times higher than the molar ratio of the As contents in fraction F4 to Amor-Fe content in the sediments of the GSPR.

## 5. Potential ecosystem risk assessment

In order to quantitatively assess As risk in the sediments of the GSPR, the As levels in the sediment were compared with the sediment quality guidelines of threshold effect level (TEL) and probable effect level (PEL) [38]. The TEL for As is  $5.9 \text{ mg kg}^{-1}$ ; concentrations below this value rarely have adverse aquatic biological effects. The PEL is  $17 \text{ mg kg}^{-1}$  and represents the concentration above which adverse effects would frequently occur. The concentrations of As in the sediments of GSPR ranged from 16.65 to  $33.42 \text{ mg kg}^{-1}$ , indicating that adverse aquatic biological effects caused by As will frequently occur. Therefore, it is necessary to remediate the sediments of the GSPR to reduce and remove the potential risk of As in the sediment.

## 6. Conclusions

The TAs content in the surface sediments of the GSPR ranged from 16.65 to  $33.42 \text{ mg kg}^{-1}$ , with an average of  $24.55 \text{ mg kg}^{-1}$ . This content was higher than the PEL, and thus, it is likely that adverse aquatic biological effects caused by As are occurring in the sediments of the GSPR. The As was mostly associated with iron oxides, followed by association with the residual fraction. The As content in the fraction F4 and F5 were correlated to the content of Amor-Fe and Cry-Fe, respectively, in the sediment. In addition, TAs was positively correlated to Sum-Fe, clay and OM contents in the sediments. The molar ratios of the As content in the fraction F4 to Amor-Fe content and the As content in the fraction F5 to Cry-Fe content roughly approached the maximum molar ratios of As to Fe for natural hematite, magnetite, and goethite. Generally, the sediments of the GSPR are seriously contaminated by As and need to be remediated to decrease the potential risks of unsafe levels of As in the sediment.

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