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Geochemistry of reduced inorganic sulfur, reactive iron and organic carbon in fluvial and marine surface sediment in the Laizhou Bay region, China

Yanqing Sheng[1,*], Qiyao Sun[1], Wenjing Shi[1], Simon Bottrell[2], Robert Mortimer[3]

[1] Research Center for Coastal Environmental Engineering Technology of Shandong Province, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

[2] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

[3] School of Animal, Rural and Environmental Sciences, Nottingham Trent University, Brackenhurst campus, Southwell, Nottinghamshire. NG25 0QF, UK

Abstract:

Understanding the geochemical cycling of sulfur in sediments is important because it can have implications for both modern environments (e.g. deterioration of water quality) and interpretation of the ancient past (e.g. sediment C/S ratios can be used as indicators of palaeodepositional environment). This study investigates the geochemical characteristics of sulfur, iron and organic carbon in fluvial and coastal surface sediments of the Laizhou Bay region, China. A total of 63 sediment samples were taken across the whole Laizhou Bay marine region and the 14 major tidal rivers draining into it. Acid volatile sulfur, chromium (II)-reducible sulfur and elemental sulfur, total organic carbon and total nitrogen were present in higher concentrations in

* Corresponding author: E-mail address: yqsheng@yic.ac.cn, Phone: +86 535 2109265; Fax: +86 535 2109000

the fluvial sediment than in the marine sediment of Laizhou Bay. The composition of reduced inorganic sulfur in surface sediments was dominated by acid volatile sulfur and chromium (II)-reducible sulfur. In fluvial sediments, sulphate reduction and formation of reduced inorganic sulfur were controlled by TOC and reactive iron synchronously. High C/S ratios in the marine sediments indicate that the diagenetic processes in Laizhou Bay have been affected by rapid deposition of sediment from the Yellow River in recent decades.

Keywords: Inorganic sulfur; Iron; River; Sediment; Laizhou Bay

1. Introduction

The global biogeochemical cycles of carbon, iron and sulfur are closely linked during early diagenesis to form sedimentary sulfide-bearing minerals (Morse and Rickard, 2004; Canfield et al., 2005; Johnston et al., 2014). Interactions and limiting components of these cycles within different formation environments can dictate the geochemistry of the sulfidic material formed **(**Morgan et al., 2012). Therefore inorganic sulfur speciation may be important as a diagnostic tool for sediment conditions during early diagenesis. The interplay of microbial iron and sulphate reduction and inorganic reactions driven by their respective products are the primary controls on the burial of reduced sulfur in anoxic sediments (Morse and Berner, 1995). Berner and Raiswell (1983) found differences in the burial ratio of organic carbon to pyrite-S in different depositional environments, suggesting C/S ratios could be a

useful tool for determining palaeodepositional environments in ancient sedimentary rocks. Berner (1982) indicated that the C/S mass ratio in normal marine sediments (deposited under an oxic water column) was between 0.75 and 1.35 (calculated from molar ratio 2.0-3.6). Research into the distribution and transformations of reduced inorganic sulfur (RIS) in freshwater, estuary, peatland, salt marsh and marine sediments (Berner 1984; Coulson et al. 2005; Bottrell et al., 2010; Sheng et al., 2011, 2013a; Mortimer et al., 2011) has shown that pyrite and ferrous monosulfide are the two major end products in sediments where dissimilatory sulfate reduction is active (Zhu et al., 2014). Although sulfate and Fe (III) reduction along with the microbially mediated formation of sulfide minerals can increase alkalinity and reduce metal availability (Burton et al., 2005; Mortimer et al., 2011), oxidation of sedimentary sulfide during sediment resuspension may cause rapid deoxygenation and acidification of overlying water, posing an environmental hazard (Morse and Rickard, 2004; Sullivan et al., 2002). Therefore, in addition to potentially recording information about the environment of deposition, sulfur geochemistry may play an important role in affecting estuarine sediment and water quality (Anthony et al., 2010; Morgan et al., 2012).

Laizhou Bay is situated in the northern part of Shandong province, east China. It is a typical semi-enclosed inner sea, one of three main bays of the Bohai Sea. This bay is an important production base for fisheries and salt in China, and marine industrial and urban developments have been booming around the bay in recent years. Over 10 rivers, notably the Yellow River, Xiaoqinghe River, Yuhe River, Dihe River, and

Jiaolaihe River, drain into the bay with high loads of sediment and industrial and municipal wastewater (Sheng et al., 2013b). The rivers and coastal zone of this area have been polluted by organochlorine pesticides (Zhong et al., 2011), antibiotics (Zhang et al., 2012), polychlorinated naphthalenes (Pan et al., 2011) and trace metals (Wang and Wang, 2007). However, there is little data about the reduced inorganic sulfur (RIS) in the region. In this study, acid volatile sulfur (AVS), chromium (II)-reducible sulfur (CRS), elemental sulfur (ES), total sulfur (TS), reactive iron, total organic carbon (TOC) and total nitrogen (TN) were analyzed in surface sediments from both rivers and the coastal zone. The environmental biogeochemical behaviour of different RIS species and relationships between organic carbon, sulfur and iron within the river-estuary-coastal zone system of Laizhou Bay were studied in order to identify the factors controlling the transformation, burial and preservation of Fe, C and S and the ratios of C/S, Fe/S that result. This allows both assessment of current and potential future impact on water quality as well as providing evidence about how sediment sulfur geochemistry reflects the depositional environment.

2. Methods and materials

2.1 Samples collection and handling

General information on Laizhou Bay and its adjacent region was introduced by Pan et al. (2011) and Zhao et al. (2013). The salinity in surface and bottom water of the offshore area of Laizhou Bay is typically 26-31 psu (increasing gradually seaward from the river mouth offshore) (Qiao et al., 2010). Water and sediment were collected

from a total of 63 sampling sites in Laizhou Bay and from rivers draining into it (Fig. 1). All sampling equipment and storage containers were cleaned with distilled water before use. All of the seawater and river water samples were collected (approximately 0-50 cm below the surface) using a stainless steel bucket and were immediately transferred to a 5-L pre-cleaned amber glass bottle. The bottle was rinsed 3 times with a sample prior to sampling. The samples were kept at 4 °C in a cold room before further treatment and analysis in the laboratory. The surface sediments (0-10 cm) from the marine region were collected using a stainless steel grab sampler, and the surface sediments (0-10 cm) from rivers were collected using a plastic spatula. All sediment samples were immediately placed into 250 ml polypropylene vials, which were fully filled with sediment and sealed with gas-tight screw-caps and immediately frozen under nitrogen in an adiabatic box until further analysis. Before analysis, all sediment samples were homogenized (mixing with a glass rod) under a stream of N_2 in a sealed chamber.

Fig. 1

2.2 Sample analysis

The reagents used were all analytical grade or above, and deionized water (milli-Q) was used to prepare reagent solutions. All glass and plastic were soaked in 10% HNO_3 for 48 h and rinsed with milli-Q water several times before use. Water samples were filtered (0.47 μm Whatman® filters) and kept cool and dark prior to analysis for total dissolved organic carbon (TDOC, calculated from the difference between total carbon and total inorganic carbon), and total dissolved nitrogen (TDN) determined

using a Shimadzu TOC-V_{CPH}/SSM-5000A (analytical relative standard deviation (RSD)≤ 5%). Salinity was determined by a BANTE531 Portable Conductivity/Salinity Meter (Shanghai, China) (RSD < 0.05%). Sediment was treated with excess 1 N HCl overnight (stirring once a while) and washed twice with deionized water to remove carbonates, then the samples were dried at ~ 60 °C for 12 h and ground to ~100 mesh before TOC analysis using a Shimadzu TOC-V_{CPH}/SSM-5000A (RSD ≤ 3%). Total nitrogen (TN) and total sulfur (TS) were determined by an Elementar vario MACRO cube CHNS analyzer (RSD < 2.5%). Prior to grain size analysis, each sediment sample was treated with sodium hypochlorite (NaOCl) to remove organic matter. Grain size was analyzed using a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2,000 μm (RSD < 2.5%). The percentages of samples in each of the following three grain-size groups were determined: < 4 μm (clay), 4-63 μm (silt), and >63 μm (sand).

The separation and determination of AVS, CRS and ES were conducted following the cold diffusion procedure described by Hsieh and Shieh (1997). Briefly, AVS, CRS and ES were separated sequentially by 6 M HCl (18 h), acidic Cr (II) (48 h) and Cr (II) plus N, N-dimethylformamide (24 h), respectively, under a pure N_2 atmosphere, at ambient temperature. The liberated H_2S was passively trapped in an alkaline Zn solution (20% ZnOAc). The quantity of S for each solid-phase RIS species trapped in ZnS was determined by iodometric titration (RSD < 8%). Sediment samples of known weight (~2 g) were loaded into centrifuge tubes containing 50 mL 1 N HCl for extraction of reactive iron under stirring. After centrifugation (3000 rpm) of the

suspensions, the resultant supernatants were filtrated for analysis of Fe^{2+} and total reactive Fe separately. The reactive iron was determined using the ferrozine method (Wallmann et al., 1993). Fe^{3+} was calculated from the difference between total Fe and Fe^{2+} (RSD <6%). All treatments were undertaken in N_2 glove box to avoid oxidation of Fe^{2+} and sulfide during sample handling.

3. Results

3.1 Grain size distribution

As shown in Fig. 2, the grain sizes of marine surface sediments were mostly dominated by silt, with the average value of 57%. The grain sizes of sediments in most rivers were dominated by sand, with the average value of 49%, and there was a fine to coarse transition in the rivers from northern/western ones to the eastern/southern ones (Fig. 1).

Fig. 2

3.2 Concentrations of TDOC, TDN and salinity in marine and fluvial water bodies

The concentrations of TDOC, TDN and salinity in the water samples are presented for the whole Laizhou Bay marine region and 14 major tidal rivers in Table 1. In the rivers, the concentrations of TDOC and TDN ranged from 2.4 to 71.9 mg L^{-1} and 2.4 to 12.4 mg L^{-1}, respectively. In the marine area, the concentrations of TDOC and TDN were much lower, ranging from 1.89 to 5.27 mg L^{-1} and 0.27 to 0.68 mg L^{-1}, respectively. In the coastal sites of E4-6 and F1, TDOC and TDN were high, suggesting pollution by terrestrial sources. The Xiaoqing River (XQH), Yuhe River

(YH) and Dihe River (DH) all receive municipal and industrial wastewater, resulting in high TDOC and TDN concentrations at site F1 (Pan et al., 2011). The Weihe River (WH) and Jiaolaihe River (JLH) also receive municipal wastewater, resulting in high TDOC and TDN at sites E4-6. These results indicate that the discharge of these heavily polluted rivers is a major source of pollutant carbon and nitrogen to the coastal zone of Laizhou Bay. The salinity ranged from 26.7 psu to 31.1 psu in the marine region. Most of salinities are similar, the lowest value being at stie A1, close to the Yellow River estuary and hence diluted by the freshwater discharge (Fig 1). For the rivers, salinities are variable but most of them are higher than average fresh water values, ranging from 0.5 psu (Yellow River, YHH-1, 2) to 31.5 psu (Bailanghe estuary, WFG, higher than seawater). Because Laizhou Bay is an important salt production area, with many plants producing salt by solar evaporation of saline groundwater, residual bitterns are discharged into local rivers directly, resulting in high salinities in some areas such as the Bailanghe River (BLH), Yuhe River (YH) and Dajiawa River (DJW).

Table 1

3.3 Distributions of TOC, TN, TS in surface sediment

In the marine sediments, TOC contents varied between 0.65 and 1.97% dry weight, with an average of 1.27% (Table 2), higher than that previously reported at a nearby site (0.87%) (Zhu et al., 2012). TN content ranged from 0.01 to 0.07% dry weight, with an average of 0.04%. TS content ranged from 0.01 to 0.09% dry weight, with an average of 0.03%. Higher TOC and TN contents were all recorded at fluvial sampling

stations. For all the rivers, TOC, TN and TS contents showed a clear decreasing trend seaward from the mainland to the estuary (Table 2). It appears that, in general, industrial and domestic wastewater discharges inland resulted in organic matter enrichment (anthropogenic inputs), causing increasing TOC, TN and TS. The highest TOC (7.04%), TN (0.53%) and TS (0.42%) were found in the upstream part of the Xiaoqing River (XQH-2). This river drains the cities (including some special industrial parks) of Jinan, Zibo and Weifang in Shandong province, and hence the water quality is heavily impacted by pollution discharge, leading to the high TOC, TN and TS in the surface sediments.

Table 2

3.4 Distribution of AVS, CRS and ES in sediment

Detailed concentrations and proportions of S in the sediments of Laizhou Bay are shown in Table 2. In most marine sites, CRS was the dominant fraction of total reduced inorganic sulfur (RIS) except for site F2 (Fig. 1). However, in most rivers, AVS was the dominant RIS, with highest concentration of 6832 μg g^{-1} in the Dihe River (DH-2). However, for the upstream of Xiaoqing River (XQH-2), Yuhe River (YH-3) and Jiaolaihe River (JLH-2), CRS was the dominant RIS. In the marine area, AVS concentrations fall in a wide range from 1.17-371 μg g^{-1}(Table 2). The higher end of this range is consistent with AVS concentrations found in northern Yellow Sea coastal surface sediments (202-344 μg g^{-1}) (Sheng, et al., 2013a), but 89% (24 of 27) of our samples fall below the lower end of their range, consistent with the high TOC/TS ratios found in these sediments (Table 3). In the rivers, the AVS levels

(6.56-6832 μg g^{-1}) are consistent with many natural estuaries (e.g. 2880 μg g^{-1}, Morse and Cornwell, 1987) and Shijing River (1043 μg g^{-1}) located in the Pearl River delta (Sheng et al, 2011).

4. Discussion

4.1 Grain size characteristics

The grain sizes of marine surface sediments of Laizhou Bay were mostly dominated by silt (57%), which is consistent with a previous report (Qiao et al., 2010). There is an anti-clockwise circulation that dominates in Laizhou Bay and the residual current near the Yellow River mouth is mainly southward, so the transport of suspended sediment (silt) off the river mouth will influence the distribution of marine sediment grain sizes directly. However, in the marine sediments, there was a definite change in grain size across the bay, with the eastern side (sites C1, D4-6, E4-6) more coarse grained, which may be influenced by the coarse sediment input of local rivers. The Weihe River (WH) and Jiaolaihe River (JLH) are two major rivers in the eastern side of Laizhou Bay and they have coarse sediment, which matches with that side of the bay. The grain sizes of sediments in most rivers were dominated by sand (49%), which may relate to the geological composition of riverbed (i.e. sandy local soil). Furthermore, the main function of rivers is draining floods, so the fine particles would be flushed and driven into the estuary by strong current during flooding in the rainy season, resulting in sand dominating the grain size distribution.

4.2 Relationships of TOC, TN, TS in surface sediment

The ratio between TOC and TN (C/N) is frequently used to discriminate between

organic matter of terrestrial and marine origin in estuarine sediments (Hedge et al., 1997). Marine algae typically have C/N ratios of 4-10 due to an abundance of protein, whereas land plants have C/N ratios of 20 or higher due to high cellulose content (Meyers, 1994). It is therefore reasonable for a mixture of both organic end-member sources to yield sediment C/N ratios between 10 and 20. In this study, except for site A5 (11.94), all ratio values are higher than 20 in the coastal area (mean value 37.4) (Table 3), which suggests the dominant source of organic matter to Laizhou Bay sediments is terrestrial material. Because site A5 is close to Longkou Port (the largest port of foreign trade in China, with a throughput of 66 million tons in 2012), so the low value of C/N may be attributed to pollutant discharge and sedimentation from boats (discharge or spill) and port, although this detailed explanation needs further study. For the rivers, the average value of C/N for rivers is 28.5 (Table 3), which is consistent with the ratio (C/N 34) of the Amazon River (Hedges et al., 1994). Because some rivers receive a combination of rainwater, residual brines from salt production, municipal and industrial wastewater and other kind pollutants, huge variations (10.7-67.3) in C/N ratios were observed between different rivers.

TOC/TS ratios (C/S) can be a useful tool for determining palaeodepositional environments in ancient sedimentary rocks. Berner (1984) found that C/S mass ratios are 1.88-3.75 in marine sediments and 18.75-93.75 in freshwater sediments (calculated from corresponding S/C molar ratios). In this study, the average C/S mass ratio is 55.91 in the marine area and 35.08 in rivers (Table 3). The highest ratio in the marine area (187.76) was for site A1, close to the Yellow River Estuary. For rivers,

the highest ratio (179.14) was at site HH3 within the Yellow River (200 Km from the estuary), and the second highest (92.23) was at site HH1, within the estuary. All the highest ratios were in the Yellow River, suggesting that the high C/S ratios in the marine area are related to the input of Yellow River sediment (Qiao et al., 2010). Interestingly, all these ratios are much higher than those in sediments off other major deltas such as the Mississippi River Delta (~ 1.05) and Amazon River Delta (~ 2.63) (Aller et al., 2004). In this study, although C/S ratios in the fluvial sediment (mean 35.08) are consistent with freshwater sediment (Berner, 1984: 18.75-93.75), the marine sediment values are exceptionally high (more than an order of magnitude above typical values quoted by Berner, 1982). This phenomenon can be explained by the following reasons: 1) high C/S ratios in sediments are associated with high TOC (Morse and Emeis, 1990); 2) the dominant source of organic matter to Laizhou Bay sediments is from terrestrial discharge. The burial of large amounts of terrestrial organic C (i.e. lignin, tannin, suberin and cutin) is more resistant to mineralization than organic C from typical marine sources, leaving high residual terrestrial organic C, and resulting in high C/S and C/N ratios; 3) influence of the input of Yellow River sediment. There is a positive correlation between TOC and TS in the fluvial sediments (R^2 of TS-TOC is 0.54). This indicates that sulfate reduction in the fluvial sediment was controlled by TOC. In contrast, there is no correlation between TOC and TS in the marine sediments (R^2 0.05). The lack of a correlation in the marine environment along with the high C/S shows that there is no overprinted pattern of early diagenetic sulfate-reduction from marine sediments in Laizhou Bay.

Table 3

4.3 AVS, CRS and ES in sediment

In the rivers and estuaries, AVS and CRS were the dominant RIS. These results are similar to those reported by Morgan et al (2012) who showed that high organic carbon content in estuarine sediments can lead to the stabilization of a significant fraction of the RIS pool as AVS. Furthermore, the relationships of TOC-AVS, TOC-CRS and TOC-ES for fluvial sediment exhibit statistically significant positive correlations ($P < 0.001$), suggesting that TOC controls sulphate reduction and formation of sulphides (Fig. 3). Southern Laizhou Bay is one of the important salt production areas of China, with many plants producing salt by solar evaporation of saline groundwater. Residual bitterns are discharged into local rivers directly, so there might be high sulphate concentrations in river water and sediments (Xue et al., 2000: average concentration of sulphate in salt and brine wells is 8.18 g L^{-1} in South coast of Laizhou Bay, 2.82 g L^{-1} in Laizhou Bay sea water and 0.04 g L^{-1} in freshwater in this area). Thode-Andersen and Jørgensen (1989) reported that ES may be the most abundant short-term sulfate reduction product in near-surface sediments, as a result of incomplete oxidation of pore-water sulfide by O_2, Fe^{3+} and Mn^{4+} species (Morse et al., 1987). However, in this study, ES was the lowest portion of RIS. The low ES concentrations in these sediments perhaps indicates that the ES had been transferred to AVS or CRS through rapid geochemical conversion.

4.4 Relationships between RIS and Fe in sediment

Gerritse (1999) showed that total Fe and TS show significant covariation in marine sediments, while in fluvial sediments they do not. However, in this study the opposite is true, with distinct positive correlation between different RIS pools and reactive Fe in fluvial sediment ($R^2 > 0.65$, Fig. 3), but not in marine sediment ($R^2 \sim 0.04$). Furthermore, the relationships of Fe^{2+}-AVS, Fe^{2+}-CRS and Fe^{2+}-ES for fluvial sediment exhibit statistically significant positive correlations ($P < 0.001$), clearly indicating that reactive Fe (Fe^{2+}) controls the formation of RIS pools in fluvial sediment in the region.

Fig.3

As shown in Fig. 2, Fe (III) dominated the total reactive Fe of the sediments, indicating iron oxide is the dominant fraction of Fe in Laizhou Bay. In the fluvial sediments, the average concentration of reactive Fe is 14137 μg g^{-1}, and the average molar ratio of reactive Fe/S is 19.96 (Table 3). This ratio is consistent with the work of Gerritse (1999), which was based on sites in Australia. As was the case for C/S, the highest Fe/S ratio in the marine area (189.46) was for site A1, close to the Yellow River Estuary. The highest fluvial ratio (178.29) was at site HH3 within the Yellow River. Furthermore, there is no correlation among three sites (HH1, HH2, and HH3) in Yellow River for total reactive Fe and TS (R^2 0.1). Therefore, high ratios of Fe/S in Laizhou Bay are related to the input of Yellow River sediment in recent years. In the fluvial sediment, the formation of RIS was controlled by TOC and reactive iron synchronously, but this was not the case in the marine sediments.

5. Conclusions

The concentrations, accumulation, and composition of several different species of inorganic sulfur have been determined in surface sediments in rivers and the coastal zone of Laizhou Bay. In fluvial surface sediments, CRS and AVS dominate RIS and concentrations of different RIS correlate with TOC and Fe. These results indicate that sulphate reduction and formation of RIS were controlled by TOC and reactive iron synchronously in the river sediments. In the marine sediments, there is no correlation between TOC and TS, but the high C/N indicates that the source of organic matter delivered to Laizhou Bay sediments is terrestrial. The high ratios of C/S and Fe/S indicate that diagenetic processes in Laizhou Bay were affected by rapid deposition of sediment from the Yellow River in recent decades.

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Table 1 The concentrations of TDOC, TDN and salinity of water samples

	TDOC (mg/L)	TDN (mg/L)	Salinity （psu)		TDOC (mg/L)	TDN (mg/L)	Salinity (psu)
A1	2.36	0.28	26.69	HH-1	2.40	2.46	0.47
A2	2.42	0.31	29.43	HH-2	2.68	2.92	0.43
A3	2.55	0.32	31.22	HH-3	2.71	4.13	0.46
A4	2.34	0.31	30.86	YHH-1	10.78	5.77	1.63
A5	1.89	0.28	29.44	GLE	8.49	3.58	27.36
B1	2.75	0.46	27.61	GLH-1	11.28	7.57	5.23
B2	3.35	0.27	27.94	GLH-2	7.09	4.68	8.69
B3	2.59	0.32	28.66	ZMG-1	4.51	2.41	7.43
B4	2.48	0.32	31.08	ZMG-2	6.41	2.51	5.26
B5	3.13	0.49	28.17	ZMG-3	9.48	2.51	3.66
C1	2.95	0.36	30.52	XQH-1	8.68	9.12	4.74
C2	1.97	0.28	29.91	XQH-2	9.34	6.71	4.31
D1	5.07	0.72	27.45	YKE	6.25	4.19	19.46
D2	4.57	0.53	27.69	YKG	15.16	8.31	13.27
D3	2.69	0.27	28.57	MH-1	6.02	2.83	2.33
D4	3.14	0.29	29.91	MH-4	13.94	5.87	17.69
D5	4.36	0.44	29.22	DJW-2	20.03	6.40	11.43
D6	3.84	0.33	27.46	DJW-4	17.21	6.09	5.27
E1	2.7	0.32	27.31	DJWE	7.13	2.16	23.79
E2	3.24	0.48	27.46	BLH-1	24.98	2.57	16.63
E3	2.45	0.33	28.53	BLH-2	3.56	1.55	29.26
E4	4.35	0.38	29.12	WFG	6.18	2.38	31.46
E5	4.52	0.39	29.77	YH-1	15.42	2.70	6.44
E6	4.13	0.29	28.49	YH-2	71.92	6.73	7.26
F1	5.27	0.62	27.46	YH-3	13.58	4.56	7.13
F2	3.48	0.68	30.66	YH-4	8.78	1.10	26.52
F3	2.42	0.31	29.87	DH-1	64.81	9.39	4.93
Mean	**3.22**	**0.38**	**28.91**	DH-2	41.47	12.39	16.23
				WH-2	3.24	3.53	1.29
				WH-3	8.524	2.43	2.67
				JLH-1	3.28	1.81	2.83
				JLH-2	15.98	4.86	12.52
				JLH-3	4.49	2.30	28.07
				Mean	**13.81**	**4.50**	**10.79**

Table 2 The spatial variations of AVS, CRS, ES, TOC, TN and TS concentrations in marine and fluvial surface sediments of Laizhou Bay.

	AVS ($\mu g\ g^{-1}$)	CRS ($\mu g\ g^{-1}$)	ES ($\mu g\ g^{-1}$)	TOC (%)	TN (%)	TS (%)		AVS ($\mu g\ g^{-1}$)	CRS ($\mu g\ g^{-1}$)	ES ($\mu g\ g^{-1}$)	TOC (%)	TN (%)	TS (%)
A1	62.77	41.75	21.31	1.26	0.03	0.01	HH-1	6.78	9.04	4.52	0.99	0.02	0.01
A2	26.07	155.87	15.14	1.95	0.06	0.09	HH-2	6.56	6.08	4.13	1.04	0.03	0.02
A3	198.18	424.59	18.19	1.92	0.07	0.05	HH-3	6.65	19.96	18.63	1.27	0.02	0.01
A4	153.87	220.77	8.10	1.34	0.05	0.03	YHH-1	3585.32	1657.45	69.28	2.24	0.19	0.27
A5	107.52	102.13	17.44	0.64	0.05	0.06	GLE	67.17	160.64	19.01	1.13	0.02	0.03
B1	47.42	33.38	20.90	1.57	0.04	0.02	GLH-1	186.30	304.49	39.26	1.83	0.07	0.06
B2	23.12	144.96	10.62	1.68	0.04	0.03	GLH-2	75.14	229.58	13.62	1.18	0.03	0.01
B3	52.20	422.67	14.51	1.10	0.03	0.05	ZMG-1	82.52	776.59	19.17	1.63	0.06	0.06
B4	41.12	224.15	11.49	0.93	0.03	0.02	ZMG-2	23.59	421.67	75.19	2.04	0.08	0.05
B5	176.83	280.30	20.46	0.75	0.03	0.06	ZMG-3	682.82	593.24	35.20	2.45	0.12	0.07
C1	11.27	93.09	27.36	0.64	0.02	0.01	XQH-1	294.76	423.56	31.03	1.57	0.05	0.04
C2	59.87	395.53	12.79	1.22	0.03	0.02	XQH-2	3054.46	3210.80	156.35	7.04	0.53	0.42
D1	3.80	12.41	5.57	1.40	0.03	0.01	YKE	611.08	500.28	24.42	1.45	0.04	0.06
D2	5.80	3.66	4.27	1.23	0.02	0.02	YKG	725.56	902.42	29.32	3.34	0.13	0.10
D3	20.57	84.87	17.68	1.97	0.07	0.04	MH-1	19.49	143.89	12.99	1.28	0.10	0.04
D4	26.15	145.39	12.65	1.07	0.05	0.04	MH-2	6.80	118.97	13.84	1.83	0.06	0.03
D5	257.44	401.83	13.24	1.29	0.04	0.07	MH-4	506.97	692.22	29.50	1.37	0.04	0.04
D6	371.01	641.55	15.42	0.93	0.03	0.04	DJW-1	1993.95	745.73	90.70	2.91	0.13	0.23
E1	18.39	76.16	13.51	1.47	0.03	0.01	DJW-2	415.25	627.08	55.20	2.21	0.05	0.09
E2	16.51	66.05	15.84	1.94	0.05	0.03	DJW-3	1149.69	619.73	39.11	1.17	0.37	0.11
E3	138.29	169.84	25.06	1.97	0.06	0.03	DJW-4	442.09	617.56	31.94	1.05	0.03	0.03
E4	21.78	49.37	10.16	0.88	0.02	0.01	DJWE	264.88	415.14	14.90	1.74	0.07	0.08
E5	8.51	48.05	6.26	0.84	0.02	0.02	BLH-1	2100.41	1556.31	35.90	2.23	0.10	0.27

E6	1.17	83.91	24.31	0.75	0.01	0.02	BLH-2	8.91	327.32	19.39	1.37	0.03	0.03
F1	18.64	62.80	13.49	1.11	0.04	0.03	WFG	146.32	333.48	31.25	1.06	0.04	0.22
F2	209.61	198.53	20.96	1.53	0.04	0.09	YH-1	487.67	358.62	15.72	1.25	0.03	0.03
F3	14.68	26.38	11.24	0.83	0.01	0.01	YH-2	3015.66	260.95	52.28	1.87	0.13	0.16
Mean	77.50	170.74	15.11	1.27	0.04	0.03	YH-3	1305.21	1483.86	54.14	2.03	0.10	0.10
							YH-4	4.39	59.69	10.75	0.89	0.01	0.04
							DH-1	4522.08	1312.47	93.81	1.50	0.07	0.21
							DH-2	6832.38	2721.09	247.37	2.88	0.05	0.03
							WH-2	897.66	318.01	43.03	1.10	0.04	0.03
							WH-3	37.86	122.24	4.17	0.39	0.06	0.06
							JLH-1	971.56	435.49	30.02	0.78	0.07	0.04
							JLH-2	367.49	681.71	27.02	1.30	0.04	0.04
							JLH-3	7.97	61.71	21.26	0.69	0.02	0.01
							Mean	969.82	645.25	42.04	1.73	0.08	0.09

Table 3 The ratios of AVS/CRS, C/N and C/S of marine and fluvial sediments in Laizhou Bay

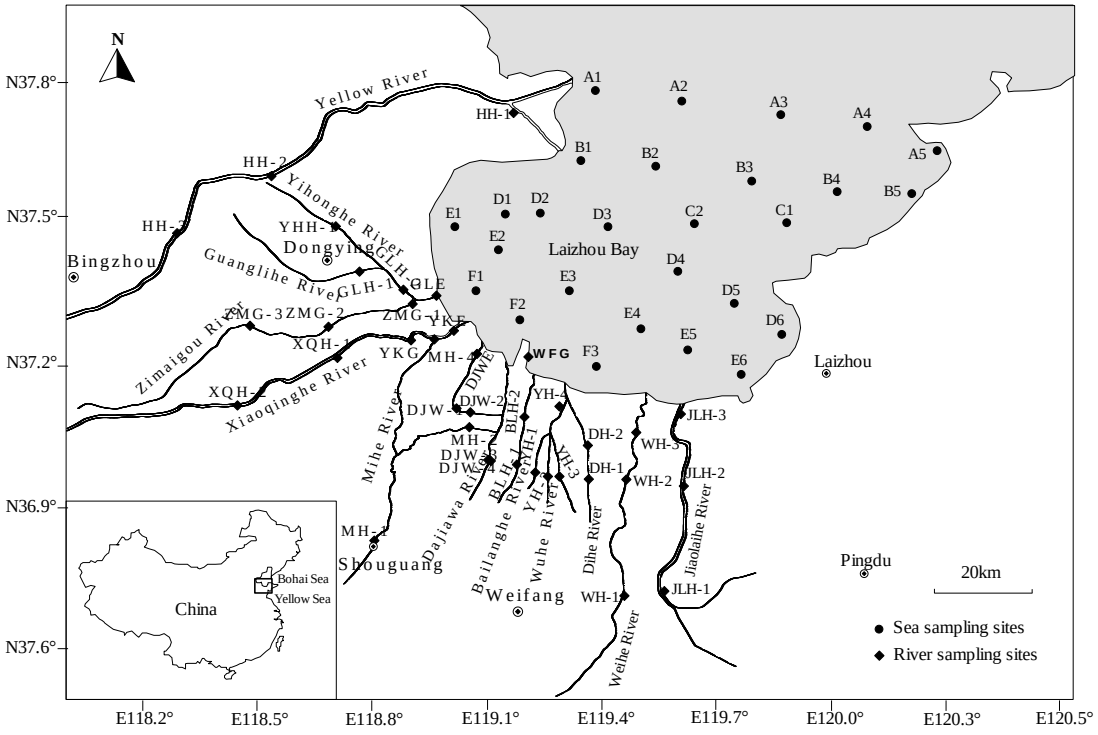
	AVS/CRS	C/N	C/S	Fe/S		AVS/CRS	C/N	C/S	Fe/S
A1	1.50	48.97	187.76	189.46	HH-1	0.75	50.96	92.93	99.10
A2	0.17	31.72	21.79	21.95	HH-2	1.08	38.26	57.44	63.40
A3	0.47	26.08	39.60	42.12	HH-3	0.33	56.87	179.14	178.29
A4	0.70	25.04	47.54	59.23	YHH-1	2.16	11.95	8.37	6.37
A5	1.05	11.94	11.10	20.78	GLE	0.42	46.41	35.76	38.71
B1	1.42	42.33	67.81	67.55	GLH-1	0.61	25.67	33.20	28.66
B2	0.16	38.24	67.03	73.35	GLH-2	0.33	43.35	82.82	79.24
B3	0.12	35.10	22.97	26.92	ZMG-1	0.11	28.12	27.74	25.35
B4	0.18	29.23	52.48	64.53	ZMG-2	0.06	25.85	38.57	32.99
B5	0.63	21.64	11.75	15.69	ZMG-3	1.15	20.10	35.41	26.12
C1	0.12	28.32	58.10	90.88	XQH-1	0.70	28.63	40.47	38.93
C2	0.15	43.72	51.48	54.88	XQH-2	0.95	13.26	16.92	8.08
D1	0.31	52.87	96.39	104.57	YKE	1.22	34.84	24.13	23.01
D2	1.58	74.78	68.66	75.24	YKG	0.80	26.62	34.17	16.59
D3	0.24	28.98	52.97	51.01	MH-1	0.14	12.99	32.57	63.67
D4	0.18	21.93	27.86	29.69	MH-2	0.06	30.77	68.44	55.73
D5	0.64	30.07	19.06	19.00	MH-4	0.73	31.54	33.89	32.14
D6	0.58	33.26	26.05	48.86	DJW-1	2.67	22.31	12.82	5.70
E1	0.24	48.38	102.25	178.83	DJW-2	0.66	40.49	25.96	17.01
E2	0.25	38.63	67.87	72.26	DJW-3	1.86	22.31	10.66	14.39
E3	0.81	31.89	75.51	73.71	DJW-4	0.72	40.51	30.87	26.35
E4	0.44	46.81	104.51	124.92	DJWE	0.64	24.06	21.80	15.97
E5	0.18	36.42	53.73	57.84	BLH-1	1.35	22.90	8.28	4.76
E6	0.01	56.74	31.80	42.82	BLH-2	0.03	50.88	53.17	46.13
F1	0.30	30.60	32.44	35.80	WFG	0.44	26.85	4.69	5.10
F2	1.06	35.13	17.74	17.81	YH-1	1.36	35.82	37.22	26.92
F3	0.56	60.92	93.37	118.62	YH-2	11.56	14.87	11.97	6.58
Mean	0.52	37.40	55.91	43.96	YH-3	0.88	19.41	19.36	7.68
					YH-4	0.07	67.25	24.17	28.29
					DH-1	3.45	21.26	6.99	7.21
					WH-2	2.82	20.06	34.38	33.68
					WH-3	0.31	10.77	14.12	37.73
					JLH-1	2.23	13.52	13.23	7.89
					JLH-2	0.54	18.05	36.62	91.90
					JLH-3	0.13	17.25	19.54	23.95
					Mean	1.27	28.45	35.08	15.98

Figure captions

Fig. 1 Locations of sampling sites in Laizhou Bay.

Fig. 2 Grain size (top) and Fe (bottom) concentrations in marine and fluvial surface sediments of Laizhou Bay.

Fig. 3 The relationships of RIS -TOC (left) and RIS - Fe^{2+} (right) in fluvial sediment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E120.5°
Yellow River
Yihonghe River
Guanglihe River
Zimaigou River
Xiaoqinghe River
Mihe River
Dajiawa River
Bailanghe River
Wuhe River
Dihe River
Jiaolaihe River
Weihe River
Laizhou Bay
Bingzhou
Dongying
Laizhou
Pingdu
Weifang
Shouguang
WFG
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HH-2
HH-3
YHH-1
GLH-1
GLE
ZMG-1
ZMG-2
ZMG-3
YKE
YKG
XQH-1
XQH-2
MH-1
MH-2
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A3
A4
A5
B1
B2
B3
B4
B5
C1
C2
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D4
D5
D6
E1
E2
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F2
F3
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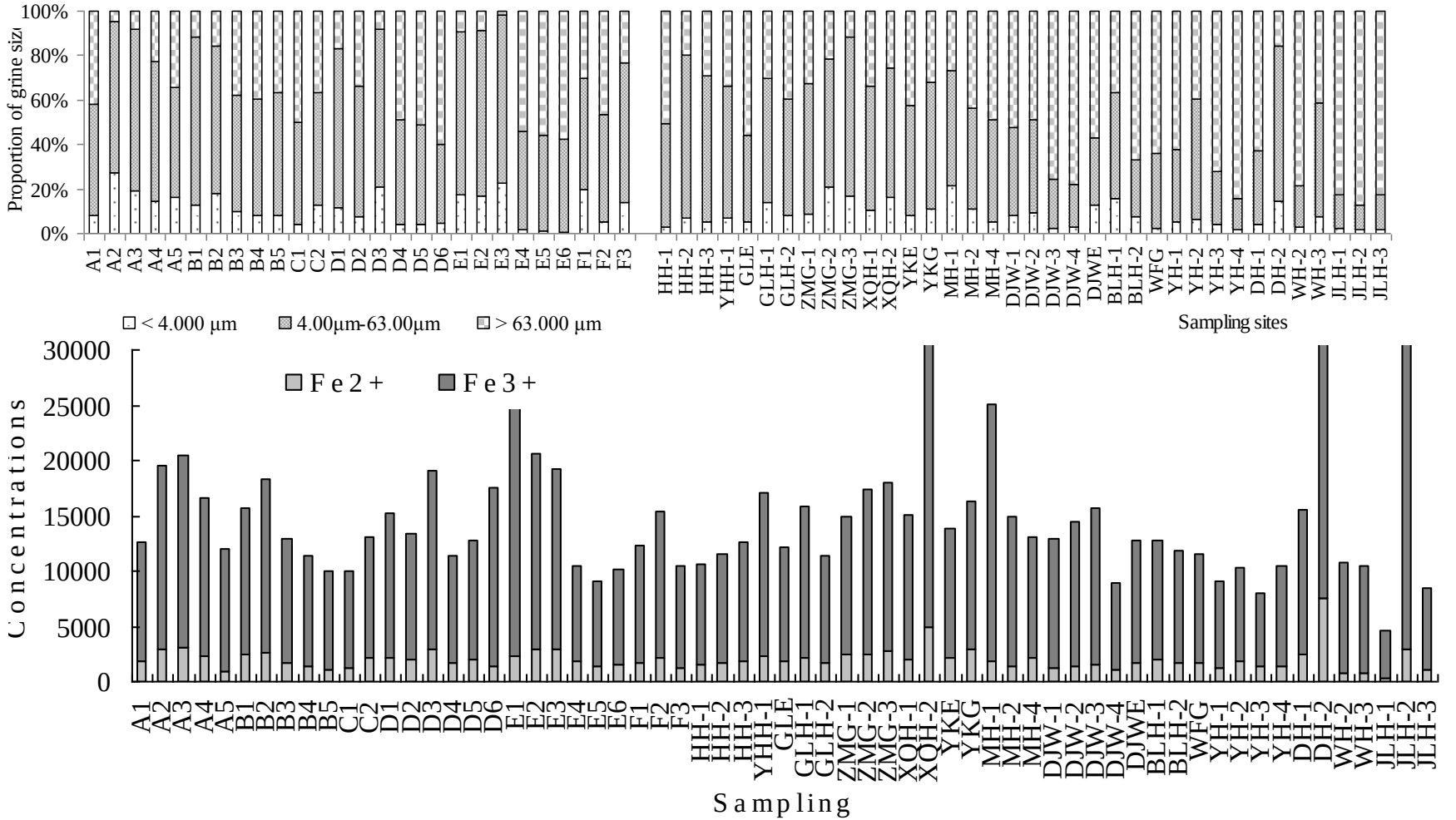
Bohai Sea
Yellow Sea
20km
Sea sampling sites
River sampling sites

Fig. 1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HH-1 HH-2 HH-3 YHH-1 GLE GLH-1 GLH-2 ZMG-1 ZMG-2 ZMG-3 XQH-1 XQH-2 YKE YKG MH-1 MH-2 MH-4 DJW-1 DJW-2 DJW-3 DJW-4 DJWE BLH-1 BLH-2 WFG YH-1 YH-2 YH-3 YH-4 DH-1 DH-2 WH-2 WH-3 JLH-1 JLH-2 JLH-3
< 4.000 μm
4.00μm-63.00μm
> 63.000 μm
Sampling sites
Concentrations
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20000
15000
10000
5000
0
Fe2+
Fe3+
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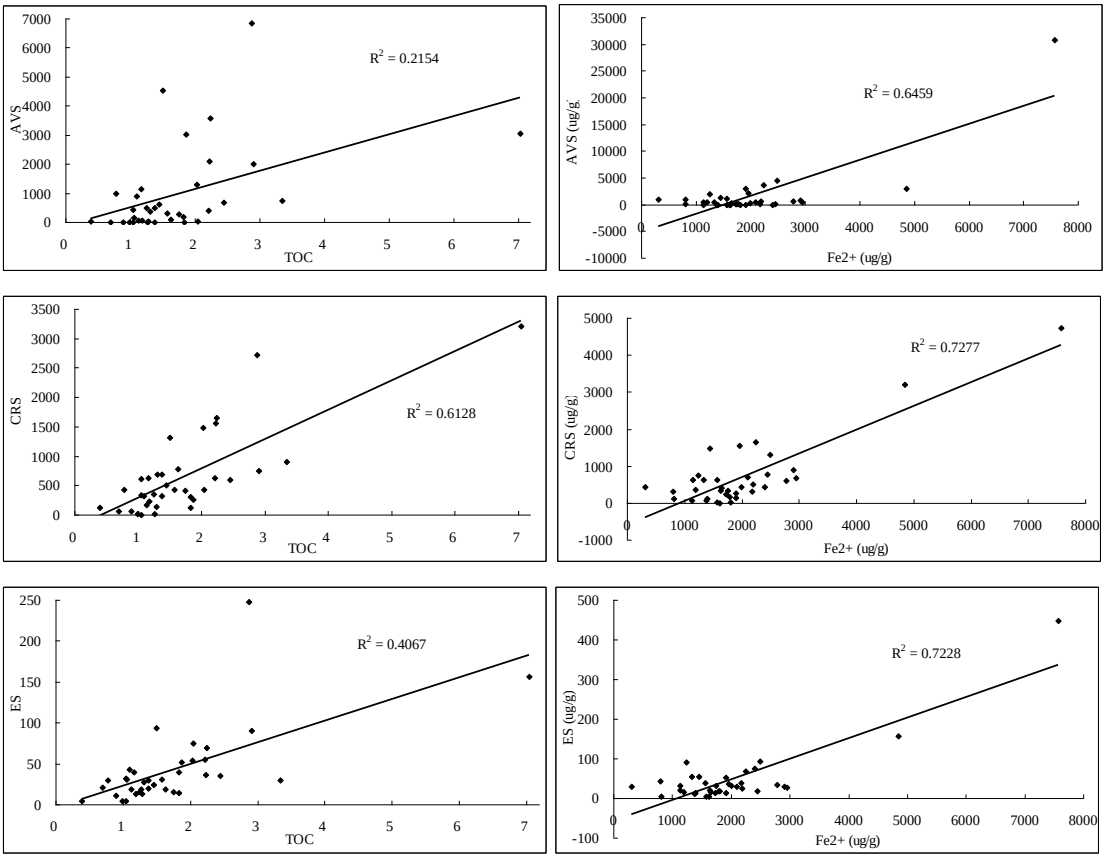
Sampling

Fig. 2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AVS (ug/g)
Fe2+ (ug/g)
R2 = 0.6459
CRS
R2 = 0.6128
CRS (ug/g)
R2 = 0.7277
ES
R2 = 0.4067
ES (ug/g)
R2 = 0.7228

Fig. 3