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1           **Reduced inorganic sulfur in surface sediment and its impact on**  
2                   **benthic environments in offshore areas of NE China**

3  
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12  
13          **Abstract**

14          Geochemical cycling and biological toxicity of sulfur in marine sediments is  
15          closely related to the activity of organisms. This study investigated the distribution  
16          and potential impact on benthic environments of acid volatile sulfur (AVS),  
17          chromium (II)-reducible sulfur (CRS), elemental sulfur (ES), total S, C, N and Fe in  
18          superficial sediments across the Bohai Sea, Yellow Sea and East China Sea. The  
19          composition of reduced inorganic sulfur in the three study areas was dominated by  
20          CRS (averaging 72% of total reduced inorganic sulfur). The low AVS content

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1 (average of  $1.12 \mu\text{mol g}^{-1}$ ) of the sediments and the low values of AVS/CRS (average  
2  $0.34 \mu\text{mol g}^{-1}$ ), degree of pyritization and degree of sulphidization indicate that there  
3 is sufficient available iron in the sediment to restrict the threat of sulphide toxicity to  
4 benthic organisms in most of the study areas. However, high organic matter loads in  
5 parts of the study areas have resulted in enhanced accumulation of AVS, resulting in a  
6 higher toxicity risk.

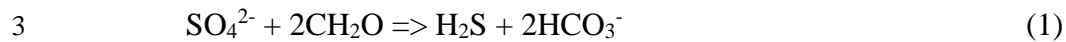
7  
8 **Keywords:** Sulfur compounds; Sedimentary environments; Offshore; Benthic  
9 environment

## 10 **1. Introduction**

11 Sulfur is essential to life and one of the key players in global biogeochemical cycles.  
12 However the most reduced form, sulfide, is generally toxic to organisms and  
13 influences water quality (Bagarinao, 1992; Sheng et al., 2011). Sulfur is cycled  
14 between and fixed in many different forms in marine sediments (Morse and Berner,  
15 1995; Canfield et al., 2005; Bottrell et al., 2009; Alvarez and Rubio, 2012). Therefore,  
16 understanding sulfur speciation in marine sediments is essential in evaluating its  
17 response to environmental change and the potential biological impact of sulfide. The  
18 availability of sulfide in the coastal environment will have implications for overlying  
19 water quality.

20 The sulfur cycle in marine sediments can be divided into reductive and oxidative  
21 processes. The reductive side of the cycle is driven by microorganisms that reduce

1 sulfate to sulfide in anaerobic environments and rates of sulfate reduction can be very  
2 high **under such conditions** (Morse et al., 2007; Tarpgaard et al., 2011).



4 In the oxidative side of the cycle sulfide reacts with a variety of oxidants **such as O<sub>2</sub>**  
5 **and Fe(III) oxides** to produce sulfate or intermediate S forms (e.g. elemental S). **The**  
6 majority of the sulfide produced in marine sediment is reoxidized (Canfield and  
7 Thamdrup 1994; Poulton 2003; Bottrell and Newton, 2006). Sulfide produced is also  
8 removed by reaction with mineral-derived Fe, initially producing a monosulfide  
9 “FeS” which transforms to more stable pyrite, FeS<sub>2</sub> (Berner 1970, 1984). However,  
10 the reactivity of mineral iron forms is highly variable (Canfield et al. 1992) and may  
11 limit the removal of sulfide. Where supply of oxidants is also restricted, production of  
12 sulfide may outcompete rates of removal and concentrations of toxic sulfide will  
13 increase in shallow pore-waters and bottom waters (Phillips et al. 1997). Furthermore,  
14 iron monosulfide species formed in sediment are often highly reactive and will rapidly  
15 react with and remove dissolved oxygen from bottom waters if sediment is  
16 resuspended.

17 The reactivity of sulfide stored in sediment when resuspension occurs is  
18 dependent on the form in which sulfide is present; dissolved sulfide is most reactive,  
19 followed by monosulfide, and pyrite is least reactive (Morse and Rickard 2004). In  
20 many sediments conversion of monosulfide to pyrite is rapid (Schoonen and Barnes  
21 1991; Butler and Rickard 2005) **such as reoxidation of AVS in the uppermost layer**

1 and thus monosulfide concentrations are low or negligible (e.g. Rozan et al. 2002;  
2 Rickard and Morse 2005). However in other situations (e.g. high pH (>7.8) sediments  
3 and under organic-rich eutrophic conditions) Fe monosulfides are persistent and  
4 represent a significant pool of reactive sulfide in the sediment (Hurtgen et al. 1999;  
5 Morse 1999; Burton et al. 2011; Morgan et al., 2012). Sulfide is toxic to aquatic plants  
6 and organisms. Its accumulation in upper sediment layers in coastal areas exerts an  
7 impact upon not only local benthos but also the pelagic biota due to the potential  
8 release of free sulfide into the water column (Bagarinao, 1992). Furthermore,  
9 re-suspension of sediment can result in oxidation of H<sub>2</sub>S and reactive sulfides,  
10 changing the redox conditions of the overlying water and leading to hypoxia at the sea  
11 floor (Phillips et al., 1997; Sorokin and Zakuskina, 2012). Oxidation of monosulfide  
12 in surface sediments may also lead to the release of toxic heavy metals (coprecipitated  
13 with FeS) into more bioavailable forms, such as dissolved Cu and Zn (Simpson et al.,  
14 2012; Rodrigues et al., 2013). Most organisms live within oxic surface sediments or in  
15 oxygenated microenvironments created within sub-oxic and anoxic sediments  
16 (Simpson et al., 2012), and hence are vulnerable to shifts in redox and associated  
17 changes in sulfur speciation and toxicity.

18 The degree of pyritization (DOP) and the degree of sulphidization (DOS) are  
19 two parameters that can be used to distinguish between situations where pyrite and Fe  
20 sulfide formation is either C- or Fe-limited and to measure the completeness of the  
21 reaction of reactive Fe (operationally defined as the fraction of Fe that is soluble in 1  
22 M HCl for 16h) with aqueous sulfide (Raiswell and Berner, 1985). In sediments that

1 contain a significant amount of Fe monosulfide, DOP underestimates the amount of  
2 Fe that has reacted with H<sub>2</sub>S (Boesen and Postma, 1988). Instead, DOS represents the  
3 degree to which reactive Fe has been transformed into sulfide and, therefore, provides  
4 a better indication of Fe limiting conditions (Yin et al., 2008). In sediments where Fe  
5 availability becomes limiting pore-water sulfide concentrations are likely to increase,  
6 enhancing the likelihood of sulfide toxicity. Conversely, if sulfide production is  
7 limited by the availability of a labile organic substrate, pore-water sulfide  
8 concentrations may be very low.

9 The Bohai Sea, Yellow Sea and East China Sea are situated north-east (NE) of  
10 China. They are important production bases for fishery and marine industries. This  
11 study area can be characterized as a region surrounded by areas of high population  
12 growth and economic development. A large amount of pollutants are discharged into  
13 these areas in industrial and municipal wastewaters via rivers (i.e. Yellow River,  
14 Yangtze River and other smaller rivers), along with excess inputs of nutrients from  
15 mariculture. This pollution may influence the cycles of iron, sulfur and phosphorus  
16 (Rozan et al., 2002), leading to offshore eutrophication and benthic macroalgal  
17 blooms, especially large offshore phytoplankton blooms e.g. *enteromorpha prolifera*  
18 in Yellow Sea (Liu et al., 2013). Previous studies on the effects of biogenic elements  
19 in sediments in these areas were focused mainly on carbon, nitrogen and phosphorus  
20 (Liu et al., 2004; Liu and Yin, 2007). However, to date, only limited effort has been  
21 devoted to the study of sedimentary geochemistry of reduced inorganic sulfur (RIS) in  
22 the offshore areas of NE China (Kang et al., 2014), and its potential impact on the

1 marine ecosystem remains unclear.

2 In this study, acid volatile sulfur (AVS), chromium (II)-reducible sulfur (CRS,  
3 pyritic sulfur), elemental sulfur (ES), total sulfur (TS), reactive iron, total organic  
4 carbon (TOC) and total nitrogen (TN) were analyzed in surface sediments from the  
5 study area. The partitioning of RIS was used to understand sulfur biogeochemistry  
6 within the sediments, and to predict the potential for ecotoxicological risk due to  
7 release of toxic sulfide.

8

## 9 **2. Methods and materials**

### 10 2.1 Samples collection and handling

11 A total of 82 sediment samples were collected from the Bohai Sea, Yellow Sea  
12 and East China Sea (Fig. 1). Surface sediments (0-20 cm) were collected using a  
13 stainless steel grab sampler and were immediately isolated from the atmosphere in  
14 plastic zip-lock bags with all air expelled by N<sub>2</sub> gas (a N<sub>2</sub> gas cylinder was aboard  
15 ship). Samples were frozen and stored in an icebox (-20°C) until arrival at the  
16 laboratory. Samples were processed immediately upon return to the laboratory. In the  
17 laboratory, the plastic sample bags were first flushed with high purity N<sub>2</sub> again.  
18 Samples were then homogenized under this inert atmosphere (a glove box) by mixing  
19 with a plastic spatula. Four replicates were used throughout.

20

21

**Fig. 1**

22

## 1 2.2 Sample analysis

2 The reagents used were all analytical grade or above, and deionized water  
3 (milli-Q) was used to prepare reagent solutions. All glass and plastic were soaked in  
4 10% HNO<sub>3</sub> for 48 h and rinsed with milli-Q water three times before use. Total  
5 organic carbon (TOC) in sediments was determined by a Shimadzu  
6 TOC-V<sub>CPH</sub>/SSM-5000A. Total nitrogen (TN) and total sulfur (TS) were determined  
7 by an Elementar vario MACRO cube CHNS analyzer. The precision of the  
8 measurements was within 5% based on three replicate sediment analyses. Prior to  
9 grain size analysis, each sediment sample was treated with sodium hypochlorite  
10 (NaOCl) to remove organic matter. Sample granulometry was analyzed using a  
11 Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes  
12 between 0.02 and 2,000 μm. The percentages of samples in each of the following  
13 three grain-size groups were determined: < 4 μm (clay), 4-63 μm (silt), and >63 μm  
14 (sand).

15 The separation and determination of AVS, CRS and ES were conducted using a  
16 modified procedure described by Newton et al. (1995) and Hsieh & Shieh (1997).  
17 Reagents and extraction steps of sulfur species separation are the same as the  
18 description of Hsieh & Shieh (1997), the detection of H<sub>2</sub>S is the same as the  
19 description of Newton et al. (1995). In this method, a thin glass pipe (with N<sub>2</sub> gas  
20 inside) was dipped into corresponding solutions (shaking occasionally) to accelerate  
21 the emission of H<sub>2</sub>S (1.5 h). All subsequent processing of sediment was performed  
22 under a N<sub>2</sub> atmosphere inside a glove box at room temperature. Briefly, AVS, CRS



1 and ES were separated sequentially by 6 M HCl, acidic Cr (II) and Cr (II) plus N,  
2 N-dimethylformamide, respectively, using pure N<sub>2</sub> as carrier gas to purge and trap  
3 H<sub>2</sub>S, at a temperature of ~ 60 °C (by electric hot plate). The liberated H<sub>2</sub>S was trapped  
4 in a 0.1 mol L<sup>-1</sup> CuCl<sub>2</sub> solution. The amount of H<sub>2</sub>S evolved from the sample for each  
5 solid-phase RIS species was determined by titrating the Cu remaining in solution with  
6 0.1 mol L<sup>-1</sup> EDTA (assuming a precipitate of CuS stoichiometry). Three to four drops  
7 of glycine cresol red (0.5% aqueous) was used as an indicator and the titration was  
8 buffered with 70 ml of 1 mol L<sup>-1</sup> sodium acetate solution (adjusted to pH 5.5 with  
9 acetic acid). The endpoint was sharp and marked by a colour change from dark blue to  
10 a light green. Sulfide solutions (Na<sub>2</sub>S) with concentrations of 0.5 and 1 mg L<sup>-1</sup> were  
11 used in recovery experiments. Average sulfide recovery rate was 96%. Measured  
12 sulfide data were converted to real sulfide contents after correction for the recovery  
13 rate. The precision of triplicate analysis was within 5% for different fractions of RIS.  
14 The fractions of Fe were determined by sequential acid digestion. Reactive Fe is the  
15 fraction of Fe that is soluble in 1 mol L<sup>-1</sup> HCl (16h, Fe<sub>R</sub>) and pyrite Fe (Fe<sub>py</sub>) is the Fe  
16 that is soluble in concentrated HNO<sub>3</sub>, after removal of the Fe associated with silicates  
17 and organic matter (Huerta-Dí'az & Morse, 1990). The concentrations of different Fe  
18 fractions (extracted by corresponding acid) were detected by an Atomic Absorption  
19 Spectrometer (TAS 990, Beijing Purkinje General Instrument Co.Ltd., Beijing),  
20 precision was to within 2% based on triplicate analysis.

21

22 2.3 Data calculation

1 DOP was taken to be the percentage of pyrite-Fe in the bioavailable iron, which  
2 was calculated as  $Fe_{py}/(Fe_R + Fe_{py})$  (Berner, 1970).  $Fe_{py}$  was calculated from  $FeS_2$   
3 stoichiometry. DOS was taken to be the percentage of Fe that has been transformed  
4 into sulfide, which was defined by  $(Fe_{py} + Fe_{AVS})/(Fe_{py} + Fe_R)$  (Boesen and  
5 Postma,1988).  $Fe_{AVS}$  is sulfide-bound Fe(II) assuming that AVS predominantly  
6 occurs as FeS, though this assumption remains controversial (Morse and Rickard,  
7 2004; Rickard and Morse, 2005).

8

### 9 **3. Results and discussion**

#### 10 3.1 Distribution of grain size

11

#### 12 **Fig. 2**

13

14 The grain size of the sediments plays a significant role in the accumulation of  
15 organic matter, and can influence the spatial distribution of C, N and S (Zhou et al.,  
16 2007). The variations of grain size in the surface sediments are shown in Fig. 2. The  
17 data reveal a predominance of silt (4-63  $\mu m$ ), which accounted for an average of 57%,  
18 57% and 47% of the particles in Bohai Sea, Yellow Sea and East China Sea,  
19 respectively. Compared to the East China Sea, high proportions of silt in the Bohai  
20 Sea and the Yellow Sea are most likely related to transport of suspended sediments  
21 down the Yellow River (Qiao et al., 2010). The surface sediments of Bohai Sea were  
22 dominated by silt, except for samples B52, B53 and B54 (Fig. 1). These sites were

1 located in the main water exchange channel between the Bohai Sea and the Yellow  
2 Sea (Liu et al., 2004), so the small particles (clay) may be winnowed by strong water  
3 currents, resulting in a predominance of sand in this area (Fig.2). In the East China  
4 Sea, driven by the Zhejiang-Fujian coastal current, a large amount of fine grained  
5 particulates from the Yangtze Estuary are transported southward along the coast and  
6 trapped in the inner shelf by the blocking of the northward warm Taiwan current  
7 offshore, developing mud wedges outside the Yangtze River mouth (Xu et al., 2009).  
8 Therefore, at site E01 (Fig. 1), the sediment was dominated by fine grained  
9 particulates, with silt and clay accounting for ~ 97% of total grains (Fig. 2).

10

### 11 3.2 Distribution of TOC, TN and TS

12 The surface sediments were characterized by variable concentrations of TN,  
13 TOC and TS. TN varied from 0.03-0.21% (% dry weight of the sediment), TOC from  
14 0.11- 2.49% and TS from 0.11-0.40%. The average TN in the Bohai Sea, Yellow Sea  
15 and East China Sea were 0.07%, 0.08% and 0.06%, respectively. The averages for  
16 TOC were 1.23%, 1.07% and 1.09% respectively (Fig. 3). The highest TOC contents  
17 were recorded at site B66 (2.3%) in the Bohai Sea, B31 (2.5%) in the Yellow Sea and  
18 E01 (1.6%) in the East China Sea. In the Bohai Sea, TN, TOC and TS exhibited high  
19 values in Bohai Bay and Laizhou Bay. In the Yellow Sea, the TOC and TS contents in  
20 sediments at B31 and B32 were high (2.5% and 1.5% respectively), indicating high  
21 organic pollution loads in these areas, most likely related to the Dalian crude oil spill  
22 in 2010 (Lv et al., 2011). This organic pollution may provide an additional substrate

1 for sulfate reduction and lead to increased sulfide production and accumulation in the  
2 sediment.

3

4 **Fig. 3**

5

### 6 3.3 Distribution characteristics of different fractions of RIS

7 Fig. 4 presents the AVS, CRS and ES concentrations in the surface sediment  
8 samples of the Bohai Sea, Yellow Sea and East China Sea. The AVS, CRS, and ES  
9 values were in the ranges 0.2-4.1  $\mu\text{mol g}^{-1}$ , 0.6-101  $\mu\text{mol g}^{-1}$ , and 0.5-3.9  $\mu\text{mol g}^{-1}$ ,  
10 respectively. AVS contents in the Bohai Sea, Yellow Sea and East China Sea are  
11 close to the ranges of AVS contents for Jiaozhou Bay sediments (0.06-13.7  $\mu\text{mol g}^{-1}$ )  
12 (Zhu et al., 2012) and East China Sea shelf sediments (0-25  $\mu\text{mol g}^{-1}$ ) (Lin et al., 2000;  
13 Zhu et al., 2013). For CRS, the concentrations are 0.6-101  $\mu\text{mol g}^{-1}$ , dominating the  
14 total RIS in all studied areas, with an average 75% share in the Bohai Sea, 59% in the  
15 Yellow Sea and 87% in the East China Sea (Fig. 4 and Table 1). This finding was  
16 consistent with the reports of Zhu et al. (2012) in Jiaozhou Bay (CRS: 8.7-51.1  $\mu\text{mol}$   
17  $\text{g}^{-1}$ ), Sheng et al. (2013) in the coastal zone of the Yellow Sea (CRS: 5.5-13.1  $\mu\text{mol g}^{-1}$ )  
18 and Zhu et al. (2013) in the East China Sea inner shelf (CRS: 2.7-38.3  $\mu\text{mol g}^{-1}$ ). In  
19 this study, although there are some values of RIS at sites B30, B31 and B32 associated  
20 with an oil spill, even these highest values (101.2  $\mu\text{mol g}^{-1}$ ) are much lower than the  
21 peak value for the southern East China Sea slope sediments (range: 0-240  $\mu\text{mol g}^{-1}$ )  
22 (Lin et al., 2002). CRS dominates over AVS in the RIS pool in the Bohai Sea, Yellow

1 Sea and East China Sea sediments and thus in all these locations AVS produced by  
2 sulfate reduction has been efficiently transformed to pyrite and there is limited  
3 accumulation of reactive monosulfide. Because of high concentrations of reactive iron  
4 (average is approximately  $100 \mu\text{mol g}^{-1}$ ) in these areas, the sulfide may be removed  
5 quickly by the formation of FeS, then it was transformed to FeS<sub>2</sub> due to sufficient ES  
6 ( $0.5\text{-}3.9 \mu\text{mol g}^{-1}$ ) is present under anoxic conditions (reoxidation of AVS would be  
7 restrained because of limited free oxygen in benthic bottom), resulting in high  
8 concentration of CRS. Overall, accumulation concentrations of labile sulfides (i.e.  
9 AVS) in the study area is much lower than levels known to be potentially toxic for  
10 aquatic biota ( $200 \text{ mg S L}^{-1}$  of wet silt, Sorokin and Zakuskina, 2012), suggesting the  
11 environmental conditions are low risk for the local marine ecosystem.

12 Generally, RIS concentrations were higher in the Yellow Sea than in the Bohai  
13 Sea and East China Sea, especially at sites B30, B31 and B32. This phenomenon is  
14 consistent with the variation of TOC and TS in same sites, and is most likely related  
15 to the Dalian crude oil spill summer 2010 (Lv et al., 2011). Deposited crude oil may  
16 result in a high load of organic pollutants in these areas, increasing TOC accumulation  
17 in the sediment (B30, B31 and B32). Furthermore, these organic compounds may  
18 provide an additional substrate for sulfate reduction and lead to increased sulfide  
19 production and accumulation in the sediment. Whilst the oil spill has modified the  
20 sediment geochemistry and increased AVS content, in the samples analyzed this  
21 increase is small and lies within the range of many sediments that have not been  
22 polluted by oil spills.

1

2

## Fig. 4

3

### 4 3.4 Relationships between C, N, S and different fractions of RIS

5 The **atomic molar** ratios of C/N, C/S and AVS/CRS are listed in Table 1. **C/N and**

6 **C/S are ratios of TOC concentrations against TN and TS concentrations, respectively.**

7 C/N is widely applied in biogeochemical studies of terrestrial, riverine, estuarine, and

8 marine environments, most commonly to estimate the fraction of terrestrially derived

9 organic matter in marine sedimentary samples (Meyers, 1997). In this study, the **C/N**

10 **ratio (molar ratio)** varied from 10.1 to 48.4 (average: 18.9) in the Bohai Sea, 7.7-41.3

11 **(average: 15.1)** in the Yellow Sea and **16.5-20.7 (average: 17.8)** in the East China Sea

12 (Table 1). These results suggest that the studied areas are abundant in

13 terrestrial-derived organic matter with high C/N ratios (always higher than 10)

14 (Meyers, 1997), associated with material rich in cellulose which originates from

15 terrestrial vascular plants and reaches the sediments via rivers, i.e. Yellow River and

16 Yangtze River.

17 **TS and TOC/TS (C/S) are used for studying oxic/anoxic conditions in marine**

18 **environments (Berner, 1984).** The C/S ratios varied from 6.1 to 37.5, with an average

19 of 12.8 in the Bohai Sea, 1.3-24.2 **(average: 10.3)** in the Yellow Sea and 6.5-**17.0**

20 **(average: 10.3)** in the East China Sea. Generally, the ratio of C/S in normal marine

21 sediment (deposited under an oxic water column) is 2.0-3.8 (Berner, 1982). Overall,

22 the C/S ratio in this study was highly variable at 1.3-37.5 (average: 11.4), with values

1 in most sampling sites higher than is normal for marine sediments. This can be  
2 explained by the impact of freshwater input and mariculture activity, which can both  
3 significantly influence C/S ratios, e.g. site B66 (37.5), is close to the Yellow River  
4 estuary (with high TOC and low RIS values in sediment); site H1 (24.3) is close to  
5 Qingdao city, where there are many large wastewater treatment plants (over 1 million  
6 tons discharged per day); site H35 (21.7) is in a mariculture area. Generally, sewage  
7 and mariculture contribute more C but not more S, resulting in high C/S ratios. The  
8 result indicates that sulfate reduction or RIS accumulation was variable in surface  
9 sediment of different areas, and may be influenced by anthropogenic activities  
10 (organic matter input) and redox conditions. AVS/CRS varied from 0.14 to 1.22, with  
11 an average of 0.48 in Bohai Sea, 0.01-1.09 (average: 0.22) in Yellow Sea and  
12 0.02-0.11 (average: 0.06) in East China Sea. Low ratios indicate that the sediment in  
13 these areas poses a low threat of toxicity to benthic organisms because CRS is more  
14 stable and less likely to release sulfide or metals than AVS, which is more soluble and  
15 reactive.

16

### 17 3.5 DOP and DOS

18 The relationship between sulfide and iron plays an important role in controlling of  
19 the sulfur cycle. As shown in Table 1, both DOP and DOS for the three areas are  
20 generally close to each other, with DOP ranging from 0.01 to 0.31 (averages of 0.02  
21 for the Bohai Sea, and 0.04 for both the Yellow Sea and East China Sea) and DOS  
22 ranging from 0.02 to 0.33 (averages of 0.04 for the Bohai Sea, 0.05) for the Yellow

1 Sea and 0.04 for the East China Sea. DOS values are slightly higher than the DOP  
2 values, which perhaps reflects the reaction of FeS and H<sub>2</sub>S to form pyrite (Rozaan et al.,  
3 2002). The three areas have much lower DOP and DOS in comparison with the  
4 averages for estuarine and bay sediments of the Gulf of Mexico (DOP 0.56-0.95 and  
5 DOS 0.63-2.66) (Morse et al., 2007), but are consistent with DOP (0.05-0.25) and  
6 DOS (0.05-0.39) for Jiaozhou Bay sediment in the Yellow Sea (Zhu et al., 2012). On  
7 the basis of the simple comparison above, it is inferred that maybe there was low  
8 availability of labile organic matter in the study areas, which has been limiting sulfide  
9 production (Zhu et al., 2012), resulting in low values of DOP and DOS. Furthermore,  
10 high concentrations of reactive iron (average is approximately 100  $\mu\text{mol g}^{-1}$ ) and low  
11 values of DOP and DOS found in the present study further indicate that pyritization  
12 and sulfidization are not being limited by the availability of reactive Fe. Thus in these  
13 sediments the supply of mineral-Fe has been amply sufficient to match net sulfide  
14 production and thus limit the sulfide toxicity hazard.

15

16

### Table 1

17

## 18 4. Conclusions

19 In order to elucidate the geochemical processes controlling the formation and  
20 stability of RIS species and its bioavailability in surface sediments, we have examined  
21 the relationship between the spatial variations in the values of sedimentary grain size,  
22 TOC, TN, TS, AVS, CRS, ES, C/N ratio, C/S ratio, AVS/CRS ratio, DOP and DOS in



1 Bohai Sea, Yellow Sea and East China Sea. In the study area, CRS was the dominant  
2 fraction of RIS, indicating the RIS is dominantly in a stable form and thus poses a low  
3 threat of toxicity to marine ecosystem. Low values of DOP and DOS indicate that  
4 pyritization and sulphidization are not being limited by the availability of reactive Fe.  
5 Sediment in these areas restricts the threat from sulfide to benthic organisms. An oil  
6 spill in part of the studied area has resulted in enhanced accumulation of AVS in  
7 marine sediment, resulting in a higher toxicity risk.

8

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14

## 15 **References**

16 Bagarinao T., 1992. Sulfide as an environmental factor and toxicant: tolerance and  
17 adaptations in aquatic organisms, *Aquatic Toxicology* 24, 21-62.  
18 Berner, R.A., 1970. Sedimentary pyrite formation. *American Journal of Science* 268,  
19 1-23.  
20 Berner, R.A., 1982. Burial of organic carbon and pyrite sulphur in the modern ocean:  
21 its geochemical and environmental significance. *American Journal of Science* 282,  
22 451-473.

- 1 Berner, R.A., 1984. Sedimentary pyrite formation: an update. *Geochimica et*  
2 *Cosmochimica Acta* 48, 605-615.
- 3 Boesen, C., Postma, D., 1988. Pyrite formation in anoxic environments of the Baltic.  
4 *American Journal of Science* 288, 575-603.
- 5 Bottrell, S.H., Newton, R.J. 2006. Reconstruction of changes in global sulfur cycling  
6 from marine sulfate isotopes. *Earth-Science Reviews* 75, 59-83.
- 7 Bottrell S.H., Mortimer R.J.G, Davies I.M., Harvey S.M., Krom M.D., 2009. Sulphur  
8 cycling in organic-rich marine sediments from a Scottish fjord. *Sedimentology* 56,  
9 1159-1173.
- 10 Burton, E.D., Bush, R.T., Johnston, S.G., Sullivan, L.A., Keene, A.F. 2011. Sulfur  
11 biogeochemical cycling and novel Fe-S mineralization pathways in a tidally  
12 re-flooded wetland. *Geochimica et Cosmochimica Acta* 75, 3434-3451.
- 13 Butler, I.B., Rickard, D. 2000. Framboidal pyrite formation via the oxidation of iron  
14 (II) monosulfide by hydrogen sulfide. *Geochimica et Cosmochimica Acta* 64,  
15 2665-2672.
- 16 Canfield, D.E., Thamdrup, B., 1994. The production of <sup>34</sup>S-depleted sulfide during  
17 bacterial disproportionation of elemental sulfur. *Science* 266, 1973-1975.
- 18 Canfield, D.E., Raiswell, R., Bottrell, S., 1992. The reactivity of sedimentary iron  
19 minerals toward sulfide. *American Journal of Science* 292, 659-683.
- 20 Canfield, D.E., Kristensen, E., Thamdrup, B., 2005. The Sulfur Cycle, *Advances in*  
21 *Marine Biology* 48, 313-381.
- 22 Hsieh Y. P., Shieh Y. N., 1997. Analysis of reduced inorganic sulfur by diffusion

- 1 methods: improved apparatus and evaluation for sulfur isotopic studies. *Chemical*  
2 *Geology*, 137, 255-261.
- 3 Huerta-Dí'az, M.A., Morse, J.W., 1990. A quantitative method for determination of  
4 trace metal concentrations in sedimentary pyrite. *Marine Chemistry* 29, 119-144.
- 5 Hurtgen, M.T., Lyons, T.W., Ingall, E.D., Cruise, A.M. 1999. Anomalous  
6 enrichments of iron monosulfide in euxinic marine sediments and the role of H<sub>2</sub>S in  
7 iron sulfide transformations: examples from Effingham Inlet, Orca basin, and the  
8 Black Sea. *American Journal of Science* 299, 556-588.
- 9 Kang, X., Liu, S. and Zhang, G. 2014. Reduced inorganic sulfur in the sediments of  
10 the Yellow Sea and East China Sea. *Acta Oceanologica Sinica* 33,100-108.
- 11 Lin, S., Huang, K.-M., Chen, S.-K., 2000. Organic carbon deposition and its control  
12 on iron sulfide formation of the southern East China Sea continental shelf  
13 sediments. *Continental Shelf Research* 20, 619-635.
- 14 Lin, S., Huang, K. M., Chen, S. K., 2002. Sulfate reduction and iron sulfide mineral  
15 formation in the southern East China Sea continental slope sediment. *Deep Sea*  
16 *Research Part I: Oceanographic Research Papers* 49, 1837-1852.
- 17 Liu H., Yin B., 2007. Annual cycle of carbon, nitrogen and Phosphorus in the Bohai  
18 Sea: A model study, *Continental Shelf Research* 27, 1399-1407.
- 19 Liu D., Keesing J.K, He P., Wang Z., Shi Y., Wang Y., 2013. The world's largest  
20 macroalgal bloom in the Yellow Sea, China: Formation and implications, *Estuarine,*  
21 *Coastal and Shelf Science* 129, 2-10.
- 22 Lv Y., Zhang W., Gao Y., Ning S., Yang B., 2011. Preliminary study on responses of

1 marine nematode community to crude oil contamination in intertidal zone of Bathing  
2 Beach, Dalian, *Marine Pollution Bulletin*, 62, 2700-2706.

3 Morgan, B., Burton, E.D., Rate, A.W., 2012. Iron monosulfide enrichment and the  
4 presence of organosulfur in eutrophic estuarine sediments, *Chemical Geology*  
5 296-297, 119-130.

6 Morse, J.W., 1999. Sulfides in sandy sediments: new insights on the reactions  
7 responsible for sedimentary pyrite formation. *Aquatic Geochemistry* 5, 75-85.

8 Morse, J.W., Berner, R.A., 1995. What determines sedimentary C-S ratios. *Geochim.*  
9 *Cosmochim. Acta* 59, 1073-1077.

10 Morse, J.W., Rickard, D., 2004. Chemical dynamics of sedimentary acid volatile  
11 sulfide. *Environmental Science & Technology* 38, 131A-136A.

12 Morse, J.W., Thomson, H., Finneran, D.W., 2007. Factors controlling sulfide  
13 geochemistry in sub-tropical estuarine and bay sediments. *Aquatic Geochemistry* 13,  
14 143-156.

15 Newton R. J., Bottrell S.H., Dean S.P., Hatfield D., Raiswell R., 1995. An evaluation  
16 of the use of the chromous chloride reduction method for isotopic analyses of pyrite  
17 in rocks and sediment, *Chemical Geology* 125, 317-320.

18 Phillips B. M., Anderson B. S., Hunt J. W., 1997. Measurement and distribution of  
19 interstitial and overlying water ammonia and hydrogen sulfide in sediment, *Marine*  
20 *Environmental Research* 44, 117-126.

21 Poulton, S.W. 2003. Sulfide oxidation and iron dissolution kinetics during the  
22 reaction of dissolved sulfide with ferrihydrite. *Chemical Geology* 202, 79-94.

- 1 Qiao S, Shi X, Zhu A, Liu Y, Bi N., Fang X., Yang G., 2010, Distribution and  
2 transport of suspended sediments off the Yellow River (Huanghe) mouth and the  
3 nearby Bohai Sea. *Estuarine, Coastal and Shelf Science* 86, 337–344.
- 4 Rickard, D., Morse, J.W., 2005. Acid volatile sulfide (AVS). *Marine Chemistry* 97,  
5 141-197.
- 6 Rodrigues S.K., Abessa D.M.S., Machado E.C., 2013. Geochemical and  
7 ecotoxicological assessment for estuarine surface sediments from Southern Brazil,  
8 *Marine Environmental Research* 91, 68-79.
- 9 Rozan, T.F., Taillefert, M., Trouborst, R.E., Glazer, B.T., Ma, S. 2002.  
10 Iron-sulfur-phosphorous cycling in the sediments of a shallow coastal  
11 bay: implications for sediment nutrient release and benthic macro-algal blooms.  
12 *Limnology and Oceanography* 47, 1346-1354.
- 13 Schoonen, M.A.A., Barnes, H.L. 1991. Mechanisms of pyrite and marcasite formation  
14 from solution: III Hydrothermal processes. *Geochim. Cosmochim. Acta* 55,  
15 3491-3504.
- 16 Sheng, Y., Fu, G., Chen F., Chen J., 2011. Geochemical characteristics of inorganic  
17 sulfur in Shijing River, South China. *Journal of Environmental Monitoring* 13, 807  
18 - 812.
- 19 Sheng, Y., Sun, Q., Bottrell, S.H., Mortimer, R.J.G., Shi, W., 2013. Anthropogenic  
20 impacts on reduced inorganic sulfur and heavy metals in coastal surface sediments,  
21 north Yellow Sea, *Environmental Earth Sciences* 68, 1367-1374.
- 22 Simpson, S.L., Ward, D., Strom, D., Jolley, D.F., 2012. Oxidation of acid-volatile

- 1 sulfide in surface sediments increases the release and toxicity of copper to the  
2 benthic amphipod *Melita plumulosa*, *Chemosphere* 88, 953-961.
- 3 Sorokin, Y.I., Zakuskina, O.Y., 2012. Acid-labile sulfides in shallow marine bottom  
4 sediments: A review of the impact on ecosystems in the Azov Sea, the NE Black  
5 Sea shelf and NW Adriatic lagoons, *Estuarine, Coastal and Shelf Science* 98,  
6 42-48.
- 7 Tarpgaard, I.H., Røy, H., Jørgensen, B.B., 2011. Concurrent low- and high-affinity  
8 sulfate reduction kinetics in marine sediment, *Geochimica et Cosmochimica Acta*,  
9 75, 2997-3010.
- 10 Xu, K., Milliman, J.D., Li, A., Liu, J.P., Kao, S.-J., Wan, S., 2009. Yangtze- and  
11 Taiwan-derived sediments on the inner shelf of East China Sea. *Continental Shelf*  
12 *Research* 29, 2240–2256.
- 13 Yin, H., Fan, C., Ding, S., Zhang, L. and Zhong, J., 2008. Geochemistry of Iron,  
14 Sulfur and Related Heavy Metals in Metal-Polluted Taihu Lake Sediments,  
15 *Pedosphere* 18, 564-573.
- 16 Zhou, J., Wu, Y., Kang, Q., Zhang, J., 2007. Spatial variations of carbon, nitrogen,  
17 phosphorous and sulfur in the salt marsh sediments of the Yangtze Estuary in China,  
18 *Estuarine, Coastal and Shelf Science* 71, 47-59.
- 19 Zhu, M., Liu, J., Yang, G., Li, T., Yang, R., 2012. Reactive iron and its buffering  
20 capacity towards dissolved sulfide in sediments of Jiaozhou Bay, China, *Marine*  
21 *Environmental Research* 80, 46-55.
- 22 Zhu, M., Shi X., Yang G., Hao X., 2013. Formation and burial of pyrite and organic

1 sulfur in mud sediments of the East China Sea inner shelf: Constraints from  
2 solid-phase sulfur speciation and stable sulfur isotope, *Continental Shelf Research*  
3 54, 24-36.

1 **Figure captions**

2

3 Fig. 1 Location of studying areas and sampling sites

4 Fig. 2 Grain size distribution of surface sediments in different sampling sites

5 Fig. 3 Concentrations of TOC, TN and TS in surface sediment in different locations

6 Fig.4 Concentrations of different fractions of RIS in surface sediments (Note: sites

7 B30, B31 and B32 were illustrated with the different scales)

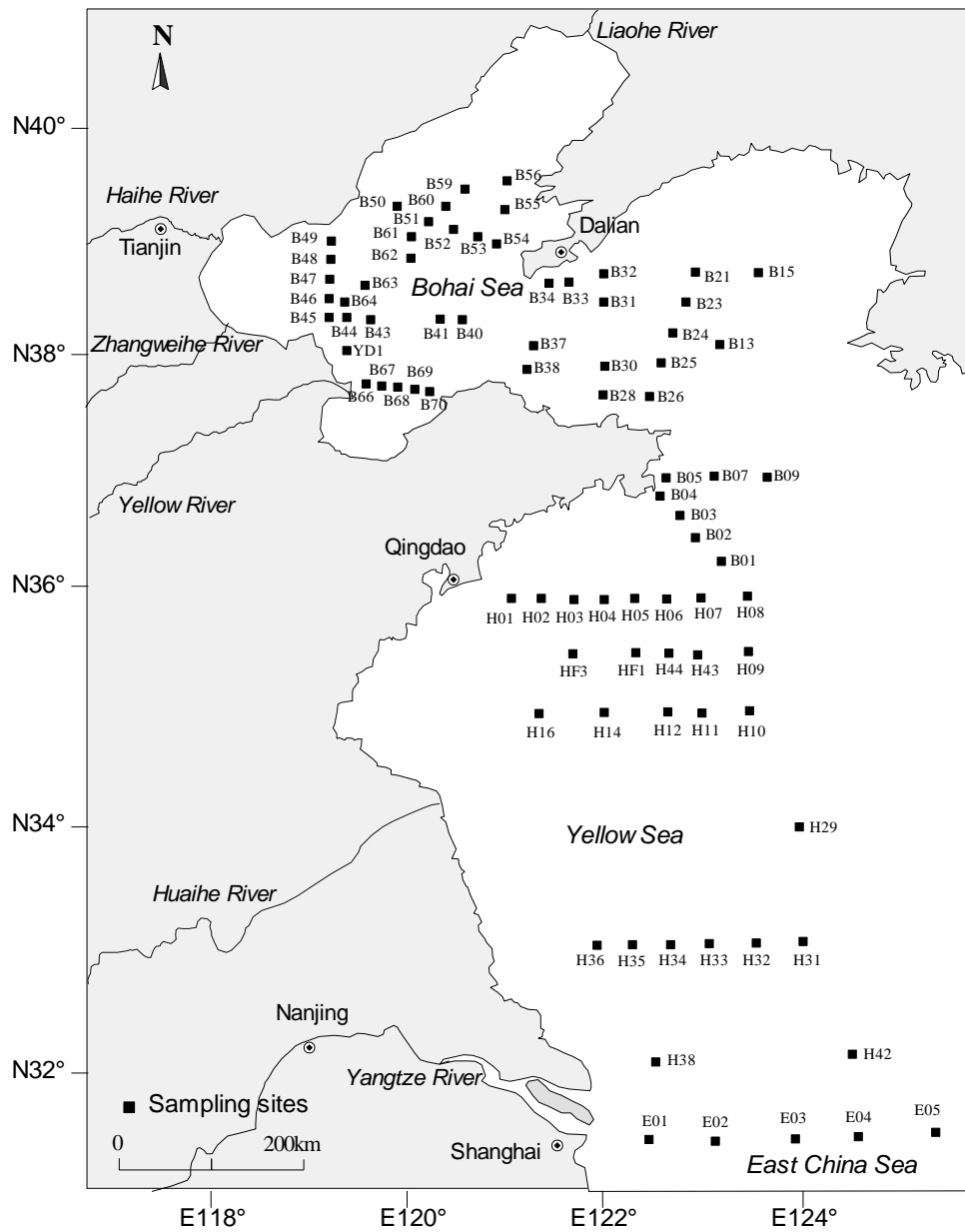
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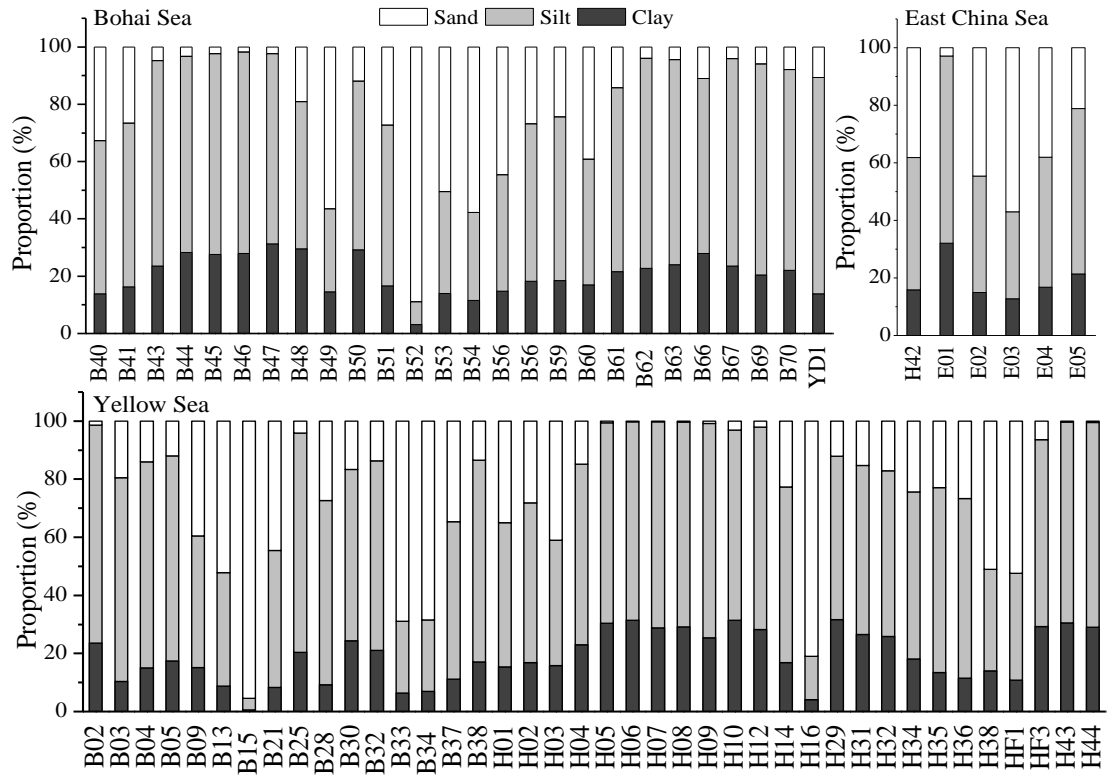
Table 1 Calculation results of different measured geochemical parameters and different iron concentrations ( $\mu\text{mol g}^{-1}$ ).

Yellow Sea	C/N	C/S	AVS/CRS	DOP	DOS	Fe <sub>R</sub>	Fe <sub>py</sub>	Bohai Sea	C/N	C/S	AVS/CRS	DOP	DOS	Fe <sub>R</sub>	Fe <sub>py</sub>
B01	7.84	6.67	0.08	0.04	0.04	147.43	5.70	B40	15.07	10.69	0.22	0.01	0.02	66.97	1.21
B02	11.92	14.70	0.23	0.03	0.05	113.41	3.85	B41	16.01	9.46	0.90	0.03	0.06	76.03	1.11
B03	17.22	11.81	0.94	0.02	0.07	65.53	1.12	B43	17.68	10.82	0.77	0.02	0.05	100.66	2.80
B04	16.43	13.29	0.12	0.01	0.01	110.69	0.77	B44	19.49	11.99	0.74	0.02	0.05	92.21	2.08
B05	16.09	17.28	0.17	0.03	0.04	71.51	2.04	B45	23.36	16.13	0.43	0.01	0.03	91.21	1.95
B07	12.99	8.74	0.07	0.04	0.05	85.19	3.72	B46	18.79	15.11	0.40	0.03	0.05	110.01	1.64
B09	10.00	11.28	0.09	0.03	0.04	65.35	2.17	B47	16.95	12.58	1.22	0.01	0.03	110.69	3.71
B13	12.52	3.50	0.05	0.09	0.10	46.95	4.39	B48	18.81	15.97	0.43	0.01	0.03	94.68	1.27
B15	8.34	1.31	0.15	0.02	0.03	22.56	0.39	B49	13.68	9.35	0.46	0.01	0.03	43.94	0.35
B21	9.71	5.35	0.14	0.03	0.05	50.42	1.73	B50	13.90	12.94	1.19	0.01	0.10	83.22	1.13
B23	11.58	5.45	0.06	0.04	0.05	63.96	3.00	B51	13.27	7.89	0.25	0.01	0.02	39.03	0.31
B24	10.40	6.81	0.16	0.03	0.04	100.27	3.19	B52	10.07	11.13	0.15	0.01	0.01	117.96	1.67
B25	9.60	9.07	0.08	0.06	0.07	84.73	5.43	B53	23.58	10.76	0.15	0.02	0.03	124.98	1.48
B26	18.50	11.33	0.53	0.01	0.03	69.19	1.03	B54	15.51	6.17	0.20	0.03	0.04	66.43	1.20
B28	24.53	18.66	0.33	0.01	0.02	56.19	0.43	B55	12.73	6.42	0.16	0.01	0.04	91.50	3.10
B30	8.16	2.60	0.01	0.27	0.28	77.35	28.79	B56	15.11	6.99	0.19	0.02	0.02	65.25	0.97
B31	41.32	12.47	0.02	0.31	0.33	39.32	17.74	B59	14.94	9.62	0.49	0.02	0.04	83.94	1.65
B32	15.81	4.82	0.04	0.28	0.32	76.56	30.24	B60	14.90	12.83	0.14	0.04	0.04	78.57	1.65
B33	20.87	10.37	0.19	0.03	0.07	28.29	0.98	B61	11.97	6.64	0.26	0.03	0.04	113.02	4.93
B34	16.08	9.35	0.40	0.01	0.02	40.57	0.54	B62	10.48	10.93	0.16	0.02	0.03	138.62	3.62
B37	14.10	12.85	0.28	0.02	0.05	53.68	1.13	B63	13.32	10.62	0.18	0.02	0.02	124.58	1.91
B38	15.29	13.56	0.39	0.02	0.03	70.55	1.29	B64	18.40	12.39	0.77	0.02	0.03	114.49	2.04
H01	24.94	24.28	0.64	0.01	0.01	102.20	0.79	B66	29.69	37.48	0.83	0.03	0.05	71.33	1.19
H02	22.77	24.22	0.16	0.01	0.01	74.91	0.62	B67	27.41	13.18	0.14	0.01	0.02	88.67	2.65

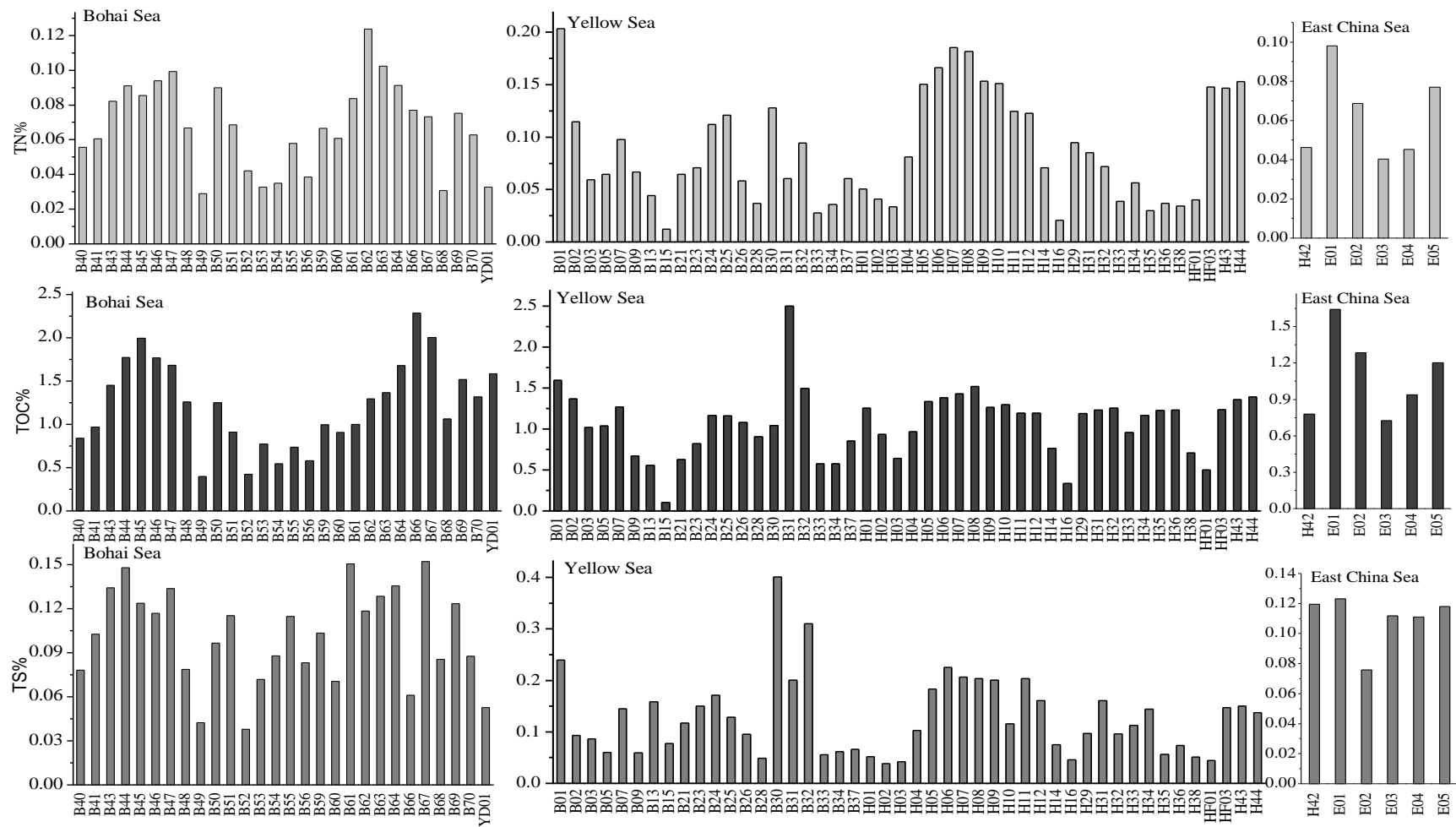
H03	19.12	15.18	0.42	0.00	0.01	71.08	0.17	B68	34.54	12.45	0.20	0.02	0.02	66.03	0.69
H04	11.89	9.41	0.51	0.01	0.02	110.87	1.55	B69	20.17	12.28	0.93	0.02	0.02	94.15	1.71
H05	8.87	7.28	0.06	0.02	0.03	165.16	4.22	B70	21.00	15.01	1.20	0.04	0.04	91.89	1.60
H06	8.32	6.14	1.09	0.02	0.03	163.58	3.16	YD1	48.41	30.10	0.36	0.01	0.02	77.82	0.68
H07	7.71	6.92	0.05	0.02	0.02	172.32	3.55	Mean	18.90	12.78	0.48	0.02	0.04	89.92	1.80
H08	8.35	7.45	0.18	0.02	0.03	185.00	3.82	<b>East China Sea</b>							
H09	8.25	6.32	0.08	0.04	0.04	159.28	6.35	H42	16.81	6.52	0.08	0.04	0.05	127.45	5.76
H10	8.57	11.20	0.10	0.03	0.03	150.15	4.57	E01	16.73	13.32	0.11	0.03	0.04	171.85	4.92
H11	9.58	5.87	0.02	0.04	0.04	179.19	7.25	E02	18.69	16.97	0.09	0.04	0.05	111.37	4.74
H12	9.69	7.40	0.12	0.02	0.03	164.26	3.24	E03	17.96	6.50	0.04	0.03	0.03	148.40	4.47
H14	10.80	10.14	0.46	0.01	0.03	91.82	1.04	E04	20.75	8.45	0.03	0.03	0.03	110.37	3.67
H16	16.18	7.27	0.96	0.01	0.02	52.46	0.59	E05	15.64	10.20	0.04	0.04	0.04	111.37	4.76
H43	9.26	9.02	0.11	0.03	0.04	181.77	5.49	Mean	17.76	10.33	0.07	0.04	0.04	130.14	4.72
H44	9.10	10.15	0.15	0.02	0.03	178.48	4.47								
HF1	12.48	11.32	0.13	0.01	0.02	50.35	0.54								
HF3	8.34	8.38	0.05	0.03	0.04	138.33	4.48								
H29	12.53	12.26	0.08	0.02	0.03	140.30	3.29								
H31	14.47	7.65	0.18	0.03	0.04	134.50	3.53								
H32	17.42	13.03	0.08	0.02	0.03	147.61	3.20								
H33	24.68	8.46	0.07	0.02	0.04	108.76	2.76								
H34	20.65	8.10	0.07	0.03	0.03	140.27	3.69								
H35	40.87	21.72	0.07	0.02	0.02	105.43	1.64								
H36	33.38	16.84	0.17	0.02	0.03	98.98	2.00								
H38	20.68	13.88	0.08	0.02	0.02	139.05	2.91								
Mean	15.17	10.44	0.22	0.04	0.05	103.04	4.14								



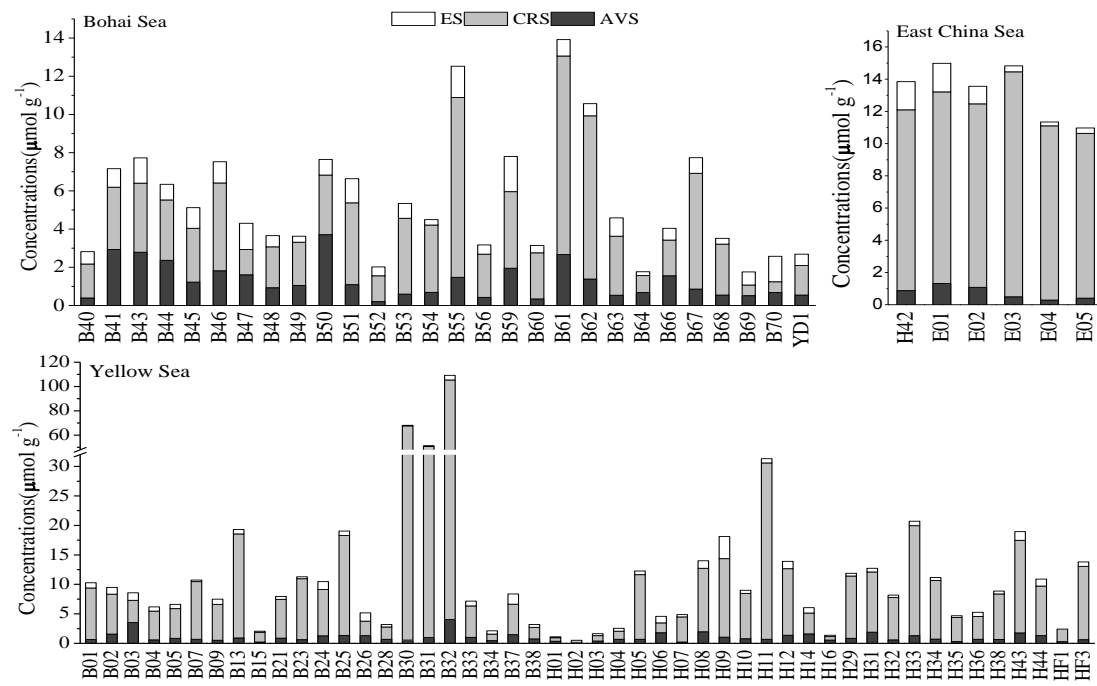
**Fig. 1**



**Fig. 2**



**Fig. 3**



**Fig.4**