



CrossMark
click for updates

Cite this: *Environ. Sci.: Processes Impacts*, 2015, 17, 1689

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

Yanqing Sheng,^{*a} Qiyao Sun,^a Simon H. Bottrell^b and Robert J. G. Mortimer^c

Geochemical cycling and biological toxicity of sulfur in marine sediments is closely related to the activity of organisms. This study investigated the distribution and potential impact on benthic environments of acid volatile sulfur (AVS), chromium(II)-reducible sulfur (CRS), elemental sulfur (ES), total S, C, N and Fe in superficial sediments across the Bohai Sea, Yellow Sea and East China Sea. The composition of reduced inorganic sulfur in the three study areas was dominated by CRS (averaging 72% of total reduced inorganic sulfur). The low AVS content (average of 1.12 $\mu\text{mol g}^{-1}$) of the sediments and the low values of AVS/CRS (average 0.34 $\mu\text{mol g}^{-1}$), degree of pyritization and degree of sulphidization indicate that there is sufficient available iron in the sediment to restrict the threat of sulphide toxicity to benthic organisms in most of the study areas. However, high organic matter loads in parts of the study areas have resulted in enhanced accumulation of AVS, resulting in a higher toxicity risk.

Received 17th April 2015
Accepted 10th August 2015

DOI: 10.1039/c5em00175g

rsc.li/process-impacts

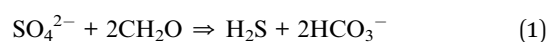
Environmental impact

This study investigated the distribution and impact on benthic environments of different fractions of reduced inorganic sulfur (RIS) in superficial sediments across the offshore areas of the Bohai Sea, Yellow Sea and East China Sea. Acid volatile sulfur (AVS), chromium(II)-reducible sulfur (CRS), elemental sulfur (ES), total sulfur, total organic carbon, total nitrogen, and reactive Fe were determined for each site. The composition of RIS in the three study areas was dominated by CRS. The low AVS content of the sediments and the low values of AVS/CRS, degrees of pyritization and degrees of sulphidization indicate that there is sufficient available iron in the sediment to restrict the threat of sulphide toxicity to benthic organisms in most of the study area.

1. Introduction

Sulfur is essential to life and one of the key players in global biogeochemical cycles. However the most reduced form, sulfide, is generally toxic to organisms and influences water quality.^{1,2} Sulfur is cycled between and fixed in many different forms in marine sediments.³⁻⁶ Therefore, understanding sulfur speciation in marine sediments is essential in evaluating its response to environmental change and the potential biological impact of sulfide. The availability of sulfide in the coastal environment will have implications for overlying water quality.

The sulfur cycle in marine sediments can be divided into reductive and oxidative processes. The reductive side of the cycle is driven by microorganisms that reduce sulfate to sulfide in anaerobic environments and rates of sulfate reduction can be very high under such conditions.^{7,8}



In the oxidative side of the cycle sulfide reacts with a variety of oxidants such as O_2 and Fe(III) oxides to produce sulfate or intermediate S forms (e.g. elemental S). The majority of the sulfide produced in marine sediment is reoxidized.⁹⁻¹¹ Sulfide produced is also removed by reaction with Fe minerals, initially producing a monosulfide “FeS” which transforms to more stable pyrite, FeS_2 .^{12,13} However, the reactivity of Fe minerals is highly variable¹⁴ and may limit the removal of sulfide. Where supply of oxidants is also restricted, production of sulfide may outcompete rates of removal and concentrations of toxic sulfide will increase in shallow pore-waters and bottom waters.¹⁵ Furthermore, iron monosulfide in sediment are often highly reactive and will rapidly react with and remove dissolved oxygen from bottom waters if sediment is resuspended.

The reactivity of sulfide in sediment when resuspension occurs is dependent of the form in which sulfide is present; dissolved sulfide is most reactive, followed by monosulfide, and pyrite is least reactive.¹⁶ In many sediments, rapid reoxidation of AVS and conversion of monosulfide to pyrite usually render monosulfide concentrations low or negligible in the uppermost layer.¹⁷⁻²⁰ However in other situations (e.g. high pH (>7.8)

^aResearch Center for Coastal Environmental Engineering Technology of Shandong Province, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, P.R. China. E-mail: yqsheng@yic.ac.cn; Fax: +86 535 2109000; Tel: +86 535 2109265

^bSchool of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

^cSchool of Animal, Rural and Environmental Sciences, Nottingham Trent University, Brackenhurst Campus, Southwell, Nottinghamshire, NG25 0QE, UK

sediments and under organic-rich eutrophic conditions) Fe monosulfides are persistent and represent a significant pool of reactive sulfide in the sediment.^{21–24} Sulfide is toxic to aquatic organisms. Its accumulation in upper sediment layers in coastal areas exerts an impact upon not only local benthos but also the pelagic biota due to the potential release of free sulfide into the water column.¹ Furthermore, re-suspension of sediment can result in oxidation of H₂S and reactive sulfides, changing the redox conditions of the overlying water and leading to hypoxia at the sea floor.^{15,25} Oxidation of monosulfide in surface sediments may also lead to the release of toxic heavy metals (coprecipitated with FeS) into more bioavailable forms, such as dissolved Cu and Zn.^{26,27} Most organisms live within oxic surface sediments or in oxygenated microenvironments created within sub-oxic and anoxic sediments,²⁶ and hence are vulnerable to shifts in redox and associated changes in sulfur speciation and toxicity.

The degree of pyritization (DOP) and the degree of sulphidization (DOS) are two parameters that can be used to distinguish between situations where pyrite and Fe sulfide formation is either C- or Fe-limited. It is also can be used to measure the completeness of the reaction of reactive Fe (operationally defined as the fraction of Fe that is soluble in 1 M HCl for 16 h) with aqueous sulfide.²⁸ In sediments that contain a significant amount of Fe monosulfide, DOP underestimates the amount of Fe that has reacted with H₂S.²⁹ Instead, DOS represents the degree to which reactive Fe has been transformed into sulfide and, therefore, provides a better indication of Fe limiting conditions.³⁰ In sediments where Fe availability becomes limiting pore-water sulfide concentrations are likely to increase, enhancing the likelihood of sulfide toxicity. Conversely, if sulfide production is limited by the availability of a labile organic substrate, pore-water sulfide concentrations may be very low.

The Bohai Sea, Yellow Sea and East China Sea are situated north-east (NE) of China. They are important production bases for fishery and marine industries. This study area can be characterized as a region surrounded by areas of high population growth and economic development. A large amount of industrial and municipal wastewaters, along with excess nutrients from mariculture, have been discharged into these areas *via* riverine inputs (*i.e.* Yellow River, Yangtze River and other smaller rivers). This pollution may influence the cycles of iron, sulfur and phosphorus,¹⁹ leading to offshore eutrophication and benthic macroalgal blooms, especially large offshore phytoplankton blooms *e.g.* *Enteromorpha prolifera* in Yellow Sea.³¹ Previous studies on the effects of biogenic elements in sediments in these areas were focused mainly on carbon, nitrogen and phosphorus.^{31,32} However, to date, only limited effort has been devoted to the study of sedimentary geochemistry of reduced inorganic sulfur (RIS) in the offshore areas of NE China,³³ and its potential impact on the marine ecosystem remains unclear.

In this study, acid volatile sulfur (AVS), chromium(II)-reducible sulfur (CRS, pyritic sulfur), elemental sulfur (ES), total sulfur (TS), reactive iron, total organic carbon (TOC) and total nitrogen (TN) were analyzed in surface sediments from the

study area. The partitioning of RIS was used to understand sulfur biogeochemistry within the sediments, and to predict the potential for ecotoxicological risk due to release of toxic sulfide.

2. Methods and materials

2.1 Samples collection and handling

A total of 82 sediment samples were collected from the Bohai Sea, Yellow Sea and East China Sea (Fig. 1). Surface sediments (0–20 cm) were collected using a stainless steel grab sampler and were immediately isolated from the atmosphere in plastic zip-lock bags with all air expelled by N₂ gas (a N₂ gas cylinder was aboard ship). Samples were frozen and stored in an icebox (–20 °C) until arrival at the laboratory. Samples were processed immediately upon return to the laboratory. In the laboratory, the plastic sample bags were first flushed with high purity N₂ again. Samples were then homogenized under this inert atmosphere (a glove box) by mixing with a plastic spatula. Four replicates were used throughout.

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% HNO₃ for 48 h and rinsed with Milli-Q water three times before use. Total organic carbon (TOC) in sediments was determined by a Shimadzu TOC-V_{CPH}/SSM-5000A. Total nitrogen (TN) and total sulfur (TS) were determined by an Elementar vario MACRO cube CHNS analyzer. The precision of the measurements was within 5% based on three replicate sediment analyses. Prior to grain size analysis, each sediment sample was treated with sodium hypochlorite (NaOCl) to remove organic matter. Sample granulometry was analyzed using a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2000 μm. 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 using a modified procedure described by Newton *et al.*³⁴ and Hsieh & Shieh.³⁵ Reagents and extraction steps of sulfur species separation are the same as the description of Hsieh & Shieh,³⁵ the detection of H₂S is the same as the description of Newton *et al.*³⁴ In this method, a thin glass pipe (with N₂ gas inside) was dipped into corresponding solutions (shaking occasionally) to accelerate the emission of H₂S (1.5 h). All subsequent processing of sediment was performed under a N₂ atmosphere inside a glove box at room temperature. Briefly, AVS, CRS and ES were separated sequentially by 6 M HCl, acidic Cr(II) and Cr(II) plus *N,N*-dimethylformamide, respectively, using pure N₂ as carrier gas to purge and trap H₂S, at a temperature of ~60 °C (by electric hot plate). The liberated H₂S was trapped in a 0.1 mol L⁻¹ CuCl₂ solution. The amount of H₂S evolved from the sample for each solid-phase RIS species was determined by titrating the Cu remaining in solution with 0.1 mol L⁻¹ EDTA (assuming a precipitate of CuS stoichiometry). Three to four drops of glycine cresol red (0.5%

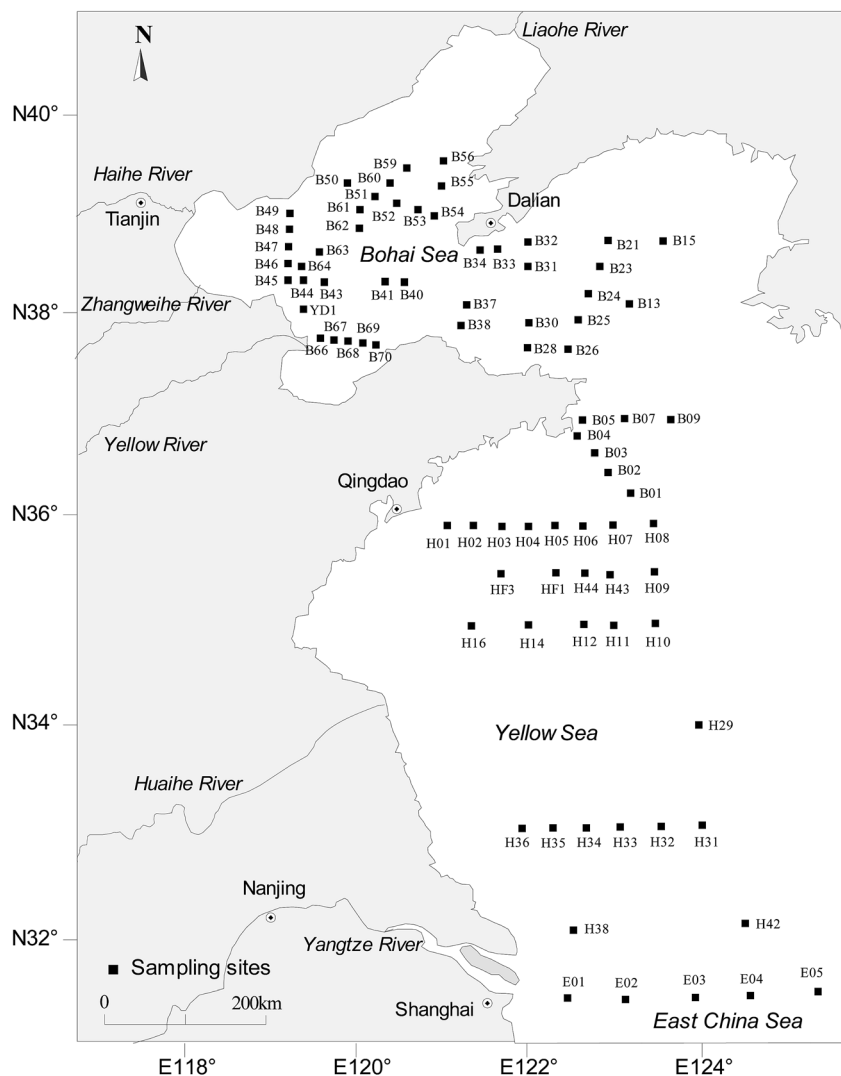


Fig. 1 Location of studying areas and sampling sites.

aqueous) was used as an indicator and the titration was buffered with 70 mL of 1 mol L⁻¹ sodium acetate solution (adjusted to pH 5.5 with acetic acid). The endpoint was sharp and marked by a colour change from dark blue to a light green. Sulfide solutions (Na₂S) with concentrations of 0.5 and 1 mg L⁻¹ were used in recovery experiments. Average sulfide recovery rate was 96%. Measured sulfide data were converted to real sulfide contents after correction for the recovery rate. The precision of triplicate analysis was within 5% for different fractions of RIS. The fractions of Fe were determined by sequential acid digestion. Reactive Fe is the fraction of Fe that is soluble in 1 mol L⁻¹ HCl (16 h, Fe_R) and pyrite Fe (Fe_{py}) is the Fe that is soluble in concentrated HNO₃, after removal of the Fe associated with silicates and organic matter.³⁶ The concentrations of different Fe fractions (extracted by corresponding acid) were detected by an Atomic Absorption Spectrometer (TAS 990, Beijing Purkinje General Instrument Co. Ltd, Beijing), precision was to within 2% based on triplicate analysis.

2.3 Data calculation

DOP was taken to be the percentage of pyrite-Fe in the bioavailable iron, which was calculated as $Fe_{py}/(Fe_R + Fe_{py})$.¹² Fe_{py} was calculated from FeS₂ stoichiometry. DOS was taken to be the percentage of Fe that has been transformed into sulfide, which was defined by $(Fe_{py} + Fe_{AVS})/(Fe_{py} + Fe_R)$.²⁹ Fe_{AVS} is sulfide-bound Fe(II) assuming that AVS predominantly occurs as FeS, though this assumption remains controversial.^{16,20}

3. Results and discussion

3.1 Distribution of grain size

The grain size of the sediments plays a significant role in the accumulation of organic matter, and can influence the spatial distribution of C, N and S.³⁷ The variations of grain size in the surface sediments are shown in Fig. 2. The data reveal a predominance of silt (4–63 μm), which accounted for an average of 57%, 57% and 47% of the particles in Bohai Sea, Yellow Sea and East China Sea, respectively. Compared to the East China

Sea, high proportions of silt in the Bohai Sea and the Yellow Sea are most likely related to transport of suspended sediments down the Yellow River.³⁸ The surface sediments of Bohai Sea were dominated by silt, except for samples B52, B53 and B54 (Fig. 1). These sites were located in the main water exchange channel between the Bohai Sea and the Yellow Sea,³¹ so the small particles (clay) may be winnowed by strong water currents, resulting in a predominance of sand in this area (Fig. 2). In the East China Sea, driven by the Zhejiang-Fujian coastal current, a large amount of fine grained particulates from the Yangtze Estuary are transported southward along the coast and trapped in the inner shelf by the blocking of the northward warm Taiwan current offshore, developing mud wedges outside the Yangtze River mouth.³⁹ Therefore, at site E01 (Fig. 1), the sediment was dominated by fine grained particulates, with silt and clay accounting for ~97% of total grains (Fig. 2).

3.2 Distribution of TOC, TN and TS

The surface sediments were characterized by variable concentrations of TN, TOC and TS. TN varied from 0.03–0.21% (% dry weight of the sediment), TOC from 0.11–2.49% and TS from 0.11–0.40%. The average TN in the Bohai Sea, Yellow Sea and East China Sea were 0.07%, 0.08% and 0.06%, respectively. The averages for TOC were 1.23%, 1.07% and 1.09% respectively (Fig. 3). The highest TOC contents were recorded at site B66 (2.3%) in the Bohai Sea, B31 (2.5%) in the Yellow Sea and E01 (1.6%) in the East China Sea. In the Bohai Sea, TN, TOC and TS exhibited high values in Bohai Bay and Laizhou Bay. In the Yellow Sea, the TOC and TS contents in sediments at B31 and B32 were high (2.5% and 1.5% respectively), indicating high organic pollution loads in these areas, most likely related to the

Dalian crude oil spill in 2010.⁴⁰ This organic pollution may provide an additional substrate for sulfate reduction and lead to increased sulfide production and accumulation in the sediment.

3.3 Distribution characteristics of different fractions of RIS

Fig. 4 presents the AVS, CRS and ES concentrations in the surface sediment samples of the Bohai Sea, Yellow Sea and East China Sea. The AVS, CRS, and ES 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 $\mu\text{mol g}^{-1}$, respectively. AVS contents in the Bohai Sea, Yellow Sea and East China Sea are close to the ranges of AVS contents for Jiaozhou Bay sediments (0.06–13.7 $\mu\text{mol g}^{-1}$)⁴¹ and East China Sea shelf sediments (0–25 $\mu\text{mol g}^{-1}$).^{42,43} For CRS, the concentrations are 0.6–101 $\mu\text{mol g}^{-1}$, dominating the total RIS in all studied areas, with an average 75% share in the Bohai Sea, 59% in the Yellow Sea and 87% in the East China Sea (Fig. 4 and Table 1). This finding was consistent with the reports of Zhu *et al.*⁴¹ in Jiaozhou Bay (CRS: 8.7–51.1 $\mu\text{mol g}^{-1}$), Sheng *et al.*⁴⁴ in the coastal zone of the Yellow Sea (CRS: 5.5–13.1 $\mu\text{mol g}^{-1}$) and Zhu *et al.*⁴³ in the East China Sea inner shelf (CRS: 2.7–38.3 $\mu\text{mol g}^{-1}$). In this study, although there are some values of RIS at sites B30, B31 and B32 associated with an oil spill, even these highest values (101.2 $\mu\text{mol g}^{-1}$) are much lower than the peak value for the southern East China Sea slope sediments (range: 0–240 $\mu\text{mol g}^{-1}$).⁴⁵ Because of high concentrations of reactive iron (average is approximately 100 $\mu\text{mol g}^{-1}$) in these areas, the sulfide may be removed quickly by the formation of FeS, then it was transformed to FeS₂ due to sufficient ES (0.5–3.9 $\mu\text{mol g}^{-1}$) is present under anoxic conditions (reoxidation of AVS would be restrained because of

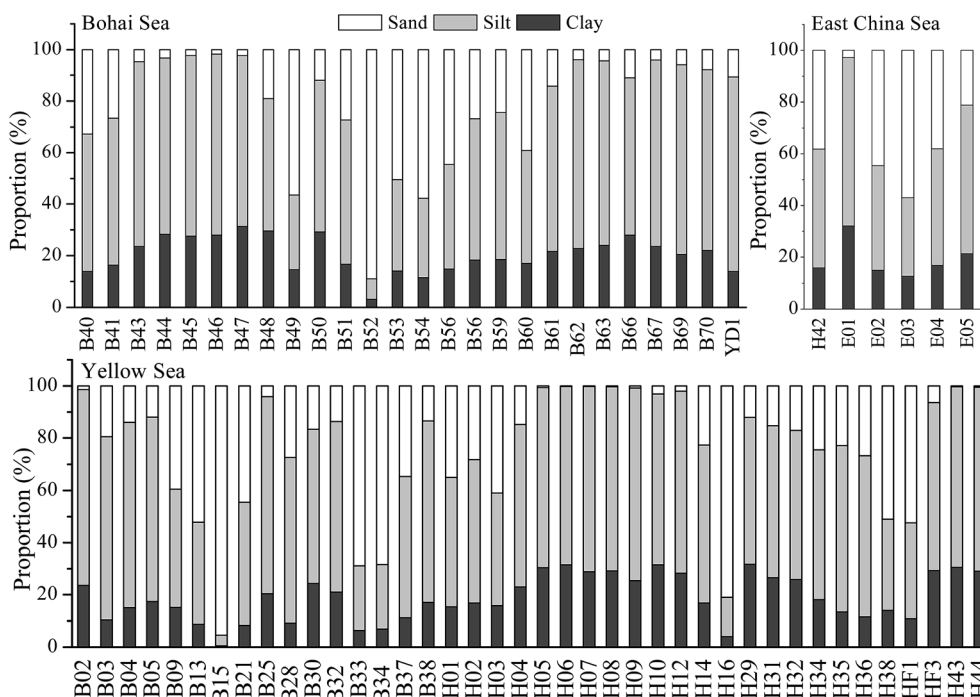


Fig. 2 Grain size distribution of surface sediments in different sampling sites.

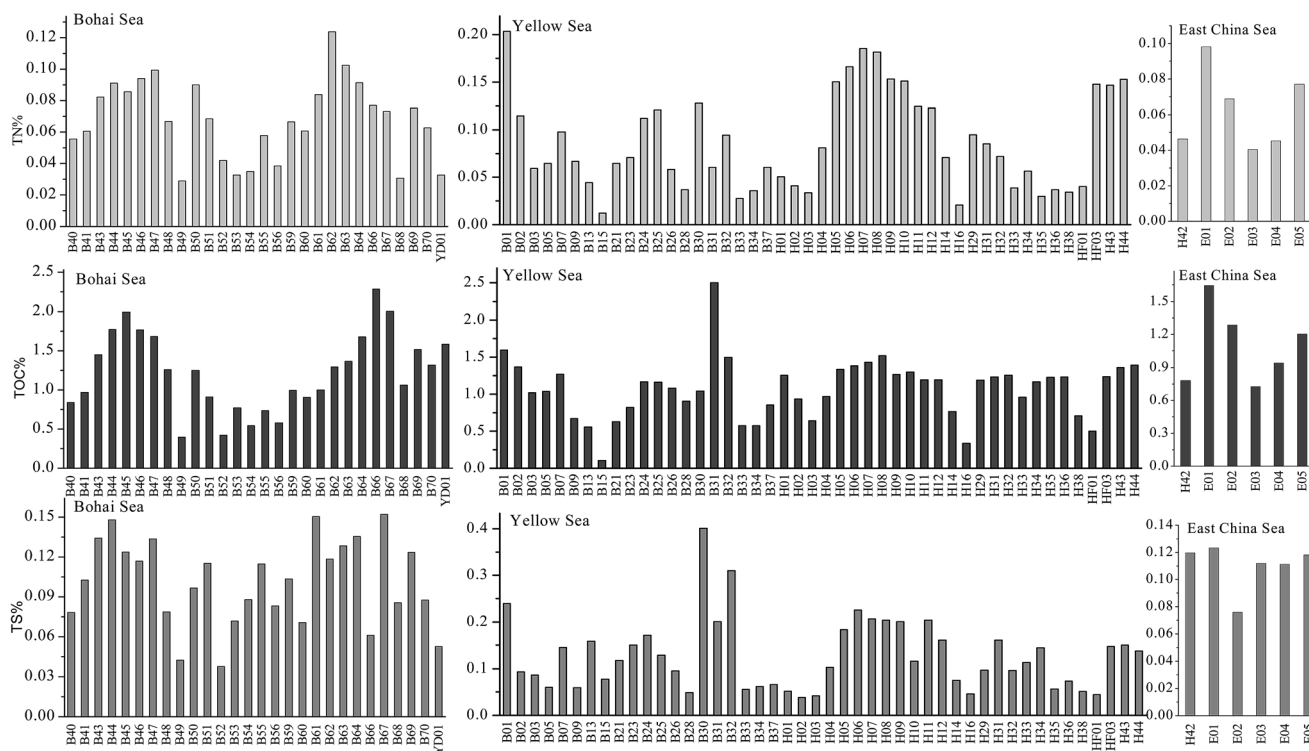


Fig. 3 Concentrations of TOC, TN and TS in surface sediment in different locations.

limited free oxygen in benthic bottom), resulting in high concentration of CRS. Overall, accumulation concentrations of labile sulfides (*i.e.* AVS) in the study area is much lower than levels known to be potentially toxic for aquatic biota (200 mg S L⁻¹ of wet silt²⁵), suggesting the environmental conditions are low risk for the local marine ecosystem.

Generally, RIS concentrations were higher in the Yellow Sea than in the Bohai Sea and East China Sea, especially at sites B30, B31 and B32. This phenomenon is consistent with the variation of TOC and TS in same sites, and is most likely related to the Dalian crude oil spill summer 2010.⁴⁰ Deposited crude oil may increase TOC accumulation in the sediment (B30, B31 and B32)

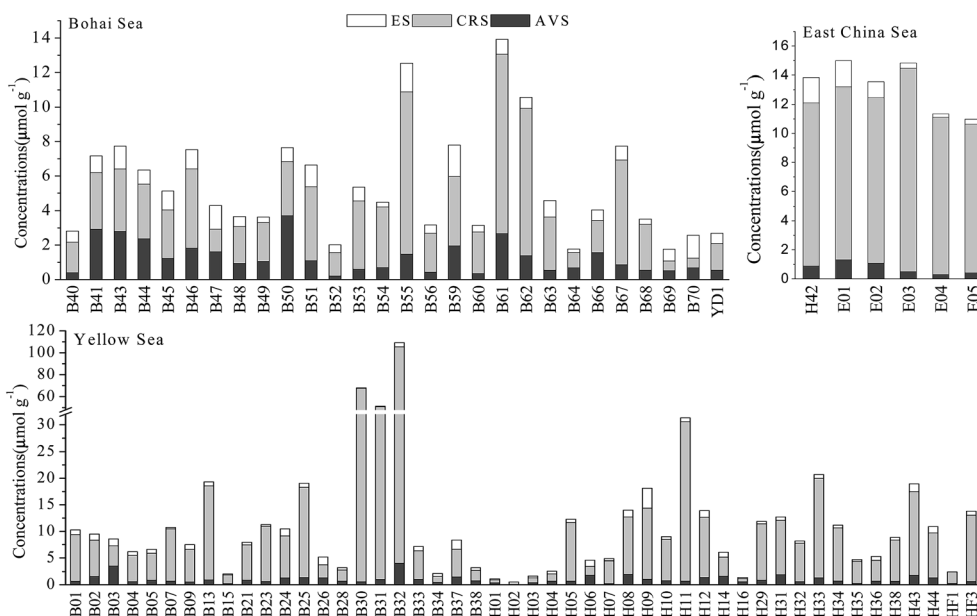


Fig. 4 Concentrations of different fractions of RIS in surface sediments (note: sites B30, B31 and B32 were illustrated with the different scales).

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

| | C/N | C/S | AVS/CRS | DOP | DOS | Fe _R | Fe _{py} |
|-------------------|-------|-------|---------|------|------|-----------------|------------------|
| Yellow Sea | | | | | | | |
| B01 | 7.84 | 6.67 | 0.08 | 0.04 | 0.04 | 147.43 | 5.70 |
| B02 | 11.92 | 14.70 | 0.23 | 0.03 | 0.05 | 113.41 | 3.85 |
| B03 | 17.22 | 11.81 | 0.94 | 0.02 | 0.07 | 65.53 | 1.12 |
| B04 | 16.43 | 13.29 | 0.12 | 0.01 | 0.01 | 110.69 | 0.77 |
| B05 | 16.09 | 17.28 | 0.17 | 0.03 | 0.04 | 71.51 | 2.04 |
| B07 | 12.99 | 8.74 | 0.07 | 0.04 | 0.05 | 85.19 | 3.72 |
| B09 | 10.00 | 11.28 | 0.09 | 0.03 | 0.04 | 65.35 | 2.17 |
| B13 | 12.52 | 3.50 | 0.05 | 0.09 | 0.10 | 46.95 | 4.39 |
| B15 | 8.34 | 1.31 | 0.15 | 0.02 | 0.03 | 22.56 | 0.39 |
| B21 | 9.71 | 5.35 | 0.14 | 0.03 | 0.05 | 50.42 | 1.73 |
| B23 | 11.58 | 5.45 | 0.06 | 0.04 | 0.05 | 63.96 | 3.00 |
| B24 | 10.40 | 6.81 | 0.16 | 0.03 | 0.04 | 100.27 | 3.19 |
| B25 | 9.60 | 9.07 | 0.08 | 0.06 | 0.07 | 84.73 | 5.43 |
| B26 | 18.50 | 11.33 | 0.53 | 0.01 | 0.03 | 69.19 | 1.03 |
| B28 | 24.53 | 18.66 | 0.33 | 0.01 | 0.02 | 56.19 | 0.43 |
| B30 | 8.16 | 2.60 | 0.01 | 0.27 | 0.28 | 77.35 | 28.79 |
| B31 | 41.32 | 12.47 | 0.02 | 0.31 | 0.33 | 39.32 | 17.74 |
| B32 | 15.81 | 4.82 | 0.04 | 0.28 | 0.32 | 76.56 | 30.24 |
| B33 | 20.87 | 10.37 | 0.19 | 0.03 | 0.07 | 28.29 | 0.98 |
| B34 | 16.08 | 9.35 | 0.40 | 0.01 | 0.02 | 40.57 | 0.54 |
| B37 | 14.10 | 12.85 | 0.28 | 0.02 | 0.05 | 53.68 | 1.13 |
| B38 | 15.29 | 13.56 | 0.39 | 0.02 | 0.03 | 70.55 | 1.29 |
| H01 | 24.94 | 24.28 | 0.64 | 0.01 | 0.01 | 102.20 | 0.79 |
| H02 | 22.77 | 24.22 | 0.16 | 0.01 | 0.01 | 74.91 | 0.62 |
| H03 | 19.12 | 15.18 | 0.42 | 0.00 | 0.01 | 71.08 | 0.17 |
| H04 | 11.89 | 9.41 | 0.51 | 0.01 | 0.02 | 110.87 | 1.55 |
| H05 | 8.87 | 7.28 | 0.06 | 0.02 | 0.03 | 165.16 | 4.22 |
| H06 | 8.32 | 6.14 | 1.09 | 0.02 | 0.03 | 163.58 | 3.16 |
| H07 | 7.71 | 6.92 | 0.05 | 0.02 | 0.02 | 172.32 | 3.55 |
| H08 | 8.35 | 7.45 | 0.18 | 0.02 | 0.03 | 185.00 | 3.82 |
| H09 | 8.25 | 6.32 | 0.08 | 0.04 | 0.04 | 159.28 | 6.35 |
| H10 | 8.57 | 11.20 | 0.10 | 0.03 | 0.03 | 150.15 | 4.57 |
| H11 | 9.58 | 5.87 | 0.02 | 0.04 | 0.04 | 179.19 | 7.25 |
| H12 | 9.69 | 7.40 | 0.12 | 0.02 | 0.03 | 164.26 | 3.24 |
| H14 | 10.80 | 10.14 | 0.46 | 0.01 | 0.03 | 91.82 | 1.04 |
| H16 | 16.18 | 7.27 | 0.96 | 0.01 | 0.02 | 52.46 | 0.59 |
| H43 | 9.26 | 9.02 | 0.11 | 0.03 | 0.04 | 181.77 | 5.49 |
| 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 |
| Bohai Sea | | | | | | | |
| B40 | 15.07 | 10.69 | 0.22 | 0.01 | 0.02 | 66.97 | 1.21 |
| B41 | 16.01 | 9.46 | 0.90 | 0.03 | 0.06 | 76.03 | 1.11 |
| B43 | 17.68 | 10.82 | 0.77 | 0.02 | 0.05 | 100.66 | 2.80 |
| B44 | 19.49 | 11.99 | 0.74 | 0.02 | 0.05 | 92.21 | 2.08 |
| B45 | 23.36 | 16.13 | 0.43 | 0.01 | 0.03 | 91.21 | 1.95 |
| B46 | 18.79 | 15.11 | 0.40 | 0.03 | 0.05 | 110.01 | 1.64 |
| B47 | 16.95 | 12.58 | 1.22 | 0.01 | 0.03 | 110.69 | 3.71 |
| B48 | 18.81 | 15.97 | 0.43 | 0.01 | 0.03 | 94.68 | 1.27 |
| B49 | 13.68 | 9.35 | 0.46 | 0.01 | 0.03 | 43.94 | 0.35 |
| B50 | 13.90 | 12.94 | 1.19 | 0.01 | 0.10 | 83.22 | 1.13 |

Table 1 (Contd.)

| | C/N | C/S | AVS/CRS | DOP | DOS | Fe _R | Fe _{py} |
|-----------------------|-------|-------|---------|------|------|-----------------|------------------|
| B51 | 13.27 | 7.89 | 0.25 | 0.01 | 0.02 | 39.03 | 0.31 |
| B52 | 10.07 | 11.13 | 0.15 | 0.01 | 0.01 | 117.96 | 1.67 |
| B53 | 23.58 | 10.76 | 0.15 | 0.02 | 0.03 | 124.98 | 1.48 |
| B54 | 15.51 | 6.17 | 0.20 | 0.03 | 0.04 | 66.43 | 1.20 |
| B55 | 12.73 | 6.42 | 0.16 | 0.01 | 0.04 | 91.50 | 3.10 |
| B56 | 15.11 | 6.99 | 0.19 | 0.02 | 0.02 | 65.25 | 0.97 |
| B59 | 14.94 | 9.62 | 0.49 | 0.02 | 0.04 | 83.94 | 1.65 |
| B60 | 14.90 | 12.83 | 0.14 | 0.04 | 0.04 | 78.57 | 1.65 |
| B61 | 11.97 | 6.64 | 0.26 | 0.03 | 0.04 | 113.02 | 4.93 |
| B62 | 10.48 | 10.93 | 0.16 | 0.02 | 0.03 | 138.62 | 3.62 |
| B63 | 13.32 | 10.62 | 0.18 | 0.02 | 0.02 | 124.58 | 1.91 |
| B64 | 18.40 | 12.39 | 0.77 | 0.02 | 0.03 | 114.49 | 2.04 |
| B66 | 29.69 | 37.48 | 0.83 | 0.03 | 0.05 | 71.33 | 1.19 |
| B67 | 27.41 | 13.18 | 0.14 | 0.01 | 0.02 | 88.67 | 2.65 |
| B68 | 34.54 | 12.45 | 0.20 | 0.02 | 0.02 | 66.03 | 0.69 |
| B69 | 20.17 | 12.28 | 0.93 | 0.02 | 0.02 | 94.15 | 1.71 |
| B70 | 21.00 | 15.01 | 1.20 | 0.04 | 0.04 | 91.89 | 1.60 |
| YD1 | 48.41 | 30.10 | 0.36 | 0.01 | 0.02 | 77.82 | 0.68 |
| Mean | 18.90 | 12.78 | 0.48 | 0.02 | 0.04 | 89.92 | 1.80 |
| East China Sea | | | | | | | |
| H42 | 16.81 | 6.52 | 0.08 | 0.04 | 0.05 | 127.45 | 5.76 |
| E01 | 16.73 | 13.32 | 0.11 | 0.03 | 0.04 | 171.85 | 4.92 |
| E02 | 18.69 | 16.97 | 0.09 | 0.04 | 0.05 | 111.37 | 4.74 |
| E03 | 17.96 | 6.50 | 0.04 | 0.03 | 0.03 | 148.40 | 4.47 |
| E04 | 20.75 | 8.45 | 0.03 | 0.03 | 0.03 | 110.37 | 3.67 |
| E05 | 15.64 | 10.20 | 0.04 | 0.04 | 0.04 | 111.37 | 4.76 |
| Mean | 17.76 | 10.33 | 0.07 | 0.04 | 0.04 | 130.14 | 4.72 |

and thus stimulate sulfate reduction and enhance sulfide accumulation. Whilst the oil spill has modified the sediment geochemistry and increased AVS content, in the samples analyzed this increase is small and lies within the range of many sediments that have not been polluted by oil spills.

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

The atomic molar ratios of C/N, C/S and AVS/CRS are listed in Table 1. C/N and C/S are ratios of TOC concentrations against TN and TS concentrations, respectively. C/N is widely applied in biogeochemical studies of terrestrial, riverine, estuarine, and marine environments, most commonly to estimate the fraction of terrestrially derived organic matter in marine sedimentary samples.⁴⁶ In this study, the C/N ratio (molar ratio) varied from 10.1 to 48.4 (average: 18.9) in the Bohai Sea, 7.7–41.3 (average: 15.1) in the Yellow Sea and 16.5–20.7 (average: 17.8) in the East China Sea (Table 1). These results suggest that the studied areas are abundant in terrestrial-derived organic matter with high C/N ratios (always higher than 10),⁴⁶ associated with material rich in cellulose which originates from terrestrial vascular plants and reaches the sediments *via* rivers, *i.e.* Yellow River and Yangtze River.

TS and TOC/TS (C/S) are used for studying oxic/anoxic conditions in marine environments.¹³ The C/S ratios varied from 6.1 to 37.5, with an average of 12.8 in the Bohai Sea, 1.3–

24.2 (average: 10.3) in the Yellow Sea and 6.5–17.0 (average: 10.3) in the East China Sea. Generally, the ratio of C/S in normal marine sediment (deposited under an oxic water column) is 2.0–3.8.⁴⁷ Overall, the C/S ratio in this study was highly variable at 1.3–37.5 (average: 11.4), with values in most sampling sites higher than is normal for marine sediments. This can be explained by the impact of freshwater input and mariculture activity, which can both significantly influence C/S ratios, e.g. site B66 (37.5), is close to the Yellow River estuary (with high TOC and low RIS values in sediment); site H1 (24.3) is close to Qingdao city, where there are many large wastewater treatment plants (over 1 million tons discharged per day); site H35 (21.7) is in a mariculture area. Generally, sewage and mariculture contribute more C but not more S, resulting in high C/S ratios. The result indicates that sulfate reduction or RIS accumulation was variable in surface sediment of different areas, and may be influenced by anthropogenic activities (organic matter input) and redox conditions. AVS/CRS varied from 0.14 to 1.22, with an average of 0.48 in Bohai Sea, 0.01–1.09 (average: 0.22) in Yellow Sea and 0.02–0.11 (average: 0.06) in East China Sea. Low ratios indicate that the sediment in these areas poses a low threat of toxicity to benthic organisms because CRS is more stable and less likely to release sulfide or metals than AVS, which is more soluble and reactive.

3.5 DOP and DOS

The relationship between sulfide and iron plays an important role in controlling of the sulfur cycle. As shown in Table 1, both DOP and DOS for the three areas are generally close to each other, with DOP ranging from 0.01 to 0.31 (averages of 0.02 for the Bohai Sea, and 0.04 for both the Yellow Sea and East China Sea) and DOS ranging from 0.02 to 0.33 (averages of 0.04 for the Bohai Sea, 0.05) for the Yellow Sea and 0.04 for the East China Sea. DOS values are slightly higher than the DOP values, which perhaps reflects the reaction of FeS and H₂S to form pyrite.¹⁹ The three areas have much lower DOP and DOS in comparison with the averages for estuarine and bay sediments of the Gulf of Mexico (DOP 0.56–0.95 and DOS 0.63–2.66),⁷ but are consistent with DOP (0.05–0.25) and DOS (0.05–0.39) for Jiaozhou Bay sediment in the Yellow Sea.⁴¹ On the basis of the simple comparison above, it is inferred that the low availability of labile organic matter in the study areas may have been limiting sulfide production,⁴¹ and resulted in low values of DOP and DOS. Furthermore, high concentrations of reactive iron (average is approximately 100 μmol g⁻¹) and low values of DOP and DOS found in the present study further indicate that pyritization and sulfidization are not being limited by the availability of reactive Fe. Thus in these sediments the supply of reactive Fe has been sufficient to match net sulfide production and thus limit the sulfide toxicity hazard.

4. Conclusions

In order to elucidate the geochemical processes controlling the formation and stability of RIS species and its bioavailability in surface sediments, we have examined the relationship between

the spatial variations in the values of sedimentary grain size, TOC, TN, TS, AVS, CRS, ES, C/N ratio, C/S ratio, AVS/CRS ratio, DOP and DOS in Bohai Sea, Yellow Sea and East China Sea. In the study area, CRS was the dominant fraction of RIS, indicating the RIS is dominantly in a stable form and thus poses a low threat of toxicity to marine ecosystem. Low values of DOP and DOS indicate that pyritization and sulphidization are not being limited by the availability of reactive Fe. Sediment in these areas restricts the threat from sulfide to benthic organisms. An oil spill in part of the studied area has resulted in enhanced accumulation of AVS in marine sediment, resulting in a higher toxicity risk.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 41373100). Additional support was provided by Science and Technology Program for Public Wellbeing of Shandong Province (Grant No. 2013kjhm060308).

References

- 1 T. Bagarinao, Sulfide as an environmental factor and toxicant: tolerance and adaptations in aquatic organisms, *Aquat. Toxicol.*, 1992, **24**, 21–62.
- 2 Y. Sheng, G. Fu, F. Chen and J. Chen, Geochemical characteristics of inorganic sulfur in Shijing River, South China, *J. Environ. Monit.*, 2011, **13**, 807–812.
- 3 J. W. Morse and R. A. Berner, What determines sedimentary C–S ratios, *Geochim. Cosmochim. Acta*, 1995, **59**, 1073–1077.
- 4 D. E. Canfield, E. Kristensen and B. Thamdrup, The sulfur cycle, *Adv. Mar. Biol.*, 2005, **48**, 313–381.
- 5 S. H. Bottrell, R. J. G. Mortimer, I. M. Davies, S. M. Harvey and M. D. Krom, Sulphur cycling in organic-rich marine sediments from a Scottish fjord, *Sedimentology*, 2009, **56**, 1159–1173.
- 6 P. Alvarez-Iglesias, B. Rubioa and J. Millosb, Isotopic identification of natural vs. anthropogenic lead sources in marine sediments from the inner Ría de Vigo (NW Spain), *Sci. Total Environ.*, 2012, **437**, 22–35.
- 7 J. W. Morse, H. Thomson and D. W. Finneran, Factors controlling sulfide geochemistry in sub-tropical estuarine and bay sediments, *Aquat. Geochem.*, 2007, **13**, 143–156.
- 8 I. H. Tarpgaard, H. Røy and B. B. Jørgensen, Concurrent low- and high-affinity sulfate reduction kinetics in marine sediment, *Geochim. Cosmochim. Acta*, 2011, **75**, 2997–3010.
- 9 D. E. Canfield and B. Thamdrup, The production of ³⁴S-depleted sulfide during bacterial disproportionation of elemental sulfur, *Science*, 1994, **266**, 1973–1975.
- 10 S. W. Poulton, Sulfide oxidation and iron dissolution kinetics during the reaction of dissolved sulfide with ferrihydrite, *Chem. Geol.*, 2003, **202**, 79–94.
- 11 S. H. Bottrell and R. J. Newton, Reconstruction of changes in global sulfur cycling from marine sulfate isotopes, *Earth-Sci. Rev.*, 2006, **75**, 59–83.

- 12 R. A. Berner, Sedimentary pyrite formation, *Am. J. Sci.*, 1970, **268**, 1–23.
- 13 R. A. Berner, Sedimentary pyrite formation: an update, *Geochim. Cosmochim. Acta*, 1984, **48**, 605–615.
- 14 D. E. Canfield, R. Raiswell and S. Bottrell, The reactivity of sedimentary iron minerals toward sulfide, *Am. J. Sci.*, 1992, **292**, 659–683.
- 15 B. M. Phillips, B. S. Anderson and J. W. Hunt, Measurement and distribution of interstitial and overlying water ammonia and hydrogen sulfide in sediment, *Mar. Environ. Res.*, 1997, **44**, 117–126.
- 16 J. W. Morse and D. Rickard, Chemical dynamics of sedimentary acid volatile sulfide, *Environ. Sci. Technol.*, 2004, **38**, 131A–136A.
- 17 M. A. A. Schoonen and H. L. Barnes, Mechanisms of pyrite and marcasite formation from solution: III hydrothermal processes, *Geochim. Cosmochim. Acta*, 1991, **55**, 3491–3504.
- 18 I. B. Butler and D. Rickard, Framboidal pyrite formation via the oxidation of iron(II) monosulfide by hydrogen sulfide, *Geochim. Cosmochim. Acta*, 2000, **64**, 2665–2672.
- 19 T. F. Rozan, M. Taillefert, R. E. Trouborst, B. T. Glazer and S. Ma, Iron–sulfur–phosphorous cycling in the sediments of a shallow coastal bay: implications for sediment nutrient release and benthic macro-algal blooms, *Limnol. Oceanogr.*, 2002, **47**, 1346–1354.
- 20 D. Rickard and J. W. Morse, Acid volatile sulfide (AVS), *Mar. Chem.*, 2005, **97**, 141–197.
- 21 M. T. Hurtgen, T. W. Lyons, E. D. Ingall and A. M. Cruise, Anomalous enrichments of iron monosulfide in euxinic marine sediments and the role of H₂S in iron sulfide transformations: examples from Effingham Inlet, Orca basin, and the Black Sea, *Am. J. Sci.*, 1999, **299**, 556–588.
- 22 J. W. Morse, Sulfides in sandy sediments: new insights on the reactions responsible for sedimentary pyrite formation, *Aquat. Geochem.*, 1999, **5**, 75–85.
- 23 E. D. Burton, R. T. Bush, S. G. Johnston, L. A. Sullivan and A. F. Keene, Sulfur biogeochemical cycling and novel Fe–S mineralization pathways in a tidally re-flooded wetland, *Geochim. Cosmochim. Acta*, 2011, **75**, 3434–3451.
- 24 B. Morgan, E. D. Burton and A. W. Rate, Iron monosulfide enrichment and the presence of organosulfur in eutrophic estuarine sediments, *Chem. Geol.*, 2012, **296–297**, 119–130.
- 25 Y. I. Sorokin and O. Y. Zakuskina, Acid-labile sulfides in shallow marine bottom sediments: a review of the impact on ecosystems in the Azov Sea, the NE Black Sea shelf and NW Adriatic lagoons, *Estuarine, Coastal Shelf Sci.*, 2012, **98**, 42–48.
- 26 S. L. Simpson, D. Ward, D. Strom and D. F. Jolley, Oxidation of acid-volatile sulfide in surface sediments increases the release and toxicity of copper to the benthic amphipod *Melita plumulosa*, *Chemosphere*, 2012, **88**, 953–961.
- 27 S. K. Rodrigues, D. M. S. Abessa and E. C. Machado, Geochemical and ecotoxicological assessment for estuarine surface sediments from Southern Brazil, *Mar. Environ. Res.*, 2013, **91**, 68–79.
- 28 R. Raiswell and R. A. Berner, Pyrite and organic matter in Phanerozoic normal marine shales, *Geochim. Cosmochim. Acta*, 1986, **50**, 1967–1976.
- 29 C. Boesen and D. Postma, Pyrite formation in anoxic environments of the Baltic, *Am. J. Sci.*, 1988, **288**, 575–603.
- 30 H. Yin, C. Fan, S. Ding, L. Zhang and J. Zhong, Geochemistry of Iron, Sulfur and Related Heavy Metals in Metal-Polluted Taihu Lake Sediments, *Pedosphere*, 2008, **18**, 564–573.
- 31 D. Liu, J. K. Keesing, P. He, Z. Wang, Y. Shi and Y. Wang, The world's largest macroalgal bloom in the Yellow Sea, China: formation and implications, *Estuarine, Coastal Shelf Sci.*, 2013, **129**, 2–10.
- 32 H. Liu and B. Yin, Annual cycle of carbon, nitrogen and phosphorus in the Bohai Sea: a model study, *Cont. Shelf Res.*, 2007, **27**, 1399–1407.
- 33 X. Kang, S. Liu and G. Zhang, Reduced inorganic sulfur in the sediments of the Yellow Sea and East China Sea, *Acta Oceanol. Sin.*, 2014, **33**, 100–108.
- 34 R. J. Newton, S. H. Bottrell, S. P. Dean, D. Hatfield and R. Raiswell, An evaluation of the use of the chromous chloride reduction method for isotopic analyses of pyrite in rocks and sediment, *Chem. Geol.*, 1995, **125**, 317–320.
- 35 Y. P. Hsieh and Y. N. Shieh, Analysis of reduced inorganic sulfur by diffusion methods: improved apparatus and evaluation for sulfur isotopic studies, *Chem. Geol.*, 1997, **137**, 255–261.
- 36 M. A. Huerta-Di'az and J. W. Morse, A quantitative method for determination of trace metal concentrations in sedimentary pyrite, *Mar. Chem.*, 1990, **29**, 119–144.
- 37 J. Zhou, Y. Wu, Q. Kang and J. Zhang, Spatial variations of carbon, nitrogen, phosphorous and sulfur in the salt marsh sediments of the Yangtze Estuary in China, *Estuarine, Coastal Shelf Sci.*, 2007, **71**, 47–59.
- 38 S. Qiao, X. Shi, A. Zhu, Y. Liu, N. Bi, X. Fang and G. Yang, Distribution and transport of suspended sediments off the Yellow River (Huanghe) mouth and the nearby Bohai Sea, *Estuarine, Coastal Shelf Sci.*, 2010, **86**, 337–344.
- 39 K. Xu, J. D. Milliman, A. Li, J. Liu, S. Kao and S. Wan, Yangtze- and Taiwan-derived sediments on the inner shelf of East China Sea, *Cont. Shelf Res.*, 2009, **29**, 2240–2256.
- 40 Y. Lv, W. Zhang, Y. Gao, S. Ning and B. Yang, Preliminary study on responses of marine nematode community to crude oil contamination in intertidal zone of Bathing Beach, Dalian, *Mar. Pollut. Bull.*, 2011, **62**, 2700–2706.
- 41 M. Zhu, J. Liu, G. Yang, T. Li and R. Yang, Reactive iron and its buffering capacity towards dissolved sulfide in sediments of Jiaozhou Bay, China, *Mar. Environ. Res.*, 2012, **80**, 46–55.
- 42 S. Lin, K. Huang and S. Chen, Organic carbon deposition and its control on iron sulfide formation of the southern East China Sea continental shelf sediments, *Cont. Shelf Res.*, 2000, **20**, 619–635.
- 43 M. Zhu, X. Shi, G. Yang and X. Hao, Formation and burial of pyrite and organic sulfur in mud sediments of the East China Sea inner shelf: constraints from solid-phase sulfur speciation and stable sulfur isotope, *Cont. Shelf Res.*, 2013, **54**, 24–36.

- 44 Y. Sheng, Q. Sun, S. H. Bottrell, R. J. G. Mortimer and W. Shi, Anthropogenic impacts on reduced inorganic sulfur and heavy metals in coastal surface sediments, north Yellow Sea, *Environ. Earth Sci.*, 2013, **68**, 1367–1374.
- 45 S. Lin, K. Huang and S. Chen, Sulfate reduction and iron sulfide mineral formation in the southern East China Sea continental slope sediment, *Deep Sea Res., Part I*, 2002, **49**, 1837–1852.
- 46 P. A. Meyers, Preservation of elemental and isotopic source identification of sedimentary organic matter, *Chem. Geol.*, 1994, **114**, 289–302.
- 47 R. A. Berner, Burial of organic carbon and pyrite sulphur in the modern ocean: its geochemical and environmental significance, *Am. J. Sci.*, 1982, **282**, 451–473.