Acid-volatile sulfide and simultaneously extracted metals in surface sediments of the southwestern coastal Laizhou Bay, Bohai Sea: Concentrations, spatial distributions and the indication of heavy metal pollution status

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A B S T R A C T

Surface sediments were collected from the coastal waters of southwestern Laizhou Bay and the rivers it connects with during summer and autumn 2012. The acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) were measured to assess the sediment quality. The results showed that not all sediments with [SEM]–[AVS] > 0 were capable of causing toxicity because the organic carbon is also an important metal-binding phase in sediments. Suppose the sediments had not been disturbed and the criteria of US Environmental Protection Agency had been followed, heavy metals in this area had no adverse biological effects in both seasons except for few riverine samples. The major ingredient of SEM was Zn, whereas the contribution of Cd – the most toxic metal studied – to SEM was <1%. The distributions of AVS and SEM in riverine sediments were more easily affected by anthropogenic activity compared with those in marine sediments.

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1. Introduction

Heavy metals in ecosystems have received extensive attention because they are toxic, non-biodegradable in environment and easy to accumulate in organisms. Heavy metal concentrations in aquatic ecosystems have increased considerably due to the inputs of industrial waste, sewage runoff, and agriculture discharges (Prica et al., 2008; Yang et al., 2012). Sediments are the main sink for heavy metals in aquatic ecosystems; however, when environmental conditions such as pH or sediment redox potential change, sediments may transform to a source of heavy metals (van Den Berg et al., 1999; Wilson and Chang, 2000; Prica et al., 2008).

Acid-volatile sulfide (AVS) is one of the major chemical components that control the speciation and the environmental risks of heavy metals in aquatic sediments. The sulfide ions can combine with most divalent metal ions to form insoluble metal sulfides in anoxic sediments (Ankley, 1996; Huerta-Diaz et al., 1998; USEPA, 2004). If the sulfide ions are in sufficient quantities, the concentrations of heavy metals will be very low in the pore water. Therefore,

sulfide in sediments has received much attention in the past decades. AVS is operationally defined as reactive solid-phase sulfide fraction that can be extracted with cold hydrochloric acid (1 M or 6 M HCl). Metals extracted during the same AVS analyzing process in the sediments are called simultaneously extracted metals (SEM), mainly including Cd, Cu, Ni, Pb and Zn (USEPA, 2004). The relationship between the molar concentration of AVS ([AVS], μmol g^{-1}) and SEM ([SEM], μmol g^{-1}) has been proposed as a possible indicator of metal toxicity in anaerobic sediments (Long et al., 1998; Liu et al., 2010). When the ratio [SEM]/[AVS] > 1 or [SEM]–[AVS] > 0, acute toxicity may be generated by heavy metals, whereas the generation of acute toxicity is less possible when [SEM]/[AVS] < 1 or [SEM]–[AVS] < 0 (Di Toro et al., 1990; Ankley et al., 1996; USEPA, 2004; Di Toro et al., 2005).

However, this approach has its limitations. When the ratio [SEM]/[AVS] > 1, or [SEM]–[AVS] > 0, heavy metal toxicity can be easily overestimated, since other constituents in sediment such as organic matter can also combine with free metal ions, which can reduce their bioavailability and ultimately reduce their toxicity (Burton et al., 2005). It is reported that theoretical expectations have high consistency with experimental results by normalizing the difference between [SEM] and [AVS] to the concentrations of total organic carbon (TOC) in sediments (f_{OC}), i.e. ([SEM]–[AVS])/f_{OC} (Burton et al., 2005; Di Toro et al., 2005; USEPA, 2005). There

are also other regulations related to sediment quality, e.g. effects range-low (ERL) and effects range-mean (ERM) concentrations which are empirical approaches based on total metal concentrations (Long et al., 1995). The results cannot provide sufficient information and sometimes it may be misleading to use only total metal concentrations in sediments to assess the toxicity or the bioaccumulation ability of metals, because bioavailability of metals in sediments not only depends on their total concentrations but also on their chemical forms (Sahuquillo et al., 2003; Gao et al., 2008, 2010; Gao and Chen, 2012; Gao and Li, 2012). Furthermore, any metal that is insoluble in the 1 M or 6 M HCl used in the AVS extraction is unlikely to be bioavailable, and therefore it is non-toxic (Allen et al., 1993; Di Toro et al., 2005). Hence, the AVS approach is suitable for heavy metal toxicity assessment in ecosystems. So far, there are a number of reports on sediment quality assessment by [SEM]/[AVS] or [SEM]–[AVS] method (e.g. Hinkey and Zaidi, 2007; Prica et al., 2008; Liu et al., 2010; Simpson et al., 2012; Gao et al., 2013), but there are only a few studies using ([SEM]–[AVS])/f_{OC} (e.g. Burton et al., 2005; Di Toro et al., 2005; De Jonge et al., 2012a; De Jonge et al., 2012b).

Laizhou Bay is one of the three major bays in Bohai Sea, making up ∼10% of its total areas, with a coastline length of ∼320 km and a surface area of ∼7000 km^2. There are several rivers running into Laizhou Bay from its southwestern coast, most of which are small and seasonal. Laizhou Bay is an important spawning and breeding ground for many marine organisms. Due to abundant seawater resources and underground brine resources, a chemical industrial base called Weifang Binhai Economic Development Zone is located along its southwestern coast. Over 400 chemical enterprises are located nearby and more than 150 kinds of chemical products are manufactured in this area. Now it is one of the biggest manufacturing bases for chlor-alkali products in the world, which produces soda ash, calcium chloride and other chemical products such as sodium silicate, bromine, bromides, and baking soda. Thus, derived from many point sources such as industrial wastewaters and agricultural discharges, non-purified or insufficiently purified wastewaters carrying heavy metals are discharged into the rivers of this area. In 2008, there were 33 tons of heavy metals carried into Laizhou Bay by Xiaoqinghe River (SOA, 2009), and the number soared to 384 tons in 2011 (SOA, 2012). The fishery development and ecological environment of Laizhou Bay have been severely threatened. Therefore it is important to monitor and understand heavy metal bioavailability and toxicity in this area.

This study examined the concentrations of AVS and SEM in the sediments of the southwestern area of Laizhou Bay and the major surrounding rivers with a purpose of trying to elucidate their distribution characteristics and assess the potential toxicity of heavy metals. The southwestern coast of Laizhou Bay was chosen because it is regarded as the most serious threatened area from anthropogenic activities in and surrounding Laizhou Bay (Xia et al., 2009; Liu et al., 2011).

2. Materials and methods

2.1. Sample collection

The research was carried out in 2012 during two periods: early summer (May–June, hereafter referred to as summer for short), which is before the peak period of the rainy season, and middle autumn (September–October, hereafter referred to as autumn for short), which is after the peak period of the rainy season. The sampling stations were arranged along the major rivers of this area extending from the land to the sea and formed five transects, covering about 15–20 km from the high tide mark to the land and about 10 km from the high tide mark to the sea (Fig. 1). The surface sediments of top 5 cm from the rivers were collected using a plastic spatula, and the surface sediments from the marine region were collected with a stainless steel grab sampler. The samples were placed in polyethylene bottles with no head space or with a nitrogen atmosphere immediately after sampling, and stored in an incubator with ice bags, and then frozen at −20 °C within 12 h until further analysis.

A total of 53 sediment samples were collected in summer and 51 were collected in autumn (Fig. 1) (samples from stations MH3 and YHH2 were collected only in summer), among which 18 marine samples were from the same stations in both sampling periods. The coordinates of corresponding sampling stations during the two periods were not exactly the same, especially in rivers with torrential water flow in autumn. However, all errors were within five meters, so the comparability was considered not to be affected.

2.2. Analytical methods

Redox potential (Eh) and pH of sediments were determined in situ immediately after sampling with redox and pH electrodes, respectively. The moisture content (MC) was determined by measuring the weight loss after drying at 105 °C for 24 h. The percentages of water were used to convert the substance contents of the
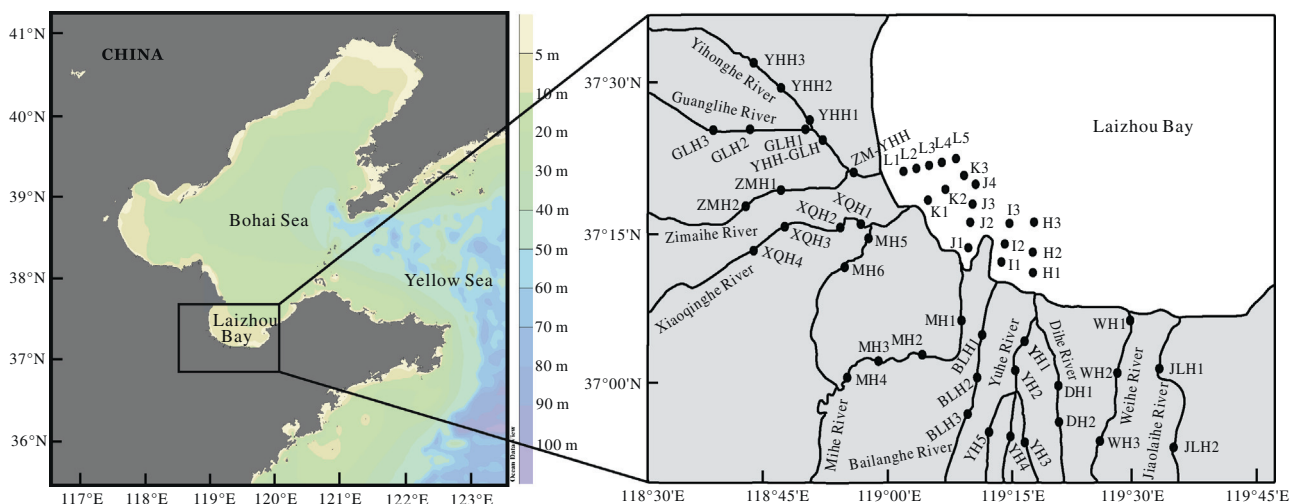

Fig. 1. Location of sampling stations in the coastal zone of SW Laizhou Bay.

sediments from a wet weight basis to a dry weight basis. The TOC in sediments was obtained by determining the total carbon with an Elementar vario MACRO cube CHNS analyzer after removing the inorganic carbon with 1 M HCl. The particle size distribution was analyzed with a particle size analyzer (Mastersizer 2000, Malvern, Britain) capable of analyzing particle sizes between 0.02 and 2000 μm. We determined the percentages of the following three groups of grain sizes: <4 μm (clay), 4–63 μm (silt), and >63 μm (sand) (Gao and Chen, 2012).

There are two methods most widely applied for AVS and SEM extraction called the purge-and-trap method (Morse et al., 1987) and the diffusion method (van Griethuysen et al., 2002), respectively. Compared with the diffusion method, it is very laborious to use the purge-and-trap method to handle a large number of samples simultaneously: a lot of glassware, gas and space are required (Brouwer and Murphy, 1994). Researchers found that the diffusion method yielded higher AVS concentrations than the purge-and-trap method. They attributed this to the higher efficiency of the diffusion method than the purge-and-trap method and to the prolonged anoxic storage of the samples (Brouwer and Murphy, 1994; Leonard et al., 1996; van Griethuysen et al., 2002). Considering the two points above, a diffusion method modified by van Griethuysen et al. (2002) was used for extracting AVS from 3 g wet sediment of each sample in this study. 5 mL 6 M HCl were chosen for AVS and SEM extraction, since it is reported that CuS phases of AVS could not be fully extracted with 1 M HCl, and it may possibly result in an underestimation of AVS concentrations in sediments (Simpson et al., 1998; De Jonge et al., 2012a). The volatile hydrogen sulfide (H_2S) was collected in 10 mL sulfide antioxidant buffer (SAOB) in which the amount of free sulfur ions was measured with an ion specific electrode (van Griethuysen et al., 2002; De Jonge et al., 2012a). The SAOB solution contained 2 M NaOH, 0.2 M ascorbic acid and 0.2 M disodium EDTA (van Griethuysen et al., 2002). The remaining sediment extracts were centrifuged for 20 min at 3000 g, and then the supernatants were collected for SEM (Cu, Pb, Zn, Ni and Cd) determination.

Apparatus blanks, reagent blanks, calibration curves, and standard recoveries were employed in the analysis. Calibration of the AVS method was done using a standard sodium sulfide to develop a calibration curve (Allen et al., 1993; Hinkey and Zaidi, 2007). Calibration series were accepted when the R^2 of the relationship between the logarithm of the sulfide concentration and the values of electric potential was above 0.999. Quality control of AVS extraction was assured by calibrating the procedure against known amounts of $Na_2S \cdot 9H_2O$ (Durán et al., 2012), and recoveries were within 85–94%. Replicates for 20% of samples were made as a part of the quality assurance and the relative standard deviations were within 10%.

Concentrations of SEM in sediments were measured by an inductively coupled plasma–optical emission spectrometer (ICP–OES; Optima model 7000DV, Perkin Elmer, USA). Standard curves of the metals were made using certified multi-element standard solution. Calibration series were accepted when the R^2 of the relationship between the concentrations of standard metals and signal values of ICP–OES was above 0.9999. Replicates for 20% of samples were made as a part of the quality assurance and the relative standard deviations were within 10% for all the metals studied. Detection limits for ICP–OES measurements (under the optimum wavelength), which were calculated as $3\times$ standard deviation of 11 measurements of Milli-Q deionized water, were 0.11 μmol L^{-1} for Cu, 0.12 μmol L^{-1} for Ni, 0.15 μmol L^{-1} for Zn, 0.005 μmol L^{-1} for Pb and 0.009 μmol L^{-1} for Cd. All results were expressed on the base of the dry weight of the sediment. All reagents were analytical or guaranteed grade and all materials (bottles, tubes, etc.) were cleaned by acid before using.

2.3. Assessment of heavy metal biotoxicity

Two methods issued by the United States Environmental Protection Agency (USEPA) were used for assessment of heavy metal biotoxicity: [SEM]–[AVS] (USEPA, 2004) and ([SEM]–[AVS])/f_{OC} (USEPA, 2005).

2.4. Statistical analysis

All data were tested for normality with the Shapiro-Wilk test before analyzing. The Spearman correlation-coefficient was used to compare the relationship between [AVS], [SEM] and other parameters in pairs. A paired samples t-test ($p < 0.05$) was performed in order to determine whether seasonal changes had significant influence on [AVS] and [SEM], respectively. The above-mentioned analyses were performed through the SPSS statistical package version 19.0 (SPSS Inc.).

3. Results and discussion

3.1. General characteristics of sediments

In summer, the mineral fraction of particles less than 4 μm (clay) varied from nearly 0% to 22.7% with an average of 9.5%. The fraction of 4–63 μm (silt) particles varied from 4.3% to 75.2% with an average of 45.6%. Sand content (>63 μm) varied from 11.0% to 94.6% with an average of 44.9%. In autumn, the ranges of clay, silt and sand were 2.0–20.1%, 8.5–81.0% and 3.2–90.0%, respectively, with their respective average of 9.0%, 47.2% and 43.8%. Therefore, the sediments in this area were mainly composed of slit and sand (Fig. 2). Marine sediments are usually finer than riverine sediments but it was not the case here. In this research, most riverine sediments were finer than marine sediments, and the components of most marine sediments became finer in the direction from the coast to the sea (Fig. 2). Other researchers also found that the sediments of the southwestern coastal Laizhou Bay were mainly composed of coarse-grained fractions (Qian et al., 2010; Hu et al., 2011). These phenomena were probably the results of the joint effects of the tidal and residual currents and the anti-clockwise circulation of Laizhou Bay which caused the re-suspension of the fine surface sediments near the estuaries and then drove them to the middle of the bay (Jiang et al., 2000; Qian et al., 2010). This was supported by the discovery of a fine-grained sediment patch that consisted of silt and clayey silt in the middle of Laizhou Bay, and this sediment patch was composed of suspended sediments derived from rivers especially the Yellow River (Qian et al., 2010).

MC varied from 16.6% to 47.1% with an average of 28.5% in summer; the corresponding data were 18.5–82.7% and 32.2% in autumn, respectively (Fig. 3). The TOC contents in sediments varied from 0.03% to 2.1% with an average of 0.3% in summer; the corresponding data were 0.2–5.5% and 0.7% in autumn, respectively (Fig. 4). The increased TOC contents from summer to autumn revealed the increased bioactivity and bioaccumulation in the aqueous system.

Eh and pH are shown in Figs. 5 and 6, respectively. Eh varied from −306 mV to 142 mV with an average of −113 mV in summer, and the corresponding data were −417 mV to 196 mV and −101 mV in autumn, respectively. Eh values in each season varied widely among stations and slightly increased from summer to autumn in general. The values of pH varied from 5.54 to 7.92 with an average of 7.32 in summer, and the corresponding data were
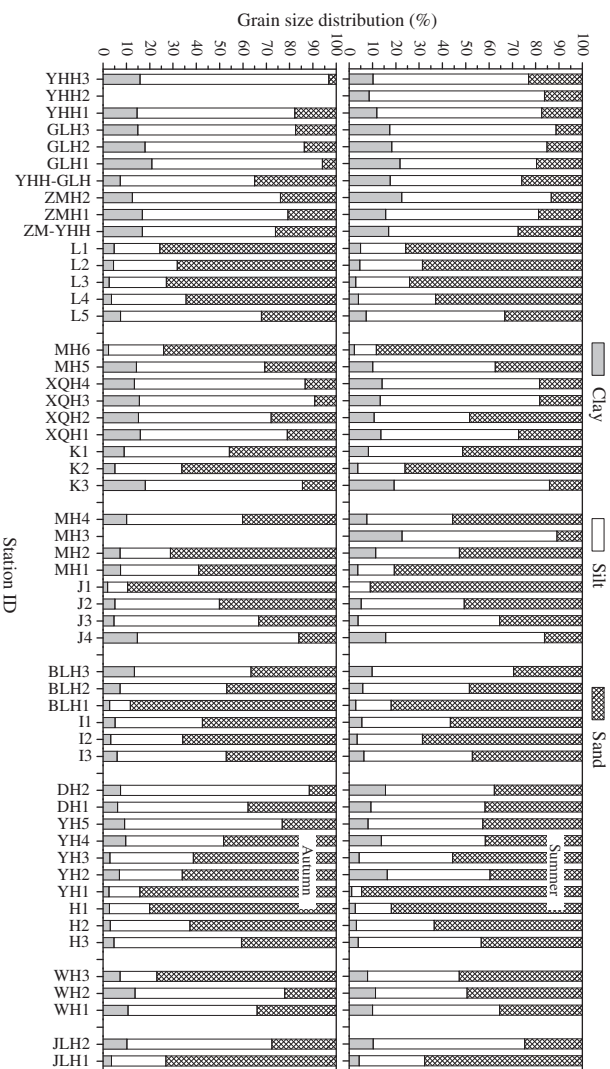
Fig. 2. Spatial distribution of clay–silt–sand composition of the surface sediments from the coastal zone of SW Laizhou Bay.
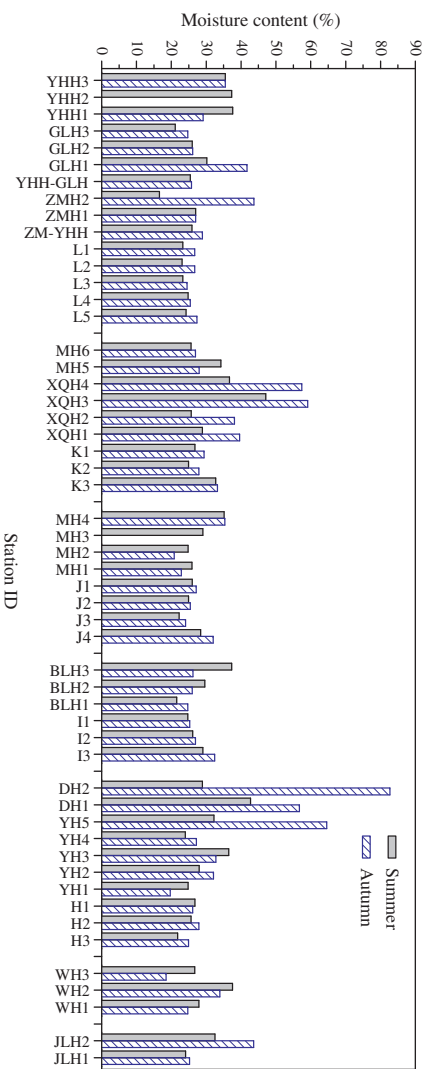
Fig. 3. Spatial distribution of moisture contents in surface sediments of the SW coastal Laizhou Bay.
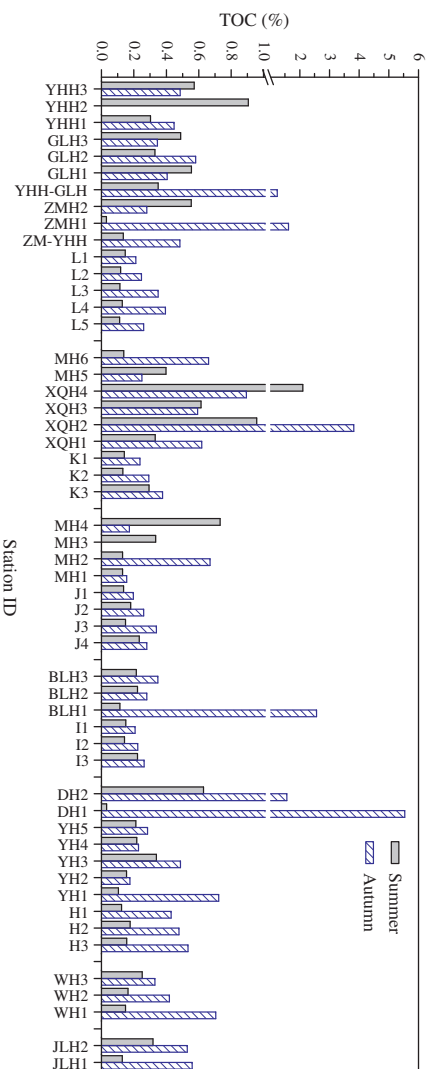
Fig. 4. Spatial distribution of TOC concentrations in surface sediments of the SW coastal Laizhou Bay.
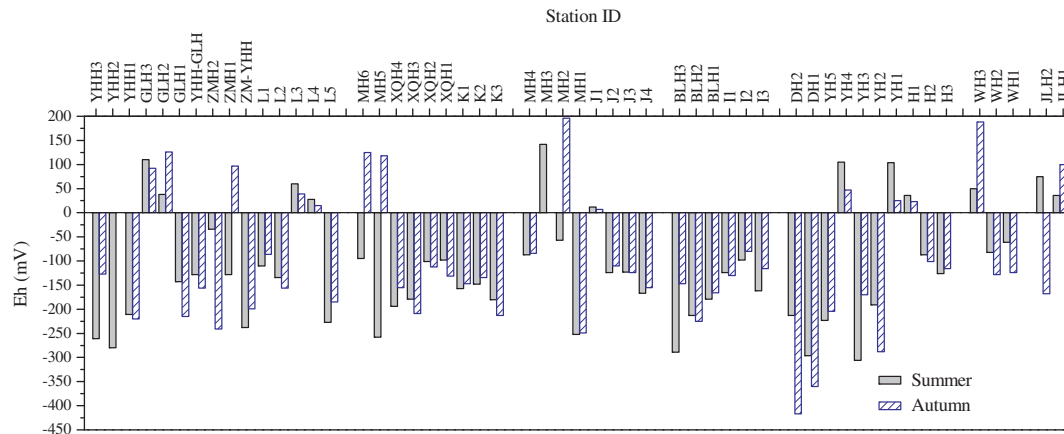
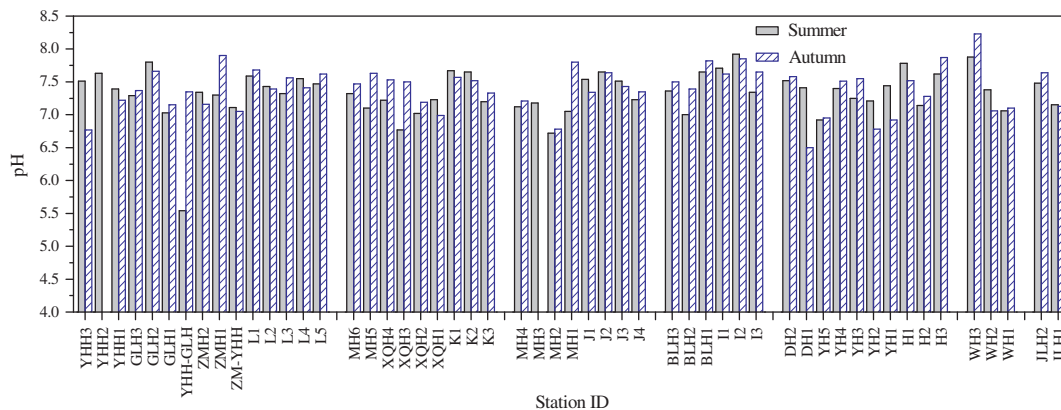**Fig. 5.** Spatial distribution of redox potential in surface sediments of the SW coastal Laizhou Bay.

Fig. 6. Spatial distribution of pH in surface sediments of the SW coastal Laizhou Bay.

6.50–8.23 and 7.39 in autumn, respectively. The range of pH value in marine sediments was narrower than that in riverine sediments.

3.2. Distribution characteristics of AVS

The spatial distribution of AVS is shown in Fig. 7 and related information is summarized in Table 1. Overall, AVS concentrations in riverine sediments were much higher than those in marine sediments; and the differences of AVS concentrations between sediments in rivers were greater than those in the marine area. The mean AVS concentrations in riverine sediments were 26.96 μmol g^{-1} and 21.83 μmol g^{-1} in summer and autumn, respectively; and the relative standard deviations (RSD) were up to 156.8 and 168.8, respectively. In the marine area, the mean AVS concentrations were 4.98 μmol g^{-1} and 3.61 μmol g^{-1} in summer and autumn, respectively; RSD were 95.0 and 65.7, respectively. The mean AVS concentration in the marine area was close to that of the surface sediments in the offshore area of Laizhou Bay in the previous study carried out in October 2011 (Gao et al., 2013). van Griethuysen et al. (2006) pointed out that sulfate was one of the prerequisites for the formation of AVS and could be a limiting factor in freshwater environments. The previous study in the off-shore area of Laizhou Bay (Gao et al., 2013) showed that the AVS concentration increased in the direction from the river outlet or coast to the sea, which was consistent with the report of van Griethuysen et al. (2006). However, the situation in this study was not the same. Much higher concentrations of AVS were observed in riverine sediments than in marine sediments. The higher AVS concentrations in riverine sediments might be

attributed to the relatively higher content of organic matter and finer particles in riverine sediments than in marine sediments, and to the rich terrigenous input and hypoxia status in rivers. Machado et al. (2008) pointed out that sediments with high TOC content and small particle size could result in anoxic conditions due to oxidation of TOC and low oxygen renewal, and then provide an ideal condition for sulfate reducing bacteria (SRB) which could reduce sulfate to sulfide. Spearman correlation analysis showed that [AVS] had significant positive correlations with clay and silt contents, and had significant negative correlation with sand content ($p < 0.05$) in both seasons (Table 2). There was also a significant positive correlation between [AVS] and TOC content ($0.001 < p < 0.01$) in summer (Table 2), which was consistent with the previous study in the off-shore area of Laizhou Bay (Gao et al., 2013); however, in autumn, there was no significant correlation between [AVS] and TOC content. TOC contents in sediments in summer were much lower than in autumn at almost all the stations; therefore, TOC might be a major limitation for the formation of AVS in summer, but not in autumn. Some other studies also showed that [AVS] and TOC content were not necessarily significantly correlated (Fang et al., 2005; Liu et al., 2007). The forming condition of AVS in riverine and in-shore sediments was much more complex than that in the off-shore area owing to the intensive interaction of a variety of natural and anthropogenic factors.

In Dihe River, Xiaoqinghe River and Yihonghe River, which are the zones with more frequent human activities, higher AVS concentrations were observed (Fig. 7); this might be attributed to the waste discharge from domestic sewage and industrial effluents. The relatively higher AVS concentrations were observed at stations
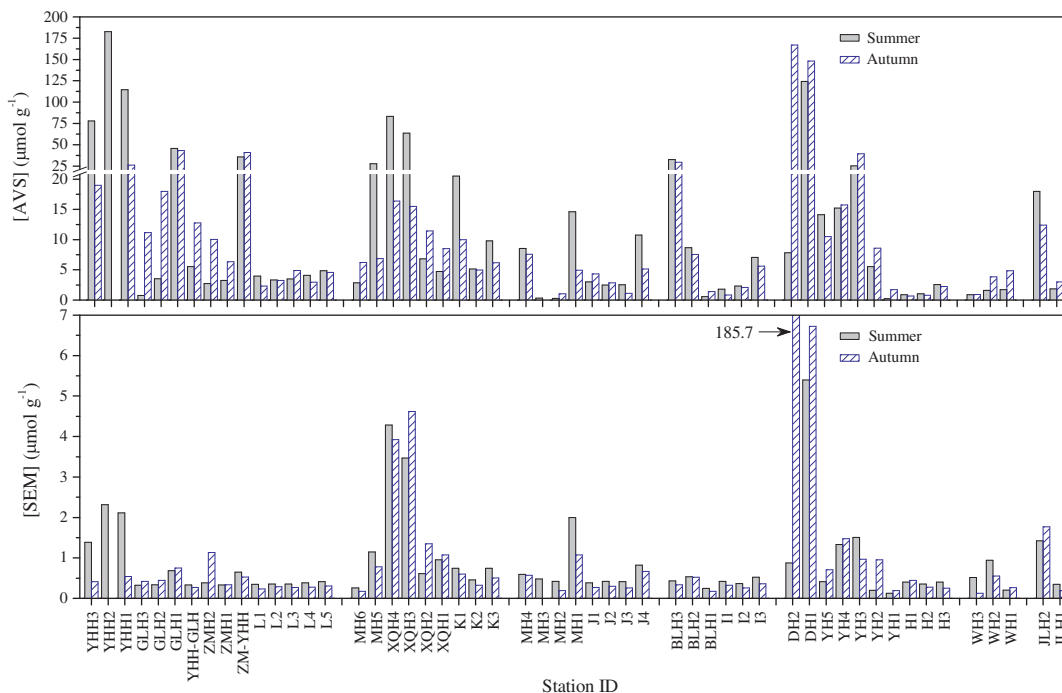
Fig. 7. Spatial distribution of AVS and SEM concentrations in surface sediments of the SW coastal Laizhou Bay.

Table 1
The summary of AVS and SEM contents in surface sediments of the SW coastal Laizhou Bay. The unit μmol g^{-1} is based on dry sediment weight for all parameters.

Sampling period	Location		[AVS]	[SEM]	[SEM]$_{Cd}$	[SEM]$_{Ni}$	[SEM]$_{Cu}$	[SEM]$_{Pb}$	[SEM]$_{Zn}$
Summer	River	Min. (μmol g^{-1})	0.25	0.13	<0.0001	0.030	0.002	0.010	0.064
		Max. (μmol g^{-1})	182.73	5.40	0.0027	0.196	1.206	0.149	4.94
		Mean (μmol g^{-1})	26.96	1.07	0.0007	0.106	0.218	0.041	0.702
		SD	42.27	1.20	0.0006	0.050	0.256	0.032	1.04
		RSD (%)	156.8	112.4	91.3	46.7	117.5	79.0	148.1
		Min. (%)			0.01	2.33	1.21	0.86	27.04
		Max. (%)			0.22	33.03	56.84	13.46	91.48
		Mean (%)			0.08	17.13	23.16	5.69	53.94
	Sea	Min. (μmol g^{-1})	0.86	0.35	0.0002	0.103	0.051	0.008	0.147
		Max. (μmol g^{-1})	20.51	0.82	0.0014	0.190	0.243	0.066	0.396
		Mean (μmol g^{-1})	4.98	0.46	0.0008	0.122	0.104	0.029	0.206
		SD	4.73	0.15	0.0004	0.025	0.057	0.015	0.066
		RSD (%)	95.0	32.3	49.0	20.5	54.9	51.9	32.0
		Min. (%)			0.05	19.12	13.22	2.08	37.03
		Max. (%)			0.33	31.32	31.30	12.26	57.64
		Mean (%)			0.18	27.28	21.46	6.12	44.96
Autumn	River	Min. (μmol g^{-1})	0.93	0.12	<0.0001	0.035	0.014	0.008	0.050
		Max. (μmol g^{-1})	167.05	185.68	0.0069	0.591	0.778	0.125	185.0
		Mean (μmol g^{-1})	21.83	6.64	0.0009	0.099	0.158	0.033	6.35
		SD	36.85	32.17	0.0016	0.096	0.172	0.024	32.1
		RSD (%)	168.8	484.3	167.9	96.6	108.8	71.8	505.4
		Min. (%)			0.003	0.32	0.01	0.04	33.15
		Max. (%)			0.64	32.67	49.10	9.35	99.64
		Mean (%)			0.08	15.49	21.28	5.01	58.14
	Sea	Min. (μmol g^{-1})	0.70	0.23	0.0001	0.047	0.029	0.005	0.077
		Max. (μmol g^{-1})	10.00	0.67	0.0011	0.174	0.186	0.053	0.342
		Mean (μmol g^{-1})	3.61	0.35	0.0004	0.087	0.072	0.023	0.163
		SD	2.37	0.13	0.0003	0.029	0.040	0.013	0.076
		RSD (%)	65.7	36.5	74.5	33.8	56.0	58.5	46.8
		Min. (%)			0.04	14.02	6.58	1.95	30.01
		Max. (%)			0.33	41.39	30.74	14.24	77.28
		Mean (%)			0.13	26.12	20.48	6.63	46.64

[SEM] = [SEM]$_{Cd}$ + [SEM]$_{Ni}$ + [SEM]$_{Cu}$ + [SEM]$_{Pb}$ + [SEM]$_{Zn}$.

YHH1 (summer), YHH2 (summer), DH1 (summer and autumn) and DH2 (autumn) (Fig. 7), and the mean Eh values at these stations were lower than −200 mV, especially in DH2 whose Eh value was even lower than −400 mV (autumn) (Fig. 5). Sediments from these stations were in severe hypoxia status. The significant negative correlation between [AVS] and Eh ($p < 0.001$) in both summer and autumn proved the relationship between AVS concentration and the redox status in sediments of the studied area (Table 2).

Table 2
Spearman correlation matrix for the components and parameters of the surface sediments from the SW coastal Laizhou Bay.

Sampling period		[AVS]	[SEM]	[SEM]$_{Cd}$	[SEM]$_{Cu}$	[SEM]$_{Ni}$	[SEM]$_{Pb}$	[SEM]$_{Zn}$	%TOC	%MC	%Clay	%Silt	%Sand	pH	Eh
Summer	[AVS]	1.000	0.717[a]	0.254[a]	0.548[a]	0.339[c]	0.583[a]	0.686[a]	0.404[b]	0.626[a]	0.319[c]	0.453[a]	−0.392[b]	−0.225	−0.698[a]
	[SEM]		1.000	0.558[a]	0.773[a]	0.603[a]	0.669[a]	0.930[a]	0.469[a]	0.660[a]	0.281[c]	0.394[b]	−0.336[a]	−0.118	−0.470[a]
	[SEM]$_{Cd}$			1.000	0.492[a]	0.468[a]	0.322[c]	0.587[a]	0.293[c]	0.301[c]	0.010	0.267	−0.197	0.129	−0.110
	[SEM]$_{Cu}$				1.000	0.688[a]	0.755[a]	0.610[a]	0.550[a]	0.506[a]	0.462[a]	0.587[a]	−0.554[a]	−0.201	−0.413[b]
	[SEM]$_{Ni}$					1.000	0.632[a]	0.509[a]	0.246	0.193	0.259	−0.227	0.007	−0.236
	[SEM]$_{Pb}$						1.000	0.584[a]	0.545[a]	0.470[a]	0.577[a]	0.650[a]	−0.640[a]	−0.169	−0.269
	[SEM]$_{Zn}$							1.000	0.424[b]	0.621[a]	0.186	0.254	−0.200	−0.086	−0.408[b]
Autumn	[AVS]	1.000	0.696[a]	0.314[c]	0.547[a]	0.409[b]	0.620[a]	0.609[a]	0.199	0.628[a]	0.622[a]	0.622[a]	−0.639[a]	−0.277	−0.439[a]
	[SEM]		1.000	0.655[a]	0.658[a]	0.507[a]	0.647[a]	0.954[a]	−0.055	0.754[a]	0.577[a]	0.578[a]	−0.600[a]	−0.204	−0.536[a]
	[SEM]$_{Cd}$			1.000	0.555[a]	0.463[a]	0.445[a]	0.619[a]	−0.085	0.570[a]	0.288[c]	0.493[a]	−0.463[a]	−0.126	−0.583[a]
	[SEM]$_{Cu}$				1.000	0.684[a]	0.754[a]	0.526[a]	−0.037	0.525[a]	0.797[a]	0.787[a]	−0.820[a]	−0.117	−0.415[b]
	[SEM]$_{Ni}$					1.000	0.749[a]	0.375[b]	−0.088	0.580[a]	0.598[a]	0.686[a]	−0.682[a]	−0.193	−0.351[c]
	[SEM]$_{Pb}$						1.000	0.520[a]	0.153	0.630[a]	0.745[a]	0.811[a]	−0.824[a]	−0.234	−0.328[c]
	[SEM]$_{Zn}$							1.000	−0.031	0.736[a]	0.464[a]	0.458[a]	−0.481[a]	−0.240	−0.495[a]

[a] $p < 0.001$.
[b] $0.001 < p < 0.01$.
[c] $0.01 < p < 0.05$.

AVS concentrations in sediments of most riverine stations increased from summer to autumn, which might be the results of the sharp metabolism of SRB with abundant nutritional materials in summer. The increased TOC concentrations from summer to autumn at most riverine stations can be good evidence for this phenomenon (Fig. 4). However, AVS concentrations in sediments of about one third of the stations in rivers decreased from summer to autumn (Fig. 7). The concentration of AVS in the sediment is determined by both the rate at which AVS is produced and the rate at which it is lost by oxidation or diffusion. It has been reported that sediments colonized by plants displayed more strongly oxidizing conditions than unvegetated sediments, and living plants can significantly decrease AVS concentrations in sediments (Jacob and Otte, 2004; Almeida et al., 2005). In middle autumn, plants were more flourishing than in early summer; this might be one of the reasons for the [AVS] decrease in sediments of some riverine stations. Moreover, AVS concentrations among stations were very different even during the same sampling period. Therefore, it is impossible to find out all the factors causing these phenomena since the dissolved sulfate concentration, organic matter availability, SRB community size, temperature, and even plants are all important variables for the fate and dynamics of AVS (Machado et al., 2008; Yang et al., 2012).

In the marine area, only in sediments of stations J1, J2 and L3 AVS concentrations were higher in autumn than in summer, and AVS concentrations at all the other 15 stations decreased from summer to autumn (Fig. 7). It has been reported that O$_2$ saturation and SRB activities played important roles in AVS formation and degradation (van Griethuysen et al., 2006). Wijsman et al. (2001) pointed out that AVS could exist near the sediment–water interface during anoxia, while it was easily oxidized under oxic conditions. In autumn the wind was stronger on the sea than in summer, and waves were much greater, which might cause the increase of the dissolved oxygen content, and then oxidize AVS. Raised Eh was observed in some marine sediments from autumn to summer (Fig. 5). Most SRB are mesophilic bacteria or thermophilic bacteria with optimum temperature ranges of 25–40 °C (Morita, 1975), and are sensitive to temperature changes (Castro et al., 2000). In summer, the mean temperature in surface seawater was above 25 °C, however, in autumn the mean temperature was only 18 °C. The decreased temperature might result in the decreased activities of SRB. Nevertheless, no information is available for this specific case study up to now. In order to ascertain whether or not SRB plays an important role in the AVS concentration changes in this area, further research is needed.

Table 3
Statistical analysis of the dependence of [AVS] and [SEM] between the sampling periods.

Location	Content	p-Value	Significant difference at level 0.05
River	[AVS]	0.853	No
	[SEM]	0.918	No
	[SEM]$_{Cd}$	0.348	No
	[SEM]$_{Ni}$	0.784	No
	[SEM]$_{Cu}$	0.293	No
	[SEM]$_{Pb}$	0.353	No
	[SEM]$_{Zn}$	0.527	No
Sea	[AVS]	0.055	No
	[SEM]	8.26×10^{-8}	Yes
	[SEM]$_{Cd}$	1.12×10^{-5}	Yes
	[SEM]$_{Ni}$	2.06×10^{-7}	Yes
	[SEM]$_{Cu}$	5.29×10^{-5}	Yes
	[SEM]$_{Pb}$	4.45×10^{-6}	Yes
	[SEM]$_{Zn}$	0.002	Yes

The paired samples t-test showed that no significant correlation existed between AVS concentrations of the two sampling phases in both riverine and marine sediments ($p > 0.05$; Table 3). Thus, AVS concentrations did not simply depend on seasonal changes, which further indicated that formation and persistence of AVS in the sediments of this area were complex.

3.3. Distribution characteristics of SEM

The spatial distribution of SEM is shown in Fig. 7 and related information is summarized in Table 1. Generally, the mean [SEM] was found to decrease from summer to autumn in marine sediments, but seemed to increase in riverine sediments. If the unusually high [SEM]$_{Zn}$ (185.0 µmol g^{-1}) in DH2 in autumn was neglected (Figs. 7 and 8), the mean [SEM] in riverine sediments in autumn was only 1.06 µmol g^{-1}, which was almost the same as that in summer (1.07 µmol g^{-1}) (Table 1). Mean [SEM] was higher in riverine sediments than in marine sediments, and this distribution characteristic was in accordance with [AVS], indicating the impact of human activities and surface runoff on the heavy metal contents. Variation ranges of SEM contents among stations and between seasons were much narrower than those of AVS, which showed that SEM was more evenly distributed compared with AVS. Relatively higher [SEM] was observed in Dihe River, Xiaoqinghe River and Yihonghe River, which was also in accordance with
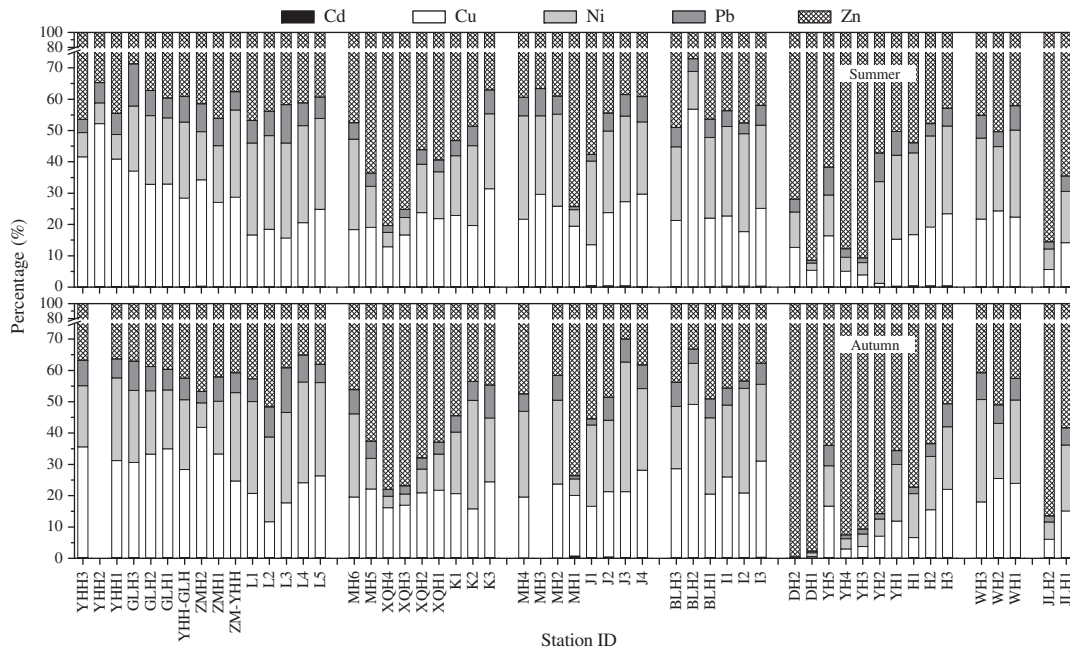
Fig. 8. Spatial distribution of relative concentrations of SEM components in surface sediments of the SW coastal Laizhou Bay.

the distribution characteristics of [AVS] (Fig. 7). The significant positive correlations between [SEM] and [AVS] ($p < 0.001$) and between components of SEM and [AVS] ($p < 0.05$) in both summer and autumn confirmed that AVS was an important carrier for SEM (Table 2).

Extremely high [SEM] (185.68 µmol g^{-1}) and [SEM]$_{Zn}$ (185.0) were found in DH2 in autumn, and the corresponding values were only 0.87 µmol g^{-1} and 0.63 µmol g^{-1} in summer, respectively (Figs. 7 and 8). It was impossible that such a big change was merely caused by natural factors, and it could be probably attributed to the wastewater discharge from factories. Several chemical plants are located near DH2, and an outfall was found in the upstream about dozens of meters away from DH2, but it could not be determined to which chemical plant it belongs. Studies showed that anthropogenic metals were more loosely bound to sediments and might be released back to the aqueous phase with the change of physical and chemical characteristics (Eh, pH, salinity and TOC) (Soares et al., 1999). Therefore, pollution risk of anthropogenic heavy metals is much higher.

Compared with other metals, Zn was the major part of SEM in all samples and accounted for approximately 27.0–99.6% of the total amount of SEM, whereas the contribution of Cd – the most toxic metal studied – to SEM was less than 1% (Fig. 8; Table 1). The average concentrations of SEM components were in the following order: [SEM]$_{Cd}$ ≪ [SEM]$_{Pb}$ < [SEM]$_{Ni}$ < [SEM]$_{Cu}$ < [SEM]$_{Zn}$ (Fig. 8), which was consistent with the order in the previous study in the off-shore area of Laizhou Bay (Gao et al., 2013). There were significant positive correlations between [SEM] and TOC and between components of SEM (except [SEM]$_{Ni}$) and TOC in summer ($p < 0.001$), but these were not true in autumn (Table 2). The results indicated that TOC might be one of the major carriers of SEM as important as AVS in summer, but SEM might be mainly combined with AVS or other substances in autumn. However, the pervious study in October 2011 showed that there was a significant positive correlation between [SEM] and TOC in off-shore sediment in Laizhou Bay (Gao et al., 2013). These facts indicated the different combined status of SEM between off-shore and in-shore sediments in Laizhou Bay. Significant positive correlations in both summer and autumn were observed between [SEM]$_{Cd}$, [SEM]$_{Pb}$, [SEM]$_{Ni}$, [SEM]$_{Cu}$, and [SEM]$_{Zn}$ in pairs, which indicated that these metals were associated with

each other and might have common anthropogenic and natural sources in the sediments (Table 2). All simultaneously extracted metals showed significant positive correlations with MC and fine-grained fractions (clay + silt) and significant negative correlations with coarse fractions (sand) in autumn as AVS did, implying the similar formative and existing conditions of AVS and SEM in this period (Table 2). However, the fine-grained fraction showed non-significant positive relationships with Cd, Ni and Zn in summer (Table 2), which was in consistence with the studies carried out by Ip et al. (2007) in Pearl River Estuary and its surrounding coastal area, implying that the concentration of heavy metals in sediments cannot be simply interpreted by changes in grain size.

The paired samples t-test showed that seasonal changes had strong effects on the distribution of SEM in marine sediments (the corresponding p-values were between 8.264×10^{-8} and 0.002) but not in riverine sediments (Table 3). The t-test results reflected that other factors (variability in terrestrial inputs, hydrodynamic process and deposition conditions, etc.) besides seasonal changes might influence the distribution characteristics of SEM in rivers. In short, formation and persistence of SEM in riverine sediments were also more complex than in marine sediments as AVS did.

3.4. Evaluation of sediment toxicity

SEM could react with AVS to form insoluble metal sulfides which are non-bioavailable for benthic organisms. If SEM is present at lower concentrations than AVS, there is a low probability of toxicity; if the concentration of SEM is greater than that of AVS, the excess fraction of the divalent metals potentially exist as free metal ions and could cause toxicity (McGrath et al., 2002; Hinkey and Zaidi, 2007). Based on this theory, each sample falls into one of the three tiers: Tier 1, associated adverse effects on aquatic life are probable ([SEM]–[AVS] > 5, unit: µmol g^{-1}); Tier 2, associated adverse effects on aquatic life are possible (0 < [SEM]–[AVS] < 5); Tier 3, there is no indication of associated adverse effects ([SEM]–[AVS] < 0) (Table 4) (USEPA, 2004). According to the AVS–SEM criterion, the surface sediment at site DH2 belonged to Tier 1 in autumn; the surface sediments at sites MH2 and MH3 belonged to Tier 2 in summer; the sediments of other sites might

Table 4
Sediment quality guidelines and the classification results.

Sediment quality guideline	Classification	Criterion used to determine classification	Reference	Number of sampling stations			
				Summer		Autumn	
				River	Sea	River	Sea
[SEM]–[AVS]	Tier 1	[SEM]–[AVS] > 5	USEPA (2004)	0	0	1	0
	Tier 2	[SEM]–[AVS] = 0 to 5		2	0	0	0
	Tier 3	[SEM]–[AVS] < 0		33	18	32	18
([SEM]–[AVS])/f_{OC}	Tier 1	([SEM]–[AVS])/f_{OC} > 3000	USEPA (2005)	0	0	0	0
	Tier 2	([SEM]–[AVS])/f_{OC} = 130–3000		0	0	1	0
	Tier 3	([SEM]–[AVS])/f_{OC} < 130		35	18	32	18

[SEM]–[AVS] unit: $\mu mol\ g^{-1}$ (dry weight); ([SEM]–[AVS])/f_{OC} unit: $\mu mol\ g^{-1}$ OC (dry weight).

Table 5
Information about the sampling stations that had potential ecological risk.

Station	Sampling period	Sediment quality guideline	Value	Classification
MH2	Summer	[SEM]–[AVS]	0.12	Tier 2
MH3	Summer	[SEM]–[AVS]	0.16	Tier 2
DH2	Autumn	[SEM]–[AVS]	18.6	Tier 1
	Autumn	([SEM]–[AVS])/f_{OC}	1189	Tier 2

[SEM]–[AVS] unit: $\mu mol\ g^{-1}$ (dry weight); ([SEM]–[AVS])/f_{OC} unit: $\mu mol\ g^{-1}$ OC (dry weight).

almost have no adverse effect on aquatic life in both seasons (Tables 4 and 5; Fig. 9).

However, not all sediments with [SEM]–[AVS] > 0 can cause increased toxicity because there are many other metal-binding phases in sediments, such as TOC (Burton et al., 2005; Di Toro et al., 2005; Brix et al., 2010; De Jonge et al., 2012a; De Jonge et al., 2012b). Hence, USEPA proposed a complementary evaluation method to evaluate the adverse biological effects of SEM taking into account the TOC concentrations in sediments, which is also a three-tier system: Tier 1, adverse biological effects may be expected (([SEM]–[AVS])/f_{OC} > 3000, unit: $\mu mol\ g^{-1}$ OC); Tier 2, adverse effects are uncertain (([SEM]–[AVS])/f_{OC} = 130 to 3000); Tier 3, adverse effects are not expected (([SEM]–[AVS])/f_{OC} < 130) (Table 4) (USEPA, 2005). According to this criterion, only the surface sediment at site DH2 fell in Tier 2 in autumn, which means its adverse biological effects are uncertain, while it had probable adverse effect on aquatic life by the AVS–SEM criterion; all the sediments of other sites might have no adverse effect in both seasons (Tables 4 and 5).

This research showed that biotoxic level of heavy metals might change from season to season. There are many factors affecting the

concentrations and biotoxicity of heavy metals in sediments. Heavy metals may enter sediments from marinas and recreational vessel operation and maintenance (Guillen et al., 1993; Fairey et al., 2004; Hinkey et al., 2005). Wastewater from factories can also cause great heavy metal pollution. Studies showed that dredging process could increase the concentrations of sediment-bound metals in overlying water or even in undisturbed watercourses (De Jonge et al., 2012a). Metals that are combined with AVS may also be released from sediments through flood, storms, oxidation, etc., and may have adverse environmental impacts (van Den Berg et al., 1999; Prica et al., 2008). Therefore the combined actions of all the factors mentioned above can lead to AVS breakdown in surface sediments, thus causing heavy metals to release into the pore water and overlying water.

3.5. The limitations of AVS–SEM evaluation method

AVS–SEM method has been proved to be an efficient ecological risk assessment method; however, it still has some limitations. AVS concentration may change when environmental conditions (pH, Eh, oxygen content, etc.) change, and then sediments without biological toxicity may produce biological toxicity. It seems that some of the sulfides measured as AVS were oxidized during the elutriation which could release metals into the water column. Therefore applying this theory to metal remobilization studies would be proper only in the case that sulfides are not oxidized during elutriation (Di Toro et al., 1990; Durán et al., 2012). During the past years, much evidence has shown that benthic invertebrates can accumulate metals, even when [SEM]–[AVS] < 0, since benthic invertebrates ingest sediment particles as their main food source disregarding AVS (Lee et al., 2000a; Lee et al., 2000b; De Jonge et al., 2009; De Jonge et al., 2010).
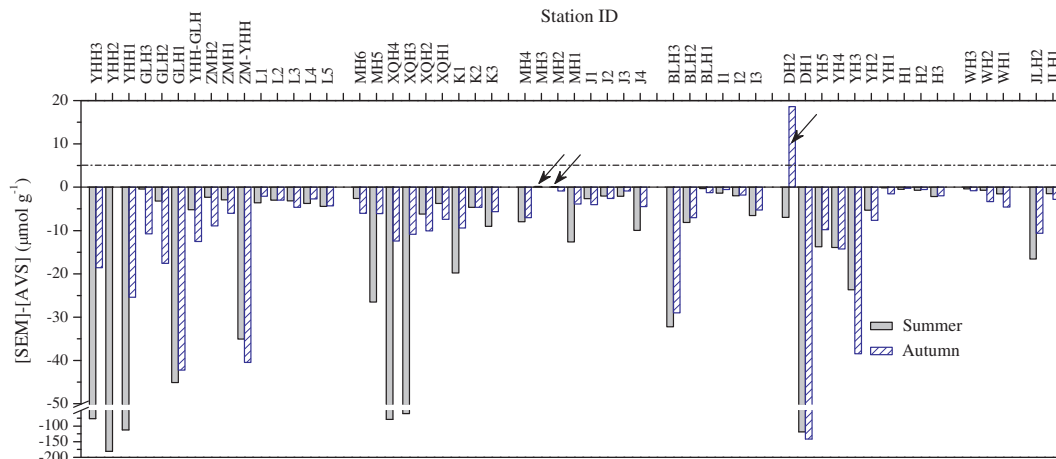

Fig. 9. Spatial distribution of [SEM]–[AVS] in surface sediments of the SW coastal Laizhou Bay. The arrows indicate the positive values.

SEMs can be combined with AVS to reduce their toxicity; however, AVS of excessively high content is also harmful to aquatic organism. AVS is usually abundant in the organic-rich and reductive environment, because AVS is mainly formed by sulfate reduction in the process of the metabolism of SRB which are anaerobic bacteria (Myhr et al., 2002; Wang et al., 2004). The serious anoxic environment may lead to the death of benthic organisms and fish. During the sample collection process of this research, dead fish or shell-fish were found at some sampling stations where very low levels of Eh were detected, e.g. DH1, YH2 and YHH1, although there was no heavy metal pollution according to AVS–SEM theory at these stations. Sulfide ions released from AVS can combine with hydrogen ions to form H_2S which has a strong neurotoxicity, and can produce toxic effects on aquatic life and even on humans; H_2S can also corrode ships, industrial equipment and pipelines (Jack et al., 1992; Kim and Kim, 2001).

Therefore using only one single approach for quality assessment of sediments may not be sufficient; a comparison of the results based on different criteria for sediment quality assessment will be more convincing. We will carry out this work later.

4. Conclusions

Because of the influence of frequent anthropogenic activities and complex natural environment, both AVS and SEM concentrations in riverine sediments were higher and had greater spatial differences among sampling sites and between different seasons than those in marine sediments. Significant positive correlations were observed between [AVS] and [SEM] in both seasons, which implied that they had similar formative and existing conditions and that AVS was an important carrier for SEM. There were also significant positive correlations between all the five simultaneously extracted metals in pairs, which indicated that these metals were associated with each other and might have common anthropogenic and natural sources in the sediments.

In accordance with the USEPA criteria, except for a few riverine samples (MH2, MH3 and DH2), heavy metals (Cd, Ni, Cu, Pb and Zn) in surface sediments of coastal Laizhou Bay had no adverse biological effects in both summer and autumn. Anthropogenic influences might be responsible for the relatively higher SEM concentrations in riverine sediments. Zn was the major component in the total amount of SEM, whereas the contribution of much more toxic Cd to SEM was no more than 0.7%. The average concentrations of SEM were in the following order: Cd $\ll$ Pb < Ni < Cu < Zn.

This study showed that biotoxic level of heavy metals might change with time, and sediments without biological toxicity in one season might produce biological toxicity in another. Biotoxic level of heavy metals could be influenced by many factors such as redox potential, dissolved oxygen, flood, and anthropogenic influences. The present research is a very beginning for a systematic assessment of sediment quality in Laizhou Bay. In the near future we hope to use more assessment methods to obtain comprehensive information on the baseline, anthropogenic discharge and bioavailability of heavy metals in this area.

Acknowledgements

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