

Distribution and pollution assessment of heavy metals in surface sediments in the central Bohai Sea, China: a case study

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Abstract The Bohai Sea is a semi-enclosed sea affected by intense industrial and maritime activities which may lead to heavy metal contamination. The major objective of this study was to reveal the distribution, and assess the potential risk of heavy metals in the sediments of the central Bohai Sea (CBS). Eight metals (Pb, Cd, Cu, Fe, Ni, Mn, Zn, and Co) in sediments obtained at 29 sites in summer and winter, 2011 were analyzed by inductively coupled plasma-mass spectrometry. The pollution assessments were carried out with three methods including marine sediment quality, the geoaccumulation index and Hakanson potential ecological risk index. Results showed that higher concentrations of heavy metals (except for Mn) were generally found in the northwest of the CBS, near the Luanhe Estuary, and higher concentrations of Mn were found in the north of the CBS. The distribution of heavy metals was mainly affected by contents of total organic carbon and clay percentage in sediment. In terms of pollution assessment, Cd was the major pollutant in the CBS.

The CBS was moderately contaminated in summer and uncontaminated in winter. The most contaminated zone was near the Luanhe Estuary, and anthropogenic sources from the Luanhe Estuary might be the main contributor. The results of three assessment methods were similar. Hakanson potential ecological risk index is more useful for the risk assessment of trace metals as it considers both potential ecological risks and biological effects. The combination of several pollution assessment methods is suggested in practice to obtain comprehensive and accurate results.

Keywords Heavy metals · Spatial distribution · Pollution assessment · Central Bohai Sea · Sediment

Introduction

Large quantities of elements and compounds are discharged into coastal seas as contaminants each year (Gao et al. 2014). Heavy metal pollution poses a serious threat to coastal and marine ecosystems as well as to the inhabitants due to its persistence, bioaccumulation and ecological damage (Gao and Chen 2012; Huang et al. 2013; Pekey 2006; Wang and Wang 2007; Xu et al. 2014). Heavy metals in the sea originate from both natural processes and anthropogenic activities. Geological and geochemical processes like tectonic activities and rock weathering processes set the geochemical background values for heavy metals (Zhang et al. 2003a). In coastal zones, metals enter the sea through atmospheric deposition of metal-contained dust from burning of fuels (Meng et al. 2008; Zhan et al. 2010; Zheng et al. 2008), surface runoff, and industrial and domestic sewage discharges (Meng et al. 2008), with the last being the most important (He et al. 2009).

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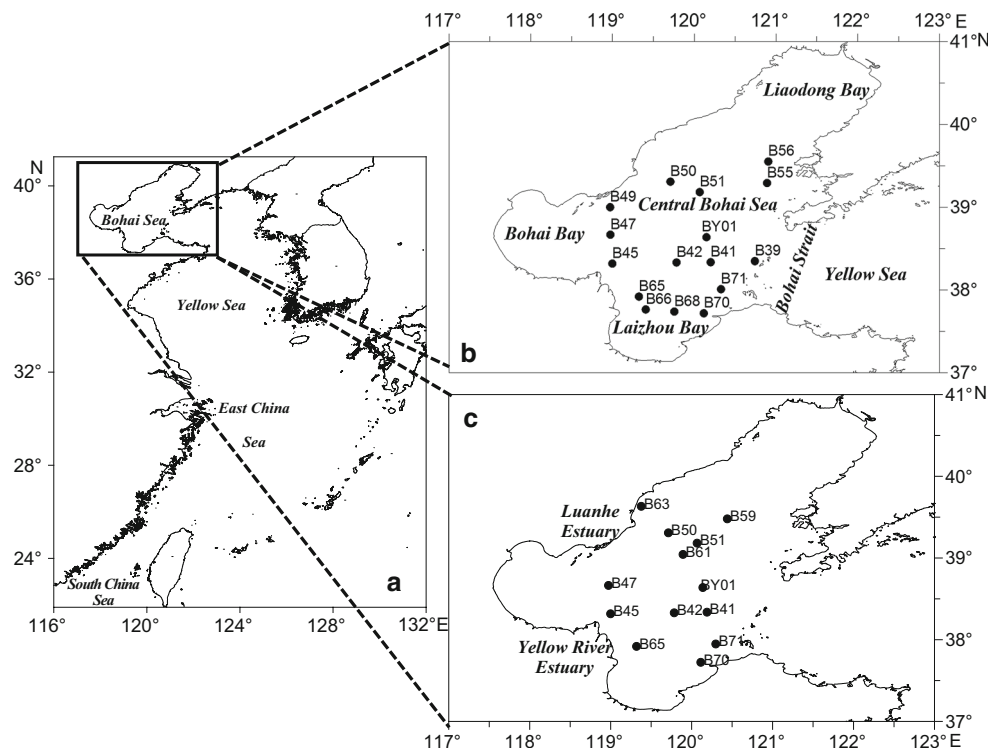
Sediments can act both as source and sink for heavy metals (He et al. 2009; Meng et al. 2008), providing a record of possible environmental changes caused by anthropogenic activities (Jiang et al. 2014; Qiao et al. 2013). The status of marine sediments is a significant criterion in the evaluation of the condition of aquatic systems (Meng et al. 2008; Xu et al. 2014; Zhan et al. 2010). Heavy metal concentrations in sediments are influenced by many factors including hydrodynamic condition (Yuan et al. 2012), sediment type (according to percentages of different-sized particles), sedimentation rate due to terrestrial input and hydrodynamic condition (Gao and Chen 2012; He et al. 2009; Teng et al. 2002), total organic carbon (TOC) (Gao and Chen 2012; He et al. 2009; Yuan et al. 2012; Zhan et al. 2010), the existing forms of heavy metals (He et al. 2009), and biological factors (Çaçador et al. 1993).

The Bohai Sea is a nearly enclosed inland sea located in northeast China (Fig. 1a) and consists of Liaodong Bay, Bohai Bay, Laizhou Bay, and the central Bohai Sea (CBS) (Fig. 1b) (Gao et al. 2014; Wang et al. 2010). It has a total area of approximately $7.7 \times 10^4 \text{ km}^2$ and a water volume of $1.7 \times 10^3 \text{ km}^3$. The mean depth is 18 m, with the deepest region of about 70 m located near the northern coast of the Bohai Strait (Gao et al. 2014). There are more than 40 rivers flowing into the Bohai Sea, among which the Yellow River, Haihe River, Luanhe River, Shuangtaizihe River and Liaohe River are the five

major ones (Gao et al. 2014; Wang et al. 2010). The amount of particulate matter inputted from the rivers into the Bohai Sea is about $1.3 \times 10^9 \text{ t-year}^{-1}$, and the sedimentation rate of the Bohai Sea is about $1.0\text{--}44.2 \text{ mm-year}^{-1}$ (Li et al. 1995). Due to intensive urbanization and industrialization, the Bohai Sea with its nearby coastal areas and estuaries has been facing severe metal pollution problems (Xu et al. 2013, 2014). The bulletins released by the State Oceanic Administration, P.R. China (SOA 2012–2014) indicated that the polluted areas of the Bohai Sea in 2012 ($13,080 \text{ km}^2$) and 2013 (8490 km^2) were significantly larger than that in 2011 (4210 km^2). The main polluted areas were Liaodong Bay, Bohai Bay, and Laizhou Bay.

Many studies have been conducted on heavy metals in surface sediments in the Bohai Sea, mainly in the three bays, but there have been few studies in the CBS. These bays were more polluted than the CBS (Gao et al. 2014; SOA 2012–2014) due to more intense port transportation, more sewage discharge, more industrial activities, and slower water-exchange rate inside the bays. Therefore, it may overestimate the contamination status of the whole Bohai Sea with ignorance of the CBS. The concentrations of Mn, Fe, and Co and their seasonal variation in the CBS have also been rarely studied. The objectives of this paper are: (1) to measure the concentrations of Pb, Cd, Cu, Fe, Ni, Mn, Zn, and Co in sediments collected from the CBS, China, (2) to analyze the relationships between

Fig. 1 Map showing **a** the location of the Bohai Sea, **b** the sampling sites during summer in 2011, and **c** the sampling sites during winter in 2011 and the locations of the Luanhe Estuary and the Yellow River Estuary



environmental variables and heavy metals, and (3) to assess pollution status of heavy metals by three methods.

Materials and Methods

Study area and sample collection

Two cruises were conducted onboard the vessel “*Dongfanghong II*” in the CBS, between 37°43′–39°38′N and 118°58′–120°55′E, from the 13th to 30th June, 2011 (summer cruise) and from the 20th November to 7th December, 2011 (winter cruise). Surface sediments were collected from 16 sites in summer (Fig. 1b) and 13 sites in winter (Fig. 1c) using a 0.1 m² stainless steel box-corer. The top 3 cm of sediment samples were sealed in polyethylene bags, and refrigerated at –20 °C.

Sample analysis

Heavy metals analysis

After transportation to the laboratory, samples were defrosted and air-dried at room temperature (20 °C) to constant weight, then ground and homogenized with a glass mortar and pestle. The dried samples were then passed through a nylon sieve of 160 meshes (96 μm) and stored in polyethylene bags. The pretreatment of sediment were according to Jiang et al. (2014). Eight heavy metals (Pb, Cd, Cu, Fe, Ni, Mn, Zn, and Co) in sediments were measured using an inductively coupled plasma-mass spectrometer (ICP-MS, Optima 2100 DV ICP System, Perkin Elmer Inc., USA). The instrument detection limits of metals are as follows: Pb, 0.0176; Cd, 0.0029; Cu, 0.0033; Fe, 0.0036; Ni, 0.0054; Mn, 0.0048; Zn, 0.0042; Co, 0.0048 mg L⁻¹, respectively. All samples were analyzed in duplicate, and the data shown herein represent the average of the duplicates.

Quality assurance and quality control (QA/QC) was assured by the analysis of a marine sediment reference material, GBW-07314 (the Second Institute of Oceanography, SOA). The materials used during analytical determinations were kept in metal-free containers. The plastic and glassware were pre-cleaned by soaking in HNO₃ (v:v = 1:3) for at least 24 h, followed by soaking and rinsing with de-ionized water. All reagents used in the analysis were of analytical grade.

TOC analysis

The water content of sediment was measured as a percentage of weight loss by drying the sediment at 60 °C for 24 h. The TOC content was determined by the (K₂Cr₂O₇–

H₂SO₄) oxidization method (SOA 2007; Mudroch et al. 1997).

Sediment type and grain size analysis

Sediment granulometry was analyzed using a Mastersizer 2000 laser diffractometer (Malvern Instrument Ltd., UK) capable of analyzing particle sizes between 0.02 and 2000 μm. The percentages of the following three groups of grain sizes were determined: <4 μm (clay, Y), 4–63 μm (silt, T), and >63 μm (sand, S). The naming of the sediment types was based on Shepard (1954).

Pollution assessment of heavy metals

Marine sediment quality (GB 18668-2002)

China national standard–marine sediment quality, GB 18668-2002 (SOA 2002), is widely used to judge the potential risks of metals in marine sediments. This standard classifies the marine sediments into three classes based on the area’s function and protection target. The first class quality area is suitable for mariculture, nature reserves, leisure activities, and industries that relate to human consumption directly; the second class quality area is used for general industry and tourism; the third class quality area is applied to sea ports and special ocean exploration.

The geoaccumulation index

The geoaccumulation index (I_{geo}) is defined by Eq. (1) (Müller 1969):

$$I_{geo} = \log_2(C_n/kB_n) \quad (1)$$

where C_n is the measured concentration of the metal (n) in the sediment, and B_n is the geochemical background value of the same metal. Factor k is the background matrix correction factor due to lithospheric effects, which is usually defined as 1.5 (Ghafari et al. 2011; Müller 1969; Rubio et al. 2000; Shafie et al. 2013; Xu et al. 2014). Samples may be classified as:

Class 0 (uncontaminated): $I_{geo} \leq 0$;

Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} \leq 1$;

Class 2 (moderately contaminated): $1 < I_{geo} \leq 2$;

Class 3 (moderately to heavily contaminated): $2 < I_{geo} \leq 3$;

Class 4 (heavily contaminated): $3 < I_{geo} \leq 4$;

Class 5 (heavily to extremely contaminated): $4 < I_{geo} \leq 5$;

Class 6 (extremely contaminated): $I_{geo} > 5$.

Ideally, B_n of heavy metals should be estimated from local sediments (Teng et al. 2002; Feng et al. 2011). The

background values of Cu, Pb, Zn, and Cd in the CBS were 22.1, 14.0, 65.2, and $0.088 \mu\text{g g}^{-1}$, respectively (Li et al. 1995). However, in the absence of the background values of Fe, Ni, Mn, and Co in the CBS, the background values of the adjacent region could be effectively substituted (Feng et al. 2011). For this reason, the B_n of the Bohai Bay sediments were chosen, i.e. 3.62 % for Fe, $36.1 \mu\text{g g}^{-1}$ for Ni, $571.0 \mu\text{g g}^{-1}$ for Mn, and $13.2 \mu\text{g g}^{-1}$ for Co (Wu and Li 1985; Feng et al. 2011; Xu et al. 2014).

Hakanson potential ecological risk index

Hakanson potential ecological risk index (RI) evaluates the combined pollution risk of an aquatic system through a toxic-response factor for a given substance (Hakanson 1980). RI is defined as follows (Eqs. (2) and (3)):

$$E_r^i = T_r^i \times C^i / C_n^i \quad (2)$$

$$RI = \sum_{i=1}^n E_r^i \quad (3)$$

where T_r^i is the toxic-response factor for a given substance, e.g., Pb = Cu = Ni = Co = 5, Mn = Zn = 1, Cd = 30 (Hakanson 1980; Xu et al. 2008, 2014), but T_r^i -Fe was unavailable. C^i and C_n^i represent the concentration of metals determined in the sediment samples and the geochemical background values of metals, respectively. The value of C_n^i is as same as B_n above. E_r^i and RI represent the monomial and sum potential ecological risk factor, respectively. Samples could be classified as:

- Low ecological risk: $E_r^i < 40$, $RI < 150$;
- Moderate ecological risk: $40 \leq E_r^i < 80$, $150 \leq RI < 300$;
- Moderate to high ecological risk: $80 \leq E_r^i < 160$;
- High ecological risk: $160 \leq E_r^i < 320$, $300 \leq RI < 600$;
- Very high ecological risk: $E_r^i \geq 320$, $RI \geq 600$.

Analysis software

Surfer 8.0 (Golden Software Inc., USA) was used for drawing the distribution maps of the TOC content and

metal concentrations in surface sediments. Microsoft excel 2010 (Microsoft Inc., USA) was used for drawing histograms and scatterplots. Statistical analyses were conducted with SPSS 18.0 software (SPSS Inc., USA).

Results and discussion

Environmental variables

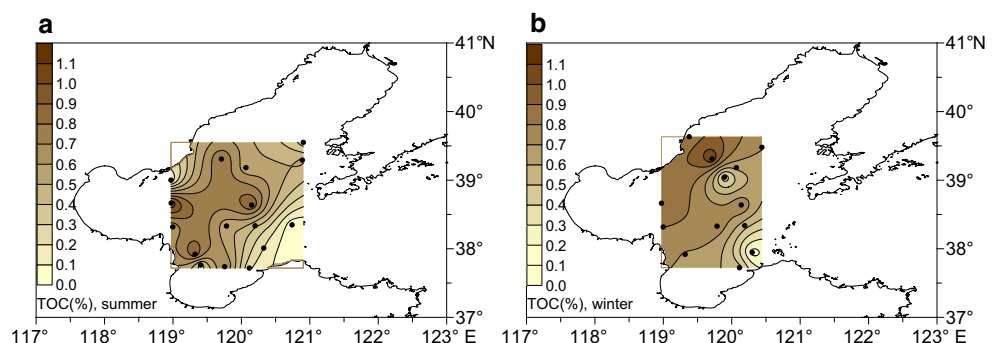
The TOC content varied between 0.02 and 1.09 % of the dry sediment weight in summer and between 0.15 and 1.08 % in winter. The spatial distributions of the TOC are shown in Fig. 2. The higher content of TOC in summer (Fig. 2a) was generally found in the west of the CBS, decreasing coastward. The content of TOC in winter (Fig. 2b) was higher in the northwest of the CBS, near the Luanhe Estuary. As shown in Fig. 3, the sediments were predominantly composed of silt. The sediment types in the CBS have been classified into four groups: S-sand, ST-sandy-silt, TS-silty-sand, and YT-clayey-silt, according to Shepard (1954). The numbers of sites of those four groups were 2, 2, 4, and 8 in summer, and 0, 4, 2, and 7 in winter, respectively. The type YT accounted for about 50 % of the sites in both seasons.

Spatial distribution of heavy metals and influencing factors

Spatial distribution of heavy metals

The metal concentrations in surface sediments collected from all sites in the CBS were ranked in decreasing order, as follows: Fe > Mn > Zn > Ni > Cu > Pb > Co > Cd in summer and Fe > Mn > Zn > Cu > Ni > Pb > Co > Cd in winter (Table 1). To compare the concentrations of these eight metals between summer and winter, an independent-sample t test was conducted and the details are represented in Table 1. There were no significant differences among them between the two seasons ($p > 0.05$)

Fig. 2 The spatial distribution of the TOC concentrations in surface sediments of the CBS in summer (a) and winter (b). The dots represent the sites (similarly hereinafter)



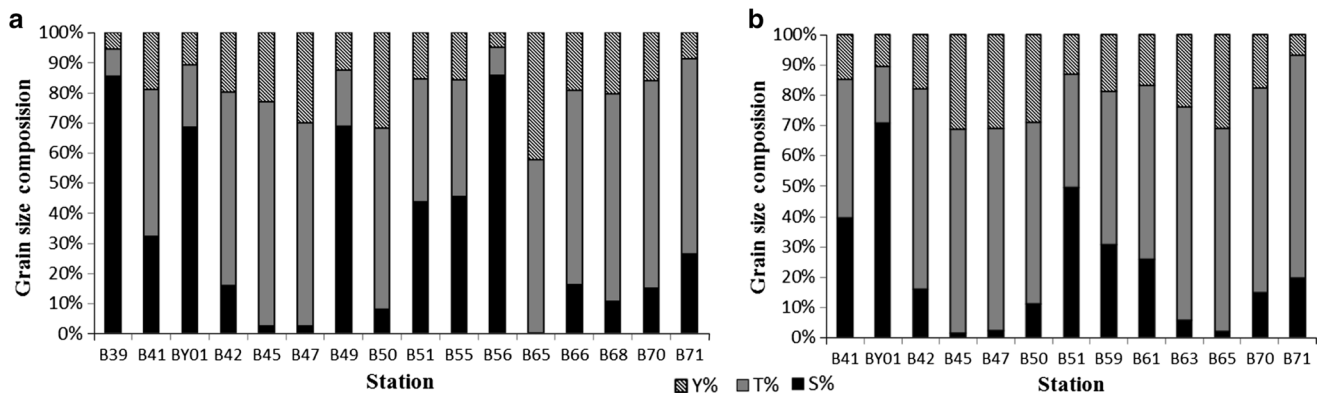


Fig. 3 The grain size compositions in surface sediments of the CBS in summer (a) and winter (b)

Table 1 Average concentrations (Mean ± SD) and details about the t test of the metals

Metal	Pb (µg/g)	Cd (µg/g)	Cu (µg/g)	Fe (%)	Ni (µg/g)	Mn (µg/g)	Zn (µg/g)	Co (µg/g)
Summer	11.36 ± 4.25	1.65 ± 1.53	16.84 ± 6.81	1.30 ± 0.34	18.50 ± 5.72	502.96 ± 204.43	41.87 ± 11.75	7.69 ± 2.09
Winter	11.98 ± 4.43	0.20 ± 0.12	18.23 ± 6.17	1.26 ± 0.29	17.44 ± 4.72	534.81 ± 155.74	39.74 ± 8.69	7.76 ± 1.83
P	0.706	0.002	0.574	0.755	0.597	0.647	0.592	0.931

with exception of Cd ($p < 0.01$). The concentration of Cd in summer was significantly higher than that in winter.

The spatial distributions of eight heavy metals are shown in Figs. 4 and 5. The distribution patterns of individual metals were as follows: (1) Fe, Ni, Zn, and Co: Higher concentrations were generally found in the northwest of the CBS, near the Luanhe Estuary. The concentrations decreased in northwest-to-southeast direction; (2) Pb and Cu: The distribution patterns were similar to (1). Another high level of Pb in both seasons and Cu in summer was found in the southwest of the CBS, near the Yellow River Estuary; (3) Cd: The distribution was similar to (1) in summer, and similar to Pb in winter; and (4) Mn: Unlike any other heavy metals, the higher concentrations of Mn were found in north of the CBS. The Site B41 in summer showed another distinct peak situated at 38.33° N and 120.20° E.

The distribution of Mn showed a distinct pattern with other metals in the sediments of the CBS. This phenomenon has also been found in many other studies (Jiang et al. 2014; Li et al. 2012; Yuan et al. 2012). The concentration of Mn may not be derived from industrial activities but from geological processes (e.g., Li et al. 2012). The dissolved Mn tends to be adsorbed on, or incorporated into freshly precipitated CaCO₃ in seawater (e.g. Wartel et al. 1990). According to V. M. Goldschmidt (Zhang et al. 2003b), heavy metals belonging to the same group have similar chemical properties.

Many studies have been conducted on heavy metals in surface sediments throughout the world. The range and

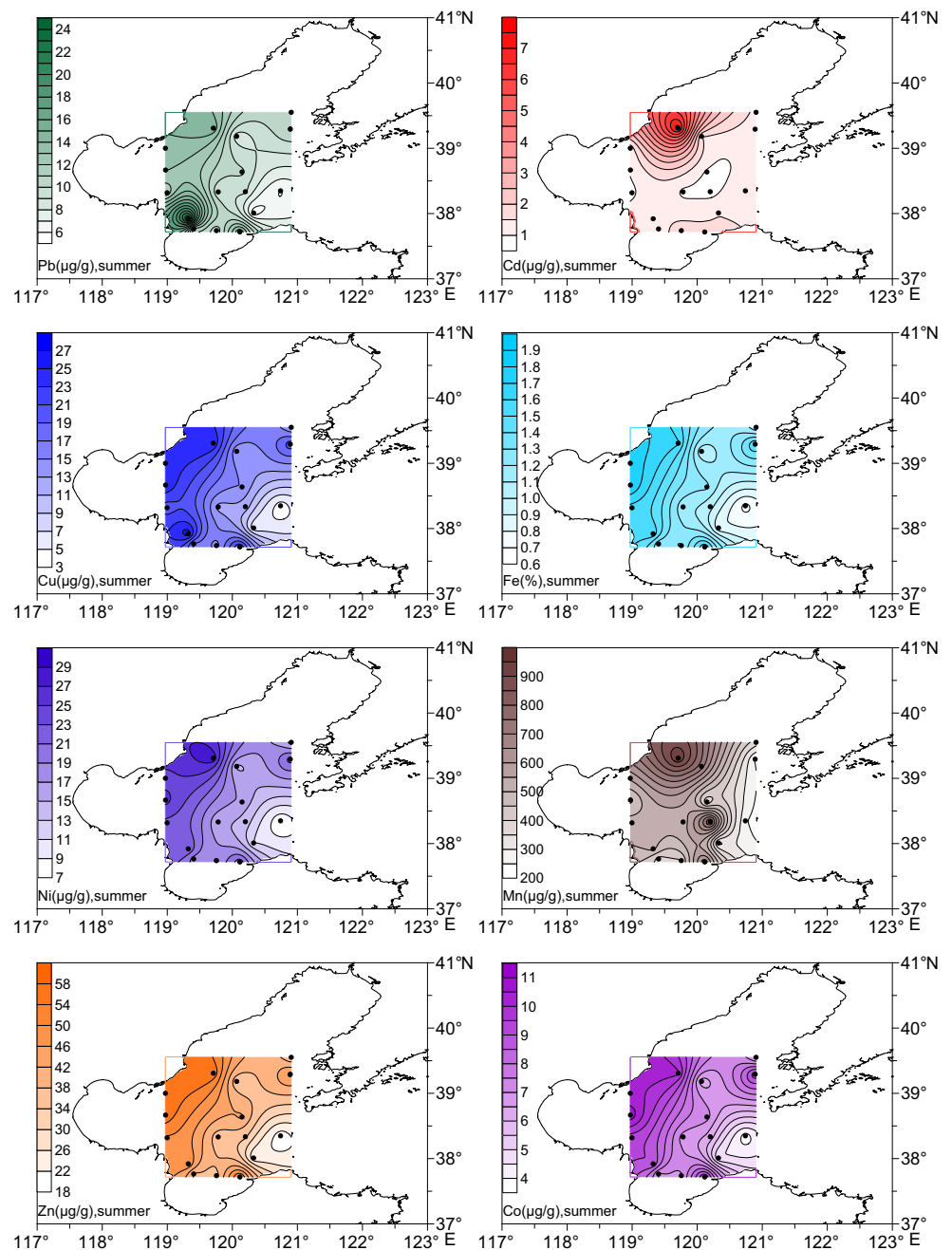
mean concentrations of metals in sediments of the Bohai Sea and other seas are summarized in Table 2. Heavy metal concentrations (except for Cd) in the CBS were comparable to others observed in the Bohai Sea or other sea areas. The contents of Cd in summer were markedly higher than the majority of the previous studies.

Statistical analysis

The relationships between every pair of heavy metals, TOC, sand %, silt %, and clay % in both seasons were analyzed and the Pearson correlation coefficients are shown in Table 3. In summer, Cd and Mn showed no significant correlation with other variables except Cd-Mn pair. Six other heavy metals showed highly significant positive correlations between each other. Clay percentage presented a significant or highly significant positive correlation with those six metals. TOC had significant positive correlations with Cu, Ni, and Co. The relationships between these variables in winter were similar to summer. Unlike the situation in summer, Cd had a highly significant positive correlations with Pb, Cu, Fe, and Ni and significant positive correlations with Zn and Co in winter. Clay percentage presented highly significant positive correlations with all heavy metals except Mn. Sand percentage and silt percentage seldom had significant correlations with heavy metals in either season.

Positive correlation between heavy metals suggests that those metals have common sources (Facchinelli et al. 2001)

Fig. 4 Spatial distribution of heavy metals in surface sediments from the CBS in summer, 2011

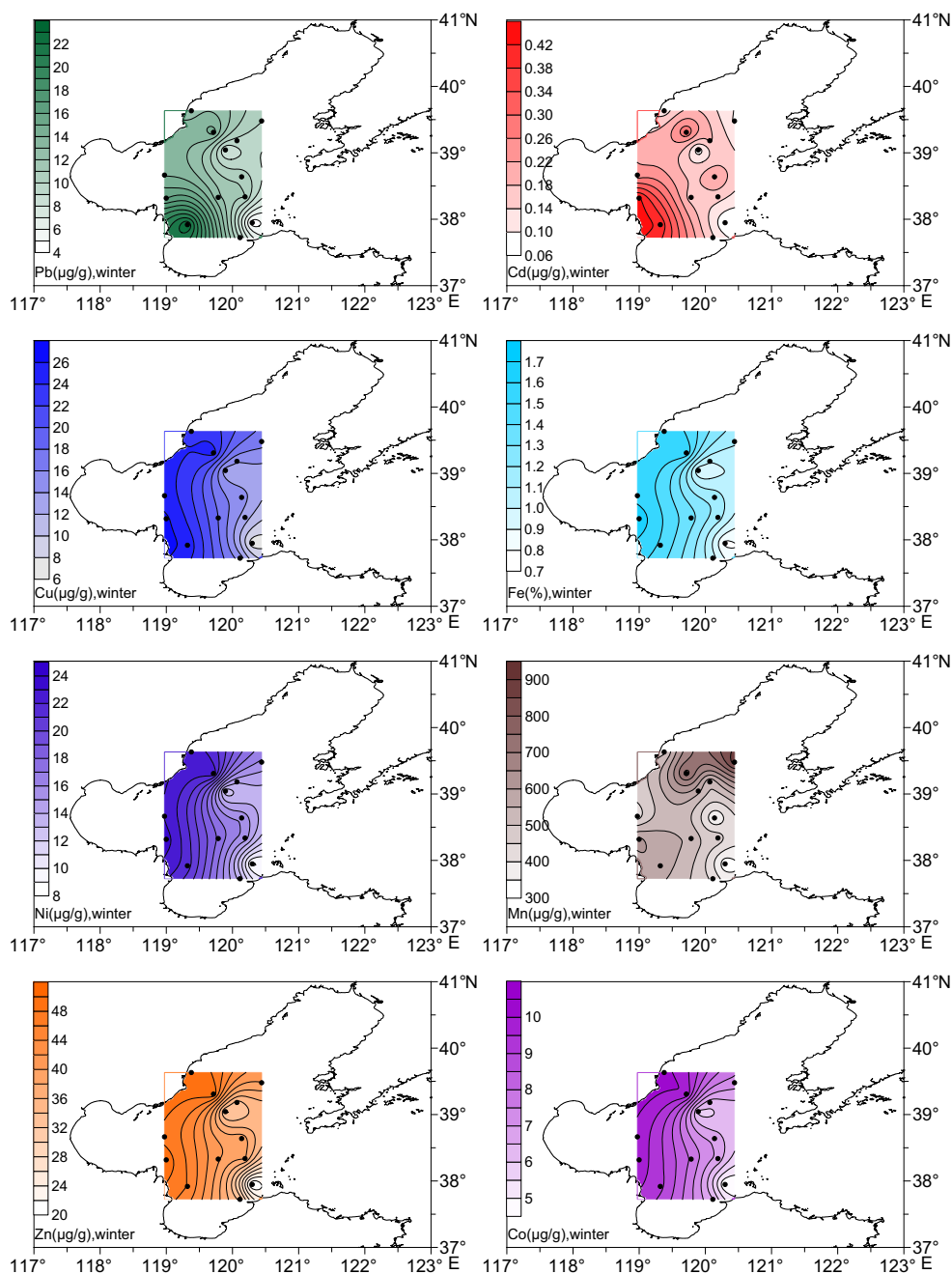


and identical behavior during transportation (Bastami et al. 2014). The concentration of Mn showed very weak correlations with the concentrations of the other metals, indicating that Mn had different sources from others. This is consistent with the discussion above about the distribution of Mn.

Grain size is one of the controlling factors affecting natural concentrations of heavy metals in sediments (Gao and Chen 2012; He et al. 2009; Jiang et al. 2014; Yuan et al. 2012). Sediment of smaller grain size such as clay tends to adsorb more heavy metals due to higher surface

area-to-volume ratio (Jiang et al. 2014; Yuan et al. 2012). For this reason, the heavy metal content increased with increasing percentage of clay in sediment. TOC is another factor that controls heavy metal concentrations in sediment (Gao and Chen 2012; He et al. 2009; Jiang et al. 2014; Yuan et al. 2012; Zhan et al. 2010). Natural organic matter shows a high affinity through adsorption or complexation of heavy metals in the aquatic environment (El Bilali et al. 2002). The TOC in sediment was adsorbed onto clay mostly (He et al. 2009), accounting for the positive correlations with clay percentage as shown in Table 3. For this

Fig. 5 Spatial distribution of heavy metals in surface sediments from the CBS in winter, 2011



reason, the percentage of clay increased with TOC, leading to the increased heavy metal content. It is noteworthy that the TOC seldom showed significant correlation with heavy metals in summer (Table 3). When several sites were excluded, as shown in Fig. 6, the TOC correlated well with heavy metals (except Cd and Mn) in summer. The concentrations of heavy metals at Sites B49 and B70 (adding B65 for Pb) in summer were somewhat higher than those in adjacent regions, suggesting the metal concentrations at those sites were probably influenced by anthropogenic activity.

Pollution assessment

Comparison of marine sediment quality

Table 2 shows the upper limits of Pb, Cd, Cu, and Zn of the first, second, and third class of marine sediment quality according to GB 18668-2002. As shown in Table 2, the Pb, Cu, and Zn concentration at all sites in both seasons and the Cd content in winter was below the upper limit for Class I sediment. That means all sampling sites in winter were clean enough to be classified as Class I marine sediment

Table 2 Comparison of heavy metal concentrations in surface sediments of seas

Location	Pb ($\mu\text{g g}^{-1}$)	Cd ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	Fe (%)	Ni ($\mu\text{g g}^{-1}$)	Mn ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	Co ($\mu\text{g g}^{-1}$)	References
The CBS (summer)	4.42–23.5 (11.4) ^a	0.842–7.28 (1.65)	3.86–26.3 (16.8)	0.668–1.80 (1.30)	7.33–28.2 (18.5)	246–945 (503)	19.5–57.2 (41.9)	3.76–10.8 (7.69)	This study
The CBS (winter)	4.42–22.9 (12.0)	0.064–0.426 (0.199)	6.84–26.3 (18.2)	0.77–1.66 (1.26)	8.77–23.4 (17.4)	315–876 (535)	19.8–49.6 (39.7)	4.49–10.1 (7.76)	This study
The Bohai Sea	(1.10)	(0.310)	(1.90)	ND	ND	ND	ND	ND	Wang and Wang 2007
Coastal Bohai Bay	20.9–66.4 (34.7)	0.120–0.66 (0.220)	20.1–62.9 (38.5)	ND	23.4–52.7 (40.7)	ND	55.3–457 (131.1)	ND	Gao and Chen 2012
Liaodong Bay	18.9–61.2 (31.8)	ND	5.7–37.1 (19.4)	ND	7.00–40.5 (22.5)	ND	14.5–145 (71.7)	ND	Hu et al. 2013
Lai Zhou Bay	11.6–33.1 (20.2)	0–0.025 (0.081)	2.9–26.4 (13.3)	ND	7.6–33.9 (19.4)	ND	34.3–93.4 (59.4)	ND	Hu et al. 2011
The Yellow Sea (summer)	4.80–21.9 (12.3)	0–8.21 (0.513)	5.93–25.7 (15.1)	0.61–2.27 (1.33)	8.43–31.1 (18.6)	84.7–1593 (410)	21.9–96.2 (47.3)	4.11–13.0 (8.24)	Jiang et al. 2014
The Yellow Sea (winter)	4.31–18.4 (11.3)	0–0.373 (0.115)	4.95–26.1 (15.9)	0.62–22.2 (1.36)	8.31–32.4 (18.8)	186–1334 (373)	18.8–82.1 (46.2)	4.31–13.3 (8.46)	Jiang et al. 2014
East China Sea	10.0–49.0 (27.0)	ND	4.30–42.0 (15.0)	0.620–3.97 (2.10)	8.20–49.0 (26.0)	152–1152 (484)	18.0–114 (60.0)	ND	Fang et al. 2009
Black Sea	14.0–35.0 (22.1)	ND	29.0–68.0 (52.1)	1.30–4.30 (2.72)	38.0–204 (67.7)	355–2495 (621)	50.0–108 (82.4)	7.00–37.0 (15.8)	Kiratli and Ergin 1996
Sea of Marmara	80.0–94.0	ND	6.00–92.0	0.42–6.31	6.00–161	152–9127	6.00–180	7.00–30.0	Bodur and Ergin 1994
Class I ^b	60.0	0.500	35.0	ND	ND	ND	150	ND	SOA 2002
Class II ^b	130	1.50	100	ND	ND	ND	350	ND	SOA 2002
Class III ^b	250	5.00	200	ND	ND	ND	600	ND	SOA 2002

ND no data

^a Values in parentheses represent average concentrations

^b Class I, II, and III = the upper limits of the first, second, and third class of marine sediment quality, respectively

Table 3 Correlation matrix for metals, TOC, sand %, silt %, and clay % in surface sediments from the CBS in summer and winter, 2011

Season	Pb	Cd	Cu	Fe	Ni	Mn	Zn	Co	TOC	Sand %	Silt %	Clay %
Summer	Pb											
	Cd	1										
	Cu	0.240	1									
	Fe	0.857**	0.965**	1								
	Ni	0.734**	0.231	0.967**	1							
	Mn	0.737**	0.436	0.971**	0.411	1						
	Zn	0.322	0.546*	0.394	0.307	0.431	1					
	Co	0.741**	0.323	0.969**	0.972**	0.431	0.987**	1				
	TOC	0.706**	0.283	0.962**	0.977**	0.352	0.490	0.501*	1			
	Sand (%)	0.434	0.209	0.513*	0.486	0.165	-0.414	-0.448	-0.538*	1		
	Silt (%)	-0.426	-0.230	-0.474	-0.465	-0.344	0.285	0.324	0.391	-0.965**	1	
	Clay (%)	0.226	0.150	0.315	0.341	0.268	0.593*	0.605*	0.722**	-0.798**	0.612*	1
Winter	Pb											
	Cd	1										
	Cu	0.855**	1									
	Fe	0.850**	0.754**	1								
	Ni	0.796**	0.725**	0.964**	1							
	Mn	0.806**	0.713**	0.976**	0.994**	1						
	Zn	0.306	0.190	0.405	0.318	0.445	1					
	Co	0.782**	0.656*	0.942**	0.959**	0.369	0.968**	1				
	TOC	0.771**	0.641*	0.971**	0.985**	0.424	0.894**	0.848**	1			
	Sand (%)	0.609*	0.564*	0.817**	0.847**	-0.218	-0.410	-0.588*	-0.184	1		
	Silt (%)	-0.468	-0.325	-0.609*	-0.561*	0.056	0.094	0.304	-0.107	-0.936**	1	
	Clay (%)	0.188	0.054	0.305	0.275	0.443	0.854**	0.907**	0.669*	-0.744**	0.462	1

* 0.01 < p < 0.05

** p < 0.01

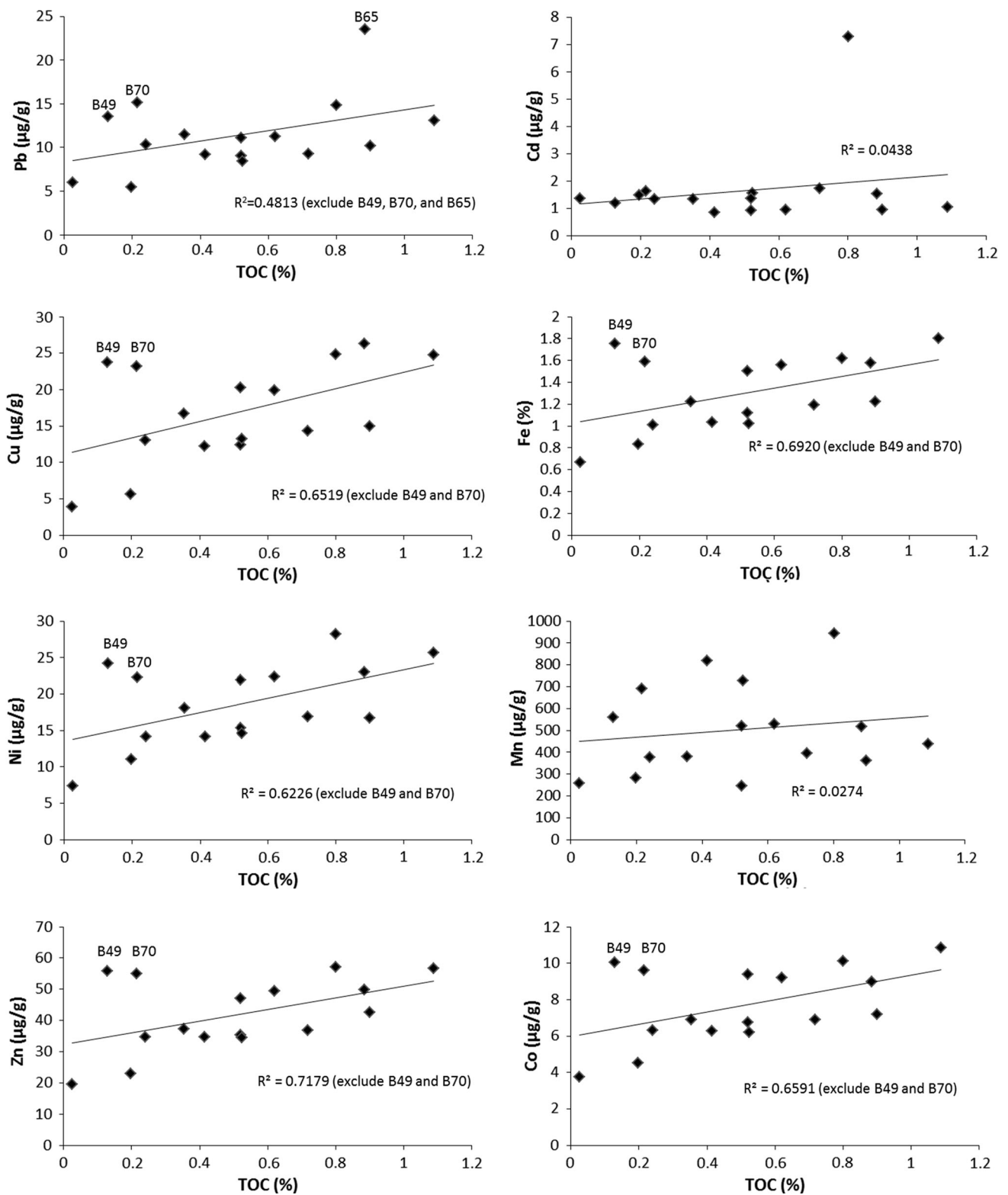


Fig. 6 Relationship between the TOC and heavy metal concentrations in the sediments from the CBS in summer, 2011

quality. In summer, however, the Cd concentration at sites 11, 4, and 1 was within the range for Class I–II, Class II–III, and above Class III threshold values, respectively. Site

B50 was heavily contaminated in summer with the Cd concentration ($7.28 \mu\text{g g}^{-1}$) in excess of Class III. According to SOA (2012–2014), with 6.25 % of sites

Table 4 The values of I_{geo} , E_r^i and RI in surface sediments in the CBS in summer and winter, 2011

Season	Site	I_{geo}/E_r^i								RI
		Pb	Cd	Cu	Fe	Ni	Mn	Zn	Co	
Summer	B39	-1.82/2.13	3.35/459.49	-3.10/0.87	-3.02/-	-2.88/1.02	-1.73/0.45	-2.32/0.30	-2.40/1.42	465.68
	B41	-1.19/3.28	2.67/286.98	-1.44/2.76	-2.39/-	-1.94/1.95	-0.06/1.44	-1.49/0.53	-1.65/2.38	299.33
	BY01	-1.04/3.65	2.83/320.45	-1.15/3.38	-2.15/-	-1.70/2.31	-1.24/0.64	-1.20/0.65	-1.46/2.73	333.81
	B42	-1.21/3.24	2.79/310.69	-1.42/2.80	-2.27/-	-1.82/2.12	-0.72/0.91	-1.47/0.54	-1.55/2.56	322.86
	B45	-0.90/4.01	2.82/316.73	-0.74/4.50	-1.80/-	-1.27/3.10	-0.70/0.92	-0.98/0.76	-1.10/3.49	333.51
	B47	-0.68/4.67	2.98/355.36	-0.42/5.59	-1.59/-	-1.08/3.56	-0.97/0.77	-0.79/0.87	-0.87/4.11	374.92
	B49	-0.63/4.84	3.18/406.84	-0.48/5.38	-1.63/-	-1.16/3.35	-0.62/0.98	-0.81/0.86	-0.98/3.81	426.05
	B50	-0.50/5.29	5.79/2481.49	-0.41/5.63	-1.75/-	-0.94/3.91	0.14/1.66	-0.77/0.88	-0.97/3.83	2502.68
	B51	-1.32/3.00	3.55/526.39	-1.32/3.00	-2.41/-	-1.89/2.02	-0.24/1.27	-1.50/0.53	-1.67/2.35	538.58
	B55	-0.92/3.97	3.35/458.79	-0.71/4.58	-1.85/-	-1.30/3.04	-1.80/0.43	-1.05/0.72	-1.08/3.56	475.09
	B56	-1.02/3.69	3.33/453.27	-1.35/2.95	-2.42/-	-1.93/1.96	-1.18/0.66	-1.50/0.53	-1.65/2.39	465.45
	B65	0.16/8.39	3.53/521.22	-0.33/5.96	-1.79/-	-1.24/3.18	-0.73/0.91	-0.97/0.77	-1.14/3.40	543.82
	B66	-0.87/4.11	3.33/451.08	-0.99/3.78	-2.15/-	-1.58/2.50	-1.18/0.66	-1.39/0.57	-1.52/2.62	465.33
	B68	-1.18/3.30	3.70/584.54	-1.21/3.25	-2.18/-	-1.68/2.34	-1.11/0.69	-1.41/0.57	-1.52/2.62	597.32
	B70	-0.47/5.40	3.63/557.80	-0.52/5.24	-1.77/-	-1.28/3.09	-0.31/1.21	-0.83/0.84	-1.04/3.64	577.23
Winter	B71	-1.95/1.94	3.48/501.28	-2.55/1.28	-2.71/-	-2.30/1.52	-1.59/0.50	-2.09/0.35	-2.13/1.72	508.59
	B41	-0.93/3.94	0.26/53.90	-1.35/2.95	-2.24/-	-1.80/2.15	-0.83/0.84	-1.36/0.59	-1.53/2.60	66.98
	BY01	-0.97/3.82	0.78/77.38	-1.14/3.40	-2.22/-	-1.77/2.19	-1.28/0.62	-1.32/0.60	-1.53/2.60	90.61
	B42	-0.78/4.37	0.27/54.12	-0.88/4.07	-2.02/-	-1.60/2.47	-0.66/0.95	-1.28/0.62	-1.32/3.00	69.60
	B45	-0.40/5.69	1.69/145.18	-0.33/5.95	-1.71/-	-1.21/3.24	-0.48/1.07	-0.99/0.75	-1.02/3.70	165.60
	B47	-0.59/4.98	0.84/80.69	-0.40/5.70	-1.79/-	-1.24/3.18	-1.01/0.75	-1.05/0.73	-1.01/3.73	99.74
	B50	-0.54/5.16	1.18/101.68	-0.41/5.63	-1.78/-	-1.26/3.14	-0.15/1.35	-0.98/0.76	-1.00/3.76	121.49
	B51	-1.12/3.46	0.48/62.77	-1.22/3.21	-2.43/-	-1.93/1.96	-0.77/0.88	-1.56/0.51	-1.67/2.35	75.15
	B59	-1.07/3.58	-0.48/32.17	-0.97/3.83	-2.28/-	-1.77/2.19	0.03/1.53	-1.29/0.61	-1.44/2.76	46.68
	B61	-1.40/2.83	-0.83/25.34	-1.37/2.91	-2.55/-	-2.13/1.71	-0.59/0.99	-1.62/0.49	-1.75/2.23	36.50
	B63	-0.75/4.47	-0.21/39.01	-0.52/5.21	-1.82/-	-1.28/3.08	-0.81/0.85	-1.01/0.75	-0.97/3.82	57.19
	B65	0.13/8.20	1.63/139.68	-0.38/5.76	-1.87/-	-1.34/2.97	-0.57/1.01	-1.09/0.70	-1.11/3.46	161.78
	B70	-1.09/3.52	0.16/50.32	-1.12/3.45	-2.38/-	-1.99/1.89	-0.96/0.77	-1.55/0.51	-1.59/2.48	62.94
	B71	-2.25/1.58	-1.04/21.86	-2.28/1.55	-2.81/-	-2.63/1.21	-1.44/0.55	-2.30/0.30	-2.14/1.70	28.75

having bad quality in summer, the CBS was moderately contaminated.

The geoaccumulation index

As shown in Table 4, the I_{geo} values (Müller 1969) of Cu, Fe, Ni, Zn, and Co at all sites and of Pb and Mn at most sites were below zero, indicating the CBS was uncontaminated by those metals. The I_{geo} values of Cd indicated the CBS was moderately ($2 < I_{geo} \leq 3$) to extremely contaminated ($I_{geo} > 5$) in summer and uncontaminated ($I_{geo} \leq 0$) to moderately contaminated ($0 < I_{geo} \leq 1$) in winter. The pollution status of the CBS in summer was more severe compared with winter. In summer higher values of I_{geo} -Cd were found in the northwest of the CBS,

especially at Site B50 located near the Luanhe Estuary. It is suggested that anthropogenic sources from the Luanhe Estuary might be the main contributor of Cd at Site B50.

Hakanson potential ecological risk index

The E_r^i and RI values (Hakanson 1980) of sediments of the CBS are shown in Table 4. In summer, 81.25 % of sites were at very high ecological risk of Cd (E_r^i -Cd > 320). In winter, the E_r^i -Cd at 4, 5, and 4 sites were low, moderate, and moderate to high ecological risk, respectively. The E_r^i values of the other seven metals at all sites were below 40 in both seasons. Because of the higher T_r^i (T_r^i -Cd = 30) and relatively higher concentration of Cd compared to the background value, Cd was the priority pollutant in the

CBS. In summer, the *RI* value at Site B50 was higher than 600, indicating a high ecological risk of metals. The *RI* values at 14 sites were above 300, which meant considerable ecological risk from metals. In winter, 84.62 % of sites were at low ecological risk ($RI < 150$). According to the values of E_r^i and *RI*, the pollution status of the CBS in summer was considerably worse than that in winter.

The results of the three methods were generally similar. The main contaminated zone was near the Luanhe Estuary. Cd was the most important pollutant in comparison with other heavy metals in the CBS. The pollution status of the CBS in summer was worse than that in winter. River runoff and anthropogenic activities are suggested as the main pollution sources in China Seas (Liu and Diamond 2005). The Bohai Sea Economic Rim, the coastal region surrounding the Bohai Sea, is one of the three most densely populated and industrialized zones in China. Due to the shallow depth, narrow connection with the outer ocean and slow water-exchange rate, the self-cleaning capacity of the Bohai Sea is very limited (Dang et al. 2013). The ecosystem of the Bohai Sea is being rapidly degraded (Gao et al. 2014). The concentrations of heavy metals in sediment may affect the heavy metal content in organisms and the bioaccumulation capacity of heavy metals by organisms (Gao et al. 2014; Liang et al. 2004). Liang et al. (2004) found that the concentrations of Cd, Cu and Zn in gastropod and oyster samples in the Bohai Sea exceeded the MPLs established by WHO (1989).

Each of the three methods has its own advantages and disadvantages. It is simple to compare the contents of the heavy metals to marine sediment quality. In terms of the concentrations of the heavy metals, this standard can classify the studied area into three classes with different function and protection target. However, the sediment qualities for many metals such as Ni, Mn, Co are not available in the standard. The geochemical background values in a certain area were not considered yet. The geoaccumulation index is used widely with the simple principle and formula, so it is convenient for comparison to previous studies. The background values of heavy metals are considered in the geoaccumulation index. Different from the above two methods, Hakanson potential ecological risk index is more complex. It is recognized as useful for the risk management of trace elements in sediments because sediment adverse biological effects and potential ecological risks are considered in Hakanson potential ecological risk index. To reduce the potential for bias and to better characterize the likelihood for adverse environmental effects in the studied sea area, the application of several metrics for pollution assessment is advisable.

Conclusions

To effectively manage potential environmental and biological impacts of contaminated sediments in a semi-enclosed sea, in the present study, the concentrations of eight metals in sediments from the CBS were measured with ICP-MS and pollution status was assessed with three methods. Higher concentrations of heavy metals (except for Mn) were generally found in the northwest of the CBS, near the Luanhe Estuary. The TOC and clay percentage were the main controlling factors affecting the distribution of heavy metals. According to the pollution assessment, the CBS was moderately contaminated in summer and uncontaminated in winter, 2011. The main contaminated zone was near the Luanhe Estuary, and Cd was the main contaminant compared to others in the CBS. Anthropogenic sources from the Luanhe Estuary might be the main contributor.

Compared the three pollution assessment methods, marine sediment quality and the geoaccumulation index methods are much simpler for calculation but they ignore the biological impacts of heavy metals in the sediments. Hakanson potential ecological risk index is a better method because biological effects and potential ecological risks are both considered. The present study provides researchers and policy makers with basic data to develop a better understanding of the geographic distribution and potential risks of metals in the CBS. In future, more background values from local sediments are needed to meaningfully assess pollution status. The combination of several pollution assessment methods is suggested in the risk management of trace metals in sediments to obtain comprehensive and accurate results.

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References

- Bastami KD, Bagheri H, Kheirabadi V, Zaferani GG, Teymori MB, Hamzehpoor A et al (2014) Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea. *Mar Pollut Bull* 81:262–267. doi:10.1016/j.marpolbul.2014.01.029

- Bodur MN, Ergin M (1994) Geochemical characteristics of the recent sediments from the Sea of Marmara. *Chem Geol* 115:73–101. doi:10.1016/0009-2541(94)90146-5
- Caçador I, Vale C, Catarino F (1993) Effects of plants on the accumulation of Zn, Pb, Cu and Cd in sediments of the Tagus Estuary salt marshes, Portugal. *Stud Environ Sci* 55:355–364. doi:10.1016/s0166-1116(08)70300-5
- Dang HY, Zhou HX, Zhang ZN, Yu ZS, Hua E, Liu XS et al (2013) Molecular detection of *Candidatus* Scalinduapacifica and environmental responses of sediment anammox bacterial community in the Bohai Sea, China. *PLoS One* 8:e61330. doi:10.1371/journal.pone.0061330
- El Bilali L, Rasmussen PE, Hall GEM, Fortin D (2002) Role of sediment composition in trace metal distribution in lake sediments. *Appl Geochem* 17:1171–1181. doi:10.1016/s0883-2927(01)00132-9
- Facchinelli A, Sacchi E, Mallen L (2001) Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Environ Pollut* 114:313–324. doi:10.1016/s0269-7491(00)00243-8
- Fang TH, Li JY, Feng HM, Chen HY (2009) Distribution and contamination of trace metals in surface sediments of the East China Sea. *Mar Environ Res* 68:178–187. doi:10.1016/j.marenvres.2009.06.005
- Feng H, Jiang HY, Gao WS, Weinstein MP, Zhang QF, Zhang WG et al (2011) Metal contamination in sediments of the western Bohai Bay and adjacent estuaries, China. *J Environ Manage* 92:1185–1197. doi:10.1016/j.jenvman.2010.11.020
- Gao XL, Chen CTA (2012) Heavy metal pollution status in surface sediments of the coastal Bohai Bay. *Water Res* 46:1901–1911. doi:10.1016/j.watres.2012.01.007
- Gao XL, Zhou FX, Chen CTA (2014) Pollution status of the Bohai Sea: an overview of the environmental quality assessment related trace metals. *Environ Int* 62:12–30. doi:10.1016/j.envint.2013.09.019
- Ghrefat HA, Abu-Rukah Y, Rosen MA (2011) Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafra Dam, Jordan. *Environ Monit Assess* 178:95–109. doi:10.1007/s10661-010-1675-1
- Hakanson L (1980) An ecological risk index for aquatic pollution-control—a sedimentological approach. *Water Res* 14:975–1001. doi:10.1016/0043-1354(80)90143-8
- He ZP, Song JM, Zhang NX, Zhang P, Xu YY (2009) Variation characteristics and ecological risk of heavy metals in the south Yellow Sea surface sediments. *Environ Monit Assess* 157:515–528. doi:10.1007/s10661-008-0552-7
- Hu NJ, Shi XF, Liu JH, Huang P, Yang G, Liu YG (2011) Distributions and Impacts of Heavy Metals in the Surface Sediments of the Laizhou Bay. *Adv Mar Sci* 29:63–72 (in Chinese)
- Hu BQ, Li J, Zhao JT, Yang J, Bai FL, Dou YG (2013) Heavy metal in surface sediments of the Liaodong Bay, Bohai Sea: distribution, contamination, and sources. *Environ Monit Assess* 185:5071–5083. doi:10.1007/s10661-012-2926-0
- Huang LL, Pu XM, Pan JF, Wang B (2013) Heavy metal pollution status in surface sediments of Swan Lake lagoon and Rongcheng Bay in the northern Yellow Sea. *Chemosphere* 93:1957–1964. doi:10.1016/j.chemosphere.2013.06.080
- Jiang X, Teng AK, Xu WZ, Liu XS (2014) Distribution and pollution assessment of heavy metals in surface sediments in the Yellow Sea. *Mar Pollut Bull* 83:366–375. doi:10.1016/j.marpolbul.2014.03.020
- Kiratli N, Ergin M (1996) Partitioning of heavy metals in surface Black Sea sediments. *Appl Geochem* 11:775–788. doi:10.1016/s0883-2927(96)00037-6
- Li SY, Miao FM, Liu GX, Hao J (1995) The primary study on the background values of heavy metals in sediments of the Bohai Sea. *Acta Oceanol Sini* 17:78–85 (in Chinese)
- Li XY, Liu LJ, Wang YG, Luo GP, Chen X, Yang XL et al (2012) Integrated assessment of heavy metal contamination in sediments from a coastal industrial basin NE China. *PLoS one* 7:e39690. doi:10.1371/journal.pone.0039690
- Liang LN, He B, Jiang GB, Chen DY, Yao ZW (2004) Evaluation of mollusks as biomonitors to investigate heavy metal contaminations along the Chinese Bohai Sea. *Sci Total Environ* 324:105–113. doi:10.1016/j.scitotenv.2003.10.021
- Liu JG, Diamond J (2005) China's environment in a globalizing world. *Nature* 435:1179–1186. doi:10.1038/4351179a
- Meng W, Qin YW, Zheng BH, Zhang L (2008) Heavy metal pollution in Tianjin Bohai Bay, China. *J Environ Sci* 20:814–819. doi:10.1016/s1001-0742(08)62131-2
- Mudroch A, Azcue JM, Mudroch P (1997) Manual of physico-chemical analysis of aquatic sediments. CRC Press, Boca Raton
- Müller G (1969) Index of geoaccumulation in sediments of the Rhine River. *GeoJournal* 2:108–118
- Pekey H (2006) The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. *Mar Pollut Bull* 52:1197–1208. doi:10.1016/j.marpolbul.2006.02.012
- Qiao YM, Yang Y, Gu JG, Zhao JG (2013) Distribution and geochemical speciation of heavy metals in sediments from coastal area suffered rapid urbanization, a case study of Shantou Bay, China. *Mar Pollut Bull* 68:140–146. doi:10.1016/j.marpolbul.2012.12.003
- Rubio B, Nombela MA, Vilas F (2000) Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. *Mar Pollut Bull* 40:968–980. doi:10.1016/s0025-326x(00)00039-4
- Shafie NA, Aris AZ, Zakaria MP, Haris H, Lim WY, Isa NM (2013) Application of geoaccumulation index and enrichment factors on the assessment of heavy metal pollution in the sediments. *J Environ Sci Health A Tox Hazard Subst Environ Eng* 48:182–190. doi:10.1080/10934529.2012.717810
- Shepard FP (1954) Nomenclature based on sand-silt-clay ratios. *J Sed Petrol* 24:151–158
- SOA (2007) The specification for marine monitoring-part 5: sediment analysis (GB17378.5-2007). Standards Press of China, Beijing
- SOA (2012) China marine environmental quality bulletin in 2011. China Oceanic Information Network. http://www.coi.gov.cn/gongbao/huanjing/201207/t20120709_23185.html
- SOA (2013) China marine environmental quality bulletin in 2012. China Oceanic Information Network. http://www.coi.gov.cn/gongbao/huanjing/201304/t20130401_26428.html
- SOA (2014) China marine environmental quality bulletin in 2013. China Oceanic Information Network. http://www.coi.gov.cn/gongbao/huanjing/201403/t20140325_30717.html
- State Oceanic Administration, P.R. of China (SOA) (2002) National standard—marine sediment quality (GB18668-2002). Standards Press of China, Beijing
- Teng YG, Tuo XG, Ni SJ, Zhang CJ (2002) Applying geoaccumulation index to assess heavy metal pollution in sediment: influence of different geochemical background. *Environ Sci Technol* 25:7–10 (in Chinese)
- Wang CY, Wang XL (2007) Spatial distribution of dissolved Pb, Hg, Cd, Cu and As in the Bohai Sea. *J Environ Sci* 19:1061–1066. doi:10.1016/s1001-0742(07)60173-9
- Wang J, Chen S, Xia T (2010) Environmental risk assessment of heavy metals in Bohai Sea, North China. *Procedia Environ Sci* 2:1632–1642. doi:10.1016/j.proenv.2010.10.174
- Wartel M, Skiker M, Auger Y, Boughriet A (1990) Interaction of manganese(II) with carbonates in seawater: assessment of the solubility product of MnCO₃ and Mn distribution coefficient

- between the liquid phase and CaCO₃ particles. *Mar Chem* 29:99–117. doi:[10.1016/0304-4203\(90\)90008-z](https://doi.org/10.1016/0304-4203(90)90008-z)
- WHO (1989) Toxicological evaluation of certain food additives and contaminants. IPCS Inchem Home. <http://www.inchem.org/documents/jecfa/jecmono/v024je01.htm>
- Wu JY, Li YF (1985) Environment geochemistry of some heavy metals in the sediments of Bohai Bay: I. The distribution pattern of heavy metals in the sediments and their background values. *Oceanologia Et Limnologia Sini* 16:92–102 (in Chinese)
- Xu ZQ, Ni SJ, Tuo XG, Zhang CJ (2008) Calculation of heavy metals' toxicity coefficient in the evaluation of potential ecological risk index. *Environ Sci Technol* 31:112–115. doi:[10.3969/j.issn.1003-6504.2008.02.030](https://doi.org/10.3969/j.issn.1003-6504.2008.02.030)
- Xu L, Wang TY, Ni K, Liu SJ, Wang P, Xie SW et al (2013) Metals contamination along the watershed and estuarine areas of southern Bohai Sea, China. *Mar Pollut Bull* 74:453–463. doi:[10.1016/j.marpolbul.2013.06.010](https://doi.org/10.1016/j.marpolbul.2013.06.010)
- Xu L, Wang TY, Ni K, Liu SJ, Wang P, Xie SW et al (2014) Ecological Risk Assessment of Arsenic and Metals in Surface Sediments from Estuarine and Coastal Areas of the Southern Bohai Sea, China. *Hum Ecol Risk Assess* 20:388–401. doi:[10.1080/10807039.2012.762281](https://doi.org/10.1080/10807039.2012.762281)
- Yuan HM, Song JM, Li XG, Li N, Duan LQ (2012) Distribution and contamination of heavy metals in surface sediments of the South Yellow Sea. *Mar Pollut Bull* 64:2151–2159. doi:[10.1016/j.marpolbul.2012.07.040](https://doi.org/10.1016/j.marpolbul.2012.07.040)
- Zhan SF, Peng ST, Liu CG, Chang Q, Xu J (2010) Spatial and temporal variations of heavy metals in surface sediments in Bohai Bay, North China. *B Environ Contam Tox* 84:482–487. doi:[10.1007/s00128-010-9971-6](https://doi.org/10.1007/s00128-010-9971-6)
- Zhang LJ, Wang G, Yao D, Duan GZ (2003a) Environmental significance and research of heavy metals in offshore sediments. *Mar Ecol Lett* 19:6–9. doi:[10.3969/j.issn.1009-2722.2003.03.002](https://doi.org/10.3969/j.issn.1009-2722.2003.03.002) (in Chinese)
- Zhang SM, Yan L, Wu JG (2003b) *Inorganic chemistry*, 3rd edn. Lanzhou University Press, Lanzhou
- Zheng N, Wang QC, Liang ZZ, Zheng DM (2008) Characterization of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China. *Environ Pollut* 154:135–142. doi:[10.1016/j.envpol.2008.01.001](https://doi.org/10.1016/j.envpol.2008.01.001)