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Extensive study of potential harmful elements (Ag, As, Hg, Sb, and Se) in surface sediments of the Bohai Sea, China: Sources and environmental risks☆

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ABSTRACT

This study analyzed 405 surface sediment samples, obtained from across the Bohai Sea, for concentrations of five potentially harmful elements (Ag, As, Hg, Sb, and Se) and several ancillary parameters (Al, Fe, Mn, total organic carbon (TOC), and grain size). Statistically, the spatial distributions of these elements were correlated positively with Al, Fe, TOC, and grain size, indicating natural sources for these elements or common accumulation mechanisms. The assessment of potential environmental risk with empirical sediment quality guidelines showed that a significant proportion of the samples had As and Sb concentrations that exceeded the effects range low (ERL) or T_{20} values in the Bohai Sea, indicating the potential for adverse biological effects. However, the assessment results differed when using evaluation methods that considered background values. Based on the geoaccumulation index (I_{geo}), Hg and Ag were found to have the highest percentages (35% and 60%, respectively) in samples that were moderately contaminated. The estimated contamination degree (C_d) suggested higher contamination levels for the entire area, with 69% of the samples being moderately contaminated. Generally, except for some local hotspots, such as Jinzhou Bay, the contamination levels of these elements in the Bohai Sea were established as slight to moderate. Samples from the Jinzhou Bay area had concentrations that were 10–100 times higher than in the rest of the Bohai Sea, indicating severe contamination.

1. Introduction

In the natural environment, As, Hg, Sb, Se, and Ag are considered potential harmful elements (PHEs) when their concentrations exceed certain levels. They can also be categorized as atmophile elements, because their mass transport through the atmosphere is often greater than via streams (Stumm and Morgan, 1996). Elements of this category are often volatile and their oxides have low ignition points. They can be transported in association with the burning of coal, gas, and methane, or released into the atmosphere during the processes of cement production or metal smelting. It is considered that Ag, Hg, and Sb are among the most potentially hazardous elements on global or regional scales (Andreae, 1986; Sposito, 1986). These B-type metals (i.e., soft Lewis acids) have a tendency to react with soft bases such as SH and NH groups in enzymes and therefore they are especially hazardous to both ecological and human health (Stumm and Morgan, 1996). Furthermore, like other metals, such elements cannot be degraded, and when deposited in surface sediments, they become a permanent threat to marine life. Following either direct consumption by bottom-feeders or re-desorption back into the overlying water, PHEs constitute a potential threat to human life, mainly through the consumption of fish products. Tragic incidents that have occurred in Japan in the 1950s, and subsequently, provide examples of Hg poisoning (Harada, 1995).

The Bohai Sea, located in northeastern China, covers an area of 77,000 km^2. It is the largest inland sea of China. As a semi-enclosed water body, the Bohai Sea is relatively shallow with a mean water depth of ~18 m. The area surrounding the Bohai Sea is one of the most developed areas in China and accounts for 25% of China's GDP (Pan et al., 2010). Following the rapid growth of industry and

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population during the past 30 years in this region, the Bohai Sea now receives considerable discharges of municipal and industrial wastewater (Wang et al., 2009). Chen et al. (2013) showed that the fluxes of As, Hg, Sb, and Se released into the air through the burning of coal in 2009 were about 236, 637, 172, and 22 tons, respectively, and these numbers are increasing annually. Consequently, the Bohai Sea is under intense pressure ecologically (SOA, 2012). In addition, the fishery stock has dropped dramatically because of overfishing, and to satisfy the large demand for seafood, extensive areas of aquaculture farming have become distributed along the Bohai Sea coast (Sun et al., 2014). The combination of the deteriorated marine environment and large-scale aquaculture operation has meant that the sediment quality of the Bohai Sea has become the focus of scientific research and environmental monitoring studies.

During 2007–2008, an extensive nearshore survey, the National Integrated Monitoring and Assessment Project in Coastal China Seas (hereafter referred to as the 908 project), was conducted along the Chinese coast and it included the Bohai Sea. Surface sediment samples were collected with high spatial resolution from across the entire area of the Bohai Sea. The 908 project analyzed the samples for most major elements but considered only a few trace elements (Shi et al., 2014). The current study selected 405 surface sediment samples from the sample repository of the 908 project and analyzed the Ag, As, Hg, Sb, and Se concentrations. The spatial distributions of these five elements were determined, their possible sources discussed, and their potential toxicity and ecological risk assessed. In recent years, extensive studies have been conducted to investigate heavy metal concentrations in the sediments of the Bohai Sea, whereas few studies have considered these five selected elements. Hg and As concentrations in surface sediment were reported more often in some specific regions of the Bohai Sea, such as the Bohai Bay (Meng et al., 2008), the Liaodong Bay (Hu et al., 2010), the Laizhou Bay (Zhuang and Gao, 2015), and nearshore areas (Li and Li, 2008). In contrast, studies on Ag in the Bohai Sea are less reported (Feng et al., 2011; Hu et al., 2012), and studies on Sb and Se are rare (Duan et al., 2010). Furthermore, it can be difficult to compare regional differences when various analytical procedures have been employed. Studies of PHEs in the Bohai Sea on such an extensive scale have not been reported before.

2. Material and methods

2.1. Sample collection

Samples of surface sediment were collected on multiple sampling expeditions during the 2-year period of 2007–2008 for the 908 project. Sediment samples were collected using either stainless steel sediment grabs or box corers. Material from the surface (<2 cm) layers was transferred into clean polyethylene bags using plastic spoons (without touching the sides of the samplers). The sediment samples were then stored onboard the survey vessel in a refrigerator at 4 °C. When transported back to shore, the samples were transferred to laboratory refrigerators until they were archived and stored in the sample storage rooms (4 °C) of the China Ocean Sediment Sample Repository, located in the First Institute of Oceanography in Qingdao, China. Here, 405 sediment samples obtained in March 2012 were selected from the sample pool of the 908 project; the sampling station locations are shown in Fig. 1. Subsamples of about 10 g (wet weight) were extracted and analyzed for the metals of interest (Ag, As, Hg, Sb, and Se). The concentrations of Fe, Al, Mn, and total organic carbon (TOC) were also determined as ancillary parameters.

The wet sediment samples were freeze-dried for 48 h and then stones, dead material of plants and animals, and shells were removed carefully using plastic tweezers. The samples were then ground to 200 mesh using either an agate mortar or grinding machine (Retsch RS200). All labware that had contact with the samples was cleaned using weak acid and deionized water in between the preparation of each sample.

2.2. Ag, As, Hg, Sb, and Se analyses

About 0.25 g of each sediment sample was weighed (to accuracy of 0.0001 g) and added to a 25-mL pre-cleaned polyethylene tube, to which 10 mL of freshly made 1:1 aqua regia solution was added. The mixture was then shaken well and placed in a water bath at 100 °C for 1 h. The 1:1 aqua regia solution was made with 1 L Milli-Q (a Milli-Q system with a resistivity of 18.2 MΩ) water (Q water) and 1 L aqua regia ($HCl:HNO_3 = 3:1$). The tubes were then removed from the water bath and diluted to 25 mL with QW. The solution was then allowed to rest overnight. Subsequently, 3 mL of the overlying solution was removed and diluted to 10 mL with 2% HNO_3 for the Ag analysis. A further 8 mL was removed for the Se and Hg analysis, and 2 mL was removed and placed in 15-mL centrifuge tubes, to which 6 mL of 33% HCl and 2 mL sulfo-carbomide–ascorbic acid solution (50 g L^{-1}, 25 g sulfo-carbomide and 25 g ascorbic acid in 1 L QW) were added. The reduction reaction was allowed to continue for over 30 min before the analysis for As and Sb was conducted. All containers and labware that had contact with the samples were pre-cleaned in acetone, followed by an alkaline detergent (cleaned thoroughly in between with deionized water), and then stored in 7% HCl for over a week. Afterwards, the containers were rinsed thoroughly (five or six times) with QW. The concentrated HNO_3 and HCl used in the experiments were distilled in the laboratory from trace metal-grade acid (National Chemical Production Inc., China) using acid purification systems (Savillex DST-1000).

The As, Hg, Sb, and Se analyses were conducted using a double-channel atomic fluorescence photometer (AFS-930, Beijing Ji-Tian Ltd., China). The analysis of Ag was performed using ICP-MS (Thermofisher XII). The detection limits were 0.04 μg g^{-1} for As, 0.002 μg g^{-1} for Hg, 0.028 μg g^{-1} for Sb, 0.006 μg g^{-1} for Se, and 0.001 μg g^{-1} for Ag. The analytical blanks were 0.39 ± 0.01 μg g^{-1} for As, 0.0005 ± 0.0007 μg g^{-1} for Hg, 0.036 ± 0.009 μg g^{-1} for Sb, 0.003 ± 0.002 μg g^{-1} for Se, and 0.0002 ± 0.0004 μg g^{-1} for Ag. Several Chinese marine sediment standards (GBW07344, GBW07345, and GBW07306 for As, Hg, Sb, and Se and GBW07309 for Ag) were analyzed ($n = 6$ for each standard) to ensure data quality, and the analytical results were all within the certified values. Replicate analyses were conducted for 10% of the samples and the relative deviations were <10% for all elements.

2.3. Other analyses

For the analyses of Al, Fe, and Mn, a sample of about 50 mg (measured to accuracy of 0.01 mg) was digested with 1.5 mL HNO_3 and 1.5 mL HF at 190 °C for 48 h. In the final step, the digested solution was diluted to 50 mL with QW before analysis with ICP-OES. The recoveries for MESS-3 and PACS-2 (Marine Sediment Reference Materials, National Research Council of Canada) were within the range 95–103% ($n = 15$) for Al, Fe, and Mn. TOC was analyzed with an elemental analyzer (Model EL-III, Vario) in triplicate and the average values were reported. The recovery of TOC was 96–104% ($n = 12$), which was assessed by analyzing Acetanilide (China Reference Material GBW060239) and the relative errors of the samples analyzed in triplicate were <6%. A laser particle size analyzer (Mastersizer, 2000; Malvern Instruments), able to analyze particle sizes within the range 0.02–2000 μm, was used to determine grain size. The particles were categorized according to the

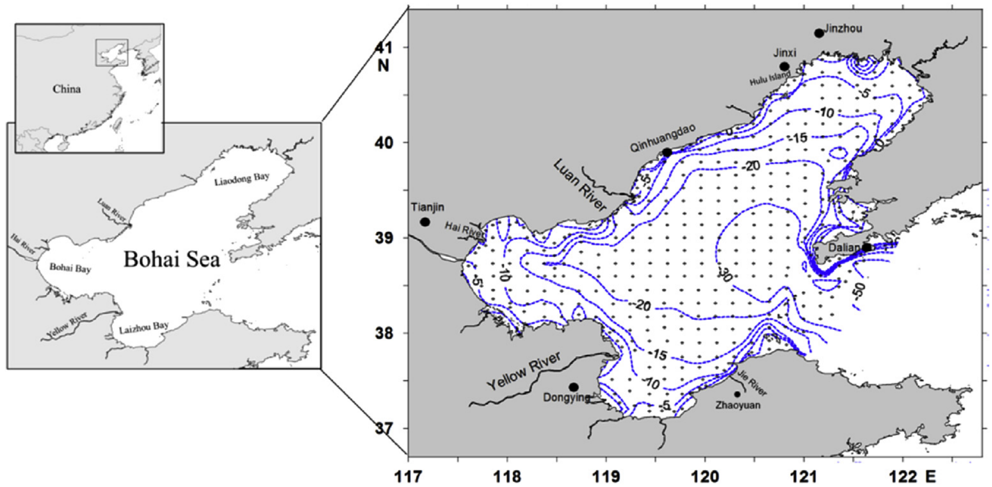

Fig. 1. Station locations ($n = 405$) in the Bohai Sea. Blue dot lines are depth contours. Open dimands are station locations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

following three size ranges: <4 μm (clay), 4–63 μm (silt) and >63 μm (sand).

3. Results and discussion

3.1. Ag, As, Hg, Sb, and Se concentrations in sediments

The average concentrations established in this study for Ag, As, Hg, Sb, and Se, together with the TOC, are reported in Table 1, in addition to data reported in previous studies of the Bohai Sea, other coastal areas of China, and other countries. Zhao and Yan (1994) reported surficial sediment data of these five selected elements based on 44 samples collected during 1958–1960 in the Bohai Sea (locations were spread evenly across the study area). Their data are comparable with the data found in this study, indicating that the average concentrations of these five elements in the Bohai Sea have not changed significantly over the past 50 years. However, the average concentrations of As, Se, and especially Hg, were all found to be slightly higher in this study compared with the values reported by Zhao and Yan (1994). The average concentration of Hg found in this study (0.054 μg g^{-1}) is 50% higher than that reported in Zhao and Yan (1994) (0.036 μg g^{-1}). In addition, the maximum concentrations found for these five elements are much higher compared with the values reported by Zhao and Yan (1994). This might indicate that some hotspots have emerged or been newly identified in this study. Indeed, some of the sampling locations in this study were closer to the shoreline compared with the locations used by Zhao and Yan (1994). Higher concentrations of Hg are often found in nearshore coastal areas or river mouths of the Bohai Sea (Li and Li., 2008; Meng et al., 2008). Zhuang and Gao (2015) reported higher Hg concentrations in river sediments (0.17–0.21 μg g^{-1}) compared with nearshore sediments (0.03–0.04 μg g^{-1}) in Laizhou Bay, while differences in concentrations of As were less apparent. The average concentration of As (9.9 μg g^{-1}) is similar to As data reported recently. Recent reports of Ag and Sb data in the Bohai Sea are scarce, although a few studies have reported higher average

Table 1
The average concentrations and ranges of As, Hg, Sb, Se, and Ag, compared with data reported in other coastal areas.

	As	Hg	Sb	Se	Ag	Reference
Bohai Sea ($n = 405$)	9.9 ± 5.6 (2.8–83.5)	0.054 ± 0.21 (0.002–4.1)	0.63 ± 0.25 (0.11–1.8)	0.16 ± 0.09 (0.02–1.3)	0.07 ± 0.04 (0.018–0.97)	*This study*
Bohai Sea ($n = 44$)	9.0 (4.1–18.8)	0.036 (0.012–0.085)	0.6 (0.3–1.3)	0.12 (0.02–0.24)	0.075 (0.041–0.14)	Zhao and Yan, 1994
Bohai Bay, Bohai Sea ($n = 27$)	5.56 (3.35–7.78)		1.51 (1.14–2.29)			Duan et al., 2010
Bohai Bay, Bohai Sea ($n = 11$)	8.7 (6.4–16.5)	0.30 (0.02–0.85)				Meng et al., 2008
Liaodong Bay, Bohai Sea ($n = 128$)	8.3 (3.1–20.3)	0.04 (0–0.4)				Hu et al., 2010
Bohai Bay, Bohai Sea (*12 sediment cores*)					0.194–2.1	Feng et al., 2011
Laizhou Bay, Bohai Sea ($n = 18$)[a]	9.5–10.5	0.035				Zhuang and Gao, 2015
Laizhou Bay, Bohai Sea ($n = 32$)					0.3 ± 0.1	Hu et al., 2012
Nearshore areas in Bohai Sea ($n = 41$)	9.7 (2.3–23.9)	0.13 (0.004–3.1)				Li and Li, 2008
Coastal and estuarine areas of the northern Bohai and Yellow Seas ($n = 35$)	8.5 (5.6–13)	0.028 (0.02–0.18)				Luo et al., 2010
Yangze River estuarine (n = 30)	4.5–30.2	0.01–0.4	0.36–1.48	0.04–0.38		Duan et al., 2014
Beibu Gulf, South China Sea ($n = 121$)	8.1 ± 5.8	0.034 ± 0.028				Gan et al., 2013
Pearl River Estuary, China ($n = 28$)	21.1 (5.5–35.6)	0.2 (0.01–0.4)				Huang et al., 2006
Jobos Bay, Puerto Rico ($n = 43$)	12.8 (1.79–28.1)	0.031 (0.001–0.144)	0.269 (0–0.589)	1.17 (0–2.74)	0.105 (0.051–0.219)	Apeti et al., 2012
South Florida, USA	2.5–10	0.1–0.2	0.2–0.6	0.2–0.8	0.1–0.3	Cantillo et al., 1999

** Numbers in the parentheses are concentration ranges

[a] Only average concentrations of coastal sediment results from Zhuang and Gao (2015) were considered here.

concentrations compared with our study, which might be due to regional differences because these other studies all focused on a specific region (Duan et al., 2010; Feng et al., 2011; Hu et al., 2012). Unfortunately, no recent Se data for the Bohai Sea are available. Studies in the Yangtze River have reported a similar range of Se concentration as found in this study, while studies conducted in Jobos Bay in Puerto Rico and in southern Florida in the United States have all reported higher Se concentrations (Apeti et al., 2012; Cantillo et al., 1999), which could be due to regional differences in background Se.

3.2. Spatial distributions

The spatial distribution of TOC and median particle size (ϕ) are shown in Fig. 2. A prevalence of finer sediments (ϕ > 6.5) was found in a band covering the area of western–central Bohai Bay and continuing all the way to northeastern parts of the central Bohai Sea, toward Qinhuangdao. Other pockets of fine-grained sediment were often observed near major cities, such as Jinxi and Dalian, and near the mouth of the Yellow River. Except for one station near Jinxi (also near Hulu Island, Jinzhou Bay) that had a TOC content of 2.7%, the average TOC content is 0.33± 0.26% (range: 0.01–1.65%) across the rest of the sea. The overall spatial distribution of higher TOC content shared many similarities with the distribution of finer sediments, indicating that TOC and PHEs are found in areas with finer particles.

The spatial distributions of PHEs are shown in Fig. 3. Generally, in the sediments, higher concentrations of PHEs are associated with higher TOC contents. Specifically, the spatial distributions of As, Sb, and Se share greater similarity with TOC and grain size, while the spatial distributions of Hg and As are similar. There are several noteworthy features of the spatial distributions of PHEs.

First, higher concentrations of all elements were found in the region of Jinzhou Bay, west of Liaodong Bay. A few stations near Jinzhou Bay had concentrations 10 to 100 times greater than the average concentrations of the Bohai Sea. The concentrations of Hg found in two stations near Jinzhou Bay (4.1 and 1.4 μg/g) were much higher than in the rest of bay (0.03–0.06 μg/g) (as shown in Fig. 3). Those stations with high Hg concentrations also had high As, Se, Sb, and Ag concentrations, although the TOC content at the two stations varied (0.66% and 2.7%). One other station with relatively high concentrations of As (51 μg g^{-1}), Ag (0.68 μg g^{-1}), and Sb (1.47 μg g^{-1}) had only a moderate TOC concentration (0.65%). Apparently, heavily contaminated stations can contain high PHE concentrations even when the TOC contents are relatively low. Jinzhou Bay, together with the coastal area of Hulu Island, is known for the heavy contamination status of its sediments (Chen et al., 2004; Luo et al., 2010; Zheng et al., 2008). Industries that include the Jinxi refinery, Huludao zinc plant (the largest zinc smelting plant in China), and Jinxi chemical complex are all located in this area, and the concentrations of metals in the sediments have been found to be increasing since the 1980s (Qiao, 1991).

Second, areas near several major cities, such as Qinhuangdao, Dalian and Tianjin, exhibited relatively high concentrations. For example, the coastal area of Qinhuangdao had an elevated concentration of PHEs, especially Hg and Ag. Qinhuangdao is a city of 3 million people and it has a large port. Coal transportation is one of the major activities of Qinhuangdao port, contributing about 40% of water-borne coal transportation in China (reaching 246 million tons of coal per year in 2014) (http://www.p5w.net/stock/hkstock/hknews/201507/t20150702_1108192.htm). We suspect that in addition to sewage discharge from the city, fly ash from the daily coal-loading activity (approximately 700,000 tons per day) in the port could have contributed to the elevated concentrations of the studied elements found in the Qinhuangdao area. Other major cities within the study area, e.g., Dalian on the east coast and Tianjin on the northwest coast of Bohai Bay, all had slightly elevated concentrations of these elements in their nearshore sediments. Tianjin and Dalian are major cities with populations of 15.2 and 6.7 million, respectively, and they both have large ports (cargo handling capacities reached 500 and 145 million tons, respectively, in 2014).

Finally, far from major cities, slight elevations of PHEs were found in two locations. One was near the Jie River, which is located in Zhaoyuan County, Laizhou Bay. Zhaoyuan County is famous for its gold mining business and therefore associated contaminants are observed in the river and nearby estuarine sediments. Concentrations of As of up to 73.9 μg g^{-1} have been found in the sediments of the Jie River (Xu et al., 2013). The other location was in the northern Bohai Strait, where higher concentrations of Sb, Se, and especially As were found in the sediments. In this area, the sediment grain size was coarse and the TOC content was low, but high Fe and Mn concentrations were also found within this area. A Spearman correlation analysis showed that As, Sb, Se, Fe, and Mn are all significantly correlated with each other ($n = 14$, $p < 0.05$). This characteristic has been found before and it might be related to the adsorption of As, Sb, and Se on Fe/Mn oxides that are coated on the sandy sediment (Rubio et al., 2000; Shi et al., 2014).

3.3. Statistical analysis of PHEs and ancillary parameters

A correlation analysis was performed for all the variables to interpret their interrelationships. The purpose of this analysis was to examine the general pattern of the large data set and therefore the high values (labeled in Fig. 3) were excluded from the statistical

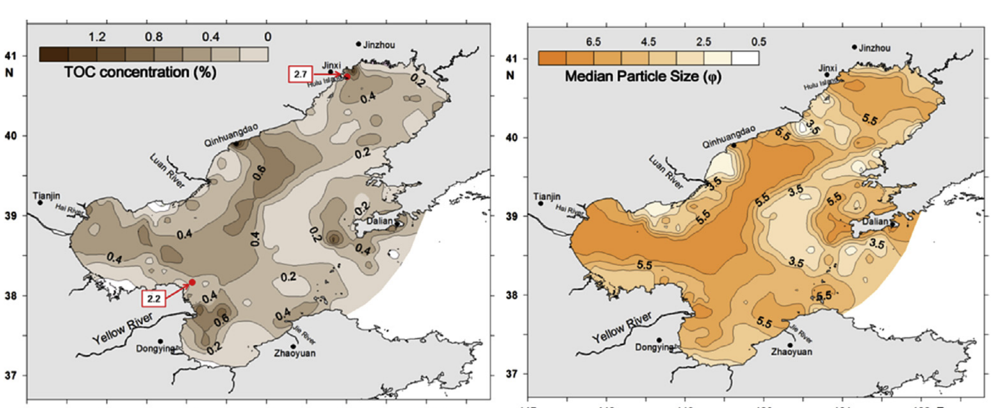

Fig. 2. Spatial distributions of the TOC content and median particle size (φ) in the Bohai Sea. Two stations with high TOC values (2.2% and 2.7% respectively) are labeled individually.

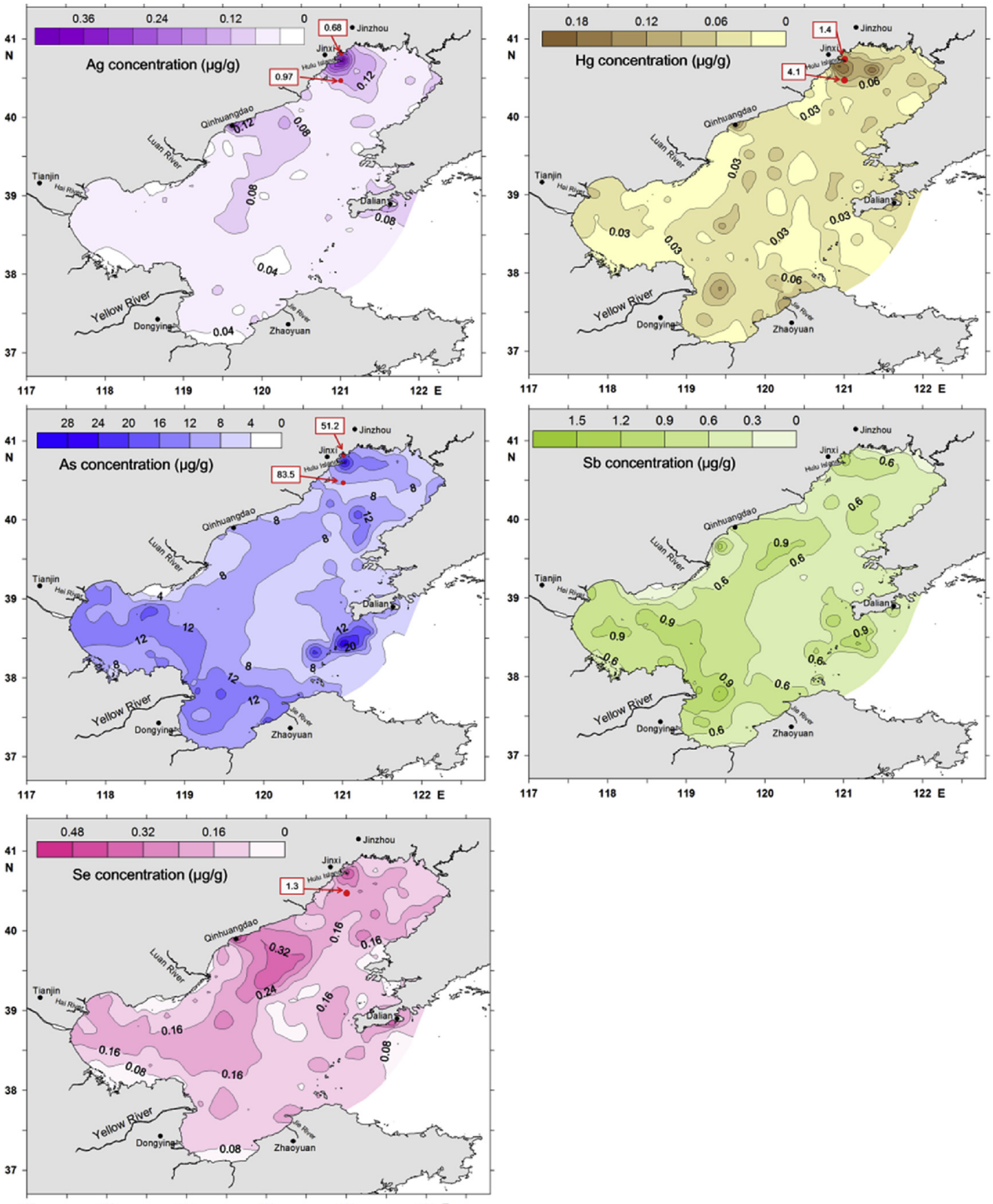

Fig. 3. The spatial distributions of Ag, Hg, As, Sb, and Se, in the Bohai Sea.

analysis. As most variables were not distributed normally, a Spearman correlation analysis was used. The results showed that all variables, including PHEs, TOC, Fe, Mn, and grain size, were significantly correlated with each other ($p < 0.01$), indicating that the accumulations of these elements in sediments are controlled largely by similar accumulation mechanisms, such as adsorption on particle surfaces or complexation with organic content. Additionally, significant correlation between Al and PHEs indicates lithogenic/natural sources for these elements. Analyses of other metals based on samples from the 908 project have suggested that grain-size distribution, which is driven by hydrodynamic forces, plays a major role in the spatial distributions of a suite of metals (e.g., Cu and Pb) in the surface sediments of the Bohai Sea (Shi et al., 2014).

A principal component analysis (PCA) was conducted for all the variables to assess their relationships and to identify possible sources for these elements. The PCA was conducted using SPSS 22.0 and the results are shown in Fig. 4. The component matrix shows that the first two principal components accounted for 74% of the total variance of the data set. Principal components 1 and 2 (PC1 and PC2) explained 58% and 16% of the variance, respectively. All other factors explained <26% of the variance and they were not retained for further evaluation. Essentially, all variances have relatively high loadings on PC1 (all values: >0.5) and the highest PC1 loadings were for Al, Fe, and TOC. High factor loadings imply that these metals contributed to and were strongly influenced by the principal component. The high PC1 loadings for Fe, TOC, and Al

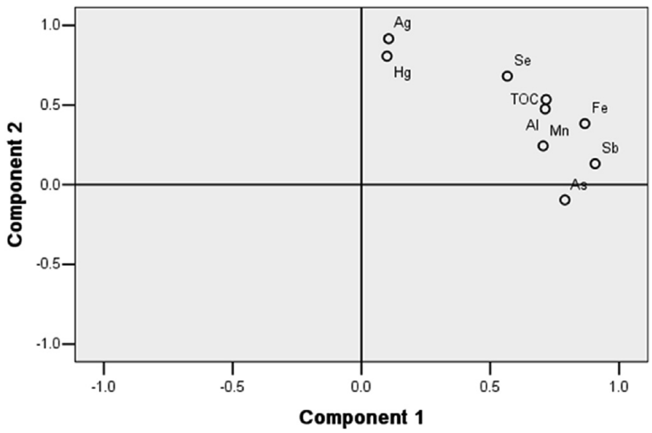

Fig. 4. Rotated diagram of principle component analysis result.

suggest that these five elements are generally derived from lithogenic sources or accumulated by similar mechanisms, which is in accordance with the results of the Spearman correlation analysis. PC2 had high loading on Hg and Ag, indicating that these two elements are heavily influenced by similar sources, such as anthropogenic contamination. It is known that Ag can be used as a tracer for sewage in seawater and sediment (Ravizza and Bothner, 1996; Sanudo-Willhelmy and Flegal, 1992). The spatial distribution of Ag showed that higher concentrations were often found in coastal areas very close to major cities, such as Jinzhou Bay, Qinhuangdao, and Dalian, as was the case for Hg.

3.4. Ecological relevance of sediment PHE concentrations

The concentrations in the sediments of the five selected elements were assessed for potential toxicity using three approaches: sediment quality guidelines (SQGs), geoaccumulation indices (I_{geo}), and contamination degree (C_d).

3.4.1. Sediment quality guidelines

The SQGs are defined based on a large data set of concentrations of certain metals associated with adverse biological effects. The SQGs employed here were the Chinese SQGs Class I and Class II (CSQG I/CSQG II) (CEPA, 2002), threshold/probable effects level (TEL/PEL), and the effects range low/median (ERL/ERM). The latter two are the SQGs used most commonly to assess marine or estuarine sediment toxicity, as recommended by the Environmental Protection Agency of the United States (USEPA) (ANZECC, 1997; Long et al., 1995; Macdonald et al., 1996). The assessment results are shown in Table 2. No SQGs were found for Se and therefore this element is not included in the table. The SQGs used for Sb are T_{20} and T_{50} values, which are defined as concentrations above which there would be 20% and 50% possibilities that adverse biological effects would occur (Field et al., 2002). Overall, only a few stations exceeded the standards of CSQG I and II for Hg and As. These stations were mainly located in Jinzhou Bay, among which two stations had very high Hg concentrations, exceeding both the CSQG Class III (1.0 μg g^{-1}) and the ERM values, indicating severe contamination within that area. A number of stations had As and Sb concentrations that exceeded the ERL/TEL or the T_{20} values (about 60% and 40%, respectively), while only a few exceeded the ERM/TEP values. Most stations had As and Sb concentrations within the range between the ERL/T_{20} and ERM/T_{50} values, indicating slight to moderate contamination for those two elements within the sediments. Based on the USEPA SQGs, a reasonably large area of the Bohai Sea was found to have anthropogenic contamination of As and Sb, categorized as moderate contamination that could cause adverse biological effects. Furthermore, in the area of Jinzhou Bay, some stations had severe contamination, indicating apparent anthropogenic sources for As and Hg.

One deficiency of the SQGs is that they do not consider natural background levels or multiple metals. For example, some elements might occur naturally in greater concentrations in specific regions. To overcome the limitations of the USEPA SQG_S, concentrations in the sediments were assessed using the geoaccumulation index (I_{geo}) and contamination degree, which are methods that include background or reference values in the calculation and assessment of the contamination level.

3.4.2. Determination of background values

To assess the sediment contamination level based on ecological risk-assessment criteria, it is important to establish appropriate background values for the elements of interest. Unfortunately, no earlier background data for the five selected elements were available for the study area. Our group has analyzed six sediment cores (140–200 cm in length) obtained from Bohai Bay, Laizhou Bay, and the central Bohai Sea (collected during 2007–2008) and studied them for background values for As, Hg, Sb, and Se (Zhu et al., unpublished data). The results of this analysis are shown in Table 3, together with data from Zhao and Yan (1994), which represent values for comparison based on samples collected in the 1960s, i.e., before the economic boom in China. In addition, the CSQG I, ERL, TEL, and T_{20} values suggest little or no adverse biological effects and therefore they are also included in the table for comparison, together with reported values for the upper continent crust in China (Li, 1994). After careful comparison of these values, the As, Hg, Sb, and Se data reported by Zhu et al. (unpublished data) were chosen as the background values for the current study. The Ag data reported by Zhao and Yan (1994) were used as the background values for Ag.

3.4.3. Geoaccumulation index

The geoaccumulation index (I_{geo}), originally introduced by Muller (1979), was employed here to separate the anthropogenic influences on the sediment from the natural influences. The index is defined by the following equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5B_n}\right)$$

Table 2
Number of stations (percentages in parentheses) that exceeded the sediment quality guidelines.

	Ag	Hg	As	Sb
CSQG I[a]	–	0.2	20	–
CSQG II[a]	–	0.5	50	–
ERL (T_{20})[b]	1.0	0.15	8.2	0.63
ERM (T_{50})[b]	3.7	0.71	70	2.4
TEL[c]	0.73	0.13	7.24	–
PEL[c]	1.77	0.7	41.6	–
> CSQG I	–	3	9	–
> CSQG II	–	2	2	–
> ERL (T_{20})	0	6	241 (60%)	174 (43%)
> ERM(T_{50})	0	2	1	0
> TEL	1	8	286 (71%)	–
> PEL	0	2	2	–

[a] CSQG I (Chinese sediment quality guideline, Class I); CSQG II (Chinese sediment quality guideline, Class II). CEPA, 2002
[b] For Hg, As, Ag, ERL/ERM values are used; for Sb, T20 and T50 values are used. ERL: effects range low; ERM: effects range median; T20: concentration when 20% adverse effect occur; T50, concentration when 50% biological adverse effect occur. Long et al., 1995; Field et al., 2002.
[c] TEL: threshold effect level; PEL: probable effect level. Macdonald et al., 1996

Table 3
Comparison of Ag, As, Hg, Sb, Se reference concentrations and the background concentrations determined.

Element *(unit: μg g⁻¹)*	CSQG I[a]	ERL[a]	TEL[a]	T_{20}[a]	CUCC[b]	Zhao and Yan (1994)[c]	Zhu et al.[d]	Background values determined
Ag	–	1	0.73	0.23	0.054	0.075	–	0.075
As	20	8.2	7.24	7.4	2.5	9	9.99	9.99
Hg	0.2	0.15	0.13	0.14	0.089	0.036	0.026	0.026
Sb	–	0.63	–	0.63	0.19	0.6	0.67	0.67
Se	–	–	–	–	0.068	0.12	0.12	0.12

[a] CSQG I (Chinese sediment quality guideline, Class I). CEPA, 2002; ERL: effects range low. Long et al., 1995; TEL: threshold effect level. Macdonald et al., 1996; T20: concentration when 20% adverse effect occur. Field et al., 2002.
[b] CUCC: Chinese Upper Continental Crust. Li, 1994.
[c] Zhao and Yan, 1994.
[d] Zhu et al., unpublished data. First institute of Oceanography, Qingdao, China.

where C_n is the measured sediment concentration of the metal of interest (n) and B_n is the geochemical background concentration of metal (n). A factor of 1.5 was used as the background matrix correction factor because of lithogenic effects (Muller, 1979). Seven classes of geoaccumulation indices were defined, ranging from class 0 ($I_{geo} \le 0$) to class 6 ($I_{geo} > 5$, i.e., extremely polluted). The I_{geo} values of 0–1 indicate slight to moderate contamination and values of 1–2 represent moderate contamination. The percentages of samples that had $0 < I_{geo} < 1$ were 5%, 35%, 6%, 28%, and 60% for As, Hg, Sb, Se, and Ag, respectively, indicating slight to moderate contamination. The percentages of samples that had $1 < I_{geo} < 2$ were 0%, 6%, 0%, 1%, and 7% for As, Hg, Sb, Se, and Ag, respectively, indicating moderate contamination. Only a few samples had $I_{geo} > 2$. Overall, based on the I_{geo} values, most sediment samples in the Bohai Sea were slightly influenced by anthropogenic sources, following in the order of Ag > Hg > Se > Sb > As. The I_{geo} values indicated that Hg and Ag had the largest areas that were influenced by anthropogenic sources. Therefore, although there was a significant proportion of samples for which the As and Sb concentrations exceeded the ERL/T_{20} values, they had the least number of samples that exceeded the I_{geo} values when background values were taken into consideration.

3.4.4. Contamination degree

The contamination degree (C_d), defined as the sum of all contamination factors (C_f^i) for a given basin, can be calculated using the following equation (Hakanson, 1980):

$$C_d = \sum_{i=1}^{5} C_f^i = \sum_{i=1}^{5} \frac{C_{sample}^i}{C_n^i}$$

where C_{sample}^i is the element concentration of the sample and C_n^i is the background concentration. Based on their degree of contamination, the sediments were classified into the following groups: $C_d < 5$ (low degree of contamination), $5 \le C_d < 10$ (moderate degree of contamination), $10 \le C_d < 15$ (considerable degree of contamination), and $15 \le C_d$ (very high degree of contamination). The spatial distribution of C_d is shown in Fig. 5. The calculated values of C_d indicate a high percentage of anthropogenically affected areas: 69% of the sites had values of $5 \le C_d < 10$, suggesting a moderate degree of contamination, 17% of the sites had values of $10 \le C_d < 15$, suggesting a considerable degree of contamination, and only 2% ($n = 7$) of the sites (mainly located in Jinzhou Bay) had values of $C_d \ge 15$. Two stations in the Jinzhou Bay area had very high C_d values (208 and 76), which indicated severe contamination status.

Compared with the SQGs, the assessment methods that consider background values should be more reliable. However, assessment methods such as C_d and I_{geo} might overestimate the contamination level because they give equal importance to all elements. For example, As and Hg are known for their toxicity, even when their concentrations are very low, and therefore when individual I_{geo} values for As, Hg, Sb, Se, and Ag are similar, one of the elements might pose a greater threat to benthic organisms than the others.

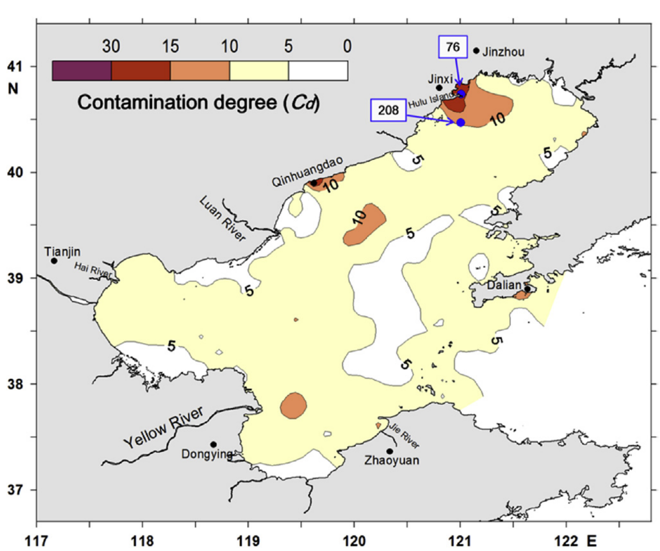

Fig. 5. The spatial distribution of the contamination degree (C_d) values. Two stations with extremely high C_d values are labeled individually.

4. Conclusions

The spatial distributions of Ag, As, Hg, Sb, and Se in the Bohai Sea have been studied in detail based on 405 surface sediment samples. Some hotspots were identified in the Bohai Sea, and Jinzhou Bay exhibited the highest contamination level. Areas near several major cities with ports, e.g., Qinhuangdao, Dalian, and Tianjin, also had elevated PHE concentrations in nearby sediments. Generally, the spatial distributions of these elements coincided with grain-size and TOC distributions, with higher concentrations found in finer sediments or sediments with higher TOC contents. Statistical analysis showed that these five elements are significantly correlated with sediment grain size, Al, Fe, and TOC contents, which indicates that these elements are derived from lithogenic sources or they are controlled by similar accumulation factors. In addition, PCA analysis showed that Hg and Ag have similar sources that could possibly be sewage discharge or aerosol dispersal from city/port areas.

An ecological assessment was conducted to assess the potential biological toxicity of these elements using SQGs and two other assessment approaches (I_{geo} and C_d). A significant proportion of samples (60%–70%) had As contents that exceeded the TEL/ERL, while about 40% of samples had Sb contents that exceeded T_{20}, indicating the potential for adverse biological effects to occur because of the concentrations of As and Sb in the surface sediments of the Bohai Sea. However, in comparison with the SQGs, the assessment methods that consider background concentrations yielded different results. Background values of the five selected elements were determined by comparing available data from the study area. The assessment with I_{geo} showed that 5%–60% of stations had slight to moderate contamination following in the order of Ag > Hg > Se > Sb > As, and <10% of stations had moderate contamination for these five elements. The calculated C_d showed that about 70% of the area had moderate contamination, about 20% had considerable contamination, and only 2% (mostly in Jinzhou Bay) had severe contamination. Overall, except for the Jinzhou Bay area, the contamination level of these five elements in the Bohai Sea is slight to moderate. Among these five elements, Ag and Hg are most concerning in terms of toxicity. The spatial distributions of Ag and Hg indicate apparent anthropogenic sources, and 35%–60% of the surface sediments in the Bohai Sea showed slight to moderate contamination with Hg and Ag.

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References

Andreae, M.O., 1986. The oceans as a source of biogenic gases. Oceanus 29 (4), 27–35.
ANZECC (Australian and New Zealand Environment and Conservation Council), 1997. ANZECC interim sediment quality guidelines. Report for the Environmental Research Institute of the Supervising Scientist, Sydney, Australia.
Apeti, D.A., et al., 2012. Characterization of land-based sources of pollution in Jobos Bay, Puerto Rico: status of heavy metal concentration in bed sediment. Environ. Monit. Assess. 184, 811–830.
Cantillo, A.Y., Lauenstein, G.G., O'Connor, T.P., Johnson, W.E., 1999. Status and trends of contaminant levels in biota and sediments of South Florida. NOAA Reg. Rep. Ser. 40 (2).
CEPA (State Environmental Protection Administration of China), 2002. Marine Sediment Quality (GB 18668–2002). Standards Press of China, Beijing, China.
Chen, J., et al., 2013. Atmospheric emissions of F, As, Se, Hg and Sb from coal-fired power and heat generation in China. Chemosphere 90, 1925–1932.
Chen, J., Liu, W., Liu, S., Lin, X., Tao, S., 2004. An evaluation on heavy metal contamination in the surface sediments in Bohai Sea. Mar. Sci. 28 (12), 16–21 (in Chinese).
Duan, L., Song, J., Xu, Y., Li, X., Zhang, Y., 2010. The distribution, enrichment and source of potential harmful elements in surface sediments of Bohai Bay, North China. J. Hazard. Mater. 183, 155–164.
Duan, L.Q., et al., 2014. Distribution, chemical speciation and source of trace elements in surface sediments of the Changjiang Estuary. Environ. Earth Sci. 72, 3193–3204.
Feng, H., et al., 2011. Metal contamination in sediments of the western Bohai Bay and adjacent estuaries, China. J. Environ. Manag. 92, 1185–1197.
Field, L.J., et al., 2002. Predicting amphipod toxicity from sediment chemistry using logistic regression models. Environ. Toxicol. Chem. 21 (9), 1993–2005.
Gan, H., Lin, J., Liang, K., Xia, Z., 2013. Selected trace metals (As, Cd and Hg) distribution and contamination in the coastal wetland sediment of the northern Beibu Gulf, South China sea. Mar. Pollut. Bull. 66, 252–258.
Hakanson, L., 1980. An ecological risk index for aquatic pollution control: a sedimentological approach. Water Res. 40 (11), 968–980.
Harada, H., 1995. Minamata disease: methylmercury poisoning in Japan caused by environmental pollution. Crit. Rev. Toxic. 25 (1), 1–24.
Hu, N.J., et al., 2012. The distribution and risk assessment of metals in surface sediments of the Laizhou Bay in the Bohai Sea. Acta Oceanol. Sin. 34 (2), 92–99 (in Chinese).
Hu, N.J., Shi, X.F., Huang, P., Liu, J.H., 2010. Distribution of metals in surface sediments of Liaodong bay, Bohai sea. China Environ. Sci. 30 (3), 380–388 (in Chinese).
Huang, X., Liang, K., Liu, X., 2006. The distribution and assessment of heavy metals in surficial sediments in the Pearl River Estuary. Trans. Oceanol. Limnol. 3, 27–36 (in Chinese).
Li, R.W., Li, Y., 2008. Environmental and sedimentological survey along the coast of Bohai Gulf. Acta Sedimentol. Sin. 26 (1), 128–138 (in Chinese).
Li, T., 1994. Element abundances of China's continental crust and its sedimentary layer and upper continental crust. Geochimica 23 (2), 140–145 (in Chinese).
Long, E.R., Macdonald, D.D., Smith, S.L., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manag. 19 (1), 81–97.
Luo, W., et al., 2010. Ecological risk assessment of arsenic and metals in sediments of coastal areas of northern Bohai and Yellow Seas, China. Ambio 39, 367–375.
Macdonald, D.D., Carr, R.S., Calder, F.D., Long, E.R., Ingersoll, C.G., 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology 5 (4), 253–278.
Meng, W., Qin, Y., Zheng, B., Zhang, L., 2008. Heavy metal pollution in Tianjin Bohai bay, China. J. Environ. Sci. 20, 814–819 in Chinese.
Muller, G., 1979. Schwermetalle in den sedimenten des Rheins-Veranderungen seitt. Unschau 79, 778–783.
Pan, T., Feng, Y., Long, L., 2010. The current development status and future trend prediction of Tianjian Port. Port. Econ. 4, 13–16 (in Chinese).
Qiao, F.Y., 1991. Monitoring of heavy metal pollution status and its future trend prediction in Jinzhou Bay. Mar. Environ. Sci. 10 (4), 69–73 (in Chinese).
Ravizza, G.E., Bothner, M.H., 1996. Osmium isotopes and silver as tracers of anthropogenic metals in sediments from Massachusetts and Cape Cod bays. Geochimica Cosmochimica Acta 60 (15), 2753–2763.
Rubio, B., Nombela, M.A., 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 (11), 968–980.
Sanudo-Willhelmy, S., Flegal, R., 1992. Anthropogenic silver in the southern California Bight: a new tracer of sewage in coastal waters. Environ. Sci. Technol. 26, 2147–2151.
Shi, X.F., Liu, Y.G., Yao, Z.Q., 2014. Coastal Seas of China – Marine Sediments. China Ocean Press, Beijing (in Chinese).
SOA (State Oceanic Administration), 2012. 2012 Marine Environmental Quality Report (in Chinese). http://www.coi.gov.cn/gongbao/huanjing/201304/t20130401_26428.html.
Sposito, G., 1986. The distribution of potentially hazardous trace metals. In: Sigel, H. (Ed.), Metal Ions in Biological Systems. Marcel Dekker, New York.
Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. John Wiley and Sons Inc., New York, p. 1022.
Sun, X.Y., Lv, T.t., Gao, Y., Fu, M., 2014. Driving force analysis of Bohai Bay coastline change from 2000 to 2010. Resour. Sci. 36 (2), 413–419 (in Chinese).
Wang, X.L., Cui, Z.G., Guo, Q., Han, X.R., Wang, J.T., 2009. Distribution of nutrients and eutrophication assessment in the Bohai Sea of China. Chin. J. Oceanogr. Limnol. 27 (1), 177–183 (in Chinese).
Xu, L., et al., 2013. Metal contamination along the watershed and estuarine areas of southern Bohai Sea, China. Mar. Pollut. Bull. 74, 453–463.
Zhao, Y., Yan, M., 1994. Geochemistry of Sediments of the China Shelf Sea. Science Publishment, Beijing, China (in Chinese).
Zheng, N., Wang, Q., Liang, Z., Zheng, D., 2008. Characterization of heavy metal concentration in the sediments of three freshwater rivers in Huludao City, Northeast China. Environ. Pollut. 154, 135–142.
Zhuang, W., Gao, X.L., 2015. Distributions, sources and ecological risk assessment of arsenic and mercury in the surface sediments of the southwestern coastal Laizhou Bay, Bohai Sea. Mar. Pollut. Bull. 99 (1–2), 320–327.