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Total petroleum hydrocarbons and heavy metals in the surface sediments of Bohai Bay, China: Long-term variations in pollution status and adverse biological risk

Ran Zhou [a,b], Xuebo Qin [b,c], Shitao Peng [b], Shihuai Deng [a,*]

[a] College of Resource and Environment, Sichuan Agricultural University, Chengdu 611130, China
[b] Tianjin Research Institute for Water Transport Engineering, Tianjin 300456, China
[c] College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

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ABSTRACT

Surface sediments collected from 2001 to 2011 were analyzed for total petroleum hydrocarbons (TPH) and five heavy metals. The sediment concentration ranges of TPH, Zn, Cu, Pb, Cd and Hg were 6.3–535 μg/g, 58–332 μg/g, 7.2–63 μg/g, 4.3–138 μg/g, 0–0.98 μg/g, and 0.10–0.68 μg/g, respectively. These results met the highest marine sediment quality standards in China, indicating that the sediment was fairly clean. However, based on the effects range-median (ERM) quotient method, the calculated values for all of the sampling sites were higher than 0.10, suggesting that there was a potential adverse biological risk in Bohai Bay. According to the calculated results, the biological risk decreased from 2001 to 2007 and increased afterwards. High-risk sites were mainly distributed along the coast. This study suggests that anthropogenic influences might be responsible for the potential risk of adverse biological effects from TPH and heavy metals in Bohai Bay.

1. Introduction

Marine sediment, which is more stable than the overlying water, is often used to monitor the environmental quality of the sea. Thus, understanding the quality of marine sediment is very helpful in setting suitable management and regulation plans. Petroleum hydrocarbons are ubiquitous pollutants in marine sediment as a consequence of industrial discharges, accidental spills, shipping activities, atmospheric fallouts, and marine oil and gas explorations (Ye et al., 2007; de Mora et al., 2010). This kind of pollutant may pose threats to the marine ecosystem, such as causing marine organism aberrant, become sterile and extinct, thus reducing the ability to exploit of marine resources (Zaghden et al., 2005; Gao and Chen, 2008). Heavy metals are another kind of prevalent contaminant in marine sediments. Unlike petroleum hydrocarbons, heavy metals cannot be biologically or chemically degraded. Heavy metals in particular can accumulate in aquatic organisms, and they are subsequently transferred to humans through the food chain, posing a huge threat to human health (Marchand et al., 2006; Kang et al., 2009). These trends indicate that both petroleum hydrocarbons and heavy metals have significant effects on the quality of marine sediments. Therefore, it is not only important to determine the concentration and distribution of petroleum hydrocarbons but also those of heavy metals in marine sediments.

Bohai Bay is a semi-enclosed bay located in the western Bohai Sea in northern China. This bay is surrounded by large cities such as Beijing (the capital city of China) and Tianjin (one of four municipalities; it is an important commercial and industrial center in China with an area of approximately 11,200 km^2 and a population of 11 million). During the last three decades, industries such as chemical industry, electronics industry, metallurgy, manufacturing, port development and marine transportation have boomed in parallel with rapid economic development (Peng et al., 2012). Large quantities of contaminants including organic pollutants and heavy metals have been discharged into Bohai Bay, causing severe risk to the marine ecosystem (Li et al., 2010). In the past few years, some publications have reported heavy metal contaminants in Bohai Bay sediments (e.g., Meng et al., 2008; Feng et al., 2011; Gao and Chen, 2012; Gao and Li, 2012). These investigations were usually carried out only once within a single year, and the results cannot describe long-term variations in sedimentary heavy metal pollution levels. Furthermore, TPH data from Bohai Bay sediments are relatively scarce. To our knowledge, little information is available on the adverse biological risks of total petroleum hydrocarbons (TPH) and heavy metals in Bohai Bay.

* Corresponding author. Tel./fax: +86 28 86291132.
E-mail address: shdeng8888@163.com (S. Deng).

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In this study, we determined the concentrations and distributions of TPH and five heavy metals (Cu, Zn, Pb, Cd and Hg) in Bohai Bay sediments collected from 2001 to 2011. The main objectives of this study were as follows: (1) to investigate spatial and temporal variations and possible sources of TPH and heavy metals in bay sediments; (2) to determine the pollution level of Bohai Bay at present; and (3) to assess the adverse biological risk.

2. Method

2.1. Sample collection

Fifteen sampling sites were selected in Bohai Bay (Fig. 1). Surface sediments were collected at each station every other May from 2001 to 2011 with a Van Veen bottom grab. The sediment samples were sieved through a 4 mm sieve to eliminate coarse rock and plant material, thoroughly mixed to ensure uniformity. In order to eliminate the variability, sediment samples were collected from three to five adjacent points for each sampling sites and then combined. The samples were placed in acid-rinsed polyethylene bags, transported to the laboratory and stored at −20 °C in the dark until analysis.

2.2. Analysis

Prior to analysis, the samples were freeze-dried for 72 h and sieved through 2 mm mesh to determine sediment physical and chemical characteristics.

For the TPH determination, 20 g of dried sediment samples were Soxhlet-extracted with a mixture of dichloromethane and hexane (v:v, 1:1) for 24 h. The TPH concentration of the extract was determined by ultra-violet fluorescence spectroscopy according to the national standard method of China (GB17378-4.1998). The method detection limit for TPH was 6.2 μg/g.

For heavy metals, 1.0 g of dried sediment was digested in a flask with $HNO_3/HClO_4$ on a heating plate. After the sample evaporated to near dryness, this digestion step was repeated. Finally, the residue was dissolved in 1.0% HNO_3, and the solution was filtered through a 0.45 μm membrane for analysis. All the metals were determined with an Agilent 7500a ICP–MS (Agilent, USA). The ICP–MS detection limits for the heavy metals were 0.01 μg/g for Cu, 0.02 μg/g for Zn, 0.005 μg/g for Pb, 0.01 μg/g for Cd, and 0.005 μg/g for Hg. The mass recoveries for Cu, Zn, Pb, Cd, and Hg were 106%, 95%, 110%, 90% and 81%, respectively.

The total organic carbon (TOC) in the sediment was determined by potassium dichromate-sulfuric acid oxidation method (Qin et al., 2010). According to multiple sediment analyses, the precision of this method was within 5.0%. The grain size composition of the sediment was analyzed with a Malvern Mastersizer 2000 laser diffractometer (Malvern Instruments Ltd., Worcestershire, UK).

2.3. Adverse biological effects

Adverse biological effects were assessed by ERM quotient method (Long et al., 1995). In theory, this method can only assess the adverse biological effects of an individual contaminant. However, in reality, many contaminants coexist in the environment. With this challenge in mind, the mean ERM quotient (mERM) method was applied to determine the adverse biological effects of coexisting contaminants (Long et al., 1998) as follows:

$$\mathrm{mERM} = \sum (C_i/ERM_i)/n$$

where C_i is the concentration of contaminant i, ERM_i is the ERM value for contaminant i and n is the number of contaminants. An mERM ⩽0.10 shows no adverse biological effect; an mERM within a range of 0.10–0.50 indicates potential adverse effects; an mERM within a range from 0.50–1.5 indicates a moderate adverse effect; and an mERM >1.5 reveals a significant adverse effect (Long et al., 2000).

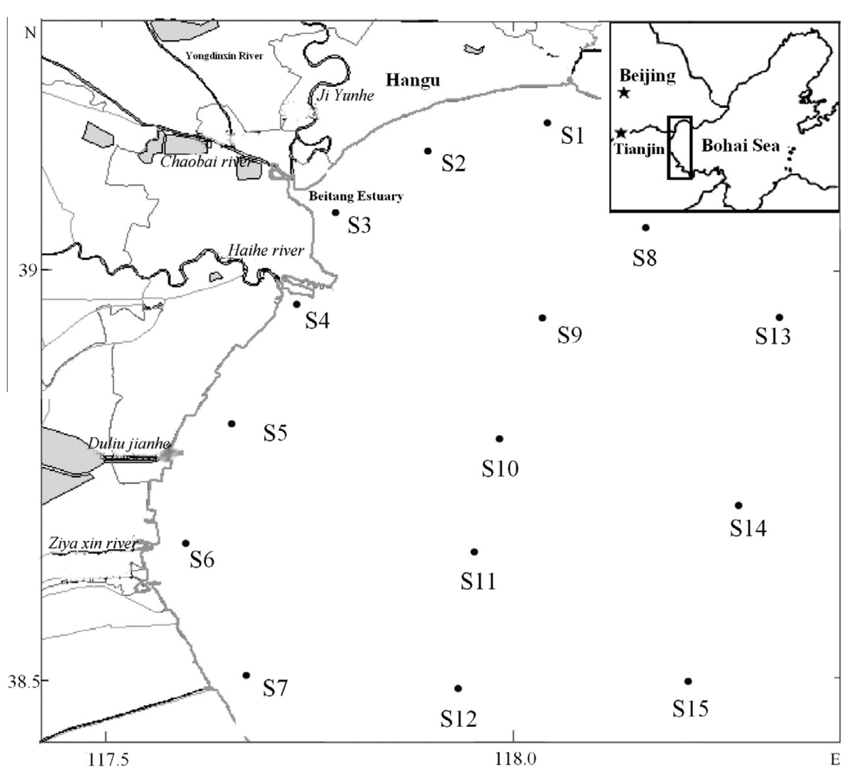

Fig. 1. Sampling sites in Bohai Bay.

2.4. Statistical analyses

A two-way analysis of variance (ANOVA) was performed to estimate the significance of differences among the different groups of data from each site or year to investigate the temporal and spatial differences in the contaminants. The relationships between the contaminants were evaluated by Pearson's correlation analysis. Statistical significance was set at $p < 0.05$.

3. Results

3.1. Sediment characteristics

In the present study, the general characteristic of the sediment was defined by its TOC content and grain composition. As shown in Fig. 2, the TOC contents ranged from 0.41% to 1.2% with an average of 0.67%. The average percentages of clay, silt and sand were 45%, 45% and 9.6%, respectively, indicating that the Bohai Bay sediment was primarily composed of clay- and silt-sized particles.

3.2. TPH and heavy metals in the sediments

The sediment TPH concentrations were significantly different in terms of both temporal and spatial variations ($p < 0.001$). As shown in Fig. 3, the temporal variations in TPH concentrations generally decreased from 2001 to 2007 and increased afterwards. The lowest and highest levels occurred in 2007 and 2011, with average concentrations of 55 μg/g and 306 μg/g, respectively. Spatial variations in TPH concentrations gradually decreased from the shoreline to offshore sites, indicating that terrestrial inputs were an important source of TPH in the bay.

The highest concentrations of all the heavy metals occurred in 2005. The concentrations increased from 2001 to 2005 and then decreased (Fig. 3). With the exception of 2005, the sedimentary Cu and Zn concentrations fluctuated from 2001 to 2011. However, the concentrations of Pb, Cd, and Hg showed strong spatial–temporal fluctuations in the bay. Like TPH, a relatively high concentration of heavy metals (Cd is an exception) was found in coastal sites, especially in estuaries. This finding suggests that riverine input was the primary source of heavy metals. Fig. 3 also shows that a high concentration of some metals, such as Pb and Hg, occurred at the offshore site (e.g., S13), indicating that other inputs may also exist for this bay.

Except for the relationships between TPH and Zn, all of the contaminants were significantly correlated amongst one another (Table 1). This trend suggests that these contaminants may share a major origin in the sediment. In addition, all of the contaminants were significantly correlated with TOC and clay, suggesting that the contaminants were influenced by both sediment organic matter and grain size composition (Table 1).

3.3. Pollution status and adverse biological risk

The overall average concentrations of all determined contaminants met the Grade-I criteria for the marine sediment quality standards of China (Table 2). However, the contaminants at some sampling sites were greater than Grade-I during certain years. For example, the highest concentration of Cu was 63 μg/g, which was 47% greater than that of Grade-I. Moreover, the Pb and Hg in some sampling sites were above the Grade-II values.

There were no sampling sites with adverse biological risks at the no harm level (Fig. 4), indicating that there was potential risk in Bohai Bay. The risk decreased from 2001 to 2007 (except in 2005) and increased afterwards. The high risk was mainly distributed along the coastal sites.

4. Discussion

4.1. TPH and heavy metal pollution

In the present study, Bohai Bay sediment was primarily composed of fine particles (Fig. 2). Such fine particles have a strong ability to adsorb contaminants (Vane et al., 2007; Qin et al., 2010). Thus, it seems that the high concentrations of TPH and heavy metals in Bohai Bay sediments resulted from accumulation. However, the overall average concentrations of all determined contaminants in the sediments were below the Grade-I criteria of the marine sediment quality standard of China (Table 2). This finding indicates that the sediment was fairly clean in terms of TPH and heavy metals. This result was consistent with the work of Feng et al. (2011), who found that the overall sediment quality generally met Chinese marine sediment quality criteria for metal concentrations in western Bohai Bay. The relatively low level of TPH occurred because this compound was not the dominant contaminant in Bohai Bay (Li et al., 2010). Nevertheless, at some sampling sites in certain years, some contaminants analyzed in the present study exceeded the Grade-I standards (Table 2). This finding indicates

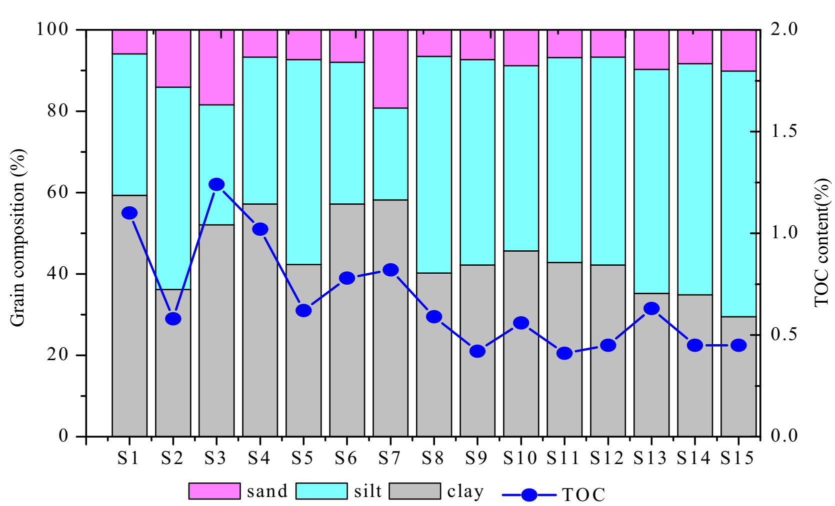

Fig. 2. Sediment TOC content and grain composition.

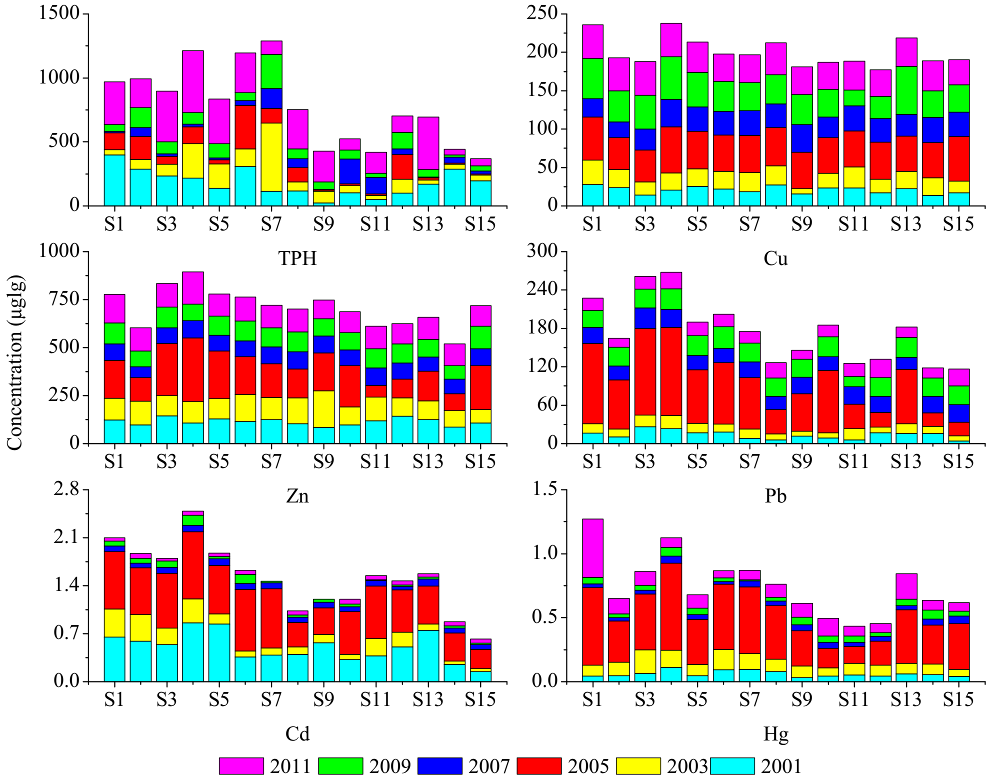

Fig. 3. Temporal and spatial variations in TPH and heavy metals.

Table 1
Pearson's correlation coefficients among contaminants, TOC and clay.

	Cu	Zn	Pb	Cd	Hg	TOC	Clay
TPH	0.56*	0.51	0.66**	0.68**	0.71**	0.699**	0.75**
Cu		0.67**	0.73**	0.69**	0.85**	0.743**	0.48*
Zn			0.78**	0.54*	0.61*	0.723**	0.64*
Pb				0.80**	0.70**	0.90**	0.73**
Cd					0.60*	0.67**	0.64*
Hg						0.82**	0.67**

* $p<0.05$.
** $p<0.01$.

that the sediments in Bohai Bay have been contaminated with TPH and heavy metals to some extent.

Total petroleum hydrocarbons concentration for surface sediments of Bohai Bay ranged from 6.3 μg/g to 535 μg/g. These values were lower than concentrations reported for heavily urbanized zones in China such as Changjiang River Estuary and Pearl River Estuary (Table 3). They were also lower than those found in sediments of Europe (e.g. UK) and North America too, whereas higher than those found in sediments of Bay of Bengal in India, Izmir Bay in Turkey, and Todos os Santos Bay in Brazil. This indicates that sediment from Bohai Bay can be categorized as a relatively low in TPH.

The levels of determined metals in surface sediment of Bohai Bay were generally comparable to those encountered in the Xiamen Harbour and Changjiang estuary in China, and were lower than concentrations reported for highly contaminated areas such as the Pearl River Estuary in China (Table 3). The Cu and Zn concentrations were also lower than marine sediments from Mediterranean Sea, Izmir Bay in Turkey, and Montevideo Harbour in Uruguay, whereas higher than those found in sediments of Todos os Santos Bay in Brazil. These suggests that the pollution level of Cu and Zn were relatively low. The concentrations of Pb, Cd, and Hg recorded in the present study were generally comparable to those encountered in the most other reported marine sediment in the world (Table 3), suggesting that the pollution level of these three metals were moderate.

Table 2
The pollution status of TPH and heavy metals.

	Marine sediment quality standard of China (upper limit)[a]			Bohai Bay		Percentage exceeding (%)		
	Grade-I	Grade-II	Grade-III	Range	Mean	Grade-I	Grade-II	Grade-III
TPH	500	1000	1500	6.3–535	159	1.1	0	0
Cu	35	100	200	7.2–63	33	47	0	0
Zn	150	350	600	58–332	118	14	0	0
Pb	60	130	250	1.3–138	29	10	2.2	0
Cd	0.50	1.5	5.0	0–0.98	0.25	20	0	0
Hg	0.20	0.50	1.0	0.03–0.68	0.12	12	4.4	0

[a] The Grade-I refer to the fairly clean sediment, which can be used for mariculture, nature reserve, endangered species reserve, and human recreation leisure activities such as swimming. The Grade-II indicates that sediment is moderately contaminated, which can be used to industry and tourism site; and the Grade-III indicates that the sediment can be used to used for harbor.

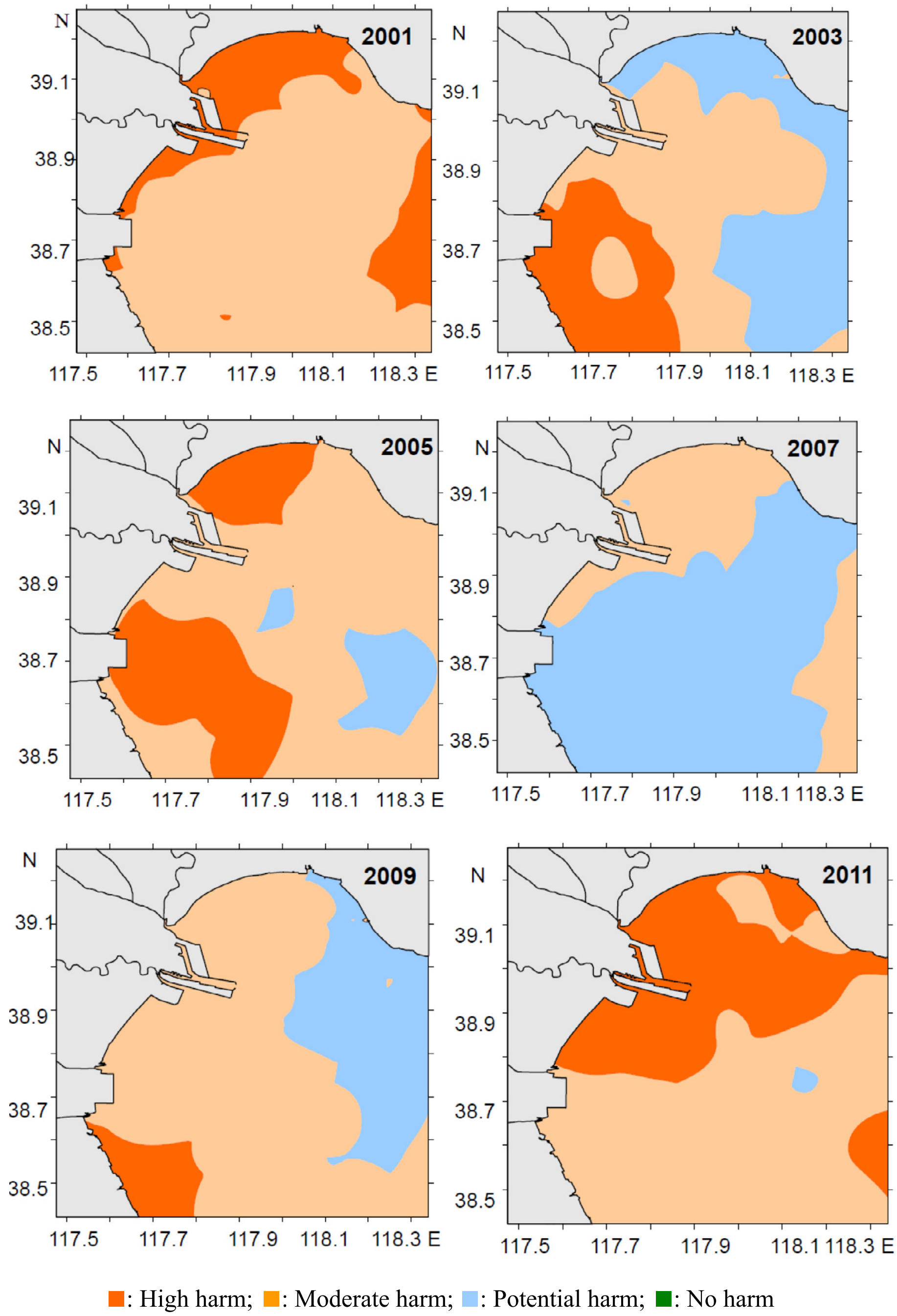

Fig. 4. Temporal and spatial variations for adverse biological risks in Bohai Bay.

To our knowledge, this is the first investigation of TPH in surface sediment from Bohai Bay. In this study, the concentration of TPH decreased from 2001 to 2007 and increased afterwards in the past decade. However, various studies were conducted to determine the heavy metals pollution in sediments of Bohai Bay in the past. For example, Meng et al. (2008) reported the sediment concentration ranges of Cu, Zn, Pb, Cd and Hg were 11–27 μg/g, 69–393 μg/g, 18–35 μg/g, 0.14–0.80 μg/g, and 0.02–0.85 μg/g, respectively, for 20 stations in coastal areas of Tianjin Bohai Bay in 2003. According to these authors, Pb, Zn, and Cd were the main polluting elements in surficial sediments from Tianjin Bohai Bay. Compared with the results of Meng et al. (2008), Zn was generally comparable, while Pb was higher in the present study. This indicates that Zn and Pb were still the main polluting elements in Bohai Bay. Comparing the means of Zn (131 μg/g) and Pb (35 μg/g) levels with the reposts by Gao and Chen (2012), who conducted in the same study area during 2008. Zinc (118 μg/g) and Pb (29 μg/g) in the present study were relatively low. This also indicates that metals concentrations increased after 2007. While compared to concentrations of Cu, Zn, Pb and Cd in the western Bohai Bay (the four metals were 26.5–45.4 μg/g, 61.6–156 μg/g, 18.3–30.7 μg/g and 0.093–0.252 μg/g, respectively, Feng et al., 2011) and intertidal Bohai Bay (the four metals were 24 μg/g, 73 μg/g, 26 μg/g, 0.12 μg/g, respectively, Gao and Li, 2012), the concentrations of these metals in the present study were relatively high. It could be explained by the fact that most of sampling sites were located in coast, where had two main origins of heavy metals including river discharge and industrial discharge. The two main origins have been considered the most

Table 3
Worldwide concentrations of TPH and heavy metals in marine sediments.

Area	TPH	Cu	Zn	Pb	Cd	Hg	Reference
Bohai Bay, China	6.3–535 (158)	7.2–63 (33)	58–332 (118)	4.3–138 (29)	0–0.98 (0.25)	0.10–0.68 (0.12)	This study
Xiamen Harbour, China μg/g	1397	19–97(44)	65–223 (139)	45–60 (54)	0.11–1.0	n.a	Ou et al. (2004); Zhang et al. (2007)
Changjiang estuary, China	2200–11820	6.9–50 (30.7)	48–154 (94)	18–44 (27.3)	0.12–0.75 (0.26)	n.a	Bouloubassi et al. (2001); Zhang et al. (2009)
Pearl River Estuary China	300–16500	15–141	240–346	29–39	2.8–4.7	n.a	Peng et al. (2005); Li et al. (2007a,b)
Bay of Bengal, India	1.8–40	385–657	71.3–201	25–40	4.6–7.5	n.a	Raj and Jayaprakash (2008); Venkatachalapathy et al. (2010)
Bizerte lagoon, Tunisia	0.05–20	n.a	n.a	32–304	0.395	n.a	Mzoughi et al. (2005); Garali et al. (2010)
Clyde estuary, UK	34–4386	n.a	n.a	6–631	n.a	n.a	Vane et al. (2011)
Humber Estuary UK	n.a	<3–83	88–395	28–145	n.a	n.a	Lee and Cundy (2001)
North Adriatic Sea, Mediterranean Sea	1520 ± 76	412 ± 12	500 ± 25	76 ± 6	n.a	n.a	Dell'Anno et al. (2009)
Izmir Bay, Turkey	0.43–7.8	66–993	217–1031	14–113	0.005–0.82	0.05–1.3	Kucuksezgin et al. (2006), Guven and Akinci (2008)
Barnegat-Bay-Little Egg Harbor Estuary, USA	47–1003 (231)	n.a	n.a	n.a	n.a	<0.02–2.6 (0.31)	Vane et al. (2008)
Galveston Bay, USA	4.2–1814	14	107	27	0.16	0.08	Rozas et al. (2000); Santschi et al. (2001)
Todos os Santos Bay, Brazil	1.6–11	21 ± 4.8	38 ± 10	15 ± 8	0.40 ± 0.20	n.a	Celino et al. (2008)
Montevideo Harbour, Uruguay	n.a	59–135	174–491	44–128	<1–1.6	0.30–1.3	Muniz et al. (2004)

All concentrations are given in μg/g. Values given in brackets are average value. n.a = not analyzed.

important reasons for the high metals concentration in seawater from coastal Bohai Bay (Wang and Wang, 2007).

4.2. The adverse biological risk in Bohai Bay

The adverse biological risk in Bohai Bay decreased from 2001 to 2007 (except for 2005) as a consequence of the decline in TPH and heavy metal concentrations (Fig. 3). Such a decrease can be at least partially explained by several causes. One cause is the establishment of some environmental protection policies. For instance, one of the most important policies, entitled *The Plan of Cleaning Bohai Sea*, was promulgated by the Central Government of China in 2001. The aim of this policy was to control the discharge of contaminants into the bay. As a result, the water quality of Bohai Sea gradually improved after the policy was put into practice. The second cause is the implementation of environmental protection programs, such as the installation of sewage treatment systems and the enforcement of water pollution control regulations over the last decade in cities along the bay (Wu and Cao, 2010). In addition, this change was also caused by public and scientific awareness related to the environmental restoration of Bohai Bay (Li et al., 2010). The highest concentration of heavy metals in 2005 can be explained by the large amount of heavy metals flowing into Bohai Bay from rivers. For example, there were 8.0 Mt of heavy metals flowing into Bohai Bay from Yongdingxin River in 2004 (SOA 2004). In 2005, Dagupaiwu River and Yongdingxin River brought 36 and 2.0 Mt of heavy metals into Bohai Bay, respectively (SOA 2005). Similar discharges might increase the heavy metals in bay sediments.

It is surprising that the biological risk has increased since 2007 (Fig. 4), but there might be several causes for this. First, wastewater discharge into the bay increased. For instance, the sewage discharge in 2011 was 628 million Mt, which is 1.1 times higher than it was in Tianjin in 2006 (Tianjin Environmental Protection Bureau, 2007, 2012). Second, pollution caused by accidents has increased in Bohai Bay in recent years. For example, there were many oil spill cases in Bohai Bay, resulting in a contaminant increase in the bay. Furthermore, other reasons, such as marine transportation and atmospheric deposition, might also lead to increases in TPH and heavy metals in the bay.

In the present study, the high-risk sites were found along the coast, especially at the estuary (Fig. 4). This finding was mainly attributed to the pollutants derived from land sources and rivers (Wang and Wang, 2007; Meng et al., 2008). In general, the estuary is in a densely populated and industrialized zone and is usually polluted more heavily than offshore areas (Pascual et al., 2012). For example, the concentration of polycyclic aromatic hydrocarbons (PAHs) in Beitang Estuary sediments was much higher than that of Bohai Bay (Qin et al., 2010). This trend was demonstrated by the high concentration of TPH (202 μg/g) found in S3, which was located in Beitang Estuary. In the present study, the highest concentrations of TPH and heavy metals were found in S4 (Fig. 3). This finding could be explained by two factors. One was that S4 was located at the Dagu River estuary, which discharged approximately 800,000 Mt/d of treated effluent into Bohai Bay (Lü et al., 2007). Another was that S4 was located near Tianjin Port, and there were many petrochemical industries around this port. In addition, there was heavy water shipping at the port. Given these reasons, it was not surprising that there was a high concentration of contaminants in this area.

The estuary had significant impacts on the coastal ecosystems as a consequence of the urbanization and industrialization around it (Lewis et al., 2001; Li et al., 2010). This finding indicates that anthropogenic inputs were most likely the major contributor to adverse biological risks in Bohai Bay.

4.3. The correlation between TPH and heavy metals in Bohai Bay

In general, several kinds of pollutants always exist simultaneously in the environment. For example, polycyclic aromatic hydrocarbons (PAHs), organic solvents, pesticides, and heavy metals often coexistent in contaminated soils (Chen et al., 2007). In the present study, both petroleum hydrocarbons and heavy metals were found in Bohai Bay sediments. A significant positive correlation was found between TPH and each heavy metal (Table 1, TPH vs. Zn was an exception). This finding indicates that the presence of heavy metals can cause a significant increase in the sorption of TPH to sediment. One reason is that the heavy metals could cause humus aggregation and flocculation in sediments and thereby increase the adsorption of petroleum hydrocarbons (Li et al., 2007a,b). The second was that the presence of heavy metals had a toxic effect on microbial communities, resulting in inhabitation of organic contaminant biodegradation (Epelde et al., 2012;

Rathnayake et al., 2013). Therefore, TPH was positively correlated with heavy metals.

In recent decades, the combined effects of heavy metals and organic contaminants have attracted substantial attention. The toxicity, mobility, bioavailability and fate of these contaminants may differ from those of a single contaminant. The additivity, antagonism or synergism of multiple contaminants may appear as a result of their combined effects (Graf et al., 2007). For instance, the combined effects of Cr and benzo(a)pyrene were more toxic to the shoot, root and germination rate of *Lolium perenne* than the single effect of Cr or benzo(a)pyrene (Chigbo and Batty, 2013). In the present study, the combination effects of these compounds were expected because of the significant correlations between TPH and heavy metals (Table 1). Such a combination effect could most likely increase the ecological risk in Bohai Bay. Therefore, it is important to better understand the co-contamination and potential interactions of different components in Bohai Bay.

5. Conclusions

In Bohai Bay sediment, the temporal variation in TPH concentrations generally decreased from 2001 to 2007 and increased afterwards, while the spatial variation gradually decreased from the coast to the offshore sites. The sedimentary Cu and Zn concentrations were constant from 2001 to 2011 with the exception of 2005, while Pb, Cd, and Hg showed strong spatial–temporal fluctuations in the bay. High concentrations of heavy metals were found along the coast, especially the sites located near the estuary. In comparison with the marine sediment quality standard of China, the overall average concentrations of all determined contaminants met the Grade-I criteria, indicating that the sediment was rather clean in terms of TPH and heavy metals. However, there was still a potential adverse biological risk in Bohai Bay. The risk decreased from 2001 to 2007 and increased afterwards. High-risk sites were mainly distributed along the coast. Anthropogenic influences were responsible for the potential adverse biological risk in Bohai Bay.

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