

Temporal and spatial trends of total petroleum hydrocarbons and heavy metals in the surface sediment of Caofeidian Sea Area, China from 2011 to 2016

Wei Huang

Tianjin Research Institute for Water Transport Engineering , Laboratory of Environmental, Protection in Water Transport Engineering, Tianjin 300456, China

E-mail: 17545011@qq.com

Abstract. The temporal and spatial distribution of total petroleum hydrocarbons (TPH) and four heavy metals in the surface sediments of Caofeidian Sea Area during 2011–2016 was investigated. The sediment concentration of TPH, Cu, Zn, Pb and Cd were 10.07-186.4 mg/L, 16.5-84.9 mg/L, 11.1-135 mg/L, 6.8-24.6 mg/L, and 0.07-0.199 mg/L, respectively. The pollution level in Caofeidian sea area is lower than those in other area in China. These results reached the highest marine sediment quality standards in China, indicating that the sediment was fairly clean. In addition, TPH at all stations decreased during 2011-2016. The highest values obtained were at stations near the port areas and estuary region.

1. Introduction

Sediments in the coastal zone are the main accumulative site of terrigenous pollutants going into the sea and main potential source of marine pollution. Petroleum hydrocarbons generated from industrial process, accidental spills, shipping activities and marine oil and gas explorations are ubiquitous pollutants in marine sediment [1]. This kind of pollutant can cause serious environmental problems because of their toxic, mutagenic and carcinogenic properties, persistence and bioaccumulation [2, 3].

Heavy metals are another kind of prevalent contaminant in marine sediments. Large quantities of untreated industrial wastewater effluents were released into marine environments during past decades. Many of these wastes were potential sources of heavy metal contamination that have the potential to threaten public health and impact the balance of the marine ecosystem. Toxicity of heavy metals in the marine environment has been a major concern since they constitute a potential risk to a number of flora and fauna species, including humans, through food chains [4, 5]. These trends indicate that both petroleum hydrocarbons and heavy metals have significant effects on the quality of marine sediments.

Bohai Bay located in the western Bohai Sea and near the city of Tianjin, the province of Hebei and Shandong, is the second largest bay of Bohai Sea. Bohai Bay is a typical semi-enclosed coastal sea, which are under constant stress from urban and industrial development [6, 7]. A large amount of pollutants were discharged into Bohai Bay annually and its geohydrologic conditions, is considered to be one of the most polluted marine areas in China. Of the many pollutants found in coastal and estuarine sediments, petroleum hydrocarbon and heavy metals are useful as markers of environmental change [8].

Caofeidian is a land reclamation-converted economic development zone in Bohai Bay located in the eponymous district of Tangshan, Hebei Province, China. The Caofeidian harbor area is located at the northern side of the mouth of the Bohai Bay and between the Tianjin Port and the Jingtang Port.



As the marine dynamic changed for project construction, Caofeidan engineering area became new enrichment pollutant areas.

Previous investigations were usually carried out only once within a single year, and the results cannot describe long-term variations in sedimentary TPH and heavy metal pollution levels. In this study, we determined the concentrations and distributions of TPH and four heavy metals (Cu, Zn, Pb and Cd) in Caofeidian sea area sediments collected from 2011 to 2016. 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 sediments; (2) to determine the pollution level of Bohai Bay at present.

2. Materials and methods

2.1. Sample collection

Twelve sampling sites were selected in Caofeidian sea area (Figure 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 -18°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, 20g 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). For heavy metals, 1.0 g of dried sediment was digested in a flask with HNO₃/HClO₄ on a heating plate. After the sample evaporated to near dryness, this digestion step was repeated. Finally, the residue was dissolved in 1.0% HNO₃, and the solution was filtered through a 0.45µm membrane for analysis. All the metals were determined with an Agilent 7500a ICP - MS (Agilent, USA).



Figure 1. Sampling sites in Caofeidian sea area

3. Results and discussion

Table 1 lists the mean, minimum and maximum concentrations of TPH and heavy metals in the surface sediments from Caofeidian sea area. The measured concentrations varied greatly as follows: TPH, 10.07-186.4 mg/L; Cu, 11.1-135.0mg mg/L; Zn, 16.5-84.9 mg/L; Pb, 6.8-24.6 mg/L; Cd, 0.01-0.199 mg/L; and the mean concentrations of TPH, Cu, Zn, Pb and Cd are 50.99 mg/L, 26.12 mg/L, 54.69 mg/L, 18.27 mg/L and 0.130 mg/L, respectively.

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 1). 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. [9], who found that the overall sediment quality generally met Chinese marine sediment quality criteria for metal concentrations in Caofeidian Sea Area. The relatively low level of TPH occurred because this compound was not the dominant contaminant in Caofeidian Sea Area [10]. Nevertheless, at some sampling sites in certain years, some contaminants analyzed in the present study exceeded the Grade-I standards (Table 1). This finding indicates that the sediments in Caofeidian Sea Area have been contaminated with TPH and heavy metals to some extent.

Table 1. The pollution status of TPH and heavy metals.

	Marine sediment quality standard of China (upper limit)			Caofeidian Sea Area	Percentage exceeding (%)			
	^a Grade-I	Grade-II	Grade-III			Range	Mean	Grade-I
TPH	500	1000	1500	10.07-186.4	50.99	0	0	0
Cu	35	100	200	11.1-135	26.12	1.7	1.7	0
Zn	150	350	600	16.5-84.9	54.69	0	0	0
Pb	60	130	250	6.8-24.6	18.27	0	0	0
Cd	0.50	1.5	5.0	0.01-0.199	0.130	0	0	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.

Compared with other reported marine sediment in China, the pollutant concentration in the study area is lower (Table 2).

Table 2. Comparison of mean contents of pollutants in surface sediments of Caofeidian sea area and other areas (mg/L).

Area	TPH	Cu	Zn	Pb	Cd	Reference
Caofeidian sea area	50.99	26.12	54.69	18.27	0.13	This study
Bohai Bay	158.00	33.00	118.00	29.00	0.25	Zhou et al.[11]
Xiamen Haobour	1397.00	44.00	139.00	54.00	0.56	Ou et al.[12]
Yangtze River Estuary	-	91.00	189.00	47.00	0.59	Chen et al. [13]
Pearl River Estuary	-	64.50	166.10	82.10	1.30	Yang et al.[14]

Total petroleum hydrocarbons concentration for surface sediments of Caofeidian Sea Area ranged from 10.07 mg/g to 186.4 mg/L. These values were lower than concentrations reported for heavily urbanized zones in China such as Yangtze river estuary and Pearl river estuary [13, 14]. This indicates that sediment from Caofeidian Sea Area can be categorized as a relatively low in TPH.

Compared to those reports in the Xiamen harbour, Yangtze river estuary and Pearl river estuary in China, the levels of determined metals in surface sediment of Caofeidian Sea Area were generally lower than the above mentioned areas [15- 17]. These suggested that the pollution level of Cu, Zn, Pb and Cd were relatively low.

The sediment TPH concentrations were significantly different in terms of both temporal and spatial variations. As shown in Fig. 2, the temporal variations in TPH concentrations generally decreased from 2011 to 2016. The lowest and highest levels occurred in 2016 and 2011, with average concentrations of 10.07 mg/L and 173.6mg/L, 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 2011. The concentrations decreased from 2011 to 2016 (Figure 2). However, the concentrations of Pb, Cd, and Zn showed strong spatial - temporal fluctuations in the bay. Like TPH, a relatively high concentration of heavy metals was found in coastal sites, especially in estuaries. This finding suggests that riverine input was the primary source of heavy metals.

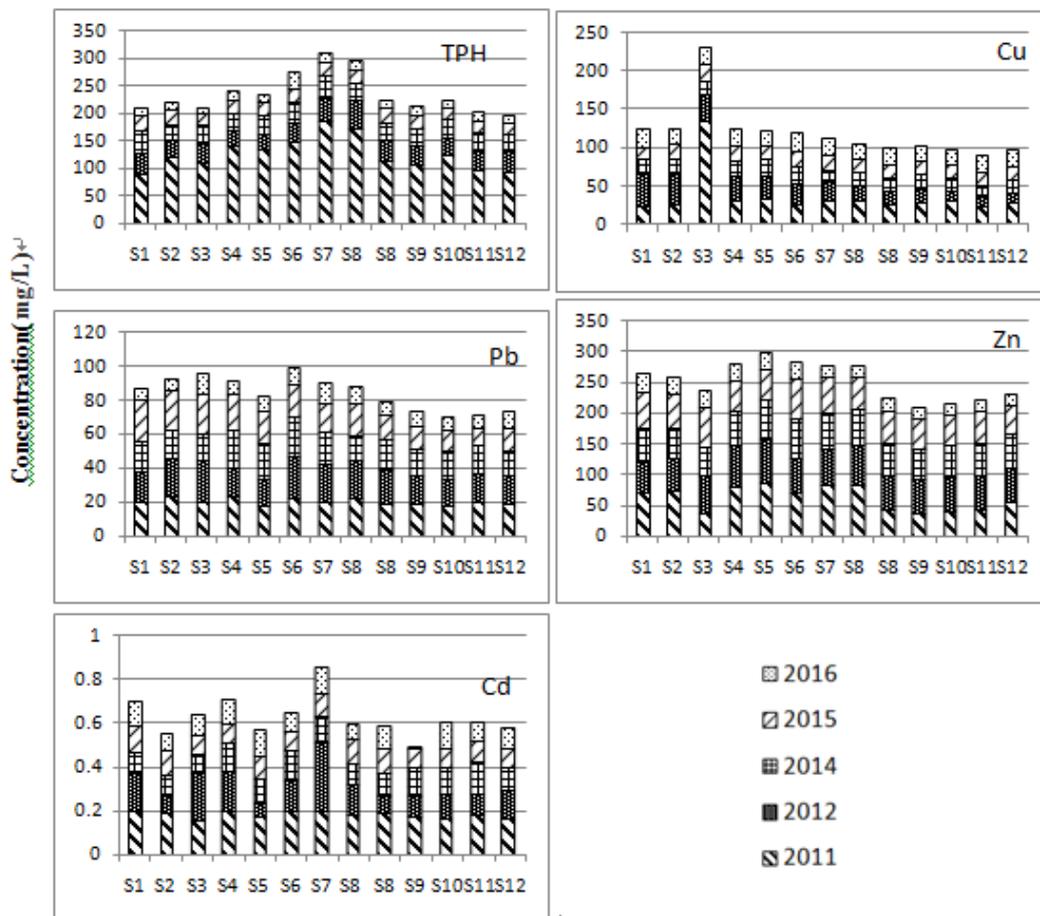


Figure 2. Temporal and spatial variations in TPH and heavy metals

In the present study, Caofeidian Sea Area sediment was primarily composed of fine particles. Such fine particles have a strong ability to adsorb contaminants [18, 19]. Thus, it seems that the high concentrations of TPH and heavy metals in Caofeidian Sea Area sediments resulted from accumulation.

In this study, the concentration of TPH decreased from 2011 to 2016. However, various studies were conducted to determine the heavy metals pollution in sediments of Bohai Bay in the past. For example, Meng et al.[20], Feng et al.[9] and Gao and Li [21] reported that Cu, Pb, Zn, and Cd were the main polluting elements in surface sediments of Bohai Bay. Compared with the results of Meng et al., Feng et al., and Gao and Li [9, 20, 21], the concentrations of these metals in the present study were relatively low. Such a decrease can be at least partially explained by several causes.

One cause is the establishment of some environmental protection policies. For instance, Bohai Blue Sea Action Plan is approved by the State Council in 2001 and the aim of this policy was to control the discharge of contaminants into the bay.

The second cause is the increasing of public awareness for environmental protection with more and more environmental propaganda, and the ecological protection and restoration projects were conducted for improving the eco-environment quality in Bohai Bay.

4. Conclusion

In Bohai Bay sediment, the temporal variation in TPH concentrations generally decreased from 2011 to 2016, while the spatial variation gradually decreased from the coast to the offshore sites. The sedimentary Cu, Zn, Pb and Cd concentrations showed strong spatial-temporal fluctuations in the area. 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.

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