The distribution, enrichment and source of potential harmful elements in surface sediments of Bohai Bay, North China

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ARTICLE INFO

ABSTRACT

A geochemical study of Bohai Bay surface sediments was carried out to analyze the potential harmful element (PHE: Ge, Mo, In, Sn, Sb, Te, Tl, Bi and V) concentrations, transportation and deposition, enrichment factors and sources. Germanium, Mo, In, Sn, Sb, Te, Tl, Bi and V concentrations in the surface sediments were: 1.43–1.71, 0.52–1.43, 0.04–0.12, 2.77–4.14, 1.14–2.29, 0.027–0.085, 0.506–0.770, 0.27–0.63 and 70.35–115.90 μg/g, respectively. The distributions of total PHE concentrations, together with sequential extraction analyses, showed that the PHEs were mainly due to natural inputs from the continental weathering delivered to the bay by rivers and atmospheric transportation and deposition. However, high Mo, Sb, Te, Bi and V occurred in non-residual fractions, suggesting some anthropogenic inputs in addition to the natural inputs. Besides sources, the distributions of PHEs were influenced by the coupling of physical, chemical and biological processes. Enrichment factor (EF) was computed for each site for each element in order to assess the polluting elements and the degree of pollution at each site. Results revealed that the EFs were generally lower than 1.0, particularly for Ge, Mo, In, Sn, Tl and V; however, the EFs were higher (>1.5), particularly for Sb, Te and Bi, revealing moderate contamination.

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1. Introduction

A good deal of research on biogeochemical processes in aquatic environment has been, and continues to be, devoted to trace elements, particularly transition metals. Rather less attention has been focused on the so-called metal and semi-metal elements, such as Ge, Mo, In, Sn, Sb, Te, Tl, Bi and V. Especially, the aquatic geochemistry of these elements is poorly known. Because of their very low abundance, these trace elements are particularly sensitive to surrounding environmental conditions, which influence their physical–chemical species and behaviors in the ecosystems. These elements are deemed serious pollutants because of toxicity, persistence and non-degradability in the environment. So, they are called "Potential Harmful Elements (PHEs)" [1]. Among them, germanium, Sn, V and Mo in trace amounts are beneficial to normal cell growth, being the so-called essential elements. However, toxicities arise when element concentrations increase to a higher level [2,3].

Antimony, Tl and their compounds are classified as priority pollutants by the Environmental Protection Agency of the United States (USEPA) [4,5]. Indium, Te and Bi are known to be non-essential and have potential toxic and harmful for living organisms [6–8]. In recent years, PHEs have been discharged into coastal oceans as a result of the rapid industrialization. Hence, although these elements except for V are found in relatively low abundances, it is possible that the high toxicities of these elements can induce environmental problems [9].

Sediments are important deposits of PHE accumulation in the aquatic environment. The large adsorption capability of sediment to accumulate compounds makes them a major repository of natural and anthropogenic PHEs and one of the most important tools to assess the contamination level of aquatic ecosystems [10]. Due to their stability within the sedimentary column, most of the contaminants can leave their fingerprint in sediments. Thus, the study of geochemical characteristics of sediment has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments. On the other hand, the non-residual fractions of PHEs (i.e., exchangeable, bound to carbonates, bound to Fe–Mn oxides and bound to organic matter
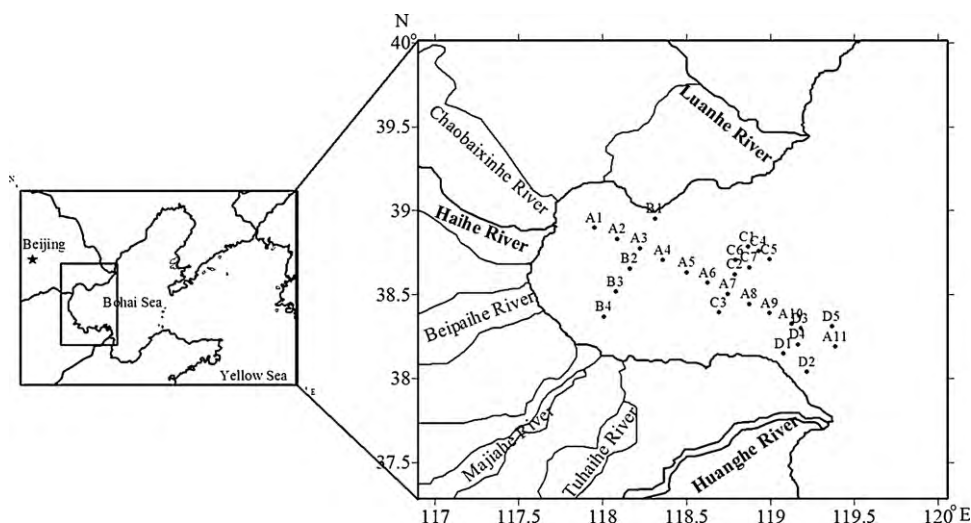
Fig. 1. Location of the stations in Bohai Bay, 2008.

fractions) can be easily released to water column through any disturbance, such as hydrological, physical, chemical and biological activities [11]. Thus, sediments are a potential source of pollution for surrounding water column. Consequently, the knowledge of the concentrations, distributions and chemical fractions of PHEs in sediments plays a key role in detecting sources of PHEs and assessing the ecological risks of PHEs in aquatic systems.

The PHEs transferred into ocean systems are associated with physical and chemical processes, such as weathering processes, subsequent riverine transportation of particulate matter, atmospheric transportation and deposition. Once entered the aquatic environment, PHEs would be adsorbed on sediment particles or precipitate into bottom sediments. The extent of PHE sorption and the factors controlling PHE distributions remarkably depend on the sediment characteristics (grain size, chemical components, organic carbon contents, mineral phases and texture), the sedimentary environmental characteristics (salinity, pH, temperature, oxidation–reduction potential (Eh), presence of ligands and ocean currents), sources whereby PHEs entered the environment and the physical, chemical and biological processes [12].

The PHEs are introduced into the oceans by natural processes including erosion of ore-bearing rocks, wind-blown dust, volcanic activity and forest fires, and processes derived from human activities by means of atmospheric deposition, rivers and direct discharges or dumping [13]. The major anthropogenic sources of PHEs are coal and fossil fuel combustion and steel manufacturing plants. So the riverine inputs and atmospheric deposition are the main carriers of PHEs to ocean. In particular, atmospheric deposition is now widely recognized as an important source of PHE contamination for surface sediments. Hence, surface sediment records provide the most compelling evidence of regional or long-range atmospheric transportation of PHEs [14].

Because of their bioavailability and toxicity, the PHEs should be of global interest and be much accounted of, but there is little information on geochemical characteristics and behaviors of PHEs in sediments. To understand behaviors and fates of PHEs and evaluate the ecological risk of PHEs, the total concentrations, distributions and chemical fractions of PHEs in the Bohai Bay surface sediments were determined. The objectives of this study were (1) to determine the PHE concentrations and their chemical fractions in the surface sediments of Bohai Bay; (2) to analyze the factors controlling the PHE distributions; (3) to evaluate the enrichments of PHEs in the surface sediments of Bohai Bay; and (4) finally to discuss the origins of PHEs in the surface sediments of Bohai Bay.

2. Materials and methods

2.1. Site description

The focus of the paper concentrated on Bohai Bay. It is a semi-enclosed bay located in the western region of the Bohai Sea in the North China. It covers an area of 1.6×10^4 km^2 with a population of about 70 million. The average depth is 12.5 m with the maximum of 32 m. Bohai Bay receives both industrial and domestic wastewater discharges from Beijing, Tianjin and Hebei province. All the wastewater through rivers and channels drains into the near-shore waters of Bohai Bay directly [15]. Approximately 87% of pollutants in Bohai Bay are discharged from land, and 95% of pollutions generated in the area are transported by river into Bohai Bay. There are several rivers (e.g., the Haihe River, Jiyunhe River, Huanghe River, Tuhaihe River and Majiahe River) emptying into Bohai Bay with a total annual water discharge of 6.5×10^9 m^3/yr and annual suspended matter input of 6.0×10^6 tons/yr [16,17].

2.2. Sampling

The present study was based on the surface sediments from Bohai Bay sampled during 21 to 28 April 2008. According to their latitude from 38°14′04″ N to 38°58′00″ N, a population of 27 sample stations were designated (Fig. 1). Position of sampling sites was recorded by the aid of a Global Positioning System (GPS) technology. Surface sediments were collected using a grab sampler. Sub-samples were taken from the center with a polyethylene spoon to avoid possible contamination by the metallic parts of the sampler. Immediately after collection, samples were placed in pre-cleaned polyethylene bags, sealed, refrigerated, and transported to the laboratory. Samples were dried in an oven at 60 °C for 72 h. Dried aliquots were ground using an agate mortar and pestle for homogenization, and prepared for analysis. Data reported in this study are calculated as dry weight.

2.3. Sediment analyses

About 0.1 g dry sample was digested in closed Teflon digestion vessel with a mixture of 0.6 ml HNO$_3$ and 2 ml HF, and then the mixture was heated on an electric heating plate at 150 °C for 24 h. Then 0.5 ml HClO$_4$ was added to the mixture, and it was evaporated to dryness. After cooling, the residue was digested again

with a mixture of 0.6 ml HNO_3 and 2 ml HF at 150 °C for 24 h, then 0.5 ml $HClO_4$ was added and heated to dryness. The residue was treated with 1 ml HNO_3 and 1 ml H_2O and heated in closed Teflon digestion vessel at 120 °C for 12 h. Next, the solution was diluted with Milli-Q water to 40 ml. Major elements (Al_2O_3, Fe_2O_3, MnO, CaO, MgO and P_2O_5) and As were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; PerkinElmer Optima 3000). Trace elements (Ge, Mo, In, Sn, Sb, Te, Tl, Bi, V, Co, Ni, Sc, Cs, Li, Zn, Pb, Cr, Cd and Cu) were measured with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; SCIEX Elan 5000). The optimum operation conditions for ICP-AES are summarized as follows: RF power, 1300 W; Coolant gas flow rate, 15 l/min; Auxiliary gas flow rate, 0.8 l/min; Delay time, 30 s; Integral, peak area. The optimum operation conditions for ICP-MS are summarized as follows: RF power, 1100 W; Coolant gas flow rate, 14 l/min; Auxiliary gas flow rate, 0.8 l/min; Nebulizer gas flow rate, 0.8 l/min; Dwell time, 20 ms; Resolution, normal.

Five fractions of PHEs in the sediment samples were obtained using the sequential selective extraction analyses. These five fractions were analogous to: exchangeable, bound to carbonates, bound to Fe–Mn oxides, bound to organic matter and residual fractions. The sequential selective extraction procedure applied to 0.1 g of dried samples with natural grain size comprised the following steps.

Extraction at room temperature for 16 h with 10 ml Milli-Q water with continuous agitation was for exchangeable fraction. The residue from the previous extraction step was subjected to further leaching with 8 ml of 0.1 M acetic acid at room temperature with continuous agitation for 16 h to receive the dissolution of carbonate fraction. The residue from the second extraction step was treated with 10 ml of 0.04 M hydroxylamine hydrochloride in 25% acetic acid at 96 °C for 6 h with continuous agitation for dissolving Fe–Mn oxides fraction. The residue from the third extraction step was leached with 1.5 ml of 0.02 M nitric acid and 4 ml of 30% hydrogen peroxide adjusted to pH 2 with HNO_3, and mixture was heated at 85 °C for 2 h with continuous agitation, followed by the addition of 1.5 ml of 0.02 M nitric acid and 4 ml of 30% hydrogen peroxide (pH 2 with HNO_3) at 85 °C for 3 h with continuous agitation. After cooling down, 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO_3 was added and the mixture was agitated for 30 min at room temperature for extracting organic matter fraction. The difference between total concentrations of elements and the sum of these four extract fractions provided information of residual fraction.

After each of these selective extractions, the samples were centrifuged at 4000 rpm for 10 min, and the supernatants were decanted into volumetric Nalgene flasks. Sediment residues were afterwards washed with Milli-Q water, centrifuged again, and the wash water was added to the supernatant. The supernatant of each fraction was determined by ICP-MS.

Total organic carbon (TOC) was analyzed by the Walkey–Blake method [18]. Sediment grain size was determined using a Laser Particle Size Analyzer. The particle sizes were less than 4 μm for clay, 4–63 μm for silt and larger than 63 μm for sand. The relative error of the duplicate samples was less than 3% ($n = 6$).

Chlorophyll-a (Chl-a) concentration was used as an indicator of the phytoplankton biomass in the surface seawater. 1 l of seawater sample was filtered quickly by vacuum filtration through Whatman GF/F glass fiber filter, and the filter samples containing chlorophyll-a were stored in dark at −20 °C until spectrophotometer analysis could be conducted. In the preparation for spectrophotometric analysis, the filter samples were immersed in 10 ml 90% acetone solution and then placed in cool, dark chambers for about 24 h to ensure extraction of Chl-a. The soaked solution was centrifuged at 3000 rpm for 10 min, and the supernatant was analyzed with a fluorescence spectrophotometer at 436 nm (Ex) and 670 nm (Em) wavelength.

2.4. Data quality

The quality assurance and quality control were controlled by method blanks, field duplicate samples, spiked samples and standard reference materials (SRMs). Field duplicate samples were collected approximately once every 10 samples while in the field. The relative percent difference for metals indentified in paired duplicate samples was all <10%. Blank samples were also performed throughout all the experiments. All element concentrations in method blanks were below the detection limits of the ICP-MS. To explicitly evaluate the analytical precision, all samples were determined in triplicate. Precision, expressed as relative standard deviation, was better than 10%. Accuracy of the analysis of the fractions was done by determining the recovery of spiked samples in the various extractant solutions. The recoveries ranged from 95 to 105%. Accuracy of the total analysis was assured using the standard reference materials (GSR-1, GSR-3, GSMS-2 and GSMS-3); their certified values and determined values are presented in Table 1. The recoveries ranged from 90 to 110%.

2.5. Calculation of enrichment factor (EF)

The EF can be used for assessing whether the presence of an element in sediment samples is due to anthropogenic activities. It is defined as the concentration ratio of a considered element to a reference element in a given sample, divided by the same ratio in earth crust, that is

$EF = (X/Y)_{sample}/(X/Y)_{crust}$,

with X = concentration of the considered element and Y = concentration of the reference element.

Table 1
Certified values and determined results of PHE concentrations (mean ±S.D. in μg/g; $n = 3$) in standard reference materials GSR-1, GSR-3, GSMS-2 and GSMS-3.

PHE (μg/g)	GSR-1		GSR-3		GSMS-2		GSMS-3	
	Certified values	Determined values	Certified values	Determined values	Certified values	Determined values	Certified values	Determined values
Ge	2.0 ± 0.3	2.0 ± 0.1	0.98 ± 0.23	1.06 ± 0.07	nd	nd	nd	nd
Sn	12.5 ± 2	11.8 ± 1	2.0 ± 0.6	1.9 ± 0.1	nd	nd	nd	nd
In	0.02	0.018 ± 0.005	0.063	0.058 ± 0.013	nd	nd	nd	nd
Mo	3.5 ± 0.3	3.3 ± 0.1	2.6 ± 0.3	2.8 ± 0.01	14 ± 1	14.7 ± 0.1	5.7 ± 0.8	5.7 ± 0.11
Sb	nd	nd	0.08 ± 0.05	0.08 ± 0.02	2 ± 0.4	2.1 ± 0.1	1.3 ± 0.3	1.3 ± 0.08
Te	0.021 ± 0.005	0.023 ± 0.002	0.022	0.021 ± 0.006	nd	nd	nd	nd
Tl	1.93 ± 0.55	1.89 ± 0.2	0.12	0.13 ± 0.01	nd	nd	nd	nd
Bi	0.53 ± 0.09	0.48 ± 0.01	0.048 ± 0.026	0.048 ± 0.01	0.9 ± 0.2	0.88 ± 0.10	0.57 ± 0.05	0.56 ± 0.01
V	24 ± 3	23 ± 1	167 ± 17	168 ± 2	101 ± 8	102 ± 1	69 ± 6	70 ± 2.2

nd: no data.

Table 2
Means, ranges and standard deviation (S.D.) of major element contents in all surface sediments of Bohai Bay ($n = 27$).

Content (%)	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	P_2O_5
Max	16.6	6.82	0.16	8.46	3.43	0.17
Min	12.9	4.78	0.09	3.69	2.49	0.14
Mean	15.2	6.11	0.12	6.83	3.09	0.16
S.D.	0.90	0.50	0.02	1.07	0.25	0.008

2.6. Statistical analysis

Statistical methods including Pearson correlation analysis and principal component analysis (PCA) were used to evaluate differences and elucidate the relationships between PHEs and other environmental parameters. In this work, a value of $p < 0.05$ was considered to indicate a significant difference in all statistical analysis. Pearson correlation analysis had been used to extract information from the chemical analysis in order to find the relationships between PHEs and major elements, and heavy metals. Principal component analysis was executed on the analytical data in order to obtain a visual representation of the main characteristics of the relationships among PHEs, major elements and TOC contents. Usually the principal components (PCs) were obtained by their eigenvalues >1. All statistical analyses were performed using the SPSS 13.0.

3. Results and discussion

3.1. Major element and PHE concentrations

The total concentrations of major elements and PHEs were measured in the surface sediment of Bohai Bay. The concentrations displayed a wide range between the elements, possibly reflecting their natural variability and sources. The contents of major elements (Al_2O_3, Fe_2O_3, MnO, CaO, MgO and P_2O_5) in surface sediments ranged from 12.9% to 16.6%, 4.78% to 6.82%, 0.09% to 0.16%, 3.69% to 8.46%, 2.49% to 3.43% and 0.14% to 0.17%, with averages of 15.2%, 6.11%, 0.12%, 6.83%, 3.09% and 0.16%, respectively (Table 2). Concerning major elements, the sediment chemical composition did not vary obviously, the respective abundance of Al and Fe + Mn remained the same whatever the sediments compared with Ca + Mg.

There was a wide range in concentrations for the different PHEs (4–5 orders of magnitude). Based on the data (Fig. 2), In, Te, Tl and Bi could be described as typically low concentration elements (0.02–1.00 µg/g). An intermediate group was formed by Ge, Mo, Sn and Sb (1–10 µg/g), whereas V was a group with relatively high concentration (100 µg/g). As shown in Fig. 2, the Ge, Mo, Sn, In, Te, Tl, Sb, Bi and V concentrations in the surface sediments of Bohai Bay were in the range of 1.43–1.71, 0.52–1.43, 2.77–4.14, 0.04–0.12, 0.027–0.085, 0.506–0.770, 1.14–2.29, 0.27–0.63 and 70.35–115.90 µg/g, with averages of 1.55, 0.84, 3.77, 0.09, 0.059, 0.685, 1.51, 0.49 and 100.40 µg/g, respectively.

The spatial patterns of surface concentrations were quite similar to PHEs. Among the PHEs, Sn and Ge showed less variability while the other PHEs showed a considerable variability in their distributions. Although the PHE concentrations varied fluctuating among the sediment samples with no regular distribution pattern (Fig. 2), all of them displayed a typical concentration gradient similar to the distribution of the clay content. Generally, the concentrations of PHEs were higher in the western part of Bohai Bay, whereas the concentrations were lower at the bay mouth. It indicated that the input of the Haihe River Basin was an important source of PHEs.
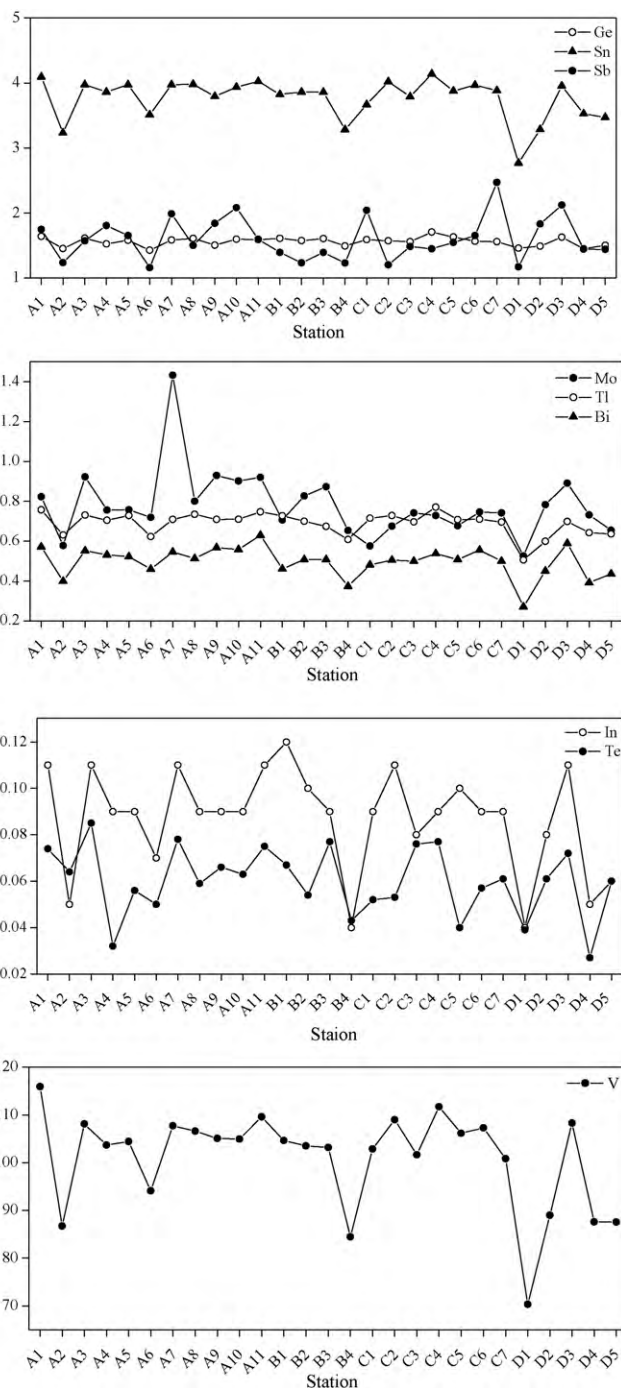

Fig. 2. Spatial variations of PHE concentrations (µg/g) in Bohai Bay surface sediments.

Table 3
Pearson correlation coefficients for PHEs and major elements (Al_2O_3, Fe_2O_3 and MnO), clay and TOC contents, reference elements (V, Co, Ni, Sc, Cs and Li) and heavy metals (Zn, Pb, Cu, Cr, Cd and As).

	Ge	Mo	In	Sn	Sb	Te	Tl	Bi	V
Al_2O_3	0.648[a]	0.314	0.757[a]	0.817[a]	0.211	0.411[b]	0.852[a]	0.663[a]	0.828[a]
Fe_2O_3	0.696[a]	0.431[b]	0.828[a]	0.901[a]	0.259	0.434[b]	0.877[a]	0.802[a]	0.909[a]
MnO	0.271	0.632[a]	0.425[b]	0.487[b]	0.357	0.463[b]	0.626[a]	0.705[a]	0.430[b]
V	0.811[a]	0.486	0.925[a]	0.970[a]	0.522[a]	0.956[a]	0.918[a]	0.292	1.000
Co	0.937[a]	0.566[a]	0.891[a]	0.959[a]	0.518[a]	0.912[a]	0.940[a]	0.222	0.964[a]
Ni	0.959[a]	0.540[a]	0.899[a]	0.974[a]	0.506[a]	0.937[a]	0.964[a]	0.255	0.981[a]
Sc	0.422[b]	0.022	0.305	0.263	0.358	0.299	0.182	0.047	0.373
Cs	0.908[a]	0.418[b]	0.814[a]	0.857[a]	0.548[a]	0.861[a]	0.866[a]	0.334[b]	0.905[a]
Li	0.787[a]	0.364	0.897[a]	0.937[a]	0.492[b]	0.956[a]	0.830[a]	0.167	0.967[a]
Zn	0.763[a]	0.533[a]	0.879[a]	0.958[a]	0.293	0.343	0.861[a]	0.853[a]	0.977[a]
Pb	0.559[a]	0.779[a]	0.752[a]	0.787[a]	0.505[a]	0.675[a]	0.779[a]	0.941[a]	0.811[a]
Cu	0.743[a]	0.517[a]	0.924[a]	0.954[a]	0.303	0.557[a]	0.938[a]	0.942[a]	0.973[a]
Cr	0.841[a]	0.538[a]	0.909[a]	0.943[a]	0.281	0.611[a]	0.912[a]	0.883[a]	0.970[a]
Cd	0.221	0.536[b]	0.398[b]	0.459	0.183	0.276	0.382[b]	0.645[a]	0.490[a]
As	0.479[b]	0.680[a]	0.789[a]	0.730[a]	0.194	0.473[b]	0.602[a]	0.842[a]	0.736[a]
Clay%	0.662[a]	0.680[a]	0.431	0.672[a]	0.728[a]	0.840[a]	0.664[a]	0.716[a]	0.750[a]
TOC%	0.731[a]	0.591[b]	0.652[a]	0.604[a]	0.464	0.565[b]	0.611[a]	0.674[a]	0.545[b]

[a] Correlation is significant at the 0.01 level (two-tailed).
[b] Correlation is significant at the 0.05 level (two-tailed).

3.2. Transportation of PHEs

The dispersal of PHEs in sediments was related to the transportation and deposition processes from sources to sinks in the bay. In particular, physical, chemical and biological processes could influence the PHE fate and transportation in sediments. Once entered aquatic system PHEs would be deposited and incorporated into sediment after these processes.

3.2.1. Physical transportation of PHEs

The physical properties of sediments (i.e., grain size and sediment components) can affect the concentrations of PHEs in the bay, since the increasing specific surface of fine sediments favored adsorption processes. The surface sediments in Bohai Bay mainly contained silty clay and clayey silt and the clay contents ranged from 25.5 to 64.3% with an average of 46.2%. Within the bay, the clay contents of sediments increased from the estuaries to the central bay and the fine-grained sediments were concentrated at the central bay. This pattern reflected a typical sediment transportation mechanism in the bay area. In addition, the physical characteristics of sediments were closely related to some major elements (i.e., Al and Fe), since clay minerals contained Al and Fe in their crystal structure. Correlation analysis suggested that the PHEs, major elements and the clay contents were significantly correlated with each other (Table 3). These correlations suggested that the PHEs were mainly combined with the fine particles. Thus, the fine particles might be a major carrier for transporting PHEs from the rivers to the central bay. So, according to the distribution of fine-grained sediment, the physical transportation of sediments and associated PHEs could be reflected.

The hydrodynamic processes and the deposition conditions were the dominant driving power affecting the sediment transportation and distribution. In the study area, the coarse-grained sediments mainly presented near the estuaries and the fine-grained sediments mainly presented at the central bay. This pattern was significantly related to the hydrodynamic conditions (i.e., tidal currents, coastal current, continental diluted current and circumfluence) in Bohai Bay. Besides, the sediment transported into the bay was mainly originated from the rivers (e.g., the Haihe River, the Huanghe River, and the Luanhe River). Detailedly, the sediments and associated PHEs of the central bay and the southern bay mainly came from the Huanghe River, the grain size of which was relatively fine [19]. The sediments and associated PHEs of the northern bay mainly came from the Luanhe River, the grain size of which was relatively coarse. However, the sediments and associated PHEs of the western bay mainly came from the Haihe River, the grain size of which was relatively fine [20]. When the sediments were transported from rivers into the bay, the coarse-grained sediments deposited quickly; however, the deposition of fine-grained sediments became slow with the increasing distance from the estuaries. Furthermore, once entered the bay, the sediments would be transported and distributed due to the effect of sediment aggregation and deposition and hydrodynamic processes such as gravitational circulation and tidal currents so that the sediment type developed. In these processes, the sediment aggregation and deposition was influenced by current velocity, salinity and suspended particulate matter concentration in the water column [21]. Therefore, most of the coarse particles tended to be deposited at the estuaries due to the sudden change in the velocity of the water currents in this area [22]. The fine particles were finally carried by waters into the central bay where the hydrodynamic processes were weak. Due to the tidal cycle, coastal current, continental diluted current and circumfluence, sediments would be agitated, resuspended and exchanged between different depositional regions, which would continue until the limited stockpile of easily eroded particles was depleted [23]. Consequently, the PHEs were transported and deposited with the fine-grained sediments, controlled by the material sources, transportation medium, transportation mode and the sedimentary environment [24].

3.2.2. Chemical transportation of PHEs

Although the elevated PHE concentrations were mainly associated with high clay content of sediment, it did not adequately account for that the concentrations of PHEs in sediments only were controlled by a change in grain size. In other words, physical transportation was not the only way to control the pattern of PHEs in the bay. Moreover, the dissolved PHEs in seawaters can be scavenged to particles, and deposited into bottom sediments via chemical processes [25]. Therefore, another important factor controlling the spatial variations of PHEs in sediments was the chemical condition of the sedimentary environment.

Information on the fractions of PHEs could provide the evidence to favor the influence of chemical condition on PHE distributions [11]. Residual fractions of PHEs mainly contained primary and secondly minerals, which may hold PHEs within their crystal structure. These portions were not released in seawaters under the conditions normally encountered in nature. Thus, the residual fractions mainly were transported by physical processes with

Table 4
Means, ranges and standard deviation (S.D.) of five fractions of PHE concentrations and their mean percentages in all surface sediments of Bohai Bay (μg/g; n = 27).

Fraction	Ge	Mo	In	Sn	Sb	Te	Tl	Bi	V
Exchangeable									
Max	0.010	0.15	nd	0.010	0.03	0.010	0.004	0.0007	2.64
Min	0.001	0.04	nd	nd	nd	nd	nd	nd	0.46
Mean	0.003	0.10	nd	0.003	0.01	0.003	0.001	0.0002	1.11
S.D.	0.0017	0.112	nd	0.004	0.009	0.003	0.0007	0.0002	0.67
Mean percentage (%)	0.19	12.86	0	0.07	0.64	5.62	0.15	0.03	1.08
Carbonates									
Max	0.03	0.050	0.010	0.020	0.29	0.02	0.003	0.12	7.1
Min	0.01	0.003	0.002	nd	nd	nd	0.001	0.04	1.5
Mean	0.02	0.015	0.007	0.006	0.07	0.01	0.002	0.09	4.1
S.D.	0.003	0.011	0.002	0.006	0.07	0.007	0.0004	0.02	1.5
Mean percentage (%)	1.25	1.84	7.64	0.17	4.40	12.70	0.23	17.97	3.97
Fe–Mn oxides									
Max	0.06	0.30	0.014	0.024	0.20	0.03	0.05	0.30	21.9
Min	nd	nd	nd	nd	nd	nd	nd	nd	9.8
Mean	0.05	0.18	0.008	0.013	0.07	0.01	0.04	0.20	16.2
S.D.	0.01	0.06	0.003	0.006	0.04	0.01	0.01	0.06	4.4
Mean percentage (%)	3.17	24.44	10.40	0.37	4.87	19.78	5.50	41.81	16.13
Organic matter									
Max	0.03	0.20	0.002	0.30	0.30	0.04	0.020	0.04	6.45
Min	0.02	0.06	nd	0.10	nd	0.01	0.010	0.01	2.80
Mean	0.03	0.12	0.001	0.14	0.18	0.01	0.017	0.02	4.63
S.D.	0.003	0.031	0.0007	0.05	0.06	0.01	0.002	0.01	0.72
Mean percentage (%)	1.86	14.65	0.65	3.77	11.16	15.63	2.41	4.46	4.56
Residual									
Max	1.60	1.10	0.10	4.00	1.80	0.10	0.72	0.40	97.9
Min	1.30	0.10	0.03	2.40	0.60	nd	0.45	0.10	53.6
Mean	1.50	0.40	0.07	3.56	1.21	0.03	0.63	0.20	75.4
S.D.	0.07	0.21	0.02	0.38	0.28	0.03	0.06	0.07	9.5
Mean percentage (%)	93.56	46.21	81.30	95.61	78.93	46.28	91.70	35.73	74.26

nd: not determined.

the clay particles. However, non-residual fractions of PHEs including exchangeable, bound to carbonates, bound to Fe–Mn oxides, bound to organic matter fractions, would be susceptible to the changes of environmental parameters (i.e., clay content, Al oxides, Fe–Mn oxides, salinity, pH, temperature and oxidation–reduction potential (Eh)). Thus non-residual fractions mainly were controlled by chemical processes. The results of PHE fractions at all the stations were analyzed to determine the mean, range and standard deviation of each fraction of PHE concentrations and their mean percentages (Table 4). It suggested that the PHEs mainly existed as residual fractions with the average percentages of 93.6% for Ge, 46.2% for Mo, 81.3% for In, 95.6% for Sn, 78.9% for Sb, 46.3% for Te, 91.7% for Tl, 35.7% for Bi and 74.3% for V, indicating that the physical transportation played an important role in PHE distributions. However, the non-residual fractions of PHEs also were higher for Mo, In, Sb, Te, Bi and V, suggesting that the PHEs also were closely related to the chemical conditions of sedimentary environment. Chemical processes mainly contained adsorption–desorption and flocculation processes, dissolution–precipitation reactions, oxidation–reduction reactions and anthropogenic pollution [26]. These processes were strongly affected by the physical–chemical parameters (i.e., clay content, Al oxides, Fe–Mn oxides, salinity, pH, temperature and Eh) of overlying waters and sediments. The salinity, pH and temperature in the overlying waters of Bohai Bay were in ranges of 30.51–32.10‰, 8.10–8.28 and 6.73–13.85 °C, with averages of 31.57‰, 8.17 and 9.17 °C, respectively.

Firstly, the adsorption–desorption and flocculation processes were mainly affected by clay content, Al oxides, Fe–Mn oxides and salinity and these processes mainly acted on the non-residual fractions. In this study, the higher percentages of PHEs bound to the non-residual fractions were found, suggesting that the PHEs might simply be affected by adsorption–desorption processes [11]. Besides, clay particles were a major carrier of PHEs from rivers to

Bohai Bay, clay particles, Al oxides and Fe–Mn oxides, very efficient scavengers for PHEs due to their larger surface coatings, were one of the factors that influenced the adsorption–desorption processes. The significant correlations between clay content, Al oxides or Fe–Mn oxides and PHE concentrations of sediments were found (Table 3), indicating that the adsorption processes increased with the increase of clay content, Al oxides and Fe–Mn oxides to some extent. Moreover, the fractions of PHEs bound to Fe–Mn oxides were dominant non-residual fractions (Table 4), further suggested that Fe–Mn oxides played an important role in adsorption processes. Besides, salinity also was an important factor affecting the adsorption–desorption and flocculation processes. There were three possible mechanisms for explaining these processes. First, PHEs could be mobilized as soluble chloride complexes. The stability and solubility of PHE complexes were relatively high while the affinity for sorption to the sediments was low. Upon the formation of these complexes, the activity of free PHEs in seawaters would decrease and desorption of sediments would increase [26]. Besides the effects of complexation, an increase of the salinity was associated with an increase in the concentrations of alkali and alkali earth metal ions that competed with PHEs for sorption sites [27]. Thus, with the salinity increase, complex ions and alkali and alkali earth metal ions increased, resulting in the adsorption and precipitation of PHEs on the sediments decreased. Second, the adsorption of PHEs on particulates intensified with the salinity increase, inducing the flocculation to enhance, and further strengthening the aggregation and deposition of sediment. Third, due to the conservative behaviors of PHEs, the dissolved PHEs in seawaters decreased with the salinity increase. Consequently, with the salinity increase, the amount of dissolved PHEs in the water column available for the process of coagulation decreased [28]. In Bohai Bay, it seemed that the complexation of PHEs, competition between adsorption of alkaline and alkaline earth metal ions and adsorption of dissolved PHEs on sediments and conservative behaviors of dissolved PHEs in

seawaters played more important roles in PHE distributions than flocculation processes. Thus, the concentrations of PHEs in the non-residual fractions of sediments decreased in higher salinity areas except for the Haihe Estuary, having more anthropogenic inputs. It was supported by the negative correlations between non-residual fractions of PHEs and salinity in Bohai Bay, with the correlative coefficients of 0.089, 0.568, 0.035, 0.749, 0.725, 0.614, 0.543, 0.439 and 0.104 for Ge, Mo, In, Sn, Sb, Te, Tl, Bi and V, respectively.

Secondly, dissolution–precipitation reactions were closely related to pH and temperature, which also worked on the adsorption–desorption process. Besides, dissolution–precipitation processes mainly acted on the exchangeable and carbonate fractions. Since pH and temperature could affect the solubility and behaviors of PHEs in aquatic environment, so they can influence PHE distributions in sediments directly [29]. With the decreasing pH and increasing temperature, the adsorption of PHEs decreased and the release of PHEs from the sediments increased. In this respect, there was only a positive correlation between exchangeable and carbonate fractions of Tl and pH ($r = 0.534$, $p < 0.05$). This may be due to the narrow variation of pH, so the influence of pH on the PHE distributions was not obvious. Besides, the concentrations of PHEs in exchangeable and carbonate fractions varied with the temperature variation. There were negative correlations between temperature and exchangeable and carbonate fractions of PHEs, with $r = -0.544$ ($p < 0.05$) for Ge, $r = -0.720$ ($p < 0.01$) for In, $r = -0.616$ ($p < 0.01$) for Sn, $r = -0.567$ ($p < 0.01$) for Te, $r = -0.642$ ($p < 0.01$) for Bi, $r = -0.553$ ($p < 0.01$) for V. This indicated that with the temperature increase, the solubility of sedimentary PHEs increased and concentrations of them decreased.

Thirdly, oxidation–reduction reactions were associated with Eh and mainly acted on the fractions bound to Fe–Mn oxides and organic matters. The Fe–Mn oxides and organic matters have a scavenging effect and may provide a sink for PHEs. The release of the PHEs from these matrixes will most likely be affected by the redox potential and pH. The PHEs transferred with the change of redox gradient of sedimentary environment, which always was indicated by the Eh value of sediment [30]. On the one hand, when the redox status of sediment changed from oxic to reductive condition, Fe(III) and Mn(IV) oxides would be reduced, and then the PHEs associated with Fe–Mn oxides would be released and scavenged by organic matters or form sulfides. On the other hand, when the redox status of sediment changed from reductive to oxic condition, organic matters or sulfides would be oxidized, and then the PHEs associated with organic matters or that existed as the sulfides would be released and re-adsorbed by Fe–Mn oxides. In this study, sedimentary environment presented the weak reductive condition in the Haihe Estuary, with the Eh value of −41 mV and sulfide of 794 ppm, whereas the sedimentary environment at the other areas of Bohai Bay was weak oxic or oxic. For example, the Eh and sulfide values in the Jiyunhe Estuary, Luanhe Estuary and Huanghe Estuary were 335.7, 102.5, and 107.3 mV and 47.2, 65, and 49 ppm, respectively [31]. It was obvious that with the increase of the Eh value, sulfide concentration decreased. Furthermore, owing to the TOC was easily conserved in reductive environment, so with the Eh increase the TOC decreased. Thus, the PHEs that existed in sediments as the sulfides or associated with organic matters decreased with the distance from the Haihe Estuary whereas the fractions of PHEs bound to Fe–Mn oxides increased with the distance from the Haihe Estuary. Moreover, the negative correlations were found between fractions bound to Fe–Mn oxides and fractions bound to organic matters, with $r = -0.635$ ($p < 0.01$) for Sb, $r = -0.541$ ($p < 0.01$) for Tl, $r = -0.577$ ($p < 0.01$) for Sn and $r = -0.617$ ($p < 0.01$) for Bi. It seemed that the PHEs could be exchanged between fractions bound to Fe–Mn oxides and fractions bound to organic matters and when the organic matter fraction decomposed, this fraction would be re-adsorbed mostly by Fe–Mn oxides and vice versa.

Fourthly, anthropogenic pollution was related to the anthropogenic discharge and mainly acted on the exchangeable and carbonate fractions [32]. The estuarine areas were close to intensive industrial and agricultural operations, so industrial and agricultural discharges may lead to a large input of PHEs to estuaries and near shore. The higher percentages of Mo, In, Te, Sb, Bi and V in exchangeable and carbonate fractions were found with 14.7%, 7.64%, 18.32%, 5.04%, 18.0% and 5.05%, respectively (Table 4), indicating the anthropogenic origin of PHEs. Consequently, the non-residual fractions were an important portion of PHEs, so the chemical conditions of the sedimentary environment were an important factor controlling the spatial variations of PHEs in sediments.

3.2.3. Biological transportation of PHEs

Organic matter accumulation in marine sediments was commonly used as a proxy for the biological productivity, so the PHEs scavenged by organic matters were strongly coupled to biological activity. The TOC contents in Bohai Bay surface sediments were 0.114–0.495%, with an average of 0.411%. The TOC contents near the estuaries were obviously high due to the abundant nutrient input mainly by rivers. Significant correlations between TOC content and PHE concentrations were found (Table 3), suggesting that the PHEs and organic matters had a common origin and PHEs were probably introduced to the system attached to organic matter.

The organic matter mainly came from the dead phytoplankton and byproduct of the zooplankton and benthos metabolic activities. These products would accelerate the release/bacterial degradation of the organic matter [33]. So, the organism biomass and the associated growth of bacteria were the controlling factors of the organic matters. Organic compounds can promote aggregation of suspended particles, which have the more efficient scavenging capability. Therefore, the deposition of aggregation led to a sudden deposition of huge amounts of organic matters, resulting in that the PHEs combined with the organic matters also transferred into the sediments.

Furthermore, marine biological productivity was an important factor for controlling the quality of organic matter. Chlorophyll-a (Chl-a) concentration was used as the most convenient index of biological productivity. The Chl-a concentrations in Bohai Bay ranged from 0.40 to 7.64 μg/l, with an average of 1.89 μg/l. There was a significant positive correlation between Chl-a concentration and TOC content, with $r = 0.566$ ($p < 0.01$). Thus, in the high productive regions, metabolisms of organisms were hearty so that the bacterial activity and growth accelerated. As a result organic matter released by lyses and bacterial decomposition of organism material initiated the formation of larger aggregates [33]. Huge amounts of these organic-rich aggregates were deposited on the sediments, thereby serving as a potential shuttle for the transfer of PHEs from the water column to the sediment layer. Thus, the transfer of PHEs to the sediments via aggregates would concentrate PHEs at the sediment/water interface.

Consequently, the coupling of physical, chemical and biological processes may be of significant relevance for PHEs. These processes played an important role in the transportation and deposition processes of PHEs in the study area.

3.3. Enrichment factors

In order to gain information about the potential sources of PHE, the enrichment factors (EFs) of them in surface sediments were calculated, choosing Cs as the reference element due to its higher percentage of residual fraction than other reference elements (V, Co, Ni, Li and Sc; Fig. 3) and significant correlation with PHEs (Table 3). This reference element had been already selected by Roussiez et al. [34] for sediments in the Gulf of Lions, and by N'guessan et al. [1] for stream bed sediments. In this study, the baseline value adopted the
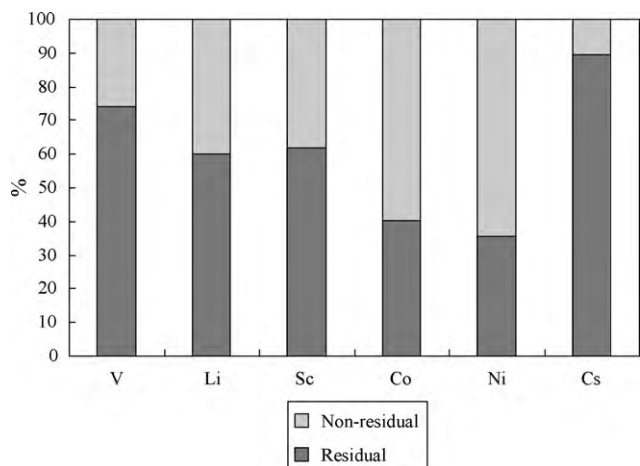
Fig. 3. Proportion of residual and non-residual fractions of reference elements (V, Li, Sc, Co, Ni and Cs) as normalizers. The non-residual fraction was the sum of exchangeable, bound to carbonates, bound to Fe–Mn oxides and bound to organic matter fractions. The residual fraction represented the elements remained in the mineral lattice.

element abundance in earth crust. It is generally accepted that EF < 2 reflects natural variability of the sample mineralogical composition [35,36]; beyond 2, a significant enrichment is suspected. Based on the research of Zhang and Liu [37], if an EF value is between 0.5 and 1.5, it suggests that PHEs may be entirely from crustal materials or natural weathering processes. If an EF is greater than 1.5, it suggests that a significant portion of PHEs are provided by other sources rather than crustal or natural origins.

The average EF values were obtained in Fig. 4 showing that the EFs of Te, Sb and Bi were higher than 1.5, while the EFs of other PHEs remained within the range of natural variability. The EFs of these PHEs lied in the sequence, Te > Bi > Sb > Sn > In > Tl > Ge > V > Mo. Te, Sb and Bi were therefore the most anthropogenic enriched elements in the surface sediment of Bohai Bay. Except for Te, Sb and Bi, the EF values of other PHEs were lower than or close to one indicating that they were derived from crust. Moreover, the high percentages of Te, Sb and Bi in exchangeable and carbonate fractions were found with 5.62% and 12.70%, 0.64% and 4.40%, and 0.03% and 17.97%, respectively (Table 4), indicating further the anthropogenic origin. Furthermore, the high percentages of Te, Sb and Bi in Fe–Mn oxides and organic matter fractions also were found with 19.78% and 15.63%, 4.87% and 11.16%, and 41.80% and 4.46%, respectively (Table 4), suggesting the high potential harm of these elements. On the whole, the pollution of PHEs in Bohai Bay was not serious based on the EF analysis.
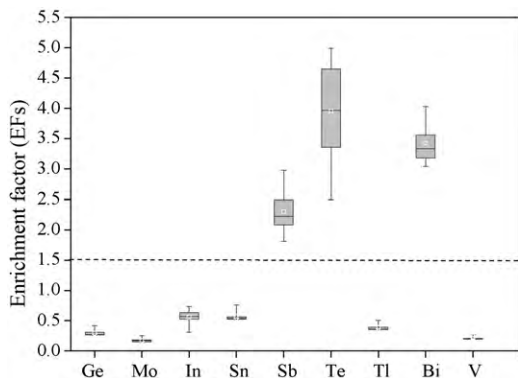

Fig. 4. Enrichment factors (EFs) for PHEs in Bohai Bay surface sediments using Cs as normalizer. Below the dot line (EF < 1.5) indicated that elements were not provided mainly from anthropogenic activities.

Furthermore, Sutherland [36] proposed that the EF values ranged between 2 and 5 indicating a moderate enrichment, EF values between 5 and 20 suggesting a significant enrichment, EF values between 20 and 40 implying a very high enrichment, and EF values higher than 40 inferring an extreme enrichment. In this respect, Bohai Bay sediments were moderately contaminated by Te, Sb and Bi.

3.4. Origins of PHEs in sediments

The PHEs were introduced in the environment naturally as well as from the anthropogenic activities. Atmosphere deposition, riverine input and food chain transportation were considered to be the major sources of PHEs in the aquatic environment.

The selective extraction studies showed that the PHEs were mainly found in the residual fractions of sediments, indicating that the main source of PHEs in the sediments of Bohai Bay was natural detrital origin delivered by the rivers and atmosphere. However, the high proportions of Mo, Sb, Te, Bi and V occurred in non-residual fractions, especially in the Fe–Mn oxides and organic matter fractions, probably indicating some anthropogenic inputs in addition to the predominant natural inputs.

Six heavy metals of Zn, Pb, Cu, Cr, Cd and As were detected in this investigation. Their concentration ranges were as follows: 78.0–110.4 µg/g, 19.0–36.1 µg/g, 19.1–41.7 µg/g, 63.4–89.3 µg/g, 0.16–0.43 µg/g and 3.35–7.78 µg/g, with averages of 98.8 µg/g, 30.0 µg/g, 35.1 µg/g, 80.2 µg/g, 0.28 µg/g and 5.56 µg/g, respectively. The maximum detection values of heavy metals were obtained at A1, C6 and A11 stations, adjacent to estuaries. This suggested that the six heavy metals in Bohai Bay surface sediments mainly came from the riverine inputs. The distribution of heavy metals in the surface sediments was similar to that of heavy metals in seawaters. So, the sources of heavy metals in seawaters also were indicatives of the origins of heavy metals in the surface sediments to some extent. High levels of heavy metals in seawaters appeared especially near the Haihe Estuary, and the same phenomenon was present in the surface sediments, indicating that the riverine input was the main source. Besides, atmospheric deposition also contributed to the Pb contamination in Bohai Bay seawaters. Meng et al. [38] reported that Pb in coastal waters of Bohai Bay originated primarily from river discharge before 2001; however Pb levels did not decrease after 2001 when annual runoff levels declined, indicating that Pb pollution by atmospheric deposition had increased. Hence, atmospheric deposition was another important source of heavy metals.

Correlation analysis results (Table 3) indicated that the six heavy metals were positively related to PHE concentrations, suggesting that they had the same source, and the factors controlling PHE distributions also worked on the heavy metals. So, the riverine input and atmospheric deposition also were the main PHE sources.

A principal component analysis (PCA) was performed on selected data of the surface sediments to reveal the interrelationships of PHEs and the major constituents (TOC, Al_2O_3, Fe_2O_3, MnO, P_2O_5 and CaO). Table 5 showed the results for the first four principal components (PCs). These four PCs were the ones with eigenvalues larger than 1, and together they described 84.7% of the variance in the data. The eigenvectors showed that the first principal component (PC1) was well related to Al_2O_3, Fe_2O_3, Ge, Bi, In, Sn, Tl and V; Mo, P_2O_5, CaO and MnO were mainly associated with PC2; Sb formed a third group; and Te and TOC represented a fourth group.

Firstly, the high loading of Al_2O_3 and Fe_2O_3 with PC1 highlighted the influence of clay minerals and iron oxides on the distributions of PHEs in Bohai Bay sediments and terrestrial source of PHEs via rivers and atmospheric transportation, except Mo was more associated with P_2O_5, Sb was influenced by anthropogenic activities, and Te was more associated with TOC.

Table 5
Rotated component matrix for data of surface sediments (PCA loadings >0.4 were shown in bold). Eigenvalues, percent of variance, and eigenvectors were given for the first four principal components (PC1–PC4).

Element	PC1	PC2	PC3	PC4
Eigenvalues	8.229	2.079	1.343	1.054
Percent of variance	54.861	13.857	8.954	7.025
Cumulative%	54.861	68.718	77.672	84.697
Eigenvectors				
Ge	**0.912**	0.018	0.109	0.176
Mo	0.275	**0.735**	0.136	0.267
In	**0.836**	0.279	0.068	0.032
Sn	**0.932**	0.258	−0.055	−0.086
Sb	0.255	0.325	**0.822**	0.079
Te	0.270	0.344	−0.298	**0.707**
Tl	**0.966**	0.060	0.043	−0.008
Bi	**0.724**	**0.601**	0.116	−0.021
V	**0.957**	0.204	0.013	0.029
Al_2O_3	**0.846**	0.212	−0.121	−0.028
CaO	0.020	**0.904**	−0.031	−0.019
Fe_2O_3	**0.870**	0.356	−0.135	−0.060
P_2O_5	0.367	**0.486**	−0.689	0.117
MnO	**0.432**	**0.835**	−0.003	0.163
TOC	−0.188	0.019	0.144	**0.797**

Secondly, the result of PCA displayed that Mo was more associated with P_2O_5, which always was used as fertilizer in agriculture, indicating therefore that they had a common origin and some Mo likely originated from fertilizer inputs. Furthermore, the riverine runoff and atmospheric deposition were the carriers of these agricultural particles to the ocean sediments. Recently, the importance of micronutrients fertilizers as sources of trace elements has come to light. Micronutrient fertilizers, which come from coal-fired power plants and mine tailings, often have other trace elements (e.g., Mo) [39].

Finally, the result of PCA displayed that Te was more associated with TOC, indicating that they had a common origin and probably Te had been introduced to the system attached to organic matters. The organic matter to marine sediments has two sources: terrestrial inputs and biogenous sources. TOC/TN ratio has been used for source identification of organic matter. It has been reported by Redfield et al. [40] to be 5–7 for marine organic matter and >15 for terrestrial organic matter by Meyers [41]. In Bohai Bay, the TOC/TN ratios varied from 4 to 13 with a mean of 7.4 suggesting a predominant marine origin. Furthermore, it has been reported that the presence of inorganic nitrogen presumably as adsorbed NH_4^+ on the clay in surface sediments can interfere with organic matter source identification especially when the TN concentrations are low [42–45]. Hence, Hu et al. [45] corrected the TOC/TN ratios ranging of 5–11, indicating that terrestrial materials from rivers could also be an important source in Bohai Bay. In conclusion, the great relationship between Te and TOC indicated that marine and terrestrial materials were the main contributions to Te sources of Bohai Bay.

4. Conclusions

The PHE horizontal distribution tendency in Bohai Bay surface sediments was similar to the distribution of clay content. The concentrations of PHEs were higher in the western Bay, whereas the concentrations were lower at the bay mouth. This distribution pattern was the result of the coupling of physical, chemical and biological processes. Besides the influence of physical processes such as clay content, sediment components and hydrodynamic conditions, another important factor controlling the spatial variations of PHEs in sediments included the chemical processes such as adsorption–desorption and flocculation processes, dissolution–precipitation reactions, oxidation–reduction reactions and anthropogenic pollution. Furthermore, the PHE concentrations also were coupled to biological activity. Normalization of PHEs to Cs and their ratios with reference materials (earth crust) showed the higher enrichment factors (>1.5) for Bi, Sb and Te, revealing anthropogenic enrichment and moderate contamination of sediment by these three elements. However, the EFs of other PHEs were close to or less than one, indicating that they mainly came from natural sources. Overall, all PHE concentrations were mainly linked to continental weathering, but there were some anthropogenic sources (i.e., agricultural, industrial emissions and gasoline combustion) which entered the bay by atmospheric deposition and riverine inputs.

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