



# Spatial distribution, enrichment and potential sources of seldom monitored trace elements in soils of Yellow River Delta, China

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**Abstract** Rapid development of industry and agriculture over the past decades have caused serious environmental impacts on the local environment. However, the spatial distribution, sources and risk assessment of seldom monitored trace elements (SMTEs) in the surface soils of Yellow River Delta (YRD) have rarely been reported. In this study, thirty surface soil samples in YRD were collected, analyzed to determine concentrations of 17 SMTEs, and evaluated based on enrichment factor (EF), geo-accumulation index ( $I_{geo}$ ), contamination factor (CF) and pollution load index (PLI). Spatial distribution results indicated that relatively high contents of SMTEs in YRD mainly occurred in the western part and oil field pumping units, which was very likely related to petroleum exploitation and refining industries. In line with spatial distributions, the assessment results using

EF,  $I_{geo}$ , CF and PLI observed potential contamination for sampling site f4, f5, f8, f13, f14, f18, f23, f30, f32, f36, f37 and f38, and reported obvious enrichment of Cs, Sn, Th, Tl and U for the surface soils of YRD. According to the multivariate statistical analysis results, 17 kinds of SMTEs could be divided into three clusters and the origins of SMTEs may differ for different clusters. Our results indicated that PC1 scores could be regarded as an “anthropogenic impact factor” and an important proxy to represent possible contamination from SMTEs in YRD. This study provides important information for the contamination status of SMTEs in the surface soils of YRD.

**Keywords** Seldom monitored trace elements · Spatial distribution · Risk assessment · Surface soils · Yellow River Delta

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## 1 Introduction

Due to the rapid development of industry and agriculture, various kinds of potential toxic elements (PTEs) have been released into the natural environment (Chen et al., 2023; Chu et al., 2019; Sabet Aghlidi et al., 2020; Song et al., 2022; Xiao et al., 2017; Xu et al., 2020; Yang et al., 2022b; Yang et al., 2021). The PTEs could gradually accumulate in the ecosystem, enrich in the food webs and ultimately pose a great threat to human health because of their toxic and non-biodegradable properties (Jiang et al., 2020; Liu et al., 2013). However, the investigation and assessment of

PTEs were mainly focused on the commonly monitored trace elements (e.g. Cu, As, Pb, Cd, Zn) in previous studies (Bai et al., 2011; Chai et al., 2014; Ding et al., 2019; Fu et al., 2014; Yang et al., 2020). Comparatively, the seldom monitored trace elements (SMTEs, such as Be, Sc, Rb, Bi, U, Mo, Tl and V) received rather less attention (Han et al., 2015; Yang et al., 2023). The sources of SMTEs may be originated from both natural process (such as weathering, volcanic eruption and wildfire) and anthropogenic activities (such as fossil fuel combustion and various kinds of chemical plants) (Chen et al., 2022; Han et al., 2015, 2016; Watts et al., 2017). Many SMTEs have been confirmed to be extremely hazardous pollutants in the environment. For example, element V could cause detrimental effects to the organisms at high levels due to the fact that phosphate mimicry in pentavalent V would cause the inhibition of phosphohydrolases and other enzymes (Nedrich et al., 2018). Low concentrations of pollutants containing Sb are also deemed to cause serious effects on human health (Kuwae et al., 2013). Moreover, Tl has been regarded to be one of the 13 priority pollutants (Keith & Telliard, 1979) and an emerging pollutant in China due to its potential risk to human health (Xiao et al., 2012). Therefore, great importance should be attached to the study of SMTEs in the natural environment.

To the best of our knowledge, few studies were reported regarding the evaluation of SMTEs contamination in soils or sediments over the past decades. In China, the spatial distribution, sources and risk assessment of SMTEs in sediments of Three Gorges Reservoir were reported, which revealed obvious contamination by Sb (Han et al., 2015). The SMTEs contamination status were also assessed for the surface sediments of Bohai Bay (Lu et al., 2013) and North Yellow Sea (Yang et al., 2023). Moreover, Li et al., (2018) assessed the anthropogenic impact and ecological risk of Tl and Co, and reported that 47.22% and 41.67% of the samples were impacted by anthropogenic activities for Tl and Co, respectively. In East Asia, Kuwae et al., (2013) reported the first historical record of Sb and In over the past 250 years, revealing intensified atmospheric pollution of Sb and In in East Asia during recent decades. Besides, investigation and assessment of various kinds of elements could be performed based on multivariate statistical methods (Sikakwe et al., 2020; Watts et al., 2017). Notwithstanding, the spatial distribution, sources and risk

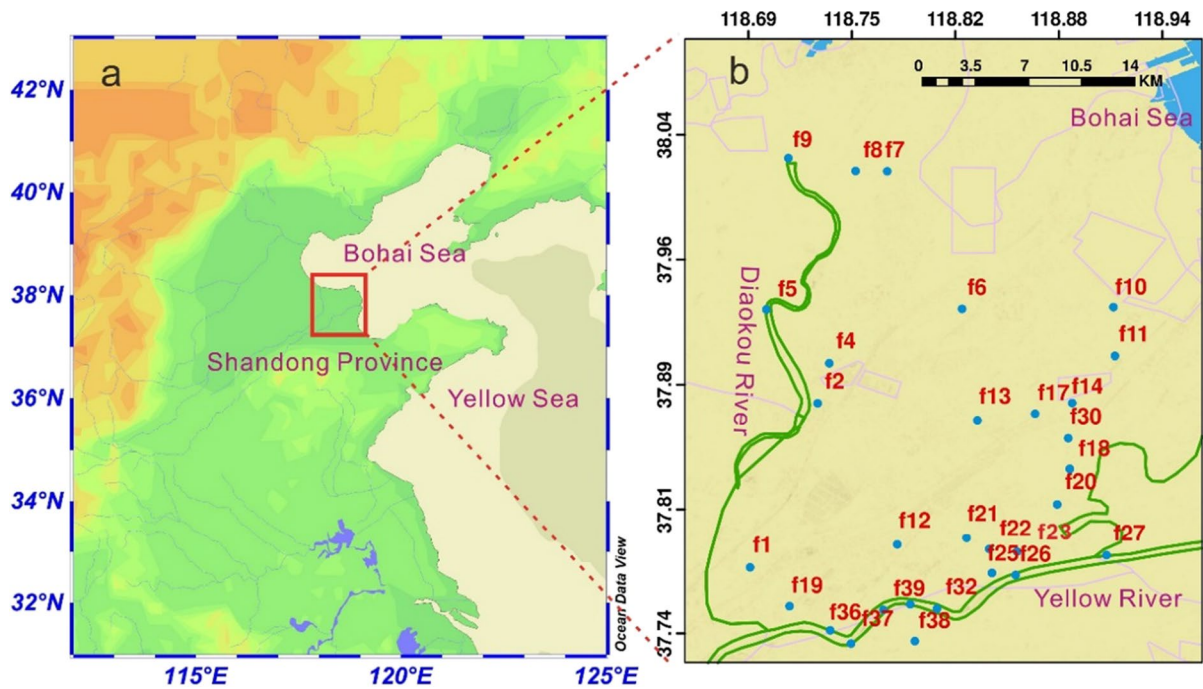
assessment of SMTEs in the soils of Yellow River Delta (YRD) still remains unclear.

The YRD is the most complete, broadest, and youngest wetland ecosystem preserved in the warm temperate zone of China. Considering that the second largest oilfield (Shengli Oilfield) is located in the YRD, rapid development of petrochemical industries and agricultural activities over the past decades have caused serious environmental impacts on the local ecosystem. Thus, China launched the ecological conservation and high-quality development of the Yellow River Basin, and regarded it as the great national strategy. Obviously, comprehensive assessment of environmental pollution status in YRD is very important for protecting the ecosystem of YRD. In order to better understand the spatial distribution, potential sources and ecological risk of SMTEs in YRD, thirty surface soil samples were collected and measured to determine concentrations of Be, Bi, Ce, Cs, Ga, Hf, La, Mo, Nb, Rb, Sc, Sn, Ta, Th, Tl, U and V. The main objectives for this study were (1) to investigate the spatial distribution of SMTEs in YRD; (2) to evaluate the concentrations and pollution status of SMTEs; (3) to assess the enrichments of SMTEs; (4) to identify the possible sources of SMTEs in YRD.

## 2 Materials and methods

### 2.1 Study area and sample collection

The YRD (118°33'~119°20' E, 37°35'~38°12' N) (Fig. 1) is located in the estuary of the Yellow River, Shandong Province. The coastal wetland of YRD was formed by the sediment transported through the Yellow River. It is a warm temperate continental monsoon climate zone, with an average annual temperature of 11.7–12.6°C and average annual precipitation of 530–630 mm (Zhang et al., 2018). Moreover, the temperature difference between four seasons is also distinct (Zhang et al., 2018). The Yellow River Delta region is low-lying, vulnerable to tides and has a high salt content in the soils. Thus, the plant species and vegetation types are simple, mainly saline meadow and saline plant community. It is worthwhile to note that the China's second largest oil field (Shengli Oilfield) is located in the Yellow River Delta, which has become an important petrochemical industry base since the 1960s. Therefore, the environmental



**Fig. 1** Map of the studied area and the sampling sites in this study

pollution status of YRD is becoming worse and worse due to the rapid development of industry and agriculture.

In this study, thirty surface soil samples were collected in the natural wetland of YRD and the sampling positions were shown in Fig. 1. In each sampling site, three surface subsamples were collected and then mixed into one composite sample. The collected subsamples were preserved in polyethylene bags, transported to the laboratory, and air-dried at room temperature. After that, the gravel and plant debris were removed, ground through a 120 mesh (0.125 mm) nylon sieve and then determined for the concentrations of various kinds of elements.

## 2.2 Analytical methods

For determination of the 17 kinds of SMTEs and Al contents in the soil samples, the powdered samples were digested by  $\text{HNO}_3\text{-HCl-HClO}_4\text{-HF}$  mix acid in a Teflon vessel, and then determined using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Agilent 5110) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Agilent 7900). The blank tests, sample replicates and standard

reference materials (OREAS 905 and OREAS-25a) were also analyzed in every batch of experimental analysis and considered in the final SMTEs contents results to validate the precision and accuracy of our results (Yang et al., 2018, 2019). The detailed analytical methods were reported in Yang et al., (2022a), and placed in the supplementary material 1.

## 2.3 Environmental risk assessment proxies

The proxy of enrichment factor (EF) is generally calculated according to comparison between the SMTEs concentrations and their geochemical baseline values, which is a helpful index for evaluating the influence of anthropogenic impacts on SMTEs contents (Kowalska et al., 2016). Considering that natural sedimentary metal loads can vary due to the provenance of metal-rich/metal-poor minerals/ compounds in the sediments (Ho et al., 2012; UNEP, 1995), element Al is widely used as the reference element to compensate for the mineralogical effect (Ho et al., 2012). In this study, we also used Al as the reference element. The index of EF could be calculated based on the following formula (Eq. 1):

$$EF = (C_m/C_{ref})/(B_m/B_{ref}) \quad (1)$$

where  $C_m$  and  $C_{ref}$  are the SMTEs concentrations and element Al contents in surface soil samples, respectively.  $B_m$  and  $B_{ref}$  are the local geochemical baseline values of SMTEs and Al, respectively. Gao et al., (1998) divided the central East China into five tectonic units and reported the crustal compositions in each tectonic unit, which was calculated by averaging relevant rock types according to their thickness and exposed area. Therefore, their geochemical compositions could roughly represent the geochemical background values. Considering that the study area was located in the Interior of North China craton (INC), their geochemical compositions of INC was selected as the geochemical background in this study (Gao et al., 1998). The EF could be classified into seven classes and the detailed classification was placed in Supplementary Table S1.

The geo-accumulation index ( $I_{geo}$ ) was proposed by Muller, (1981), which is also widely used to assess the pollution status of soil samples compared with the

geochemical baseline values.  $I_{geo}$  could be calculated according to the following formula (Eq. 2):

$$I_{geo} = \log_2 [C_m / (1.5 \times C_b)] \quad (2)$$

where  $C_m$  is SMTEs concentrations in soils, and  $C_b$  is the local geochemical baseline values of SMTEs (Gao et al., 1998). The  $I_{geo}$  values could also be classified into seven classes (Muller, 1981) and the detailed classification was placed in Supplementary Table S1.

Contamination factor (CF) is the ratio of SMTEs concentrations ( $C_m$ ) and the local geochemical baseline values (Gao et al., 1998), and can be divided into four classes (Valdelamar-Villegas et al., 2021): no contamination ( $CF < 1$ ); moderate contamination ( $1 < CF \leq 3$ ); considerable contamination ( $3 < CF \leq 6$ ); high contamination ( $CF > 6$ ). In addition, the pollution load index (PLI) could be calculated based on the geometric mean of the CF values of different SMTEs (Valdelamar-Villegas et al., 2021). The formula of CF (Eq. 3) and PLI (Eq. 4) are as follows:

$$CF = C_m / C_b \quad (3)$$

$$PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \times \dots \times CFn} \quad (n \text{ is the number of SMTEs}) \quad (4)$$

## 2.4 Statistical analysis

The Principal Component Analysis (PCA), Correlation Matrix (CM), and Cluster Analysis (CA) was performed according to 17 kinds of SMTEs values for the surface wetland soil samples in YRD. Among these analysis methods, PCA and CM were conducted based on the Origin 2017 software, while CA and One sample T test were performed via SPSS 25.0 software and the CA analysis was analyzed utilizing hierarchical clustering based on Pearson correlation.

## 3 Results and discussion

### 3.1 Concentrations and spatial distributions of SMTEs in YRD

The SMTEs concentrations in the surface soil samples of YRD were shown in Table 1 and compared

with those of different river/marine sediments and the geochemical background values (Table 1). The results showed that the SMTEs levels showed a relatively small variation range and no outlier values were observed. According to the SMTEs contents, the average values of Be, Bi, Ce, Cs, Ga, Hf, La, Mo, Nb, Rb, Sc, Sn, Ta, Th, Tl, U and V were 1.78, 0.29, 62.90, 6.28, 14.21, 2.21, 31.37, 0.76, 11.46, 89.88, 9.94, 2.39, 0.83, 10.47, 0.52, 2.20 and 70.17  $\mu\text{g/g}$ , respectively. Ta, Mo, Tl and Bi could be regarded as low concentration SMTEs (0–1  $\mu\text{g/g}$ ), while Be, Cs, Ga, Hf, La, Nb, Sc, Sn, Th and U could be regarded as moderate concentration SMTEs (1–30  $\mu\text{g/g}$ ). Moreover, Ce, Rb and V were higher than 50  $\mu\text{g/g}$ , and can be classified as high concentration SMTEs.

In order to better understanding the SMTEs concentrations and their pollution status in YRD, the SMTEs of different river/marine sediments and geochemical background values were also summarized and compared with those in the soil samples of YRD (Table 1). The SMTEs levels in YRD

**Table 1** The concentrations of SMTEs in the surface soils of YRD compared with geochemical background values as well as those in the sediments from different sampling sites

	Be	Bi	Ce	Cs	Ga	Hf	La	Mo	Nb	
YRD soils	Min Max Average	1.50 2.10 1.78	0.21 0.41 0.29	51.5 70.3 62.90	4.52 9.03 6.28	12.30 17.50 14.21	1.8 2.5 2.21	25.7 34.8 31.37	0.51 1.06 0.76	10.4 12.5 11.46
Bohai Bay	Core 2 Core 6	0.38–0.52 0.35–0.56			16.56–21.15 13.70–20.84				0.54–1.50 0.53–1.75	
Surface sediments of Bohai Bay		0.27–0.63					0.52–1.43			
Stream sediments in northern Japan	1.05	0.365	23.8	3.57	15.2	12.7	1.31	5.12		
Marine sediments in northern Japan	1.04	0.30	21.8	2.78	12.3	11.3	1.57	4.73		
Colombia Santa Marta sediments	0.9 ± 0.1	0.1 ± 0.0	36.8 ± 4.7	0.4 ± 0.3	123.7 ± 11.5	0.5 ± 0.1	18.2 ± 2.6	0.6 ± 0.1	6.6 ± 0.6	
Three Gorges Reservoir sediments	2.82	0.56		37.09						
Hugli river estuary sediments	3.6 ± 0.8	0.7 ± 0.2	78.8 ± 9.4	10.8 ± 1.8	19.1 ± 2.8	1.0 ± 0.2	41.6 ± 13.6	0.40 ± 0.13	13.1 ± 0.8	15.13
Brahmaputra River of Bengal Basin	0.47		20.11		4.82		0.39			
Shandong Province Background	1.94	0.27	66.8	15.77		34.2	0.58	13.5		
Interior of the North China craton	1.29	0.38	56.2	15	4.11	27.1	0.6	10		
UCC	2.1	0.16	63	17.5	5.3	31	1.1	12		
Rb	Sc	Sn	Ta	Tl	U	V	Reference			
79.7	8.0	2.0	0.73	0.46	1.9	57	This study			
106.5	12.60	3.0	0.91	0.64	2.5	91				
89.88	9.94	2.39	0.83	0.52	2.20	70.17				
		3.20–4.08		0.60–0.74		86.73–111.23	Duan et al., (2011)			
		2.65–4.34		0.49–0.75		75.67–114.62				
		2.77–4.14		0.506–0.770		70.35–115.90	Duan et al., (2010)			
49.7	18	1.87	0.49	0.40	1.11	157.00	Ohta et al., (2010)			
42.2	12.1	1.35	0.4	0.34	1.05	102.00				
30.9 ± 4.5	14.8 ± 0.8	1.4 ± 0.1	0.5 ± 0.0	0.2 ± 0.0	1.5 ± 0.3	115.9 ± 6.4	Caballero-Gallardo et al., (2015)			
		3.51		0.75		143.77	Han et al., (2015)			
171 ± 19		5.6 ± 0.6	1.2 ± 0.1	0.83 ± 0.08		107 ± 17	Watts et al., (2017)			
	15.8	1.27	17.58	0.8	3.19		Khan et al., (2020)			

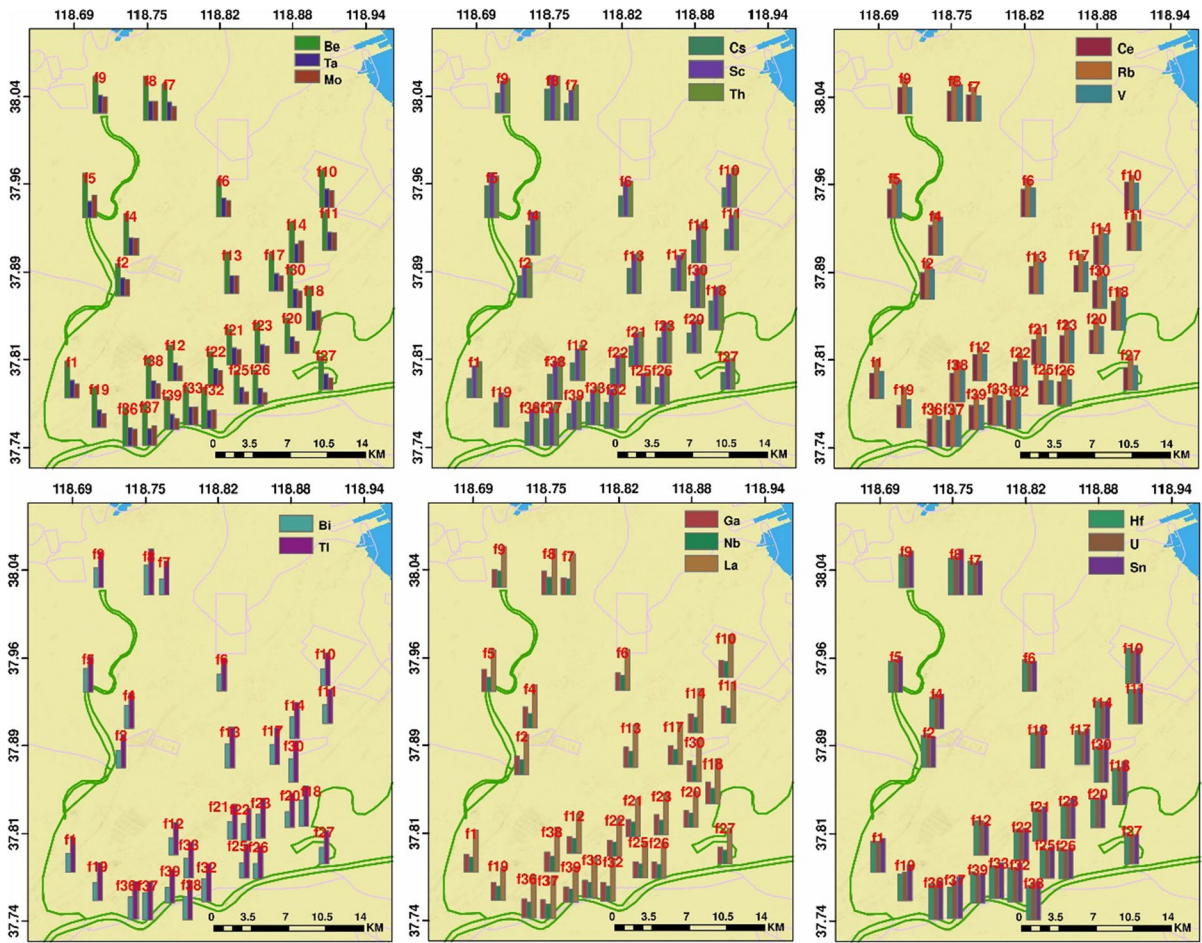


Table 1 (continued)

		Be	Bi	Ce	Cs	Ga	Hf	La	Mo	Nb
94.7	10.2	2.80		10.7	0.59	2.16	75.6	Pang et al., (2019)		
71	14	1.40	0.61	6.97	0.36	1.23	88	Gao et al., (1998)		
84	14	2.1	0.9	10.5	0.9	2.7	97	Rudnick et al., (2003)		

surface soils were slightly lower than those in sediments of the Bohai Bay (Duan et al., 2010, 2011), which was very likely related to the anthropogenic activities in the important industrial base of Beijing-Tianjin-Tangshan area. However, compared with the stream/marine sediments in northern Japan (Ohta et al., 2010), obvious differences among these SMTEs were observed. The Be, Ce, Cs, Hf, La, Nb, Rb, Sn, Ta, Th, Tl and U concentrations in the sediment of northern Japan were slightly lower than those of surface soils in YRD, while the Bi, Mo, Sc and V contents were higher than those of YRD soils. It is worthwhile to note that the Ga and V levels in Colombia Santa Marta sediments (Caballero-Gallardo et al., 2015) were significantly higher than those of YRD soils, while the other SMTEs were obviously lower. As for the SMTEs concentrations in the sediments of Three Gorges Reservoir (Han et al., 2015), the average Be, Bi, Ga, Sn, Tl and V levels were higher than those in YRD soils. Similar results were also observed when the SMTEs levels in YRD were compared with those in sediments of Hugli river estuary (Watts et al., 2017) and Brahmaputra River (Bengal Basin) (Khan et al., 2020). Overall, the SMTEs levels in YRD were comparable with those of the Shandong Province Background (Pang et al., 2019), Interior of the North China craton (Gao et al., 1998) and the upper continental crust (UCC) (Rudnick et al., 2003). Notwithstanding, the Cs levels of YRD soils were significantly higher than those of the Interior of the North China craton and UCC.

The spatial distributions of these SMTEs were shown in Fig. 2 and obvious differences of SMTEs concentrations could be found among different sampling sites. Based on the comprehensive analysis of the spatial variation patterns of SMTEs, relatively higher concentrations were observed at the sampling sites f4, f5, f8, f13, f18, f23, f30, f32, f36, f37 and f38 for most of the SMTEs. Therefore, potential enrichment of SMTEs mainly occurred at the northwest and southwest of the study area, which was consistent with heavy metal variation patterns (Yang et al., 2022a). The SMTEs enrichment could be related to the petroleum exploitation and refining industries. It is noteworthy that relatively high SMTEs concentrations were also observed in sampling sites f13, f18, f23 and f30, though these samplings sites were located in the eastern part of the study area. In fact,



**Fig. 2** The concentrations and spatial distributions of 17 kinds of SMTEs in the surface soils of YRD

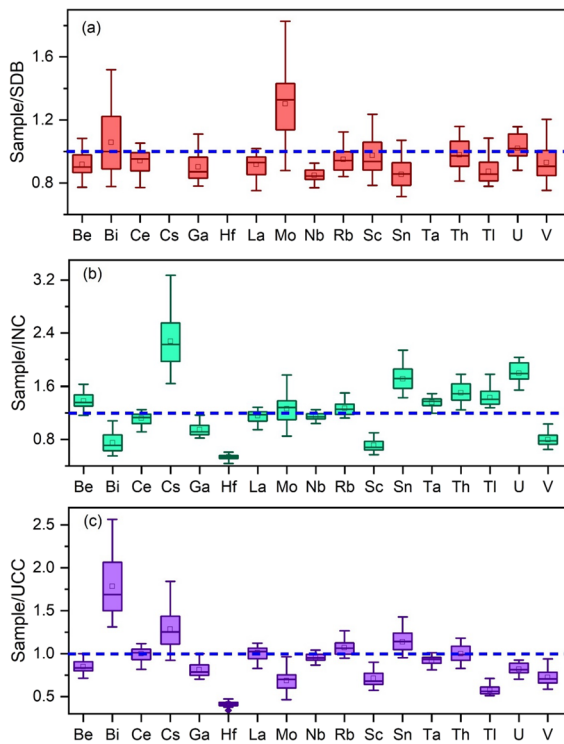
many oil field pumping units were distributed surrounding the sampling sites f13, f18, f23 and f30, and thus the petroleum extraction activities may account for the enrichment of SMTEs. Overall, the spatial distributions of SMTEs in the surface soils of YRD were mainly related to the anthropogenic activities, such as petroleum exploitation and refining industries.

### 3.2 Geochemical background normalized patterns for YRD sediments

The geochemical background normalized pattern was represented by the ratio of SMTEs contents and background values, which has been widely utilized to reflect the enrichment or depletion of elements in the analyzed samples (Khan et al., 2020; Yang et al., 2022a). The background from Shandong Province

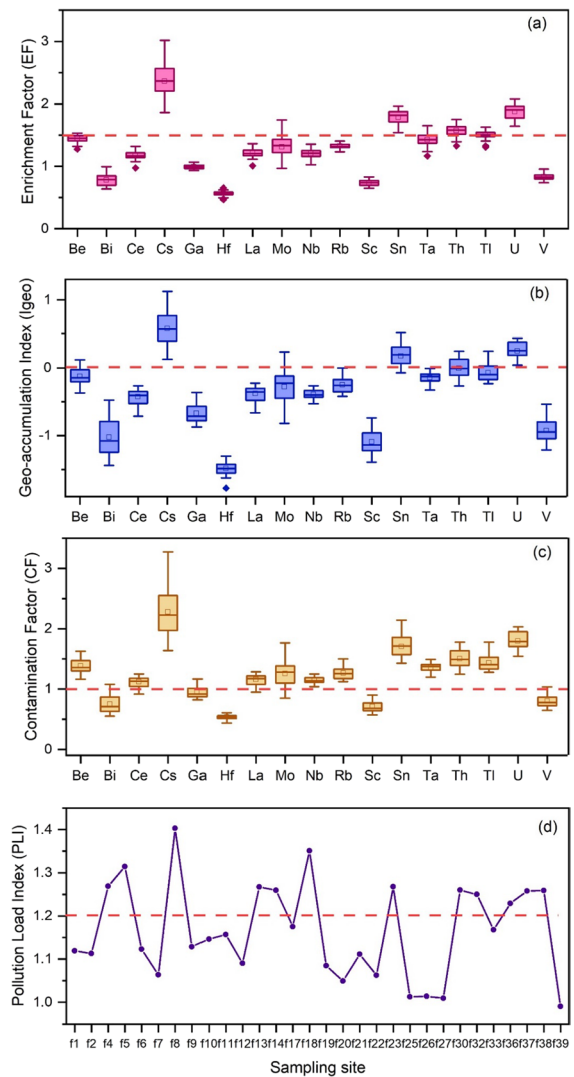
(SDB) (Pang et al., 2019), North China (INC) (Gao et al., 1998), and Upper Continental Crust (UCC) (Rudnick et al., 2003) were used to normalize SMTEs contents of YRD surface soils, and the results were shown in Fig. 3. In addition, one sample T test was analyzed to examine their difference. Results showed that the mean values for majority of the SMTEs were significantly different from those of the SDB, INC and UCC background ( $p < 0.01$ ), except for the difference between the SDB background and the average contents of Bi ( $p = 0.14$ ), Sc ( $p = 0.286$ ), Th ( $p = 0.251$ ) and U ( $p = 0.262$ ), and between UCC background and the average contents of Ce ( $p = 0.916$ ), La ( $p = 0.412$ ) and Th ( $p = 0.868$ ).

As shown in Fig. 3, most of the SMTEs fluctuated in a narrow range around the geochemical background values, notwithstanding, there are still several



**Fig. 3** The variation patterns of SDB-normalized (a), INC-normalized (b) and UCC-normalized (c) SMTEs levels for the surface soils of YRD. The blue line in this figure indicates that SMTEs levels of the YRD soils are equal to the geochemical background values. If the ratios are higher than 1, it means the enrichment of SMTEs levels, and vice versa

SMTEs displaying significant enrichment or depletion compared with the SDB, INC and UCC background values. For example, the variation patterns of SDB-normalized SMTEs (Fig. 3a) showed significant enrichment of Bi and Mo, and depletion of La, Nb and Tl, while the variation patterns of INC-normalized SMTEs (Fig. 3b) displayed positive Be, Cs, Sn, Ta, Th, Tl and U anomalies, and negative Bi, Ga, Hf, Sc and V anomalies. Moreover, the variation patterns of UCC-normalized SMTEs (Fig. 3c) indicated that the levels of Bi, Cs, Rb and Sn were significantly enriched, and the levels of Be, Hf, Mo, Sc, Tl, U and V were significantly depleted compared with the UCC geochemical background. Therefore, the normalized variation patterns based on different geochemical background values showed small differences when it was specific to detailed elements. To sum up, potential enrichment of Bi, Cs, Mo, Sn, Rb, Th and U may occur in the surface soils of YRD.



**Fig. 4** The box plots of EF (a) and  $I_{geo}$  (b) and CF (c) for 17 kinds of SMTEs analyzed in this study, as well as the variation patterns of PLI values for all the surface soil samples in YRD

### 3.3 Contamination assessment of SMTEs

Many studies have confirmed that the SMTEs could cause adverse effects on the natural environment and organism’s health (Duan et al., 2010, 2011; Gao et al., 2014; Khan et al., 2020; Li et al., 2018). However, the levels, sources and pollution status of SMTEs have rarely been studied for the surface soils of YRD. In order to further investigate the contamination status of SMTEs and assess its potential risks in YRD soils, the proxies of EF,  $I_{geo}$ , CF and PLI were calculated



based on the SMTEs levels in this study and the results are shown in Fig. 4.

The contamination degree of SMTEs levels in YRD were evaluated using the proxy of EF, which could discriminate possible influence of human activities (Duan et al., 2010). Previous results have showed that the SMTEs could be significantly influenced by human activities if the EF values are higher than 1.5, while the EF values of 0.5–1.5 may indicate mainly natural sources (Hu et al., 2013; Xu et al., 2016). The average EF values of Be, Bi, Ce, Cs, Ga, Hf, La, Mo, Nb, Rb, Sc, Sn, Ta, Th, Tl, U and V were 1.44, 0.78, 1.17, 2.36, 0.99, 0.56, 1.21, 1.31, 1.20, 1.32, 0.74, 1.78, 1.43, 1.57, 1.50, 1.88 and 0.83, respectively. As shown in Fig. 4a, obvious enrichment of Cs, Sn, Th, Tl and U was observed ( $EF > 1.5$ ), which suggested that these SMTEs in the surface soils of YRD could be significantly influenced by human activities. The EF values of Bi, Ga, Hf, Sc and V are lower than 1, indicating main contribution from natural sources. In addition, the EF values for rest of the SMTEs fell in the range of 1–1.5, which suggested that the origins of these SMTEs in YRD soils may be related to both natural weathering and human activities.

The results of  $I_{geo}$  are similar with those of EF (Fig. 4b). The average  $I_{geo}$  values of Be, Bi, Ce, Cs, Ga, Hf, La, Mo, Nb, Rb, Sc, Sn, Ta, Th, Tl, U and V were -0.13, -1.02, -0.43, 0.58, -0.67, -1.49, -0.38, -0.28, -0.39, -0.25, -1.09, 0.18, -0.15, -0.01, -0.07, 0.25 and -0.92, respectively. According to the evaluation standard (Muller, 1981), the average  $I_{geo}$  values of Cs (0.58), Sn (0.18) and U (0.25) are higher than 0, and should be regarded as the “slightly polluted” level. The average  $I_{geo}$  values for the rest of SMTEs suggested that the surface soils of YRD may be unpolluted with other SMTEs except for several sampling sites. Overall, the evaluation results of  $I_{geo}$  are consistent with those of EF.

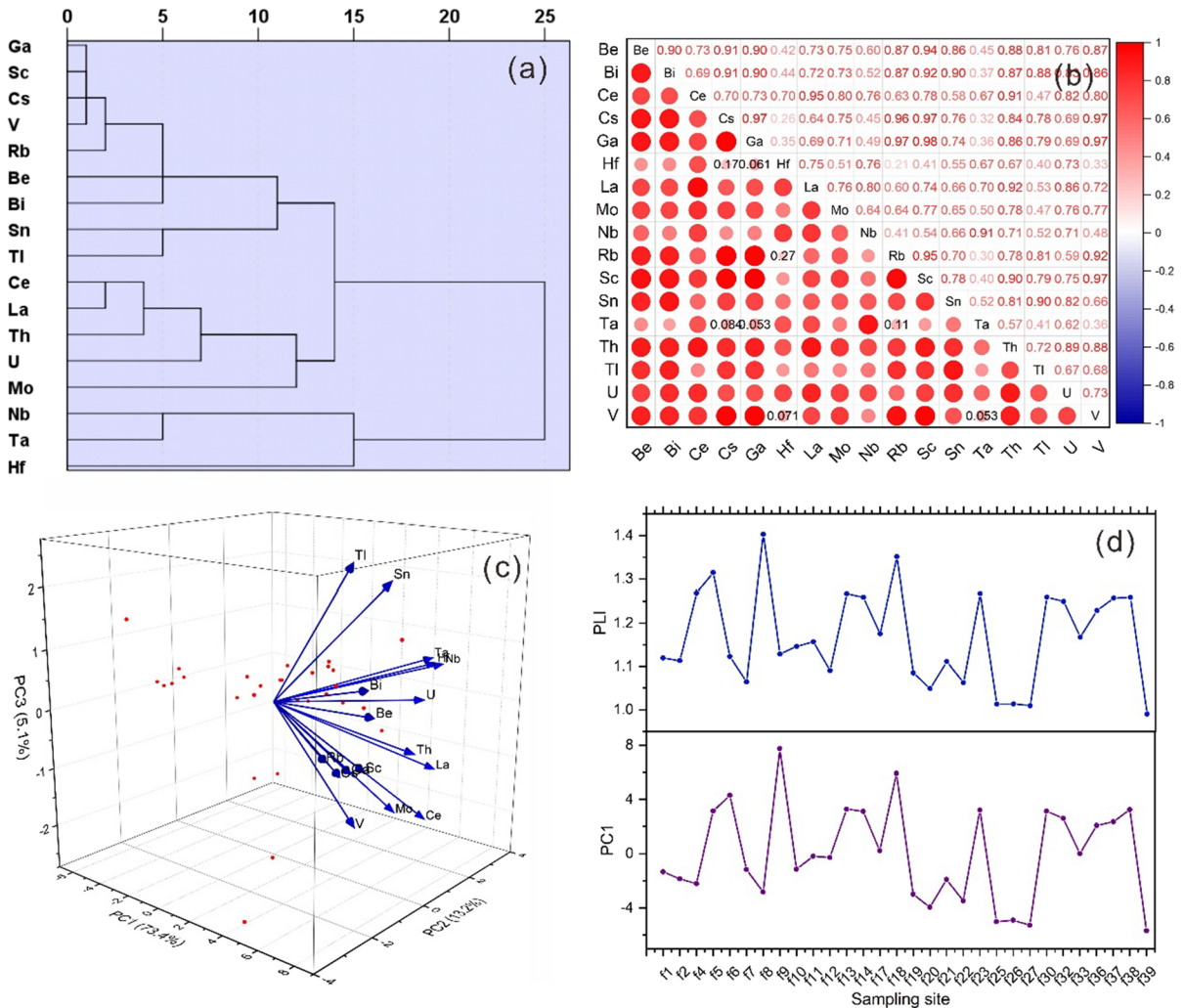
In this study, the proxy of PLI was also utilized to comprehensively assess the pollution status and potential risks for each sampling site. Considering that the PLI was calculated based on the geometric mean of the CF values of different SMTEs, the results of CF was also presented in Fig. 4c. The CF values indicated that the majority of SMTEs ( $1 < CF < 3$ ) were slightly to moderately polluted except for the elements Bi, Hf, Sc and V. The trends of CF results showed similar variation patterns with those of EF and  $I_{geo}$ . Based on the results of CF, the PLI for all the

surface soils samples were calculated and displayed in Fig. 4d. In general, if  $PLI > 1$ , potential contamination by SMTEs may occur for the sampling site (Khan et al., 2020; Yang et al., 2020). However, the SMTEs contents may maintain the baseline levels if  $PLI < 1$ . Our results indicated that the PLI values for most of the sampling sites are higher than 1, which suggested possible contamination caused by these SMTEs. It is worthwhile to note that the PLI values for sampling site f4, f5, f8, f13, f14, f18, f23, f30, f32, f36, f37 and f38 are all higher than 1.2, thus the contamination status for these positions could be much more serious than other sampling sites. Therefore, the assessment results are consistent with the spatial distribution variation patterns, and the potential contamination mainly occurred in the western part of the study area as well as the dense oil field pumping units area.

### 3.4 Potential sources SMTEs in YRD

The SMTEs are regarded as harmful pollutants owing to their toxic, persistent and non-degradable properties, and their major sources are related to the natural process and human activities (Duan et al., 2010; Han et al., 2015). The natural origins mainly consist of chemical weathering, volcanic eruptions, sand dust and wildfires, while the anthropogenic sources are mainly linked to the human activities such as fossil fuel combustion and industrial plants (Han et al., 2015). To further explore the interrelationship and potential sources of the analyzed SMTEs, three multivariate statistical analysis methods were analyzed, and the results are displayed in Fig. 5.

The cluster analysis results (Fig. 5a) indicated that the 17 kinds of SMTEs could be divided into three clusters. Cluster 1 includes Ga, Sc, Cs, V, Rb, Be, Bi, Sn and Ta, while cluster 2 was composed of Ce, La, Th, U and Mo. The rest of SMTEs (Nb, Ta and Hf) was classified as cluster 3. The relative long distance between cluster 3 and the other two clusters indicated that the sources of these SMTEs from different clusters could be different, which was further testified by the correlation analysis results. As shown in Fig. 5b, most of the SMTEs were significantly correlated with each other. However, the Ta and Hf had no significant correlations with many other SMTEs. In addition, the correlations between SMTEs in cluster 1 or cluster 2 are more significant than those between cluster 1 and cluster 2. Overall, the cluster analysis results are



**Fig. 5** The cluster analysis (a), correlation matrix (b) and principal component analysis (c) results based on 17 kinds of SMTEs in the surface soils of YRD. (d) comparison between the PC1 scores and PLI variations for the YRD soils from different sampling sites

consistent with those of correlation analysis results, and the origins of SMTEs may differ for different clusters.

The principal component analysis is a commonly used statistical method for dimension reduction for huge amounts of data, and the new extracted variables could indicate the main information of the analyzed dataset (Han et al., 2016; Xu et al., 2016). The KMO values and Bartlett’s test results are 0.839 and 1005.565, respectively (df=136,  $p < 0.01$ ), indicating that PCA analysis results could be used to reduce dimensionality. Thus, PCA analysis was performed based on all the analyzed SMTEs to investigate the main factors for their different variation patterns. Our

results indicated that all the SMTEs could be reduced to 3 principal components (Fig. 5c), and the extracted PCs (PC1, PC2 and PC3) can explain 91.7% of the total variances. PC1 (explained 73.4% of the total variances) had high loadings on Ga, Sc, Cs, V, Rb, Be, Bi, Sn and Ta, while PC2 (explained 13.2% of the total variances) had high positive loadings on Nb, Ta and Hf. In addition, PC3 (explained 5.1% of the total variances) had relatively high loadings on Ce, La, Th, U and Mo. Considering that the PC1 explained 73.4% of the total variances, and thus we extracted the scores for PC1. It is worthwhile to note that the variation patterns of PC1 scores are similar with those of PLI (Fig. 5d), and the correlations are significant

( $r=0.635$ ,  $p<0.01$ ). Therefore, PC1 scores could be regarded as an “anthropogenic impact factor” and an important proxy to indicate possible contamination from SMTEs.

Based on previous studies, different geochemical elements could be regarded as tracers of different kinds of anthropogenic activities (Conti et al., 2022; Karbowska, 2016; Frasca et al., 2018; Massimi et al., 2020). In general, Cu, Sb, Sn, Fe and Mn are usually deemed as tracers of vehicular traffic (Karbowska, 2016; Frasca et al., 2018; Massimi et al., 2020), which was very likely related to the fact that these elements exist in vehicles brakes and released by mechanical abrasion, thus tracing vehicular traffic sources (Abbasi et al., 2012; Marconi et al., 2011). In addition, Cs, Li, Ta and Rb are generally released from domestic heating (Szidat et al., 2007), wildfires (Van Drooge et al., 2012) and burning of agricultural waste in rural areas (Lee et al., 2008), and thus could be deemed as tracers of biomass burning. Considering that Cs, Sn and U were obviously enriched in the surface soils of YRD (Figs. 3 and 4), their sources could be linked to biomass burning, vehicular traffic and chemical industry due to intensive human activities in recent years. Therefore, the SMTEs in cluster 1 (associated with PC1) are very likely influenced by human activities, which should attract more attentions in future soil environmental protection of YRD. As for the rest SMTEs, their origins could be mainly related to natural sources. Similar results were also observed for a sediment core in North Yellow Sea, and Yang et al., (2023) reconstructed the pollution history of SMTEs and reported significant anthropogenic influence over the past 300 years based on PCA analysis. In addition, the environmental risk assessment of SMTEs for Bohai Bay surface sediments also indicated that the SMTEs were mainly related to natural weathering, but there were still non-negligible anthropogenic sources (Duan et al., 2010).

#### 4 Conclusions

This study reported the levels, sources, spatial distribution and risk assessment of SMTEs in the surface soils of YRD. The SMTEs levels were slightly lower than those in the sediments of Bohai Bay and comparable with those of the Shandong Province Background. Based on the spatial distributions, relatively

high levels of SMTEs were observed in the western part and oil field pumping units, and this distribution pattern was the result of petroleum exploitation and refining industries. Compared with the geochemical background, potential enrichment of Bi, Cs, Mo, Sn, Rb, Th and U may occur in the surface soils of YRD. The contamination assessment results using proxies of EF,  $I_{geo}$ , CF and PLI further testified this. Obvious enrichment of Cs, Sn, Th, Tl and U was observed ( $EF>1.5$ ) and the average  $I_{geo}$  values of Cs (0.58), Sn (0.18) and U (0.25) are higher than 0. Moreover, the PLI values for sampling site f4, f5, f8, f13, f14, f18, f23, f30, f32, f36, f37 and f38 are all higher than 1.2, indicating potential contamination, which was consistent with the spatial distribution patterns. Multivariate statistical analysis was further performed to investigate the potential sources of SMTEs, and our results indicated that PC1 scores could be regarded as an “anthropogenic impact factor” and an important proxy to represent possible contamination from SMTEs in YRD. Notwithstanding, more studies regarding the threshold concentrations, ecotoxicity and remediation of these SMTEs in YRD should be performed in future studies.

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**Data availability** Data and materials will be made available on request.

**Declarations**

**Ethical approval** Not applicable.

**Consent to participate** Not applicable.

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