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ORIGINAL PAPER

Spatial distribution of heavy metals and their potential sources in the soil of Yellow River Delta: a traditional oil field in China

Xiongyi Miao · Yupei Hao · Fawang Zhang · Shengzhang Zou · Siyuan Ye · Zhouqing Xie

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Abstract In this study, soil samples were collected from different layers throughout the whole Yellow River Delta (YERD), in north China. The total concentration of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb) and zinc (Zn) was determined to demonstrate their spatial distribution and pollution status in different layers of soils throughout the whole YERD. The obtained results suggested a relatively low contamination of heavy metals as observed through the evaluation of CF and RI. The potential ecological risk of Hg is not so severe. Also, the maximum potential threat could be noted only from Cd instead of Hg based on the widespread degree of pollution, which breaks traditional concept that oil production escalates mercury in the soil. The obtained value of EF proves a higher enrichment of heavy metals in the surface soil than in the layer of deep soil induced by human activities. Human activities only slightly elevate As, Cd and Pb. As has the strongest ability downward to lower layer, followed by Cd and Pb in YERD. The source of heavy metals predominantly stems from natural deposits, and their concentrations are controlled by the nature of their association with the mineral. Overall, it shows that the petroleum industry instead of agriculture could be treated as an important source to bring anthropogenic heavy metals in the soils. The human influence only elevated the concentration of heavy metals in the soil of the areas corresponding to the intensive production of oil. In this study some of the measures have also been proposed to avoid and control soil pollution as well as the health risk caused by heavy metals.

Keywords Yellow River Delta · Soil · Heavy metal elements · Contamination assessment · Oil field

The original version of this article was revised: In the original publication of the article, the sixth author name was misspelt. The correct spelling is given in the article.

X. Miao · Z. Xie (✉)
Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China
e-mail: zqxie@ustc.edu.cn

X. Miao
e-mail: miaoxy@karst.ac.cn

S. Ye (✉)
Key Laboratory of Coastal Wetlands Biogeosciences, China Geologic Survey, Qingdao Institute of Marine Geology and Laboratory for Marine Geology, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266071, China
e-mail: ye_syuan@sina.com

Y. Hao · F. Zhang · S. Zou
Key Laboratory of Karst Dynamics, MNR&GZAR, Institute of Karst Geology, CAGS, Guilin 541004, China

Introduction

Soil contamination by heavy metals is a global issue due to their adverse effects to the environment and potential threat to public health. Unlike many organic pollutants, heavy metals are highly resistant to degradation by the environment, and thus their bioaccumulation poses a significant threat to microbiota, flora and fauna (Gitet et al. 2016; Hu et al. 2017; Leung et al. 2017), more importantly once they have been transformed from solid form into ionic moieties or into organometallic moieties through biomethylation (Gitet et al. 2016; Hu et al. 2017; Leung et al. 2017). Therefore, the excess amount of trace metals present in the soils can threaten human health through the consumption of infected crops produced in polluted areas. Besides, the chronic low-level intake of soil heavy metals through ingestion or inhalation has a serious negative effect on human health (Cao et al. 2016; Wang et al. 2017). Earlier studies demonstrated that the exposure to heavy metals could lead to harmful diseases such as cancer, kidney dysfunction, nephropathy and central nervous system disorders, and currently, there is no known medical treatments available to reverse the above health defects (Javed et al. 2016; Jaishankar et al. 2014; Zheng et al. 2007). Over the last few decades, a continuous industrialization and urbanization resulted in the accumulation and elevation in the concentration of heavy metals in the soils. Therefore, investigations on the spatial distribution of heavy metals in soil are critical to assess their level and impact on pollution. Many sources of pollution have already been investigated, which include industrial and domestic wastewater emissions, sewage irrigation, chemicals (Yu-Mei et al. 2016) and electronic products processing (Tang et al. 2010), vehicle exhaust (Ying-Chun et al. 2016), overuse of pesticides and fertilizers (Yang et al. 2017; Padoan et al. 2017) and mining (Li and Ji 2017). However, to the best of our knowledge, the contamination of heavy metals in soil caused by oil production is rarely reported. One of the key reasons is that various hydrocarbons as compared to heavy metals will be added more significantly into the soil during oil production. Due to crude oil which is commonly abundant with various heavy metals (Agbogidi et al. 2007), a small increment in heavy metals in the soil that stems from oil production can easily surpass the safety thresholds and poses a great threat to the safety of the environment. Therefore, it is of great importance to strengthen the investigation of heavy metals pollution in the soil around oil fields.

The global common issue of limited land resources leads to difficulty in the effective separation of industries from agriculture in the same area, as it not only brings more challenges to various pollutants accumulated in the soil, but also increases the possibility to degrade the crop production affected by other sources of contaminants.

The previous studies mainly focused on the heavy metals pollution in the soil around a specific industry (Duong and Lee 2011; Chary et al. 2008; Murati et al. 2015), but not on the combined influences of the elevation of heavy metals in the soil from farming and other industries that coexist in a particular area. To meet the needs of regional pollution control and rational distribution of different industries, it is necessary to focus on the studies which not only aim at the survey of heavy metals pollution in the soil around a single industry but extend it to the interaction of farming and other industries, which is lacking at this stage. In addition, the earlier studies mainly centered on the developed cities or densely populated areas (Long et al. 2013; Huo et al. 2012; Chabukdhara and Nema 2013; Rocher et al. 2004). However, the underdeveloped areas have not been given enough attention, where a continuous industrial development without any environmental regulation will deteriorate the environment which in turn is more likely to destroy the economic development. So, it is of great significance to strengthen the environmental research in the underdeveloped areas.

The Yellow River Delta (YERD) is one of the most active regions of land–ocean interaction and is a habitat for many rare and endangered species. In particular, it provides overwintering and breeding shelter for migrating birds in the inland of Northeast Asia and the western Pacific Rim (Hua et al. 2012). This delta originally formed in a channel of the Yellow River in 1855 due to the movement of large volumes of sediment for a long distance and deposited into the Bohai Sea (Yongquan 2007). The YERD is not only a vital wetland of north China, but it is also an important crop production area and contains the Shengli Oil Field, a site which has been operational since 1960s. In view of the low background of heavy metals in the sediments of the Yellow River (Yuan et al. 2008; Ma et al. 2016), the background value of heavy metals in the soils of YERD should also be low. However, from earlier studies an elevated concentration of heavy metals in the soils has been observed before, and a considerable contamination was disclosed, which suggested an intense influence of an increase in the heavy metals in the soils from industrial and agricultural developments in this short period of 10 years (Bai et al. 2011a, 2012; Xie et al. 2014; Yao et al. 2016; Li et al. 2014). In fact, due to the relatively simple industrial system, YERD can be used as an ideal area, not only to identify the combined contamination, but also to check the independent contamination feature of oil production or agricultural contamination. However, earlier researches had lesser regional research or centered on the studies of heavy metal pollution of soil around a single industry (oil producing or agriculture) (Bai et al. 2011a, 2012; Xie et al. 2014; Yao et al. 2016; Li et al. 2014), which leads to different results, and the contribution of oil exploitation and agricultural production to the accumulation of heavy metals in the soil throughout the whole YERD becomes difficult to understood. Besides, most of the available information on the distribution of heavy metals has been determined only in the samples of topsoil. Also, only a little is known about the movement of heavy metals throughout the soil profile. Therefore, it is necessary to identify the distribution and possible sources of heavy metals in different soil layers under high density of oil production and high frequency of agriculture in order to propose a comprehensive soil management for YERD. The above will not only assist in the local development of ecological agriculture and tourism, but will also produce a positive environmental research for the areas of coexistence of multiple industries around the world.

The YERD is one of the coastal wetlands with protected values, but a continuous development of oil industry and agriculture is a potential threat to soil environment. The outcome of this research is expected to provide some insights into the origin and accumulation of heavy metals in the soil profiles. On this context, the primary objectives of this study were: (1) to examine the spatial distribution of heavy metals (As, Hg, Cd, Cr, Cu, Pb and Zn) in the soil profiles of YERD, (2) to assess the contaminant status of heavy metals in the soil profiles of YERD and (3) to identify the potential sources of the heavy metals from oil industry, agriculture or natural deposit using multivariate analysis.

Materials and methods

Study area description

The Yellow River Delta, spanning 37°30′–38°08′N and 118°18′–119°19′E (Fig. 1), is located in the northern Shandong province, north of China. The delta is situated on the south edge of the Bohai Sea and has a temperate, semi-humid continental monsoon climate. Average annual temperature is 11.7–12.6 °C, and average annual precipitation is 530–630 mm, of which 70% occurs during the summer (May–July). Average annual evaporation is 1900–2400 mm (Yu et al. 2011). The YERD originally formed in a channel of the Yellow River in 1855 due to large volumes of sediment being deposited by the Yellow River into the Bohai Sea. The Yellow River is the main river in the YERD, entering the study area from Nansong village of Lijin County and flowing to the northeast through Kenli County into the Bohai Sea. The length of the YERD is 128 km. The YERD is a low-lying area which is commonly affected by tides and resulted in high salinity of soils. The main soil types are sandy and clayey fluvisols. The YERD is an important agricultural base in the north of China, producing cotton, rice, wheat, vegetables and fruits. The YERD also contains the second largest oil field in China (Shengli Oil Field, operating since 1960s), having an annual production of crude oil ranging from 400,000 to 30,000,000 tons (Linsheng et al. 1998).

Sample collection and analysis

The sampling location from the coast to inland was chosen covering the entire Yellow River Delta (YERD) region, and the seasonal variation of heavy metals was neglected in line with previous research, which demonstrated the concentrations of soil heavy metals generally remain almost constant between seasons in the natural state (Grabowski et al. 2001; Bragato et al. 2009). The general layout of sampling covered densely populated and industrial concentrated areas of YERD. The three sample horizons of 0–20 cm (surface, directly influenced by anthropogenic activity), 20–50 cm (subsurface, moderately influenced by anthropogenic activity) and 50–80 cm (bottom, expressing natural states) were determined based on the intensity of anthropogenic influence from surface to bottom. Thus, the chemical constituents in deep soil

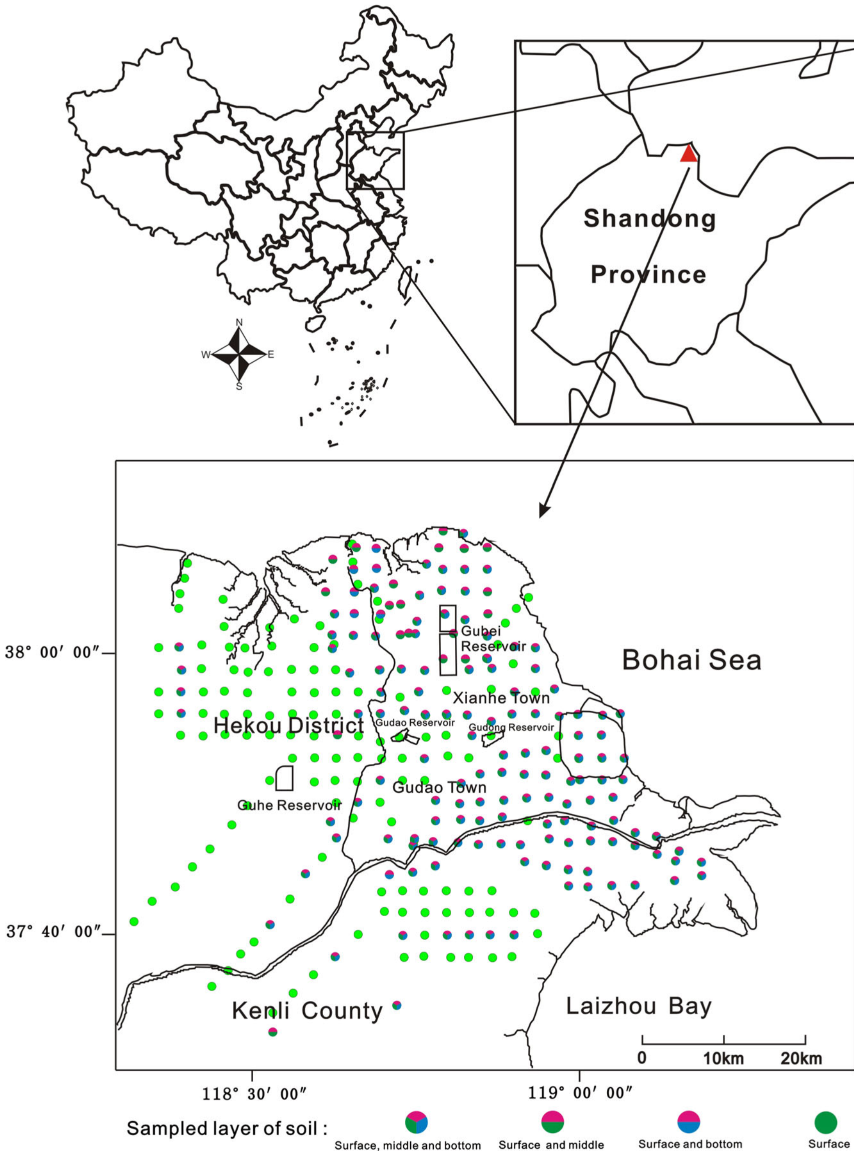


Fig. 1 Sample plots in the Yellow River Delta

will become more stable so that the amount of samples should decrease with an increase in depth. The bottom layer is less affected by human activities than the top layer, so the composition is more uniform. Therefore, the sample collection decreases with an increase in the depth. 290, 164 and 162 samples were collected from the surface, subsurface and bottom levels of soil, respectively. Two or three subsamples were collected among 100 m and combined into a test sample with weight of 1 kg in each sample site. A stainless steel spade was used to take samples and was cleaned before each sampling to avoid cross-contamination and growth of mild-dew. The samples were refined using a 2-mm nylon sieve to remove large stones, debris and pebbles. The product was oven-dried (< 60 °C) and crushed to fine powder (< 63 μm) for further analysis. 0.2 g of the powdered samples was digested by a solution of HNO_3 + HCl + HF (5:4:1 v/v) in a Teflon digestor at 140 °C for 6 h. Then, the residue obtained was diluted to make up the volume and extracted using nitric acid. The soil organic matter (SOM) was obtained using an elemental analyzer

Table 1 Global maximum background value (c_n^i) and toxic factor (T_r^i) of heavy metal elements

Item	Cr	Cu	Zn	Pb	Cd	As	Hg
$C_n^i/(\times 10^{-6})$	61	22.6	74.2	26	0.097	11.2	0.065
T_r^i	2.00	5.00	1.00	5.00	30.00	10.00	40.00

(Vario EL-III). Elemental constituents such as Si, Al, Fe, Mn, I, P and S were measured using an X-ray fluorescence spectrometer (XRF, Axios PW4400), while constituents such as Mn, Ni, Cu, Pb, Zn, Cd and Cr were analyzed by an inductively coupled plasma mass spectrometry (ICP-MS, Thermo X series). As and Hg were measured with an atomic fluorescence spectrometer (AFS-920).

The process of maintaining quality assurance and quality control for each batch of the sample (for example 1 blank and 1 standard for every 10 samples) includes obtaining standards (reference materials), duplicates and methods from the Chinese Academy of Measurement Sciences. High sample recovery between 95 and 105% was reported and used toward QA/QC compliance (Hu et al. 2013a, b; Dou et al. 2013).

Statistical analysis

Commercial software SPSS 12.0 was used for the data analysis. Pearson correlation was conducted to reveal their relationships between soil properties and heavy metals and to identify the pollution sources of soil heavy metals. Differences were considered significant if $P < 0.05$. The contour of heavy metals is obtained by kriging interpolation in Surfer 13, and line charts were drawn using Graph 10.

Assessment method

Potential ecological risk index

The potential ecological risk index (RI) could be used to assess the ecological risk of toxic substances and contaminants on the biological community (Zhao and Li 2013). Hence, this index was selected to evaluate the combined effect of pollution from multiple metals. The RI was calculated using the following equation (Hakanson 1980):

$$E_r^i = T_r^i \cdot c_f^i \quad (1)$$

$$\mathrm{RI} = \sum E_r^i = \sum T_r^i \cdot c_f^i = \sum T_r^i \cdot c_s^i / c_n^i \quad (2)$$

where E_r^i is the monomial potential ecological risk index of heavy metal i; T_r^i is the toxic response factor for a specific heavy metal i (Table 1); c_f^i is the contamination factor of heavy metal i; c_s^i is the content of heavy metal i in the samples (mg kg^{-1}); and c_n^i is the background value of heavy metal i in the study area (mg kg^{-1}). In this study, soil background values of Chinese soil (Fusheng 1991) were used as c_n^i (Table 1).

According to Hakanson (1980), the contamination factor (CF) of less than unity indicates low levels of contamination with CF between 1 and 3 ($1 < \mathrm{CF} < 3$) and is considered to be moderate level of contamination, while $3 < \mathrm{CF} < 6$ is considered to be a significant contamination, and $\mathrm{CF} > 6$ indicates a very high contamination. The contamination degrees and potential ecological risk of a heavy metal (E_r^i) were classified as low degree ($E_r^i < 40$), moderate degree ($40 \le E_r^i < 80$), considerable degree ($80 \le E_r^i < 160$), high degree ($160 \le E_r^i < 320$) and very high degree ($E_r^i \ge 320$). However, according to Li et al. (2015), the RI is modified on the basis of all the heavy metals examined and the classification is defined as low risk ($RI < 110$), moderate risk ($110 \le RI < 220$), high risk ($220 \le RI < 440$) and very high risk ($RI \ge 440$).

The index of enrichment factor

For the estimation of the status of heavy metal contamination and distinction of the potential sources (anthropogenic vs natural origin), it is more useful to calculate the non-dimensional enrichment factor (EF). Al is the most common choice for normalization to minimize the grain size effect on the heavy metal values (Rule 1986; Roussiez et al. 2005; Chen et al. 2007; Xia et al. 2012; Hu et al. 2013b). The EF is calculated as follows:

Table 2 Enrichment factor and degree of contamination

Enrichment factor	Degree of contamination
$0.5 < EF < 1.5$	No enrichment
$1.5 \leq EF < 3$	Minor enrichment
$3 \leq EF < 5$	Moderate enrichment
$5 \leq EF < 10$	Moderately severe enrichment
$10 \leq EF < 25$	Severe enrichment
$25 \leq EF < 50$	Very severe enrichment
$EF > 50$	Extremely severe enrichment

$$EF = \frac{\left(\frac{C_x}{C_{Al}}\right)\text{sample}}{\left(\frac{C_x}{C_{Al}}\right)\text{baseline}} \quad (3)$$

where (C_x/C_{Al}) is the ratio of metal to Al in the sample measured and (C_x/C_{Al}) is measured at the baseline as previous studies have shown that the regional background values might be more appropriate to calculate the EF (Rubio et al. 2000; Kersten and Smedes 2002; Christoforidis and Stamatis 2009). Hence, in the present work, the average metal concentrations were used as the background metal values (Table 4) sourced from the upper continental crust of North China (Gao et al. 1998). The EF between $0.5 < EF < 1.5$ indicates that the metals are entirely from crustal contribution (e.g., weathering product), while the value of $EF > 1.5$ shows the proportion of heavy metals being delivered from non-crustal materials (e.g., biota and/or pollution drainage) (Zhang and Liu 2002). According to Sutherland and Tolosa (2000) and Chen et al. (2007) the degree of contamination is listed (Table 2).

Results

The content of heavy metals in YERD

The descriptive statistics of the concentrations of heavy metals in the soils are summarized in Table 3. The content of heavy metal elements is higher on the surface than in the deep layers, whereas its content on the subsurface layer is closer to the bottom layer. The coefficient of variation of surface soil was generally the highest among the soil horizons, which suggests an enlarged variation related to human may come out. In the whole soil profile it has been observed that mercury had the highest coefficient of variation as compared to other heavy metals. This may be due to the active chemical properties of mercury, which determine the mobility, and it may be activated by the biota of soil and also gradually accumulates upward to the surface. The lowest coefficient of variation was observed with Cr and Pb, which indicates a minimal fluctuation in the concentration of these two elements. The coefficients of variation of Cd, As, Cu and Zn were approximately the same, which displays a moderate fluctuation in their concentration. The results of this investigation agree well with the results of Li et al. (2014) and Rui et al. (2008), whereas they are lower than that reported by Bai et al. (2012). The content of heavy metals generally demonstrates deviations owing to the differences between the sampling area and its considered range. However, the concentration of heavy metals nearly meets Class I criterion of soil quality standards of China. As compared to the national deltas such as Yangtze River Delta and Pearl river delta, the concentration of heavy metals in the soil of YERD is relatively low, which approaches or slightly lower than the baseline of Chinese soil, but slightly higher than the baseline of world soil, besides Cr. It is due to the result of different soil baselines arising from variations in the distribution of elements. The concentration of heavy metals in the soil of YERD is still relatively low as compared to the delta of famous rivers around the world, such as Mekong, Han and Mississippi Rivers.

The distribution and assessment of heavy metals

The contamination factor (CF) displays the distribution of heavy metals more clearly and eliminates the need to compare each of the heavy metals at different magnitudes. The observed values of CF are listed in Table 4. Firstly, the consistent changes of CF in three different depths of soils manifest the variation of heavy metals mainly controlled by the parental material of soil. Also the values of CF in the surface soils are significantly higher compared to other depths of soil which suggest that the heavy metals tend to concentrate on the surface soil and are considered to be an additional input induced by humans. Only the average CF of Cd in the surface soil surpasses 1, and hence, the status reached moderate contamination, whereas the average CF of all other heavy metals is below 1, reflecting their low contamination. The

Table 3 Content of heavy metal elements of the Yellow River Delta and the other regions

Location	Item	Sample num	As	Cd	Cr	Cu	Hg	Pb	Zn
Surface	Average	290	(5.38–1.89)	(0.077–0.277)	(46.51–96.97)	(9.17–43.88)	(0.0035–0.1746)	(13.44–39.15)	(34.07–102.63)
			10.31	0.134	62.89	19.62	0.0232	19.35	57.48
	STDEV		3.45	0.041	10.45	7.16	0.0195	4.11	15.92
	σ		0.33	0.31	0.17	0.36	0.84	0.21	0.28
Middle	Average	164	(4.13–21.95)	(0.071–0.262)	(46.43–105.85)	(10.11–43.48)	(0.0037–0.1830)	(13.37–36.73)	(35.27–104.26)
			9.41	0.115	60.94	17.85	0.0226	18.57	53.22
	STDEV		3.30	0.037	10.32	6.51	0.0155	3.62	15.19
	Σ		0.35	0.33	0.17	0.36	0.68	0.19	0.29
Bottom	Average	162	(4.003–21.94)	(0.072–0.247)	(47.55–97.62)	(9.52–43.10)	(0.0043–0.1409)	(13.37–36.45)	(32.92–105.28)
			9.47	0.114	60.95	17.90	0.0232	18.64	53.56
	STDEV		3.25	0.033	9.96	6.14	0.0146	3.63	14.70
	Σ		0.34	0.29	0.16	0.34	0.63	0.19	0.27
Soil of Yellow River Delta (2012) (Bai et al. 2012)			–	0.394	59.08	22.37	–	14.34	75.22
Sediment of Yellow River Delta (2006) (Rui et al. 2008)			18.16	0.040	–	12.48	–	10.99	39.18
Estuarine Sediment of Yellow River (2007) (Bai et al. 2012)			27.60	0.570	–	26.70	–	27.23	78.00
Sediment of Laizhou Bay			13.10	0.081	57.10	13.30	0.0530	20.20	59.40
Estuarine (Hu et al. 2011) Sediment of Yangtze River			11.68	–	73.33	38.50	0.1900	28.41	111.65
Estuarine (Bi 2004) Sediment of Pearl River (Gan et al. 2010)			22.90	0.200	81.10	38.60	0.1700	44.00	100.70
Class I criteria of soil quality criteria of China (GB15618-1995)			15	0.2	90	35	0.15	35	100
Soil baseline of China (Chen et al. 2005)			9.60	0.097	61.00	22.60	0.0650	23.60	67.70
Soil baseline of World (Chen et al. 2005)			5.00	0.060	100.00	20.00	0.0100	10.00	54.00
Sediment of Mekong River (Fu et al. 2012)			19.28	–	183.44	22.08	–	36.73	82.71
Sediment of Han River (Lai et al. 2013)			6.77	0.220	61.70	29.70	0.0830	35.10	126.00
Sediment of Mississippi River (Santschi et al. 2001)			–	0.175	68.32	21.31	0.1390	27.41	144.00

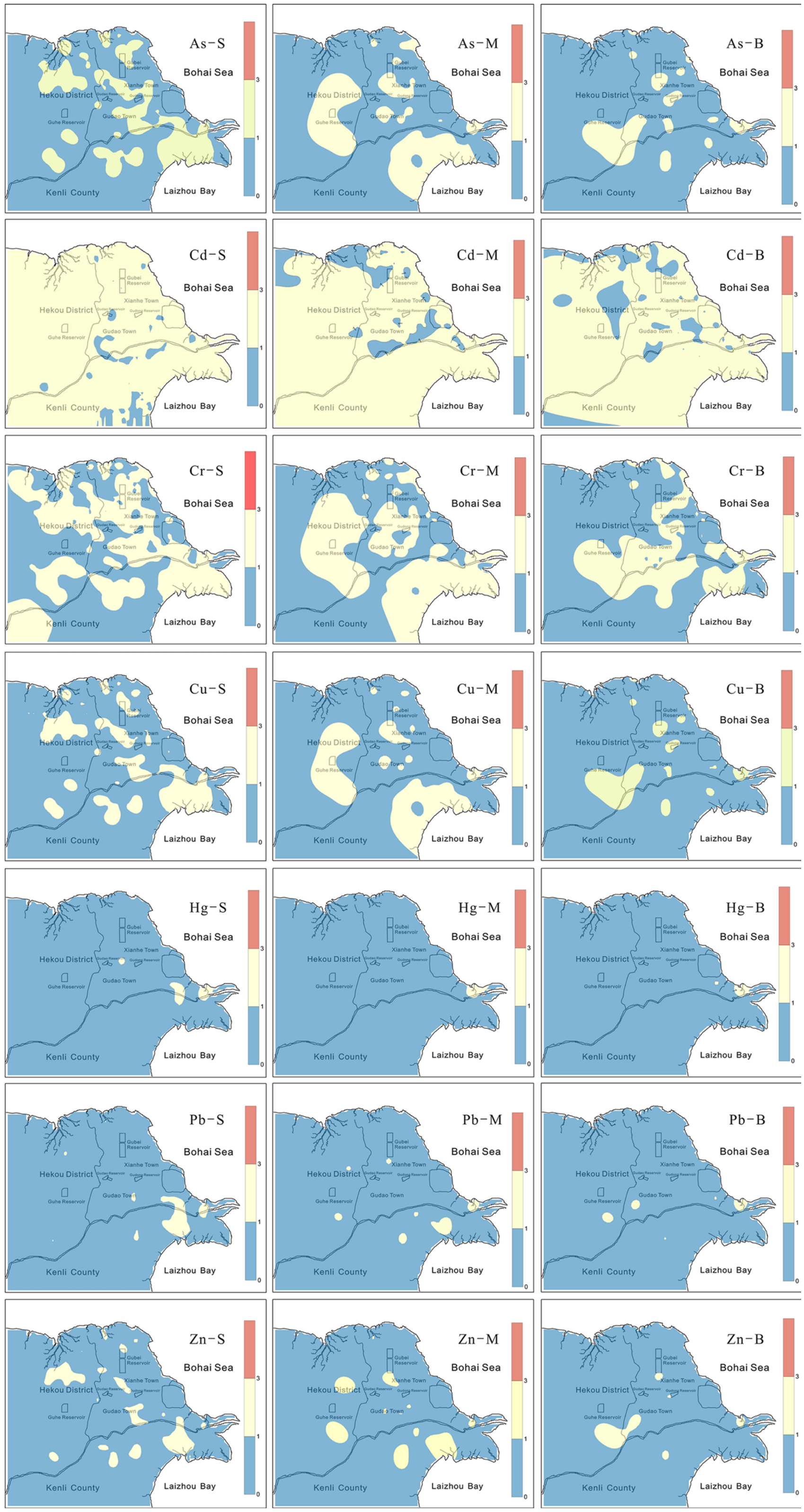
Table 4 Potential ecological risk factors (E_r^i) and risk indices (RI) of heavy metals in Yellow River Delta

Location	E_r^i							RI
	As	Cd	Cr	Cu	Hg	Pb	Zn	
Surface	4.80–19.54	23.95–85.67	1.52–3.18	2.03–9.71	2.14–107.46	2.59–7.53	0.46–1.38	40.48–211.73
	9.21	41.42	2.06	4.34	14.27	3.72	0.77	75.78
Middle	3.68–19.60	21.96–81.03	1.52–3.47	2.24–9.62	2.28–112.64.	2.57–7.06	0.48–1.41	43.89–231.36
	8.40	35.48	2.00	3.95	13.93	3.57	0.72	68.05
Bottom	3.57–19.59	22.27–76.39	1.56–3.20	2.11–9.53	2.67–86.68	2.57–7.01	0.44–1.42	45.51–201.53
	8.46	35.15	2.00	3.96	14.31	3.59	0.72	68.18

distribution demonstrates their moderate contamination (Fig. 2), where Cd shows the widest distribution covering the entire soil of YERD in different layers. However, other heavy metals indicate a low contamination. The second widest distribution area was displayed by Cr; the distribution area of As is approaching Cu; and the distribution area of Pb, Zn and Hg is smaller. The distribution of moderate contamination is noted in the north shore of Yellow River and adjacent to estuary. With an increase in the depth of soil, the content of heavy metals is not only simply reduced, but a reverse in the concentration of heavy metals in the soil profile could be noted. A relatively uniform distribution of heavy metals is noticed in the same layer, which could be related to the similar source of heavy metals in each of the layers (Fig. 3).

To gain an insight into the potential ecological risk arising from heavy metals, the values of E_r^i and RI were calculated as shown in Fig. 4. The potential ecological risk decreases with an increase in the depth of soil, and the potential ecological risk of surface soil is higher, which is consistent with the higher content of heavy metals in the surface soil. The potential ecological risk of soils in different layers throughout YERD is of low degree, and hence, the overall environmental condition is healthy. The main ecological risk derived from Cd, Hg and As is in agreement with the contribution rate to RI (Fig. 5), especially for Cd, where the monomial contribution rate is beyond 50%. These results are not completely consistent with the results evaluated by CF. Due to the differences in the toxicity coefficient, although the CF value of Cr is high and the distribution area of moderate contamination is large, the potential ecological risk is low. Similarly, the CF value of Hg is low, but its higher toxicity coefficient among heavy metals elevated its potential ecological risk. Contrasting from Cd and Hg, the potential ecological risk caused by As does not exist with the E_r^i values of As (all below 40). Even though Hg has the highest risk and is reaching a considerable degree, the spatial distribution is too small and restricted to Hongliu oil fields, which was constructed to restore the wetland (Zheng et al. 2015). The maximal risk degree of Cd is moderate, and the distribution area is the widest among heavy metals and is mainly restricted to north shore and near estuary, where it is covered by a high density of oil-producing wells, and thus the potential ecological threat mainly

Fig. 2 CF distribution of heavy metal elements in the Yellow River Delta's surface soil. The data expressed above are compared to the background in Table 1



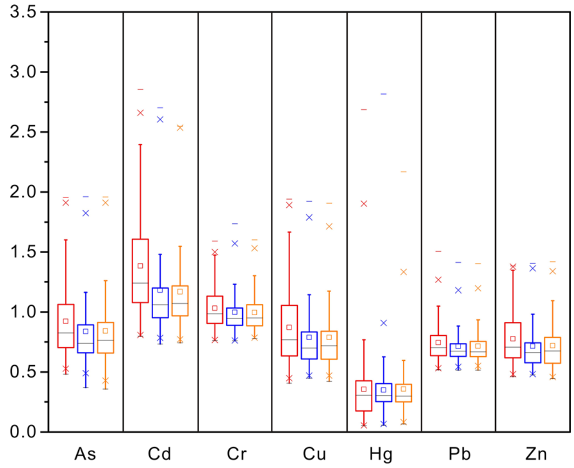


Fig. 3 Contamination factor of heavy metal elements in Yellow River Delta. Red, blue and orange indicate the respective surface layer, middle layer and bottom layer. The data expressed above are compared to the background in Table 1

stems from Cd instead of Hg in YERD, which breaks the traditional concept that oil production may escalate mercury in the soil. The soils of YERD are close to low risk based on the distribution of RI values, which discloses a good ecological environment (Fig. 6).

The impact of a continuous increase in the concentration of heavy metals in the soils induced by humans is the most and a serious concern behind their threat, and thus the EF value is calculated to gain an insight into the cumulative effect of heavy metals. The highest EF values in the surface layer than in the deep layer demonstrate a higher influence posed by anthropogenic activity which is more prone to accrete in the surface layer and leads to a higher potential ecological risk in the surface layer. The EF values of As, Cd and Pb are relatively higher and near to or slightly beyond 1.5, indicating a minor enrichment, whereas the EF values of others are lower than 1.5, illustrating an insignificant enrichment with a smaller influence from humans. According to the distribution of EF values above 1.5 in the deep soils, it can be concluded that exogenic As has the strongest ability to migrate downward to lower layer, followed by Cd and Pb in YERD. Affected by human activities, As can accumulate in the surface soil and migrated gradually to deeper soil in various forms of metalloid ions. The Cd mainly concentrated in the surface soils, partly transferred to the middle layer, but the enrichment was rarely found out in the bottom layer. Pb is enriched only in the surface soil, while there is no significant rise in the deep soil (Fig. 7).

The potential source of heavy metals

Influence of soil parent material on heavy metals

YERD is a modern depositional system silted by a large amount of sand from Yellow River after its diversion into Bohai Sea (Yuanfang 1991). The silt-carrying capacity of Yellow River is huge, which is approaching 1.6 billion tons per year (Mei-e and Xianmo 1994), where a considerable amount of detrital materials from Loess plateau of western China moves into sea. Therefore, the soil material of YERD is inevitable sediment of Yellow River. SiO_2, Al_2O_3 and Fe_2O_3 are the critical components of soil, and also the embodiment inherits from the parent materials of soil which are chemically stable and thus difficult to decompose in the environment. In general, a higher concentration of SiO_2 in the soil leads to a lower content of Al_2O_3 and Fe_2O_3, and the longer the soil parent material is transported, the stronger the intensity of weathering. This principle can be used for judging the degree of chemical weathering (Belousova 2006). The average contents of SiO_2, Al_2O_3 and Fe_2O_3 are close irrespective of the depth of soil. The spatial distribution is merely fluctuating between maximum and minimum (Table 5), which illustrates that weathering and transportation are dominated by the climatic characteristics within the entire river basin that control the source and physicochemical properties of the sediments reaching YERD by means of flow regulation (Shi and Wang 2015).

The heavy metals in the soil show a well natural source because of a significant correlation with SiO_2, Al_2O_3 and Fe_2O_3. The contents of Cr, Cu and Pb that were controlled by the natural deposit have been reported (Wen et al. 2015). The correlation between heavy metals and SiO_2 is negative, whereas between heavy metals and Al_2O_3, Fe_2O_3, it is positive. It indicates that the heavy metals of soil in YERD are inherited from sediments of Yellow River and could be determined by their mineral assemblage characteristics. It is also a good indication of the environmental conditions in the Yellow River Delta. A lower but a significant correlation of Hg suggests a poor control from the combination of mineral corresponding to the

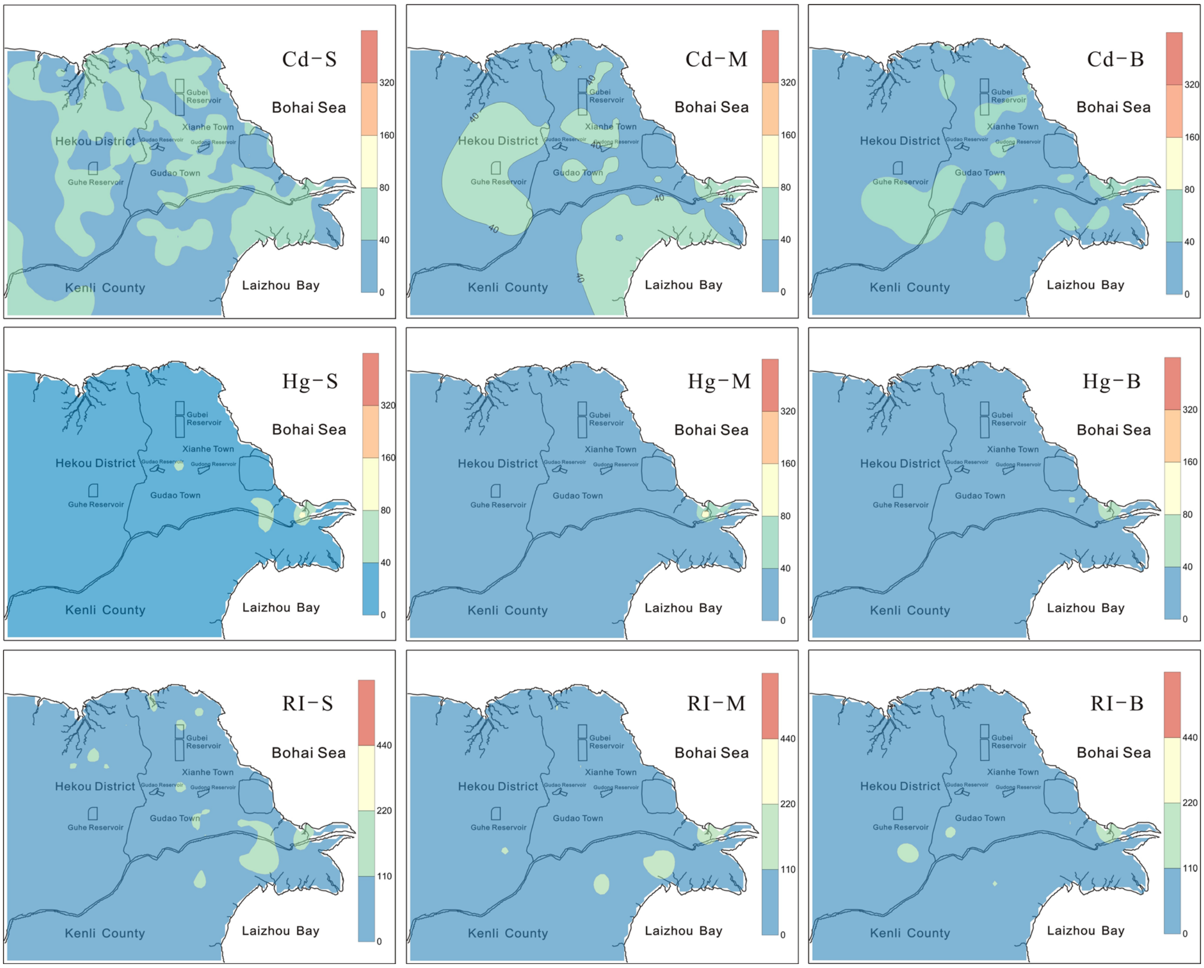


Fig. 4 E_r^i and RI distribution of heavy metals in the Yellow River Delta's soil. SRI, MRI and BRI are the risk indices (RI) of heavy metals in the surface, middle and bottom layers, respectively

relevant and active chemical properties, where Hg confined in the minerals of soil may dissociate and reach the environment and exists in the soil microbes (Robles et al. 2015). A part of activated mercury may move into the atmosphere, whereas the remaining part may complex with chloride in the soil originated from the intrusion of saltwater, which leads to non-uniform distribution of Hg to other heavy metals and impacts the mineral assemblage on Hg.

In general, SiO_2 and Fe_2O_3 are ubiquitous in all types of rocks in various speciations of minerals. However, the distributions of SiO_2 and Fe_2O_3 in various minerals are uneven. SiO_2 is the main component of quartz and more concentrated in felsic minerals, while Fe_2O_3 is more centralized in dark minerals, such as pyroxene and olivine (Kong et al. 2011). Although both felsic and dark minerals are formed by magmatic diagenesis, dark minerals lack stability to resist weathering in the surface environment of earth compared to felsic minerals (Bazilevskaya et al. 2015). Quartz has the strongest resistance to weathering than other minerals. Therefore, the strength of weathering can be revealed according to the main chemical composition of the characteristic minerals such as, SiO_2 and Fe_2O_3 which are often treated as chemical weathering index. With the deepening of weathering, quartz gradually accumulates and dark minerals suffer a massive loss, where only a small part of dark the minerals such as biotite and hornblende which do not decompose completely is left over. The heavy metals are mainly present in the dark minerals, such as olivine, pyroxene and

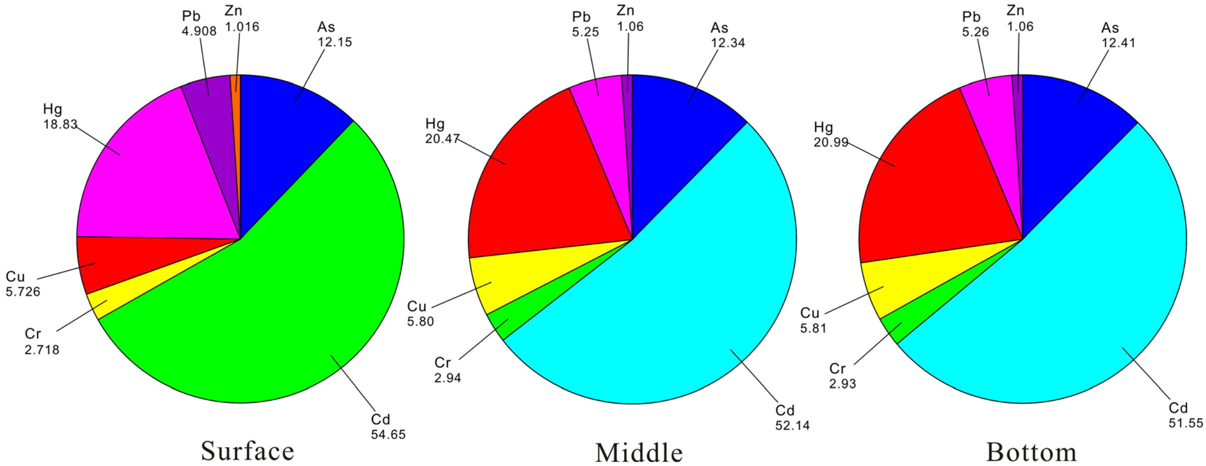


Fig. 5 Pie chart showing the contribution rate of E_r^i to RI

hornblende. It has been well explained that the natural abundance of heavy metals in the sediment will significantly decrease with an increase in quartz, which weakens the existence of dark minerals to promote the accumulation of heavy metals in the sediment. This result is consistent with the high content of quartz (commonly $> 50\%$) of the sediments in YERD (Xiong et al. 2003).

Additionally, original silicate minerals convert into secondary minerals which primarily consist of clay minerals and hydrous oxides with iron, manganese and aluminum through chemical and biochemical weathering under the conditions of suitable temperature and humidity. The granular size of such minerals is too small with a high specific surface area, which poses a negative electricity under alkaline conditions and is prone to adsorb ions of heavy metals. This may be the reason that heavy metals indicate a stronger correlation with SiO_2 as compared to Al_2O_3 and Fe_2O_3.

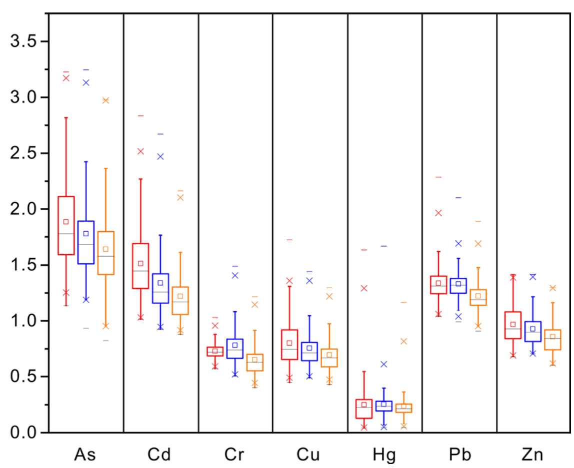


Fig. 6 Enrichment factor of heavy metal elements in the Yellow River Delta. Red, blue and orange indicate the surface, middle and bottom layers, respectively

Influence of human activities on heavy metals

Anthropogenic heavy metals often refer to the by-products that stem from industrial and agricultural activities that have not been effectively managed, but their release to soil, water and air cause adverse effects to the environment. These heavy metals usually have strong mobility and bioavailability, which cause their bioaccumulation in biota and eventually affecting human health. Due to this, the anthropogenic heavy metals are becoming a hot topic in the current research (Bazilevskaya et al. 2015). The third largest oil field is located in Yellow River Delta, which is also a critical agricultural base of North China (Cui et al. 2009), and thus, the anthropogenic heavy metals are inevitable in the soil arising from oil processing and applications of fertilizer.

The Yellow River Delta, the main production area for grain, cotton and vegetables in China, is experiencing a rapid development since the introduction of reforms and policies. There is 700,000 hectares of arable land in the Yellow River Delta (Zhao et al. 1994); however, 70% of soil in this area is salinated. The production techniques in this fragile ecological environment rely heavily on pesticides and fertilizers (Xiao-Min 2008). It is therefore inevitable that heavy

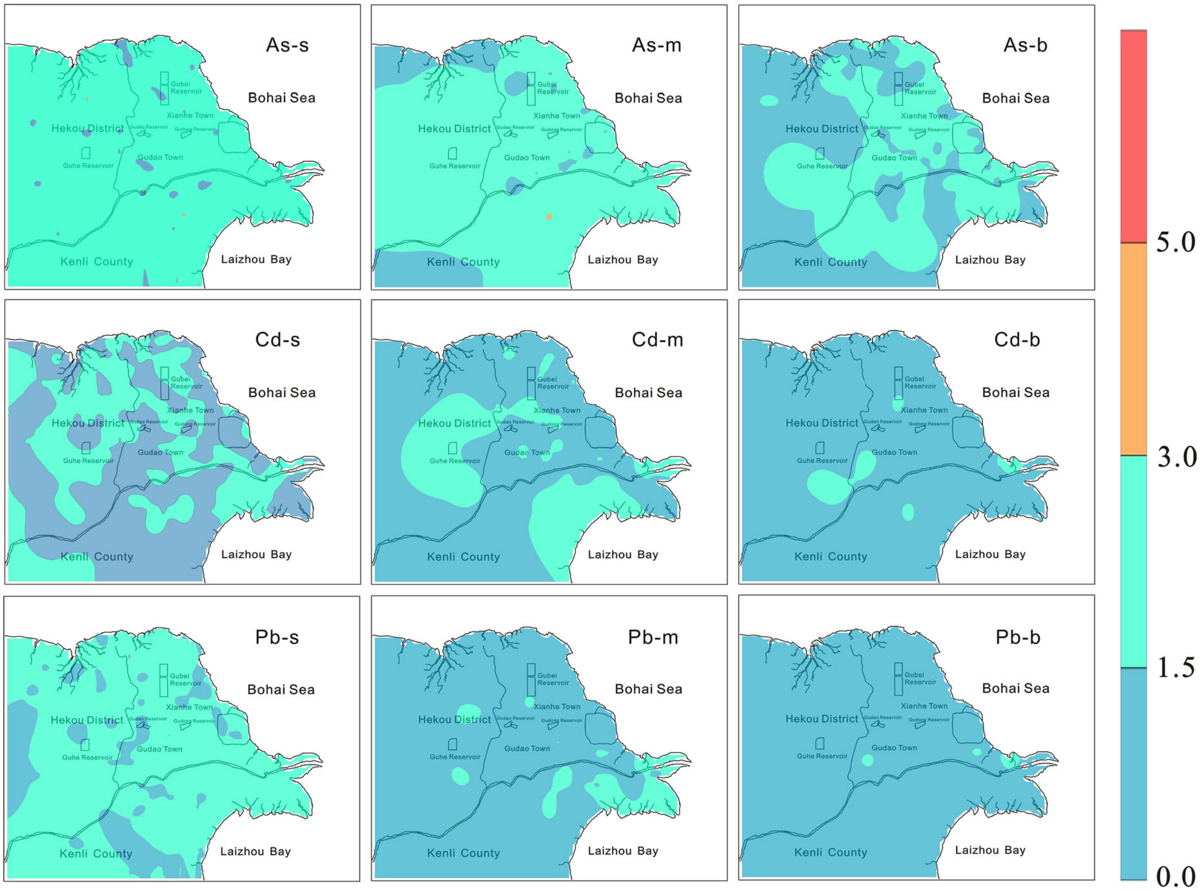


Fig. 7 EF distribution of heavy metal elements in the Yellow River Delta's soil

metals used in the chemical fertilizers have become an important source for heavy metal contamination in the soil and have resulted in potential environmental threats (Atafar et al. 2010). Nitrogen and phosphorus are the two most important elements that affect the growth of crops, with nitrogen-based fertilizers being readily applied to promote the growth of crops. Previous studies have shown that more than 160,000 tons and 90,000 tons of nitrogen and phosphorus fertilizers, respectively, were added to the soil in this area in order to improve the soil condition for the cultivation of crops (Shan et al. 2017). If only heavy metals are derived from agriculture, they must be fixed in phosphates and accumulate with the input dosage of fertilizers to the soil. Thus, the correlation with nitrogen and phosphorus must be significant in order to express the relation. However, a correlation just expressed with nitrogen is significant. Even though a significant correlation between As, Cr, Cd, Cu, Ni, Pb, Zn and P has been reported (Bai et al. 2011b), which is obviously different from the current results of insignificant correlation with phosphorus, and the congregated plow lands are thought to be the main reason within a small area of YERD. Only a significant correlation found out with nitrogen cannot confirm the elevation in the concentration of heavy metals in the soil corresponding to farming, as oil production can also affect the enrichment of heavy metals in the soil. Additionally, the spatial trending of cultivated land is relatively dispersive and limited so that the heavy metals introduced by fertilization cannot be effectively accumulated in the soil. This infers that agriculture contributes a little to elevate the concentration of heavy metals in the soils of YRED and, moreover, it eliminates the suspicion that agriculture plays a vital role in the soil pollution in that area.

Table 5 Physical and chemical indexes of soils in each sampling site

Location	Item Unit	SiO_2 mg/g	Al_2O_3 mg/g	Fe_2O_3 mg/g	SOM mg/g	TP mg/kg	TN mg/kg	I mg/kg	pH –
Surface	Average	(47.19–68.33)	(9.58–15.59)	(2.75–6.85)	(0.07–1.53)	(336.07–886.69)	(25.08–1445.37)	(0.08–7.96)	(7.32–9.93)
		61.28	11.35	3.96	0.36	629.80	375.80	1.32	8.35
Middle	Average	(47.77–67.68)	(9.35–14.31)	(2.85–6.86)	(0.04–0.80)	(484.01–780.75)	(70.58–795)	(0.16–4.23)	(7.78–9.63)
		61.74	10.97	3.77	0.21	608.63	254.86	1.02	8.49
Bottom	Average	(47.18–67.68)	(9.42–14.42)	(2.83–6.95)	(0.04–0.70)	(490.58–780.75)	(24.37–931.51)	(0.14–4.33)	(7.97–9.67)
		61.98	10.96	3.78	0.19	607.99	239.95	0.99	8.47

The Yellow River Delta contains a wealth of oil and gas resources, where the Shengli Oil Field has oil and natural gas geological reserves approaching 300 million tons and 23,000 million m^3, respectively. Moreover, the associated gas resources are around 1 million m^3 (Hu 2013). Hence, the oil production has become the breadwinner of regional economy, but poses a potential menace to the local environment. Petroleum contains petrobenzene and hydrocarbons and is the effective component used for fuel. However, with the exception of organic compounds, the oil and gas reservoirs absorb heavy metals, alkaline earth metals and halogen elements which are present in the nearby areas and formed during the whole geological period of which generates an abnormal content of these elements surrounded by the soil. This is treated as a signal to trace oil, which is the basis of oil exploration with a long history and mature technology. Thus, if the signals can work to locate oil, then they can also have the effect on pollution derived from oil production. Generally, alkaline earth metals and halogen elements can provide a strong indication to oil industry, but they are not suitable in YERD because of the intrusion of seawater that accumulates multiple ions referring to ocean in soil owing to coastal wetland attributes of YERD, such as Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Br^- etc. The above ions are present in higher amounts than the background levels (Zhang et al. 2016), and thus, the signals are weakened. However, as one of the halogen elements, the concentration of iodine in the soil is not affected significantly by seawater intrusion, where the average concentration of iodine in YERD is in the midst of normal soil content (0.7–2.0 mg/kg) (Fuge and Johnson 1986).

During production, once oil spills into soil, stable compounds such as methyl iodide, ethyl iodide, propyl iodide, etc., would be formed by means of replacement of one or more hydrogen atoms by iodine in the presence of sunlight and aggregate gradually. Previous research demonstrated that the concentration of iodide in the soil would escalate 1.5–50 times than the baseline with the existence of lighter hydrocarbons (Schumacher 1996). Thus, the presence of iodine is a good indication to oil industry (Tedesco and Bretz 1995), and thus iodine should be considered as a signal to identify heavy metals from oil industry. Some of the areas in YERD demonstrate higher iodine content than the corresponding baseline even more than 3 times as observed in this study. Such a higher fluctuation in the concentration of iodine suggests a close relationship with the oil production. Thus, the soil heavy metals affected by oil production have been demonstrated; however, the influence is not much more important than the traditional concept. It is to be noted that the contaminated area is limited and not spread to the whole YERD based on the significant correlation between iodine, SiO_2, Fe_2O_3 and Al_2O_3 which implies the dominance of mineral iodine, but not oil iodine, in the entire soil profile. This is in accordance with the previous reports which indicated oil production only elevated C/N of soil as compared to normal soil, but heavy metals tend to accumulate in the soil close to oil wells (Wang et al. 2010; Obiajunwa et al. 2002). Therefore, the enrichment of multiple heavy metals commonly occurs in the traditional oil fields such as Gubei, Gudong, Hongliu, Xianhe and Hekou (Wang et al. 2002). A significant correlation observed between heavy metals, SOM and TN is shown in Table 6. The close relationship between TN and SOM indicates that nitrogen is an indispensable element of soil organic matter, while the close relationship between TN and heavy metals is more likely indicating the pollution from oil production. Wang et al. (2002) found that in YERD the leaking of oil failed to increase the nitrogen in the soil significantly. Actually, the organic matter of petroleum generally accumulated with heavy metals from the spilled oil. Furthermore, the increasing amount of organic matter of petroleum in the soil elevates the negative electricity and reducibility, which intensifies the concentration of exogenous heavy metals owing to the positive electricity of heavy metals, which also indicates that multiple heavy metals and organic matters inclined to accumulation in the soil around the oil wells (C.-y. WANG et al. 2010; Obiajunwa et al. 2002). It is the reason why three large oil production plants located in Hekou district, Gudao town and Xianhe town fall into the hot spots of RI and EF in north of YERD. However, it does not indicate the intensive oil production will significantly elevate the heavy metals in the soil. The concentration of exogenous heavy metals in the soils should be more related to net accumulation, in other words, or the loss in the volume of heavy metals must be less than the input volume of heavy metals in the soil, and then the concentration of heavy metals in the soil will increase; otherwise, the concentration of heavy metals in the soil will remain constant. This is the reason that the concentration of heavy metals in the soils of intensive oil fields along the northeast coast is low. Even though a large amount of heavy metals from oil production will input into soils, the wash effect caused by sea intrusion will sweep away more heavy metals. Therefore, it can be concluded that oil production close to coast will not significantly increase the heavy metals in the soil. But, more attention should be paid to seawater or sediment which is present nearby. The hot spot of heavy metals in Huanghe town should be linked to other sources because of the oil production in the blank area. Thus, the petroleum industries could be treated as a considerable source to bring anthropogenic heavy metals present in the soils.

Only Cd, As and Pb instead of all heavy metals in the soils are significantly elevated and affected by oil production. This result is close to the previous study in the oil field of Southern Nigeria (Iwegbue et al. 2009), which demonstrated that oil spillage mainly contributes to the significant increase in Cd, Cr and Pb in the topsoil and subsoil. But the significant increase in Cr did not come out in YERD because of the lower local baseline compared with global baseline. Even through As did not appear in Iwegbue's research, arsenic has a high content in petroleum, which often causes severe pollution in the traffic areas. The concentration of arsenic in residuals released by oil combustion is commonly several-fold to dozens of times higher than the baseline of soil in accordance with the previous reports (Duong and Lee 2011; Johansson et al. 2009; Lu et al. 2009). However, the degree of elevation in the concentration of heavy metals affected by oil production in YERD is relatively small due to lower EF. Hg is also present abundantly in petroleum (Lu et al. 2009; Shi 2008), but the EF values of Hg are all below 1.5. In addition, Hg demonstrates a significant but a lower correlation as compared to other heavy metals. All these imply a nonsignificant effect of anthropogenic activities to soil mercury, which seems to be a paradox corresponding to a higher content of Hg in the oil. In fact, Hg in petroleum is mainly as elemental mercury and mercury halide (Gajdosechova et al. 2015). Once the oil fell into the soil, elemental Hg would gradually evaporates into air, and mercury halide would break away from other heavy metals in the existence of exceeded complex radical to make complexation in

Table 6 Correlation coefficients between contents of heavy metals and chemical indexes

Item	Location	As	Cd	Cr	Cu	Hg	Pb	Zn	SOM	TN	TP	I
SiO_2	Surface	− 0.898**	− 0.883**	− 0.815**	− 0.882**	− 0.489**	− 0.863**	− 0.889**	− 0.552**	− 0.699**	0.123**	− 0.647**
	Middle	− 0.875**	− 0.841**	− 0.832**	− 0.884**	− 0.529**	− 0.904**	− 0.881**	− 0.550**	− 0.789**	0.221**	− 0.780**
	Bottom	− 0.870**	− 0.831**	− 0.818**	− 0.883**	− 0.569**	− 0.873**	− 0.870**	− 0.605**	− 0.883**	0.193*	− 0.695**
Fe_2O_3	Surface	0.968**	0.885**	0.917**	0.940**	0.356**	0.873**	0.979**	0.614**	0.727**	0.005**	0.675**
	Middle	0.975**	0.908**	0.910**	0.981**	0.472**	0.897**	0.991**	0.676**	0.831**	− 0.061**	0.803**
	Bottom	0.966**	0.917**	0.910**	0.980**	0.541**	0.887**	0.991**	0.720**	0.896**	− 0.034	0.746**
Al_2O_3	Surface	0.939**	0.874**	0.859**	0.924**	0.421**	0.866**	0.947**	0.595**	0.706**	0 − .070**	0.671**
	Middle	0.957**	0.888**	0.861**	0.949**	0.469**	0.879**	0.972**	0.656**	0.814**	− 0.164**	0.808**
	Bottom	0.938**	0.886**	0.842**	0.947**	0.537**	0.856**	0.960**	0.716**	0.879**	− 0.127	0.709**
SOM	Surface	0.600**	0.661**	0.591**	0.633**	0.328**	0.605**	0.650**	–	0.832**	0.205**	0.520**
	Middle	0.685**	0.639**	0.589**	0.706**	0.431**	0.592**	0.679**	–	0.708**	− 0.062**	0.543**
	Bottom	0.740**	0.756**	0.653**	0.736**	0.505**	0.702**	0.732**	–	0.730**	− 0.075	0.552**
TN	Surface	0.702**	0.746**	0.668**	0.703**	0.285**	0.687**	0.735**	–	–	0.170**	0.568**
	Middle	0.824**	0.737**	0.707**	0.825**	0.478**	0.816**	0.823**	–	–	− 0.158**	0.660**
	Bottom	0.887**	0.851**	0.829**	0.896**	0.553**	0.878**	0.888**	–	–	− 0.135	0.704**
TP	Surface	− 0.055	0.086	0.051	− 0.085	− 0.086	− 0.054	− 0.016	–	–	–	0.879
	Middle	− 0.071	− 0.064	0.071	− 0.061	− 0.081	− 0.135	− 0.097	–	–	–	− 0.079**
	Bottom	− 0.086	0.020	0.084	− 0.045	− 0.074	− 0.114	− 0.057	–	–	–	− 0.017
I	Surface	0.68**	0.638**	0.626**	0.632**	0.209**	0.611**	0.666**	–	–	–	–
	Middle	0.803**	0.773**	0.737**	0.796**	0.475**	0.764**	0.802**	–	–	–	–
	Bottom	0.749**	0.682**	0.664**	0.754**	0.456**	0.686**	0.735**	–	–	–	–

**Correlation is significant at the 0.01 level (two-tailed)

*Correlation is significant at the 0.05 level (two-tailed) the soil. This is the reason that oil industries fail to cause an obvious enrichment of mercury in the soil.

Suggestion

The security of ecological environment is of great importance in the light of the special status of oil and agricultural industries in China. Some measures could be taken to avert and control soil pollution as well as the health risk caused by heavy metals. First, regulating the land usage on the basis of environmental assessment, where the compromised land should be found out and converted to a more suitable type for the usage. Second, establishing the buffers between the oil field and farmland can completely eradicate the contamination from the activities of oil production activities which degrade the farm production. Last, strengthening the monitoring and conducting relevant remediation of polluted areas, especially in the past oil fields. Some attempts have been done adjacent to estuary in Hongliu oil field (Zheng et al. 2015), which was abandoned about a decade before and has become a restored wetlands, where the degradation due to pollution has also been found out.

Conclusion

The potential ecological risk is mainly from Cd based on the largest distribution area of considerable degree instead of Hg based on the widespread degree of pollution, which breaks the traditional concept that oil production may escalate mercury in the soil. The value of EF proves a higher enrichment of heavy metals in the surface soil induced by human activities than in the deep layers of soil. As has the strongest ability to move downward to lower layer, followed by Cd and Pb in YERD. The source of heavy metals dominantly stems from natural deposits and the concentration of heavy metals controlled by their association with minerals. The human influence only elevates the heavy metals of soil in some of the areas, but not in all the areas of YERD, and thus the petroleum industries could be treated as a considerable source to bring anthropogenic heavy metals into soils instead of agriculture. Only Cd, As and Pb instead of all heavy metals in the soils are significantly elevated and affected by oil production, where the degree of elevation of concentration is relatively small in YERD.

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