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ABSTRACT

This study investigated the dissolved trace metal contamination levels of Zn, Sr, B, Al, Ba, Fe, Mn, Li, V, Be, Cd, Cr, Cu, Mo, Ni, Se, and Pb in 23 surface waters of the Yellow River Delta (YRD) in China. Coefficients of variation with 66–260% reflected large spatial variations of concentrations of metals. Compared to drinking water guidelines established by the World Health Organization and the U.S. Environmental Protection Agency, the primary trace metal pollution components (Al, B, V, and Zn) were above drinking water standard levels by 82.6%, 47.8%, 52.2%, and 52.2%, respectively. Preliminary risk assessments were determined via the Hazard Quotient (HQ) to evaluate the human health risk of these metals. $HQ_{ingestion}$ of V indicated potential deleterious health effects for residents. Hierarchical cluster results revealed that clusters 1, 2, and 3 were primarily affected by pollution from industrial and domestic activities, natural and agriculture activities, and oil fields, respectively. Principal component analysis results indicated Fe, Mn, Al, and Ba were controlled by natural sources, whereas anthropogenic activities led to high pollution levels of Al, B, V, Zn, and Sr.

Key Words: trace metals, source, risk, surface water, Yellow River Delta, anthropogenic.

INTRODUCTION

Rapid industrial development in the last few decades has added huge loads of pollutants to rivers (Kaushik *et al*. 2009). Particularly important are the high

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concentrations of heavy metals, as these contaminants persist in the environment and their adverse effects are increased as a result of biomagnification. Heavy metals enter the aquatic environment mainly by direct discharges from industrial sources (Nriagu and Pacyna 1988). More than 90% of the heavy metals in aquatic systems were accumulated via several pathways (Luo *et al*. 2010), which are contributed by disposal of liquid effluents, terrestrial runoff, atmospheric deposition, and leachate from numerous urban, industrial, and agricultural activities. Such accumulation can be greater in enclosed and semi-enclosed areas where exchange of water with the open sea is limited (Karageorgis *et al*. 2002).

Distributions of dissolved trace metals in surface water can provide evidence of the effects of human activities on ecosystems and aid in assessing the risks associated with the discharge of human waste. Dissolved trace metals in aquatic systems can have adverse effects for human health and the organisms that make up the base of the food chain (Azevedo *et al*. 2009; Christophoridis *et al*. 2009). Also, surface water is a vital resource for local development and ecological sustainability, and recycling of heavy metal pollutants in stream water can lead to further risks to human health and aqueous ecosystems (Rai 2008). For example, soils that are exposed to a higher level of heavy metals due to wastewater irrigation can lead to accumulation of these pollutants in crops and transfer them to higher trophic levels (Green *et al*. 2010). Adverse effects such as deformities, cancer, and death of aquatic animals together with their terrestrial predators may also be induced (Coeurdassier *et al*. 2010; Volpe *et al*. 2009).

The Yellow River Delta (YRD) is a developing region in China and is also suffering from enormous environmental deterioration from industrialization. Extremely high sediment loads (>1000 million tones per year, Mt/yr) have been discharged to the sea over thousands of years as a result of poor agricultural practices in the loess region (Saito *et al*. 2001); however, sediment loading has decreased rapidly over the past 60 years in response to climate changes, dam construction, and soil-conservation practices in the river basin (Wang *et al*. 2006a). The high sediment loading from the river and transport by hyperpycnal flows into the estuary have made a considerable contribution to the deltaic depositional system (Wang *et al*. 2010). In the last decades, with the rapid economic development in Asian countries, environmental pollution caused by heavy metals has been identified in several delta areas, for example, the Mekong Delta (Cenci and Martin 2004), the Pearl River Delta (Ouyang *et al*. 2004), and the Yangtze River Delta (Yang *et al*. 2009). Most investigations of pollutants in the YRD have focused on hydrocarbon, nitrate, polychlorinated biphenyls (PCB_S), and polycyclic aromatic hydrocarbon pollutants (Chen *et al*. 2007; Li *et al*. 2006; Li *et al*. 2001b; Xing *et al*. 2005). Only a few reports of trace metal concentrations in the YRD are available, and most focus exclusively on sediments (Guo 2007; Li *et al*. 2001a; Wang *et al*. 2009b; Zhang *et al*. 1988). A comprehensive investigation of the distributions of dissolved trace metals in the YRD will be useful to determine the sources, associated ecological risks, and strategies for remediation of heavy metal pollutants.

The present study investigated concentrations and distributions of several trace metals (Zn, Sr, B, Al, Ba, Fe, Mn, Li, and V) dissolved in surface waters in the YRD. Multivariate statistical techniques were used to analyze the similarities or dissimilarities between sampling sites, to illustrate the relationship of heavy metal variables

responsible for spatial distributions, and to identify the influence of possible sources. These data will be valuable for water quality and public health assessments in the YRD during the current state of rapid socioeconomic development in this region.

METHODS AND MATERIALS

Description of Study Sites

The Yellow River is a sediment-filled river that flows from the Bayan Har Mountains to the Bohai Sea, where it builds and rebuilds the Yellow River Delta. Study sites were selected in the zone of the YRD, between 37° 26′–38° 10′ N and 118° 21′–119° 20′ E. Mean annual precipitation in the study area is 590 mm, mostly occurring from July to September, and mean annual air temperature is 11.9°C. The average maximum and minimum temperatures are 26°C in July and −4°C in January. The geographic location of sediment accumulation forming the YRD has shifted several times due to the complicated imbrication pattern of the lower river channel (Wang *et al*. 2006b). The modern Yellow River Delta, formed since 1855, caused by erosion and settling along the old channel hosts the delta's natural wetlands and is subject to environmental pollution due to an extensive field of oil and gas exploitation, as well as agricultural and industrial development in this region (Wang *et al*. 2009a).

Sampling and Analysis

Samples were collected in the end of the flood season, October 2010, from sites (Table 1) encompassing the entire Yellow River Delta region (n = 23), including old channels, irrigation ditches, surrounding cities and towns, nature reserves, and oil production sites (Figure 1). Surface water samples were collected manually at <1 m depth in the center of the river. The samples were immediately filtered through acid-treated millipore filters (0.45 μm mesh) into polyethylene terephthalate (PET) bottles in the field. The filtered samples were acidified to pH < 2 with ultra-purified 6M HNO_3 and then stored at 4°C until analysis in the laboratory.

Total concentrations of Zn, Sr, B, Al, Ba, Fe, Mn, Li, V, Be, Cd, Cr, Cu, Mo, Ni, Se, and Pb were analyzed using inductively coupled plasma-optical emission spectrometer (ICP-OES). Calibration curves were made after measurements of samples and data were evaluated by the determination of quality control standards. Reagents, procedural blanks, and samples were measured six times in parallel and we report the average of the last three values.

Data Treatment and Multivariate Statistical Methods

Kolmogorov-Smirnov statistics were used to assess the goodness of fit of log-normal distribution. Spearman rank-order correlations were used to study the correlations between the non-normal water quality parameters. Because most values of Be, Cd, Cr, Cu, Mo, Ni, Se, and Pb were small or less than the detection limits, Zn, Sr, B, Al, Ba, Fe, Mn, Li, and V were selected to analyze the distribution by multivariate statistical methods, and then identified the influence of possible sources. All the metals were used to evaluate the health risk. All mathematical and statistical computations were made using SPSS 17.0 for Windows.

Table 1. Sample sites information.

ID	Address	Coordinates	Types	Remarks
32	Northwest of Hekou district	37.94262 118.4693	Side stream	Waste land and no village around. Water flows from the Hekou district where many factories are located, such as oil production factory, printing factory, papermaking factory.
35	Yellow River NO.5 Pile in Hekou district	38.01687 118.9112	Side stream; coastal site	Waste land, no oil field around. It's 4000 m from the Shengli Oil Production Plant.
37	NO.3 old channel of Yellow River	38.05552 118.7232	Side stream; coastal site	Waste land. Phragmites communis and low red plants. No village.
39	NO.2 old channel of Yellow River	38.0503 118.7513	Side stream; coastal site	Waste land in the oil field. It's about 150 m near to oil wells.
41	NO.4 Team of oil field	38.01922 118.6762	Side stream	Waste land in the oil field. It's near the oil wells.
43	Gudong Town in Hekou district	37.88748 118.7275	Side stream	Farmland around. It's near the Gudong Town, but the river doesn't flow through this town.
45	The middle of Bonantiao River Bridge in Dongying City	37.89887 118.6008	Side stream	Farmland and grassland around. The concentration of suspended particles is high.
47	Old channel of Yellow River in the east of Xiaoshengmiao Village	37.70445 118.6205	Irrigation channel	Farmland and some villages around. Receives water from the main Yellow River. Slight eutrophication.
49	Old channel of Yellow River in Lijin County	37.78642 118.6367	Side stream	Farmland. Villages around.
52	Kaiyuan Bridge of Yellow River	37.73933 118.7623	Main stem river	Yellow River water.
53	East of Xianhe Town	37.9418 118.8653	Side stream	The center of the town. Surface water may be affected by factories and residents.
56	Oil field of Gudong Town in Dongying City	37.87988 119.043	Side stream; coastal site	Oil field in the waste land. Oil factories around.
58	NO.3 north of Yellow River in Kenli County	37.81143 119.0117	Main stem river	Wetland of National Reserve in Yellow River Delta.
59	Protected area in Kenli County	37.7865 119.044	Main stem river	Wetland of National Reserve in Yellow River Delta. Yellow River water. Main stem river.
61	NO.1 protected area of Yellow River mouth in Kenli County	37.76718 119.1596	Main stem river	Sea water mixed with surface water was sampled from the Yellow River mouth.
63	NO.2 protected area of Yellow River in Kenli County	37.77155 119.1086	Main stem river	Main stem river. Wetland of National Reserve in Yellow River Delta. Estuarine site.
66	West of Hexing Village in Kenli County	37.60135 118.6195	Side stream	Farmland and villages around. Water is from the Yellow River and flows through the north of Kenli county.

(Continued on next page)

Table 1. Sample sites information. *(Continued)*

ID	Address	Coordinates	Types	Remarks
70	Hongguang Village in Kenli County	37.52927 118.8414	Side stream	Dirty water around farmland and villages. Water flows from the center of Kenli county, where lots of factories are located, such as oil production and papermaking factories.
72	Zhimai River in the southeast of Dongying City	37.35207 118.7606	Side stream	No village. Wasteland and farmland around.
74	Xiying Village in Dongying City	37.48165 118.4968	Side stream	Site is in the center of Dongying district. Water is impacted by human activities.
75	Yellow River Bridge in Lijin County	37.48722 118.271	Main stem river	Yellow River water.
77	The middle of West Yongxin River Bridge in Xiwei Village, Lijin County	37.68447 118.457	Side stream	Beside the town, around the villages. Cotton and oil plants here.
79	Houjia Village of Hekou district in Dongying City	37.84187 118.4098	Side stream	Farmland and villages around. We don't find factories here.

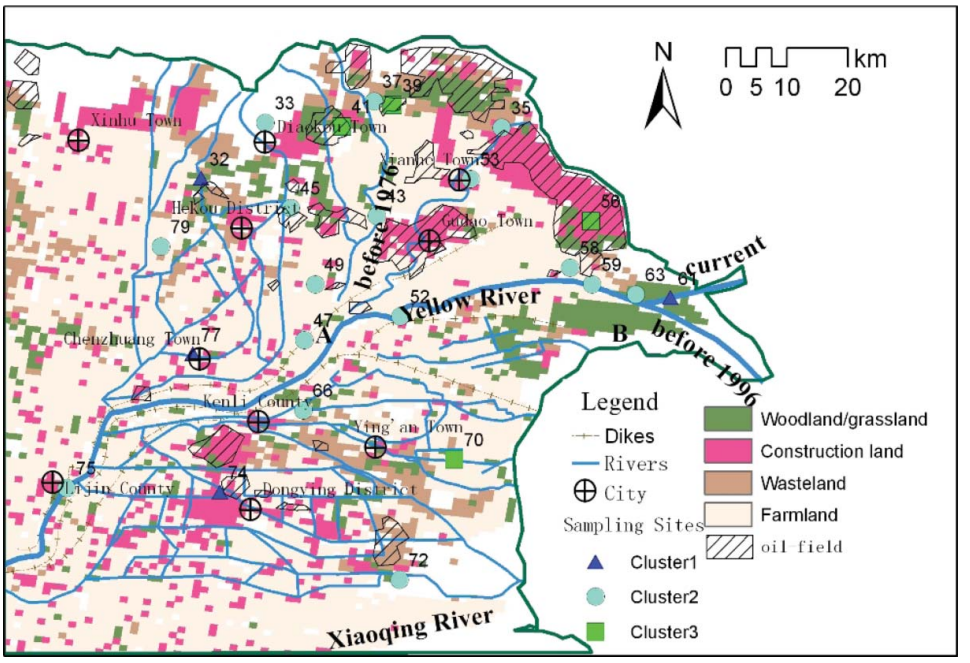

Figure 1. Sampling sites in the Yellow River Delta. (Color figure available online.)

Principal component analysis (PCA) was used to identify the possible trace metal sources. Kaiser-Meyer-Olkin (KMO) and Bartlett's tests (Shrestha and Kazama 2007) were performed to examine the suitability of the data for PCA. Results show that all the variables are log-normally distributed with higher confidence and suitable for PCA tests. In the present study, PCA was performed by the method of Varimax rotation with Kaiser Normalization.

We performed hierarchical methods, which form clusters sequentially, beginning with the most similar pair of objects and forming higher clusters step-by-step. These data produce a dendrogram that provides a visual summary of the clustering processes, depicting clustering groups with a dramatic reduction in dimensionality of the original data (Alkarkhi *et al*. 2008; Li and Zhang 2010; Pekey *et al*. 2004; Yalcin and Ilhan 2008). In the present study, hierarchical agglomerative cluster analysis (CA) was performed on the z-scale normalized variables by the average linkage method (Shrestha and Kazama 2007), using Squared Euclidean distances as a measure of similarity.

Risk Assessment

Humans' exposure to trace metals include ingestion and dermal absorption, which are the main routes of exposure in surface water environments (Wu *et al*. 2009). Considering these two pathways, hazard quotients (HQs) associated with corresponding metals were assessed via a risk assessment model. The exposure dose and HQs are calculated using Eqs. (1)–(3), adapted from the U.S. Environmental Protection Agency (USEPA) (De Miguel *et al*. 2007; Karim 2011; Wu *et al*. 2009):

$$\mathrm{D}_{\mathrm{ingestion}} = \frac{C_w \times IRW \times EF \times ED}{BW \times AT} \tag{1}$$

$$\mathrm{D}_{\mathrm{dermal}} = \frac{C_w \times SA \times K_p \times ABS \times ET \times EF \times ED \times CF}{BW \times AT} \tag{2}$$

$$\mathrm{HQs} = \mathrm{D}/\mathrm{RfD} \tag{3}$$

where D: exposure dose contacted through ingestion of water ($\mathrm{D}_{\mathrm{ingestion}}$) and dermal absorption ($\mathrm{D}_{\mathrm{dermal}}$), mg/kg/day; C_w: average concentration of trace metal in water, mg/L; *IRW*: drinking water ingestion rate, in this study, 2 L/day; *EF*: exposure frequency, in this study, 350 day/year; *ED*: exposure duration, in this study, 30 years; *BW*: average body weight, in this study, 70 kg; *AT*: averaging time, for non-carcinogens and carcinogens, 10,950 days; *SA*: exposed skin area, in this study, 2,800 cm^2; K_p: Dermal Permeability Constant, cm/hr, in this study, Co: 0.0004, Ni: 0.0002, Zn: 0.0006, other metals: 0.001; *ABS*: dermal absorption factor, 0.001; *ET*: exposure time, in this study, 0.6 h/day; *CF*: unit conversion factor, for water: 1 L/1,000 cm^3; RfD is the reference dose for different analytes, expressed in μg/kg/day (Table 3), which is based on U.S. risk-based assessments (USEPA 2006b).

RESULTS AND DISCUSSION

Descriptive Statistics

The distribution of dissolved trace metals, Al, B, Ba, Fe, Li, Mn, Sr, V, and Zn, within the YRD are summarized in Figure 2; and the mean, standard deviation, maximum, and minimum values for each trace metal are presented in Table 2. Mean trace metal concentrations in the surface water ranked in the following order: Zn > Sr > B > Al > Ba > Fe > Mn > Li > V. The mean concentrations of Sr and Zn were the largest in river water, and V, Mn, Li, Fe were consistently the lowest (Table 2). Coefficients of variation reported in Table 2 reflect the wide spatial variation of individual elements. In particular, Mn, V, Zn, and Al exhibit large spatial variation. For example, site 37 has a high Zn concentration (11.52 mg/L), but the neighboring site 39 has only 3.92 mg/L.

The Spearman rank-order correlation coefficient matrix of heavy metals in the YRD indicated that there were significant relationships among trace metals (Table 3). Li and Sr were significantly positively correlated, suggesting that Sr and Li had similar origins and transport pathways. There were strong positive correlations between B

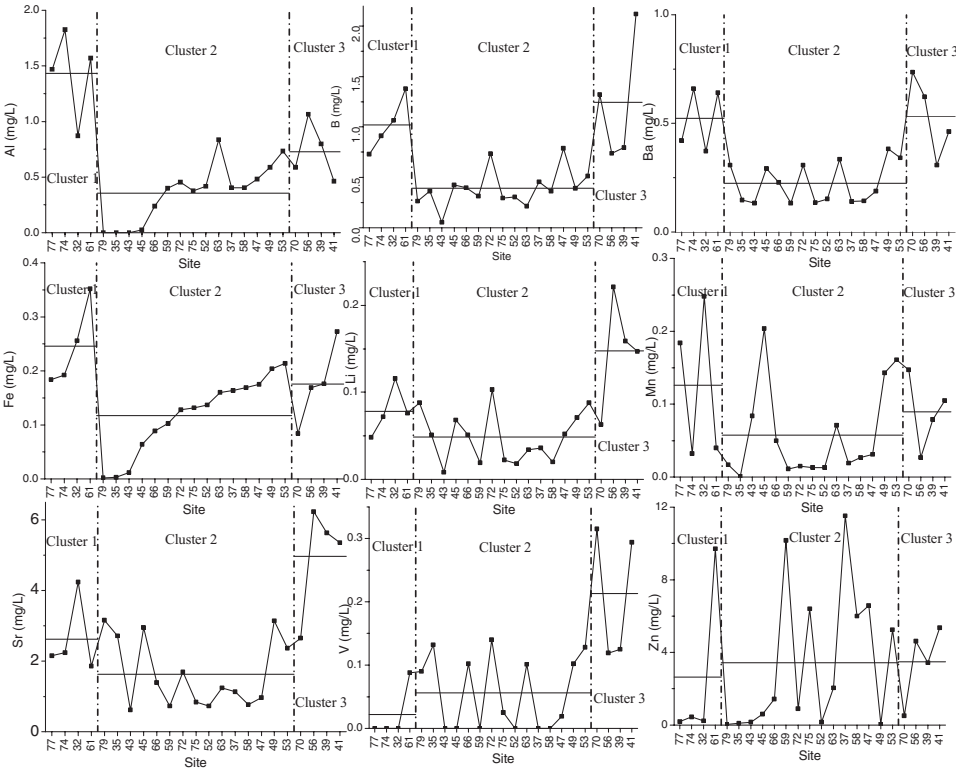

Figure 2. Spatial cluster analysis of heavy metals' concentrations (solid horizontal lines denote mean concentration for sites in cluster; vertical dotted lines divide sampling sites into three groups determined by cluster analysis of all metals; zero values represent non-detects).

Table 2. Descriptive statistics of heavy metals concentrations in the Yellow River Delta (mg/L).

Heavy metals	Minimum	Maximum	Mean	Coefficient of variation
Al	0.00	3.93	0.49	142.86%
B	0.05	2.92	0.62	83.87%
Ba	0.05	1.43	0.31	80.65%
Fe	0.00	0.66	0.12	100.00%
Li	0.01	0.22	0.06	83.33%
Mn	0.00	1.72	0.10	260.00%
Sr	0.51	6.23	2.25	66.22%
V	0.00	0.32	0.05	160.00%
Zn	0.03	11.52	2.33	145.06%

0.00 = less than the detection line limit.

and Ba, Fe, Li, and Sr; between Al and B, Ba, and Fe; between Ba and Fe, Sr and Li. V, and Li were also significantly positively correlated. Zn concentrations were not correlated with other trace metals.

Principal Component Analysis (PCA)

Results of the PCA performed on the trace metal data are reported in Table 4. The five principal components (PCs) explained 94.5% of the total variance within the sample set. The first PC accounted for 44.1% of the total variance, and was mostly determined by distributions of Al, Ba, and Fe with high value indicators, and, to a smaller degree, B. The second PC explained 19.7% of the total variance and was determined largely by Li and Sr. The third PC explained 13.6% of the total variance and was associated with distributions of B and V.

Hierarchical Cluster Analysis

In order to further evaluate the spatial variation of heavy metals, hierarchical cluster analysis (CA) was used to divide sampling sites into three different groups

Table 3. Spearman rank-order correlation coefficient matrix for selected heavy metals in the Yellow River Delta.

	Al	B	Ba	Fe	Li	Mn	Sr	V	Zn
Al	1								
B	0.64*	1							
Ba	0.77*	0.71*	1						
Fe	0.78*	0.62*	0.54*	1					
Li	0.45	0.69*	0.68*	0.43	1				
Mn	0.40	0.40	0.52	0.41	0.32	1			
Sr	0.33	0.54*	0.66*	0.28	0.87*	0.42	1		
V	0.07	0.32	0.41	0.00	0.54*	0.03	0.03	1	
Zn	0.15	0.25	−0.18	0.32	−0.04	−0.37	−0.20	−0.04	1

*Correlation is significant at the .01 level (2-tailed).

Table 4. Total variance explained (a) and component matrixes for trace metal contents (b).

(a) Component Initial Eigenvalues					
	Total	% of Variance	Cumulative%		
1	3.971	44.121	44.121		
2	1.774	19.717	63.838		
3	1.225	13.611	77.449		
4	0.777	8.639	86.088		
5	0.726	8.062	94.150		
(b) Component Matrix (Rotated)					
Variables	1	2	3	4	5
Al	**0.972**	0.105	−0.058	0.112	0.043
B	0.416	0.293	**0.681**	0.321	0.241
Ba	**0.748**	0.297	0.486	−0.173	0.091
Fe	**0.638**	0.156	0.093	**0.620**	0.292
Li	0.211	**0.937**	0.230	0.038	0.022
Mn	0.114	0.131	0.056	−0.165	**0.954**
Sr	0.113	**0.926**	0.253	−0.065	0.188
V	−0.041	0.277	**0.927**	−0.087	−0.023
Zn	0.005	−0.079	−0.028	**0.916**	−0.267

Extraction method: principal component analysis; bold characters are similar sources in factors.

to detect the similarity groups (Figure 3). Members of a cluster are considered to have similar features of heavy metals' contaminations and are likely to be influenced by similar land use practices, pollutant sources, and transport pathways. Cluster 1, consisting of sites 32, 77, 61, and 74, corresponds to relatively high Al, B, Ba, Fe, Mn, and low V (Figure 2). In cluster 1, sites 32, 77, and 74 are situated at the relative upstream sites and site 61 is in the sea estuary. Cluster 3, consisting of sites 39, 41, 56, and 70, corresponds to relatively high B, Ba, Li, Sr, and V (Figure 2). Almost all these stations are located along the coast and may be affected by seawater. The remaining 15 sites composed cluster 2 and exhibited relatively low average concentrations of heavy metals (Figure 2).

The dendrogram (Figure 3) generated by CA rendered spatial similarity of heavy metal concentrations in aggregation (Figure 2). Sites 32, 74, and 77 in cluster 1 are located northwest of the Hekou District, Xiying District, and Chenzhuang Town, respectively. These sites are all located near populous areas and numerous industrial plants (Table 1). They are significantly impacted by human activities and receive pollution mostly from domestic wastewater and industrial effluents located in city areas. However, site 61 (cluster 1), is located in the mouth of the Yellow River and is influenced by the high flow and suspended solids, and also affected by sediment resuspension (Liu *et al*. 2008). Although sites 37 (cluster 2), 39 (cluster 3), and 41 (cluster 3) are very close in proximity, results showed they exhibited significant differences in trace metal concentrations (Figure 2). Site 37 is located at the old channel of the Yellow River, and the river flow velocity is larger than at sites 39 and 41. The latter sites are located in oil extraction plants (Figure 1 and Table 1) and are

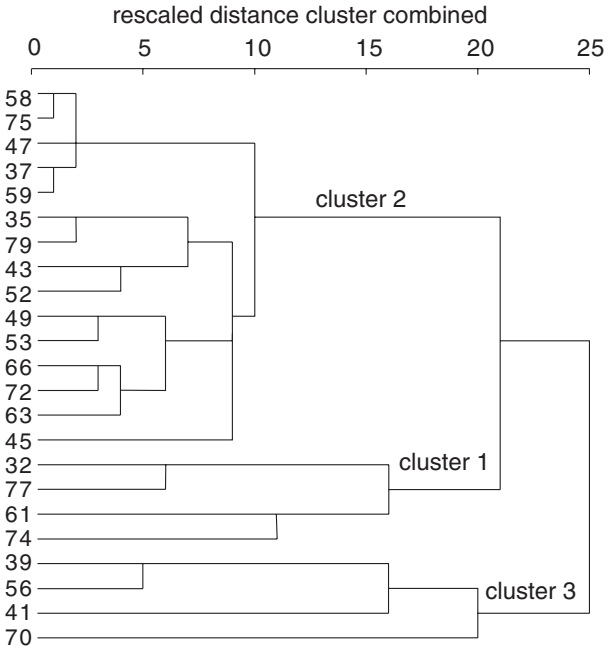

Figure 3. Dendrogram showing clustering of monitoring sites.

affected by pollution from extraction processes and industrial wastewater produced by oil extraction processes (Figure 1 and Table 1) (Han 2009). Site 56 in cluster 3 is also located near an oil field in Gudong Town in Dongying City. Site 70, located in the lower Yongfeng River, Kenli County, is impacted by upstream factories and residents (Table 1), which was influenced by anthropogenic activities. Most sites in cluster 2 are located in farmland and wasteland (Figure 1) and the concentrations of heavy metals may receive pollution from non-point sources (*i.e.*, agricultural activities and orchard plantations), point sources from the upper stream, and natural processes (*i.e.*, weathering) (Lee *et al*. 2010; Li and Zhang 2010).

Risk Assessment

Concentrations of many trace metals in surface waters of the YRD are above the drinking water quality guidelines established by the World Health Organization (WHO 2006) and the U.S. Environmental Protection Agency (USEPA 2006a). The primary components of trace metal pollution are Al, B, V, and Zn, and the average concentrations of each are greater than the standard levels by 82.6%, 47.8%, 52.2%, and 52.2%, respectively. Cd, Cr, Cu, Pb, Co, and Se are seen as the priority toxic pollutants for aquatic life and exceeded protection guidelines established by the USEPA by 4.3%, 0, 0, 21.7%, 8.7%, and 13%, respectively. Pb concentrations in five sites exhibited greater than drinking water standard levels, as was the case for one site for Cd and Ni, two sites for Co, and three sites for Se. The higher concentrations of Cd, Pb, Co, and Se occur presumably at sites 41 and 70, likely due to oil exploration, use of fertilizers and pesticides, metal smelting and refining, manufacturing

processes, automobile exhausts, waste incineration, and other industrial activities in these anthropogenic areas.

The HQs of trace metals for local residents through oral and dermal routes are summarized in Table 5. HQs > 1 suggest that the water could possibly have deleterious effects on the residents' health (Karim 2011). In this study, the HQ_{dermal} values were found less than unity, which indicates that the dermal adsorption of trace metals may have little or no health threat. Most of the $HQ_{ingestion}$ values were smaller than unity, which indicate these trace metals could pose little or no risks to local residents (Wu *et al*. 2009). However, $HQ_{ingestion}$ of V in clusters 2 and 3 were 1.5 and 5.8 (Table 5), suggesting V could have deleterious health effects concerns for the local residents at the sites represented in these clusters. The oxide and some other salts of vanadium have moderate toxicity (Hosokawa and Yoshida 1989). Although vanadium compounds are poorly absorbed through the gastrointestinal system, high doses of V by oral ingestion may alter blood conditions, or cause liver or kidney damage (Hosokawa and Yoshida 1989). In addition, Han (2009) reported Zn, Sr, Cu, Pb, Hg, Ce, Ti, and hexavalent Cr are the main heavy metal components in water bodies near oil fields in the YRD. $HQ_{ingestion}$ of Cd and Co at site 70 were 1.15 and 1.92, respectively, suggesting that Cd and Co may be among the serious health concerns for residents in this area. $HQ_{ingestion}$ of Zn at sites 59, 61, and 75 along the Yellow River Channel ranged from 0.58 to 0.93, and the value for Pd at site 41 was 0.82, suggesting these elements also could pose a mild hazard to local residents.

Source Identification

Generally, Ba and Mn in surface waters primarily derive from natural sources of weathering and subsequent pedogenesis (Krishna *et al*. 2009; Li and Zhang 2010); while Al and Fe mainly originate from Earth's crust (Pekey *et al*. 2004). In this study, distributions of these elements dominated the variability captured by the first and fifth PCs; therefore, these PCs predominantly originate from natural processes (*i.e.*, pedogenic process and mineral weathering). Concentration patterns of Al, Fe, and Ba exhibit substantial spatial differences, however (Figure 2). For example, high concentrations of Ba, Fe, and Al in sites 32, 74, and 77 are predominantly affected by the anthropogenic factors in the upper stream (Table 1); whereas, the observation of remaining sites may reflect the integration of strong geochemical correlations in crustal contribution, petroleum mines and other anthropogenic additions.

High values of Li and Sr in the second PC and of the strong Spearman rank-order correlation between Li and Sr indicate similar source and transport pathways for these elements. Natural Sr is usually stored in the minerals celestine and strontianite in the crust (Obut 2007). Crude oil also contains Sr, Ba, and other elements (Duyck *et al*. 2002). Li is also found widely in many rocks and some brine on Earth, but it is a comparatively rare element and generally very low in concentration (Krebs 2006). However, oilfield brines exhibit significant enrichment of Sr and Li (Chan *et al*. 2002). Li concentration is high (from 0.147 to 0.221 mg/L at sites 39, 41, and 56) in oil fields and very low (from 0.019 to 0.034 mg/L at sites 58, 59, 63, 75, and 52) in the main Yellow River channel. Sr exhibits a similar spatial variation, from 5.355 to 6.228 mg/L at sites 39, 41, and 56 in the oil field, and comparatively low concentrations in the main Yellow River channel. These observations explain three

Table 5. Reference dose and hazard quotient for each element.

Element	$RfD_{ingestion}$ (μg/kg/day)	RfD_{dermal} (μg/kg/day)	$HQ_{ingestion}$				HQ_{dermal}				$\sum HQ_s$ = (a) + (b)
			Average of sites (a)	Cluster1	Cluster2	Cluster3	Average of sites (b)	Cluster1	Cluster2	Cluster3	
Al	1.0E+03	1.0E+02	1.7E-02	3.9E-02	9.8E-03	2.0E-02	1.4E-07	3.3E-07	8.2E-08	1.7E-07	1.7E-02
B	2.0E+02	1.8E+02	8.9E-02	1.4E-01	5.4E-02	1.7E-01	1.5E-05	1.3E-07	5.0E-08	1.6E-07	8.9E-02
Ba	7.0E+01	1.4E+01	1.3E-01	2.0E-01	8.8E-02	2.1E-01	7.6E-06	8.6E-07	3.7E-07	8.7E-07	1.3E-01
Fe	3.0E+02	4.5E+01	1.4E-02	2.2E-02	1.1E-02	1.6E-02	3.4E-06	1.3E-07	6.0E-08	9.0E-08	1.4E-02
Li	2.0E+01	1.0E+01	9.7E-02	1.1E-01	6.7E-02	2.0E-01	1.6E-06	1.8E-07	1.1E-07	3.4E-07	9.7E-02
Mn	2.0E+01	8.0E-01	1.0E-01	1.7E-01	7.9E-02	1.2E-01	1.7E-06	3.6E-06	1.6E-06	2.6E-06	1.0E-01
Sr	6.0E+02	1.2E+02	1.1E-01	1.2E-01	7.4E-02	2.3E-01	5.5E-05	5.0E-07	3.1E-07	9.5E-07	1.1E-01
V	1.0 E+00	1.0E-02	*2.1E+00	6.0E-01	*1.5E+00	*5.8E+00	1.8E-06	5.1E-05	1.3E-04	4.9E-04	*2.1E+00
Zn	3.0E+02	6.0E+01	3.0E-01	2.4E-01	3.1E-01	3.2E-01	4.6E-05	6.1E-07	7.9E-07	8.0E-07	3.0E-01
Mo	5.0 E+00	1.9E+00	2.3E-02	0	3.5E-02	1.4E-03	9.8E-08	0	7.8E-08	3.0E-09	2.3E-02
Ni	2.0E+01	5.4 E+00	3.8E-03	6.8E-03	1.6E-03	9.2E-03	1.3E-08	4.3E-09	9.7E-10	5.8E-09	3.8E-03
Pb	1.4 E+00	4.2E-01	1.1E-01	2.2E-01	2.7E-02	3.1E-01	1.3E-08	6.0E-08	7.7E-09	8.6E-08	1.1E-01
Se	5.0 E+00	2.2 E+00	2.1E-02	0	2.3E-02	3.4E-02	8.8E-08	0	4.4E-08	6.5E-08	2.1E-02
Cd	5.0E-01	5.0E-03	7.1E-02	5.5E-02	1.8E-02	2.9E-01	3.0E-08	4.6E-06	1.5E-06	2.4E-05	7.1E-02
Co	3.0E-01	3.0E-04	1.4E-01	2.7E-01	6.1E-03	5.0E-01	1.4E-08	9.2E-05	2.0E-06	1.7E-04	1.4E-01
Cr	3.0 E+00	1.5E-02	8.3E-03	0	0	4.8E-02	2.1E-08	0	0	8.1E-06	8.3E-03
Cu	4.0E+01	1.2E+01	2.4E-03	7.5E-03	7.8E-04	3.6E-03	8.2E-08	2.1E-08	2.2E-09	1.0E-08	2.4E-03

*HQ values >1.

sites are affected by an oil field in the second PC; the five sites with low background concentrations (Krebs 2006) in the main Yellow River Channel are affected by natural factors, and the remaining sites are affected by anthropogenic and natural factors (Li and Zhang 2010).

B is a low abundance element in the earth crust, but water-soluble boride on Earth, such as borax and kernite, is concentrated by natural processes. B could be enriched in oil field brines (Tan *et al*. 2011). However, substantial spatial differences of B (Figure 2 and Table 1) are indicative of anthropogenic signatures, that is, agrochemical industries and insecticides containing boric acid (Ghassempour *et al*. 2002). High concentrations of B and V in sites 39, 41, and 56 are affected by the oil field (Table 1), and the high B concentrations in sites 77, 74, 32, 61, and 70 are associated with factories, agrochemical process from the upper stream (Table 1). V is greatly impacted by anthropogenic activities, such as mining and agricultural processes (Li *et al*. 2008). Therefore, the third PC may be determined by natural and agrochemical process (Yalcin and Ilhan 2008).

The correlation coefficients of Zn reveal that Zn is not related to other chemical elements, suggesting that the origin and transport pathways of Zn are different from other trace metals. In the coastal environment, Zn is generally shown to accumulate to highest levels (Lee *et al*. 2010) through biological activities (Alkarkhi *et al*. 2008) and accumulation of allochthonous Zn in the coastal environment (Lee *et al*. 2010). However, we observed large spatial variations in Zn concentrations in this study. Concentrations were high along the mainstream of the Yellow River (sites 75, 47, 58, 59, and 61 are 6.40, 6.59, 6.00, 10.17, 9.70, and 8.61 mg/L, respectively). These data suggest that Zn in the YRD mainly originates from the upper stream region and likely from anthropogenic activity (Han 2009) (*i.e.*, industrial activities). Concentrations of Zn at the sites 39, 41, and 56 are 3.43, 5.35, and 4.62 mg/L in the oil field and Zn in these sites could be affected by oil extraction. The remaining sites with relatively low concentrations of Zn mostly located in the farmland and wasteland were observed similarly with the Han's results (2009) and these sites may be affected by anthropogenic and natural factors.

CONCLUSIONS

Based on the results of dissolved trace metal contaminations as well as multivariate statistical techniques for identifying the relative contribution of trace metals, it concluded that (1) Large spatial variations of metals' concentrations were associated with natural and anthropogenic factors. Anthropogenic activities led to a high pollution of Al, B, V, Zn, and Sr, and the potential pollutants of Ba, Cr, Hg, Se, and Pb. Pedogenic process and mineral weathering affected the concentrations of Fe, Mn, Al, and Ba. (2) Oil extraction directly influenced the trace metals of the surface water in the oil field. (3) Special attention should be paid to Al, B, V, and Zn that were above standard levels of drinking water guidelines. Zn pollution is more serious than other heavy metals in the main Yellow River channel. (4) $HQ_{ingestion}$ value of V indicated potential deleterious health effects for residents. Preliminary risk assessments also showed Cd, Co, and Pb presented high HQ values.

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