Influence of coastal groundwater salinization on the distribution and risks of heavy metals

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HIGHLIGHTS

- Southwestern coastal plains of study area showed significant groundwater salinization.
- About 13.27% of sampling sites showed moderate or more serious heavy metal pollution.
- Heavy metals in groundwater exerted low ecological risks.
- Heavy metals in groundwater exerted high cancer risks for adults and children.
- Salinization of coastal groundwater caused the increase in pollution and risks.

GRAPHICAL ABSTRACT
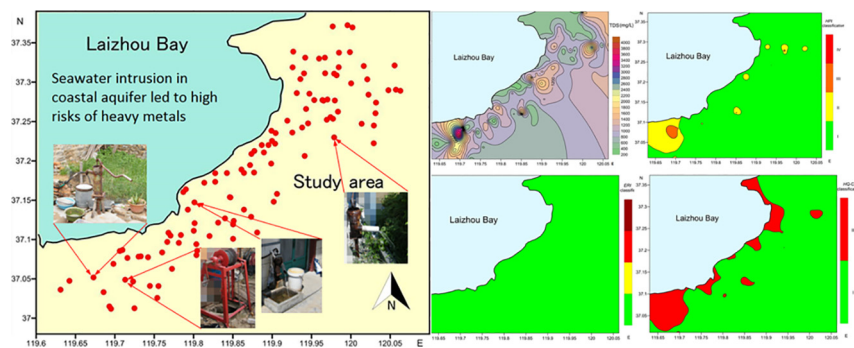
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ABSTRACT

Coastal groundwater quality significantly affects the regional sustainable development, due to the water resource shortage in coastal zone. Current studies on coastal groundwater have mainly focused on saline water intrusion and over-extraction. Information on the heavy metal pollution of coastal groundwater with salinization trend is limited. This study investigated heavy metals in groundwater from a typical coastal region with intensive anthropogenic activities and saline water intrusion. The southwestern coastal plains of the study area showed significant groundwater salinization trend. Heavy metals in the coastal groundwater mainly originated from anthropogenic activities and groundwater salinization according to principal component analysis. Relative high concentrations of As, Co, Cr, Cu, Fe, Mn, and Ni occurred in the southwestern coast of the study area with high TDS level, indicating that the concentrations of these heavy metals in shallow aquifer of the study area might be influenced by the groundwater salinization. Average concentrations of heavy metals in groundwater of the study area ranged from 0.03 (Cd) to 686.92 (Fe) μg/L. Fe was the dominant heavy metal in groundwater with the maximal concentration of 2333.76 μg/L and exceeding-standard rate reaching 98.23%. Approximately 13.27% of sampling sites showed moderate or higher heavy metal pollution of groundwater based on heavy metal pollution index. Heavy metals in groundwater exerted low ecological risks. Elements Fe, Ni, and As were the main contributors for ecological risks. Cancer risks of heavy metals for both adults and children were high at all sampling sites. Non-cancer risks for adults and children were unacceptable at 4.42% and 17.70% of sampling sites, respectively. The

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salinization of the coastal groundwater could also lead to the increase in the ecological and health risks of heavy metals in coastal groundwater. These findings provide initial and important information on heavy metals pollution in coastal aquifer with saline water intrusion.

1. Introduction

Groundwater is an important type of water resource to play a critical role in the regional development (Béjar-Pizarro et al., 2017; Gholami et al., 2015; Li et al., 2018), especially in areas with limited water resource including coastal regions, arid regions, and megacities (Sefelnasr et al., 2015; Vandenbohede et al., 2009; Zhu et al., 2015). Half of the global megacities are estimated to depend on the groundwater resources for development (Bricker et al., 2017). Groundwater is also important drinking/domestic water resource in many countries and regions (Béjar-Pizarro et al., 2017; Eschauzier et al., 2013; Fram and Belitz, 2011). Groundwater has attracted wide attention due to various problems caused by over-extraction such as land subsidence (Zhu et al., 2015) and seawater/salt-water intrusion (Tam et al., 2014) as well as groundwater quality deterioration such as salinization (Du et al., 2015; Han et al., 2014) and pollution (Santucci et al., 2018; Wen et al., 2018; Wu et al., 2018a).

Groundwater pollution is caused by various substances including nitrogen and phosphorous chemicals (Ağca et al., 2014; Wen et al., 2018; Wu et al., 2018a), heavy metals (Ağca et al., 2014; Chaturvedi et al., 2018), organic pollutants (Eschauzier et al., 2013; Fram and Belitz, 2011; Szekeres et al., 2018), and microbial contaminants (Szekeres et al., 2018). Heavy metals, frequently-detected pollutants in various environmental matrices, attract wide attention due to toxicity, persistence, bioaccumulation, and potential risks to the ecosystems and humans (Burges et al., 2015; Wu et al., 2018b). Therefore, heavy metals in groundwater are a study hotspot (Ağca et al., 2014; Chaturvedi et al., 2018).

Coastal regions usually carry a lot of population to increase water resource demand (Han et al., 2014). Coastal bays are a kind of important geological unit, especially in north China. However, current studies on groundwater from coastal bays of north China focus on salinization and evolution (Du et al., 2015; Han et al., 2014) as well as submarine groundwater discharge (Zhang et al., 2016). Rare information is available on heavy metal pollution of coastal groundwater with salinization trend. The saline water intrusion could change the physical-chemical characteristics of soil, which could subsequently have great influence on the solid-water interface behaviors of heavy metals (Stumm, 1992). Therefore, this study performed field sampling, laboratory analysis, pollution determination, and risk assessment to explore heavy metal pollution and potential ecological-health risks of groundwater in a coastal region with saline water intrusion, severe water shortage and intensive anthropogenic activities. The final aim is to provide initial information on heavy metals pollution in coastal aquifer with saline water intrusion.

2. Materials and methods

2.1. Study area, sampling strategy, and chemical analysis

Laizhou Bay, a typical coastal bay located in the northern Shandong Peninsula of China, is one of three bays in the Bohai Sea. Due to extremely intensive anthropogenic activities and groundwater over-extraction, seawater intrusion in the coastal aquifer of Laizhou Bay coastal area has become the most serious in China (Wen et al., 2018). Laizhou Bay is critical to the sustainable development in coastal regions of Shandong and thus obtains wide investigations (Du et al., 2015; Han et al., 2014). Therefore, this study selected southern Laizhou Bay and shallow groundwater samples were collected from total 113 wells (Fig. 1). The population of the study area was approximately 5 million in 2017 with percentage of non-agricultural population <15% according to Shandong Statistical Yearbook. The study area covers gentle hills,
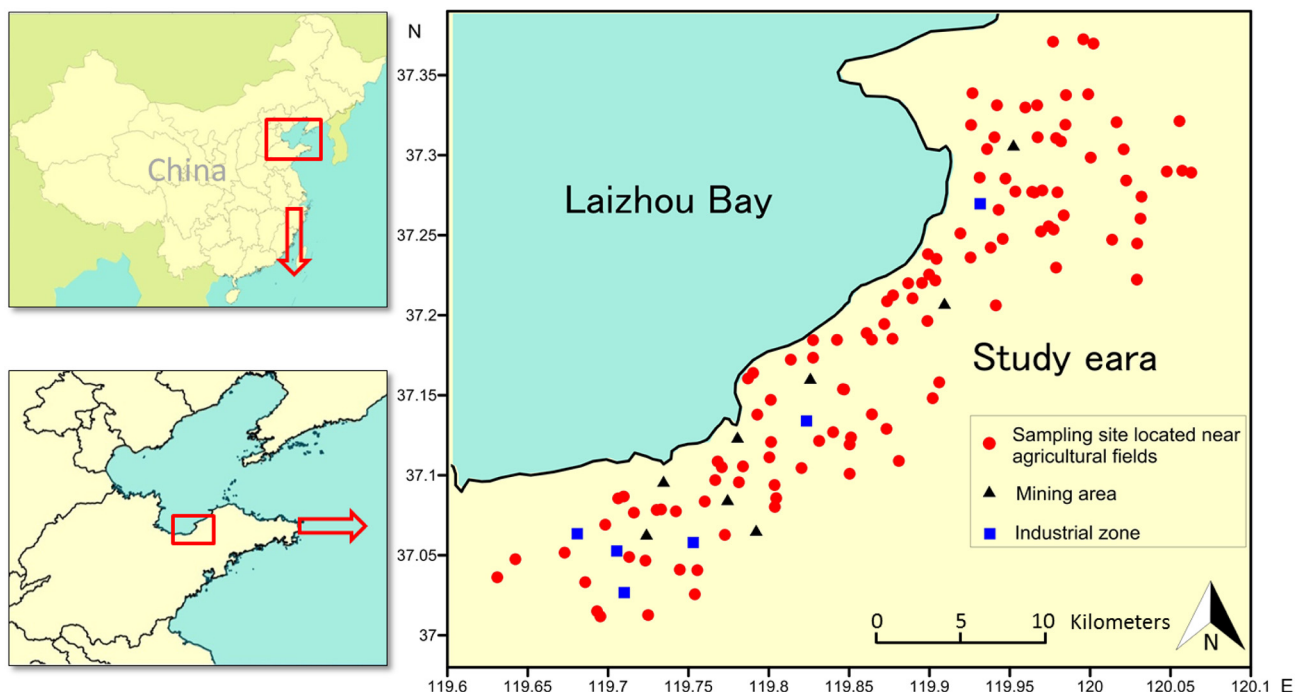

Fig. 1. Study area and the sampling sites of the southern Laizhou Bay. Agricultural fields are located in the surroundings of sampling sites.

sloping plains, saline-alkali depressions, coastal estuaries, and tidal flats. Lots of villages randomly distribute on the study area so that the quality-centralized water supply is not available for 60% of residents in the study area. Mining in the study area has been extensively performed for decades. Agriculture is another major anthropogenic activity in the study area so that fertilizers and pesticides are also widely used in this area. Recently, industry is also in development in the study area. Sampling was performed from May to October 2013. All wells, located at the yards of the residents to collect shallow groundwater, provided daily drinking water as well as shower water for them. The water quality was not further controlled. The depth of shallow aquifers that were mainly made up of fine sands, medium-fine sands, and sand loams ranged from 2 to 30 m (Fig. S1). Each groundwater sample with 500-mL volume was stored in a pre-cleaned armor glass bottle and transported back to the laboratory as soon as possible. The groundwater samples were filtered through 0.45 μm membrane filters (Pall Life Sciences, Ann Arbor, MI, USA) and stored at 4 °C until analysis.

Total dissolved solids (TDS), pH, and electrical conductivity (EC) of each groundwater sample were *in situ* monitored using an Ultrameter II™ 6P (Myron L Company, USA). Concentrations of 10 typical heavy metals in groundwater samples including arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn) were determined by an ELAN DRC II inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer Ltd., MA, USA). Limits of detection (LOD) and limits of quantity (LOQ) of target heavy metals in coastal groundwater were shown in Table S1. Method blank (Millipore ultrapure water), spiked blank (Millipore ultrapure water spiked by mixture solution of target heavy metals), and spiked sample (one real groundwater sample spiked by mixture solution of target heavy metals) were analyzed in duplicate for every 10 real groundwater samples to assure quality control of analysis. Recoveries of target heavy metals were in the range of 89.5%–107.2% for spiked blanks and in the range of 87.6%–109.6% for spiked samples.

2.2. Heavy metal pollution of groundwater

Three methods including heavy metal pollution index (HPI), the Nemerow index (NI), and contamination degree (CD) were employed to determine groundwater heavy metal pollution of southern Laizhou Bay. The most serious evaluation results would be used to exhibit the final pollution status based on the worst scenario.

HPI was calculated by the following equation (Qu et al., 2018):

$$HPI = \frac{\sum_{i=1}^{n} \left(\frac{MC_i}{SC_i} \times 100 \right) \times \left(\frac{1}{SC_i} \right)}{\sum_{i=1}^{n} \frac{1}{SC_i}}$$

where SC_i and MC_i refer to assessment standard concentration (μg/L) and the measured concentration (μg/L) of the target heavy metal in groundwater; n represents the numbers of target heavy metals. SC_i value of target heavy metal was set as Class III concentration threshold of "Standard for groundwater quality (GB/T 14848-2017)". Pollution ranking criteria of HPI referred to Table 1.

The following equation showed how NI was calculated (Liu et al., 2015a; Vu et al., 2017):

$$NI = \sqrt{\frac{\left(\frac{MC_i}{SC_i} \right)^2_{mean} + \left(\frac{MC_i}{SC_i} \right)^2_{max}}{2}}$$

where $\left(\frac{MC_i}{SC_i} \right)_{max}$ and $\left(\frac{MC_i}{SC_i} \right)_{mean}$ refer to the maximal value and average value of $\left(\frac{MC_i}{SC_i} \right)$ among all target heavy metals. Pollution evaluation criteria based on NI referred to Table 1.

CD was calculated according to the following equation (Sharifi et al., 2016):

$$CD = \sum_{i=1}^{n} \frac{MC_i}{SC_i}$$

Table 1 also provided the pollution evaluation criterion of CD.

2.3. Ecological risks of heavy metals in groundwater

Ecological risk index (ERI) model was employed to evaluate the potential ecological risks posed by heavy metals in groundwater of the study area (Sharifi et al., 2016):

$$ERI = \sum_{i=1}^{n} T_i \times \frac{MC_i}{SC_i}$$

where T_i is the biological toxicity factor of a target heavy metal. The values of T_i for all target heavy metals were selected from the literatures

Table 1
Ranking criteria of pollution, ecological risk, and cancer risk.

Method	Pollution or risk level	Classification	Value	References
Heavy metal pollution index (HPI)	Low pollution	I	$HPI < 15$	Edet and Offiong, 2002; Qu et al., 2018
	Moderate pollution	II	$15 \leq HPI \leq 30$	
	Moderate-to-heavy pollution	III	$30 < HPI \leq 100$	
	Heavy pollution	IV	$HPI > 100$	
Nemerow index (NI)	Insignificant pollution	I	$NI < 1$	Liu et al., 2015a; Vu et al., 2017
	Slight pollution	II	$1 \leq NI < 2.5$	
	Moderate pollution	III	$2.5 \leq NI < 7$	
	Heavy pollution	IV	$NI \geq 7$	
Contamination degree (CD)	Low pollution	I	$CD < 6$	Sharifi et al., 2016
	Moderate pollution	II	$6 \leq CD < 12$	
	Considerable pollution	III	$12 \leq CD < 24$	
	Very heavy pollution	IV	$CD \geq 24$	
Ecological risk index (ERI)	Low risk	I	$ERI < 110$	Sharifi et al., 2016
	Moderate risk	II	$110 \leq ERI < 200$	
	Considerable risk	III	$200 \leq ERI < 400$	
	Very high risk	IV	$ERI \geq 400$	
Cancer risk (CR)	Very low risk	I	$CR \leq 1 \times 10^{-6}$	Ge et al., 2013
	Low risk	II	$1 \times 10^{-6} < CR \leq 1 \times 10^{-4}$	
	Moderate risk	III	$1 \times 10^{-4} < CR \leq 1 \times 10^{-3}$	
	High risk	IV	$1 \times 10^{-3} < CR \leq 0.1$	
	Very high risk	V	$CR > 0.1$	

(Hakanson, 1980; Sharifi et al., 2016). Ecological risk levels were determined based on the ranking criteria (Table 1).

2.4. Health risks of heavy metals in groundwater

Heavy metals in groundwater exert health risks through ingestion (drinking water) and dermal contact (such as shower). The health risks are evaluated using cancer risks (CR) and hazard quotients (HQ).

Health risks through ingestion pathway posed by heavy metals in groundwater of the study area were calculated by the following equations (Liu et al., 2015b; USEPA, 2016):

$$CR_{ingestion}(individual) = \frac{MC_i \times DR \times EF_i \times ED_i}{BW \times AT} \times SF$$

$$HQ_{ingestion}(individual) = \frac{MC_i \times DR \times EF_i \times ED_i}{BW \times AT \times RfD}$$

$$CR_{ingestion} = \sum CR_{ingestion}(individual)$$

$$HQ_{ingestion} = \sum HQ_{ingestion}(individual)$$

where DR means water consumption rate; EF_i means ingestion exposure frequency; ED_i refers to ingestion exposure duration; BW refers to body weight; AT means average lifespan; SF refers to cancer slope factor; RfD refers to the reference dose of the chemical through oral exposure route. The values of SF and RfD could be obtained from the USEPA guidelines (USEPA, 2016). The values of other parameters referred to Wu et al. (2016). The values of parameters were briefly shown in Table S2.

Health risks through dermal contact were calculated by the following equations (USEPA, 2004):

$$CR_{dermal}(individual) = K_P \times MC_i \times t_{event} \times \frac{EV \times ED_d \times EF_d \times SA}{BW \times AT} \times \frac{SF}{GIABS}$$

$$HQ_{dermal}(individual) = K_P \times MC_i \times t_{event} \times \frac{EV \times ED_d \times EF_d \times SA}{BW \times AT} \times \frac{1}{RfD \times GIABS}$$

$$CR_{dermal} = \sum CR_{dermal}(individual)$$

$$HQ_{dermal} = \sum HQ_{dermal}(individual)$$

where K_P refers to dermal permeability coefficient of pollutant; t_{event} represents event duration; ED_d, EV, and EF_d represent dermal contact exposure duration, the event frequency, and dermal contact exposure frequency, respectively; GIABS is the fraction of chemical absorbed in gastrointestinal tract; SA refers to skin surface area. The values of parameters were obtained from the references and shown in Table S2 (Akhbarizadeh et al., 2016; IRIS, 2018; Ranjbar Jafarabadi et al., 2017; Sarria-Villa et al., 2016; USEPA, 2004; USEPA, 2016).

Health risks posed by heavy metals in groundwater were calculated by the following equations:

$$CR = CR_{ingestion} + CR_{dermal}$$

$$HQ = HQ_{ingestion} + HQ_{dermal}$$

Cancer risk ranking criteria were listed by Table 1. Inadmissible non-cancer risk threshold was set to 1 (Qu et al., 2018).

2.5. Data processing

All data of concentrations, pollution, ecological risks, and health risks were processed using Surfer 11 (Golden Software LLC, Colorado, USA) to obtain the corresponding distribution/contour maps. The relationship among TDS, pH, and heavy metals in groundwater was determined using the Pearson correlation coefficients calculated by SPSS 19.0 (IBM, New York, USA). Principal component analysis (PCA) was also performed by SPSS 19.0.

3. Results and discussion

3.1. Distribution of pH, TDS, and heavy metals in the coastal groundwater

Distribution of pH and TDS was shown in Fig. 2. Except 6 wells with pH ranging from 6.80 to 6.96, groundwater of the remaining sites exhibited neutral to alkaline with pH varying from 7.00 to 8.63 (Table S3). In general, pH of groundwater showed site-specific feature that weak acidic groundwater mainly existed in the southwestern part of the study area. Interestingly, TDS concentrations of groundwater in this area were the highest in contrast to those in the rest of regions (Fig. 2). Concentrations of TDS ranged from 246.79 to 3858.02 mg/L with the average value of 972.27 mg/L (Table S3). Groundwater type at approximately 59.29% of sampling sites was fresh water (TDS < 1000 mg/L) according to classification criterion (Liu et al., 2017) and groundwater quality at these sites was classified into Class III representing that groundwater was suitable for drinking based on "Standard for groundwater quality (GB/T 14848-2017)". In contrast, groundwater type at approximately 38.94% of sampling sites was brackish water (1000 < TDS ≤ 3000 mg/L) while that at about 1.77% of sampling sites with shallow aquifer depth of 2–8 m was saline water (3000 < TDS ≤ 50,000 mg/L). Based on the ranking criteria of "Standard for groundwater quality (GB/T 14848-2017)", groundwater quality at about 35.40% and 5.31% of sampling sites was classified into Class IV (1000 < TDS ≤ 2000 mg/L) representing that groundwater was suitable for drinking after treatment and Class V (TDS > 2000 mg/L) representing that groundwater was not suitable for drinking. The southwestern coastal plains of the study area showed significant groundwater salinization trend, similar to the previous reports (Du et al., 2015; Han et al., 2014). EC values ranged from 490.00 to 6332.00 µS/cm with the average value of 1673.06 µS/cm (Fig. S2 and Table S3). Distribution of groundwater EC exhibited the similar variation patterns of TDS.

Concentrations of heavy metals in groundwater of the southern Laizhou Bay ranged from BDL (below detection limit, As at 1 site, Cd at 2 sites, and Cr at two sites) to 2333.76 (Fe) µg/L with the mean values varying from 0.03 (Cd) to 686.92 (Fe) µg/L (Fig. 2 and Table S3). The maximal and average concentrations of As/Cd/Cr in groundwater were 7.63/0.26/37.43 and 1.56/0.03/6.27 µg/L, respectively (Table S3). Concentrations of As, Cd, and Cr were all below the corresponding Class III thresholds of "Standard for groundwater quality (GB/T 14848-2017)". Concentrations of Pb and Co were in the range of 0.06–14.52 and 0.12–3.41 µg/L with the similar average values of 0.65 and 0.52 µg/L, respectively, all below the Class III thresholds (Table S3). Concentrations of Ni ranged from 2.05 to 32.12 µg/L while those of Zn were in the range of 0.35–195.30 µg/L (Table S3). The average concentrations of Ni and Zn were 8.03 and 17.16 µg/L, respectively. Cu and Mn showed the similar concentration distribution that the concentrations were in the ranges of 0.22–6.04 (mean: 1.15) µg/L for Cu and 0.11–8.73 (mean: 1.03) µg/L for Mn (Table S3). Cu, Fe, Mn, and Zn are essential elements for humans. World Health Organization (WHO) provides provisional guideline values for Cu (2000 µg/L), Fe (2000 µg/L), Mn (400 µg/L), and Zn (3000 µg/L) in drinking water (WHO, 2017). However, more strict thresholds for these metals in groundwater of China are provided in "Standard for groundwater quality (GB/T 14848-2017)" to evaluate the groundwater quality by classifying groundwater quality into 5 levels. Groundwater with Class I, II, or III is suitable for drinking while it with Class IV or V is not suitable for drinking. Therefore, "Standard for groundwater quality (GB/T 14848-2017)" was used to evaluate the groundwater quality of the study area. Concentrations of Pb, Co, Cu, Zn, and Mn in groundwater were all below the corresponding Class III thresholds of "Standard for groundwater quality (GB/T 14848-2017)"
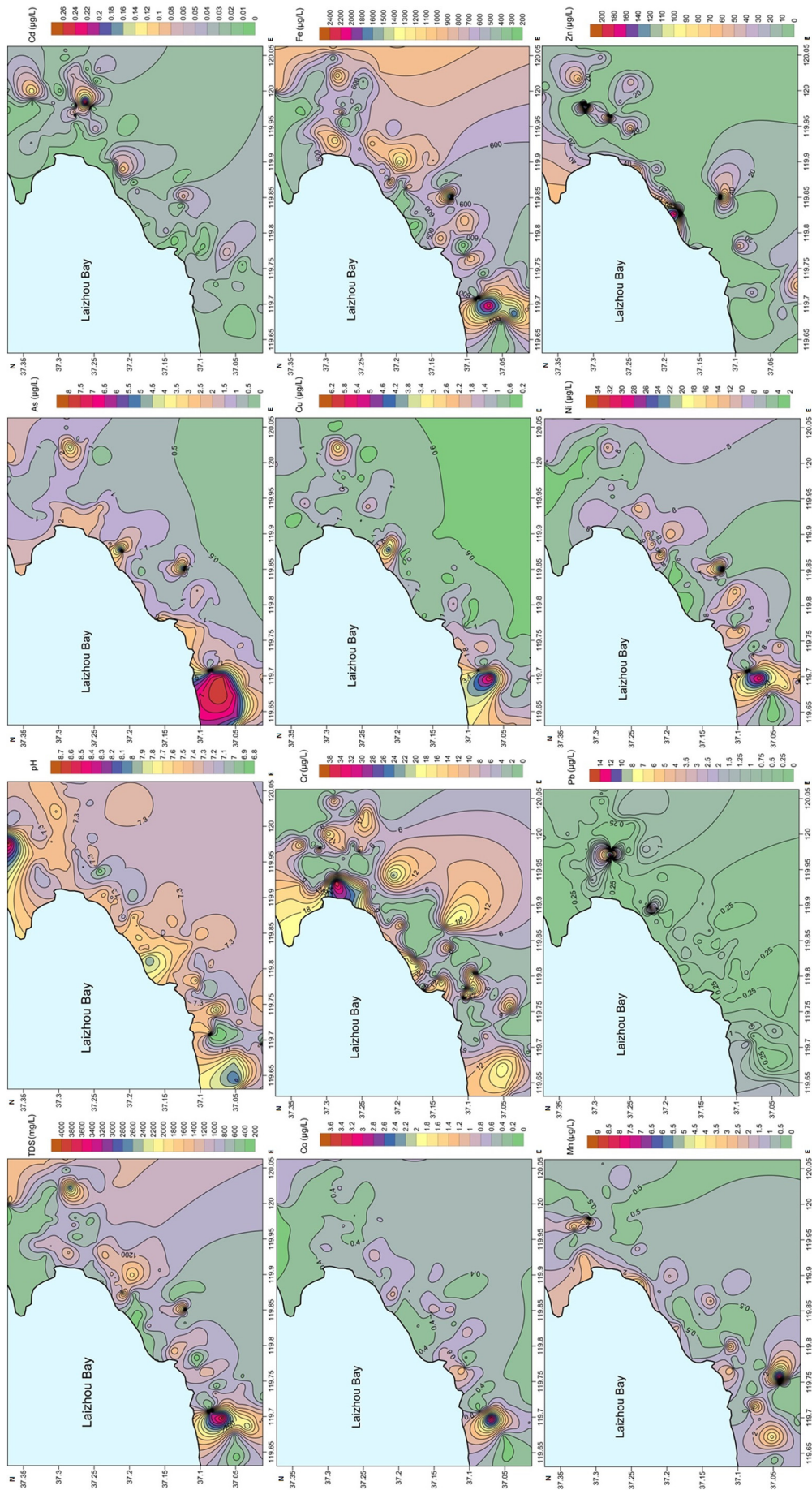
Fig. 2. Distribution of TDS, pH, and target heavy metals in coastal groundwater of the study area.

Table 2
Pearson correlation matrix of TDS, pH, EC, and heavy metals in coastal groundwater.

	Pb	Cr	Co	Ni	Cu	Zn	As	Cd	Fe	Mn	TDS	pH	EC
Pb	1.000												
Cr	−0.171	1.000											
Co	0.001	−0.096	1.000										
Ni	0.004	−0.152	0.823**	1.000									
Cu	0.045	−0.169	0.618**	0.537**	1.000								
Zn	−0.076	0.200*	−0.180	−0.208*	−0.029	1.000							
As	−0.005	0.135	0.514**	0.536**	0.659**	−0.114	1.000						
Cd	0.238*	−0.339**	0.057	0.093	0.167	0.061	0.010	1.000					
Fe	0.087	−0.119	0.785**	0.894**	0.448**	−0.212*	0.484**	0.148	1.000				
Mn	−0.097	0.269**	0.012	0.001	−0.022	0.240*	0.110	−0.170	−0.054	1.000			
TDS	0.043	−0.115	0.801**	0.887**	0.610**	−0.222*	0.551**	0.122	0.930**	−0.062	1.000		
pH	0.053	0.036	−0.441**	−0.562**	−0.203*	0.072	−0.049	−0.072	−0.484**	−0.072	−0.497**	1.000	
EC	−0.042	0.134	0.766**	0.867**	0.534**	−0.147	0.575**	−0.024	0.844**	0.099	0.895**	−0.535**	1.000

Note: symbols * and ** mean the significant level at $p < 0.05$ and $p < 0.01$, respectively.

at all sampling sites. Concentrations of Ni in groundwater at 3 sites exceeded the Class III threshold (20 μg/L) and those at the remaining sites were below the threshold. Interestingly, concentrations of Fe in groundwater were larger than Class III threshold (300 μg/L) of "Standard for groundwater quality (GB/T 14848-2017)" at 98.23% of sampling sites, suggesting that Fe pollution of groundwater occurred in the study area. Mining activities in the study area are frequently performed to cause transport of iron into groundwater. Industrial sewage and agricultural activities such as fertilizer usage are also important sources of iron pollution in the groundwater. Concentrations of heavy metals in fresh groundwater, brackish groundwater, and saline groundwater showed different variations. Concentrations of heavy metals in fresh groundwater of the southern Laizhou Bay ranged from BDL (Cr) to 915.00 (Fe) μg/L with the average values varying from 0.03 (Cd) to 496.13 (Fe) μg/L. Concentrations of heavy metals in brackish groundwater of the southern Laizhou Bay ranged from BDL (Cr, Cd, and As) to 1879.90 (Fe) μg/L with the average values varying from 0.04 (Cd) to 920.80 (Fe) μg/L. Concentrations of heavy metals in saline groundwater of the southern Laizhou Bay ranged from 0.03 (Cd) to 2333.76 (Fe) μg/L with the average values varying from 0.03 (Cd) to 1933.16 (Fe) μg/L. Distribution of heavy metals in groundwater also showed significant site-specific and chemical-specific features (Fig. 2). The salinity could increase the aqueous concentrations of some heavy metals in soil-water systems (Lu et al., 2004). The salinity could also increase the mobility of heavy metals in the soil (Acosta et al., 2011). Seawater intrusion or salinization was reported to account for increased concentrations of heavy metals in groundwater (Basahi et al., 2018; Kampouroglou and Economou-Eliopoulos, 2017). The highest concentrations of As, Co, Cu, Fe, and Ni occurred in the southwestern coast of the study area, similar to TDS, indicating that the concentrations of these heavy metals in shallow aquifer of the study area might be possibly influenced by the groundwater salinization mainly caused by seawater intrusion. This was also proved by the high concentrations of As (73.34–73.87 μg/L), Co (1.06–1.36 μg/L), Cu (128.39–210.08 μg/L), Fe (2020.00–3940.00

μg/L), and Ni (13.25–19.21 μg/L) in 3 seawater samples simultaneously collected from the southwestern coast of the study area. Moreover, some research results further exhibited that increased concentrations of heavy metals in groundwater were attributed to seawater intrusion or salinization (Basahi et al., 2018; Kampouroglou and Economou-Eliopoulos, 2017). The highest concentrations of Cr occurred along the coastline of the northeastern study area while those of Mn occurred in the southern inland part of the study area. However, relatively high concentrations of Cr and Mn were also found in the southwestern coast of the study area, similar to TDS. The highest concentrations of Zn occurred in the central part of the study area while those of Cd and Pb occurred in the central part of the northeastern study area. The distribution of heavy metals in groundwater suggested that the complex factors including groundwater salinization and anthropogenic activities might influence these chemicals in shallow aquifer of the study area.

Groundwater hydrochemical type in the study area mainly included HCO₃-Cl-Ca, HCO₃-NO₃-Ca, SO₄-HCO₃-Cl-Ca, SO₄-HCO₃-Na-Ca, HCO₃-Ca, Cl-Ca, HCO₃-Cl-Na-Ca, HCO₃-NO₃-Cl-Ca, SO₄-Cl-Na-Ca, and HCO₃-Cl-Ca with the major cation of Ca^{2+} and major anions of HCO_3^- and Cl^-. Groundwater with low concentrations of heavy metals generally exhibited hydrochemical types of SO₄-HCO₃-Cl-Ca, SO₄-HCO₃-Na-Ca, and HCO₃-Ca while groundwater with high concentrations of heavy metals usually showed hydrochemical types of SO₄-Cl-Na-Ca, Cl-Ca, and HCO₃-Cl-Ca.

3.2. Possible sources of heavy metals in the coastal groundwater

Correlation analysis on TDS, pH, EC, and heavy metals in groundwater was shown in Table 2. Significantly positive correlation existed in Pb-Cd, Zn-Mn, and Cr-Zn at $p < 0.05$ as well as in Cr-Mn, Cu-As, Cu-Fe, and As-Fe at $p < 0.01$. Co was positively correlated with Ni, Cu, As, and Fe at significance level of $p < 0.01$ while Ni was positively correlated with Cu, As, and Fe at $p < 0.01$. Significantly negative correlation existed in Cr-Cd at $p < 0.01$ and Zn-Fe at $p < 0.05$. TDS was significantly positively correlated with Co, Ni, Cu, As, and Fe at $p < 0.01$ while it was negatively correlated

Table 3
Total variance explained and component matrix for heavy metals in coastal groundwater.

Component	Initial eigenvalues			Elements	Component		
	Total	% of variance	Cumulative %		1	2	3
1	3.630	36.304	36.304	Pb	0.080	−0.482	0.313
2	1.729	17.287	53.590	Cr	−0.190	0.732	−0.018
3	1.156	11.565	65.155	Co	0.894	0.104	−0.053
4	0.883	8.830	73.985	Ni	0.915	0.054	−0.082
5	0.780	7.800	81.785	Cu	0.753	0.047	0.255
6	0.686	6.861	88.647	Zn	−0.260	0.319	0.730
7	0.583	5.835	94.481	As	0.712	0.323	0.106
8	0.304	3.041	97.523	Cd	0.181	−0.589	0.556
9	0.157	1.567	99.089	Fe	0.880	−0.013	−0.076
10	0.091	0.911	100.00	Mn	−0.048	0.627	0.353

with Zn at $p < 0.05$. Similar with TDS, EC was significantly positively correlated with Co, Ni, Cu, As, and Fe at $p < 0.01$. Moreover, EC was also significantly positively correlated with TDS and negatively correlated with pH at $p < 0.01$. In contrast, pH was only negatively correlated with Co, Ni, Cu, Fe, and TDS. These results showed that Co, Ni, Cu, As, and Fe might be influenced by the same factors or originate from the same/similar sources.

PCA was performed to explore the possible sources of heavy metals in groundwater. Three components with the eigenvalues >1.0 were obtained to explain 65.155% of the total variance (Table 3). The first

principal component accounting for the largest variance of 36.304% was mainly composed of the elements Co, Ni, Cu, As, and Fe (Table 3), which was similar to the results of correlation analysis. Cr and Mn were included in the second principal component that explained 17.287% of total variance. Moreover, Cd might negatively contribute to the second principal component. The third principal component was only composed of Zn, accounting for 11.565% of the total variance (Table 3). Elements Co, Ni, Cu, As, and Fe might originate from the seepage of industrial and mining wastewater as well as saline water intrusion. Cr and Mn might mainly come from the industrial activities. Zn
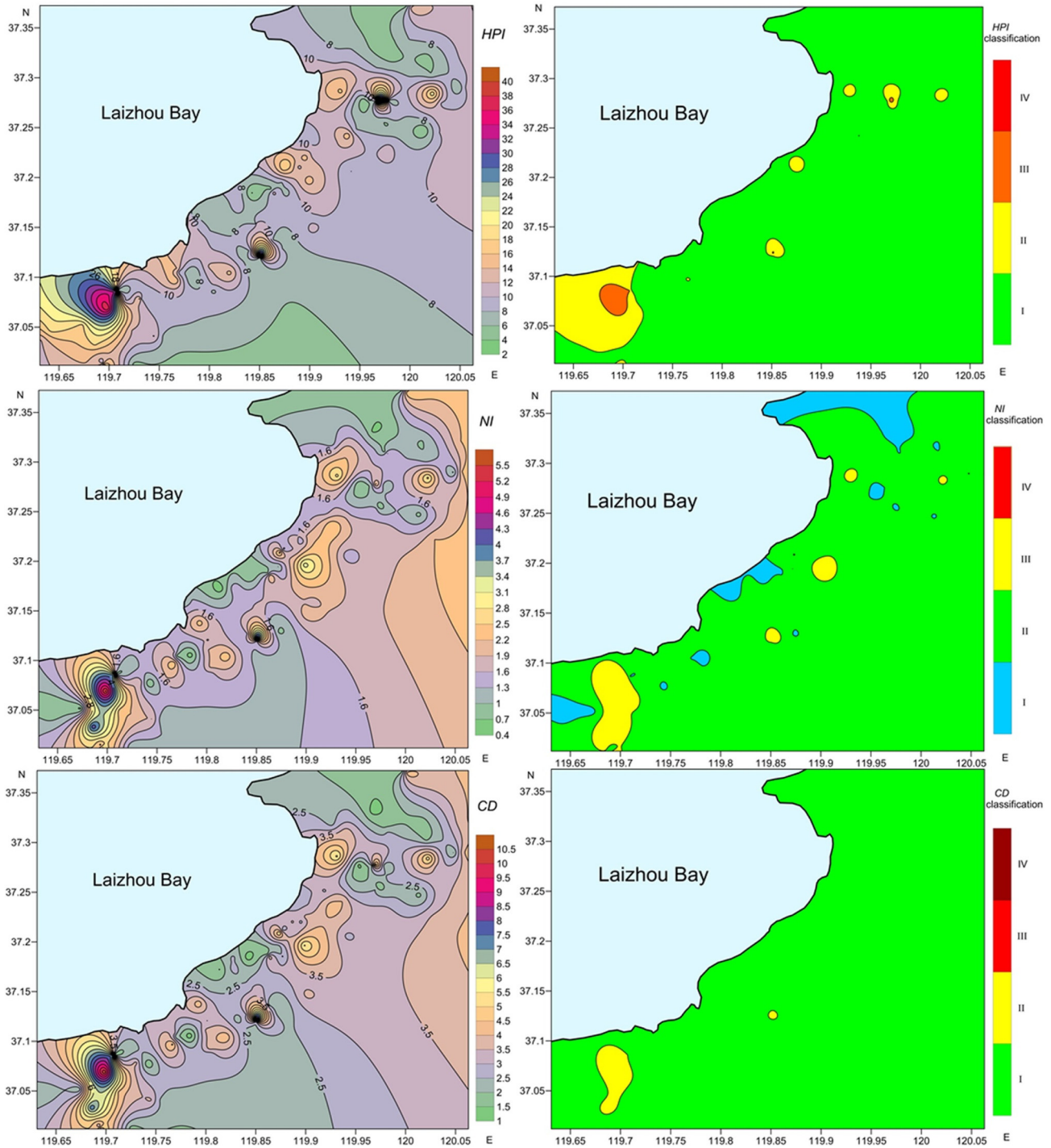
Fig. 3. Coastal groundwater heavy metal pollution evaluated by *HPI*, *NI*, and *CD*. Levels I, II, III, and IV of *HPI* mean low, moderate, moderate-to-heavy, and heavy pollution, respectively; Levels I, II, III, and IV of *NI* refer to insignificant, slight, moderate, and heavy pollution, respectively; Levels I, II, III, and IV of *CD* represent low, moderate, considerable, and very heavy pollution, respectively.

might originate from feces and usage of fertilizers and pesticides. Cd and Pb might be influence by mixed sources. Therefore, heavy metals in groundwater might mainly originate from anthropogenic activities and saline water intrusion.

3.3. Pollution of heavy metals in the coastal groundwater

Except Fe, the concentrations of the remaining heavy metals in groundwater were generally below the Class III thresholds. However, more information on the comprehensive pollution caused by all heavy metals in groundwater was needed to provide the basis for the environmental management in this region. Therefore, pollution of all target heavy metals in groundwater of southern Laizhou Bay was determined by three methods including HPI, NI, and CD (Fig. 3). HPI values of all sampling sites ranged from 3.92 (GW25) to 38.34 (GW38) with the average of 10.66. Based on the HPI ranking criteria, approximately 98, 11, and 4 sampling sites showed low, moderate, and moderate-to-high groundwater pollution by heavy metals, respectively. Moderate and moderate-to-high heavy metal pollution mainly occurred in the southwestern region

of the study area (Fig. 3), which was identical with the regions where the highest concentrations of As, Co, Cu, Fe, and Ni occurred. Elements including Ni, As, Fe, and Pb were the main contributors for pollution, averagely accounting for 90.99% of heavy metal pollution. NI values were in the range of 0.54 (GW70)-5.55 (GW107) with the average of 1.63. Approximately 19.47%, 71.68%, and 8.85% of sampling sites showed slight, low, and moderate heavy metal pollution, respectively. Moderate pollution mainly occurred in the southwestern and central regions of the study area (Fig. 3). In general, pollution evaluated by HPI was more serious than that assessed by NI. Fe was the dominant contributor for pollution evaluated by NI. CD values of the sampling sites ranged from 1.20 (GW7) to 10.40 (GW107) with the average of 3.08. Approximately 109 and 4 sampling sites were endured low and moderate pollution, respectively. Moderate pollution mainly occurred in the southwestern and central regions of the study area (Fig. 3). Pollution assessed by NI was generally more serious than that evaluated by CD. Similar to NI results, Fe was also the dominant contributor for pollution evaluated by CD.

According to the "worst-scenario", approximately 86.73% and 13.27% of sampling sites showed low and moderate or higher
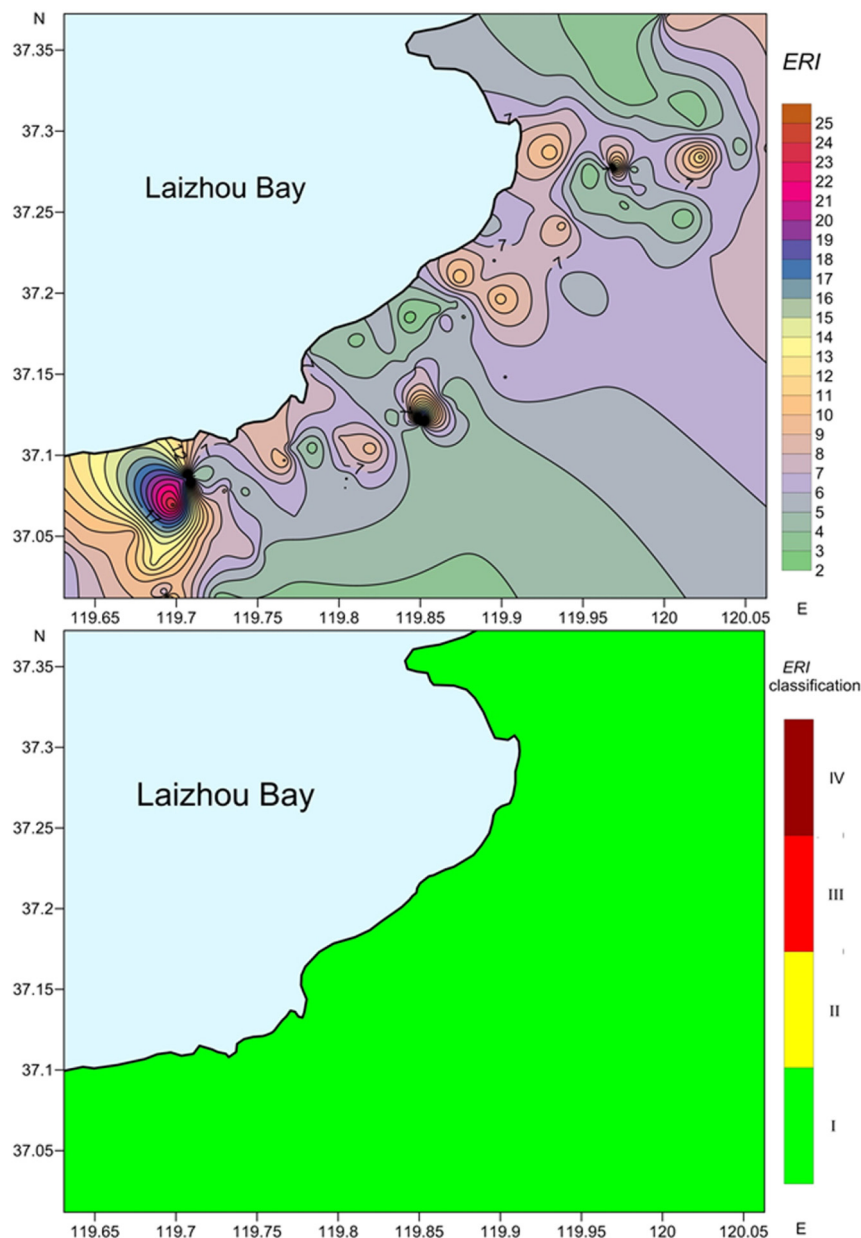

Fig. 4. Ecological risks posed by heavy metals in coastal groundwater. Levels I, II, III, and IV refer to low, moderate, considerable, and very heavy ecological risk, respectively.
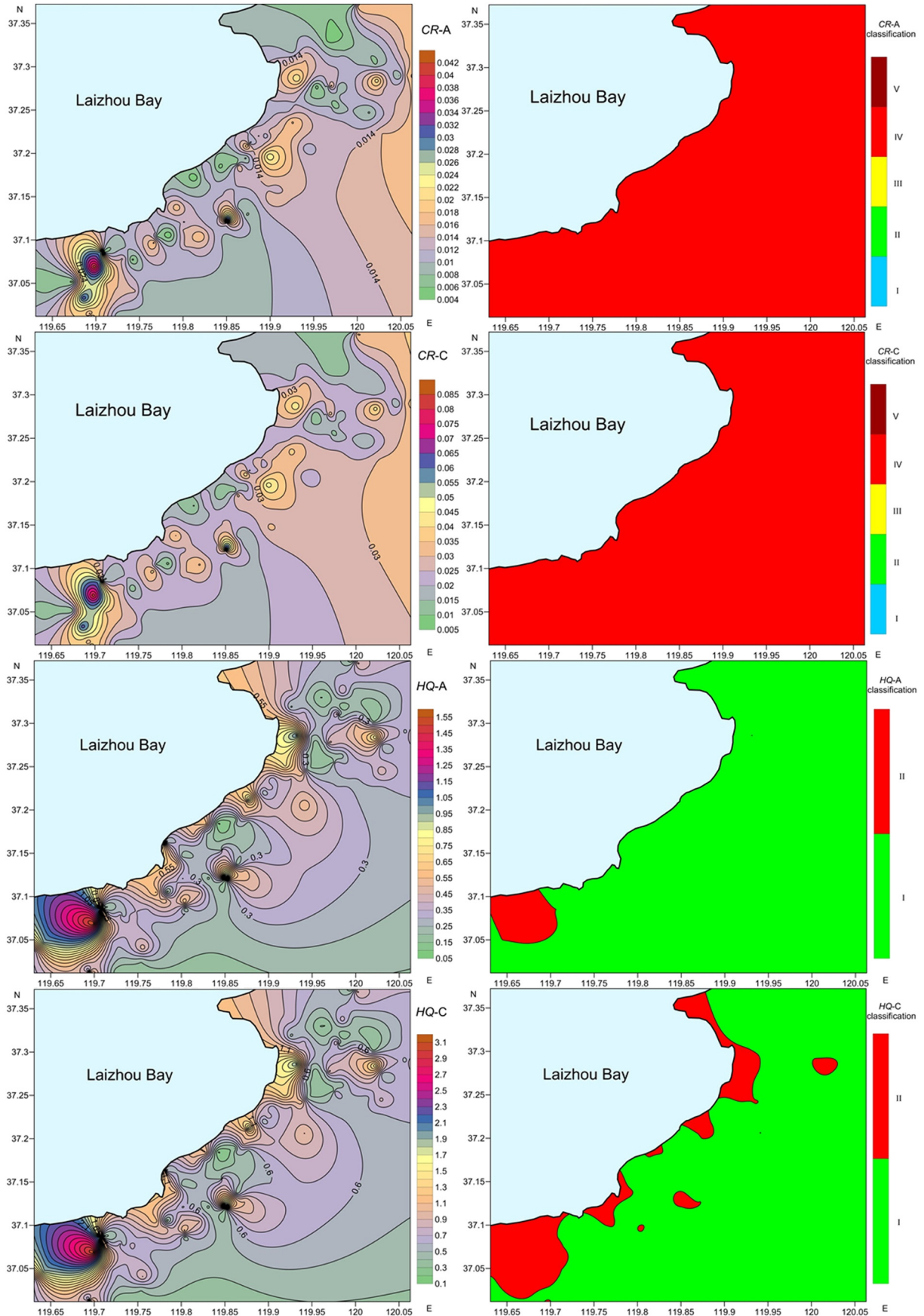
Fig. 5. Health risks of heavy metals in coastal groundwater. *CR* and *HQ* refer to cancer risk and hazard quotient, respectively; A and C represent adults and children; Levels I, II, III, IV, and V for *CR* refer to very low, low, moderate, high, and very heavy cancer risks, respectively; Levels I and II for *HQ* mean acceptable and unacceptable non-cancer risks, respectively.

groundwater heavy metal pollution, respectively. Moreover, relatively high *HPI*, *NI*, and *CD* values were found in the southwestern coast of the study area where severe groundwater salinization occurred, indicating that coastal groundwater salinization could lead to the increase in the pollution of heavy metals in the coastal aquifers. Considering that all water samples were collected from the drinking wells, groundwater pollution needs more attention and effective control.

3.4. Ecological risks posed by heavy metals in the coastal groundwater

Potential ecological risks of heavy metals in groundwater of the study area were evaluated using *ERI* model. *ERI* values ranged from 2.45 to 24.39, which suggested that heavy metals exerted low ecological risks to groundwater systems of all sites (Fig. 4). The *ERI* values of southwestern coast of the study area where severe groundwater salinization occurred were much higher than those of other areas, indicating that the salinization led to the increase in the ecological risks in the coastal groundwater. Fe was the dominant risk contributor with the contribution percentage ranging from 9.23% to 44.37% and the average percentage of 34.67%. Ni was the second risk contributor with contribution percentage in the range of 6.12%–43.44% and the mean value of 29.41%. Metalloid As averagely contributed to approximately 22.04% of ecological risks. Cu and Mn were the weakest risk contributors with the average contribution percentages of 0.09% and 0.18%, respectively. Therefore, effective control of Fe, Ni, and As in groundwater will significantly decrease the potential ecological risks posed by heavy metals in groundwater of the study area.

3.5. Health risks posed by heavy metals in the coastal groundwater

Health risks of heavy metals in groundwater were evaluated by cancer risks and hazard quotients through ingestion (drinking water) and dermal contact pathways. Cancer risks and hazard quotients of heavy metals for adults and children were illustrated by Fig. 5. Both the cancer risks and hazard quotients of heavy metals in southwestern coastal groundwater of the study area where severe groundwater salinization occurred were much higher than those of the remaining areas, indicating that the salinization led to the increase in the health risks in the coastal groundwater.

Cancer risks of heavy metals in groundwater for adults varied from 4.39×10^{-3} to 4.15×10^{-2} with the mean value of 1.25×10^{-2} while those for children ranged from 8.79×10^{-3} to 8.32×10^{-2} with the average of 2.50×10^{-2}. Cancer risks of heavy metals for children were generally twice for adults. Cancer risks through ingestion pathway accounted for about 98.92%–99.91% and 98.09%–99.84% of total risks for adults and children, respectively. Cancer risks for both adults and children were classified into high levels at all sampling sites. Fe was the dominant contributor for cancer risks through ingestion and dermal contact pathways. Cr and Ni also contributed to cancer risks through dermal contact to some extent.

Hazard quotients of heavy metals in groundwater for adults ranged from 9.58×10^{-2} to 1.55 with the mean value of 3.95×10^{-1} while those for children varied from 1.91×10^{-1} to 3.07 with the average of 7.72×10^{-1}. Hazard quotients of heavy metals for children were generally 1.96 times those for adults. Hazard quotients through ingestion accounted for approximately 78.98%–99.66% of total non-cancer risks for adults while those accounted for 85.06%–99.78% of total risks for children. Non-cancer risks for adults were acceptable at 108 sampling sites and unacceptable at 5 sites. Non-cancer risks for children were classified into unacceptable at 20 sampling sites and acceptable at 93 sites. Metalloid As was the dominant contributor for hazard quotients through ingestion, and followed by Co, Fe, Ni, and Cr. Fe was the dominant contributor for non-cancer risks through dermal contact, and followed by Cr and Ni.

4. Conclusions

The investigation provided initial and important information on heavy metals pollution in coastal aquifer with saline water intrusion. The heavy metal pollution in the coastal groundwater of Laizhou Bay was mainly caused by anthropogenic activities and groundwater salinization according to PCA analysis. Fe was the dominant heavy metal in groundwater with the maximal and average concentrations reaching 2333.76 and 686.92 μg/L, respectively. Concentrations of Fe in groundwater exceeded Class III threshold (300 μg/L) at 98.23% of sampling sites. Approximately 86.73% and 13.27% of sampling sites showed low and moderate or higher groundwater heavy metal pollution based on *HPI* evaluation. *ERI* values ranged from 2.45 to 24.39, which suggested that heavy metals exerted low ecological risks to groundwater systems of all sites. Cancer risks for both adults and children were classified into high levels at all sampling sites. Non-cancer risks for adults were unacceptable at 4.42% of sampling sites while those for children were unacceptable at 17.70% of sampling sites. Effective control of heavy metals in coastal groundwater of Laizhou Bay is needed. The southwestern coastal plains of the study area showed significant groundwater salinization trend. The salinization of the coastal groundwater could lead to the increase in the heavy metal pollution and ecological-health risks in coastal groundwater.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.10.250.

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