water

MDPI

Article

Assessment of Potential Ecological Risk of Heavy Metals in Surface Soils of Laizhou, Eastern China

Zhigang Zhao [1,2], Haishui Jiang [1,*], Linghao Kong [2], Tianyi Shen [1], Xionghua Zhang [1], Songsong Gu [2], Xiangcai Han [2,3] and Yachao Li [2]

1 School of Earth Sciences, China University of Geosciences, Wuhan 430074, China; 2202010051@cug.edu.cn (Z.Z.); shenty@cug.edu.cn (T.S.); zhangxh@cug.edu.cn (X.Z.)
2 Yantai Coastal Zones Geological Survey, China Geological Survey, Yantai 264000, China; knowledge0103@163.com (L.K.); gusongsong@163.com (S.G.); 2001200152@cugb.edu.cn (X.H.); 18033738050@sina.cn (Y.L.)
3 School of Ocean Sciences, China University of Geosciences, Beijing 100083, China
* Correspondence: jiangliuis@cug.edu.cn

Abstract: With the rapid industrialization and urbanization, more attention is turning to heavy metal contamination in the soil environment. To assess the potential environmental risk on soil, a comprehensive geochemistry study on heavy metal was performed in Laizhou, eastern China, using 3834 surface soil samples (0–20 cm, regular grid of 1×1 km^2) and 60 layered soil samples (0–200 cm) were analyzed. The average concentrations of As, Cd, Cr, Cu, Hg, Ni, Zn and Pb were 7.60 mg·kg^{-1}, 0.15 mg·kg^{-1}, 45.50 mg·kg^{-1}, 19.10 mg·kg^{-1}, 44.00µg·kg^{-1}, 18.70 mg·kg^{-1}, 51.40 mg·kg^{-1} and 29.00 mg·kg^{-1}, which were lower than the threshold levels of the Grade II criteria of China national environment quality standard for soil, but the contents of As, Cd, Hg, and Pb were higher than background values of eastern Shandong Province surface soil. Fractionation analysis showed that the potential bioavailability in surface soils decreases in the order of Cd > As > Cu > Ni > Zn > Cr > Pb > Hg. Soil assessments with enrichment factor, contamination factor, Nemerow composite index, geo-accumulation index and potential ecological risk index, indicate the soil in Laizhou is contaminated strongly with As, Cd and Hg and a moderately Cr, Ni, Cu and Zn. The level of Pb pollution is between moderate to high. Multivariate analyses suggest that Cr and Ni were derived mainly from natural sources, and As, Cd, Pb, while Hg mostly came from anthropogenic sources. Cu and Zn were from a mixture of anthropogenic and natural sources. Our results demonstrate that more attention should be paid to monitoring soil quality in the heavily polluted site.

Keywords: heavy metal; soil; spatial distribution; contamination assessment; Laizhou

check for updates

Citation: Zhao, Z.; Jiang, H.; Kong, L.; Shen, T.; Zhang, X.; Gu, S.; Han, X.; Li, Y. Assessment of Potential Ecological Risk of Heavy Metals in Surface Soils of Laizhou, Eastern China. *Water* **2021**, *13*, 2940. https://doi.org/10.3390/w13212940

Academic Editors: Patrizia Brunetti and Giuseppe Capobianco

Received: 13 August 2021
Accepted: 27 September 2021
Published: 20 October 2021

1. Introduction

Heavy metals contaminations in soil has generated great concern as an urgent environment problem worldwide due to toxicity, bioaccumulation, and persistence properties [1–5]. As, Hg, Pb, Cd, Cr, Ni, Cu and Zn, have been listed as the priority control contaminants by the United States Environment Protection Agency [6]. They accumulate in agricultural soil and migrate into human bodies through food chains, threatening the natural ecosystem and public health [7–12]. Heavy metal contamination in agricultural soil has became a serious concern in China with rapid industrial development and increased human activities [13,14]. Approximately 1/6 of the cultivated land in China may suffer from heavy metal pollution currently [15,16].

Under the influence of rapid industrialization and urbanization, the concentrations of heavy metals in peri-urban areas are significantly higher than in rural areas [1,2,17,18]. A plethora of evidence showed that heavy metals contaminations occurred universally in industry-based peri-urban areas [18–20]. The pollution of heavy metals in peri-urban soil is mainly associated with human activities, such as mining and smelting, industrial wastes (waste water, waste gas and waste residue), coal burning, household wastes and automobile exhaust emissions [18,21–24]. The peri-urban areas are still an important part of agricultural production, providing grains and vegetables to local and urban residents [20]. More fertilizers and pesticides were used in agricultural land to achieve high yield, which could exacerbate the heavy metal accumulation in soil. Therefore, it is necessary to determine the distribution pattern and contamination level of the heavy metals in contaminated soils and assess their potential risks to the soil so that remedial plans can be developed.

Given the main origins of vegetables and fruits, heavy metals level in Laizhou should be a matter of concern, especially as it is also an important gold mining area in China. However, the spatial distribution and ecological risk assessment of heavy metals in the soil of Laizhou is relatively little known. An accurate and complete assessment of the potential risks induced by heavy metals is necessary for restoring the local ecosystem. In this paper, the characteristics of heavy metals in the surface soil of Laizhou were analyzed, aiming to investigate the geochemistry features of heavy metals and evaluate the regional ecological risk. The enrichment factor, contamination factor, Nemerow composite index, geo-accumulation index, and potential ecological risk index were applied to evaluate the pollution level and ecological risk of heavy metals in soil, which can provide references for the control of the heavy metal pollution. Analysis of variance, Pearson correlation coefficient and principal component analysis were used to identify the sources of heavy metals.

2. Methods and Materials

2.1. Study Area and Soil Sampling

The study area is located in Laizhou (119°33′ E–120°18′ E, 36°59′ N–37°28′ N), Eastern Shandong Province, China, covering about 985 km^2 (Figure 1). Laizhou has a warm temperate continental climate with an average annual temperature of 16 °C. Its mean annual rainfall is 471 mm, mostly between June and September. The terrain is higher in the southeast and is lower in the northwest, ranging from 0 to 430 m above sea level (Figures 1 and 2a). Rocks in Laizhou are mainly consisted of granite, gneissic granite, marble schist, basite and granulite in the southeastern hill area, while a few gneissic granites and pluvial alluvial sediments in the northwestern plains area (Figure 2b). Inside the study area, about 53% of the land was used for agricultural faring, 45% of the land was occupied by factories and residential settlements, and the rest were water bodies and roads (Figure 2c).

In this study, 3834 surface soil samples (0–20 cm depth) were collected from June to September 2020 from Laizhou (Figure 1) by multipoint mixing and systematic gird sampling (1×1 km^2).To study the distribution patterns of heavy metals in the vertical direction, three soil profiles were measured in the heavily polluted and slightly polluted sites, respectively (Figure 1). Each site includes 10 distinct soil horizons, with 20 cm intervals from 0–200 cm. Each soil sample was collected simultaneously in triplicate from the same location. All samples were put in polyethylene bags and brought back to the laboratory, which were subsequently air dried at room temperature and passed through a 2 mm sieve.

2.2. Chemical Analysis

Soil pH value was determined by the electrode method. The organic matter (OM) content of the sample was determined by the dichromatic oxidation titration method. Total nitrogen (TN) was measured by Kjeldahl after digested by the concentrated H_2SO_4 (95.0–98.0%). Total phosphorus (TP) content was measured by the molybdate colorimetric method after digested by $HClO_4$ (70.0–72.0%). Total organic carbon (TOC) was determined by the potassium dichromate volumetric method. Cation exchange capacity (CEC) was measured by ammonium acetate method [25–27]. For Cd, Cu, Zn, Cr, Ni and Pb analysis, 0.5 g of each soil sample was digested with $HClO_4$ (70.0–72.0%)/HNO_3 (65.0–68.0%)/HF (≥40.0%) (2:10:5 *v*/*v*/*v*) in Teflon tubes, while for As and Hg, 0.5g of each soil sample was digested with HNO_3 (65.0%)/HCL (36.0–38.0%) (1:3, *v/v*) [21]. The speciation of heavy metals was measured using the modified European Communities Bureau of Reference (BCR) extracted method [28–30], which means that these soil samples were separated into water soluble fraction, Ion exchangeable fraction, carbonate bound, Fe-Mn oxide, humic acid bound, strong organic bound and residual fraction. In all cases, the heavy mental recovery degree was calculated as the following: Recovery (%) = (Heavy metal extracted by single extraction/Heavy metal extracted by Sequence BCR) × 100 [30]. The values of Recovery (%) were between 90 and 105. The contents of Cd, Cu, Zn, Cr, Ni, and Pb, from the digested soil samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS 1260). The analysis of As and Hg was performed using one atomic fluorescence spectrometer (AFS-8220) in triplicate. The national certified materials (GBW07403a) and parallel samples were used to check the quality of the analysis results. The relative standard error of the test results was 0.48–2.88%, which met the quality control requirements.

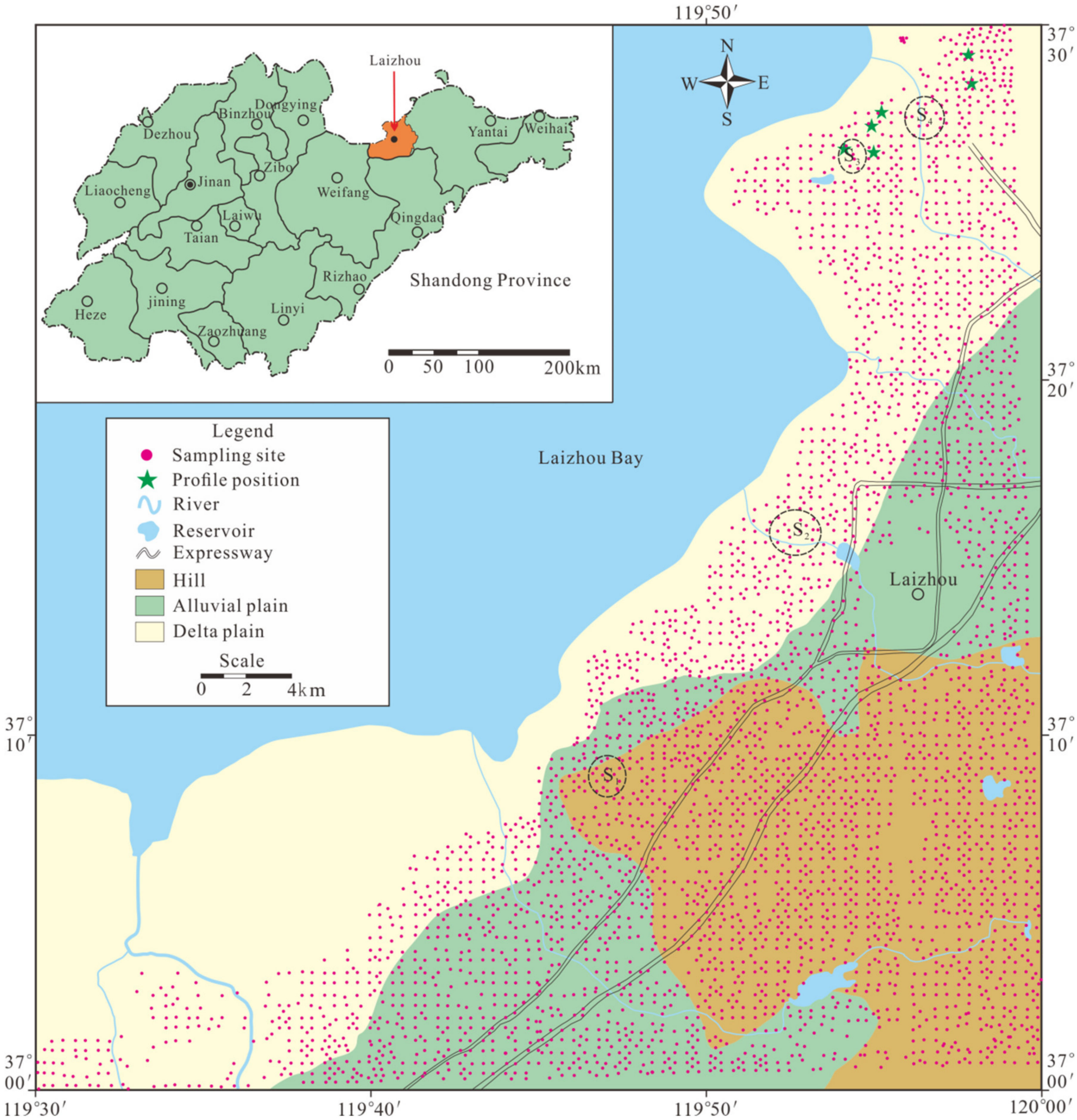

Figure 1. Geographical location of study area with indication of the sampling sites (the geographical location map is derived from the administrative zoning map of Shandong Province, 2019).

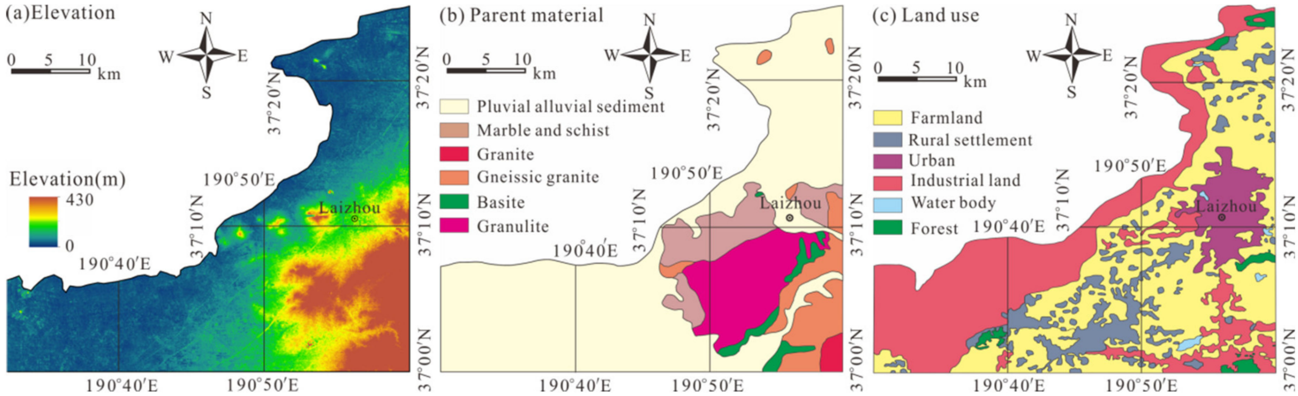

Figure 2. Land use, parent material and topography in Laizhou ((**a**) from the SRTMDEM 90M; (**b**) was adapted from the geological map of Yantai city (map scale, 1:250,000); (**c**) was interpreted in GF-2 1M).

2.3. Assessment of Potential Risk and Criteria

2.3.1. Enrichment Factor (EF)

The EF is the ratio calculated by dividing the normalizing concertation of each element in soil by the chosen baseline. It is an effective method to distinguish whether heavy metals are derived from natural or anthropogenic sources [31,32]. Fe was chosen as the reference element to calculate the EF value owing to minor influence of anthropogenic activities [33–35]. It is calculated as follows: EF = $(Me/Fe)_{sample}/(Me/Fe)_{baseline}$, where Me_{sample} and Fe_{sample} represent the heavy metal and Fe concentration in the sample, respectively. $Me_{baseline}$ and $Fe_{baseline}$ represent the background value of heavy metal and Fe, respectively. The average metal concentrations of surface soil in eastern Shandong Province were taken as the background values [36]. The principle of grading for EF is listed in Table 1 [37,38]. EF > 1 indicates anthropogenic sources and EF < 1 implies a possible mobilization or depletion of metals [39].

Table 1. Principle of grading for enrichment factor.

EF	Class	Degree
EF ≤ 1	0	Non-pollution
1 < EF ≤ 2	1	Slight pollution
2 < EF ≤ 5	2	Moderately polluted
5 < EF ≤ 20	3	Heavy pollution
20 < EF ≤ 40	4	Moderately severe
40 < EF	5	Severe pollution

2.3.2. Contamination Factor (CF) and Nemerow Composite Index (NI)

The CF was applied to assess the pollution level of a single heavy metal and NI was used to reflect the comprehensive pollution degree of all the heavy metals studied. The indices are calculated by using the following equation: (1) CF = C_i/S_i; (2) NI = $[(CF^2{}_{max} + CF^2{}_{ave})/2]^{1/2}$, where C_i represents the heavy metal (i) concentration in soil sample; S_i is the risk screening value of the heavy metal (i) in soil. The risk screening values of the heavy metal were obtained from soil environmental quality-risk control standard for soil contamination of agricultural land in China. CF_{max} and CF_{ave} represent the maximum and average value of EF, respectively. The principle of grading for CF and NI are listed in Table 2 [40].

Table 2. Principle of grading for contamination factor and Nemerow composite index.

Class	CF	NI	Contamination Degree
0	<0.7	<0.7	Safety
1	0.7–1.0	0.7–1.0	Warning
2	1.0–2.0	1.0–2.0	Slight pollution
3	2.0–3.0	2.0–3.0	Moderate pollution
4	>3.0	>3.0	Heavy pollution

2.3.3. Geo-Accumulation Index (I_{geo})

The geo-accumulation index (I_{geo}) was applied to eliminate the influence of geological contributions in the assessment of heavy metal pollution [41]. It is calculated with the equation of $I_{geo} = \log_2 [C_i/(k \times B_i)]$, where C_i is the measured concentration of the heavy metal (i) in sample; B_i represents the background value of the heavy metal (i) in soil. The average metal concentrations in Eastern Shandong Province surface soil was used as the background values [17]. The factor k is generally 1.5, which represents a background matrix correction factor owing to lithogenic variation [42,43]. The contamination degrees of heavy metals based on the I_{geo} value were presented in Table 3 [44,45].

Table 3. Contamination Degree Based on Geo-Accumulation (Igeo) Values.

I_{geo}	Class	Degree
$I_{geo} < 0$	0	Unpolluted
$0 \leq I_{geo} < 1$	1	Unpolluted to moderate
$1 \leq I_{geo} < 2$	2	Moderately polluted
$2 \leq I_{geo} < 3$	3	Moderately to strongly polluted
$3 \leq I_{geo} < 4$	4	Strongly polluted
$4 \leq I_{geo} < 5$	5	Strong to very strong pollution
$5 \leq I_{geo}$	6	Very strong pollution

2.3.4. Potential Ecological Risk Index (RI)

The RI was used to emphasize the toxicology of heavy metals and evaluate its potential ecological risk. It is developed based on the superposition of various heavy metals and the different risk levels they pose to organisms [46]. RI is calculated as the following equation: $RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_i/B_i$, where E_r^i and T_r^i represents the potential ecological risk factor and the toxicity response coefficient of single heavy metal (i), respectively. The toxicity response coefficient values are Cd = 30, Cu = 5, Pb = 5, Ni = 5, Cr = 2, Zn = 1, As = 10, Hg = 40 [46,47]. C_i is the heavy metal (i) concentration in soil sample. B_i represents the background value of the heavy metal (i) [38]. The contamination levels based on E_r and RI values are listed in Table 4 [45–48].

Table 4. Contamination levels based on potential ecological risk values.

Class	Er	Degree	RI	Degree
1	<40	Low	<150	Low
2	40–80	Moderate	150–300	Moderate
3	80–160	High	300–600	High
4	160–320	Moderately severe	600–1200	Moderately severe
5	>320	Severe	>1200	Severe

2.4. Statistical Analysis

Summary statistics, such as the maximum, minimum, arithmetic mean values, standard deviation (SD), and coefficient of variation (CV) were calculated based on the heavy metals concentration. Analysis of variance (ANOVA), Pearson correlation and principal component analysis (PCA) were carried out using SPSS 22.0 to identify the potential sources of heavy metals. Spatial distributions of heavy metals were elucidated using the Kriging method via Geochemical Studio 2.5.7 software.

3. Results and Discussion

3.1. Soil Physicochemical Properties

The descriptive statistics of surface soil basic physicochemical properties in 62 samples are presented in Table 5. The average pH value of 6.9 for the surface soils suggests that the soil in Laizhou in total had neutral properties. The average concentrations of TN, TP, TOC and OM were 0.77 g·kg^{-1}, 0.34 g·kg^{-1}, 9.36 g·kg^{-1} and 16.13 g·kg^{-1}, respectively. The variation in CEC ranged from 0.42 to 15.41 cmol·kg^{-1}. The OM can affect heavy metal behaviors in soils, such as speciation, mobility and migration, due to the large CEC and high affinity on the particle surface of the OM, which is beneficial for the adsorption of heavy metal [49]. Therefore, the low values of OM in soil from the study area may aggravate the migration of heavy metal [49].

Table 5. Descriptive statistics of physicochemical properties of surface soils in Laizhou.

Property	pH	OM (g·kg^{-1})	CEC (cmol·kg^{-1})	TP (g·kg^{-1})	TN (g·kg^{-1})	TOC (g·kg^{-1})
Range	5.36–7.57	3.68–31.52	0.42–15.41	0.08–1.52	0.10–1.52	2.14–18.30
Mean	6.90	16.13	9.71	0.34	0.77	9.36
Standard deviation	0.46	5.69	4.00	0.26	0.35	3.30
Coefficient of variation	0.07	0.37	0.49	0.48	0.44	0.37

3.2. Horizontal Distribution Patterns of Heavy Metals

The descriptive statistical results presented that none of the eight heavy metals concentration exceed the Grade II criteria of China national environment quality standard for soil (Table 6), suggesting insignificant pollution of eight heavy metals in Laizhou. Nevertheless, the average concentrations of As, Cd, Hg, and Pb are higher than background values of eastern Shandong Province surface soils (Table 6), indicating enrichment of these four heavy metals. In particular, the maximum contents of Cd and Hg in surface soils almost reached 100 and 200 times of their background values of eastern Shandong Province surface soil, respectively, implying intensive anthropogenic activities on some samples.

Table 6. Descriptive Statistic of Eight Heavy Metals Concentrations in Surface Soils from Laizhou.

Metal	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Range	0.50–98.30	0.03–11.90	5.00–472.00	2.30–556.00	1–6544	2.00–203.00	4.10–429.00	3.10–1100.00
Mean	7.60	0.15	45.50	19.10	44.00	18.70	29.00	51.40
SD	4.30	0.31	22.10	18.60	115.00	10.50	18.80	32.50
CV	0.58	2.10	0.49	0.97	2.62	0.56	0.65	0.63
Background values [38]	6.30	0.108	56.20	19.60	29.00	23.5	25.4	56.1
Grade II criteria values	30.00	0.30	200.00	100.00	2400.00	100.00	120.00	250.00

Hg is in μg·kg^{-1}, other heavy metals are in mg·kg^{-1}.

The horizontal distribution patterns of eight heavy metals in the surface soil (0–20 cm) were greatly influenced by the sampling location, characterized by '*hotspot*' patterns, where a high concentration of heavy metal was surround by relatively lower concentration (Figure 3). The pollution patterns were similar with the heavy metals contamination in the industry-based Peri-urban area of Wuxi, China, and Pb contamination in the Quseburn Catchment, UK [20,50]. For example, the soils surrounding industrial areas and rural settlements had higher concentrations of As, Cd and Pb, while the soils with higher Hg concentrations were adjacent to urban, rural settlement and quarries. The soils with higher Cr and Ni contents show NE-SW distribution in the central and southern part of study area, which is consistent with the distribution of the basite (Figure 2b), indicating the parent rock weathering source. The CV of Cd and Hg in surface soils were significantly higher than background value of eastern Shandong Province surface soils (Table 6), which were due to the existence of some outliers from human activities.

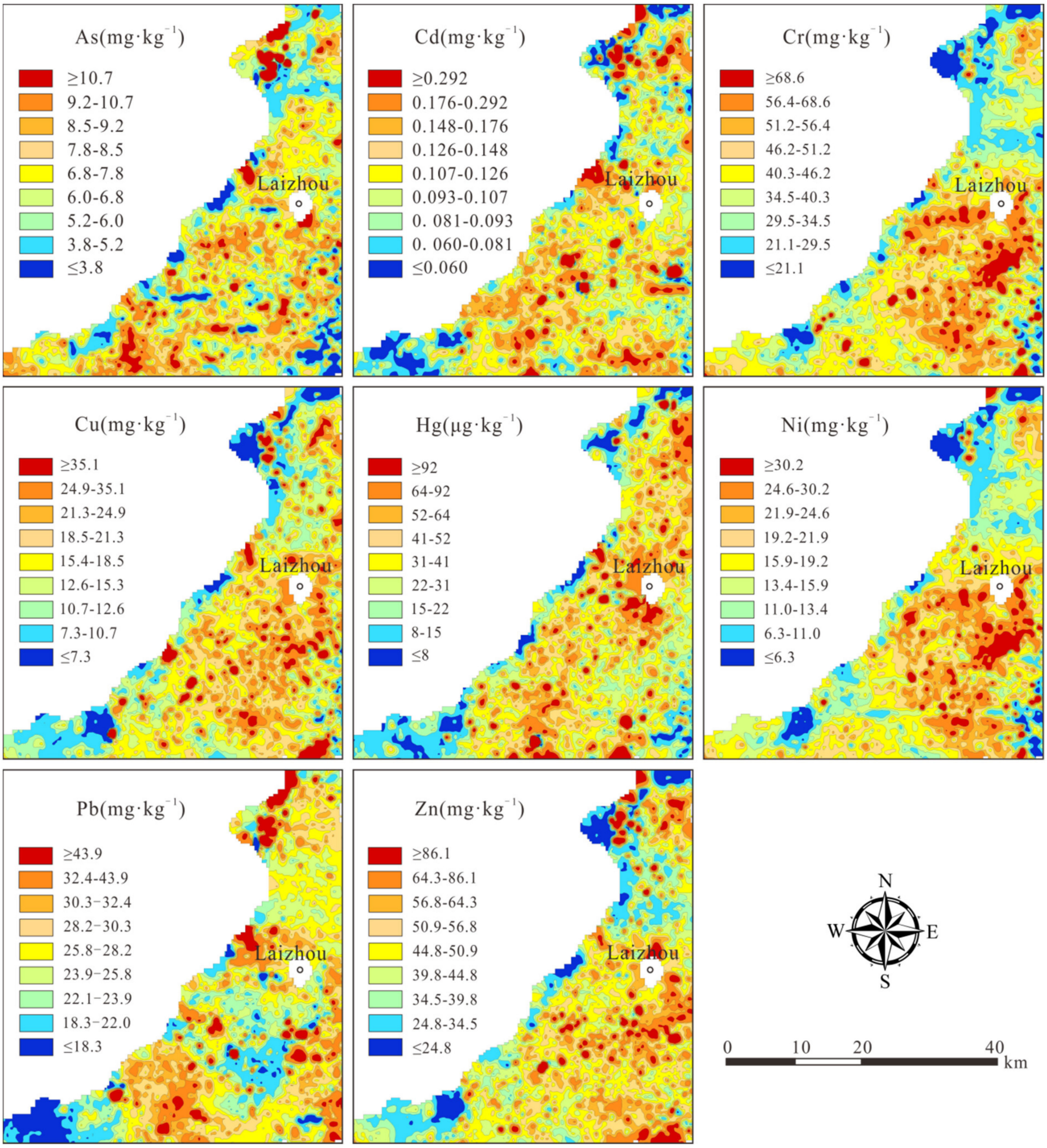

Figure 3. Horizontal distribution of heavy metal (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) in the study area.

3.3. Vertical Distribution Patterns of Heavy Metals

The vertical distribution plots of eight heavy metals in the soil profiles of the slightly and heavily polluted sites are presented in Figure 4. In slightly polluted sites, the average concentrations of Cd, As, Hg and Pb show slight change throughout the soil profile. The mean concentrations of Cr, Ni, Cu and Zn were increased in subsoil (140–160 cm), indicating the four metals were enriched significantly due to the downward eluviation process. In heavily polluted sites, the mean concentrations of heavy metals are higher than background values of eastern Shandong Province surface soils with the exception of Cr and Ni (Table 6). The results suggest that As, Cd, Cu, Hg, Pb and Zn are significantly accumulated in the heavily polluted sites, posing a potential risk to ecological security.

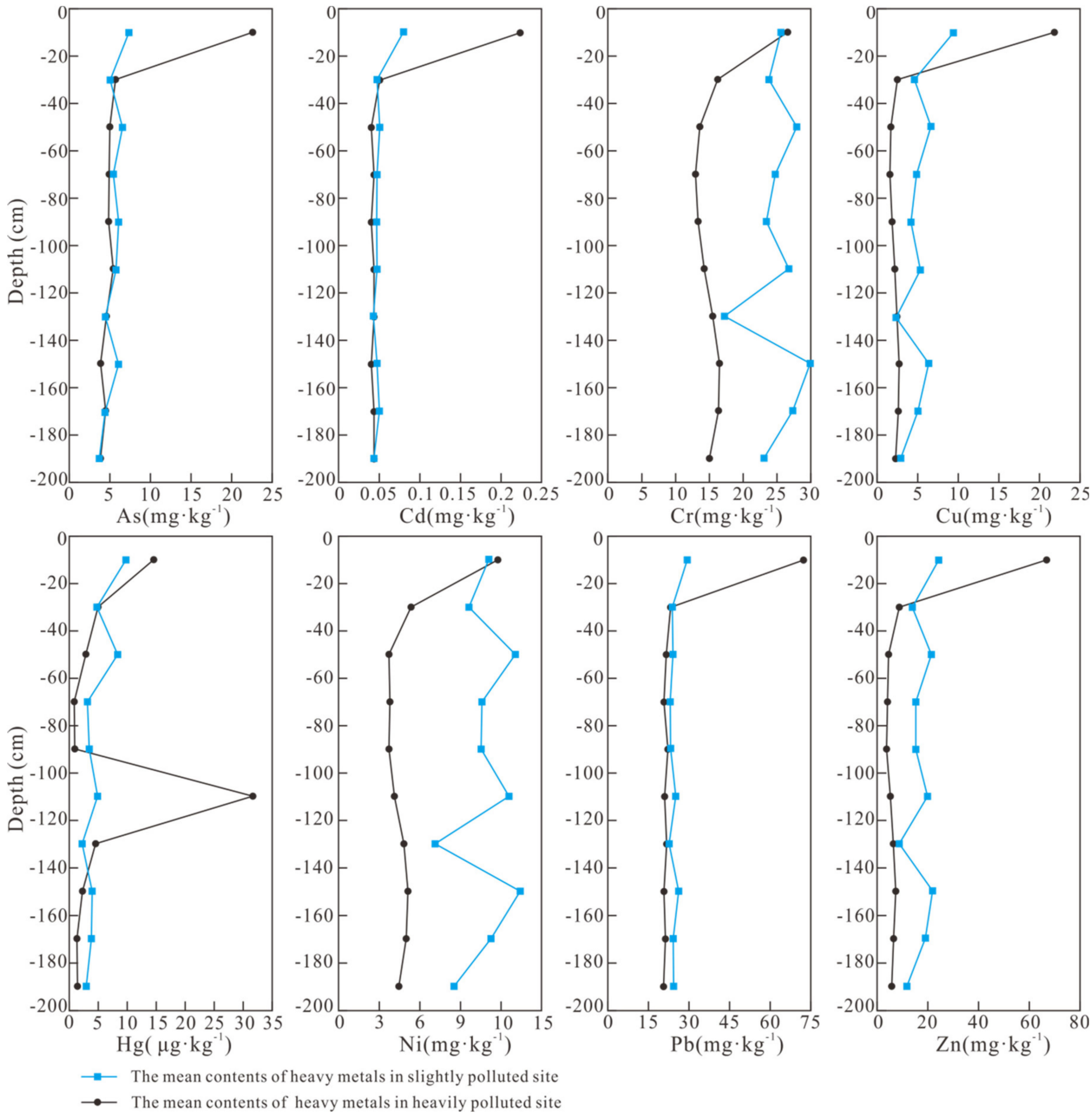

Figure 4. Vertical distribution plots of heavy mental in slightly and heavily polluted site.

The concentrations of As, Cd, Cu, Pb and Zn were the highest in 0–20 cm of soil profile, and then obviously decreased below 20 cm, which was closer the tailings pond, implying significant enrichment of these heavy metals with anthropogenic input. The concentration of Hg peaked in 100–120 cm of soil profile, which may be related to the downward eluviation process.

3.4. Speciation of Heavy Metals

The speciation of heavy metals is significant for revealing the possible environmental effects of heavy metals in soil by evaluating their mobility, activity, bioavailability and eco-toxicity among different chemical fractions [51,52]. The chemical fractions of heavy metal in soil are divided into water soluble, ion exchange, carbonate bound, humic acid bound, Fe/Mn oxide, strong organic bound and residue in this paper. According to the stability of chemical binding and bioavailability, the chemical fraction of heavy metals could be divided into the most bioavailability fraction (water soluble, ion exchange, carbonate bound), the medium bioavailability fraction (humic acid bound and Fe/Mn oxide) and the inert bioavailability (strong organic bound and residue) [53–55].

Fifty typical surface soil samples from four sites (S1, S2, S3 and S4) in the study area were analyzed in this paper (Figure 1). The results show that the heavy metals dominated in the soil residuals with the exception of Hg, Cr and Pb are the most abundant element in this fraction (Figure 5). Residual phases of metals are generally much less toxic to organisms [56].

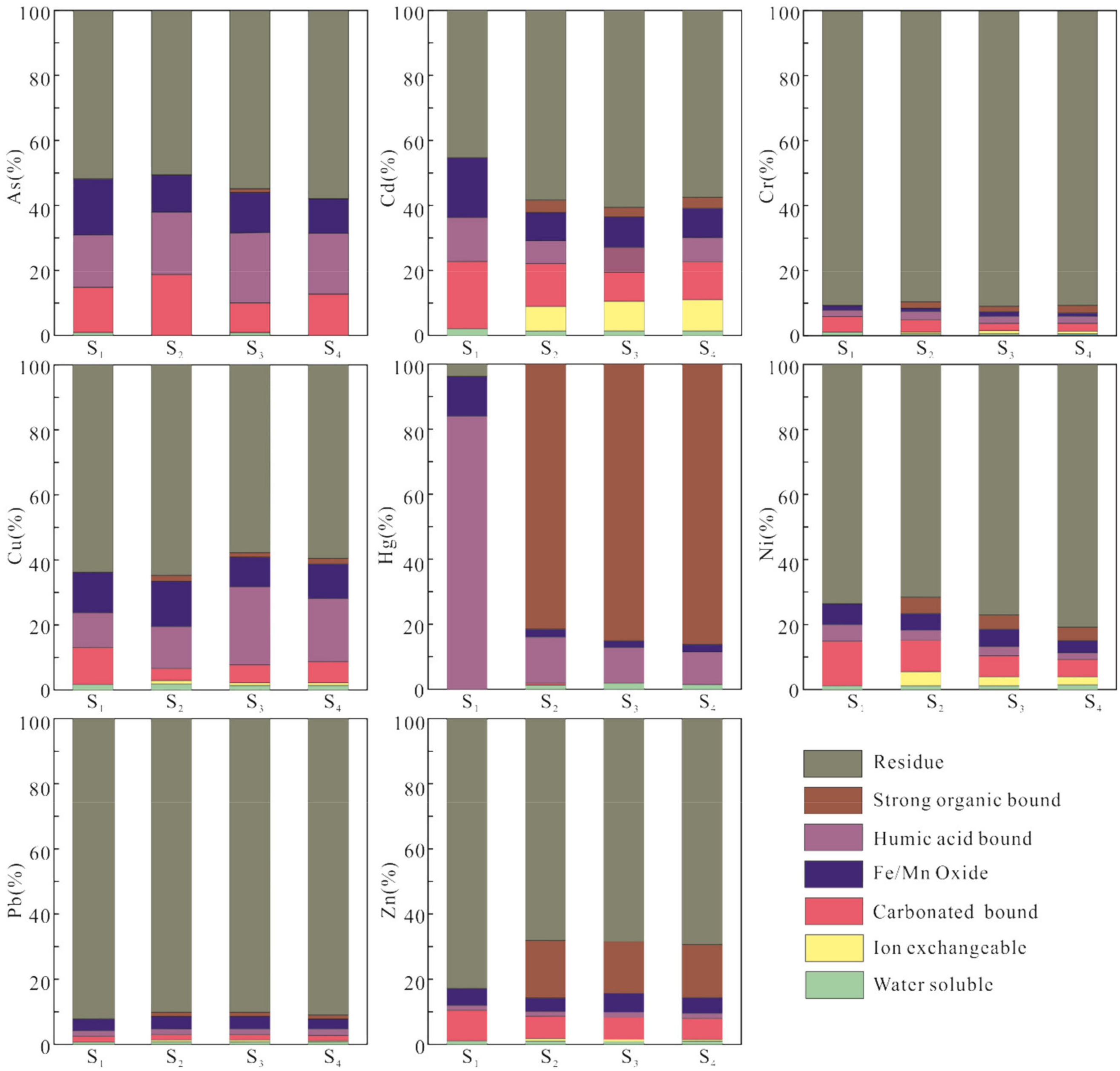

Figure 5. Speciation of heavy metals in surface soils from four sites of the study area.

The largest bioavailability fractions of As, Cd and Cu accounted for 14%, 21.7% and 8.9% on an average and the mean percentages of them in the medium bioavailability fraction were 32%, 20.3% and 28.3% respectively. The proportion of As, Cd and Cu in the bioavailability fraction was close to 1/2, 2/5 and 2/5, respectively. In addition, the mean concentrations of As and Cd in the mining area of Laizhou were high, which deserves more attention.

The speciation of Cr and Pb are very similar, which dominate in soil residue. The mean percentages of most bioavailability fractions of Ni and Zn were below 13%, while the mean percentages of them in a medium bioavailability fraction were 8.4% and 6.5%. Ni and Zn mostly existed in the inert fraction. Hg was the most abundant element in humic acid bound form, constituting 84.1% of the total concentration in the soils from S1, which was dominate in strong organic bound form (82.2–86.2%) in soil samples from another three sites. The results indicate that Hg in soil from site S1 mostly existed in medium bound fraction, which deserves more attention.

3.5. Assessment of Soils Pollution

3.5.1. Enrichment Factor

The mean EF values decreased in the order of Hg > Cd > Pb > As > Cu > Zn > Cr > Ni (Table 7 and Figure 6). The EF values of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn exceeded 2 in 22.87%, 23.50%, 1.51%, 7.20%, 37.45%, 1.12%, 23.60% and 6.39% of the samples, respectively. The average EF values of eight heavy metals were higher than 1. Furthermore, the maximum EF value of As, Cd, Cu and Hg are higher than 40. In particular, the maximum value of Hg reacheed 268.41 (Table 7). The results indicate that As, Cd, Pb and Hg are enriched significantly in surface soils [39].

Table 7. Enrichment factor (EF), contamination factor (CF), geo-accumulation index (I_{geo}) and potential ecological risk index (Er) values of heavy metals in study area.

Parameters		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
EF	Range	0.03–44.41	0.25–113.36	0.16–15.16	0.22–69.48	0.02–268.41	0.13–10.27	0.05–18.19	0.43–35.41
	Mean	1.75	1.94	1.10	1.32	2.13	1.03	1.77	1.27
CF	Range	0.02–3.28	0.1–39.67	0.03–2.36	0.02–5.56	0.01–2.73	0.02–2.03	0.03–3.58	0.01–4.40
	Mean	0.25	0.49	0.23	0.19	0.02	0.19	0.24	0.21
I_{geo}	Range	−4.15–3.47	−2.31–6.32	−3.98–2.58	−3.53–4.40	−5.24–7.45	−3.99–2.67	−3.15–3.56	−4.67–3.80
	Mean	−0.36	−0.33	−0.91	−0.69	−0.24	−0.96	−0.42	−0.76
E_r	Range	0.85–166.61	9.09–3606.06	0.19–17.91	0.65–157.95	1.58–10470.40	0.47–47.88	0.84–88.64	0.06–20.91
	Mean	12.81	44.48	1.73	5.44	70.37	4.41	5.99	0.98

3.5.2. Contamination Factor and Nemerow Composite Index

The CF values in surface soils are summarized in Table 7 and Figure 6. The mean CF values decrease in the order of Cd > As > Pb > Cr > Zn > Cu = Ni > Hg. The percentages of CF values of heavy metals exceeding 1 in the surface soil samples were Cd (0.65%) = Pb (0.65%) > Cu (0.42%) > As (0.34%) > Cr (0.29%) > Ni (0.16%) > Hg (0.03%). Although the mean CF values based on risk screening values for eight heavy metals were lower than 1, the mean CF based on background values from eastern Shandong Province surface soil for As, Cd, Hg and Pb are higher than 1. The results indicate that As, Cd, Hg and Pb were significantly enriched in the surface soils of the study area. Therefore As, Cd, Hg and Pb in surface soils from the study area deserve more attention. In addition, the results of NI values showed that 2.69% of the surface soil samples were polluted. The proportions of slight, moderate and heavy pollution were 1.75%, 0.47% and 0.47%, respectively.

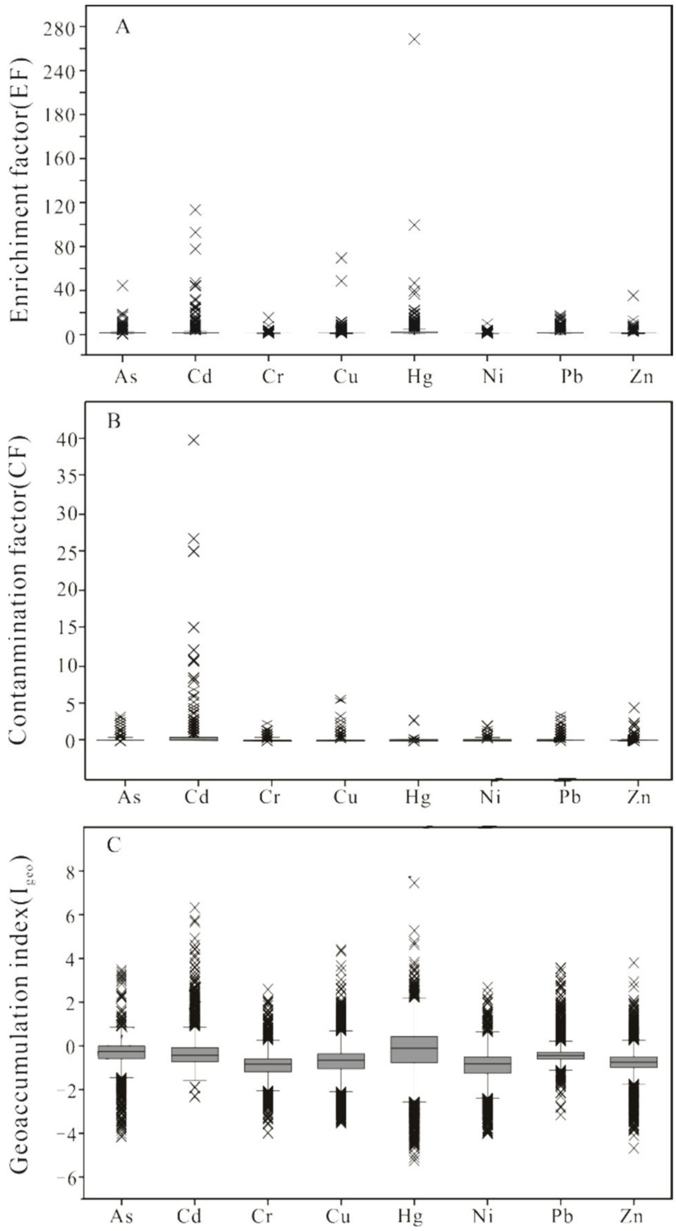

Figure 6. Box-plots display the distributions of the pollution indexes of heavy metals in surface soils of the study area. (**A**) enrichment factor (EF); (**B**) contamination factor (CF); (**C**) geo-accumulation index.

3.5.3. Geo-Accumulation Index

Similar to the results of CF, Cr, Ni and Zn were the three heavy metals with low pollution levels of I_{geo} in the study area (Table 7 and Figure 6). The percentages of the surface soil samples not contaminated by Cr, Cu, Ni, Pb and Zn were 96.64%, 87.72%, 95.28%, 92.54% and 93.17%, respectively, indicating slight pollution of these metals in Laizhou surface soils. The proportions of I_{geo} values of As, Cd and Hg exceeding 1 in surface soil samples were 24.47%, 24.23% and 45.04%, respectively. Such results imply that As, Cd and Hg were enriched significantly in some surface soil samples.

3.5.4. Potential Ecological Risk Index

The results suggest that the average Er values for eight heavy metals followed the decreasing order as: Hg > Cd > As > Pb > Cu > Ni > Cr > Zn (Table 7). The proportions of surface soil samples with low potential ecological risk of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn were 99.58%, 69.54%, 100%, 99.79%, 30.59%, 99.97%, 99.71% and 100%, respectively

(Figure 7). Depending on the sampling station location and each metal, the Er values showed low to severe potential ecological risk in Laizhou. Cr, Ni and Zn presented low potential ecological risk, while As, Cu and Pb presented low to high potential ecological risk. Again, Cd and Hg were significantly accumulated in the surface soils and their Er values indicated low to severe potential ecological risk (Table 7 and Figure 7). The high ecological risk values of Cd and Hg were due to the high toxicity coefficient and the accumulation from human activities [57]. The results of RI suggested that 30.78% of the surface soil samples were a potential risk, with the percentages of moderate potential ecological, high potential risk, moderately severe ecological risk and severe potential risk in surface soil samples were 27.49%, 2.58%, 0.47% and 0.23%, respectively (Figures 7 and 8).

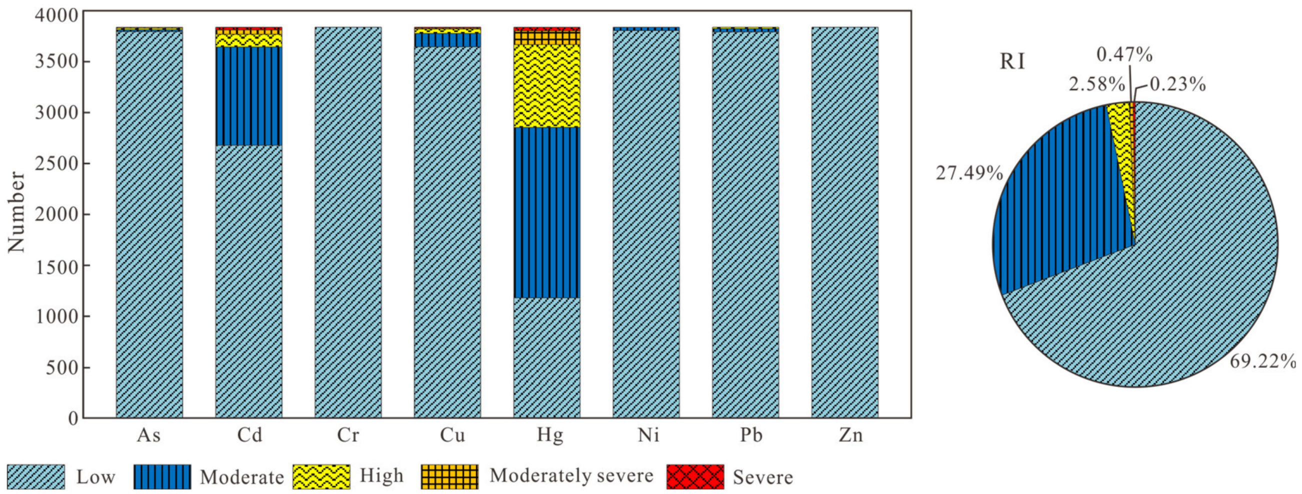

Figure 7. Potential Ecological Risk Classification of Heavy Metals in Surface Soil.

3.6. Source Identification of Heavy Metals

3.6.1. Relationships of Heavy Metal and Environmental Factors

The ANOVA and Pearson correlation analysis were useful tools for testing relationships between the heavy metal concentrations in surface soils and environmental factors. ANOVA was used to compare the mean concentration of heavy metal in soil samples among the land use group and parent material group, and Pearson correlation analysis was used to identify the relationships between the concentrations of heavy metals and topography. Statistically significant differences were observed for total concentrations of heavy metals among five land types and six parent materials, indicating that the land types and parent materials had significant effects on the spatial distribution of heavy metals. The average concentrations of As and Pb in industrial land were significantly higher than that in other land types (Table 8), suggesting that they were mainly influenced by industrial waste. The mean concentrations of Hg surrounding urban, rural settlements and quarries were higher than those of other land types (Table 8), suggesting that it was mainly from automotive exhaust, coal-burning and industrial dust. Furthermore, the average concentrations of Cd, Cu and Zn were higher in industrial land and rural settlements (Table 8), suggesting that the intensive anthropic activities affected the elevated concentrations of these three heavy metals in soils. The mean contents of Cr and Ni in all types land use were lower than the background values in eastern Shandong Province surface soils (Tables 6 and 8), indicating that these two heavy metals were mainly from natural sources.

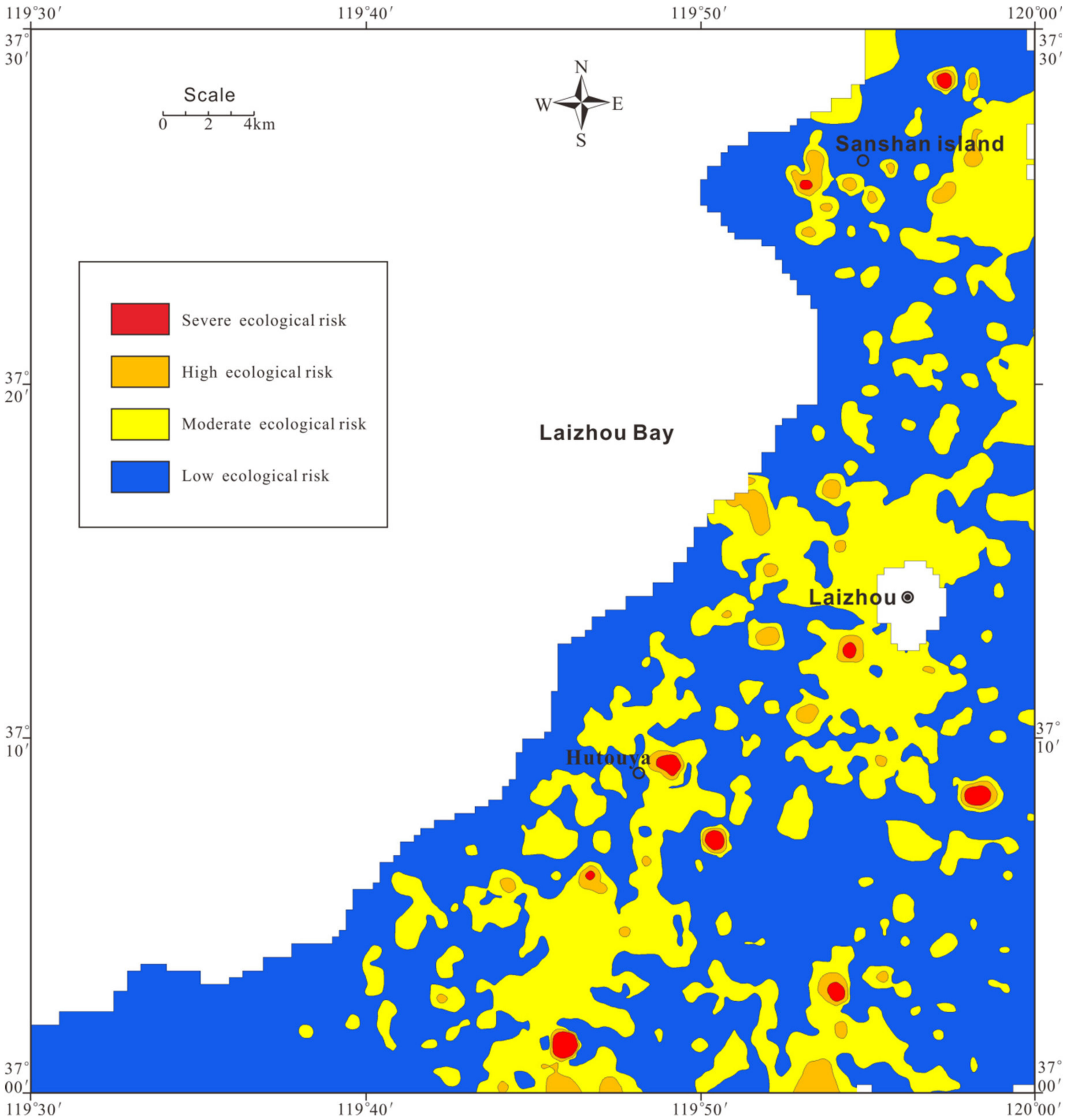

Figure 8. Degree of Composite Potential Ecological Risk of Heavy Metals in Surface Soil.

Table 8. Results of Analysis of Variance (ANOVA) for the Concentration of Heavy Metal in Surface Soils by Land Use and Parent Material Types.

	N	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Farmland	1618	7.30	0.132	44.11	17.87	36.38	17.96	30.00	49.85
Forest	636	6.10	0.121	40.01	17.43	21.81	15.67	28.58	45.18
Industrial Land	261	10.50	0.162	48.77	20.84	63.60	20.63	36.23	56.39
Rural settlement	1191	8.10	0.179	49.29	21.14	59.43	20.57	30.47	55.42
Urban	128	7.50	0.130	49.26	21.40	66.47	21.62	28.12	55.48
	F	57.796 **	5.402 **	23.068 **	7.773 **	16.428 **	30.587 **	16.548 **	13.529 **
Pluvial alluvial sediments	2018	7.58	0.132	38.85	16.25	46.88	15.18	29.31	45.08
Marble and schist	492	7.57	0.142	53.49	20.48	47.79	22.29	27.52	53.08
Granite	69	5.07	0.104	32.61	22.89	18.24	9.40	37.23	56.25
Gneissic granite	464	7.45	0.214	47.64	21.23	33.87	20.03	33.80	62.93
Basite	124	8.32	0.152	68.97	24.75	41.40	30.27	28.54	64.33
Granulite	666	7.68	0.151	55.40	23.96	42.51	24.59	25.08	58.58
	F	5.464 **	5.658 **	127.797 **	23.900 **	1.809 *	174.925 **	15.541 **	39.853 **

* Statistically significant at the 0.05 level, ** Statistically significant at the 0.01 level, Hg is in $\mu g \cdot kg^{-1}$, other heavy metals are in $mg \cdot kg^{-1}$.

The average contents of Cr, Cu, Ni and Zn were higher in soil from basite than those of other parent materials, indicating that their parent material is an influence. As, Cd, Hg and Pb exhibited high level in surface soils due to these soils being mainly covered by the industrial land and urban areas with intensive anthropic input.

The Pearson correlation between As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, and elevation were lower (Table 9), which suggested that the topography has no significant influence on the concentrations of eight heavy metals in Laizhou.

Table 9. Correlation Matrix for Heavy Metals.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Elevation
As	1									
Cd	0.222 **	1								
Cr	0.113 **	0.103 **	1							
Cu	0.254 **	0.313 **	0.409 **	1						
Hg	0.037 *	0.029	0.024	0.023	1					
Ni	0.147 **	0.096 **	0.796 **	0.319 **	0.029	1				
Pb	0.426 **	0.399 **	0.151 **	0.258 **	0.044 **	0.052 **	1			
Zn	0.284 **	0.478 **	0.497 **	0.641 **	0.045 **	0.378 **	0.372 **	1		
Fe	0.235 **	0.079 **	0.677 **	0.366 **	0.032 *	0.783 **	0.029	0.384 **	1	
Elevation	−0.087 **	−0.002	0.168 **	0.083 **	−0.050 **	0.164 **	−0.002 **	0.0145 **	0.275 **	1

* Statistically significant at the 0.05 level (two-tailed), ** Statistically significant at the 0.01 level (two-tailed).

3.6.2. Correlation of Heavy Metals

A high positive correlation between heavy metals may indicate they have similar sources [31,33]. Significantly and positively correlated at the 0.01 level were found between Cr—Ni, Cr–Fe, Cr–Cu, Cr–Zn and Ni–Fe, indicating they might be derived mainly from natural sources due to Fe is influenced slightly by human activities [34,35]. Such results are consistent with the horizontal distribution patterns of heavy metals. There are statistically significant and positive relationships between As and Pb, Cd and Pb, Cd and Zn at the 0.01 level, indicating that they might be derived from similar sources. Hg seems to be an isolate heavy metal, weakly correlated with other metals.

3.6.3. Principal Component Analysis

PCA with a varimax rotation is used to identify the potential pollution sources of heavy metals [34,58,59]. Three principal components with eigenvalues greater than 0.990 (before and rotation) were extracted. The PCA method leads to a reduction of the initial dimension of the dataset to three components explaining 68.483% of the total variability. Based on the correlation analysis results of heavy metals, eigenvalues > 0.990 and the first three principal components covering most of the information of heavy metals, the first three eigenvalues were selected for further analysis and eigenvalues < 0.9 were discarded for identifying sources of heavy metals [35] (Figure 9). The contribution of PC1 is 38.285% (Table 10, Figure 9), showing very high loadings of Cr, Ni and Fe, and moderate loading of Cu and Zn. The PC1 should represent natural sources due to Fe is influenced slightly by human activity [34,35].

The 19.106% of total variance is explained by PC2, and has high loadings in favor of As, Cd, Cu, Pb and Zn (Table 10). According to the spatial distribution of As, Cd and Pb, the highest concentration of these heavy metals occurs in industrial land, rural settlement and urban (Figures 2c and 3). Therefore, PC2 represents industrial and domestic pollution sources. In addition, the similar loading of Cu and Zn observed on PC1 and PC2 suggest that they have a mixed source (Figure 9), being derived from both anthropogenic activities and natural sources.

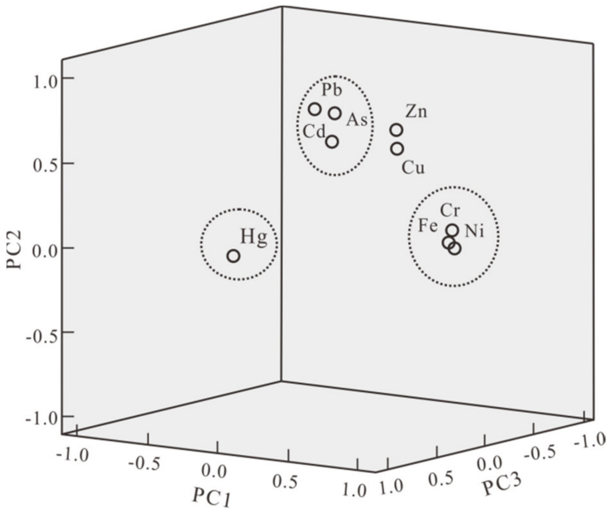

Figure 9. Loading plot of principal components (PCs) for heavy metals in surface soils of the study area using principal component analysis (PCA) after varimax rotation.

Table 10. Loading of surface soil and eigenvalues, percentage of variance, and eigenvectors for the three principal components (PC1, PC2 and PC3).

Parameter	PC1	PC2	PC3
As	0.093	0.599	0.097
Cd	0.004	0.735	−0.045
Cr	0.886	0.144	−0.004
Cu	0.446	0.572	−0.068
Hg	0.024	0.045	0.989
Ni	0.920	0.041	0.024
Pb	−0.054	0.772	0.056
Zn	0.466	0.688	−0.039
Fe	0.882	0.073	0.033
Eigenvalues	3.466	1.720	0.998
Percentage of variances	38.285	19.106	11.092
Cumulative % eigenvectors	38.285	57.391	68.483

The contribution of PC3 is 11.092% and is dominated exclusively by Hg (Table 10, Figure 9). Investigation shown that Hg pollution areas match well with the location of the expressway, peri-urban, rural settlement and quarries. Previous studies reveal that Hg concentrations in surface soils are mainly attributed atmospheric deposition [60–63]. The results of the air pollution monitor show that the concentration of Hg is relatively high in heavily polluted areas (Unpublished data). Hg was derived mainly from the atmospheric pollution, so that PC3 represents the atmospheric deposition pollution.

4. Conclusions

This study examined the distribution of heavy metals in surface soils from Laizhou, Eastern Shandong Province, China. Through analysis of enrichment factor, contamination factor, geo-accumulation index and potential ecological risk index, the surface soils were significantly enriched with As, Cd, Hg and Pb, while the concentrations of Cr, Cu, Ni and Zn were mostly within the normal range. Fractionation analysis results shown that the potential bioavailability of selected heavy metals in surface soils decrease in the order of Cd > As > Cu> Ni > Zn > Cr > Pb > Hg. According to the results of analysis of variance, Pearson correlation and principal component analysis, among the selected heavy metals in surface soil, Cr and Ni originated from parent material, and came from natural source. As, Cd, Hg, Pb were mainly derived from anthropic inputs, and Cu and Zn were derived from the combination of lithogenic nature and anthropogenic activities. Industrial, traffic emission and coal-burning are the main anthropogenic sources of these heavy metals. The results suggest that more attention should be paid to monitoring soil quality in the heavily polluted site.

Author Contributions: Conceptualization, Z.Z. and H.J.; methodology, Z.Z. and H.J.; writing—original draft preparation, Z.Z. and H.J.; writing—review and editing, Z.Z. and T.S.; visualization, Z.Z. and X.Z.; supervision, L.K., S.G., X.H. and Y.L.; funding acquisition, L.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the China Geological Survey (DD20208080).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: We are grateful to four anonymous reviewers and the academic editor for the detailed and constructive comments.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Radwan, E.K.; Kafafy, H.; El-Wakeel, S.T.; Shaheen, T.I.; Gad-Allah, T.A.; El-Kalliny, A.S.; El-Naggar, M.E. Remediation of Cd(II) and reactive red 195 dye in wastewater by nanosized gels of grafted carboxymethyl cellulose. *Cellulose* **2018**, *25*, 6645–6660. [CrossRef]
2. Hossain, M.I.; Soliman, M.M.; El-Naggar, M.E.; Sultan, M.Z.; Kechi, A.; Abdelsalam, N.R.; Abu-Saied, M.A.; Chowdhury, M. Synthesis and characterization of Graphene Oxide-Ammonium Ferric Sulfate composite for the removal of dyes from tannery wastewater. *J. Mater. Res. Technol.* **2021**, *12*, 1715–1727. [CrossRef]
3. Yang, J.C.; Wang, W.G.; Zhao, M.W.; Chen, B.; Dada, O.A.; Chu, Z.H. Spatial distribution and historical trends of heavy metals in the sediments of petroleum producing regions of the Beibu Gulf, China. *Mar. Pollut. Bull.* **2015**, *91*, 87–95. [CrossRef] [PubMed]
4. Dassenakis, M.; Scoullos, M.; Gaitis, A. Trace metals transport and behavior in the Mediterranean estuary of Acheloos river. *Mar. Pollut. Bull.* **1997**, *34*, 103–111. [CrossRef]
5. Bryan, G.W.; Langston, W.J. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: A review. *Environ. Pollut.* **1992**, *76*, 89–131. [CrossRef]
6. Cravotta, C.A., III; Brady, K.B.C. Priority pollutants and associated constituents in untreated and treated discharges from coal mining or processing facilities in Pennsylvania, USA. *Appl. Geochem.* **2015**, *62*, 108–130. [CrossRef]
7. Li, X.X.; Wang, X.L.; Chen, Y.D.; Yang, X.Y.; Cui, Z.J. Optimization of combined phytoremediation for heavy metal contaminated mine tailings by a field-scale orthogonal experiment. *Ecotoxicol. Environ. Saf.* **2019**, *168*, 1–8. [CrossRef] [PubMed]
8. Olawoyin, R.; Oyewole, S.A.; Grayson, R.L. Potential risk effect from elevated levels of soil heavy metals on human health in the Niger delta. *Ecotoxicol. Environ. Saf.* **2012**, *85*, 120–130. [CrossRef]
9. Cao, H.C.; Luan, Z.Q.; Wang, J.D.; Zhang, X.L. Potential ecological risk of cadmium, lead and arsenic in agricultural black soil in Jilin Province, China. *Stoch. Environ. Res. Risk Assess.* **2009**, *23*, 57–64. [CrossRef]
10. Gu, J.G.; Lin, Q.Q.; Hu, R.; Zhu, Y.P.; Zhou, Q.X. Heavy metals pollution in soil-plant and its research prospect. *Chin. J. Soil Sci.* **2005**, *36*, 128–133.
11. Margin, M.; Rossier, D.; Crettaz, P.; Jolliet, O. Life cycle impact assessment of pesticides on human health and ecosystems. *Agric. Ecosyst. Environ.* **2002**, *93*, 379–392. [CrossRef]
12. McLaughlin, M.J.; Parker, D.R.; Clarke, J.M. Metals and micronutrients-food safety issues. *Field Crops Res.* **1999**, *60*, 143–163. [CrossRef]
13. Cai, K.; Duan, Y.M.; Luan, W.L.; Li, Q.; Ma, Y.C. Geochemical behavior of heavy metals Pb and Hg in the farmland soil of Hebei plain. *Geol. China* **2016**, *43*, 1420–1428.
14. Wong, S.C.; Li, X.D.; Zhang, G.; Qi, S.H.; Min, Y.S. Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environ. Pollut.* **2002**, *119*, 33–44. [CrossRef]
15. Zeng, S.Y.; Yu, H.C.; Ma, J.; Liu, J.N.; Chen, F. Identifying the Status of Heavy Metal Pollution of Cultivated Land for Tradeoff Spatial Fallow in China. *Acta Pedol. Sin.* **2021**, in press.
16. Song, W.; Chen, B.M.; Liu, L. Soil heavy metal pollution of cultivated land in China. *Res. Soil Water Conserv.* **2013**, *20*, 293–298.
17. Dai, J.R.; Pang, X.G.; Song, J.H.; Dong, J.; Hu, X.P.; Li, X.P. A study of geochemical characteristics and ecological risk of elements in soil of urban and suburban areas of Zibo City, Shandong Province. *Geol. China* **2018**, *45*, 617–627.
18. Zhang, L.; Song, F.B.; Wang, X.B. Heavy metal contamination of urban soils in China: Status and countermeasures. *Ecol. Environ.* **2004**, *13*, 258–260.

19. Yao, D.; Sun, M.; Yang, F.; Jiang, H.Y.; Li, G.S.; Ding, C.X. Environmental geochemistry of heavy metals in urban soils of Qingdao City. *Geol. China* **2008**, *35*, 539–550.
20. Zhao, Y.F.; Shi, X.Z.; Huang, B.; Yu, D.S.; Wang, H.J.; Sun, W.X.; Oboern, I.; Blomback, K. Spatial Distribution of Heavy Metals in Agricultural Soils of an Industry-Based Peri-Urban Area in Wuxi, China. *Pedosphere* **2007**, *17*, 44–51. [CrossRef]
21. Sun, Z.H.; Xie, X.D.; Wang, P.; Hu, Y.N.; Cheng, H.F. Heavy metal pollution caused by small-scale metal ore mining activities: A case study from a polymetallic mine in South China. *Sci. Total Environ.* **2018**, *639*, 217–227. [CrossRef]
22. Cheng, H.F.; Hu, Y.N.; Luo, J.; Xu, B.; Zhao, J.F. Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. *J. Hazard. Mater.* **2009**, *165*, 13–26. [CrossRef]
23. Zhuang, P.; Zou, B.; Li, N.Y.; Li, Z.A. Heavy metal contamination in soils and food crops around Dabaoshan mine in Guangdong, China: Implication for human health. *Environ. Geochem. Health* **2009**, *31*, 707–715. [CrossRef]
24. Szatyłowicza, E.; Krasowskab, M. Assessment of heavy metals leaching from fly ashes as an indicator of their agricultural use. *Desalin. Water Treat.* **2000**, *199*, 288–296. [CrossRef]
25. Ye, M.H.; Yuan, X.Y.; Li, G.P.; Wan, J.; Xu, J. Distribution and ecological risk assessment of nutrient elements in surface sediments of Jianxi Watershed in northern Fujian. *Environ. Chem.* **2018**, *37*, 2481–2488.
26. Ye, M.H.; Yuan, X.Y.; Zhou, R.; Wan, J.; Xu, J. Distribution and environmental significance of phosphorus forms in riparian soils and river sediments of Jianxi Basin, Fujian province. *Pol. J. Environ. Stud.* **2017**, *26*, 2331–2341. [CrossRef]
27. Li, J.F.; Qu, M.K.; Huang, B.; Liu, G.; Zhao, Y.C.; Sun, W.X.; Hu, W.Y. Spatially non-stationnary relationships between cation exchange capacity and related control factors. *Acta Pedol. Sin.* **2017**, *54*, 638–646.
28. Cui, X.W.; Geng, Y.; Sun, R.R.; Xie, M.; Feng, X.W.; Li, X.X.; Cui, Z.J. Distribution, speciation and ecological risk assessment of heavy metals in Jinan Iron & Steel Group soils from China. *J. Clean Prod.* **2021**, *295*, 1–9.
29. Wen, Z.; Li, J.; Wang, X.; Zhang, X.X. Fractionation and Environmental Assessment of Heavy Metals in Sewage Sludge from Municipal Wastewater Treatment Plants of Guizhou Province. *China Rural. Water Hydropower* **2016**, *12*, 67–78.
30. Arain, M.B.; Kazi, T.G.; Jamali, M.K.; Jalbani, N.; Afridi, H.I.; Baig, J.A. Speciation of heavy metals in sediment by conventional, ultrasound and microwave assisted single extraction methods: A comparison with modified sequential extraction procedure. *J. Hazard. Mater.* **2008**, *154*, 998–1006. [CrossRef]
31. José, M.N.; José, P.H.; Sergi, D. Assessment of heavy metal pollution, spatial distribution and origin in agricultural soils along the Sinú River Basin, Colombia. *Environ. Res.* **2017**, *154*, 380–388.
32. Taylor, S.R. Abundance of chemical elements in the continental crust: A new table. *Geochim. Cosmochim. Acta* **1964**, *28*, 1272–1285. [CrossRef]
33. Lv, J.S.; Liu, Y.; Zhang, Z.L.; Dai, J.R.; Dai, B.; Zhu, Y.C. Identifying the origins and spatial distributions of heavy metals in soils of Ju country (Eastern China) using multivariate and geostatistical approach. *J. Soils Sediments* **2015**, *15*, 163–178. [CrossRef]
34. Fang, G.C.; Wu, Y.S.; Chang, S.Y.; Huang, S.H.; Rau, J.Y. Size distributions of ambient air particles and enrichment factor analyses of metallic elements at Taichung Harbor near the Taiwan Strait. *Atmos. Res.* **2006**, *81*, 320–333. [CrossRef]
35. Kartal, S.; Aydin, Z.; Tokalioglu, S. Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data. *J. Hazard. Mater.* **2006**, *132*, 80–89. [CrossRef]
36. Dai, J.R.; Pang, X.G.; Yu, C.; Wang, C.L.; Wang, Z.H.; Hu, X.P. Geochemical baselines and background values and element enrichment characteristics in soils in eastern Shandong Province. *Geochimica* **2011**, *40*, 577–587.
37. Sutherland, R.A. Bed sediment -associated trace metals in an Urban stream, Oahu, Hawaii. *Environ. Geo.* **2000**, *39*, 611–627. [CrossRef]
38. Fan, X.T.; Jiang, Y.X.; Cui, B.; Chao, S.H.; Zhu, M.L.; Zeng, X.C.; Liu, J.W.; Cao, H.B. Selection of a reference element for enrichment factor: A case study on the pollution evaluation of heavy metals in the sediment of Yuan River. *Acta Sci. Circumstantiae* **2016**, *36*, 3795–3803.
39. Szefer, P.; Glasby, G.P.; Sefer, K.; Pempkowiak, J.; Kaliszan, R. Heavy-metal pollution in superficial sediments from the southern Baltic Sea off Poland. *J. Environ. Sci. Health* **1996**, *31*, 2723–2754.
40. Jiang, Y.F.; Wang, X.T.; Wu, M.H.; Sheng, G.Y.; Fu, J.M. Contamination, source identification, and risk assessment of polycyclic aromatic hydrocarbons in agricultural soil of Shanghai, China. *Environ. Monit. Assess.* **2011**, *183*, 139–150. [CrossRef]
41. Muller, G. Index of geoaccumulation in sediments of the Rhine River. *Geojournal* **1969**, *2*, 108–118.
42. Muller, G. Schwermetalle in den sediments des Rheins-Veranderungen seitt 1971. *Umschau* **1979**, *79*, 778–783.
43. Stoffers, P.; Glasby, G.P.; Wilson, C.J. Heavy metals pollution in Wellington harbour. *N. Z. J. Mar. Fresh.* **1986**, *20*, 495–512. [CrossRef]
44. Forstner, U.; Ahlf, W.; Calmano, W. Sediment quality objectives and criteria development in Germany. *Water Sci. Technol.* **1993**, *28*, 307–314. [CrossRef]
45. Guo, W.H.; Liu, X.B.; Liu, Z.G.; Li, G.F. Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. *Procedia Environ. Sci.* **2010**, *2*, 729–736. [CrossRef]
46. Hakanson, L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res.* **1980**, *14*, 975–1001. [CrossRef]
47. Xu, Z.Q.; Ni, S.J.; Tuo, X.G.; Zhang, C.J. Calculat ion of Heavy Metals'Toxicity Coefficient in the Evaluat ion of Potent ial Ecological Risk Index. *Environ. Sci. Technol.* **2008**, *31*, 112–115.

48. Bao, L.R.; Deng, H.; Jia, Z.M.; Li, Y.; Dong, J.X.; Yan, M.S.; Zhang, F.L. Ecological and health risk assessment of heavy metals in farmland soil in northwest Xiushan, Chongqing. *Geol. China* **2020**, *47*, 1625–1636.
49. Diagboya, P.N.; Olu-Owolabi, B.I.; Adebowale, K.O. Distribution and interactions of pentachlorophenol in soils: The roles of soil iron oxides and organic matter. *J. Contam. Hydrol.* **2016**, *191*, 99–106. [CrossRef]
50. Mellor, A.; Bevan, J.R. Lead in the soils and stream sediments of an urban catchment in Tyneside, UK. *Water Air Soil Pollut.* **1999**, *112*, 327–348. [CrossRef]
51. Han, C.M.; Wang, L.S.; Gong, Z.Q.; Xu, H.X. Chemical forms of soils heavy metal and their environmental significance. *Chin. J. Ecol.* **2005**, *24*, 1499–1502.
52. He, Y.S. Pollution characteristics and ecological risk assessment of heavy metals in Haikou urban soil. *Chin. J. Ecol.* **2014**, *33*, 421–428.
53. Sun, J.L.; Wu, W.J.; Zhao, R.X.; Zhang, X.X. Studies on pollution of heavy metals in soils and technology of plant remediation. *J. Chang. Univ. Sci. Technol.* **2003**, *26*, 46–48.
54. Wu, X.M.; Pan, G.X. The correlation analysis between the content of heavy metals and the factor influencing the pollution of heavy metals in urban soils in Nanjing city. *Acta Pedol. Sin.* **2003**, *40*, 921–928.
55. Yang, Y.G.; Pateson, E.; Campbell, C. Environment effects of heavy mental accumulation in urban soils by application of Biolog method. *Geochimica* **2001**, *30*, 459–464.
56. Shibini, M.P.A.; Sujiatha, C.H. Distribution and geochemical speciation of sediment bound heavy metals in the specific zones of central Kerala, India. *Environ. Nanotechnol. Monit. Manag.* **2020**, *14*, 1–10. [CrossRef]
57. Ilyas, S.; Lee, J.; Kim, B. Bioremoval of heavy metals from recycling industry electronic waste by a consortium of moderate thermophiles: Process development and optimization. *J. Clean Prod.* **2014**, *70*, 194–202. [CrossRef]
58. Qiu, J.D.; Liu, J.Q.; Li, M.N.; Wang, S.; Bai, W.M.; Zhang, D.L. Assessment of heavy metal contamination in surface sediments from the nearshore zone, southern Jiangsu Province, China. *Mar. Pollut. Bull.* **2018**, *133*, 281–288. [CrossRef]
59. Winner, D.A.; Cass, G.R. Modeling the long-term frequency distribution of regional ozone concentrations using synthetic meteorology. *Environ. Sci. Technol.* **2001**, *35*, 1191–1200. [CrossRef] [PubMed]
60. Landis, M.S.; Keeler, G.J.; Al-Wali, K.I.; Stevens, R.K. Divalent inorganic reactive gaseous mercury emissions from a mercury cell chlor-alkali plant and its impact on near-field atmospheric dry deposition. *Atmos. Environ.* **2004**, *38*, 613–622. [CrossRef]
61. Heckel, P.F.; Lemasters, G.K. The Use of AERMOD Air Pollution Dispersion Models to Estimate Residential Ambient Concentrations of Elemental Mercury. *Water Air Soil Pollut.* **2011**, *219*, 377–388. [CrossRef]
62. Sun, G.Y.; Li, Z.G.; Bi, X.Y.; Chen, Y.P.; Lu, S.F. Distribution, sources and health risk assessment of mercury in kindergarten dust. *Atmos. Environ.* **2013**, *73*, 169–176. [CrossRef]
63. Garcia, G.F.; Alvarez, H.B.; Echeverria, R.S.; Alba, S.R.; Rueda, V.M.; Dosantos, E.C.; Cruz, G.V. Spatial and temporal variability of atmospheric mercury concentrations emitted from a coal-fired power plant in Mexico. *J. Air Waste Manag. Assoc.* **2017**, *67*, 973–985. [CrossRef]