



Geochemical baseline establishment, pollution level and health risk assessment of soil heavy metals in the upper Xiaowen River Basin, Shandong Province, China

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Abstract This study analyzed the distribution and content of eight heavy metals (Cu, Pb, Zn, Ni, Cr, As, Cd, and Hg) in 221 surface soil samples from the upper reaches of the Xiaowen River. Environmental geochemical baselines were established for the eight heavy metals, and the pollution status was assessed on the basis of these baselines and the soil background value of Weifang City. The calculation results of Nemerow pollution index and the potential ecological hazard index (PEHI)- R_i showed that the overall pollution degree and ecological hazard in the study area were at a slight level. 49% (calculated by baseline value) and 24% (calculated by background value

of Weifang City) samples were at moderate or above pollution level. 9% (calculated by baseline value) and 42% (calculated by background value) samples were at the level of moderate potential ecological hazards or above. According to the calculation results of I_{geo} and PEHI- E_i , the main pollutant in the study area was Hg, followed by Cd. 3% (calculated by baseline value) and 12% (calculated by background value) of Hg samples were at moderate or above contamination levels. 5% (calculated by baseline value) and 38% (calculated by background value) of Hg samples were at the level of strong potential ecological hazard or above. The western, central, and eastern parts of the study area were mainly the primary areas of pollution and ecological hazards. The non-carcinogenic risk was at an acceptable level, the carcinogenic risk was at a tolerable level, and the main risk pathway was oral intake, with Cr being the main contributor. Source apportionment indicated that soil heavy metals primarily originate from soil parent material, transportation, agricultural fertilization, and industrial emissions (waste gas, waste water and solid waste).

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Introduction

Soil is a major component of the human environment, serving as the foundation for agriculture. The safety of agricultural products is affected by many factors, including soil heavy metal pollution. Heavy metals are a type of ubiquitous pollutants that not only lead to decreased yield, but also affect the quality of crops and endanger human health. Therefore, heavy metal pollution of agricultural soil has been consistently been a hot topic.

At present, research on soil heavy metals is focused on pollution assessment, health risk assessment, and source apportionment. Soil heavy metal contamination has been assessed using a variety of methodologies, including the single factor pollution index (SFPI), geo-accumulation index (I_{geo}), and Nemerow pollution index. For example, Dina et al. (2023) evaluated soil pollution in Vienna, Austria, using SFPI and reported that the SFPI value exhibited a gradient along the city, with higher concentrations of Pb, Cu, Zn, and Sr in urban and suburban areas compared to the countryside. In contrast, the contamination levels of Zn, Cu, Cr, Pb, and Ni were low. Furthermore, the source of metal pollution in Vienna was found to be anthropogenic contamination, with transportation exhaust potentially being the primary contributor. In order to prevent further soil degradation in Beijing, Zou et al. (2018) collected samples from the suburbs and evaluated the contamination level using the Nemerow pollution index. Only 3% of the samples were found to be slightly contaminated and affected by human beings, and some areas had relatively high levels of Cd and Hg pollution. Therefore, farmland soil in the suburbs of Beijing was designated to be suitable for cultivation, but attention should be paid to the levels of Cd and Hg. Wang et al. (2018) analyzed the deposition fluxes of 50 heavy metals in atmospheric dust in Zhuzhou City using the composite pollution index and pointed out that atmospheric dust is likely to cause heavy metal pollution in soil. The largest pollutant was Cd, followed by Pb, As, and Hg, which Cr was at a safe level, mainly from natural sources. Heavy metal pollution poses major ecological risks in urban agriculture. A study using the Nemerow pollution index reported a very high level of pollution in 60% of agricultural soil samples from Yaounde, Cameroon (Amina et al., 2021). The potential

ecological hazard index (PEHI) has been used to assess possible ecological dangers. According to the PEHI of soil near a coal mine in Tai'an City, the principal pollutants were found to be Cd and Hg, with Cd being the primary contributor (Yan et al., 2022).

As industrial and agricultural production increase, human activities are exerting increasingly more serious effects on soil. If the soil standard is unified for a large area, the phenomenon of 'over protection' or 'pre-protection' is likely to occur in the evaluation and treatment of pollution (Sun et al., 2019). Therefore, the concept of geochemical environmental geochemical baseline value was introduced for pollution and ecological risk assessment. The environmental geochemical baseline for soil considers the effects of human activity on the environment in addition to reflecting the outcomes of the natural geochemical evolution. Unlike the large-scale soil background value, the environmental geochemical baseline reveals the influence of human production and life on chemical substances in the local soil (Fan et al., 2021). For example, in order to explain the relationship between the chemical composition of surface soil and potential pollution sources, Ana et al. (2021) determined the environmental geochemical baseline of the O'Higgins area in Chile; the eastern part of O'Higgins features major Cu–Mo deposits. The results show that the basement lithology controls the distribution of most major elements and some trace elements. The primary sources of pollution in the study area were found to be the extraction of Cu, metal alloys, and oil combustion. In addition to vehicle fuel combustion, pesticide and fertilizer use in agricultural soils could also be tracked. Wang et al. (2022) established the geochemical baseline values of 46 elements in the soil of the Bayan Obo mining area in Inner Mongolia, China, by combining the soil geochemical baseline values calculated using a standardization method and the relative cumulative frequency curve method. Owing to the complex geological processes in the mining area, the geochemical baseline values of most elements were higher than the average values of soil elements determined using various methods in the literature. Heavy metals in soil can have positive or negative effects on human health through various exposure pathways (skin contact, nasal inhalation, oral intake, etc.). The health risk assessment model released by the US EPA has been used to provide reference for

rational planning and utilization of soil and residents' health. Qi et al. (2023) analyzed the potential of the non-ferrous metal smelting industry in heavy metal pollution and endangering human health by collecting surface soil samples from a smelting area. They reported that human activity has led to Zn, Cd, Cu, Pb, and As pollution in the vicinity of the non-ferrous metal smelting area, with high exposure risk for adults. Source analysis can be performed to avoid and control pollution from the source, and the rational use of principal component and correlation analysis is more convenient for identifying the source. Chang et al. (2023) evaluated the pollution of farmland soil around a pyrite waste residue pile in southern Sichuan by combining PEHI and I_{geo} . Their results showed that Ni and Cr in the farmland soil primarily originate from the soil parent material, with runoff and leaching as the primary mechanisms of Cr, Cd, Pb, and As entering the soil from the waste pile. Moreover, atmospheric deposition and diffusion of dust produced by the waste pile affected the nearby soil. Therefore, they suggested urgent risk management and control of the pyrite waste pile, as well as restoration and repair of the nearby damaged agricultural area.

The upper reaches of the Xiaowen river in Shandong Province represent an important area for agricultural production. Considering the susceptibility of crop yield and residents' health to the enrichment of heavy metals in soil, a wide range of extensive research has been carried out in this area. However, the degree of research has been low, and the methods used have been relatively simple. Based on the investigation of element content, ArcGIS has been used to generate a spatial distribution map, and I_{geo} has been used to evaluate pollution. It was pointed out that most of the soil in Weifang City is not polluted by heavy metals, but local pollution was observed in some areas. For example, a correlation was observed between Cu–Cr–Ni pollution, which was concentrated at the junction of Qingzhou-Linqu-Changle and Anqiu-Zhucheng (Liu et al., 2016). Eight heavy metal elements such as Cd and Hg were tested and analyzed by means of geoscience statistics and multivariate statistics. The content of Cd, Hg, and As in Anqiu City, Shandong Province (average value) is equivalent to the soil background value of Weifang City, and the content of other elements (average value) is slightly higher than the soil background

value of Weifang City, all of which are below the risk screening value of each element (Zhao et al., 2020). However, pollution in the upper reaches of the Xiaowen River has not been evaluated thus far. Therefore, it is necessary to carry out a detailed study of the upper reaches of the Xiaowen River.

In this study, the environmental geochemical baseline value and the background value of Weifang City were used for comparative evaluation. This method is more suitable for local agricultural planting and factory planning, thus ensuring more objective evaluation. In order to determine the pollution of heavy metal elements in soil and its risks to human health in the study area, based on high-density sampling, the geochemical baseline values of soil in the upper reaches of the Xiaowen River were determined, and pollution was evaluated using I_{geo} and the Nemerow pollution index. Potential ecological hazard assessment was carried out, and the evaluation results were spatially characterized using ArcGIS. The non-carcinogenic and carcinogenic risks were analyzed, and source analysis was performed to provide a reference for soil management and maintaining the safety of residents' health.

Materials and methods

Overview of the study area

The upper reaches of the Xiaowen River are located west of Weifang City in the middle of the Shandong Peninsula (Fig. 1). The average annual temperature is 12.3 °C, precipitation is 792.5 mm, and evaporation is 1912 mm. The average sunlight duration has been 2367.9 h over the years. The research region is traversed by the Weifang-Rizhao Expressway (G1815) in a northwest–southeast direction and by Shandong 102 Provincial Highway (S102) in an east–west direction. The industrial cluster in the research area predominantly involves food processing, packaging, and shipping of watermelon, strawberry, and asparagus crops. Before 1962, the source of the Xiaowen River was Daicunba. In 1962, the channel above Caoying of the Quanhe River was diverted into the Xiaowen River, and the two upstream branches in the northern part of the Quanhe River became the upstream of the Xiaowen River.

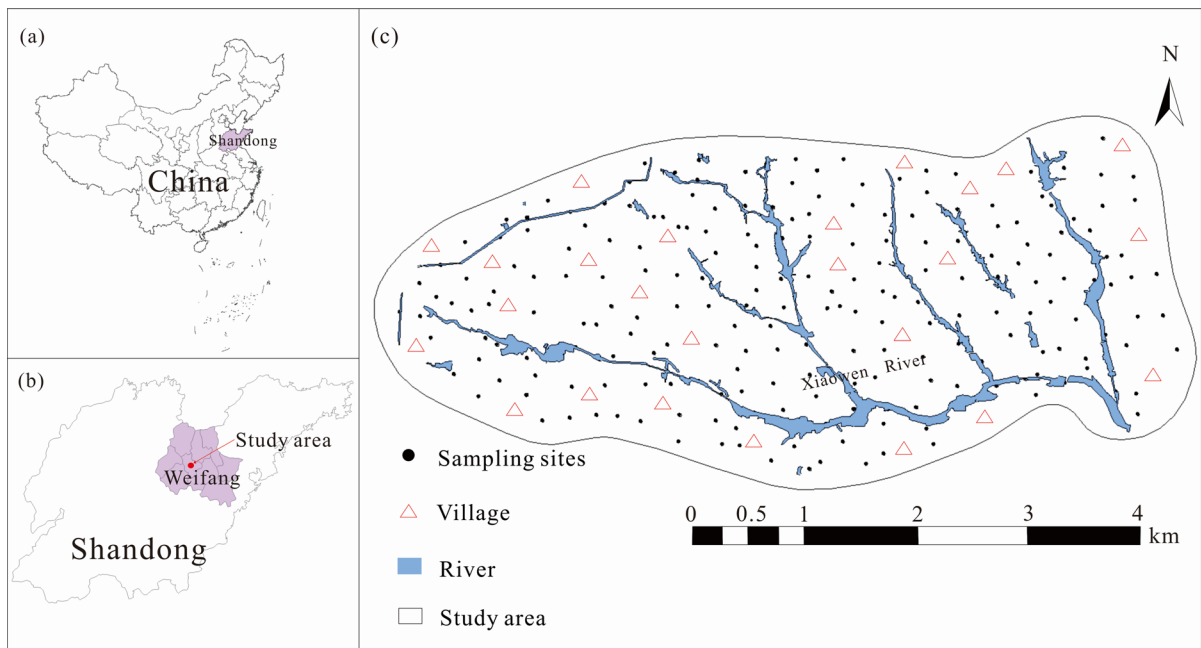


Fig. 1 Location map of the study area

Soil sample collection, processing and analysis

The soil surface sampling points were arranged in a grid on a 1:50,000 land use status map, and the sampling points are laid out in a grid pattern in units of 1 km², with an average soil sample sampling density of 5 pieces/km². Sampling points were set with a radius of 20–50 m, and the center point was determined using GPS. Soil samples were taken from 0 to 20 cm of the soil layer, and 2–6 sub-samples were combined in equal quantities to form a mixed sample. The soil of each sampling point was broken, and roots, straws, stones, worms, and other impurities were removed. After fully mixing, 1–1.5 kg of the sample was retained using the quartering method and placed in a sample bag. Repeated sampling was performed for different groups at different times. In the process of repeated sampling, the hole position of the first sampling was located first, and the second sampling was carried out in the range of 50–100 cm from the first sampling point following the same method as that for the first sample. The weight of the original sample was greater than 1500 g. Cu, Pb, Zn, Ni, Cr and V were analyzed using the X-ray fluorescence spectrometry (XRF). The standard curve constants and matrix correction coefficients

were obtained by regression of a series of standard samples, which were prepared using the powder pressure cake method, and the interference and matrix effect were corrected using the background subtraction method. The elements were using the computer automatic correction. As and Hg were analyzed using the atomic fluorescence spectrometry (AFS). The sample was decomposed with aqua regia, extracted with 50% HCl. In 10% HCl medium, the soil samples were determined with thiourea as a pre-reducing agent and potassium borohydride as a reducing agent. Cd was analyzed using the inductively coupled plasma mass spectrometry (ICP-MS). After decomposition by HF, HNO₃ and HClO₄, fluorine removal, HNO₃ extraction, and determine capacity, the working curve was prepared using a mixed standard, and the soil samples were determined using a plasma mass spectrometer with 2% HNO₃ solution. In order to ensure strict quality control, standard substances were added into every 50 samples, and the accuracy and precision were calculated, requiring accuracy ≤ 0.10 and precision ≤ 0.17 . The accuracy of each element was calculated to be 0.0017–0.0095, and the precision was calculated to be 0.038–0.063. 1 piece of replicate was inserted into every 50 samples, and the relative deviation (RD) between the original

analytical data and the reproducibility test data was calculated, requiring $RD \leq 40\%$, and the qualification rate was required to be greater than 95%. The relative deviation (RD) between the original analytical data and the repeatability test data was calculated, and the RD was required to be $\leq 40\%$, and the pass rate was required to be greater than 95%. The pass rate of each element was calculated to be more than 97%. The accuracy, precision and relative deviation are in accordance with the quality inspection requirements of the Specification for Geochemical Evaluation of Land Quality (DZ/T0295-2016).

Establishment of the environmental geochemical baseline

The reference element standardization method is used to select an appropriate inert element as the standard factor to perform linear fitting with the active element, and the inert element content is used to assess the enrichment level of the active element. This method is widely used to eliminate the influence of soil particle size and other factors on element content to a certain extent (Lu et al., 2018). The linear regression equation of the two was constructed under the 95% confidence level test based on the correlation between active elements (pollution elements) and inert elements (standard elements), which is the baseline model:

$$C_m = aC_n + b \tag{1}$$

where C_m represents the measured concentration of active elements, C_n represents the measured concentration of inert elements, and a and b are regression constants. Samples that fall within the 95% confidence interval are considered to be uncontaminated and can be used as data points to establish the regression equation when determining the geochemical baseline. In contrast, samples that fall outside the 95% confidence interval are considered to be artificially contaminated and should be disregarded when establishing the regression equation.

Calculations were made for the regression constants a and b . The average anticipated value of active elements B_{mm} , that is, the average content of inert elements in the research region, may be derived:

$$B_{mm} = a\bar{C}_n + b \tag{2}$$

where B_{mm} represents the baseline of element m , and \bar{C}_n represents the average content of standard elements. When using the standardized method to determine the geochemical baseline, the standard elements must be selected first. Previous studies mostly used Al, Fe, Ti, V, Se, Li, La, etc., as reference elements.

Heavy metal pollution assessment

Among many soil pollutants, heavy metals are one of the most influential, which can be determined through comparison with the reference value. Therefore, it is very important to select appropriate parameters. In this study, the background value of Weifang City (Cd 0.081 mg/kg, Hg 0.015 mg/kg, As 8.1 mg/kg, Pb 20.3 mg/kg, Cr 65 mg/kg, Cu 0.1 mg/kg, Ni 27.7 mg/kg, Zn 52.8 mg/kg) and the environmental geochemistry baseline were used as the reference values of I_{geo} . The Nemerow pollution index was used to evaluate the pollution status, and the PEHI level was determined.

Geo-accumulation index (I_{geo})

I_{geo} , which was first proposed by the German scientist Müller (1969), was used to assess the level of pollution of each element. It was initially used for the quantification of heavy metals in sediments and then applied to the evaluation of heavy metals in soil. Most of the previous evaluation methods considered the environmental geochemical background value and human pollution, ignoring background value changes caused by diagenesis. In I_{geo} , changes in the background value caused by rock differences are taken into consideration. The formula for calculating I_{geo} is as follows:

$$I_{geo} = \log_2(C_i/K \times C_{Bi}) \tag{3}$$

where C_i is the measured value of “ i ” (mg/kg). K , which is typically used to characterize sedimentary characteristics and other effects, is the correction coefficient of background value change produced by soil rock difference. It typically takes 1.5. C_{Bi} is the background value of “ i ” (mg/kg), with the geochemical baseline value and the soil background

value of Weifang City as the reference values. I_{geo} is the geo-accumulation index of "i." I_{geo} is divided into seven levels (Table S1).

Nemerow pollution index

In "Scientific Analysis of River Pollution," American scholar Nemerow proposed a pollution index for a thorough assessment of pollution levels in a study area, taking into account the weighted multi-factor environmental quality index for the most serious pollution factor (highlighting the maximum value). The equation for calculating the Nemerow pollution index is as follows (Haque et al., 2020):

$$P_i = \frac{C_i}{S_i} \quad (4)$$

$$P_N = \sqrt{\frac{(P_{I_{ave}})^2 + (P_{I_{max}})^2}{2}} \quad (5)$$

where P_N is the Nemerow pollution index, $P_{i_{ave}}$ is the average value of each heavy metal pollution index, and $P_{i_{max}}$ is the maximum value. The grading standards are shown in Supplementary Table S2.

Potential ecological hazard index (PEHI)

In 1980, Swedish scientist Lars Hakanson (Sun et al., 2021) proposed the use of PEHI to carry out ecological risk assessment. Based on the characteristics of heavy metal properties and environmental behavior, the concentration of heavy metals is combined with environmental studies and toxicology to evaluate the potential risks of metal pollutants in sediments and soils to organisms. The calculation formula is as follows:

$$P_i = \frac{C_i}{C_{Bi}} \quad (6)$$

$$E_i = T_i \times P_i \quad (7)$$

$$R_i = \sum_1^n E_i \quad (8)$$

where P_i is the single factor pollution index of heavy metals; C_{Bi} is the background value of heavy metal

element "i" (mg/kg). T_i is the toxicity coefficient of a given heavy metal "i" (Cd (30), Hg (40), As (10), Pb (5), Cr (2), Cu (5), Ni (5), Zn (1)); E_i is the PEHI of a single element; R_i is the comprehensive PEHI. PEHI is divided into five grades according to E_i and R_i (Table S3).

Health risk model

The health risk assessment model proposed by the US EPA was used for evaluation (USEPA, 2001). It is characterized by the non-carcinogenic risk index (HI) and carcinogenic risk index (CRI), and the following pathways of exposure are considered: skin contact, oral and nasal inhalation, and oral intake.

Exposure calculation

The calculation methods of the daily average exposure of heavy metals through oral intake, oral and nasal inhalation, and skin contact are as follows:

$$ADD_{ing} = \frac{C_s \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (9)$$

$$ADD_{inh} = \frac{C_s \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (10)$$

$$ADD_{dermal} = \frac{C_s \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (11)$$

where ADD_{ing} , ADD_{inh} , and ADD_{dermal} are the average daily exposure of heavy metals through oral intake, inhalation, and skin contact, respectively [$mg/(kg \cdot day)^{-1}$]. C_s is the content of heavy metals in soil (mg/kg). The other parameters are shown in Supplementary Table S4.

Health risk characterization

HI is the sum of the non-carcinogenic risk quotient (HQ) attributable to different exposure pathways. HQ is the ratio of the average daily exposure dose (ADD) to the corresponding reference dose (RfD) of a heavy metal under various exposure pathways (Table S5). THI is the total HI of each heavy metals through various exposure pathways. The calculation equations for HQ, HI, and THI are as follows:

$$HI = \sum HQ_i = \sum \frac{ADD_i}{RfD_i} \tag{12}$$

$$THI = \sum HI \tag{13}$$

THI or HI values less than 1 indicate acceptable levels for the human body, whereas THI or HI values greater than 1 indicate significant risks, with larger values reflecting higher risks.

The carcinogenic risk is characterized by CRI, which is calculated by the sum of the carcinogenic risk quotient (CR) attributable to different exposure routes. CR is the product of the daily average ADD of each exposure route and the corresponding slope factor (SF) (Table S5). The total carcinogenic risk index (TCRI) is the combination of the CRI of heavy metals through various exposure pathways. CRI, CR, and TCRI are calculated as follows:

$$CRI = \sum CR_i = \sum ADD_i \times SF_i \tag{14}$$

$$TCRI = \sum CRI \tag{15}$$

TCRI or $CRI < 10^{-6}$ indicates no carcinogenic risk, $10^{-6} < TCRI$ or $CRI < 10^{-4}$ indicates tolerable carcinogenic risk for humans and $TCRI$ or $CRI > 10^{-4}$ indicates intolerable carcinogenic risk for humans.

Data statistics and analysis

The statistical analysis of content was executed in Excel and IBM SPSS software. At the same time, ArcMap, Origin, and CorelDRAW were used to construct data charts.

Results and discussion

Descriptive statistics

The average content of each element is as follows: Cr (55.17) > Zn (52.03) > Pb (23.38) > Ni (22.15) > Cu (17.01) > As (7.43) > Cd (0.11) > Hg (0.03) mg/kg, among which the contents of Pb, Cd, and Hg were higher than the soil background values of Weifang City (Table 1). When comparing the average contents, because the data dimensions are different, it is not appropriate to use the standard deviation directly. Therefore, the coefficient of variation was introduced. The coefficient of variation is a normalized measure of the degree of dispersion of the probability distribution. It is defined as the ratio of the standard deviation to the mean value, which is meaningful only when the mean value is not zero. The grading standard is as follows: $C_v < 0.1$ indicates weak variability; $0.1 < C_v < 1$ indicates moderate variability; $C_v > 1$ indicates strong variability. All 8 heavy metals showed moderate variability, with Hg (0.63) > Cu (0.46) > Cd (0.4) > As (0.26) > Pb (0.24) = Ni (0.24) = Zn (0.24) > Cr (0.21), indicating that soil heavy metals were affected by human activities (Table 1). The coefficients of variation of Hg, Cu, and Cd were relatively large, which may indicate the risk of pollution. Accordingly, soil pollution was evaluated.

Establishment of the environmental geochemical baseline

The samples within the 95% confidence interval of the measured values of Cu, Pb, Zn, Ni, Cr, As, Cd, and Hg were used as baseline samples. The regression baseline model of active components and standard components was determined through linear regression analysis, and the geochemical baseline values were obtained (Table 2). In this study, V was

Table 1 Descriptive statistics of soil heavy metals in the study area

| Parameter | Cd | Hg | As | Pb | Cr | Cu | Ni | Zn |
|--------------------------|------|-------|-------|-------|-------|-------|-------|-------|
| Maximum value (mg/kg) | 0.37 | 0.17 | 13.51 | 81.4 | 138.8 | 112.3 | 72.1 | 131.7 |
| Minimum value (mg/kg) | 0.02 | 0.005 | 0.78 | 12.5 | 29 | 5.2 | 11.7 | 19.3 |
| Mean value (mg/kg) | 0.11 | 0.03 | 7.43 | 23.38 | 55.17 | 17.01 | 22.15 | 52.03 |
| Standard deviation | 0.05 | 0.02 | 1.92 | 5.72 | 11.51 | 7.82 | 5.42 | 12.49 |
| Coefficient of variation | 0.4 | 0.63 | 0.26 | 0.24 | 0.21 | 0.46 | 0.24 | 0.24 |

Table 2 Geochemical baseline data of soil heavy metals based on standardized methods

| Element | Regression equation | R^2 | Base value(mg/kg) |
|---------|------------------------------------|-------|-------------------|
| Cu | $Cu = 1.86 + 0.23 V$ | 0.065 | 16.86 |
| Pb | $Pb = 23.67 - 4.45E - 3^{\wedge}V$ | 0.000 | 23.38 |
| Zn | $Zn = 9.42 + 0.65 V$ | 0.201 | 51.82 |
| Ni | $Ni = -5.43 + 0.42 V$ | 0.448 | 21.97 |
| Cr | $Cr = -0.02 + 0.85 V$ | 0.398 | 55.43 |
| As | $As = 2.58 + 0.07 V$ | 0.111 | 3.04 |
| Cd | $Cd = 0.05 + 9.15E - 4^{\wedge}V$ | 0.029 | 0.11 |
| Hg | $Hg = 0.03 + 4.56E - 5^{\wedge}V$ | 0.000 | 0.03 |

selected as the standard component; its content was between 30 and 104.5 mg/kg, the standard deviation was 8.58, and the coefficient of variation was 0.13. Accordingly, the relationship between heavy metals and standard element “V” was determined (Fig. 2).

Heavy metal pollution

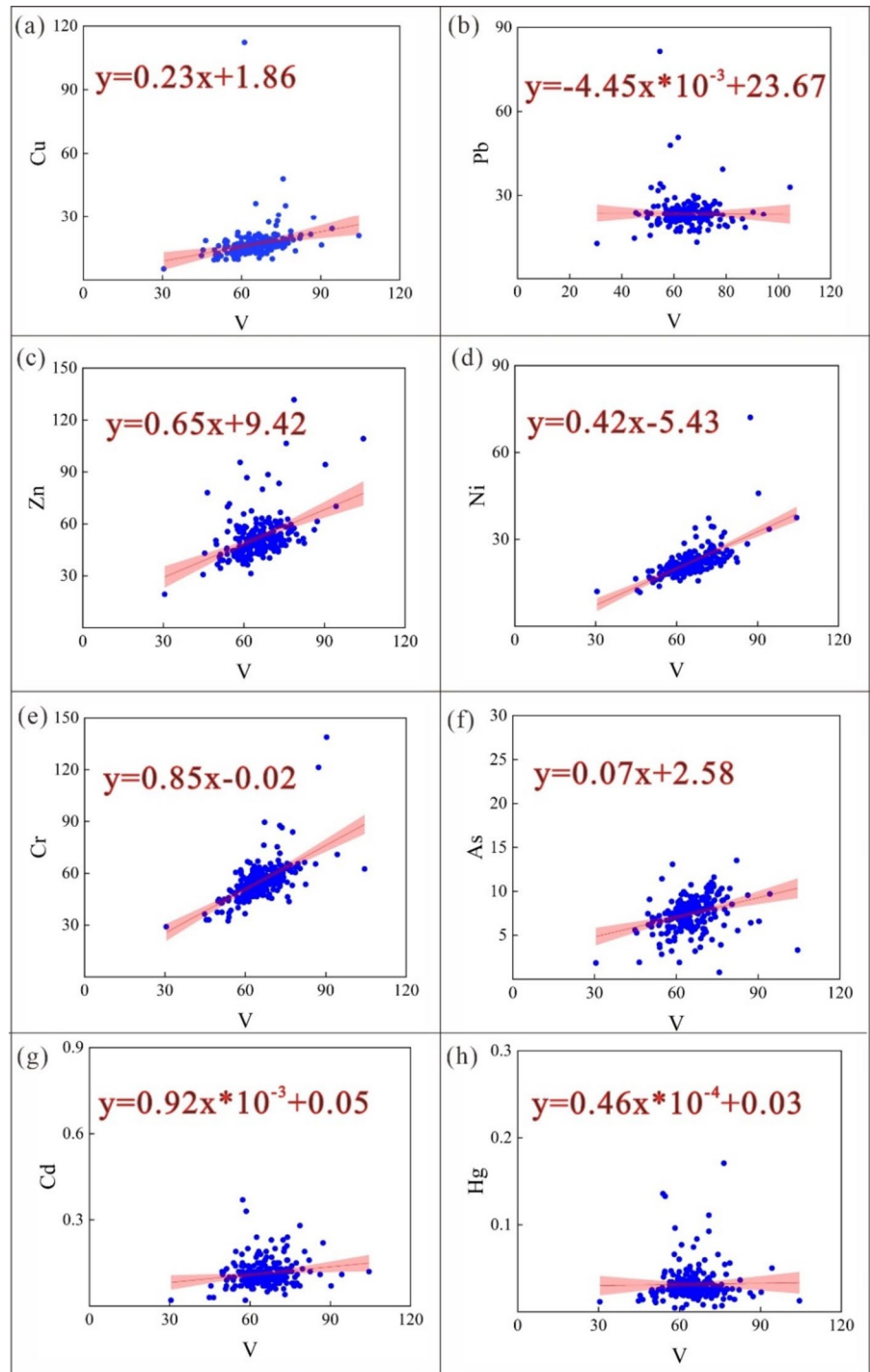
As mentioned earlier, the environmental geochemical baseline value and the background value of Weifang City were used for evaluation. Affected by human production and living activities, the environmental geochemical baseline values of Cd and Hg were higher than the background values of Weifang City. Therefore, when the background value of Weifang City was used as the reference value, the pollution degree of Cd and Hg obtained was relatively serious, but the direction of contamination was consistent. According to I_{geo} , the pollution levels of Cu, Pb, Zn, Ni, Cr, and As were non-moderate pollution at only a few points, and the rest of the area was pollution-free. Cd and Hg showed different degrees of accumulation, and their large coefficients of variation may be attributable to pollution. Cd contamination was moderate at 1% (calculated by background value) of the sampling sites, and the contamination was concentrated in the western and eastern parts of the study area (Fig. 3a and b). Moderate or above Hg contamination was present at 3% (calculated by baseline value) and 12% (calculated by background value) of the sampling sites, with contamination concentrated in the west, central, and east (Fig. 3c and d). According to the Nemerow pollution Index, 51% (calculated by baseline

value) and 73% (calculated by background value) of the sampling sites had mild pollution, and a small number had moderate or above pollution. The pollution was concentrated in the western, central, and eastern regions (Fig. 3e and f). A pollution distribution map drawn according to I_{geo} and the Nemerow pollution index displays the same pollution pattern (Fig. 3). Therefore, Cd and Hg can be considered the primary pollutants.

Evaluation of potential ecological hazard index (PEHI)

According to the classification criteria (Table S3), descriptive statistical analysis and grading evaluation were carried out on the PEHI of heavy metal elements. The ecological hazards of Cu, Pb, Zn, Ni, Cr, and As were low. The PEHI of Cd and Hg was higher than that of other elements, but the overall ecological hazard was mild (Fig. 4). Affected by anthropogenic activities, the environmental geochemical baseline values of Cd and Hg in the study area were higher than their background values. Therefore, the $PEHI-E_i$ calculated using the background value of Weifang City (Figs. 4b, 5b, d) was higher and more serious than the environmental geochemical baseline (Figs. 4a, 5a, c), but the distribution maps of PEHI drawn were similar between the two reference values. E_i values indicated that Cd at 1% (calculated by baseline value) and 4% (calculated by background value) sampling points had strong ecological hazards, and Hg at 5% (calculated by baseline value) and 38% (calculated by background value) sampling points had strong ecological hazards. A distribution map of ecological risk was drawn according to E_i , and the potential hazards of Cd were concentrated in the western region (Fig. 5a and 5b). The potential hazards of Hg were concentrated in the western, central, and eastern parts. R_i showed that 9% (calculated by baseline value) and 42% (calculated by background value) of the sampling sites had moderate or above ecological hazards. Overall, the western, central, and eastern regions showed higher PEHI, essentially consistent with distribution of more serious pollution according to I_{geo} and the Nemerow pollution index (Fig. 5e and f).

Fig. 2 Relationship between heavy metal elements and V (a Cu; b Pb; c Zn; d Ni; e Cr; f As; g Cd; h Hg)



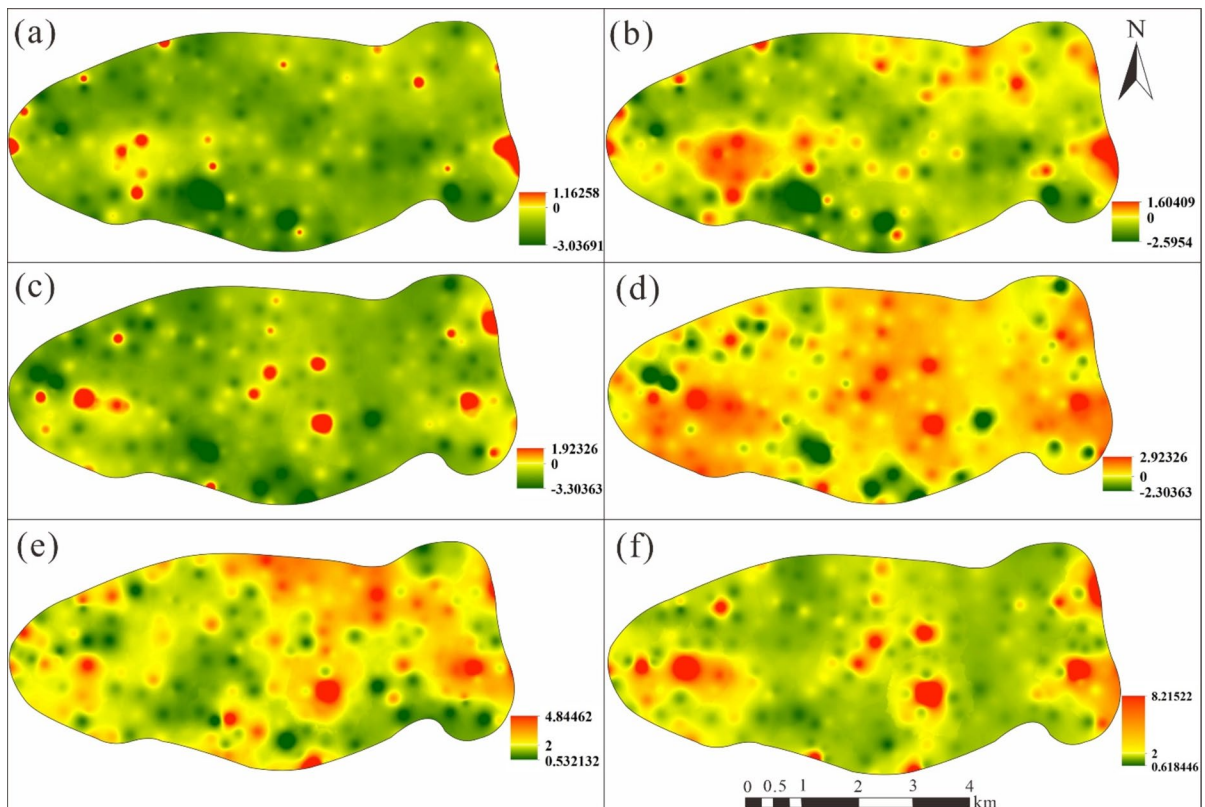


Fig. 3 Heavy metal pollution distribution map (**a** I_{geo} (Cd)-environmental geochemical baseline; **b** I_{geo} (Cd)-soil background value of Weifang City; **c** I_{geo} (Hg)-environmental geochemical baseline; **d** I_{geo} (Hg)-soil background value of

Weifang City; **e** Nemerow pollution index-environmental geochemical baseline; **f** Nemerow pollution index-soil background value of Weifang City)

Human health risk assessment

Non-carcinogenic risk

Cu, Pb, Zn, Ni, Cr, As, Cd, and Hg were selected for non-carcinogenic risk assessment. The daily doses of different heavy metals under different pathways were calculated for non-carcinogenic exposure. According to different reference doses of heavy metals, HQ, HI, and THI were obtained (Table 3).

The HQ of all heavy metals was less than 1 for both adults and children. The main exposure pathway was oral intake, with contribution rates of 86.03% and 91% for adults and children, respectively. The HQ of different heavy metals followed the order $\text{Cr} > \text{Pb} > \text{Ni} > \text{Cu} > \text{Zn} > \text{Cd} > \text{Hg} > \text{As}$.

The HI values of heavy metals were significantly higher for children than for adults (Fig. 6a). The THI values for adults and children under each exposure

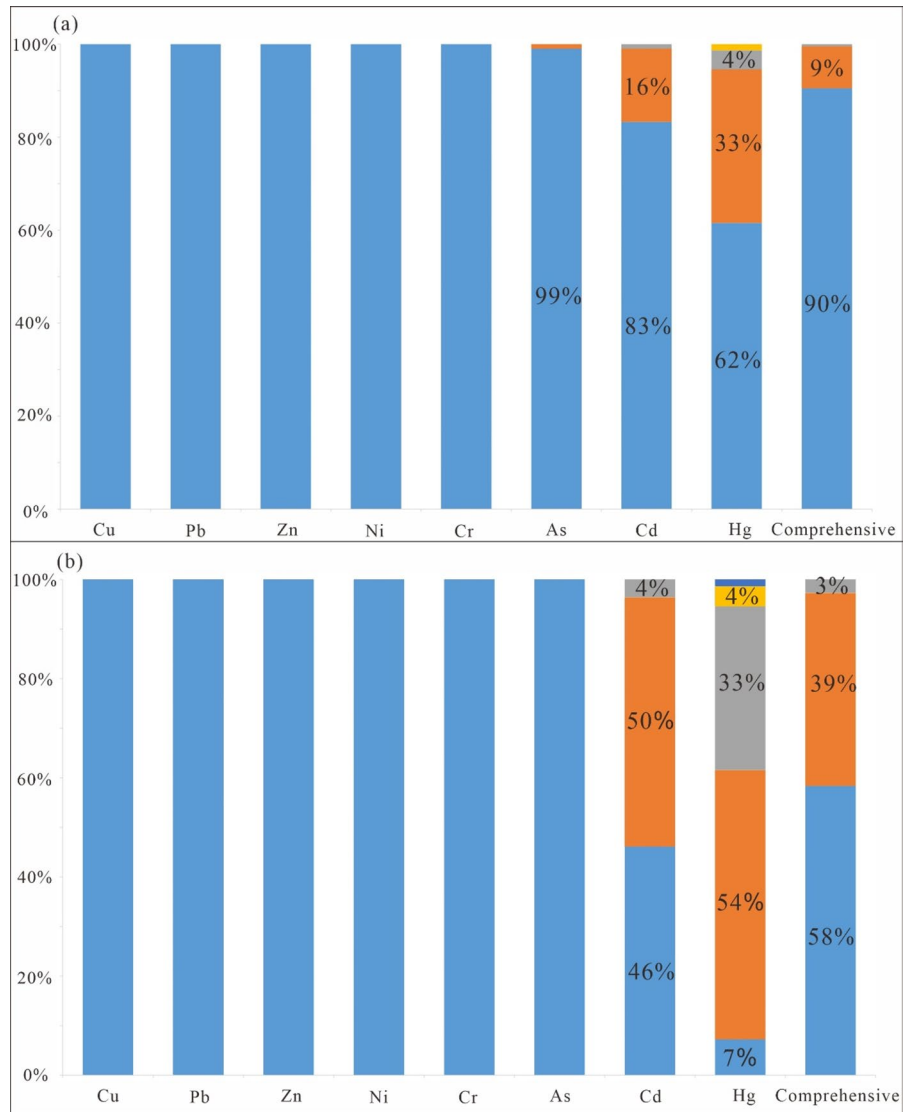
pathway were 0.04 and 0.38, respectively, which are both less than 1, indicating an acceptable non-carcinogenic risk level. In particular, Cr contributed 71 and 69.8% of the risks to adults and children, respectively (Fig. 6c).

Carcinogenic risk

Ni, Pb, As, Cr, and Cd were selected for carcinogenic risk assessment. The carcinogenic exposure was calculated and the ADD of each heavy metal under the three exposure pathways was obtained. CR, CRI, and TCRI were calculated according to the SF of each heavy metal element (Table 4).

The CRs of As and Cr under each exposure pathway were at tolerable levels, and those of the other elements were at no carcinogenic risk. The main exposure pathway was oral intake, contributing 89 and 93% to TCRI in adults and

Fig. 4 Proportion of PEHI (a environmental geochemical baseline as the background value; b Weifang City as the background value)



children, respectively. For oral intake, CR followed the order $Cr > As > Pb > Cd$ (Table 4).

The carcinogenic risk was higher for children than for adults (Fig. 6b), with TCRI of $4.58E-05$ and $2.23E-05$, respectively, which are within the tolerance range of the human body. The contribution rate of the CRI of each metal to TCRI for adults and children is shown in the figure (Fig. 6d). The contribution rates of Cr to TCRI were 73.6 and 72.5% for adults and children, respectively.

Analysis of heavy metal sources

At present, the primary sources of heavy metals in soil are soil parent material and human production and livelihood activities. Heavy metals from the same source exhibit a correlation. The information of the eight heavy metals could be expressed by three principal components, with eigenvalues (λ) of 2.365, 1.486, and 1.45, respectively; the cumulative contribution rate was 66.266%. The levels of Ni and Cr showed larger positive loads, at 0.900 and

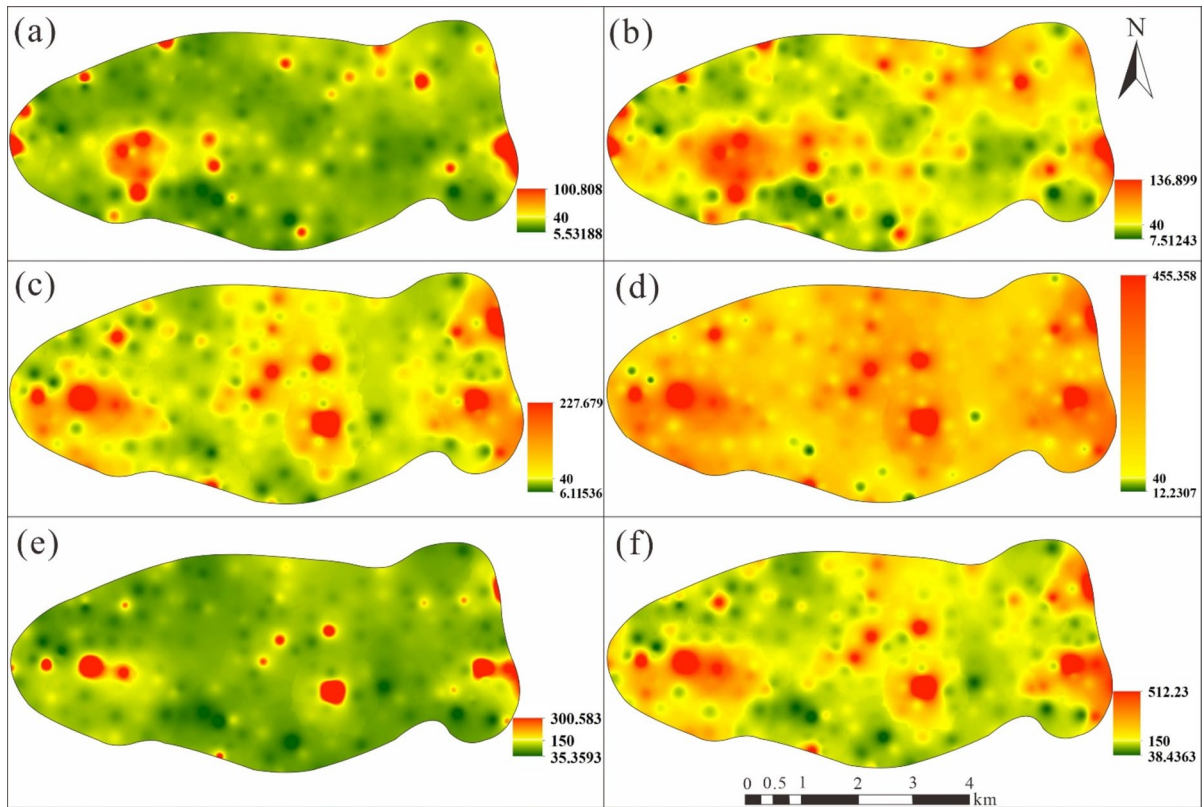


Fig. 5 Distribution of PEHI (a PEHI (Cd)-environmental geochemical baseline; b PEHI (Cd)-background value of Weifang City; c PEHI (Hg)-environmental geochemical base-

line; d PEHI (Hg)-background value of Weifang City; e PEHI (Comprehensive)-environmental geochemical baseline; f PEHI (Comprehensive)-background value of Weifang City)

Table 3 Non-carcinogenic risk assessment of heavy metals under different exposure conditions

| | HQ _{oral ingestion} | | HQ _{inhalation} | | HQ _{skin exposure} | | HI | |
|-----|------------------------------|----------|--------------------------|----------|-----------------------------|----------|----------|----------|
| | Adult | Child | Adult | Child | Adult | Child | Adult | Child |
| Cu | 5.83E-04 | 5.44E-03 | 6.39E-08 | 1.49E-07 | 7.75E-06 | 4.30E-05 | 5.90E-04 | 5.48E-03 |
| Pb | 9.15E-03 | 8.54E-02 | 1.01E-06 | 2.36E-06 | 2.43E-04 | 1.35E-03 | 9.40E-03 | 8.68E-02 |
| Zn | 2.38E-04 | 2.22E-03 | 2.62E-08 | 6.11E-08 | 4.74E-06 | 2.63E-05 | 2.42E-04 | 2.24E-03 |
| Ni | 1.52E-03 | 1.42E-02 | 1.62E-07 | 3.79E-07 | 2.24E-05 | 1.24E-04 | 1.54E-03 | 1.43E-02 |
| Cr | 2.52E-02 | 2.35E-01 | 2.91E-04 | 6.80E-04 | 5.03E-03 | 2.79E-02 | 3.05E-02 | 2.64E-01 |
| As | 3.24E-08 | 3.03E-07 | 3.74E-06 | 8.74E-06 | 3.30E-04 | 1.83E-03 | 3.34E-04 | 1.84E-03 |
| Cd | 1.56E-04 | 1.46E-03 | 1.72E-06 | 4.02E-06 | 6.23E-05 | 3.46E-04 | 2.20E-04 | 1.81E-03 |
| Hg | 1.45E-04 | 1.35E-03 | 5.59E-08 | 1.30E-07 | 8.66E-06 | 4.81E-05 | 1.53E-04 | 1.40E-03 |
| THI | - | - | - | - | - | - | 4.30E-02 | 3.78E-01 |

*En dash (-) denotes an absence of related THI

0.926, respectively, and the contribution rate of the first principal component was 29.566%. As a marker element of the soil formation process, Ni is often

used as an indicator of natural sources. Ni and Cr presented a strong correlation, which is consistent with the principal component analysis (Fig. 7). The

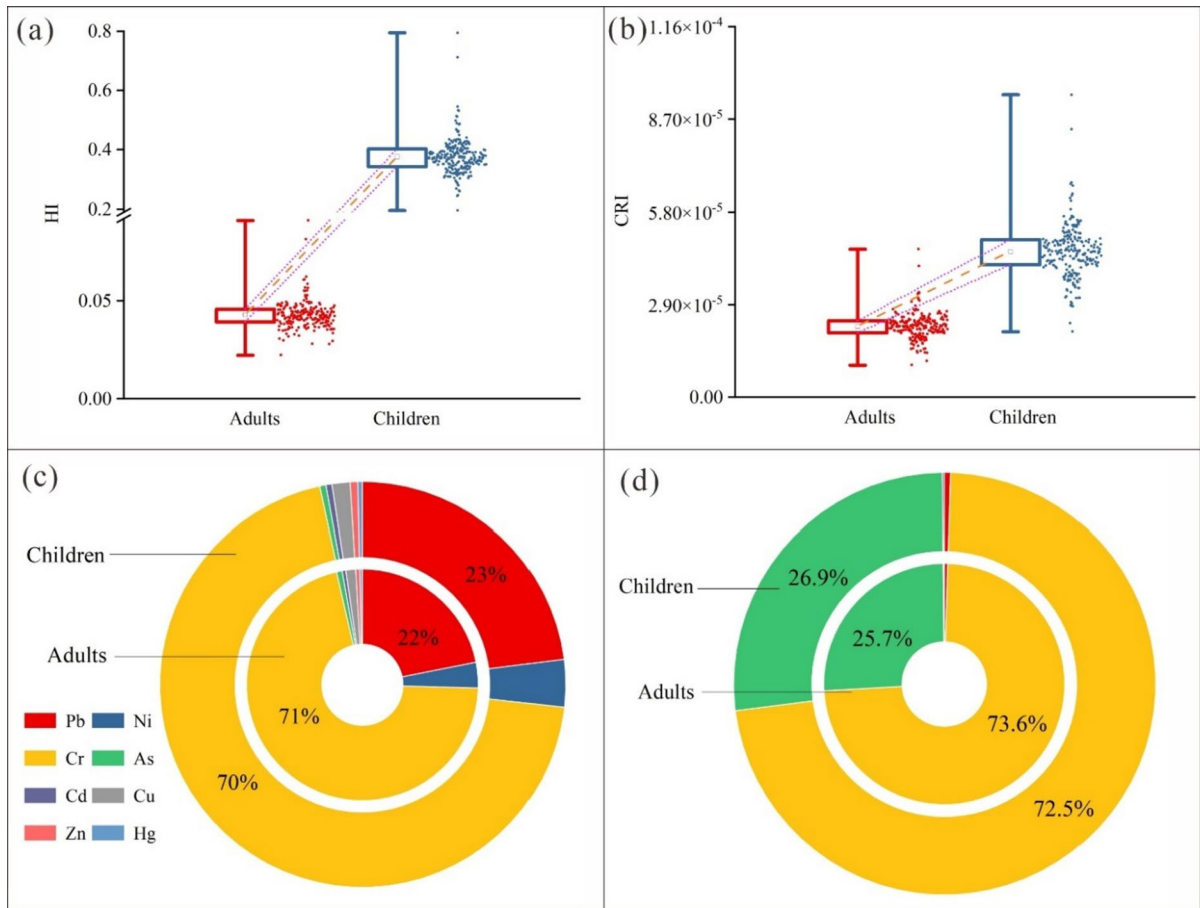


Fig. 6 (a) Comparison of HI between adults and children at sampling point; **b** Comparison of CRI between adults and children at each sampling point; **c** Contribution of heavy metal HI to THI; **d** Contribution of heavy metal CRI to TCRI)

Table 4 Carcinogenic risk assessment of heavy metals under different exposure conditions

| | CR _{oral ingestion} | | CR _{inhalation} | | CR _{skin exposure} | | CRI | |
|-----|------------------------------|------------|--------------------------|------------|-----------------------------|------------|------------|------------|
| | Adult | Child | Adult | Child | Adult | Child | Adult | Child |
| Ni | – | – | 1.04E – 09 | 1.50E – 14 | – | – | 1.04E – 09 | 5.62E – 10 |
| Pb | 1.01E – 07 | 2.18E – 07 | – | – | – | – | 1.01E – 07 | 2.18E – 07 |
| As | 5.67E – 06 | 1.22E – 05 | 6.30E – 09 | 3.39E – 09 | 5.52E – 08 | 5.52E – 08 | 5.74E – 06 | 1.23E – 05 |
| Cr | 1.40E – 05 | 3.02E – 05 | 1.30E – 07 | 7.00E – 08 | 2.24E – 06 | 2.87E – 06 | 1.64E – 05 | 3.32E – 05 |
| Cd | 2.96E – 08 | 6.38E – 08 | 4.03E – 11 | 2.17E – 11 | 4.63E – 09 | 5.93E – 09 | 3.43E – 08 | 6.97E – 08 |
| TCR | – | – | – | – | – | – | 2.23E – 05 | 4.58E – 05 |

*En dash (–) denotes an absence of related CR

contents of Cr and Ni in farmland soil were lower than their background values in Weifang soil, indicating that Ni and Cr were less affected by human disturbance (Zhang et al., 2023). Therefore, the first

principal component can be attributed to a natural source. The contribution rate of the second principal component was 18.579%. The contents of Cu, Pb, and Zn had higher positive loads at 0.680, 0.582, and

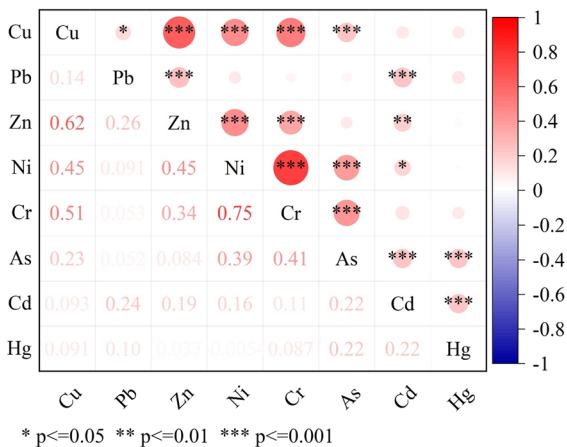


Fig. 7 Heat map of correlation analysis

0.819, respectively, similar to the results of the correlation analysis. Studies have shown that the wear and corrosion of motor vehicle engines, brake pads, galvanized parts, and tires, as well as traffic activities such as fuel combustion and vehicle exhaust emissions, release Pb, Cu, and Zn to the surrounding environment (Li et al., 2023a, 2023b). The main source of Pb is automobile exhaust emissions and a large amount of harmful gases and dust deposition containing heavy metals produced by automobile tire wear (Pu et al., 2022). The Pb content in this area was higher than the local background value. Studies have shown that Pb emitted by automobile exhaust enters the atmosphere, through migration, and finally

settles in the soil. Although leaded gasoline has been banned, 'unleaded' gasoline refers to gasoline with a Pb content below 0.013 g/L. Consequently, a small amount of lead-containing compounds and particles is still discharged into the atmosphere with tail gas, which results in Pb pollution of the soil after migration (Shen et al., 2023). According to the survey, the study region contains two major thoroughfares G1815 and S102, and considering the high traffic volume in the area, the second principal component can be attributed to the traffic source. The contribution rate of the third principal component was 18.121%, and Pb, As, Cd, and Hg showed high positive loads at 0.510, 0.579, 0.692, and 0.631, respectively. With wide acreage, agriculture is the main industry in the studied area. According to studies, the main contributors to Cd contamination in China's agriculture soils include industrial air deposition, organic fertilizers, chemical fertilizers and pesticides, and sewage irrigation (Li et al., 2023a, 2023b). Long-term use of As-containing pesticides, insecticides, and herbicides in farmland is likely to cause As accumulation (Liao et al., 2023). Hg is commonly used as an additive in herbicides, pesticides, fertilizers, and insecticides and thus used as a key indicator of agricultural activities (Chen et al., 2023; Zhang et al., 2023). The second industry is industries. According to the survey, the study area contains many factories, such as glass steel plant, plastic processing plant, steel casting plant, and sand field. Industrial emissions of 'waste gas, waste water and

Table 5 Total variance explanation

| Item | Principal component 1 | Principal component 2 | Principal component 3 |
|--------------------------------------|-----------------------|-----------------------|-----------------------|
| Cu | 0.197 | 0.680 | -0.195 |
| Pb | -0.244 | 0.582 | 0.510 |
| Zn | 0.247 | 0.819 | 0.137 |
| Ni | 0.900 | 0.202 | 0.024 |
| Cr | 0.926 | 0.139 | 0.022 |
| As | 0.441 | -0.384 | 0.579 |
| Cd | 0.130 | 0.201 | 0.692 |
| Hg | -0.072 | -0.087 | 0.631 |
| The variance contribution eigenvalue | 2.365 | 1.486 | 1.450 |
| Contribution rate/% | 29.566% | 18.579% | 18.121% |
| Accumulative contribution rate/% | 29.566% | 48.145% | 66.266% |

Bolditalics values show higher factor loadings

solid waste' from facilities such as steel smelters and metal processing are important sources of Pb and Cd in soils (Lv & He, 2018). Therefore, the third principal component can be attributed to the combination of industry and agriculture. These findings can plausibly explain the reason for Weifang City's soil background value being lower than the environmental geochemical baseline value (Table 5).

Conclusion

On the basis of regional investigation and sampling, this study analyzed eight heavy metals in soil from the upper reaches of the Xiaowen River. Except for Hg, Cu, and Cd, all heavy metals showed moderate variability, indicating that the contents of these three elements are highly dispersed. The environmental geochemical baseline values are as follows: Cu (16.86), Pb (23.38), Zn (51.82), Ni (21.97), Cr (55.43), As (3.04), Cd (0.11), and Hg (0.03) mg/kg. The environmental geochemical baseline value or the soil background value of Weifang City was taken as the reference value for pollution assessment and PEHI assessment, and the pollution patterns were found to be essentially the same. However, under the influence of human production and livelihood activities on local areas, the environmental geochemical baseline values of most elements were lower than the local background values, and Cd and Hg were abnormal. Therefore, when the environmental geochemical baseline was used as the reference value, I_{geo} showed that Cd did not have moderate or above pollution, and Hg had moderate pollution at 3% sampling points. PEHI- E_i showed that Cd had strong potential ecological hazards at 1% sampling point, and Hg had strong potential ecological hazards or above at 5% sampling point. According to the Nemerow pollution index, 49% of the sampling points had moderate or above pollution. PEHI- R_i showed that 9% of the sampling sites had moderate potential ecological hazards. When the soil background value of Weifang City was used as the reference value, I_{geo} showed that 1% of the sampling points had moderate pollution of Cd, and 12% of the sampling points had moderate and above pollution of Hg. PEHI- R_i showed that 4% of the sampling sites had strong potential ecological hazards of Cd, and 38% of the sampling sites had

strong potential ecological hazards and above of Hg. According to the Nemerow pollution index, 24% of the sampling points had moderate and above pollution. Cd pollution was mainly distributed in the west, and Hg pollution was mainly distributed in the west, middle, and east. The overall pollution degree of the study area was relatively light, and the pollution was concentrated in the west, middle, and east, which was basically consistent with the pollution direction of Cd and Hg, so the main pollutants were Cd and Hg. The health risks to humans are at an acceptable risk; Cr is the main risk factor, and the main exposure pathway is oral intake. The primary sources of heavy metal contaminants include emissions from vehicles, emissions from natural sources, fertilizer application in agriculture, and 'waste gas, waste water and solid waste' emissions from factories.

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Data availability The data will be shared on reasonable request to the corresponding author.

Declarations

Conflict of interests The authors declare that there is no conflict of interest.

Ethical approval Not applicable.

Consent to participate We confirm that all authors of the paper consent to participate.

Consent for publication This manuscript was approved for publication by all the authors.

Human or animal rights Not applicable.

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