Soil Heavy metals contamination of a typical calcium carbide slag dump sites: source apportionment and risk assessment

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Abstract: Source identification and risk assessment of heavy metals were the necessary preliminary work for the contaminated sites remediation. In this report, the As, Cd, Cr, Cu, Hg, Ni, Pb and Zn concentration in a typical calcium carbide slag dump site of thirty-four soil samples were collected to test. The source of heavy metals was analyzed by PMF model, and the apportionment of ecological risk and health risk with different pollution sources were calculated. The results show that Hg was the main polluted heavy metal in the site, with a maximum concentration of 112.19 mg.kg⁻¹, and the soil in the site was accompanied by As, Cu and Pb co-contamination. The average Hg concentration in farmland samples was 0.13 mg.kg⁻¹, which also exceeded the local soil background values, indicating that soil Hg contamination in the site had spread outwards. The sources of eight heavy metals were divided into oil refinery waste water and parent material mixed source (As, Cr, Cu and Pb), vinyl chloride waste source (Hg) and parent material source (Cd, Ni and Zn), respectively. The average potential ecological risk of soil in the site was 22344.39 and vinyl chloride waste source contributed 99.85% to ecological risk. The average CR of oil refinery waste-water and parent material mixed source for children and adults were 9.06×10⁻⁶ and 6.36×10⁻⁶, accounting for 99.9% and 99.48% of the total average CR for children and adults, respectively. The average HI of vinyl chloride waste source to children and adults were 0.6 and 0.38, accounting for 64.13% and 52.34% of the average total HI of child and adult, respectively. This indicates that children were more vulnerable to heavy metals. Compared with adults, the major pollution sources were more harmful to children.

Keyword: Heavy metals. PMF. Source apportionment. Ecological risks. Human health risks

Introduction

With the increasing importance of soil environment, the treatment of industrial pollution sites has gradually become a hot research topic of soil restoration in recent years. Among them, the evaluation and repair of heavy metal pollution sites is an important part of the treatment of industrial pollution sites. Soil heavy metal pollution has long-term and stable. Studies have shown that Cds can stay in soil for 75 to 380 years, Hg pollution for 500 to 1000 years, Ag, Ni, Cu, Pb, Zn, etc. for 1000 to 3000 years (Zhang et al. 2017). The excess heavy metal content in the soil not only destroys the ecological environment, but also migrates to other environmental media such as the atmosphere and water bodies, and endangers animal and human health through
food chain, breathing, drinking water and skin contact (Lu et al.2015). Lead excess can cause damage to organs such as the human reproductive system, immune system and kidneys (Silva et al.2016), and cadmium excess can lead to bone loosening, kidney damage and cancer (Itoh et al.2014). Therefore, it is of great significance to investigate the pollution status of soil heavy metal industrial pollution sites, systematically evaluate the degree of soil heavy metal pollution, and evaluate the health risk of the population.

Unlike other types of land, such as farmland, heavy soil metals in industrial pollution sites are closely linked to industrial production activities. Yan (2020) analysis of soil heavy metal sources in the northern estuary area of Liaodong Bay shows that heavy metals Cu, Zn and Pb are mainly affected by natural factors, and Cr and Ni are mainly due to domestic and industrial wastewater discharge. The heavy use of phosphorus fertilizer, petrochemical production and industrial activities as the main man-made sources. Tai (2018) analysis shows that Zn in the soil around waste incineration sites is mainly from waste incineration plants, Pb, Cu and Cd are mainly affected by waste incineration plants, followed by natural sources, Cr and Ni are mainly affected by natural sources, Hg is mainly affected by waste incineration plants and coal-fired emissions, and As is mainly due to specific industrial pollution. Han (2012) analysis of heavy metals in Shougang and surrounding soils shows that Ni and As are mainly from soil-based mother metals, Cu, Zn, Pb and Cd are mainly from industrial smelting and traffic emission sources, and Cr is controlled by soil-based mother metals and man-made pollution. Xie (2018) analysis shows that Pb, Cd, Cu, Zn and As at a steel plant in western Fujian Province are mainly affected by pollutants emitted by steel mills, and Cr and Ni are mainly affected by native mother quality. Bilal (2019) used positive matrix decomposition model to analyze the surface soil heavy metal pollution sources in the east open-pit mining area and showed that the contribution rates of five pollution sources were 20.79 percent, 16.83 percent, 16.83 percent, 27.72 percent and 17.82 percent, respectively. Analysis of soil heavy metal sources at shou steel pollution sites by Wu (2020) shows that Cu, Cr, Pb and Zn come from steel smelting, Cd and Sb from traffic pollution, and Hg comes mainly from coal combustion.

With the precise analysis of heavy metal sources, some scholars have evaluated the ecological and human health risks of heavy metals in soil by using pollution sources. Liu (2018) evaluation of soil heavy metal sources and human health risks in Silver City shows that coal combustion and other related activities are the most influencing sources of soil heavy metals cancer risk and non-carcinogenic risk in the region, and he believes that using pollution sources for human health risk assessment is more meaningful than using only carcinogenic risk thresholds and non-carcinogenic risk thresholds for human health risk assessment.Yang (2019) research on farmland soil health risks in Wenling area showed shows that parent material and plant, fertilizer application, industrial discharge, and vehicle emission accounted for 52.9, 19.0, and 28.1% of total non-cancer risk, and 39.2, 45.3, and 15.5% total cancer risk, respectively. Huang (2020) analysis shows that the main sources of heavy metals in farmland soil in Kowloon River basin are natural sources, agricultural activities,
coal-fired release and industrial activities, and their combined contribution rate to heavy metals in farmland soil is 37.0%, 26.7%, 17.6% and 18.7%. In addition, Wu (2020) believes that the use of pollution sources for human health risk assessment is also important to guide similar enterprises production activities.

This study analyzed the degree and source of soil heavy metal pollution in mercury-containing waste landfill sites, and calculated the ecological and human health risks based on pollution sources. The aim are: first, to understand the soil contamination of the site; second, to analyze whether the pollution in the site spread outwards, and third, to identify the ecological and human risks of the greatest impact on the source of pollution.

Materials and methods

Study area and sample collection

The geographical coordinates of the study area are 123°53′53.70″ east longitude and 47°08′46.98″ north latitude, 22km away from Qiqihar city (Figure 1). The northeast of the study area was the production enterprises of caustic soda, PVC, oil refining, etc., and the southwest was farmland. The study area is about 28.57×10⁴ m². Since the 1950s, industrial sites have started production, and a large amount of production waste was discharged into the research area in the form of waste water and waste residue.

In this study, the judgment method was used to sample the soil under the waste residue in the site, and thirty-four sampling points were arranged in the study area. The soil 0.5m deep below the mercury-containing waste residue was collected for analysis. Three boreholes F1, F2 and F3 were arranged in the farmland around the study area for soil sampling and analysis for comparison.

Sample preparation and measurement of HMs

The concentrations of Cu, Zn, Cr and Ni were measured by flame atomic absorption spectrophotometry. The concentration of Pb and Cd were measured by graphite furnace atomic absorption spectrophotometry. The concentration of As and Hg were measured by atomic fluorescence method. In addition, soil pH, organic matter, cation exchange capacity, hydrolyzable nitrogen, available phosphorus, available potassium, and redox potential were measured in the laboratory.
Positive matrix factorization (PMF)

PMF relies on a receptor model that quantifies the contribution of sources to samples based on the compositions or fingerprints of the sources. In this study, PMF version 5.0 (U.S. EPA, Washington, DC) was used for source apportionment. This model decomposes the original matrix $x_{ij}$ into two factor matrices $g_{ik}$ and $f_{jk}$ and a residual matrix $e_{ij}$; the basic equation is as Eq. (1):

$$x_{ij} = \sum_{k=1}^{n} g_{ik} \cdot f_{kj} + e_{ij}$$  \hspace{1cm} (1)

where $x_{ij}$ is the content of the jth HM in sample i; $g_{ik}$ is the contribution of the kth source for sample i; and $f_{kj}$ is the source profile of the jth HM in source k. The residual error matrix $e_{ij}$ is calculated as the minimum value of the objective function $Q$:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{n} \left( \frac{|e_{ij}|}{u_{ij}} \right)^2$$  \hspace{1cm} (2)

where $u_{ij}$ refers to the uncertainty of the jth HM in i number of samples. The main feature of PMF is that the model requires the HM contents of samples and uncertainties of the contents that are used to analyze the quality of the content values individually. The uncertainty can be calculated through various methods (Reff et al, 2007). In this study, the uncertainty was calculated using Eq. (3) and Eq. (4) as follows:

If $c \leq \text{MDL}$,

$$u_{ij} = \frac{5}{6} \times \text{MDL}$$  \hspace{1cm} (3)

If $c > \text{MDL}$,

$$u_{ij} = \frac{1}{10} \times c$$  \hspace{1cm} (4)

where $c$ is the content of the element and MDL is the method detection limit.

Statistical analysis method

Descriptive and multivariate statistical analysis methods were used to analyse the sample data. The descriptive analysis statistics included the maximum value, minimum value, average value, median value, skewness, kurtosis and coefficient of variation. SPSS 21.0 software was used for the statistical analysis, and EPA PMF5.0 software was used for the pollution source analysis, while ArcGIS 10.6 software was used for pollution distribution analysis and mapping.

Ecological risk assessment

The calculation formula of single pollution index is (Liu, 2013):

$$P_i = \frac{C_i}{S_i}$$  \hspace{1cm} (5)

Where, $P_i$ is the single pollution index of heavy metal I; $C_i$ is the measured content of heavy metal I in soil (mg.kg$^{-1}$); $S_i$ is the environmental standard value of heavy metal I in soil (mg.kg$^{-1}$). In this study, the second-level environmental quality
standard value of soil heavy metal pollutants in "soil environmental quality standard" (GB15618-2008) was adopted to evaluate the soil heavy metal pollution status of the site. Usually, Pi< 1 indicates that the soil is not polluted by heavy metal; 1 ≤ Pi< 2 indicates the soil is slightly polluted by heavy metal; 2 ≤ Pi< 3 indicates the soil is moderately polluted by heavy metal; Pi≥ 3 indicates that the soil is heavily polluted by heavy metal.

Potential ecological hazard index method is a set of methods established by Hakanson (1980) from the perspective of sedimentology to evaluate the potential ecological hazard of heavy metals based on the properties and environmental behavior characteristics of heavy metals (Chen, 2017). The potential ecological risk factor \( E_r^i \) of a single heavy metal calculated as follows:

\[
E_r^i = T_r^i \times \frac{C_i}{C_{rn}}
\]

Where, \( C_i \) is the content of \( i \) heavy metals. \( C_{rn} \) is the reference value of \( i \) heavy metal, and the arithmetic mean value of soil background value in Heilongjiang province is adopted in this evaluation (Zhang et al. 2018). \( T_r^i \) is the toxicity response coefficient of a heavy metal, reflecting the toxicity level of heavy metal and the sensitivity of soil to heavy metal pollution. Reference related research (Wei, 1991; Zhan, 2017), the corresponding toxicity coefficients of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn, are 10, 30, 2, 5, 40, 5, 5 and 1, respectively.

The comprehensive potential ecological harm index RI (table 1) of heavy metals expressed as the sum of \( E_r^i \) of each heavy metal:

\[
RI = \sum_{i=1}^{m} E_r^i
\]

### Table 1 Grading standards of Hakanson potential ecological risk

| Level                  | Score   | Level            | Score   |
|------------------------|---------|------------------|---------|
| Low ecological risk    | <40     | Low ecological risk | <150   |
| Medium ecological risk | 40-80   | Medium ecological risk | 150-300 |
| Higher ecological risk | 80-160  | High ecological risk | 300-600 |
| High ecological risk   | 160-320 | Extremely high ecological risk | >600   |

**Human health risk assessment**

The human health risk assessment is carried out according to the methods specified in the Technical guidelines for risk assessment of contaminated sites (HJ 25.3-2019). The second category land use was chosen as the exposure scenario, and the sensitive receptor was adult. The human health risk contribution of each pollution source was quantitatively examined by using the PMF model. The mathematical quantitative analysis expressions are shown in equations (8)-(17) (Liu et al. 2018), and the parameters of each equation can be found in HJ 25.3-2019. Due to the limited volatility of HMs and PAHs, only oral ingestion, skin contact and particles inhalation are considered as the main exposure routes. Table S1 shows the non-carcinogenic reference dose and carcinogenic slope factor of the three exposure pathways of each pollutant. Table S2 shows the values of relevant parameters of human health risk assessment.
\[
\text{Con} (CR_{obs})_{ij} = \text{Con}_{ij} \times SF_{0} \times \frac{ABS_{0} \times (\text{OISER}_{a} \times \text{ED}_{a} \times \text{EF}_{a})}{BW_{a} \times AT_{ca}} \times 10^{-6} \tag{8}
\]
\[
\text{Con} (HI_{ois})_{ij} = \frac{\text{Con}_{ij} \times (\text{CON}_{10} \times \text{ST}_{R} \times \text{ED}_{c} \times \text{EF}_{c})}{BW_{c} \times AT_{nc}} \times 10^{-6} \tag{9}
\]
\[
\text{Con} (CR_{dsc})_{ij} = \text{Con}_{ij} \times SF_{0} \times \frac{ABS_{d} \times EF_{v} \times (\text{SAF}_{a} \times \text{SSAR}_{c} \times \text{ED}_{c} \times \text{EF}_{c})}{BW_{a} \times AT_{ca}} \times 10^{-6} \tag{10}
\]
\[
\text{Con} (HI_{dsc})_{ij} = \frac{\text{Con}_{ij} \times (\text{CON}_{10} \times \text{ST}_{R} \times \text{ED}_{c} \times \text{EF}_{c})}{BW_{c} \times AT_{nc}} \times 10^{-6} \tag{11}
\]
\[
\text{Con} (CR_{pis})_{ij} = \text{Con}_{ij} \times \left( \frac{14R \times BW_{a}}{DAIR_{a}} \times PM_{10} \times \frac{DAIR_{a} \times PLAF \times ED_{a} \times (fsp \times EFO_{a} \times fsp \times EFI_{a})}{BW_{a} \times AT_{ca}} \times 10^{-6} \right) \tag{12}
\]
\[
\text{Con} (HI_{pis})_{ij} = \frac{\text{Con}_{ij} \times PM_{10}}{BW_{c} \times AT_{nc}} \times \left( \frac{DAIR_{a} \times PLAF \times ED_{a} \times (fsp \times EFO_{a} \times fsp \times EFI_{c})}{BW_{c} \times AT_{nc}} \times 10^{-6} \right) \tag{13}
\]
\[
\text{Con} (CR_{k})_{ij} = \text{Con} (CR_{ois})_{ij} + \text{Con} (CR_{dsc})_{ij} + \text{Con} (CR_{pis})_{ij} \tag{14}
\]
\[
\text{Con} (HI_{k})_{ij} = \text{Con} (HI_{ois})_{ij} + \text{Con} (HI_{dsc})_{ij} + \text{Con} (HI_{pis})_{ij} \tag{15}
\]
\[
\text{Con} (Total - CR_{k})_{ij} = \sum \text{Con} (CR_{k})_{ij} \tag{16}
\]
\[
\text{Con} (Total - HI_{k})_{ij} = \sum \text{Con} (HI_{k})_{ij} \tag{17}
\]

Where, \(\text{Con}_{ij}\) is the pollutant content of the \(i\)th element and the \(j\)th source; \(\text{Con} (CR_{ois})_{ij}\) is the oral carcinogenic risk of the \(i\)th element and the \(j\)th source; \(\text{Con} (HQ_{ois})_{ij}\) is a non-carcinogenic risk of the oral pathway of the \(i\)th element and the \(j\)th source; \(\text{Con} (CR_{des})_{ij}\) is the carcinogenic risk of skin contact pathway from the \(i\)th element and the \(j\)th source; \(\text{Con} (HQ_{des})_{ij}\) is the \(i\)th element of the \(j\)th source of skin contact route non-carcinogenic risk; \(\text{Con} (CR_{pis})_{ij}\) is the carcinogenic risk of the \(i\)th element and the \(j\)th source in the respiratory inhalation pathway; \(\text{Con} (HQ_{pis})_{ij}\) is the \(i\)th element of the \(j\)th source of respiratory inhalation pathway is not carcinogenic risk; \(\text{Con} (CR_{k})_{ij}\) is the carcinogenic risk of the \(i\)th element and the \(j\)th source in three ways; \(\text{Con} (Hl_{k})_{ij}\) is the third pathway of the \(i\)th element and the \(j\)th source, which is not carcinogenic risk; \(\text{Con} (total-CR_{k})_{ij}\) is the Total carcinogenic risk of the \(i\)th element from the \(j\)th source; \(\text{Con} (total-Hl_{k})_{ij}\) is the total non-carcinogenic risk of the \(i\)th element from the \(j\)th source.

Results and discussion

HMs concentrations in study area

The statistical results of heavy metal content in thirty-four soil samples in the study area as shown in Table b2. The results showed that the maximum concentrations of As, Cu, Hg and Pb were 16.88, 29.20, 112.19, 120.00 mg.kg\(^{-1}\), all exceeded the background value. The maximum concentration of Cd, Cr, Ni, Zn were 0.06, 45.30, 20.60 and 54.50 mg.kg\(^{-1}\), and did not exceed the local soil background value, this indicates that the four heavy metals were not contaminated. The smaller variation
coefficient of heavy metal concentration with the smaller difference and dispersion
degree, and more uniform distribution. On the contrary, the greater the difference and
dispersion degree, the more uneven the distribution (Zhao et al. 2012; Chen et al
2017). The variation coefficients of Hg of soil samples were 2.73, and the differences
in concentration and dispersion degree were large, indicating Hg were unevenly
distributed. The variation coefficients of other seven heavy metals were relatively
small (all less than 1), indicating they were evenly distributed in the soil of the site.
The single-factor pollution index of Hg and Pb were 5609.50 and 5.29 indicates that
these two heavy metals were heavily polluted. The single-factor pollution index of As
and Cu were 1.81 and 1.56, indicates these two heavy metals were slightly polluted.
The single-factor pollution index of Cd, Cr, Ni, Zn were 0.75, 0.89, 0.85 and 0.95,
This was further proof that these four heavy metals were not polluted. The soil in the
site was mainly seriously polluted by Hg. The detection of heavy metal concentration
in the soil at three sampling points of farmland showed that the concentration of
heavy metals in the soil did not exceed the local soil background value except Hg,
which indicated that the farmland soil had not been polluted by Hg.

In addition, the physical and chemical properties of the soil was also analyzed in
order to better understand the state of the soil on the site. The average soil organic
matter content in the site was 0.57, the maximum organic matter content was 2.49,
and the organic matter content was low. The average soil pH value is 9.7 (>8.5),
which was a strong alkaline soil. A higher pH will greatly reduce the availability of
soil phosphorus, potassium and nitrogen (Zhang et al. 2017). Therefore, in addition to
heavy metal elements, the soil in this area was affected by mercury-containing waste
residues, and the physical and chemical properties of the soil have also been severely
damaged.
### Table 2 Heavy metal concentrations in the soil of the study area (n=34)

| HMs          | Study area | Farmland | Background value | Screening value | Single factor pollution index $P_i$ |
|--------------|------------|----------|------------------|-----------------|-------------------------------------|
|              | Average    | MAX      | MIN  | MED  | SD   | CV  | SKEW | KURT | Average | Value | Value |                          |
| As (mg.kg⁻¹) | 7.37       | 16.88    | 3.39 | 6.76 | 2.85 | 0.39 | 1.71 | 3.56 | 6.10    | 9.33  | 20    | 1.81                      |
| Cd (mg.kg⁻¹) | 0.03       | 0.06     | 0.01 | 0.03 | 0.01 | 0.39 | 0.29 | -0.84| 0.06    | 0.08  | 20    | 0.75                      |
| Cr (mg.kg⁻¹) | 26.98      | 45.30    | 8.99 | 26.70| 9.40 | 0.35 | 0.11 | -0.46| 1.77    | 50.82 | -     | 0.89                      |
| Cu (mg.kg⁻¹) | 11.72      | 29.20    | 3.72 | 10.16| 5.28 | 0.45 | 1.41 | 2.88 | 11.50   | 18.74 | 2000  | 1.56                      |
| Hg (mg.kg⁻¹) | 8.82       | 112.19   | 0.01 | 0.07 | 24.33| 2.73 | 3.23 | 10.57| 0.13    | 0.02  | 8     | 5609.50                   |
| Ni (mg.kg⁻¹) | 11.78      | 20.60    | 1.61 | 11.50| 4.41 | 0.37 | 0.22 | 0.11 | 10.69   | 24.16 | 150   | 0.85                      |
| Pb (mg.kg⁻¹) | 26.41      | 120.00   | 14.30| 19.00| 23.27| 0.88 | 3.26 | 10.42| 21.67   | 22.70 | 400   | 5.29                      |
| Zn (mg.kg⁻¹) | 32.57      | 54.50    | 10.50| 32.00| 9.59 | 0.29 | 0.30 | 0.43 | -       | 57.34 | -     | 0.95                      |
| pH           | 9.70       | 11.25    | 7.82 | 9.78 | 0.86 | 0.09 | -0.20| -0.53| -       | -     | -     | -                        |
| Organic matter (%) | 0.57       | 2.49     | 0.19 | 0.50 | 0.47 | 0.82 | 2.99 | 9.94 | -       | -     | -     | -                        |

Note: - means no data.
Source analysis of heavy metals

Correlation analysis

The correlation between elements was significant or extremely significant, it indicates that there was homology or compound pollution between elements (Guo et al. 2012; Zhang et al. 2014). Pearson correlation analysis results of heavy metal content in soil (Figure 2) showed that Cu, Hg and Pb were significantly correlated (P<0.01) and the correlation coefficients were all over 0.7, indicating that these three elements had the same source. As also significantly correlated (P<0.01) with Cu, Hg and Pb, but the low correlation coefficients (<0.65) indicated that As has similar sources with these three heavy metals. Cd and Zn were extremely significantly correlated (P<0.01), but the correlation coefficient of the two heavy metals was low (<0.5), and there was no correlation between Cd and other six heavy metals, which indicates that Cd has other sources. Except for Hg and Pb, the concentrations of the other six soil heavy metals were normally distributed, which indicates that Hg and Pb may have been contaminated by some anthropogenic sources (Zhang et al.2006).

PMF

US EPA PMF model was used to analyze the contribution rate of different pollution sources to eight heavy metals from thirty-four sampling points. The correlation coefficients between the predicted concentrations and the measured concentrations of the eight pollutants obtained by the PMF model simulation were 0.89, 0.92, 0.91, 0.85, 0.83, 0.95, 0.88 and 0.91 (Figure 3), respectively, and the fit was good. On the basis of a strong explanatory ability and low Q value (0.1), three main factors were selected, as shown in Figure 4. The results show that using the analytical value could meet the needs of the simulation results (Dong et al. 2018).
Fig. 3 Comparison of prediction results and measured results of eight heavy metals concentration
As (45.5%), Cr (59.8%), Cu (59.3%) and Pb (54.6%) had higher loads on factor 1. The average concentration of As, Cr, Cu and Pb did not exceed the background values, it shows that these four heavy metals were mainly derived from parent material (Zhang et al. 2017). However, the concentrations of As, Cu, and Pb at six, two, and six sampling points respectively exceeded the local soil background value, indicating that the soil has suffered man-made pollution, too. Analysis shows that the higher concentrations of As, Cu, and Pb in the site were mainly related to the waste-water discharge in the northern industrial production area (Ma et al. 2019). A large amount of sulfide will be generated during the refining process in the industrial zone, which will be discharged into the site through the sewage outlet. Therefore, factor 1 represents oil refinery waste-water and parent material a mixed source.

Hg (83.8%) has a relatively high load on factor 2. The Hg concentration in twenty-nine sampling points in the site exceeded the soil background value (0.02 mg/kg). Among them, the soil Hg concentration in six sampling points exceeded the screening value (8 mg/kg), which indicates that the soil Hg in the site mainly comes from human pollution (Han et al. 2019). The production process in the northern industrial zone of the site shows that a large amount of mercury-containing waste was generated during the production of PVC (Feng 2016; Gao 2020). These mercury-containing wastes were discharged into the site along with the waste-water, which was the main factor that causes the Hg concentration pollution in the site. Therefore factor 2 represents the vinyl chloride waste source.

Cd (79.5%), Ni (61.1) and Zn (55%) had higher loads on factor 3. The maximum value of these three heavy metals does not exceed the local soil background value, which indicates that the three metals mainly come from the parent material (Wei et al. 2018). Therefore, factor 3 represents the source of parent material.

Oil refinery waste-water and parent material mixed source, vinyl chloride waste source, parent material source were identified by analyzed the eight heavy metals in the thirty-four samples using the PMF model, as shown in Figure 5. The proportions of these three pollution sources in the total concentrations of heavy metals were 58 %, 3.9 % and 38.1%, respectively. The heavy metals contamination levels at the site were significantly affected by the industrial production processes and had the characteristics of point source pollution.
Fig. 4 Contribution rates of different sources on eight HMs based on positive matrix factorization (PMF)

Ecological risk

Hakanson potential ecological risk index method was used to measure the ecological risk of heavy metals in soil to the contaminated site. This method not only considers the concentration of heavy metals in soil, but also links the ecological effects, environmental effects and toxicology of heavy metals, which comprehensively reflects the stress degree of heavy metals on the ecological environment (Shi et al. 2019; Zhang et al. 2020). The average potential ecological risk
factor ($E_i$) of As, Cd, Cr, Cu, Ni, Hg, Pb and Zn were 3.05, 0.37, 1.41, 5.13, 60818, 5.14, 0.91 and 0.17 (Figure 6). Except for Hg, the ecological risks of the other seven heavy metals were all low ecological risk. Analysis of the ecological risk of heavy metals in each drill hole shows that the ecological risks of eight heavy metals at 34 sampling points range from 56.54 to 280529.1, the average was 22344.39 with extremely high ecological risk. The sampling sites with extremely high ecological risk were mainly located in the eastern part of the study area. The contribution rate of vinyl chloride waste source to ecological risk reaches 99.85%, and was the main cause of high ecological risk of site soil, as shown in Figure 7. The sum of the contribution rate of the other two sources of heavy metals to the total ecological risk of the site is 0.15%, basically low ecological risk.

**Fig.6** Potential ecological risk of heavy metals in the surface soil of the contaminated sites

**Fig.7** Ecological risk contribution rate of each pollution source

**Human health risk assessment**

**Deterministic risk assessment**

Three heavy metals, As, Cd and Ni, were associated with carcinogenic risk, and As, Cd, Cr, Cu, Hg, Ni, Pb and Zn have a hazard index, as show in Table S1.
According to HJ 25.3-2019-Technical guidelines for risk assessment of contaminated sites, this contaminated site was industrial land and belongs to category I land, and the heavy metal risk assessment considers adult and child carcinogenic and hazard index.

Figure 8A and Figure 8B shows the carcinogenic risk (CR) values of the three exposure pathways of As, Ni, and Cd at thirty-four sampling points with child and adult. The CR of three exposure pathways with As were all exceeded the acceptable level ($1 \times 10^{-5}$), but did not exceed the tolerance value ($1 \times 10^{-4}$), among them, the carcinogenic risk of oral ingestion was the highest. The CR of the three exposure pathways of Cd and Ni did not exceed the acceptable level ($1 \times 10^{-6}$). The CR of heavy metals in children was generally higher than that in adults, indicating that children were more vulnerable to soil heavy metals.

The HI for the eight heavy metals in thirty-four borehole of three exposure pathways with child and adult were shown in Figure 8C and Figure 8D. Both child and adult HI of Hg with oral ingestion at the B6, B10, B11 and B13 sampling points were exceed the tolerance value (>1). The HI of the three exposure pathways of the other seven heavy metals did not exceed the tolerance value (1). Same as CR, The HI of heavy metals in children was generally higher than that in adults, too.

**Source risk assessment**

According to the sources of As, Cd and Ni pollution, the CR at the thirty-four sampling sites contaminated by each source with child and adult were analyzed, as shown in Figure 9A and Figure 9B. The total CR value of child was between $4.17 \times 10^{-6}$ and $2.08 \times 10^{-5}$. The CR of heavy metals in all the sampling sites was greater than the acceptable level ($1 \times 10^{-6}$), but did not exceed the tolerance value ($1 \times 10^{-4}$). The oil refining waste-water and parent material mixed source (As) and soil parent material sources (Cd and Ni) of the average total CR of child were $9.06 \times 10^{-6}$ and $8.68 \times 10^{-6}$, with CR contribution rates of 99.9 % and 1%, respectively. The oil refining waste-water and parent material mixed source (As) and soil parent material sources (Cd and Ni) of the average total CR of adult were $6.36 \times 10^{-6}$ and $3.3 \times 10^{-8}$, with CR contribution rates of 99.48 % and 0.52 %, respectively. The oil refining waste-water and parent material mixed source was the main factor causing carcinogenic risk of
heavy metals in the site. Both sources increase the CR in children compared to adults. At the same time, the proportion of pollution sources that dominate the child CR (oil refining waste-water and parent material mixed source) will increase compared to adults.

The HI of three pollution sources with child and adult was shown in Figure 9C and Figure 9D. The total HI of thirty-four sampling points with child was between 0.22 and 8.4. There were four sampling sites where the total HI exceeded the tolerance value (>1). The HI were the largest at the B10 and B13 sampling point. The total average HI of the oil refining waste-water and parent material mixed source, vinyl chloride waste source, and soil parent material sources were 0.31, 0.6 and 0.02, respectively, with contribution rates for the total average HI of 33.27%, 64.13% and 2.6 %, respectively. The total HI of thirty-four sampling points with child was between 0.19 and 5.44. There were four sampling sites where the total HI exceeded the tolerance value (>1). The HI were the largest at the B10 and B13 sampling point, too. The total average HI of the oil refining waste-water and parent material mixed source, vinyl chloride waste source, and soil parent material sources were 0.29, 0.38 and 0.05, respectively, with contribution rates for the total average HI of 40.39 %, 52.34 % and 6.36 %, respectively. The solid waste source of chlor-alkali was the main pollution source that affects the HI of heavy metals at the site. Similar to the CR, the proportion of primary pollution sources (solid waste source of chlor-alkali) in the HI of children increases compared with adults.

Fig.9 CR and HI assessment based on pollution sources. A CR of child; B CR of adult; C HI of...
Child; D HI of adult

CR of child and adult did not exceed the tolerance value \((1 \times 10^{-4})\), the HI value of soil heavy metals in the four sampling sites exceeded the tolerance value \((>1)\). All the four sampling points were located at the eastern boundary of the site, and on-site exploration shows that the area was originally an industrial sewage outlet. Therefore, this area was the key area of soil remediation in the site. The heavy metal concentration analysis of the farmland adjacent to the site showed that the Hg concentration in the farmland had exceeded the local soil background value, which indicated that the pollution in the site had spread to the farmland.

Compared with deterministic risk assessment, risk assessment based on pollution sources could better reflect the sources of pollutants in the contaminated site and the level of pollution on the soil of the site, and then provide a reference for the next step of soil remediation, and could also provide evidence production for management of similar industrial sites.

**Conclusion**

Mercury pollution was most severe in landfills where mercury-containing waste was found, as well as arsenic, copper and lead contamination. Analysis of heavy metals in farmland soil around the site shows that mercury in the soil has migrated outward. There three sources of pollution, were oil refinery waste-water and parent material a mixed source, vinyl chloride waste source and parent material source, of the eight heavy metals in the site were identified. Vinyl chloride waste source contributed 99.85% to ecological risk, the most significant impact on soil ecological risk was Hg. Oil refinery waste-water and parent material mixed source contributed 99.9% and 99.48% of the total average CR for children and adults, respectively. Vinyl chloride waste source contributed 64.13% and 52.34% of the average total non-carcinogenic risks with children and adult. Children’s health was more susceptible to major pollution sources.

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**Compliance with ethical standards**

**Conflict of interest** The authors declare no conflicts of interest

**Animal research**

Not applicable

**Consent to participate**

Written informed consent for participate was obtained from all participants.

**Consent to publish**

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