Evaluating Metal(loid)s Contamination in Soil of a Typical Industry Smelting Site in South Central China: Levels, Possible Sources and Human Health Risk Analysis

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Abstract: Soil pollution by metal(loid)s caused by smelting activities is a severe problem posing a great threat to environmental and human health. In this study, the concentrations, sources and human health risks posed by six potentially toxic elements (Cr, Mn, Zn, Pb, Cd, and As) were determined in the soil of a typical alloy smelting site in South Central China. The results showed that the concentrations of metal(loid)s were in the descending order of Mn > Cr > Zn > Pb > As > Cd. Additionally, the selected elements were classified into different pollution degrees using geo-accumulation index and pollution load index. The entire study area had a high pollution level with relatively severe and extensive contamination by Cr, Cd, and Mn. The combined application of principal component analysis and positive matrix decomposition model revealed that the major sources of these elements include smelting activities (48.68%), waste residue stacking (22.95%), and natural sources (28.37%). According to the results of the human health risk assessment, the non-carcinogenic risk was insignificant as a whole; however, the carcinogenic risk had an unacceptable level. Among them, Cr was the main driver of carcinogenic risk, which needs special attention.

Keywords: metal(loid)s pollution; source identification; human health risk assessment; smelting site; PMF; PCA

1. Introduction

The metal(loid)s contamination of soils has become an increasingly severe concern in many parts of the world, it has a profound effect on the ecological environment and human health [1–4]. The metal(loid)s in the environment usually come from industrial activities and agricultural production [1,5–7]. As one of the largest global metal producers and consumers [8,9], China has had rapid industry development, creating much wealth from non-ferrous metal smelting in the past few decades [8]. However, smelting activities have also brought a heavy burden to the surrounding environment, especially to soil [10]. Fly ash, wastewater, and slag, which are side products of smelting processes, such as material preparation, smelting, and casting processes, contain toxic elements that enter the soil environment through rainfall, sedimentation, leakage, and other means, thus causing severe pollution [11,12]. Due to the obvious toxicity, difficult degradation, and outstanding persistence of metal(loid)s [13,14], it deteriorates soil quality and enters the human body through food intake, skin contact, and other ways, inducing diseases such as cancer and harming human health [15–18].

Mounting evidence indicates that people’s exposure to these potentially toxic metal(loid) elements will adversely affect many human organs [19]. For instance, Cr(VI) is a harmful carcinogenic pollutant with high toxicity, which causes diseases of the respiratory tract,
digestive tract, and skin [18]. Excessive intake of Cd can cause renal dysfunction, hypercalciuria, bone damage, hypertension, and lung inefficiency in humans [16,20,21]. Excessive As can also cause skin cancer, gastrointestinal diseases, and cardiovascular disease [22–24]. Additionally, long-term intake of food grown in Pb-contaminated soil will increase the incidence of gastrointestinal cancer [1]. Some studies have also found that Mn, Pb, Zn, Cd, and other elements are also related to human neurological diseases [25]. For instance, manganese can induce Parkinsonism by affecting the frontal cortex of the brain, leading to early dementia [17,19]. Moreover, workers exposed to excessive Pb often show neurocognitive impairments, e.g., dizziness, amnesia, and schizophrenia [19]. Thus, it is of great significance and scientific value to investigate the concentrations, sources, and human health risks of metal(loids) in the soil of polluted industrial sites.

Hunan province of South Central China is well-known for its abundant reserves of non-ferrous metals [3,26,27]. In the last century, many factories have focused on smelting, mining, electroplating, and other industries in this area. The study area is a typical abandoned smelter, which is one of the representative smelting enterprises established and key ferroalloy enterprises in the last century in China. Due to the long history of industrial smelting activities, the production area has accumulated much smelting waste. The pollutants contained therein entered the soil in various ways, resulting in a significant metal(loid) pollution problem. Therefore, our study area has become a typical abandoned site severely polluted by smelting activities. Although many studies are already available on soil pollution in smelting sites, most previous studies have focused on the impact of the smelter on the surrounding soil, and relatively few studies have targeted the pollution characteristics of the soil inside the smelter [28–31]. Under the background of ecological restoration and industrial transformation in China, it is necessary to solve the pollution problem in the south. Meanwhile, deep knowledge of the pollution situation and source identification of pollution elements in the soil inside the smelter is key to subsequent soil remediation. However, the priority pollutants inside the smelting area, spatial characteristics of pollutants, pollution source and risks to the surrounding people are unclear. Therefore, a thorough investigation of metal(loid) pollution in the soil inside the smelter is prompted to conduct targeted remediation of the smelter site in the future.

Recently, various pollution indices, such as contamination factor, enrichment factor, geo-accumulation index \( I_{geo} \), pollution ecological risk index, and pollution load index \( (PLI) \), have been extensively used to evaluate the degree of metal(loid)s pollution in the soil [32,33]. Moreover, exploring the pollution sources and spatial distribution of metal(loid)s has provided an important reference for identifying the pollution degree and formulating pollution prevention strategies [8]. Currently, kriging interpolation combined with correlation analysis, principal component analysis (PCA), and positive matrix factorization model (PMF), have been considered as highly effective methods used to determine the possible sources of pollutants [34–36], and allocate natural or anthropic contribution [8,35]. Furthermore, the influence of metal(loid)s on human health can be examined by determining whether the carcinogenic risk and hazard quotient of elements exceed the risk acceptance threshold. The model proposed by the United States Environmental Protection Agency (USEPA) has been widely used [37]. However, it has some parameters that do not conform to the actual human exposure characteristics in China, causing the deficiency of inaccurate risk assessment [38]. For example, we believe that parameters such as average weight, average height, and respiratory rate of adults significantly correlate with the actual living environment and race of various countries. Additionally, and different races in different regions will have differences in such parameters. Therefore, to solve this problem, this study focuses on using the Chinese technical guidelines for the risk assessment of soil contamination of land for construction (HJ 25.3-2019) [39]. However, the risk assessment of China is still in the developmental stage, and some parameters in the guidelines have not been specified. Thus, we combine some parameters of the USEPA model for human health risk assessment to provide more accurate evaluation results.
Accordingly, the present study focuses on: (1) determining the contamination levels and distribution of metal(loids) in the selected smelter area; (2) identifying the possible sources of metal(loids) in the soil; (3) assessing the human health risks through different exposure pathways. The outcomes of this study could provide basic data for metal(loids) pollution control and for policy decisions based on the accurate confirmation of regional pollutants. In addition, this study provides a reference case for the systematic evaluation of soil contamination, which can be used for other related studies in similar smelting sites around the world.

2. Materials and Methods

2.1. Study Area and Sampling

The study area, which is an abandoned smelting factory located in Hunan Province, South Central China, belongs to the subtropical monsoon humid climate, has four distinct seasons. Founded in 1958, the plant was once one of the key ferroalloy enterprises in China, with an annual production capacity of 148,000 tons. Production stopped recently and the factory closed down. The industrial site primarily consists of the NO. 3 smelting workshop, NO. 4 smelting workshop and blast furnace smelting workshop, as shown in Figure 1, which mainly produced Fe-Mn products and chromium-related products. Due to the simple traditional smelting process, remedial nature of environmental treatment measures and the random discharge of industrial pollutants, the soil in the study area has been heavily polluted.

![Study area and soil sampling locations.](image)

Figure 1. Study area and soil sampling locations.

Based on the production history and prevalent processes at the time of operation, 40 sampling points were set up on the site, as shown in Figure 1. The surface soil (20–50 cm) was collected within a single sampling site using a shovel, and then mix them thoroughly. Subsequently, 1000 g of the mixed sample was put it into a sealed bag. Before loading soil samples into the sealed bags, stones, plant debris, and other sundries on the soil surface...
were discarded. After all the sampling work was completed, it was sent to the laboratory for analysis.

2.2. Sample Pretreatment and Analysis

The soil samples were aired-dried at room temperature in an indoor ventilated place, ground thoroughly with an agate mortar, and passed through a 200-mesh (0.75 µm) nylon sieve. To measure the concentration of metal(loid)s, 0.1 g of each soil sample was placed in a crucible and digested in 2 mL HNO₃ and 2 mL HCl on a hot plate for 1 h at 110 °C. Afterwards, 1 mL HF and 1 mL HClO₄ were added, the temperature was increased to 250 °C, and digestion was continued until the white smoke disappeared. Once the sample was allowed to cool down, it was diluted with 2 mL of HCl (1 + 1) and transferred into a 10 mL polyethylene container. The resulting solution was diluted with deionized water to the scale mark, and the concentrations of Pb, and Cd were determined by ICP–MS (Thermo fisher X2, Bremen, Germany), while Cr, Mn, Zn and As were analyzed by ICP-AES (ICAP6300, USA). All readings were taken in three replicates.

2.3. Quality Assurance and Quality Control

The accuracies of the soil sample analysis were controlled using the standard reference materials (GBW07429 and GBW07404) of the National Certified Reference Materials Research Center of China. All analyses were carried out in triplicate, and the recoveries of each element were were within the range of 89–106%. The relative standard deviations of all elements ranged from 1% to 7%, and the analytical precision was within ±10%.

2.4. Pollution Indices

In order to evaluate the pollution level of selected elements in the soil of the study area, Igeo and PLI was introduced. Igeo is a classical method widely used for the soil pollution level of selected elements [40,41]. The relevant equation is as follows:

\[ I_{geo} = \log_2 \left( \frac{C_n}{K \times B_n} \right) \]  

where \( C_n \) represents the measured concentration value; \( B_n \) represents the background value of elements, and in this study, it denotes the soil background value of Hunan Province [42]; \( K \) is the change of background value caused by diagenesis (generally \( k = 1.5 \)). 

Igeo can be classified into seven categories, as shown in Table S1. PLI is a screening tool to evaluate the extent of pollutants of a particular location [43], which has been widely used to measure the cumulative pollution degree [44,45]. The following formula was used to calculate the PLI:

\[ CF = \frac{C_n}{B_n} \]

\[ PLI = \sqrt[\text{CF}_1 \times \text{CF}_2 \times \ldots \times \text{CF}_n} \]

where CF represents the pollution factor of single element, \( C_n \) is the measured concentration value, and \( B_n \) represents the background value. The values of PLI are generally classified into six categories, as shown in Table S1.

2.5. Multivariate Statistical Analysis

PCA is a dimension reduction method widely used to distinguish the different origin of metal(loid)s groups [36]. PMF combined with PCA could quantitatively identify pollution sources and their contributions [44].
PMF is an effective source analysis model, which mainly uses the minimum iterative double multiplication to determine the main pollution sources and contribution rate. PMF mainly used uncertainty to weight all data [34,36]. The relevant equation is as follows:

$$x_{ij} = \sum_{k=1}^{n} g_{ik} f_{kj} + e_{ij}$$  \hspace{1cm} (4)

where $x_{ij}$ represents the measured concentration of the selected element; $g_{ik}$ represents the contribution matrix of the $k_{th}$ source factor; $f_{kj}$ represents the source profile of element for the $k_{th}$ source factor; $e_{ij}$ represents the residual for each sample; $i$ and $j$ are the number of samples and chemical elements. The minimum value of the objective function $Q$ was calculated by the following equation:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left( \frac{x_{ij} - \sum_{k=1}^{n} g_{ik} f_{kj} u_{ij}}{u_{ij}} \right)^2$$  \hspace{1cm} (5)

The uncertainty was calculated using the following formula:

$$Unc = \frac{5}{6} \times MDL$$  \hspace{1cm} (6)

$$Unc = \sqrt{(Error\ fraction \times \ concentration)^2 + MDL^2}$$  \hspace{1cm} (7)

where $Unc$ refers to the uncertainty, and $MDL$ is the detection limit. If the concentration value $\leq MDL$, the uncertainty is calculated using Equation (6); if the concentration value $> MDL$, Equation (7) is used.

2.6. Human Health Risk Assessment

The human health risk assessment was conducted according to the Chinese guideline (HJ 25.3-2019) [39] and the “Exposure Factors Handbook of US Environmental Protection Agency” [37], including the carcinogenic risk assessment and the non-carcinogenic risk assessment. The health risk assessments of the present study mainly considered three different pathways: ingestion, dermal contact and inhalation. The cancer risk (CR) was used to evaluate the carcinogenic risk, while the hazard quotient (HQ) index was employed to evaluate the non-carcinogenic risk. Equations (8)–(11) were used to calculate the carcinogenic risk, while Equations (12)–(15) were applied to calculate the non-carcinogenic risk.

$$CR_{ois} = OISER_{ca} \times C_{sur} \times SF_o$$  \hspace{1cm} (8)

$$CR_{dcs} = DCSER_{ca} \times C_{sur} \times SF_d$$  \hspace{1cm} (9)

$$CR_{pis} = PISER_{ca} \times C_{sur} \times SF_i$$  \hspace{1cm} (10)

$$CR_n = CR_{ois} + CR_{dcs} + CR_{pis}$$  \hspace{1cm} (11)

where $C_{sur}$ denotes the measured value of metal(loids); $CR_{ois}$, $CR_{dcs}$, and $CR_{pis}$ represent carcinogenic risk via ingestion, dermal contact, and inhalation, respectively; $OISER_{ca}$, $DCSER_{ca}$, $PISER_{ca}$ represent the soil exposure dose (carcinogenic) of three exposure pathways, and their equations are given in Table S2. The total carcinogenic risk ($CR_n$) is the sum of risks posed by the three pathways. The other corresponding parameter values were summarized in Tables S2 and S3. According to previous studies, when $CR_n < 10^{-6}$,
the carcinogenic risk can be ignored; when $10^{-6} < CR_n < 10^{-4}$, it is generally considered acceptable; and when $CR_n > 10^{-4}$, it is considered unacceptable [6,14].

\[
\begin{align*}
HQ_{ois} &= OISER_{nc} \times \frac{C_{sur}}{RFD_o \times SAF} \quad (12) \\
HQ_{dcs} &= DCSER_{nc} \times \frac{C_{sur}}{RFD_d \times SAF} \quad (13) \\
HQ_{pis} &= PISER_{nc} \times \frac{C_{sur}}{RFD_i \times SAF} \quad (14) \\
HI &= HQ_{ois} + HQ_{dcs} + HQ_{pis} \quad (15)
\end{align*}
\]

where $HQ_{ois}$, $HQ_{dcs}$, and $HQ_{pis}$ are the hazard quotients of exposure to metal(loid)s via ingestion, dermal contact, and inhalation, respectively; $OISER_{nc}$, $DCSER_{nc}$, and $PISER_{nc}$ represent soil exposure dose (non-carcinogenic) via three pathways, as shown in Table S2. The hazard index ($HI$) represents the sum of $HQ$ of different pathways for individual elements, indicating the total risk, whereas other parameters are presented in Tables S2 and S3. When $HI < 1$, it is generally considered that there is no significant non-carcinogenic risk, and when $HI > 1$, it indicates that there is a non-carcinogenic human health risk.

2.7. Statistics Used

The descriptive statistical analysis was conducted using SPSS 25.0 (IBM, Armonk, NY, USA) and Microsoft Excel 2010 (Microsoft, Redmond, WA, USA). Descriptive data were calculated, such as the minimum, maximum, mean and coefficients of variation. The Pearson’s correlation and PCA analysis were also carried out by SPSS 25.0. Origin 2018 (OriginLab, Northampton, MA, USA) was used to convert the data into graphics to make the data more visual. The PMF model analysis was calculated by the EPA PMF 5.0 (United States Environmental Protection Agency, Washington, DC, USA) to explore the sources of metal(loid)s. All spatial distribution maps were made through kriging interpolation using Surfer 16.0 (Golden Software LLC, Golden, CO, USA).

3. Results

3.1. Concentration of Metal(loid)s in the Soil

The average concentrations of Cr, Mn, Zn, Pb, Cd, and As in the study area soil were 1930, 13,256, 326, 216, 2.43 and 22.78 mg/kg, respectively, which exceeded the background values of Hunan Province by 28.81, 26.78, 3.44, 8.00, 30.76, and 1.63 times, respectively (Table 1). Furthermore, the excess level in descending order was Cd > Cr > Mn > Pb > Zn > As. The coefficient of variation (CV) can reflect the effect of soil properties by the surrounding environment [46]. Generally, CV is classified into four types: CV < 20%, low variability; CV from 20% to 50%, moderate variability; CV from 50% to 100%, high variability; CV > 100%, exceptionally high variability [47,48]. The CV values of Cr, Mn, Zn, Pb and Cd were all greater than 100%, and this exceptionally high variability indicated that they were strongly impacted by external factors and human activities (Table 1). The CV of As in the soil was 47.01%, exhibiting moderate variability, indicating that the pollution caused by As might be influenced by human activities, but was not excessively strong.

In order to figure out the pollution level, the metal(loid)s were evaluated by the $I_{geo}$ and $PLI$ indices. The ranges of $I_{geo}$ for Cr, Mn, Zn, Pb, Cd, and As were from $-0.61$ to $7.40$, $-3.01$ to $6.73$, $-0.66$ to $3.98$, $-0.93$ to $5.63$, $-2.57$ to $6.80$, and $-1.31$ to $1.54$, respectively (Figure 2). The average $I_{geo}$ value of the six elements in the soil decreased in the following order: Cr (3.37) > Cd (3.24) > Mn (2.94) > Pb (1.51) > Zn (0.81) > As (0.03). Based on the average values, it could be found that, in terms of Cr and Cd, the soil was classified as heavily polluted, and 52.5% of Cr and 61.1% of Cd exhibited $I_{geo}$ values greater than 3 (Figure 2). Based on the Mn, Pb, and Zn average values, the soil was evaluated as moderately polluted to heavily polluted, moderately polluted, and unpolluted to moderately...
polluted, respectively. The average $I_{\text{geo}}$ value of As showed that industrial soils were unpolluted to moderately polluted, the pollution degree was the lightest, and only one sample had an $I_{\text{geo}}$ value above 1. The results showed that six elements caused pollution at different levels, among which Cr, Mn and Cd pollutions were comparatively serious, while As pollution was only slight (Figure 2). The PLI values of Cr, Mn, Zn, Pb, Cd, and As were 15.49, 11.54, 2.64, 4.29, 14.15, and 1.53, respectively, and the PLI values were also in the descending order of Cr > Cd > Mn > Pb > Zn > As. Overall, the PLI values in all of the soil samples varied from 0.75 to 39.53 with an average of 7.83, showing that the industrial soil was strongly polluted by metal(loids).

Table 1. Descriptive statistics of metal(loids) concentrations in soil samples.

|        | Cr   | Mn   | Zn   | Pb   | Cd   | As   |
|--------|------|------|------|------|------|------|
| Minimum (mg·kg$^{-1}$) | 66   | 92   | 78   | 21.3 | 0.02 | 7.15 |
| Maximum (mg·kg$^{-1}$)  | 17,000 | 78,600 | 2250 | 2010 | 13.20 | 61.17 |
| Mean (mg·kg$^{-1}$)     | 1930 | 13,256 | 326 | 216 | 2.43 | 22.78 |
| Median (mg·kg$^{-1}$)   | 565  | 4430 | 178 | 87.02 | 1.38 | 2.00 |
| SD                  | 3283 | 19,389 | 515 | 352 | 3.36 | 1.07 |
| C.V. (%)            | 170.09 | 146.26 | 157.80 | 163.13 | 138.20 | 10.71 |
| Skewness          | 2.19 | 2.06 | 3.29 | 4.02 | 2.30 | 1.05 |
| Kurtosis          | 3.81 | 3.86 | 10.21 | 19.14 | 4.91 | 3.54 |
| Background Values (mg·kg$^{-1}$) | 67 | 495 | 95 | 27 | 0.079 | 14 |
| LOD (mg·kg$^{-1}$) | 1.025 | 0.630 | 0.03 | 0.50 | 0.014 | 0.09 |
| LOQ (mg·kg$^{-1}$) | 3.417 | 2.100 | 0.10 | 1.67 | 0.047 | 0.30 |

SD: standard deviation; C.V. (%): coefficient of variation. (soil data were referred to dry weight). *a*: Background values of soil elements in Hunan Province [42].

Figure 2. Geo-Accumulation Index ($I_{\text{geo}}$) of the metal(loids).

3.2. Spatial Distribution of Metal(loids)

The spatial distribution of metal(loids) in this study area are presented in Figure 3. The spatial distribution of Zn, Pb, and Cd exhibited similar patterns, and particularly high concentrations of them accumulated near the blast furnace smelting workshop in the southwest corner and the NO. 3 smelting workshop (Section 304), which indicated that the source of Zn, Pb, and Cd might be related to the former industrial activities in these two areas. The spatial distribution of Mn was concentrated in its slag landfill in
the southeast and the NO. 3 smelting workshop (Section 304). The hot spots of Cr were located in the chromium slag yard in the central area. However, the spatial pattern of As was distinct from the other metal(loid)s; its spatial variation was not significant, which was consistent with the analysis of CV. The concentration of As in the site was relatively uniform and was slightly higher in Section 304 in the north. Overall, most of the hot spots of these elements were clearly associated with the NO. 3 smelting workshop (Section 304), which had mainly produced chromium-related products, including roasting, reduction, calcination, smelting and other processes, with Section 304 mainly responsible for the smelting process. Therefore, the smelting process of Section 304 could provide a reference for determining the source of these elements.

Figure 3. Spatial distribution of metal(loid)s in the soil of study area.

3.3. Statistical Analysis

Correlation analysis (CA) and PCA can reflect the correlation among metal(loid)s levels to some extent and distinguish the different groups of metal(loid)s [44], which was used to reveal the association of the source of metal(loid)s in the study area. A strong correlation can reveal the close relationship between elements, indicating that these elements may have common sources and similar migration pathways [35,49], which can provide a reference for the traceability of metal(loid)s. The relationships among Cr, Mn, Zn, Pb, Cd, As, and pH were examined by Pearson’s correlation analysis, as shown in Table 2. The correlations among Pb, Zn and Cd were highly significant at the $p < 0.01$ level ($r > 0.77$). Similarly, Mn with Cd and Zn were strongly correlated at the $p < 0.01$ level ($r > 0.53$), indicating that these elements might share a common pollution source. And the correlation between As and Cd was significant at the $p < 0.05$ level. In particular, Cr was correlated with none of the other metal(loid)s, but had a significant correlation with pH, indicating that it has a unique source and is related to pH.
Table 2. Pearson correlation coefficient matrix between metal(loid)s in the soil.

|       | Cr   | Mn   | Zn   | Pb   | Cd   | As   | pH  |
|-------|------|------|------|------|------|------|-----|
| Cr    | 1.000|      |      |      |      |      |     |
| Mn    | 0.097| 1.000|      |      |      |      |     |
| Zn    | 0.101| 0.576**| 1.000|      |      |      |     |
| Pb    | 0.055| 0.292| 0.776**| 1.000|      |      |     |
| Cd    | 0.185| 0.530**| 0.998**| 0.848**| 1.000|      |     |
| As    | 0.219| 0.055| 0.314| 0.289| 0.411*| 1.000|     |
| pH    | 0.376*| 0.068| 0.166| 0.062| 0.211| 0.060| 1.000|

* Correlation is significant at the 0.05 level (p < 0.05), ** Correlation is significant at the 0.01 level (p < 0.01).

Prior to PCA, KMO and Bartlett’s spherical tests (KMO = 0.679, Sig = 0.000 < 0.001) were performed on the data to determine their suitability for PCA. Three principal components (PC1, PC2, and PC3) (eigenvalues > 1) were obtained from the data for the metal(loid)s in the soil, representing almost 81.04% of the total variance of explanatory variables, with 47.01 % of the variance explained by PC1, 19.10 % by PC2, and 14.93 % by PC3 (Figure 4). Loading of Cd, Zn, Pb, and Mn were shown by PC1, that of Cr by PC2, and that of As by PC3. According to their strong correlations in PC loadings, six elements could be classified into Group 1 (Cd, Zn, Pb, and Mn), Group 2 (Cr), and Group 3 (As) (Table 3; Figure 4).

Table 3. Rotated component matrix for metal(loid)s in the soil.

| Component | Initial Eigenvalues | Element | Rotated Component |
|-----------|---------------------|---------|------------------|
|           | % of Variance       |         |                  |
| 1         | 3.291               | Cr      | -0.034           |
| 2         | 1.337               | Mn      | 0.652            |
| 3         | 1.045               | Zn      | 0.951            |
| 4         | 0.607               | Pb      | 0.857            |
| 5         | 0.517               | Cd      | 0.944            |
| 6         | 0.162               | As      | 0.277            |
| 7         | 0.041               | pH      | 0.129            |

Figure 4. Loading plot of principal component analysis. (Extraction method: Principal component analysis; Rotation method: Varimax with Kaiser normalization. Rotation converged in three iterations.)

3.4. PMF Modeling

The PMF model were utilized to better identify the sources of metal(loid)s in this study area and quantify their corresponding contribution of sources to each element. To ensure high accuracy of program results, the Q value was minimized and different factors (2, 3, and 4) were selected to control the residual matrix E, and the base runs were performed.
20 times to find the most ideal solution. When the number of factors was 3, the \( Q \) value was the smallest (\( Q = 0.5 \)), and the residuals of each element were between \(-3\) and \(3\). The \( R^2 \) values for each element were as follows: \( \text{Cr} \) (0.97), \( \text{Mn} \) (0.61), \( \text{Zn} \) (0.62), \( \text{Pb} \) (0.74), \( \text{Cd} \) (0.63), and \( \text{As} \) (0.99). The \( R^2 \) of all six elements were greater than 0.6, suggesting high correlations, therefore, the positive matrix factorizing model (PMF) was applicable, and the results could be considered reliable.

The operation results of PMF 5.0 were shown in Figure 5, which was consistent with the grouping result of PCA. The first factor (Factor 1) was mainly dominated by \( \text{Cr} \), accounted for 22.95% of the total variance and \( \text{Cr} \) had the highest concentrations (its contribution was 87.0%) in Factor 1. Factor 2 was characterized by \( \text{Cd}, \text{Zn}, \text{Pb}, \) and \( \text{Mn} \) (their contributions were 82.6%, 43.7%, 68.3%, and 82.2%, respectively), accounting for 48.68% of the total variance, which was the largest among the three factors. Factor 3 was mainly dominated by \( \text{As} \) (the contribution was 83.8%), which accounted for 28.37% of the total variance.

![Base Factor Profiles - Run 18](image)

**Figure 5.** Source profiles and source contributions of soil metal(loid)s from PMF model.

### 3.5. Cancer Risk and Hazard Quotient

Based on the guideline (HJ 25.3-2019) [39], the study area belonged to category II industrial land, and its human health risk assessment only considered adults. Three elements, \( \text{Cr}, \text{Cd}, \) and \( \text{As} \), were associated with carcinogenic risk, and all six elements were associated with non-carcinogenic risk. However, the method we selected (Chinese guideline and
USEPA model) did not estimate the relevant parameters of Pb and was not fit for the risk assessment of Pb. Therefore, only the other five elements were evaluated.

Table 4 and Figure 6 show the adult CR and HQ results under different exposure routes. CR of Cr ranged from $1.15 \times 10^{-5}$ to $2.97 \times 10^{-3}$ (average $= 5.40 \times 10^{-4}$), indicating an unacceptable carcinogenic risk; the CR of Cd ranged from $5.25 \times 10^{-10}$ to $3.46 \times 10^{-7}$ (average $= 6.75 \times 10^{-8}$), indicating no obvious carcinogenic risk of Cd; the CR of As ranged from $6.00 \times 10^{-9}$ to $4.33 \times 10^{-5}$ (average $= 1.66 \times 10^{-5}$), indicating an existing but acceptable carcinogenic risk. Overall, the average total carcinogenic risks of Cr, Cd, and As ($CR_{n} = 1.85 \times 10^{-4}$) suggested that the smelting area posed an unacceptable carcinogenic risk of the surrounding populations. Cr consists of the highest carcinogenic risk contribution (97.30%), most of the computed carcinogenic values for Cr were greatly more than the threshold limit of $1 \times 10^{-4}$, whereas As and Cd rarely exceeded the limit. Based on the exposure pathways, the relationship among the carcinogenic risk of the three exposure pathways was $CR_{\text{inh}} > CR_{\text{d} \text{i} \text{a} \text{s}} > CR_{\text{d} \text{e} \text{r} \text{a} \text{c} \text{t} \text{a} \text{l}}$ (Figure 6 and Table 4), and the inhalation route was the main source of carcinogenic risk.

Table 4. Human health risk of metal(loid)s in the study area soil.

| Type of Risk | Exposure Pathway | Cr   | Mn   | Zn   | Cd   | As   |
|--------------|------------------|------|------|------|------|------|
| Carcinogenic | Ingestion        | /    | /    | /    | /    | 1.3 $\times 10^{-5}$ |
|              | Dermal contact   | /    | /    | /    | /    | 2.3 $\times 10^{-6}$ |
|              | Inhalation       | 5.4 $\times 10^{-4}$ | /    | /    | 6.7 $\times 10^{-8}$ | 1.5 $\times 10^{-6}$ |
|              | CR$_{n}$         | 5.4 $\times 10^{-4}$ | /    | /    | 6.7 $\times 10^{-8}$ | 1.7 $\times 10^{-5}$ |
| Non-carcinogenic | Ingestion   | 2.3 $\times 10^{-1}$ | 2.1 $\times 10^{-1}$ | 2.9 $\times 10^{-3}$ | 5.7 $\times 10^{-3}$ | 1.7 $\times 10^{-1}$ |
|              | Dermal contact  | 1.4 $\times 10^{-2}$ | 1.3 $\times 10^{-3}$ | 1.8 $\times 10^{-5}$ | 1.4 $\times 10^{-3}$ | 3.1 $\times 10^{-2}$ |
|              | Inhalation       | 6.4 $\times 10^{-1}$ | /    | /    | 2.3 $\times 10^{-2}$ | 1.4 $\times 10^{-1}$ |
|              | HI               | 2.9 $\times 10$ | 2.2 $\times 10^{-1}$ | 2.9 $\times 10^{-3}$ | 3.0 $\times 10^{-2}$ | 3.4 $\times 10^{-1}$ |

Figure 6. CR and HQ of five elements in all sampling sites of three pathways.

The ranges of HI value for Cr, Mn, Zn, Cd, and As were from $6.28 \times 10^{-2}$ to $1.62 \times 10^{1}$, $1.47 \times 10^{-3}$ to $1.25 \times 10$, $6.69 \times 10^{-4}$ to $1.67 \times 10^{-2}$, $2.32 \times 10^{-4}$ to $1.53 \times 10^{-3}$, and $1.24 \times 10^{-1}$ to $8.95 \times 10^{-1}$, respectively. Adults under different exposure pathways showed that the order of average non-carcinogenic risk (HI) of metal(loid)s was Cr ($2.93 \times 10$) > As ($3.43 \times 10^{-1}$) > Mn ($2.16 \times 10^{-1}$) > Cd ($2.98 \times 10^{-2}$) > Zn ($2.92 \times 10^{-3}$). The average values of HI for four metal(loid)s were less than $1 \times 10$, indicating that these elements did not pose a non-carcinogenic health risk, except Cr. Additionally, the contribution of the three exposure routes to total HI was $HQ_{\text{d} \text{i} \text{a} \text{s}} > HQ_{\text{i} \text{n} \text{h} \text{a} \text{l} \text{i} \text{t} \text{a} \text{t} \text{i} \text{o} \text{n}} > HQ_{\text{d} \text{e} \text{r} \text{a} \text{c} \text{t} \text{a} \text{l}}$, and the ingestion route was the main source of non-carcinogenic risk.
4. Discussion

4.1. Pollution Sources

The CA, PCA, and PMF results were combined with the concentration and spatial distribution of metal(loid)s to identify the source of each element. Factor 1 was mainly defined by Cr. Generally, Cr in the soil was considered to be from a natural source and significantly influenced by the parent material. Many previous studies on industrial areas have also obtained this point of view [14,50,51]. However, the concentration of Cr in the smelter we studied was far beyond the supply of natural sources. According to the previous descriptive analysis, the concentration of Cr was much higher than the background value (more than 28.81 times) and showed exceptionally high variability. Thus, Factor 1 could be excluded from the soil-forming parent material source. Based on the spatial distribution results, Cr was enriched near the chromium slag yards. Due to a historical reason, these two large chromium slag yards were formed near the NO. 3 smelting workshop to stack the waste slag produced using the process of chromium-related products, with 200,000 tons of chromium slag accumulated. This chromium slag infiltrated into deep soil and groundwater through leaching and was gradually enriched in the soil. Additionally, according to the CA results, the source of Cr had a certain correlation with pH. Some studies have also shown that pH is an essential factor in the migration of Cr in the soil [52]. The pH level can affect the chemical transformation of Cr in the soil and change its occurrence form, subsequently impacting its migration capacity in the soil. For example, carbonate bound chromium in the soil can easily be transformed into water-soluble chromium at low pH, increasing its migration ability in the soil environment to increase the migration range and depth of Cr [52]. Therefore, it could be inferred that Cr pollution was mainly caused by the centralized stacking of chromium slag; thus, Factor 1 could be considered due to the stacking of waste slag.

Factor 2 was characterized by Cd, Zn, Pb, and Mn. According to the spatial distribution, the contents of Cd, Pb, and Zn near the blast furnace smelting workshop and the NO. 3 smelting workshop (Section 304) were much higher than their background values. The blast furnace smelting workshop mainly smelted pig iron, manganese residual, and other Fe-Mn products, while Section 304 was also mainly responsible for the smelting process. Some previous studies have several Pb, Zn, and Cd in the ash produced in the material preparation and purification of the smelting process; these ashes can increase the content of Pb, Zn, and Cd in the topsoil [53]. It is generally considered that the main source of Pb, Zn, and Cd is industrial smelting [8]. Although many previous studies reported that Mn in the soil might be controlled by the soil parent material [50,54,55], in the smelting site of our study, manganese ore, as an important raw material, easily accumulated in the soil during the smelting process. In the process of iron tapping, a large amount of dust removal ash and Mn-rich slag were produced. This fly ash and waste residue could enter the soil through atmospheric sedimentation, direct discharge and infiltration [56], resulting in the enrichment of Mn. Obviously, smelting activities were a key pollution source of these four elements in the soil across the study area. Therefore, Factor 2 could be ascribed to the source smelting activities.

Factor 3 was mainly dominated by As. Many previous studies attributed the source of As to agricultural input [36,57], and considered that the use of pesticides and chemical fertilizers leads to the enrichment of As [36]. However, the study area has been used as industrial land for more than 60 years, and most of the surrounding land was industrial land. Therefore, we believe that As in the study area was less likely to come from agricultural input. According to the previous analysis, the As content generally fluctuated around the soil background value of Hunan Province, and it was slightly higher than this background value. In addition, CV was 47.01%, and it differed from other exceptionally high elements, indicating that it was less impacted by human activities in the study area. Thus, we tend to think that As comes from natural input. Some previous studies have also confirmed that As in the soil may come from soil parent material [46,58]. Therefore, Factor 3 could be considered to be affected by a natural source.
4.2. Human Health Risk

According to the International Agency for Research on Cancer guidelines [59], Cr poses a significant carcinogenic risk [32,59]. The risk assessment results in this study also indicate the leading contribution of Cr in carcinogenic risk. Therefore, in this smelting site, significant attention should be paid to the risk and migration changes of Cr. Among the three exposure routes, inhalation by respiration is the most important exposure route, indicating that the downwind direction of the smelter might have higher carcinogenic risks than the other areas. Therefore, when entering or passing near the site, people should wear dust masks to prevent inhalation of soil dust particles. Additionally, during subsequent urban construction, residential areas, parks, and other densely populated areas should not be built downwind of the smelting site during subsequent urban construction.

Among the non-carcinogenic risks, only the average hazard quotient of Cr exceeds the threshold, showing an unacceptable non-carcinogenic risk as a whole. However, we found that although other elements have no significant non-carcinogenic risk as a whole, but the HI values of Mn at some sites exceeded the threshold. It showed that, while overall, the region did not present a significant non-carcinogenic risk, some sites might show considerable non-carcinogenic risks for humans, such as slag yard stacking areas with highly concentrated pollutants and waste residues. Therefore, more attention should be paid to sampling sites that exceeded the acceptable hazard quotient in the study area. For instance, for Cr, in 45% of the sites, the HI value exceeded 1, and the maximum HI value reached 16.17; thus, requiring significant attention. Additionally, the risk assessment results showed that oral intake was the main exposure route of non-carcinogenic risk. However, our study area was an industrial land, and the main people concerned were adults. Previous studies also showed that geophagism (soil ingestion) was rarely observed in few adults [32]; thus, avoiding agricultural development in the study area can inhibit the risks brought by the ingestion pathway. Therefore, we believe that the inhalation route needs more attention.

5. Conclusions

The present study evaluated an industrial smelting site in South Central China for contamination by metal(loids), their source, and associated human health risks. Although the smelting site had been dormant for several years, soil samples with high concentrations of metal(loids) were still detected. The average concentrations of Cr, Mn, Zn, Pb, and Cd were much higher than the background value of the Hunan Province. As evidenced by the Igeo and PLI analysis, the pollution order was Cr > Cd > Mn > Pb > Zn > As. Among the six elements, the most heavily polluted by Cr and Cd, whereas it was only slightly polluted by As. The study area was highly contaminated by metal(loids) as a whole, especially near the smelting workshop and slag yards. The statistical analysis revealed three primary sources of elements, with the main source of Mn, Zn, Pb, and Cd being smelting activities. In contrast, Cr was attributed to the stacking of chromium slag, and As was related to a natural source. Among them, smelting activities constituted the main pollution source with the highest contribution to the human health risk in the study area. Moreover, human health risk assessment indicated that there was no severe non-carcinogenic risk at the time of evaluation, but the carcinogenic risk was unacceptable across the entire study area. Cr was the major element affecting CR and HQ, which significantly contributed to the non-carcinogenic and carcinogenic risks for local residents. Therefore, priority should be given to the remediation of Cr contamination. The existing carcinogenic and non-carcinogenic risks of Cr should be promptly addressed and require appropriate control and protection strategies. Additionally, environmental management and control must find measures to cut off the main receptor exposure pathways—namely, inhalation, and targeted pollution source control is urgently necessary.
Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su132011294/s1, Table S1: Criteria for soil classification using pollution indices, Table S2: Major parameters in the formulas of human health risk assessment, Table S3: Summary of SF values and reference dose (RfD) of the selected elements.

Author Contributions: Conceptualization, C.L. and L.Y.; methodology, C.L.; software, C.L.; validation, C.L., L.Y. and B.X.; formal analysis, C.L.; investigation, H.P.; resources, A.L.; data curation, C.L.; writing—original draft preparation, C.L.; writing—review and editing, L.Y., B.X. and A.L.; project administration, L.Y. and A.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (2019YFC1805900).

Institutional Review Board Statement: Not applicable.

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

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