

Article

Spatial Distribution and Migration Mechanisms of Toxic Elements in Farmland Soil at Nonferrous Metal Smelting Site

Buxing Shi ^{1,2,3}, Kui Cai ^{1,2,*}, Xiulan Yan ⁴, Zhaoshu Liu ⁴, Qian Zhang ⁵, Jun Du ¹, Xiao Yang ^{4,*} 
and Wenlou Luan ⁶

¹ Hebei Key Laboratory of Strategic Critical Mineral Resources, Hebei GEO University, Shijiazhuang 050031, China; bkysts@163.com (B.S.); 15233657683@163.com (J.D.)

² Institute of Geological Survey, Hebei GEO University, Shijiazhuang 050031, China

³ China North Industries Norengo Ltd., Shijiazhuang 050011, China

⁴ Key Laboratory of Land Surface Pattern and Simulation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China; yanxl@igsnrr.ac.cn (X.Y.); lzs954246998@126.com (Z.L.)

⁵ Hydrogeology and Engineering Geology Exploration Institute of Hebei Province, Shijiazhuang 050000, China; zhang_q16@163.com

⁶ Institute of Resource and Environmental Engineering, Hebei GEO University, Shijiazhuang 050031, China; wenloul1958@163.com

* Correspondence: kcai@hgu.edu.cn (K.C.); yangx@igsnrr.ac.cn (X.Y.)

Abstract: Nonferrous metal smelting is a potential emission source of trace elements. However, it is vital to identify the dominant factors in determining toxic element (TE) spatial distribution and migration behaviors. We hypothesize that soil clay is the key factor in agricultural land around nonferrous metal smelting areas. Hence, this study focused on Qingyuan Town, a typical nonferrous metal smelting base. From this site, 95 soil samples (0–20 cm) were collected from cultivated land around the nonferrous metal smelters. Eight soil samples were analyzed for TE speciation and clay minerals in hot spot and non-hot spot areas following the TE distribution. A geographical detector (Geodot) showed that the distributions of total and exchangeable TE were affected by multiple factors (clay, CaO, and Fe₂O₃). X-ray diffraction (XRD) showed that the clay was mainly comprised of an illite and smectite mixed layer (67.13%), illite (15.38%), chlorite (9.25%), and kaolinite (8.25%). Moreover, correlation analysis showed that the exchangeable As was positively correlated with illite ($R^2 = 0.76$, at $p < 0.01$ level), kaolinite ($R^2 = 0.43$, at $p < 0.01$ level), and chlorite ($R^2 = 0.59$, at $p < 0.01$ level) in the hot spot, but negatively correlated with a mixed layer of illite and smectite ($R^2 = 0.83$, at $p < 0.01$ level). In contrast, the cases of Cd, Cu, Pb, and Zn presented an opposite trend with As. The positive matrix factorization (PMF) results showed that the contribution rate of nonferrous metal smelting to soil As was 42.90% and those of Cd, Cu, Pb, and Zn were 84.90%, 56.40%, 59.90%, and 59.20%, respectively. These results can provide guidance for controlling the TE risk associated with agricultural land management.

Keywords: nonferrous metal smelting; toxic elements; clay minerals; geographical detector; positive matrix factorization



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1. Introduction

Nonferrous metal smelting is considered to be one of the most important sources of anthropogenic arsenic (As) and other trace element (TE) emissions [1,2]. TEs such as anthropogenic arsenic (As), cadmium (Cd), lead (Pb), and copper (Cu) in nature are all sulfurophilic elements, which are often associated with each other in the mineralization process. Hebei Province in northern China is a major province in the metallurgical industry, with 3022 nonferrous metal smelting and processing enterprises. During the smelting process, these TE as products are discharged into the environment with waste gas, wastewater, and waste slag, leading to accumulation in agricultural soils that threatens human

health [1–3]. TE pollution is very prominent in the province due to a large emission of complex TE pollutants. The agricultural land area polluted by As, Cd, Cu, Zn, and Pb has reached 120 km² [2]. For arsenic in particular, the United States Agency for Toxic Substances and Disease Registry (ATSDR) places inorganic As or arsenic oxides at the top of the toxicity list, based on their toxicity and potential for human exposure [3]. Due to its high toxicity, TE have caused increasing soil environmental concerns, and people are increasingly aware of its harm to plant, animal, and human health [4,5].

Nonferrous metal smelting is considered to be a main source for inducing TE pollution [6–9]. The migration and transformation abilities of TE in soil depend on the clay type and amounts of Fe₂O₃, MnO, Al₂O₃, and CaO, as well as on the total organic carbon (TOC), soil pH and cation exchange capacity (CEC) [10–12]. Clay minerals in natural soil (smectite, illite, kaolinite, and chlorite) play a crucial role in TE migration via adsorption [5,10,13,14]. The affinity of TE to clays depends on the composition and type of clay minerals [5,10]. For instance, a 2:1 layer of smectite, illite, and chlorite has high CECs and numerous adsorption sites for metal cations [15]. Smectite, illite, and chlorite can form polyhydroxyl-stable complexes with TE ions or adsorb cations through cation exchange [16]. Moreover, the adsorption of TE on clay minerals involves a series of complex adsorption mechanisms such as direct binding, surface complexation, and ion exchange between metal cations and clay minerals [10,13,14]. Meanwhile, as CaO can regulate the pH in soil, it affects the ability of clay minerals to adsorb TE, induces the formation of hydrophyrite, hematite, and goethite from iron oxide, and changes the mobility of TE [13]. The adsorption capacity of clay minerals to different TE ions will change under the change of soil environment [17]. The aforementioned factors not only affect the migration and transformation ability of TE in natural soil in isolation, but also determine their interactions [11,18–21]. Previous studies on the distribution of TE have been limited to interpolation analyses, which cannot explain how interactions of the soil properties affect the distribution characteristics of TE [19–21]. Hence, the key issue is how to link these soil factors (such as clay, pH, CEC, CaO, TOC, Fe, and Mn oxides) with TE distribution patterns in farmlands around nonferrous metal smelting areas.

The high-risk area of soil composite TE pollution around nonferrous metal mining and smelting areas has reached thousands of square kilometers [9,22]. The potential TE (As, Cd, Pb, Cu, and Zn) in the soil in northern China have been saturated, reaching a critical overflow point. Hence, accurately quantifying the contributions of important factors (such as clay, pH, CEC, CaO, TOC, Fe, and Mn oxides) to the spatial distribution of TE is an important task [23–27]. Traditional multivariate analysis is based on the distribution characteristics of TE and could be used to predict possible influencing factors. However, it cannot quantify the extent of each specific factor's influence. The spatial variability of pollutants and their concentrations in specific soil layers varies with the influencing factors. The Geodot theory is mainly based on the spatial variability of pollutants. If a particular impact factor causes soil pollution, the pollutant will exhibit spatial distribution and variability similar to that of the impact factor. Geodot explains the effects of various factors and their interactions on the spatial variation of pollutants [28,29]. Hence, it helps to quantify the contribution level of soil factors to TE. Meanwhile, the PMF model is an important means of quantitative analysis of environmental pollution sources. It is one of the source contribution methods recommended by the USEPA. Moreover, the PMF model has been applied in research on the source contribution of TE, which can obtain accurate results and demonstrate the good performance of this model. As a novel-source analytic receptor model, PMF has been investigated, and in the solution process, non-negative constraints on the factor load and factor score have been made, and using data standard deviation has been shown to optimize the factor load and scores and have made them more interpretable with a clear physical meaning [28].

In this study, we aimed to predict the distribution of TE in agricultural land in Qingyuan in Baoding, Hebei Province, China. The objectives of this present study were to (a) determine the factors that influence the distribution of TE at multiple factors us-

ing Geodor; (b) reveal the relationship between soil clay minerals and TE exchangeable fractions in the hot spot area using correlation analysis; and (c) analyze the rate of source contribution for TE in soils affected by nonferrous metal smelting activities using PMF. Our study provides important theoretical support for understanding the mobility and transformation of TE in agricultural land around nonferrous metal smelting activities.

2. Materials and Methods

2.1. Study Area

The town of Qingyuan (113°40′–116°20′ E, 38°10′–40°00′ N) is located in Hebei Province, China (Figure 1). The town covers an area of 867 km², including 922 km² of cultivated land. The total population is about 338,295. The topography of this area is an alluvial depression plain, a low-lying flat land, and the soil type is mainly fluvo-aquic soil. The study area has a warm, temperate, continental, monsoon-type, sub-humid, and semi-arid climate, with a mean annual temperature of 12.7 °C. It has a metallurgical development history that has lasted decades. Moreover, the rural population has continued to increase. For local residents' health, the government has gradually intensified its efforts to improve the environment during this period. Some metallurgical enterprises have stopped production, but there are still hundreds of nonferrous metal recycling, smelting, casting, and processing enterprises. Over the course of its development, the town has gradually formed a complete industrial chain integrating recycling, electrolysis, cable processing, and precision instrument manufacturing. Due to smelting activities, Cu, Zn, Cd, and Pb have seriously polluted cultivated land according to the risk screening values for soil contamination of agricultural land (soil environmental quality risk control standard for soil contamination of agricultural land (GB15618-2018)) [30].

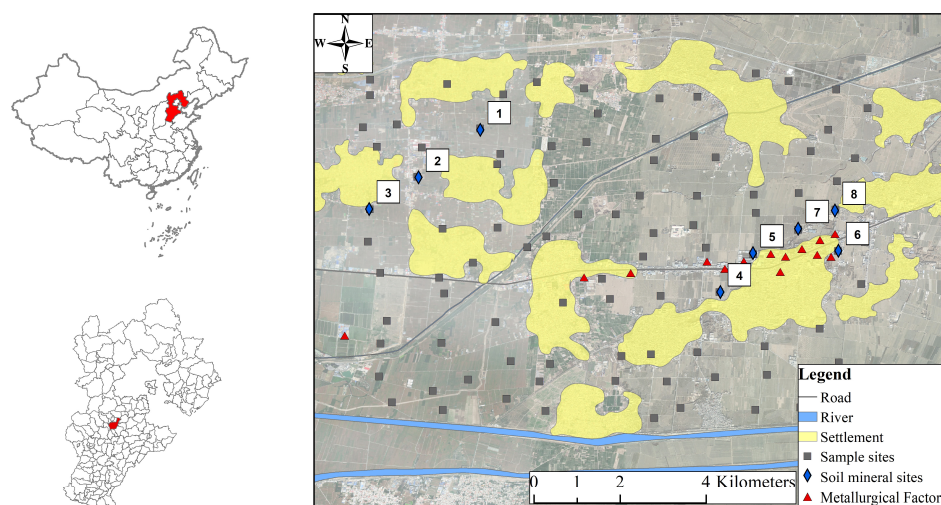


Figure 1. Sampling locations in the study area. The samples of 1, 2, 3 were collected at non hot-spot and 4, 5, 6, 7, 8 were collected at hot-spot.

2.2. Sample Collection and Preparation

The samples were collected in the east of Baoding, Hebei Province, China, where numerous nonferrous metal smelters exist. Following the plum blossom method, 95 soil samples (0–20 cm cultivated horizon) were collected from the farmland around the nonferrous metal smelters using a predetermined grid system. Approximately three to five subsamples were collected and thoroughly mixed as an analysis sample. Consider that soil properties are affected by surrounding land use. During sampling, geographical information such as location land-use type, metallurgical enterprise site, coordinates, and elevation were recorded. The samples were then air-dried for approximately two weeks at room temperature. Subsequently, they were sieved through a 1 mm nylon sieve to remove stones and plant residues, after which they were immediately transported to the laboratory.

2.3. Chemical Analysis

The samples were digested by $\text{HNO}_3\text{--HF--HClO}_4$ (3:1:1) in a microwave digestion tube prior to inductively coupled plasma mass spectrometry (ICP-MS; NexION 350X, PerkinElmer, Waltham, MA, USA). The detection limits of the TE in this study ranged from 0.001–0.015 mg/kg; the relative standard deviations of all heavy metals were less than 5%.

Soil pH was analyzed following the standard method HJ 962-2018 (F50A). The Fe_2O_3 content was determined using the potassium dichromate volumetric method, and the content of CaO and Mn was determined using the atomic absorption method. The TOC content was determined using an Elementar (Vario EL, Elementar, Frankfurt, Germany). Soils were treated with 1 M HCl to remove carbonates before determination.

CEC was determined following reference HJ 889-2017; soil samples were digested in an advanced microwave digestion system to determine the heavy metal pseudo-total concentrations following the United States Environmental Protection Agency (USEPA) method 3051A. Cd, Cr, Cu, Ni, Pb, and Zn concentrations were measured via ICP-MS (NexION 350X, PerkinElmer). Further, As and Hg were measured via hydride generation atomic fluorescence spectrometry (DZ/T 0279.13-2016) and vapor generation–cold atomic fluorescence spectrometry (DZ/T 0279.17-2016, AFS-2202E). The detection limits of the heavy metal(loid)s were as follows: As, 0.4 $\mu\text{g/g}$; Cd, 0.2 $\mu\text{g/g}$; Cu, 4 $\mu\text{g/g}$; Zn, 5 $\mu\text{g/g}$; Pb, 1 $\mu\text{g/g}$; Ni, 1 $\mu\text{g/g}$; Cr, 10 $\mu\text{g/g}$; and Hg, 0.1 ng/g.

Additionally, TE speciation chemical analysis was conducted following the TESSIER five-part extraction method using ICP-MS [31]: (1) the exchangeable was extracted by adding 8 mL 1 mol/L ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$); (2) carbonate was extracted by adding 8 mL 1 mol/L sodium acetate (NaAc); (3) Fe–Mn oxidation was extracted by adding hydroxylamine hydrochloride (NH_2OHHCl); (4) organic bound was extracted by adding 3 mL 0.02 mol/L nitric acid (HNO_3) and 5 mL 30% (*v/v*) hydrogen peroxide (H_2O_2); and (5) the residual was digested and analyzed using the nitric acid(HNO_3)–hydrofluoric acid(HF)–perchloric acid(HClO_4) digestion method. The difference in value of the total and sum of (1) + (2) + (3) + (4) + (5) for heavy metals was below 15%. The results of speciation met the test requirements.

The spatial distribution map of TE was mapped following the detection results, and then eight soil samples in the TE hot spot (4–8) and non-hot spot (1–3), serving as controls were selected for clay mineral analysis (Figure 1). Clay minerals were analyzed via X-ray diffraction (XRD, D8 Advance) reference SY/T 5163-2018 (analysis method for clay minerals and ordinary nonclay minerals in sedimentary rocks by X-ray diffraction).

2.4. Evaluation Method

2.4.1. Geographical Detector

The geographical detector (Geodot) is a statistical tool to determine the spatial differentiation of environmental factors and reflects the driving forces for the distribution of TE [32,33]. Q-statistics were used to quantitatively analyze the contribution rate of the given environmental factors. This method has been successfully used in the last decade to understand the relationship between environmental factors and TE [33–35]. In this study, we assessed major variable factors, including soil clay, pH, TOC, Fe_2O_3 , Mn, CaO, and CEC. Different q values were calculated using the following formula:

$$q = 1 - \frac{\sum_{h=1}^L N_h \sigma_h^2}{N \sigma^2} \quad (1)$$

where h represents the subregion of independent variable X , N_h represents the number of samples in the subregion of h , N represents the number of spatial units in the whole region, σ_h^2 represents the variance of the subregion, and σ^2 represents the total variance of the whole region [35]. An interaction detector was used to detect the interaction between the two factors. The q value was used to evaluate whether the interaction of these two environmental factors enhanced or weakened the explanatory ability of a single factor to the

dependent variable Y or was consistent with the effect of two independent environmental factors on Y [29].

2.4.2. Positive Matrix Factorization

PMF is a mathematical method that uses a sample of receptor models or fingerprints for quantitative analyses of TE pollution sources. Paatero and Tapper (Paatero and Tapper, 1994) proposed for the first time that the least iterative square algorithm decomposes the original matrix E_{ik} into two factor matrices, A_{ij} and B_{jk} , and a residual matrix ε_{ik} [36]. The basic equation is as follows:

$$E_{ik} = \sum_{j=1}^p A_{ij}B_{jk} + \varepsilon_{ik} (i = 1, 2, \dots, m; k = 1, 2, \dots, n) \quad (2)$$

where E_{ik} is the concentration of k pollutant in the i sample; A_{ij} is the contribution of the i sample to the j source, that is, the source sharing ratio matrix; B_{jk} is the contribution concentration of the k pollutant in the j source, namely the source component spectrum matrix; and ε_{ik} is a random error. PMF decomposes the original matrix through multiple calculations to obtain the optimal matrices A and B , making the output objective function reach the minimum value, and the objective function Q is:

$$Q = \sum_{i=1}^m \sum_{k=1}^n \left(\frac{\varepsilon_{ik}}{\sigma_{ik}} \right)^2 \quad (3)$$

where σ_{ik} represents ε_{ik} uncertainty. The concentration data and uncertainty data should be loaded during the operation process. The calculation method for the uncertainty is as follows:

When the TE concentration is less than or equal to the corresponding method detection limit (MDL), the uncertainty value is:

$$Unc = \frac{5}{6} \times MDL \quad (4)$$

When the potential trace elements concentration is greater than the corresponding MDL , the uncertainty value is:

$$Unc = \sqrt{(\sigma \times c)^2 + (MDL^2)} \quad (5)$$

where σ is the relative standard deviation and c is the TE concentration. Since there is no clear number of factors, there will be some errors in the results. Many factors cause a source to be decomposed into two or even more, while some do not exist. If the number of factors is minimal, different pollution sources will be combined into one. Therefore, residual matrix E is controlled by finding the minimum value Q . It is very important to determine the number of factors involved. In this study, the rotation coefficient F_{peak} is set as -0.1 , and 20-factor iteration operations were carried out to obtain a low Q value. Most of the residual values were between -3 and 3 . With the adjustment of the factor number, the calculation results tended to be stable, and finally, four factors were determined.

2.5. Statistical Analysis

SPSS 24.0 was used for all descriptive statistics of TE and soil properties. The distribution map of the soil sample sites and the predicted distribution map of soil TE were completed using the Geostatistical Analyst module of ArcGIS10.5. The chord diagram, percentage histogram, and correlation analysis were completed using Origin Pro 2022. The source analysis of soil TE was completed using PMF5.0

3. Results and Discussion

3.1. Concentration and Soil Properties

3.1.1. Concentration and Distribution

The average contents of As, Cd, Cu, Zn, Pb, Ni, Cr, and Hg were 27.67, 3.91, 143.90, 355.95, 201.64, 25.5, 67.57, and 0.06 mg/kg in cultivated land surrounding nonferrous metal smelting enterprises in the east of Baoding, Hebei Province, respectively. The mean values of As, Cd, Cu, Zn, and Pb exceeded the risk screening values for soil contamination of agricultural land (soil environmental quality risk control standard for soil contamination of agricultural land (GB15618-2018)) by 29.75%, 551.67%, 43.90%, 18.65%, and 18.61%, respectively. We further analyzed the distribution of TE pollution features in cultivated land surrounding nonferrous metal smelting.

The spatial distribution maps for TE (As, Cd, Cu, Zn, and Pb) were mapped using the inverse distance weighted method (Figure 2a–e). Following this method, the overall distribution characteristics of the TE in cultivated land in polluted and non-polluted areas were identified. This indicated that the hot spot of the TE area was distributed in the soil surrounding the industrial zone of nonferrous metal smelting. Moreover, the TE content showed a decreasing trend farther away from the nonferrous metal smelting industrial zone. The areas with high TE content were mainly concentrated in the northeast direction, consistent with the distribution of nonferrous metal smelters. This result clearly demonstrates that nonferrous metal smelting enterprises were the main contributor to TE pollution.

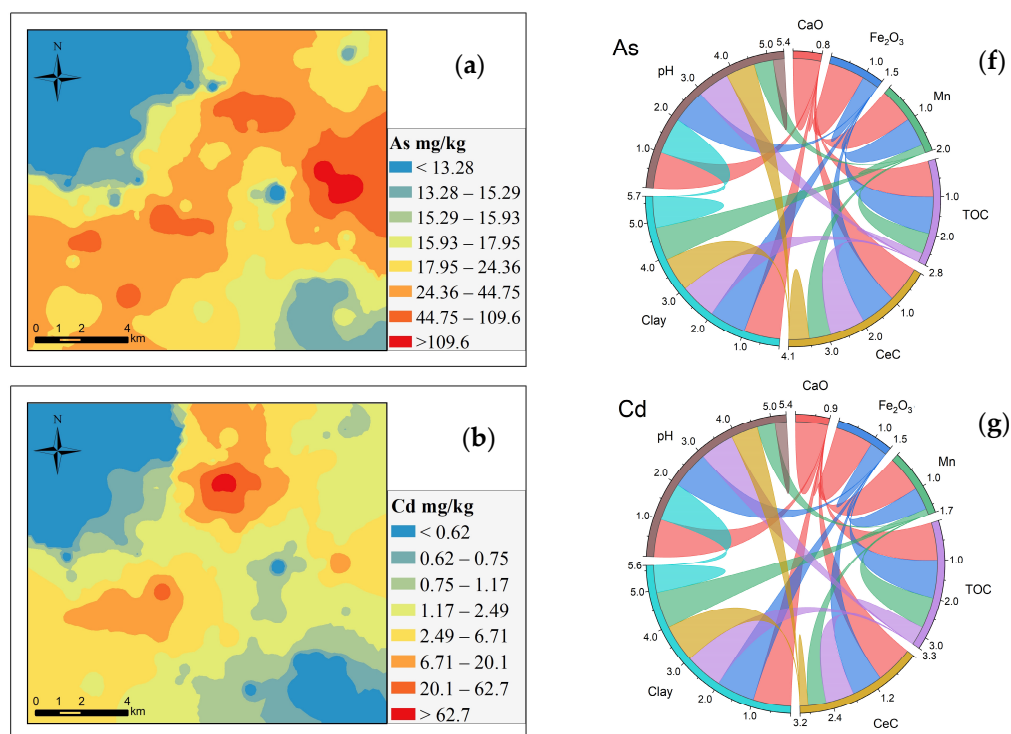


Figure 2. Cont.

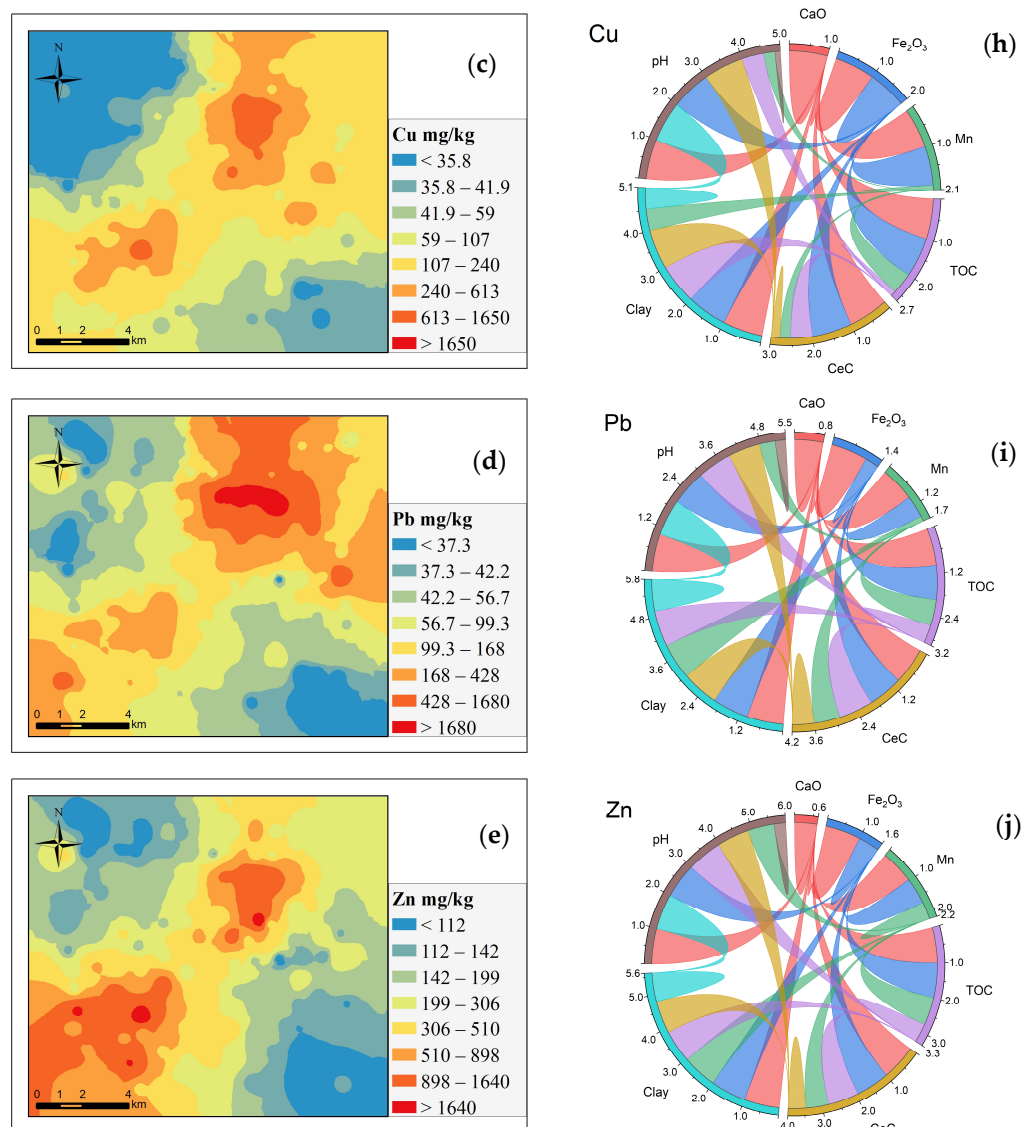


Figure 2. Distribution map of TE and contributions in this study to TE contributions of interactions between total TE and different factors. (a), (b), (c), (d), (e) denote distribution maps of As, Cd, Cu, Pb, Zn, respectively. And (f), (g), (h), (i), (j) mean contributions of interactions between total As, Cd, Cu, Pb, Zn and soil properties, respectively.

3.1.2. Soil Properties

Table 1 summarizes the statistical analysis of the soil properties in the study area, which belongs to the generally weak alkaline soil. The coefficient of variation of the clay, CaO, TOC, and CEC was greater than that of Fe_2O_3 , Mn, and pH. In particular, the variation of clay and CaO was significant, and the coefficient of variation was more than 40%, which belongs to a moderate variation. This indicated that the soil clay and CaO were affected by external factors. Meanwhile, the large coefficient of variation also indicated that the ability of clay to adsorb TE in the soil of the study area differed. Studies have confirmed that clay minerals in soil are the main sources of TE adsorption sites [12,24]. CaO also has the same capacity as clay to adsorb TE [1,37,38]; the variation of both was large, indicating the heterogeneity of the soil adsorption capacity of TE in the study area.

Table 1. Soil properties and q -statistics of different factors on TE.

Types	Clay	CaO	Fe ₂ O ₃	Mn	TOC	CEC	pH
Coefficient of Variation	41.44%	41.29%	11.26%	11.50%	33.14%	23.44%	3.89%
Mean values	78.39 g/kg	3.55 (10 ^{−2})	4.39 (10 ^{−2})	577.73 (10 ^{−6})	1.10 (10 ^{−2})	9.73 (10 ^{−6})	8.15
Total As (q statistic)	24.70%	22.18%	13.68%	6.98%	7.08%	16.41%	8.98%
Total Cd (q statistic)	22.20%	26.78%	14.19%	5.03%	15.35%	6.84%	9.60%
Total Pb (q statistic)	24.52%	22.06%	10.65%	4.07%	13.70%	16.82%	8.18%
Total Cu (q statistic)	17.19%	31.14%	31.83%	3.89%	4.42%	7.11%	4.43%
Total Zn (q statistic)	21.14%	16.29%	15.35%	12.57%	13.55%	12.70%	8.40%

3.2. Driving Mechanism and Contribution of Soil Property Factors to the Spatial Distribution of TE

Studies have shown that pH is a key factor affecting the ability of soil minerals to carry TE. Soil pH is crucial in the mobility and bioavailability of TE in the soil and could affect the complex reaction of cations on the surface of clay minerals in the soil, ion exchange, and other metal-binding processes [39,40]. TOC indirectly affects soil TE behavior by influencing soil microbial activity [41,42]. Soil clay enriches TE through specific surface areas, thus affecting their migration behaviors [43]. Furthermore, several studies have shown that pH, TOC, and soil clay must be considered when studying the behavior of TE in soil [44,45]. CEC reflects the ability of soil to exchange TE cations [27,46].

Numerous results have proven that the oxides of Fe and Mn have a good adsorption effect on TE [47–49]. CaO is also the most effective mineral for absorbing TE in soil [1,50,51]. Therefore, the spatial distribution of TE is intertwined with many factors, including soil clay, pH, TOC, CEC, Fe₂O₃, Mn, and CaO. These factors have different degrees of impact on As. The effects of these factors may be independent, implying that there is no interaction between the two factors, but somehow may be complicated. This means that one factor can weaken or strengthen another due to reciprocal action. The contribution of soil factors to TE can be quantified by further determining the mechanism driving the spatial distribution of TE using Geodot [29,52].

3.2.1. Dominant Factors of Spatial Distribution

Table 1 shows the contribution of the main factors that affect the spatial distribution of TE. For total As, the first three main contributing factors were soil clay, CaO, and CEC. However, the contribution rate of these three main influencing factors to the spatial distribution of As differed. The clay had the greatest contribution ($q = 24.70\%$), the second was CaO ($q = 22.18\%$), and the third was soil CEC ($q = 16.41\%$). In addition, the contributions of Fe₂O₃, Mn, TOC, and pH were 13.68%, 6.98%, 7.08%, and 8.98%. The results of soil mineral analysis confirmed that the percentage of clay in the hot spot was higher (25%) than that in the non-hot spot (15.33%). Meanwhile, the percentage of calcium carbonate in the hot spot (7.6%) was higher than that in the non-hot spot (3.67%). These results indicate the effects of clay and CaO on As and other TE in the polluted soil and further confirm the contribution of clay and CaO to the spatial distribution of As. Mn and TOC in the soil can also affect the migration and transformation of As. However, the contribution of Mn and TOC to As was relatively low, indicating that the two-soil factors have a tiny impact on As migration. For other TE, the top three contributing factors to Cd, Pb, Cu, and Zn were soil clay, CaO, and Fe₂O₃. The contributions of clay ($q = 22.20\%$, 24.52%, 17.19%, 21.14%) and CaO ($q = 26.78\%$, 22.06%, 31.14%, 16.29%) were highly similar and both factors exerted almost identical effects on the TE. The contribution of Fe₂O₃ for TE exceeded those of Mn,

CEC, and pH. However, the q values of Fe_2O_3 and TOC for Cd and Pb were smaller than As, Cu, and Zn.

Based on the aforementioned results, in situ clay minerals might be safely applied as remediation agents on cultivated land contaminated by TE in the study area. The contribution of CaO to As, Cd, Pb, Cu, and Zn were 22.18%, 26.78%, 22.06%, 31.14%, and 16.29%, close to that of clay. Moreover, numerous studies have confirmed that lime is an effective nonclay mineral for adsorbing heavy metal ions [1,23,53,54]. This is because Ca^{2+} and other divalent cations form ternary complexes on the surface of clay minerals to enhance the adsorption of TE [5,55]. Especially for total Cu, the q values of Fe_2O_3 were 31.83% similar with CaO (31.14%), but higher than the other TE's q values of Fe_2O_3 , possibly because Cu is more likely to adsorb iron-oxidized and CaO surfaces [56,57].

3.2.2. Contribution of Multivariate Interaction

Figure 2f–i shows the influence of the interaction between the factors on the spatial differentiation of total TE. The results show that the interaction between all factors was greater than any single factor. This indicates that the factors are mutually and nonlinearly enhanced. Moreover, it shows that the combined effect is greater than the synthesis of any single effect. For total As, the contribution of the interaction between the clay and CaO explains the 99.99% contribution, much larger than the sum of its contribution (46.88%). Moreover, the contribution of the interaction between the clay and the TOC (99.29%) is much greater than any additive effect alone (31.78%). The interactions between clay and CaO and between clay and Fe_2O_3 explain 99.99% of the contribution to As; much larger than the sum of their individual contributions. For other TE, As and Cd, Pb, Cu, and Zn are close to the contribution of the interaction. Figure 2 and Table 1 show that the interaction between the factors emphasizes that the factors affecting the spatial distribution of TE were not the result of a simple additive relationship. Conversely, it results from the superposition of spatial distribution features of different factors [52]. When a single factor is considered, its explanation is not obvious. However, its explanation is greatly enhanced when the combined effects of soil factors are considered. The results indicate that changes in soil clay, CaO, and Fe_2O_3 directly and significantly affect the spatial distribution of TE.

Currently, most studies on the relationship between TE and soil clay minerals in contaminated cultivated land, especially the basic analysis of clay minerals, are insufficient. This makes it difficult to show the complex situation of a real contaminated site. The blind selection of passivating agents induces poor long-term performance and stability, damaging the local soil's structure [4,5,26]. Hence, it is difficult to maximize economic and ecological benefits. Field investigation and research should be combined with the combined action of multiple factors to optimally understand the binding relationship among TE, CaO, Fe_2O_3 , and clay minerals.

3.3. Relationship between Exchangeable TE and Clay Content

Figure 3a–e summarizes the speciation composition of TE. The results of As show that an exchangeable fraction accounts for 16.43% higher than carbonate (4.63%), Fe–Mn oxidation (6.25%), and organically bound fractions (1.5%) in hot spots. However, the results also show that residual fraction accounts for 72% (Figure 3a). The results of Cd, Pb, Cu, and Zn show that an exchangeable fraction accounts for 8.67%, 0.39%, 1.0%, and 0.92% smaller than carbonate (26.69%, 29.78%, 8.92%, 12.19%) and Fe–Mn oxidation (24.07%, 26.57%, 11.65%, 28.79%). Meanwhile, the result of organically bound fractions accounts for 4.9%, 14.71%, 5.54%, 16.46%, respectively. The results show that the residual fraction of Cd, Pb, Cu, and Zn accounts for 35.67%, 28.56%, 52.57%, and 61.96%. The percentage of the residual fraction of TE is relatively high compared with other fractions in hot spots, especially As. This further explains why TE are fixed by silicate mineral lattices. The percentage of exchangeable TE in the non-hot spot was higher than in the hot spot. These results might have been caused by low clay levels in the hot spot area (Figure 3f).

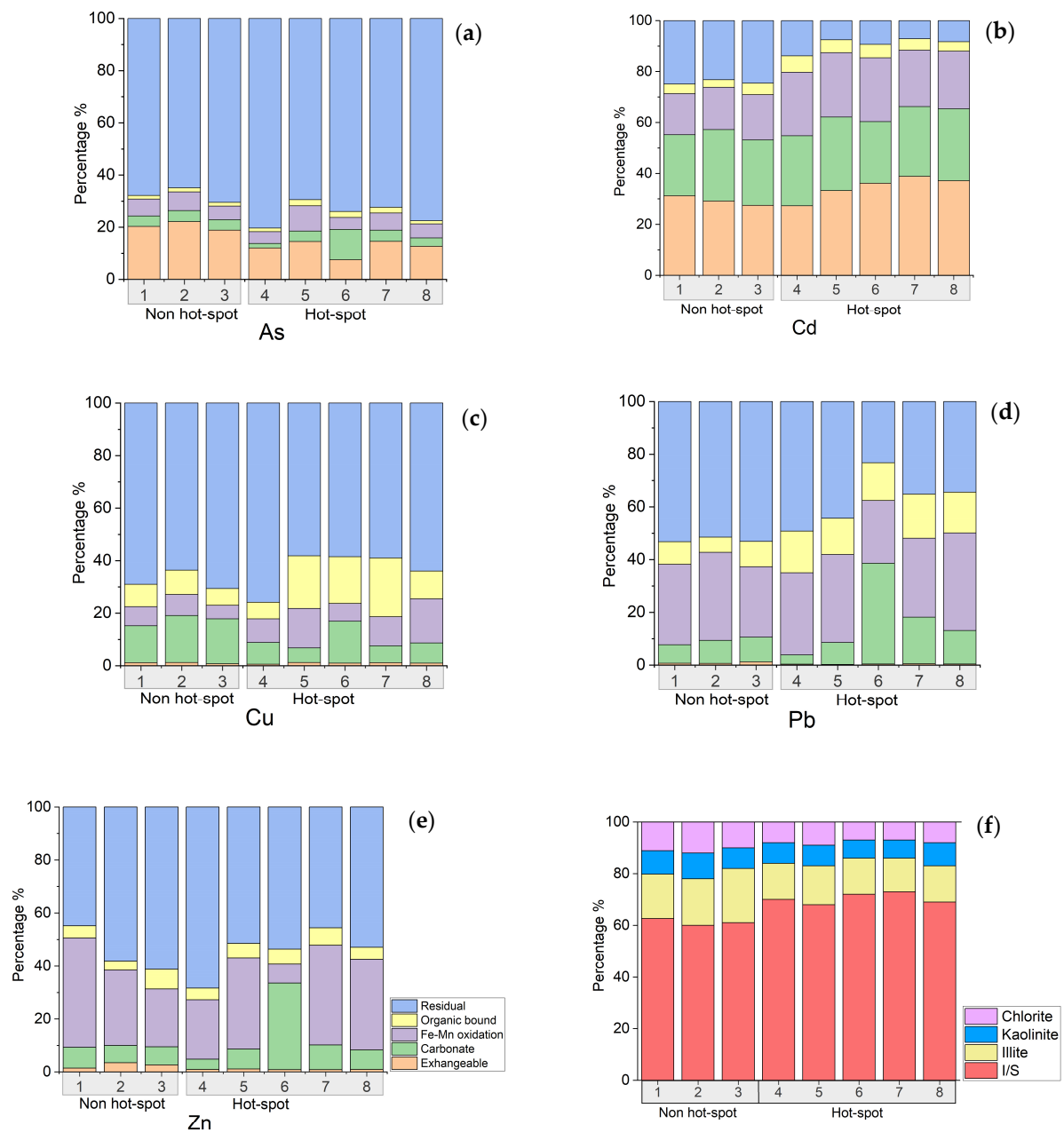


Figure 3. Histogram of percentage of speciation TE, and histogram of a percentage of clay minerals. (a), (b), (c), (d), (e) mean the speciation percentage of As, Cd, Cu, Pb, Zn in non hot-spot and hot-spot in the study, respectively. (f) imply clay minerals percentage in non hot-spot and hot-spot in the study.

Based on the above analysis, we speculate that clay is the main controlling factor for TE migration and transformation. Therefore, we analyzed clay mineral types and the percentage content via XRD (Figure 3f). The results showed that the clay minerals in the study area included an illite and smectite mixed layer, illite, kaolinite, and chlorite, with an average percentage content of 67.13%, 15.38%, 8.25%, and 9.25%. The mixed layer of illite and smectite was the dominant clay mineral in the area, and the proportion was four to nine times that of the other clay minerals. However, the percentage content of mixed layers of illite and smectite was higher in the hot spot (69.6%) than in the non-hot spot (63%). The existence of illite and smectite greatly affected the migration and transformation ability of As and other TE (Cd, Pb, Cu, and Zn) in the hot spot.

Figure 4 shows the relationship between exchangeable TE and clay (mixed layers of illite and smectite, illite, kaolinite, and chlorite). The exchangeable fraction of As was observed to be significantly and negatively correlated with the illite and smectite mixed layers, and the correlation coefficient R^2 was 0.83 (at $p < 0.01$ level) following the correlation analysis. However, illite, kaolinite, and chlorite showed a significant positive correlation, and the correlation coefficients R^2 were 0.76, 0.43, and 0.59, at the $p < 0.01$ level, respectively. In addition, the exchangeable fractions of Cd, Pb, Cu, and Zn were observed to be significantly and positively correlated with the illite and smectite mixed layers, and the correlation coefficient R^2 were 0.29, 0.53, 0.22, and 0.79 (at $p < 0.01$ level) following the correlation analysis (Figure 5).

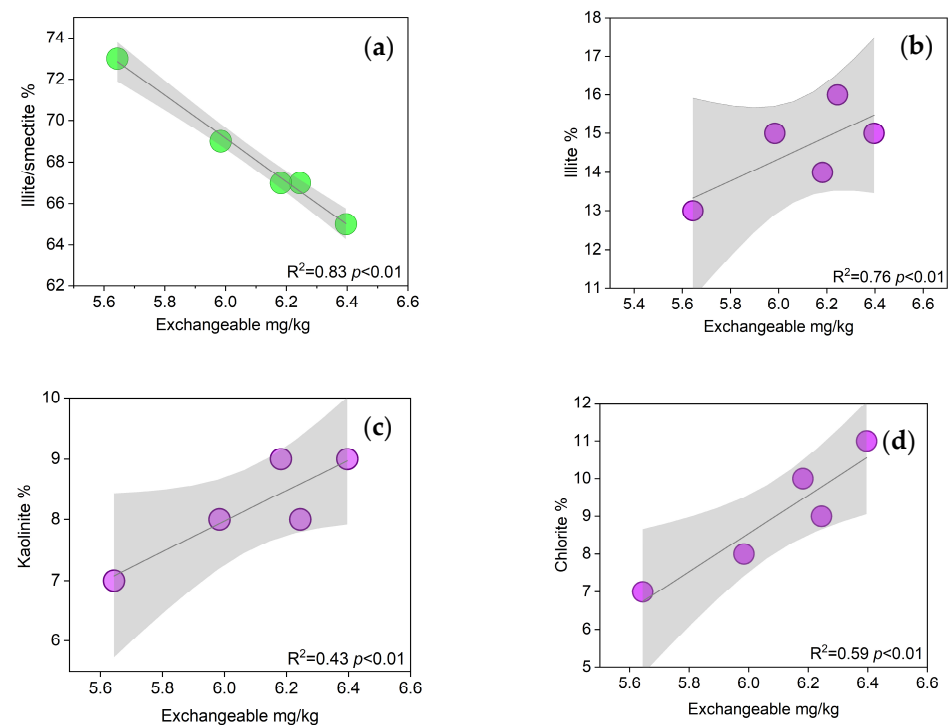


Figure 4. The relationship between exchangeable As and clay (mix clay of illite and smectite, illite, kaolinite, and chlorite) in a hot spot in the study area (samples 4, 5, 6, 7 and 8). (a), (b), (c), (d) stand for the relationship of mix clay of illite and smectite, illite, Kaolinite, Chlorite, and exchangeable of As, respectively.

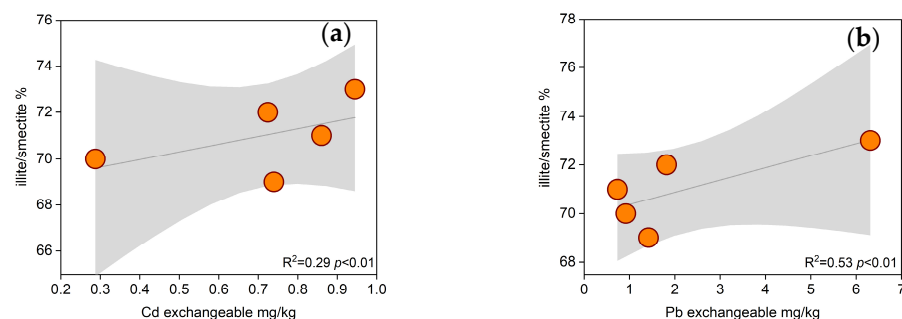


Figure 5. Cont.

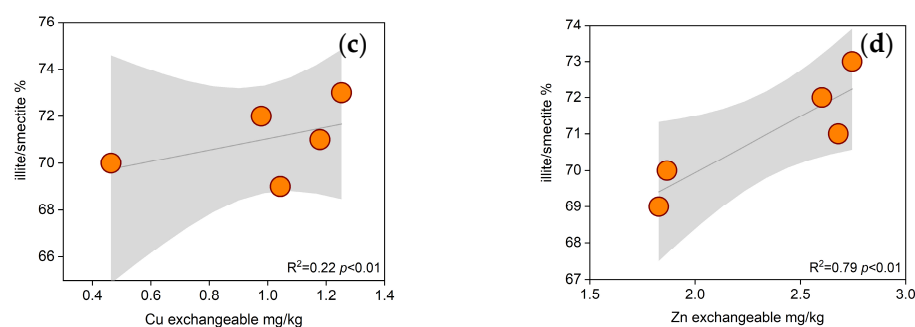


Figure 5. The relationship between exchangeable Cd, Pb, Cu, Zn and clay (mix clay of illite and smectite) in a hot spot in the study area (samples 4, 5, 6, 7 and 8). (a), (b), (c), (d) indicate the relationship of mix clay of illite and smectite, and exchangeable of Cd, Pb, Cu and Zn, respectively.

There are two important reasons for this result in our analysis. Firstly, the speciation results show that the carbonate (4.63%), Fe–Mn oxidation (6.25%) and organically bound fractions (1.5%) occupy a certain proportion. In addition, soil factors CaO (41.29%), Fe_2O_3 (11.26%), Mn (11.50%), and TOC (33.14%) were important factors driving the spatial distribution of As. Therefore, these soil factors and clay minerals will produce competitive adsorption behaviors with As ions, resulting in the occurrence of the above relationship. Secondly, this also indicates that clay minerals in soil have an adsorption competition mechanism for As and other TE. Smectite is often used as a remediation material for soils contaminated by As, Cd, Cu, Pb, and Zn [14,58,59]. Smectite and illite are 2:1 clays (two tetrahedral and one octahedral sheet). Moreover, smectite mainly absorbs TE through cation exchange and has more adsorption sites for TE than illite. TE ions might be adsorbed on the surface of the smectite. Moreover, adsorbed TE are easily released with the “occupying” of other TE ions, affecting their long-term performance and stability [24,59]. Kaolinite is a 1:1 clay (one tetrahedral and one octahedral sheet per layer) and does not occur in cation substitution. Chlorite is a 2:1 clay containing a hydroxyl sheet. Studies have confirmed that the adsorption of kaolinite and chlorite for As (V) is 25–35 times larger than that of other clay minerals [10].

Currently, studies have shown that the opposite properties of As and Cd, Pb, Zn, and Cu are difficult to fix simultaneously [19,20,60]. Since conventional remediation measures cannot simultaneously reduce the availability of As and Cd, Pb, Zn, and Cu in soil [19,61,62], a more comprehensive remediation strategy must be developed for pollution due to nonferrous metal smelting activities.

3.4. Source Contribution

It is necessary to identify each source contribution for each TE, which can be easily determined by the factor score derived from the PMF model. Figure 6 shows the contribution rates of each factor source analyzed by PMF to soil TE. This indicates that the As, Cd, Cu, Pb, and Zn have high concentration values in Factor 1, and the contribution rates are 42.90%, 84.90%, 56.40%, 59.90%, and 59.20%, respectively. The proportions of As, Cd, Cu, Pb, and Zn samples exceeding the risk screening value (mg/kg) of agricultural land soil pollution are 29.75%, 80.38%, 36.71%, 20.25%, and 34.81%, respectively. The main source of TE is the secondary product of smelting metal sulfide mines [63,64].

Meanwhile, Cr and Ni contribute 67.10% and 67.50%, to Factor 2. The average concentrations of Cr and Ni were lower than the soil environmental background values in Hebei Province. Moreover, some studies have also demonstrated that Cr and Ni in the soil is mainly affected by the parent material [65,66]. Hence, Factor 2 can be interpreted as a natural source. TE have a higher value in Factor 2, and the contribution rate of As, Cd, Cu, Pb, and Zn were 53.40%, 13.80%, 41.90%, 37.30%, and 37.90%. In addition, the amount of As, Cd, Cu, Pb, and Zn in Factor 3 and Factor 4 also had small values, contributing 1.20%, 1.10%, 1.70%, 2.30%, 2.90% and 2.60%, 0.20%, 0.01%, 0.60%, 0.01%, respectively.

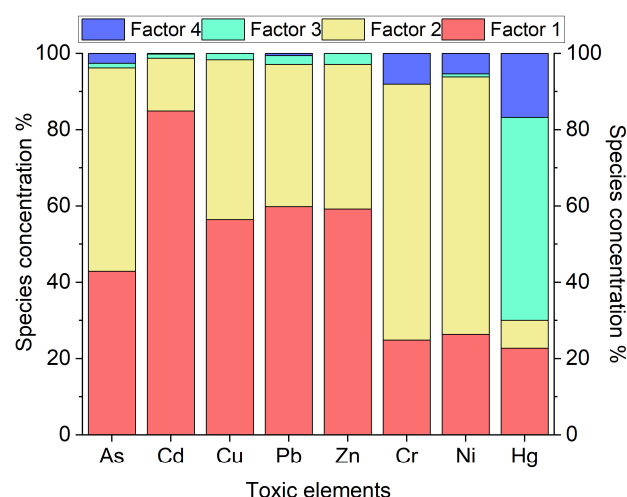


Figure 6. Contribution rate of each factor source to soil TE in this study area.

4. Conclusions

In this study, we observed that clay was the key factor for TE migration and transformation at multiple factors. There was a significant positive correlation between clay minerals and the exchangeable fraction As in the polluted area. However, the relationship of As was opposite to Cd, Cu, Zn, and Pb with clay minerals. As prefers to be adsorbed to illite, kaolinite, and chlorite compare with Cd, Cu, Zn, and Pb. The contribution rate of nonferrous metal smelting to As, Cd, Cu, Zn, and Pb in this area was 84.90%, 56.40%, 59.90%, and 59.20%, respectively. Next, we should focus on adsorption and desorption batch experiments to explore the competitive mechanism of As and clay minerals (illite, smectite, kaolinite, and chlorite) based on their relationship in the presence of other TE (Cd, Pb, Cu, and Zn).

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