

# Determining environmental risk and source of heavy metal(loid)s in the surrounding farmland soil of a zinc smelter in water source area, Northwest China

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## Research Article

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# Abstract

Risk and source of heavy metal(loid)s (As, Cu, Cr, Pb, Mn, Ni, V, and Zn) were determined in the surrounding farmland soil of a zinc smelter in the water source area of the Mid–route of South–North Water Transfer Project of China to explore the impact of smelting activity on local environment. The heavy metal(loid)s contents were analyzed by X–ray fluorescence spectrometry and their pollution levels and ecological risks were assessed by geoaccumulation index, Nemerow synthetic pollution index and potential ecological risk index. The possible sources of the heavy metals(loid)s were identified by multivariate statistical analysis methods. The mean contents of the heavy metal(loid)s in the farmland soil were above the local soil background values except Mn. The contents of As, Cu, Pb, Zn, and Ni in the downwind direction soil decreased with the distance increasing between the sampling site and the zinc smelter. The investigated soils were moderately to seriously polluted by heavy metal(loid)s and the heavy metal(loid)s presented moderately ecological risk as a whole. As, Cu, Pb, and Zn mainly originated from zinc smelting activities. Cr, Mn, and V primarily derived from natural source. Ni mainly came from zinc smelting activities, partly from natural source. The zinc–smelting activity influenced the heavy metal(loid)s content, particularly Zn and Pb, in the surrounding farmland soil. The local government should strengthen the cooperative monitoring of heavy metal(loid)s in farmland and agricultural products, as well as pollutant emission monitoring and control.

# Introduction

With the development of industry, the acceleration of urbanization, and the increase of agricultural chemicals using, soil pollution problems have become increasingly prominent and attract more and more attention worldwide in recent decades (Zhao et al. 2020; Kumar et al. 2019; Zhang et al. 2019; Akopyan et al. 2018; Yang et al. 2018; Li et al. 2017 ). Among all kinds of soil pollutants, heavy metal(loid)s cause more attention due to their high toxicity and non–biodegradability (Wu et al. 2020). Heavy metal(loid)s in soil can be absorbed and enriched in plants and transferred to animals and human bodies via food chains (Liu et al. 2017; Zhang et al. 2016). When people eat grains or vegetables polluted by heavy metal(loid)s, their survival and health will be threatened (Baltas et al. 2020; Zhou et al. 2020; Bhatti et al. 2018; Li et al. 2019, 2018). High contents of heavy metal(loid)s in the body can interfere with the physiological process of the body, and injure human organs such as heart, bone, kidney, small intestine, reproductive system and nervous system (Csavina et al. 2012). Hence studying and evaluating the ecological risk of heavy metal(loid)s in farmland are important for understanding soil environmental quality, strengthening comprehensive prevention of soil pollution and safeguarding human health.

The major sources of soil heavy metal(loid)s are natural sources and anthropogenic sources (Jiang and Guo 2019). Weathering of rocks, volcanic eruptions, splashing waves, vegetation discharge are the main natural sources (Lee et al. 2020). While mining, beneficiation, metal smelting, electroplating, dyes, textiles, burning of fossil fuels, agricultural pesticides, fertilizers, sludge application and sewage irrigation are the main anthropogenic sources (Wang et al. 2019; Peng et al. 2019; Ettler 2016; Lu et al. 2014a). Among various soil heavy metal(loid) sources, nonferrous metal smelting is one of the significant (Kang et al.

2019; Křibek et al. 2019; Ghayoraneh and Qishlaqi 2017; Shiel et al. 2010; Wang et al. 2010). In the metal smelting process, large quantities of heavy metal(loid)s discharge into surrounding soil through sewage irrigation, waste residue infiltration and atmospheric sedimentation, resulting in heavy metal(loid)s pollution in farmland soil around smelter (Shen et al. 2017; Wen et al. 2015). These metals cannot be degraded naturally in soil, but through continuous enrichment in the soil to achieve a high level. Many studies have shown that contaminated soils around smelters have become high-risk areas for safe production of agricultural products (e.g. Lee et al. 2020). There are lots of literatures on soil heavy metal(loid)s pollution around smelters in China, but most of which are concentrated in the eastern and southern areas of the country (e.g. Zhao et al. 2020; Li et al. 2018; 2011). Whereas, up to now, few researches on farmland soil pollution around metal smelters have been launched in the water source area of the Mid-route of South-North Water Transfer Project.

Shangluo city (33°2'30"–34°24'40" N, 108°34'20"–111°1'25" E) is located in the upstream of Danjiang valley, the water source area of Mid-route South-North Water Transfer Project of China (Zhuang and Lu 2020). With abundant non-ferrous metal resources, such as zinc, lead, copper, molybdenum and gold, Shangluo is the important mineral resources base in Northwest China. Many metal mining and smelting industries are distributed in Shangluo, which may cause heavy metal(loid)s pollution in agricultural soil and water. Heavy metal(loid)s in agricultural soil would enter into surface water with runoff or soil erosion excepting pollute agricultural products, leading to the deterioration of water quality. South-North Water Transfer Project is a national water resource allocation project for solving the water shortage in North China. Water security is crucial to South-North Water Transfer Project. Shangluo has abundant rainfall and complex topography and geomorphology, which result in serious soil erosion in that area.

To understand the impact of metal smelting activities to farmland soil in the water source area, the farmland around a zinc-smelting plant with no other large-scale anthropogenic source in its vicinity in Shangluo, Northwest China was investigated in this study. The primary purposes of this study are (1) to determine the contents of heavy metal(loid)s in the farmland soil around the zinc smelter; (2) to evaluate the contamination degrees and ecological risks of the investigated heavy metal(loid)s in the farmland soil; and (3) to identify the sources of heavy metal(loid)s in the farmland soil. The findings of this study would help us to understand the impact of metal-smelting activities on the environment of the water source area and would offer the basic information for regulators in environmental protection of the water source area.

## **Materials And Methods**

### **Study area**

Shangluo is a mountainous valley city with a permanent population of 2.50 million (up the end of 2019) about 110 km southeast of the provincial capital Xi'an. The climate of Shangluo is semi-humid monsoon mountain climate in warm temperate zone. January is the coldest month with a mean temperature of 7.8 °C while July is the hottest with a mean temperature of 13.9 °C. The annual mean

precipitation is 696.8–830.1 mm. Affected by the terrain, the annual wind direction in Danjiang valley is mainly east (E), east–south–east (ESE), and west (W), and the mean wind speed is circa  $2.4 \text{ m s}^{-1}$ . The main crops in Shangluo are wheat and corn, and the main cash crops are vegetables and walnuts.

The investigated zinc smelter, located at the hillside of the north bank of Danjiang valley about 7 km southeast of Shangluo city, was built in 1987 with 50 thousand tons of zinc productivity per year. Meanwhile, precious metals such as silver (Ag) and indium (In) are recovered and produced in the zinc smelting process. The main raw ore of the zinc smelter is sphalerite (ZnS), associated galena (PbS) and chalcopyrite ( $\text{CuFeS}_2$ ). In addition, it also contains cadmium, indium, silver and other metals.

Considering the influence of topography, wind direction and villages distribution, three plots of farmland (marked A, B and C, respectively) in different directions near the smelter were selected for soil sampling (Fig. 1). Plot A is located on the hillside in the northwest direction of the zinc smelter. There are no villages near this plot and the traffic is inconvenient as only farmland paths lead to there. The altitude of the terraced farmland on the hillside is about 700–720 m and about tens of meters higher than the smelter. Plot B is located in the southwest of the smelter and next to a village. The altitude of plot B is about 647–649 m which is lower than that of the smelter. There are hardened rural cement roads around Plot B. Luxuriant trees and shrubs grow on the hillsides between plot B and the smelter. Plot C is located in a valley to the east of the smelter and a small seasonal stream flows through the valley. The altitude of plot C is about 680–690 m which is slightly lower than that of the smelter. There is barely vegetation between plot C and the smelter. All three plots are wheat and corn rotation, and grains grown on the farmland are consumed by the local residents. The soil type of the investigated farmland is yellow–brown soil with a pH from 7.2 to 8.3. The mean value of soil organic matter, total nitrogen, total phosphorus, available nitrogen, available phosphorus and available potassium was  $20.1 \text{ g kg}^{-1}$ ,  $1.2 \text{ g kg}^{-1}$ ,  $0.6 \text{ g kg}^{-1}$ ,  $108.9 \text{ mg kg}^{-1}$ ,  $17.9 \text{ mg kg}^{-1}$  and  $113.7 \text{ mg kg}^{-1}$ , respectively. Texture analysis indicates that soil is silty clay loam, composed of sand (26.3%), silt (56.0%), and clay (17.7%). The mean contents of major elements, i.e.  $\text{Fe}_2\text{O}_3$ , CaO,  $\text{K}_2\text{O}$ , MgO,  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  were 6.7%, 0.9%, 1.5%, 1.8%, 2.0%, 33.1%, and 7.8%, respectively.

## Sampling and analytical methods

Soil samples were collected in July 2017. A hand–held GPS was used to record the longitude, latitude, altitude and other information of sampling location. A total of 25 topsoil (0–20 cm) samples were taken from plot A (9 samples, numbered A1–A9), plot B (8 samples, numbered B1–B8) and plot C (8 samples, numbered C1–C8) (Fig. 1). At each point, a composite soil sample was fully mixed and retained at 1 kg in accordance with the four–point method in an area of about  $2 \text{ m} \times 2 \text{ m}$ . All soil samples were kept in polythene bags.

In the laboratory, all soils were air–dried naturally, and then the impurities were removed. Agate mortar and pestle were used to ground the samples to pass through  $75 \mu\text{m}$  nylon mesh. The processed samples were stored in polyethylene plastic bags. Preventing from the cross–contamination between different

samples, all processing was performed avoiding touching with metallic object. 4 g of treated soil and about 2 g of boric acid which used as the substrate were pressed by the molding press to form a circular sheet sample to be tested (Chen et al. 2013). The contents of heavy metal(loid)s (As, Cu, Cr, Pb, Mn, Ni, V, and Zn) in soil were tested using X-ray fluorescence spectrometer (XRF, Panalytical, PW2403) according to the method in literature (Pan et al. 2017). The national standard material samples and parallel samples were adopted for quality guarantee and control in the experiment. Relative error between the detected value and reference value of elements in standard sample is less than 10%, and that of the duplicate sample is less than 5%.

### Assessing methods of pollution and ecological risk

The geoaccumulation index ( $I_{geo}$ ) and Nemerow synthetic pollution index ( $NSPI$ ) were respectively used to assess the single pollution level and comprehensive pollution level of heavy metal(loid)s in the farmland soil. The  $I_{geo}$  is calculated using the following formula (Zhang et al. 2019; Chakraborty et al. 2017; Duodu et al. 2016)

$$I_{geo} = \log_2 \frac{C_i}{k \times B_i} \quad (1)$$

where  $C_i$  is the content of heavy metal(loid)  $i$  in the soil ( $\text{mg kg}^{-1}$ ); constant  $k$  is a change in reference value that may be caused by diagenesis, here 1.5 was accessed;  $B_i$  refers to the reference value of heavy metal(loid)  $i$  in parent rock, here refers to the soil element background value of Shaanxi (CNEMC 1990). The grades of pollution were distinguished in 6 levels proposed by Müller (1969) (Table S1 in Supplementary Materials).

The  $NSPI$  is calculated by formula (2) (Zhang et al. 2019)

$$NSPI = \sqrt{\frac{P_{iave}^2 + P_{imax}^2}{2}} \quad (2)$$

where  $P_{iave}$  and  $P_{imax}$  respectively represents the mean and the maximum of single pollution index  $P_i$  of all heavy metal(loid)s in a sample.  $P_i$  is equal to the ratio of the content of heavy metal(loid)  $i$  in the farmland soil and its corresponding background value in Shaanxi soil. The grades of  $P_i$  and  $NSPI$ , as well as the corresponding pollution levels are listed in Table S2 and Table S3 (Supplementary Materials).

Potential ecological risk index ( $PERI$ ), proposed by Hakanson (1980) to evaluate the ecological hazard effect resulted from toxic pollutants in sediments, has been widely applied to assess the environmental risk of heavy metal(loid)s in soil (Zhang et al. 2019; Ke et al. 2017; Suresh et al. 2012). The  $PERI$  is calculated using the formula (3) (Zhang et al. 2019).

$$PERI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times C_f^i = \sum_{i=1}^n T_r^i \times \frac{C_s^i}{C_b^i} \quad (3)$$

where  $C_s^i$  represents the determined value of heavy metal(loid)  $i$  in the soil, while  $C_b^i$  represents the corresponding reference value (CNEMC 1990).  $T_r^i$  is the toxic response factor of different substance (As, Cu, Cr, Mn, Ni, Pb, V, and Zn are 10, 5, 2, 1, 6, 5, 2, and 1, respectively) (Yuan et al. 2014; Lu et al. 2014b).  $E_r^i$  is the potential ecological risk index of heavy metal(loid)  $i$  while  $PERI$  is the comprehensive potential ecological risk index. The evaluation criteria for  $E_r^i$  and  $PERI$  are listed in Table S4 (Supplementary Materials) (Yuan et al. 2014; Lu et al. 2014b).

### Statistical analysis methods of data

Descriptive statistical analysis, Pearson correlation analysis, cluster analysis (CA) and principal component analysis (PCA) were conducted using the commercial statistics software package SPSS version 21.0 for Windows (IBM Company, Chicago, USA). Descriptive statistics of heavy metal(loid) contents in the farmland soil samples, including minimum (Min), maximum (Max), mean, standard deviation (SD), coefficient of variation (CV), skewness and kurtosis, were applied to analyze the content characteristics of heavy metal(loid)s in the farmland soil. Pearson correlation analysis, CA and PCA, the extensively used multivariate statistical analysis methods in pollution studies (Wang et al. 2019; Zhang et al. 2019; Ke et al. 2017; Pan et al. 2017; Lu et al. 2014a), were adopted to determine the relationships among heavy metal(loid)s and to identify their possible sources combining their content characteristics and pollution levels in the farmland soils near the zinc smelter.

## Results And Discussion

### Heavy metal(loid) contents

The determination results of the heavy metal(loid)s contents from the farmland soil samples together with the reference value (CNEMC 1990) are presented in Table 1. As shown in Table 1, the mean contents of As, Cu, Cr, Pb, Mn, Ni, V, and Zn were 17.3, 39.5, 135.7, 143.3, 571.1, 35.8, 82.4, and 771.9 mg kg<sup>-1</sup>, respectively. Except for Mn, the mean contents of As, Cu, Cr, Pb, Ni, V, and Zn were above their corresponding reference value, which were 1.6, 1.8, 2.2, 6.7, 1.2, 1.2, and 11.1 times the reference, respectively. The coefficient of variation (CV), the ratio of the standard deviation and the mean, is a statistical measure reflecting the variability of the observed value. In general, a CV ≤ 20% indicates low variability, a CV range of 21–50% indicates moderate variability, a CV range of 51–100% shows high variability, and a CV >100% is regarded as very high variability (Pan et al. 2017; Phil-Eze 2010). Table 1 shows that the contents of heavy metal(loid)s determined in the farmland soil around the zinc smelter presented different variance. The contents of Zn, Pb, and Cu presented high variability (51% < CV ≤ 100%), the content of As presented moderate variability, and the other heavy metal(loid)s showed low variability. The large CV values of Zn, Pb, Cu, and As reveal their heterogeneity in the farmland soil around the zinc smelter, which might demonstrate the existence and impact of anthropogenic sources (Pan et al. 2020, 2017; Karim et al. 2014).

Kurtosis and skewness values indicated whether the concentrations of the studied heavy metal(loid)s follow a normal distribution. The kurtosis values of As, Cu, Pb, and Zn are 2.7, 3.7, 1.8, and 2.5 respectively, showing that these four elements deviated from the normal distribution. The absolute kurtosis values of Cr, Mn, Ni, and V are less than 1, indicating that their contents in the soil samples were close to the normal distribution. Skewness values of 9.9, 15.9, 5.1, and 8.8 further indicated that As, Cu, Pb, and Zn were skewed positively towards the higher concentration. While, the skewness values of Cr, Mn, Ni, and V are close to 0, showing that the content distribution of these four elements was relatively uniform.

Fig. 2 shows that the investigated heavy metal(loid)s in the farmland soils of three plots have diverse variation features. The contents of As, Cu, Pb, and Zn in the farmland soils of three plots have remarkable difference, while the content diversities of Cr, Mn, Ni, and V in the farmland soils of three plots are indistinct. The mean contents of As, Cu, Pb, and Zn in the farmland soils of three plots presented plot A > plot C > plot B. According to Chinese soil environmental quality–Risk control standard for soil contamination of agricultural land (GB 15618–2018) (MEE 2018), the contents of Pb in 67% soil samples of plot A and 50% soil samples of plot C, and the contents of Zn all soil samples of plot A and plot C are larger than their corresponding risk screening values for soil contamination of agricultural land of China, implying the soil environment and agricultural products may exist pollution risk of Pb and Zn.

Fig. 3 shows that the contents of As, Cu, Pb, Zn, and Ni in the farmland soil samples from plot A present decreasing trend with the increase of the distance between the sampling site and the zinc smelter, while the contents of Cr, Mn, and V in the farmland soil have not distinct trend. The contents of As, Cu, Pb, and Zn decreased 88%, 76%, 71%, and 83% respectively and Ni contents declined 28% in the farmland soil with the distance of soil sampling site to the zinc smelter increasing from 100 m to 300 m (Fig. 3). Plot A is situated in the downwind direction of the zinc smelter. Considering no other pollution sources existing in the vicinity of the zinc smelter, we think the aforementioned variation characteristics of heavy metal(loid)s content in the farmland of plot A reflecting the impact of zinc–smelting activity on the contents of As, Cu, Pb, Zn, and Ni.

### **Pollution and ecological risk of heavy metal(loid)s**

The results of  $P_i$  and  $NSPI$  are shown in Table 2 and Fig. 4. The determined heavy metal(loid)s presented pollution at different extent in three plots, except for As in plot B and Mn in plot C. The mean  $P_i$  values of As, Cu, Pb, and Zn in the farmland soil decrease in the order of plot A > plot C > plot B. Especially Pb and Zn, their  $P_i$  values are 10.31 and 15.92 in plot A, and 6.80 and 14.64 in plot C respectively, presenting severe pollution. The pollution diversity of heavy metal(loid)s in three plots may be related with their position and terrain. Plot A is located in downwind of the zinc smelter and its terrain is higher than the zinc smelter. The special topography hinder the further diffusion of smoke and dust with heavy metal(loid) particles and promote pollutants sinking, which may be the cause of severe soil pollution in plot A. Plot B is not in the dominant wind direction, and there are lush trees and vegetation between plot B and the smelter. Plot C is situated in the east of the smelter (downwind) and its terrain is lower than the

smelter. The diffusion of pollutants discharged from the smelter in plot C is easier than in plot A. Fig. 4 shows that the *NSPI* values of heavy metal(loid)s in the farmland soils from plot B are in range of 2–3 presenting moderate pollution, while which in the farmland soils from plot A and plot C are all larger than 3 except sample C3 indicating serious pollution. The comprehensive pollution degree of heavy metal(loid)s in three plots decreases in the order of plot A > plot C > plot B.

The computed results of  $I_{geo}$  for elements in the farmland soil around zinc smelter of Shangluo are presented in Table 3 and Table S5 (Supplementary Materials). In plot A, the  $I_{geo}$  of Mn and V are all below zero, indicating no pollution of these two metals in samples from plot A. Most of the  $I_{geo}$  value of Ni are under zero, which indicated no pollution, except two  $I_{geo}$  values 0.03 (A4) and 0.09 (A7) (Table S5 in Supplementary Materials) slightly greater than zero. The  $I_{geo}$  value of As range from -0.44 (A3) to 1.66 (A7) which corresponded to level 0 of unpolluted to level 2 of moderately polluted. The mean  $I_{geo}$  value of 0.31 indicated As is slightly polluted. As for Cr, the  $I_{geo}$  value of which range from 0.30 to 0.68 with the mean value of 0.55, indicated Cr was slightly polluted in plot A. The mean  $I_{geo}$  value of Cu is 0.51, which corresponded to level 1 of slightly polluted. Sample from A7 is an exception, the  $I_{geo}$  value of which is 2.03 corresponded to level 3 of moderately severely polluted. Pb and Zn showed more accumulation in plot A as compared to other seven elements. The mean  $I_{geo}$  value of Pb is 2.66 which corresponded to level 3 of moderately severely polluted. The max  $I_{geo}$  value of 3.95 (A7) corresponded to level 4 of severely polluted. The mean  $I_{geo}$  value of Zn is 3.12 which corresponded to level 4 of severely polluted. Sample from A7 was extremely polluted with the  $I_{geo}$  value of 5.14.

In plot B, the  $I_{geo}$  of As, Mn, Ni and V are all below zero, which indicated no samples are polluted by these four elements in plot B. The mean  $I_{geo}$  value of Cu is -0.11, corresponding to level 0 of unpolluted, but the  $I_{geo}$  value 0.10 and 0.05 from B5 and B8 are two exceptions. As for Cr, Pb and Zn, the  $I_{geo}$  of them are all between 0 and 1, showed samples from plot B were slightly polluted by these elements.

In plot C, the  $I_{geo}$  values of Mn, Ni and V are all below zero, which indicated no samples are polluted by these elements in plot C. For As, Cr and Cu, their mean  $I_{geo}$  values are between 0 and 1, indicating that these three elements corresponded to level 1 of slightly polluted. Samples from C2 and C3 were unpolluted with As. The  $I_{geo}$  value of Cr has little change, the maximum and minimum values are 0.46 and 0.33 respectively. As for Cu, the  $I_{geo}$  value of samples from C1, C2, C3 and C4 are < 0, corresponding to level 0 of unpolluted. The  $I_{geo}$  value of samples from C5, C6, C7 and C8 are between 0 and 1 (Table S5 in Supplementary Materials), corresponding to level 1 of slightly polluted. Similar to plot A, Pb and Zn are also accumulated obviously in plot C. The  $I_{geo}$  value of Pb ranged from 1.05 (C3) to 2.68 (C8) which corresponded to level 2 of moderately polluted and level 3 of moderately to severely polluted. The mean  $I_{geo}$  value 2.06 of Pb indicated moderately polluted in plot C. The mean  $I_{geo}$  value of Zn is 3.15 which corresponded to level 4 of severely polluted. The same as Pb, the minimum  $I_{geo}$  value of Zn 1.74 appears at C3 and maximum  $I_{geo}$  value 4.07 appears at C8.

The  $E_r^i$  values of heavy metal(loid)s in the farmland soils are shown in Fig. 5. It can be found from Fig. 5, the  $E_r^i$  values of Cr, Mn, Ni, and V in soil samples and Cu in most soil samples (except soil sample A7 in plot A) are  $< 15$ , indicating low ecological risk level. As and Zn in some soil samples of plot A and plot C have moderate and considerable ecological risk. Pb in the farmland soils from three plots possesses different ecological risk levels, i.e. in plot A presenting considerable to high ecological risk, in plot B presenting low ecological risk, while in plot C presenting moderate to considerable ecological risk. The *PERI* values of heavy metal(loid)s determined in the farmland soil near the zinc smelter range from 43.5 to 261.5 with an mean of 83.5, showing the investigated soils have wide ecological risk levels, i.e. low to high ecological risk. The comprehensive ecological risk levels of heavy metal(loid)s in the farmland soils of three plots are low in plot B, moderate in plot C and considerable in plot A. Pb is the main contributor of the comprehensive ecological risk, then are As, Cu and Zn, which respectively contributes 37.2%, 19.3%, 11.7%, and 11.3% to *PERI*.

## Multivariate Statistical results and source identification

### Pearson's correlation analysis results

Studying the correlation between elements can predict whether the sources of heavy metal(loid)s are same owing to different heavy metal(loid)s in soil have different migration and enrichment trends. If there is a correlation between them, the source may be similar, otherwise the source may be different (Dong et al. 2019). The Pearson correlation analysis results of heavy metal(loid)s in the farmland soil around the zinc smelter are displayed in Table 4. Table 4 displays that there are very significantly positive correlations ( $P < 0.01$ ) among As, Cu, Pb, and Zn, and the correlation between each other is highly correlated. Similarly, positive correlations ( $P < 0.01$ ) were found among Cr, Mn, and V. Different from the other seven elements, Ni appeared moderately positive correlation with As, Cu, and Pb ( $P < 0.01$ ). At the significant level of 0.05, Ni has a positive correlation with Cr, Mn, V, and Zn, but the correlation degree is low.

To some extent, the correlation between heavy metal(loid) elements reflects the similarity of pollution degree or the similar sources of heavy metal(loid)s. The correlation coefficient analysis also suggested that As, Pb, Cu, and Zn may have the same source or similar geochemical properties. Pb–Zn minerals are often accompanied by heavy metal(loid) elements such as Cu, As, etc., which are the main characteristic pollutants of nonferrous smelting industry (Félix et al. 2015; Tembo et al. 2006). In addition, the combustion of coal during metal smelting may be a source of As (Lu et al. 2009). The correlation coefficient analysis also indicated that Cr, Mn, and V may have the same source.

### PCA results

Table 5 shows the PCA results of heavy metal(loid)s determined in the farmland soil around the zinc smelter. It can be seen from Table 5, two factors with the eigenvalues  $> 1$  were extracted in PCA, which explains 92.2% of the total variance. The contribution rate of the first factor is 52.9%, and the factor loads of As, Cu, Ni, Pb, and Zn are 0.982, 0.961, 0.679, 0.972, and 0.960, respectively. The second factor

explains 39.3% of the total variance and the factor loads of Cr, Mn, V, and Ni are 0.956, 0.950, 0.974, and 0.575, respectively.

## **CA results**

The CA results are shown in Fig. 6. As, Cu, Pb, Zn, and Ni are the first category, which can be further divided into 2 sub-clusters, i.e., As–Zn–Pb–Cu and Ni. Cr, V, and Mn are the second category. The result of cluster analysis is consistent with that of PCA.

## **Heavy metal(loid) source identification**

Eight elements were divided into two groups based on the multivariate statistical analysis results together with their contents characteristics in the soil. The first group of elements are As, Cu, Pb, Zn, and Ni. In Pearson's correlation analysis and PCA, these five elements have strong positive correlation, and are clustered together in cluster analysis. Combining the content characteristics and pollution levels of As, Cu, Pb, Zn, and Ni in the soil, as well as their spatial variation trend in the downwind farmland of the zinc smelter, we think these elements in the farmland soil around the zinc smelter mainly came from the emission of zinc smelter. It should be noted that there is a certain difference between As and other four metals. The results of correlation analysis and PCA indicate that As in the farmland soil has other source yet.

The second group is composed of Cr, Mn, and V. Compared with the first group of elements, the coefficients of variation of these three metals are comparatively small, indicating that their contents variations in the investigated soil samples are minor. Combined the results of multivariate statistical analysis and pollution assessment, as well as the field investigation, we consider that these metals in the farmland soil mainly originated from natural source. As has a certain correlation with Cr, Mn, and V in correlation analysis and PCA, showing that As in the farmland soil partly originated from natural source.

## **Conclusions**

The farmland soils around a zinc smelter in Shangluo, the water source area of the Mid–route of South–North Water Transfer Project of China have elevated heavy metal(loid)s except Mn. The zinc–smelting activity influenced the heavy metal(loid)s content, particularly Zn and Pb, in the surrounding farmland soil. The contents of Zn in the farmland soil of the northwest and the east of the zinc smelter and the contents of Pb in more than half of soil samples of the northwest and the east of the zinc smelter exceed the risk screening values for soil contamination of agricultural land of China. The determined heavy metal(loid)s in the farmland soil presented diverse pollution level and spatial diversity. Zn was moderately to severely polluted, Pb was moderately polluted, Cr and Cu were slightly polluted, and other elements were unpolluted. The comprehensive pollution of heavy metal(loid)s in the farmland were extreme as a whole. The comprehensive ecological risk of heavy metal(loid)s in the farmland soils was moderate as a whole, which mainly contributed by Pb, then As, Cu, and Zn. As, Cu, Pb, and Zn in the soil mainly originated from the emission of the zinc smelter. Cr, Mn, and V primarily came from natural

source. Ni in the farmland soil mainly derived the emission of the zinc smelter, partly came from natural source. According to this research, the local government should pay attention to the elevated As, Cu, Pb, Zn, and Ni content, particularly Zn and Pb, in the farmland soil caused by zinc–smelting activities and strengthen the cooperative monitoring of heavy metal(loid)s in farmland and agricultural products, as well as pollutant emission monitoring and control. In addition to, the environmental impact and risk of other mining and smelting activities in the water source area should be investigated in the future.

## Declarations

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**Authors' contribution** SZ: field sampling, methodology, statistical analysis, writing—original draft. XL: funding acquisition, conceptualization, writing—review & editing.

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## Tables

**Table 1** Descriptive statistics of heavy metal(loid) concentrations ( $\text{mg kg}^{-1}$ ) in soil around the zinc smelter.

Element	As	Cr	Cu	Mn	Ni	Pb	V	Zn
Max	51.3	150.1	130.8	632.1	45.9	495.5	94.3	3678.7
Min	9.7	115.1	20.4	416.8	29.7	50.1	63.5	123.1
Mean	17.3	135.7	39.5	571.1	35.8	143.3	82.4	771.9
SD	8.6	10.1	21.0	58.1	4.2	100.6	8.2	752.9
CV(%)	49.7	7.4	53.2	10.2	11.7	70.2	10.0	97.5
Kurtosis	2.7	-0.5	3.7	-0.9	0.8	1.8	-0.5	2.5
Skewness	9.9	-0.9	15.9	0.3	0.3	5.1	-0.8	8.8
Reference <sup>a</sup>	11.1	62.5	21.4	557.0	28.8	21.4	66.9	69.4

Notes: <sup>a</sup> CNEMC 1990. SD: standard deviation; CV: coefficient of variace.

**Table 2** The  $P_i$  of heavy metal(loid)s in the soil samples.

Element	Plot A		Plot B		Plot C	
	Mean	Range	Mean	Range	Mean	Range
As	2.02	1.10–4.62	0.93	0.87–0.99	1.67	1.14–2.25
Cr	2.21	1.84–2.40	2.29	2.18–2.40	2.01	1.89–2.06
Cu	2.36	1.65–6.11	1.40	1.26–1.60	1.71	0.95–2.86
Mn	1.02	0.75–1.12	1.11	1.09–1.13	0.94	0.89–0.99
Ni	1.39	1.14–1.59	1.20	1.10–1.26	1.13	1.03–1.23
Pb	10.31	6.17–23.15	2.52	2.34–2.86	6.80	3.10–10.91
V	1.24	0.95–1.36	1.35	1.30–1.41	1.11	1.09–1.15
Zn	15.92	7.82–53.01	2.22	1.77–2.68	14.64	5.02–25.16

**Table 3** The  $I_{geo}$  of heavy metal(loid) in farmland soil around Shangluo zinc smelter.

Element	As	Cr	Cu	Mn	Ni	Pb	V	Zn
Plot A								
Max	1.62	0.68	2.03	-0.42	0.09	3.95	-0.14	5.14
Min	-0.44	0.30	0.14	-1.00	-0.39	2.04	-0.66	2.38
Mean	0.31	0.55	0.51	-0.56	-0.12	2.66	-0.28	3.12
Plot B								
Max	-0.60	0.68	0.10	-0.40	-0.25	0.93	-0.09	0.84
Min	-0.78	0.54	-0.25	-0.47	-0.45	0.64	-0.23	0.24
Mean	-0.68	0.61	-0.11	-0.43	-0.32	0.75	-0.16	0.55
Plot C								
Max	0.58	0.46	0.93	-0.60	-0.28	2.86	-0.38	4.07
Min	-0.40	0.33	-0.65	-0.76	-0.54	1.05	-0.46	1.74
Mean	0.13	0.42	0.12	-0.67	-0.42	2.06	-0.43	3.15

**Table 4** Pearson's correlation matrix between the concentration of heavy metal(loid)s in soil around the smelter.

Metal	As	Cr	Cu	Mn	Ni	Pb	V	Zn
As	1	-0.076	0.924**	-0.039	0.606**	0.947**	-0.166	0.973**
Cr	0.716	1	0.019	0.860**	0.480*	-0.070	0.930**	-0.230
Cu	0.000	0.927	1	0.029	0.621**	0.905**	-0.046	0.925**
Mn	0.853	0.000	0.891	1	0.476*	-0.125	0.919**	-0.180
Ni	0.001	0.015	0.001	0.016	1	0.627**	0.438*	0.463*
Pb	0.000	0.741	0.000	0.552	0.001	1	-0.188	0.930**
V	0.428	0.000	0.828	0.000	0.028	0.368	1	-0.312
Zn	0.000	0.269	0.000	0.389	0.020	0.000	0.130	1

The right upper part is correlation coefficient; the left lower part is significant level.

\*\*Correlation is significant at  $P \leq 0.01$  (two-tailed).

\* Correlation is significant at  $P \leq 0.05$  (two-tailed).

**Table 5** Rotated component matrix for data of soil around the zinc smelter.

Elements	Component		Communality
	1	2	
As	<b>0.982</b>	-0.046	0.967
Cr	-0.033	<b>0.956</b>	0.916
Cu	<b>0.961</b>	0.050	0.925
Mn	-0.023	<b>0.950</b>	0.902
Ni	<b>0.679</b>	<b>0.575</b>	0.791
Pb	<b>0.972</b>	-0.071	0.950
V	-0.122	<b>0.974</b>	0.963
Zn	<b>0.960</b>	-0.208	0.965
Eigenvalue	4.232	3.148	
%of total explained variance	52.9%	39.3%	
%of cumulative explained variance	52.9%	92.2%	

Extraction method: Principal Component Analysis.

Rotation method: Varimax with Kaiser normalization.

Rotation converged in 3 iterations.

## Figures

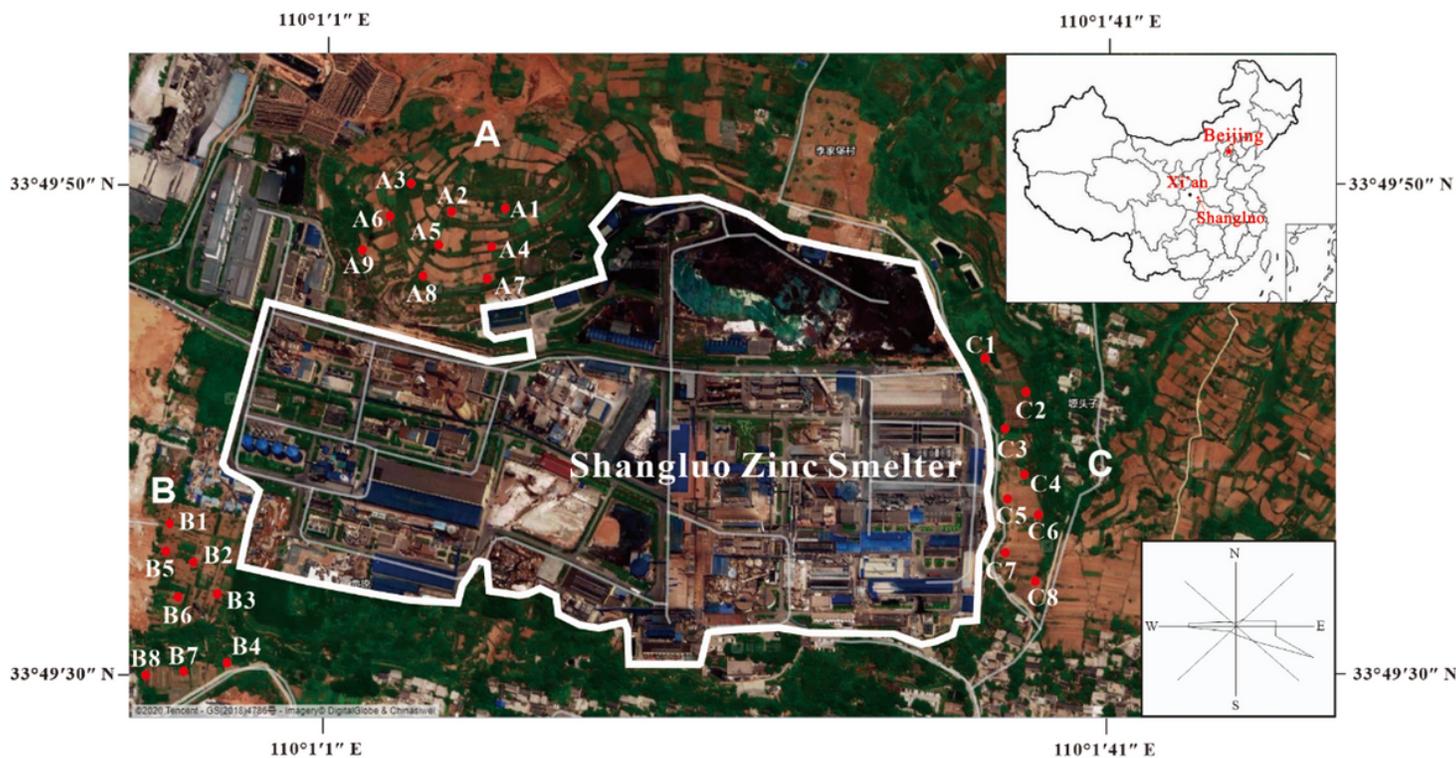
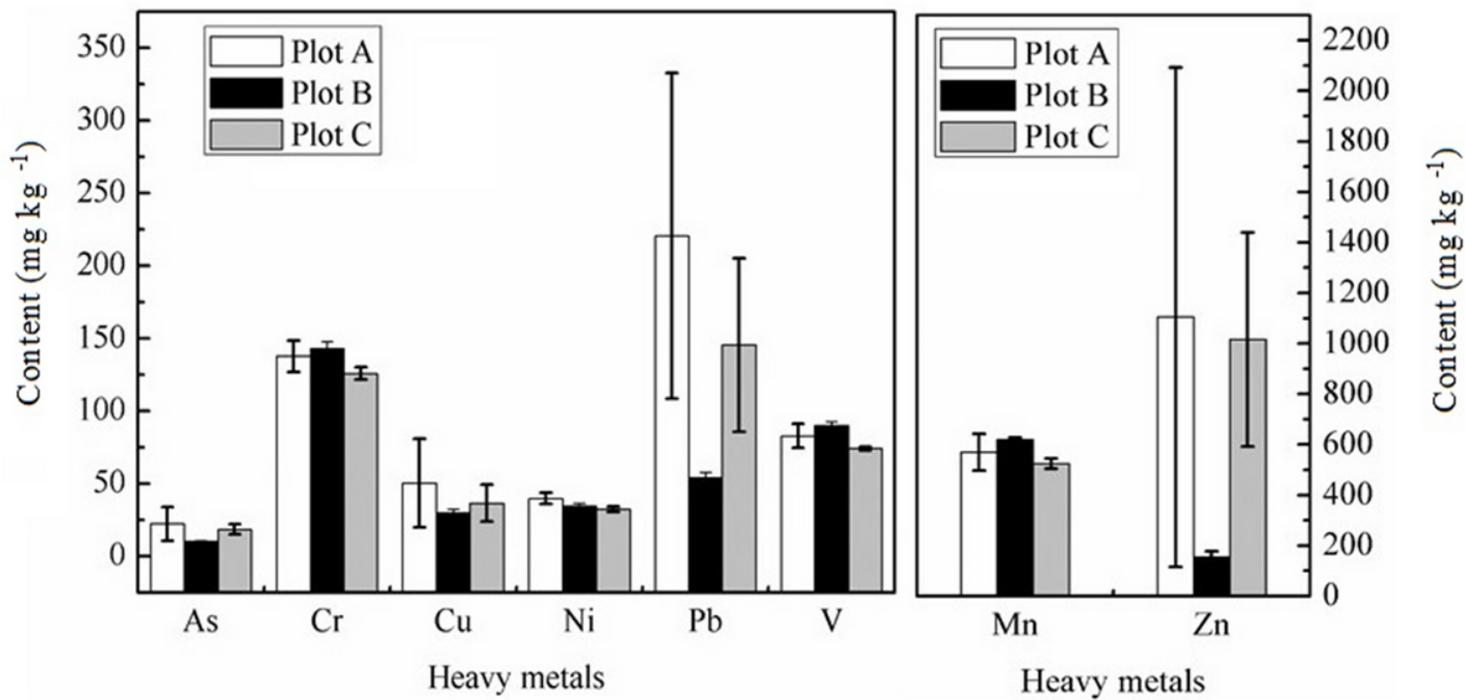


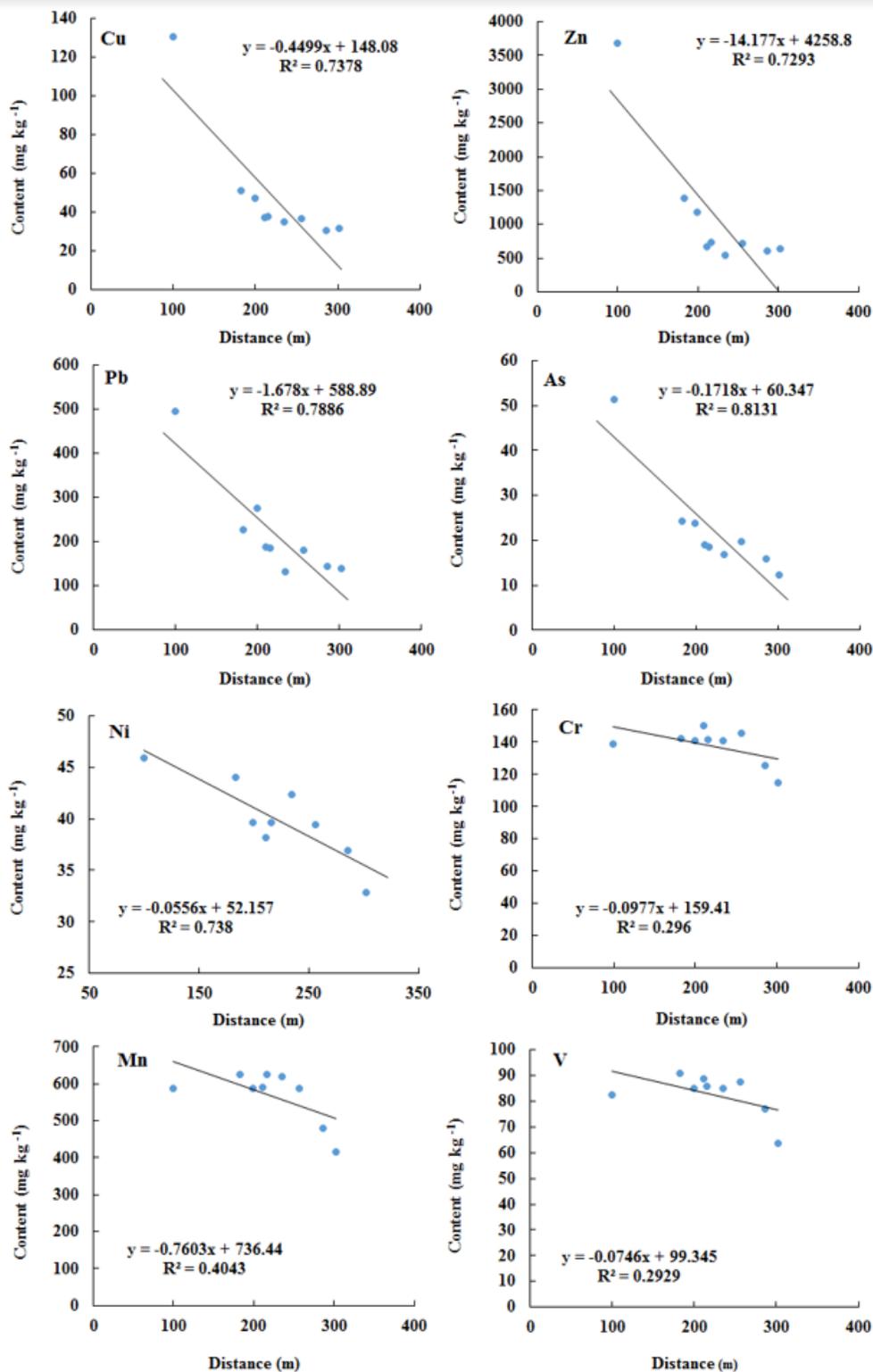
Figure 1

Location of the zinc smelter and soil sampling sites. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.



**Figure 2**

Heavy metal(loid) contents in the farmland soil of Plot A, Plot B and Plot C.



**Figure 3**

Relationship between heavy metal(loid) concentration and distance (Plot A).

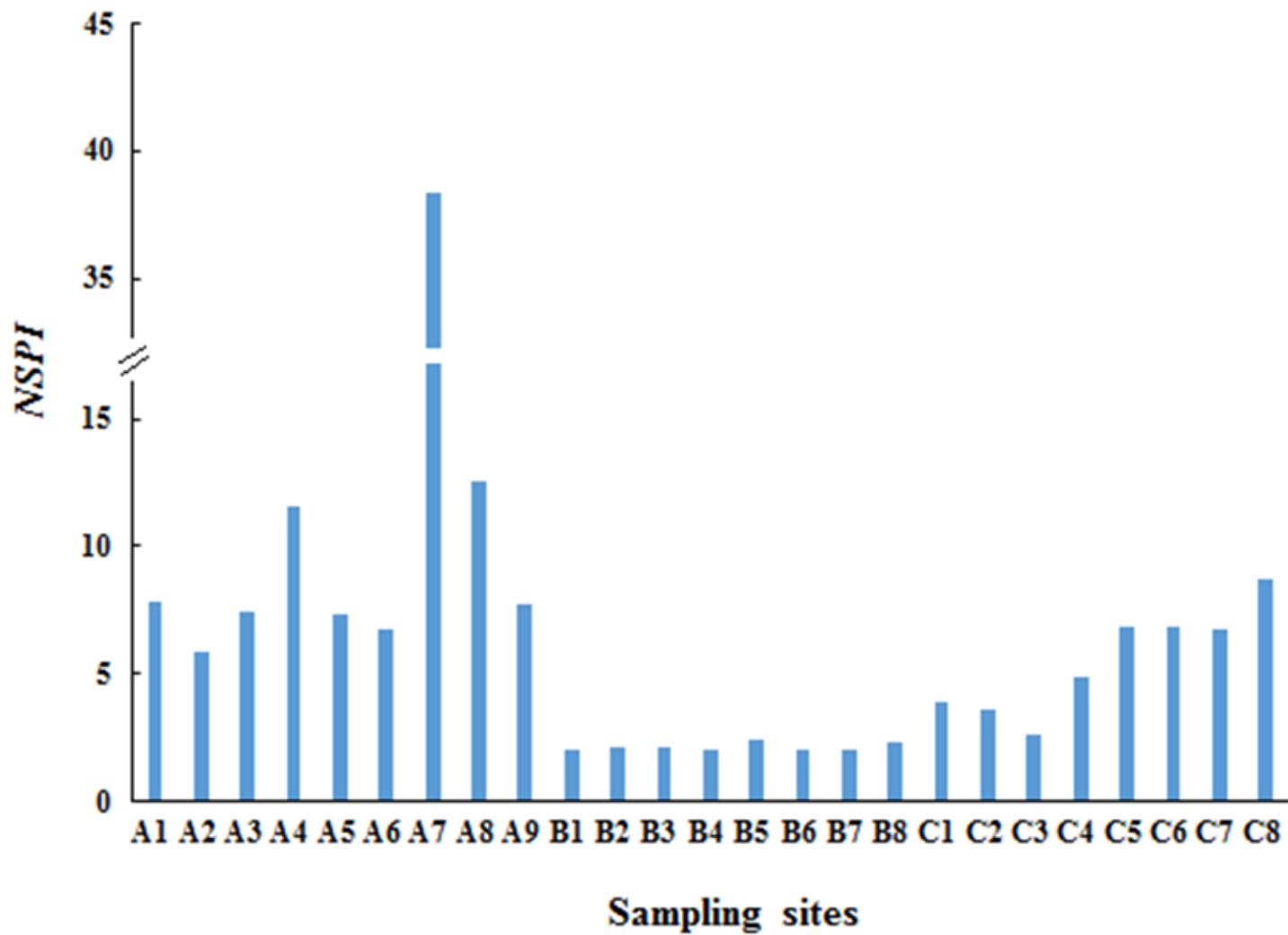


Figure 4

The NSPI values of heavy metal(loid)s in the farmland soils.

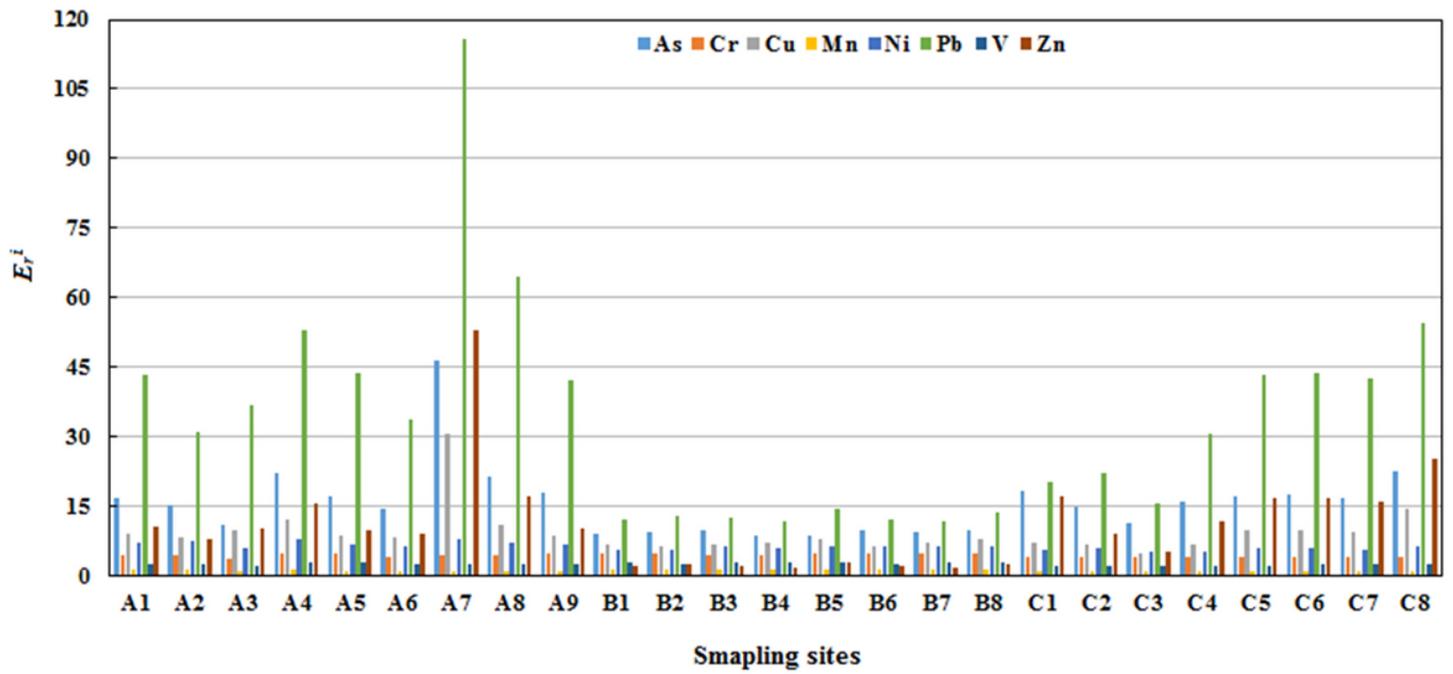


Figure 5

The  $Er^i$  values of heavy metal(loid)s in the farmland soils.

## Rescaled distance cluster combine

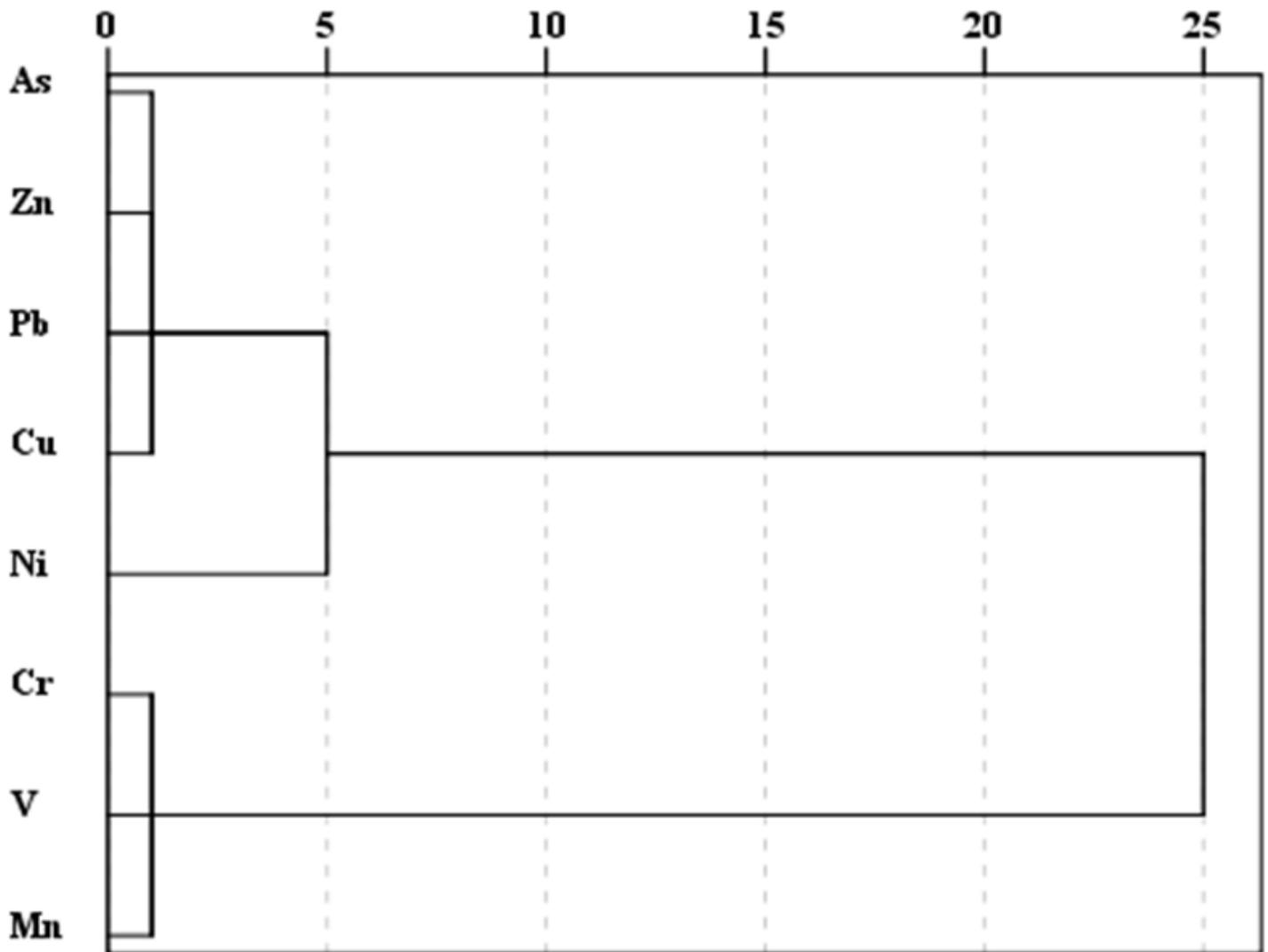


Figure 6

Dendrogram results from Ward method of hierarchical cluster analysis for 8 elements

## Supplementary Files

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