Source Apportionment and Health Risk Assessment of Zn (II) Ions Based on Gridded Spatial Interpolation and Geochemical Equilibrium Simulation

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Source apportionment and health risk assessment of Zn (II) ions based on gridded spatial interpolation and geochemical equilibrium simulation

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Abstract

Soil heavy metal pollution had become a global issue involving environmental safety and human health risks. A methodology was explored to quantify the sources of heavy metals in the soils and investigate the spatial distributions of heavy metals by the gridded spatial scale. The case study was implemented in the industrial waste sites in Suzhou city, Jiangsu province. Zinc (Zn) was screened out as the targeted metal (TM) through the potential ecological risk assessment, the species of which was simulated by the geochemical software PHREEQC. The aim of this research was to determine the dominant metal species of TM with potential hazardous health risk to local people to achieve key prevention and pollution control. Herein, according to the morphological evolution of metal species, the activity and concentration of the Zn species was calculated for both carcinogenic and non-carcinogenic health risk assessment. The evaluation of the optimized human health risk demonstrated that the associated health risk of Zn (II) depended predominantly on its metal speciation and was also affected by acidity and soil organic matter. Overall, the optimized carcinogenic and non-carcinogenic risk value of Zn\textsubscript{2}S\textsubscript{2}- for adults was 2.01E-04 and for children was 1.31 respectively, resulting in corresponding hazardous risk to human, which accounted for high risk level of 61.5% and
58.5%, respectively. This method could provide a reference for the decision-making of soil heavy metal pollution control and targeted hypotoxic conversion of metal species and remediation for certain heavy metal of polluted area.

**Keywords:**

Health risk assessment; Metal morphological evolution; Positive matrix factorization; Grid spatial distribution; Zinc speciation

### 1. Introduction

With the development of economy and urbanization, many cities had carried out the adjustment of industrial structure and the transformation of land use mode in China, which required some polluting enterprises in the main urban area to move into the government planning area according to the industrial category (Cai et al., 2018; Xiao et al., 2019). Some of them were shut down, went bankrupt or carried out rectification according to the requirements of environmental remediation (Noli and Tsamos, 2016; Wcisło et al., 2016; Cheng et al., 2017). However, due to the limitations of the enterprise's previous technology and awareness of environmental protection, the waste water and other pollutants discharge will inevitably leak into the environmental media, leading to soil pollution (Gu et al., 2014; Zhang et al., 2018). After the relocation and shutdown of these industrial enterprises, a large number of contaminated sites had been left behind. When the heavy metal contaminated sites were redeveloped and utilized, the heavy metal pollutants will have a certain impact on the environmental media of the site, and may cause harm to the health of the population (Khoshgoftarmanesh et al., 2006; Liu et al., 2013; Li et al., 2014; Peñafernández et al., 2014; Shrestha et al., 2016). After entering the soil, heavy metal pollutants were transported or accumulated by a variety of media, which will affect the growth and reproduction of plants and animals, and even the survival of human beings, and brought a variety of potential risks such as health risks and ecological risks (Du et al., 2014; Chakraborty et al., 2015; Liu et al., 2015; Wali et al., 2015; Wang et al., 2015). Therefore, it was of great significance to evaluate the pollution status of contaminated sites for environmental and human health risks and site remediation. At present, in the process of redevelopment and utilization of contaminated sites in China, the problem of soil pollution was very prominent.
Heavy metals in the field of environmental pollution mainly referred to the elements with significant toxicity to organisms, such as As, Cr, Cd, Hg, Zn, Co, Cu, Ni, Sb, Ba, etc. Heavy metal pollution mainly came from traditional industrial production such as mining and metal smelting (Zhang et al., 2012). The source of heavy metal pollution was mainly due to the leakage of raw materials during transportation and storage, the leakage of pollutants in the process of production and waste discharge and even unreasonable storage and discharge of solid waste (Rodríguez Martín et al., 2006; Morjani et al. 2007; Shi et al., 2008). Heavy metal in the contaminated areas can not be decomposed by organisms, most of which can not be removed by incineration, but it was easy to accumulate in organisms. Some heavy metal elements may be transformed into more toxic methyl compounds, and some may even accumulate in the human body at harmful concentrations through the food chain, seriously endangering human health (Zhang et al., 2014). Furthermore, most of heavy metal pollution was complex and most of them had poor mobility or short migration distance, so they were easy to accumulate in environmental media (Dehghani et al., 2017; Li et al., 2017). Health risk assessment of contaminated sites was a local risk assessment based on specific sites. By evaluating potential carcinogenic and non-carcinogenic human health risks of site pollutants to human health, it can provide decision-making basis for site pollution control and site restoration (Chen et al., 2009; Xu et al., 2014). In view of the serious harm of contaminated sites to human health, human health risk assessment had been carried out from all aspects at home and abroad (Tang et al., 2013).

The premise of effective implementation of comprehensive prevention and control of heavy metal pollution was to understand the pollution degree, source and spatial-temporal distribution characteristics of soil heavy metals. At present, the analysis of the sources of heavy metals in site mainly focused on the general analysis of whether they were from natural or anthropogenic sources, and rarely combines with the site functional areas to explore the specific industrial pollution sources. Researchers had mostly studied the level of soil heavy metal contamination from an overall regional perspective, but there was a lack of screening of target metals ($TM$), not to mention further
contamination evaluation of the target heavy metal speciation. In addition, the research on health risk of heavy metals in contaminated sites was mostly based on the total concentration of pollutants. However, it was not enough to only use total concentration to assess health risk, mainly because the toxicity and mobility of heavy metals in the environment depended on the specific chemical forms and states of metals. An important factor in determining human health risks was the effect of chemical forms on bioavailability (Reis et al. 2004; Mashal et al., 2015; Yang et al., 2015; Gu et al., 2016). Domestic and foreign scholars began to study the forms of heavy metals in the environment in the 1970s and found that the biological activity and environmental behavior of heavy metals in the environment are not only related to their total concentration, but also determined by their forms in the environment to a greater extent, especially their bioavailability (Fernández et al., 2000; Impellitteri et al., 2003; Sastre et al., 2003). The activities and eco-environmental effects of different forms of heavy metals directly affected their bioavailability, toxicity, migration and transformation ability, as well as their circulation in nature (Reis et al., 2014; Mashal et al., 2015; Yang et al., 2015; Gu et al., 2016). However, due to the complexity of heavy metal elements in contaminated soil, it was very difficult to determine the ion speciation of heavy metal elements, and the use of numerical simulation software could provide a certain convenience for the study of the physical and chemical property of heavy metal elements in soil (Gu et al., 2007).

In view of the above problems, this paper aimed to use field sampling data to evaluate the relationship between the degree of soil heavy metal pollution and its existing spatial distribution and pollution sources, and then comprehensively analyzed the potential health risk level of soil heavy metals to screen out the target heavy metals. Morphological evolution of $TM_{ion}$ species was incorporated into the optimized human health risk assessment model. Based on the comprehensive consideration of the influence of the existing metal speciation and activities of heavy metals on the health risks of heavy metals, a heavy metal speciation health risk assessment model combining the characteristics of targeted metal was established. Thus, accurate quantitative assessment can be realized and scientific basis can be provided for the prevention and control of heavy metal pollution in the site.
2. Frameworks of the methodology in the study area

An optimized human health risk assessment methodology based on the screening of targeted metal and morphological evolution of metal species was proposed to quantify and distinguish the contribution of carcinogenic and non-carcinogenic health risk effects of metal species on people. Different from the traditional health risk assessment methods, it used the ion speciation of the target metal to assess the health risk, which made up for the shortcomings and inaccuracy of the traditional methods (Li et al., 2013; Olujimi et al., 2015; Liu et al., 2016; Ogunbanjo et al., 2016). The framework of the methodology was shown in Fig. 1. Targeted metal was screened out by potential ecological risk assessment and the spatial distribution of each heavy metal was illustrated on the PMF spatial interpolation. Concentrations and activities of each targeted metal species were obtained by geochemical simulation and the support of PHREEQC software was employed. Carcinogenic and non-carcinogenic health risk assessment was carried out to evaluate the hazard of each metal species of **TM** both for adults and children. Optimized and non-optimized risk index were compared for the interrelation between ion activity and weight analysis. It was helpful to determine the policy decision for the management of abandoned industrial sites. For example, based on the health risk values and characteristics of specific metal species, targeted restoration treatment measures were proposed to save budget and time. Changes in soil environmental conditions can also help predict risks. The approach was applicable to any contaminated sites and uncontaminated sites except mercury for its volatility.
2.1. Data Analysis

The data underwent by statistical analysis using SPSS Statistics 25 (IBM Inc., CO, USA) and Microsoft Office (version 2010, USA). The spatial distribution of heavy metal species was mapped by the Surfer v.12.0 (Golden Software Inc., CO, USA). The data was performed by EPA-PMF 5.0 to assess the sources of soil heavy metals with a 95% confidence interval (significance p < 0.05) (S Zhang et al., 2008; aha et al., 2017). Visual MINTEQ was used to simulate concentrations and activities of target metal speciation (Lai et al., 2019).

2.2. Spatial interpolation based on quantitative source apportionment

2.2.1 Positive matrix factorization

Positive definite matrix factor analysis was a relatively mature quantitative source analysis method in the field of environmental pollution source analysis (Paatero et al., 1994; Chen et al., 2011). Through non-negative constraint factor analysis and iterative calculation with the least square method, the objective function was minimized to solve chemical mass balance (CMB) between the measured heavy metal concentration and pollution source (Franco et al., 2009; Dong et al., 2018; Guan et al., 2018). On one hand, the obtained source component spectrum and source
contribution rate can be explained and had clear physical significance (Lv et al., 2019). On the other hand, the PMF method did not require the measurement of the source component spectrum, and used error estimates for each individual data point in order to cope with missing and inaccurate data more reasonably (Mamut et al., 2017). The data entered into the program include concentrations and equation-based uncertainties (Jiang et al., 2019).

Compared with the traditional source apportionment methods, the PMF method could weigh all data that can analyze the contribution rate of target variables (Tian et al., 2018). The sample metal concentration data matrix was defined as:

$$C_x^t = \sum_{y=1}^{p} (g_{xy} f_{yt} + e_x)$$

Where, the $C_x^t$ represented concentration of the $t$ compound at the sampling point $x$; $g_{xy}$ represented contribution rate of the $y$th source at the sampling point $x$; $f_{yt}$ was the mass fraction of the $y$th source at the metal $t$; $e_x$ was the deviation of the metal $t$ at sample point $x$; Objective function $Q$ was defined by Eq. (2) (Duan et al., 2020).

$$Q = \sum_{x=1}^{n} \sum_{t=1}^{m} \left( \frac{e_x^t}{u_x^t} \right)^2$$

Where the $u_x^t$ was the uncertainty of the metal $t$ at the sampling point $x$ (De Miranda et al., 2018).

### 2.2.2 Spatial interpolation method

To analyze all sources of soil heavy metals in the study area, it was not feasible to rely on the analysis results of sample data alone (Szopka et al., 2013). Through the analysis of the whole area, it was helpful to detect all the sources of heavy metals. With the Ordinary Kriging interpolation method, the values of soil heavy metals can be obtained from all the grids with a small number of samples. For grid A, under the condition that the spatial trend of metal content was unknown constant, the Ordinary Kriging method can predict the metal content $K$ ($C_{(A_0, K)}$) in any non-sampled grid as (Yang et al., 2017),

$$\hat{C}_{(A_0, K)} = \sum_{i=1}^{n} \hat{\lambda}_{(i,k)} C_{(A_i, K)}$$

where, $C_{(A_0, K)}$ represents the content value of $K$ in adjacent grid elements, $A_i$ $i=1, 2...n$. $\hat{\lambda}_{i}$ $i=1, 2...n$ is the
The corresponding equation based on unbiased estimation and minimum variance is as follows:

\[ \sum_{i=1}^{n} \lambda_i y_i (x_{A_i} - x_{A_0}) + \mu = \gamma (x_{A_0} - x_{A_j}) \]  

where \( \gamma \) was the variation function of a certain lag distance and \( \mu \) was the Lagrange normal number.

\[ \sum_{i=1}^{n} \lambda_i = 1 \]

According to the above steps, the spatial distribution of content of soil heavy metals in the scale grids can be effectively generated.

2.3. Potential ecological risk assessment

Ecological risk index was used to assess environmental sensitivity and the pollution degree of soil heavy metals (Kusin et al., 2018). The standardized heavy metal \( T_r^i \) developed by Hakanson was used for evaluation basis (Hakanson, 1980). It was calculated by the following equation for the potential ecological risk index of an individual metal \( E_r^i \).

\[ E_r^i = T_r^i \times \frac{c}{c_0} \]  

Where \( c \) represented the measured concentration of heavy metal and \( c_0 \) was the background value of heavy metal in soil. \( E_r^i \) represented the environmental risk index of heavy metal \( i \) and \( T_r^i \) represented the toxicity response coefficient of heavy metal \( i \), which mainly reflected the toxicity level of heavy metals and the sensitivity of the environment to heavy metal pollution.

The potential ecological risk index (RI), based on heavy metal concentration and toxicity, was conducted to calculate the integrated potential environmental risk for the total hazard heavy metal (Zhu et al., 2012; Wu et al., 2017). The following equation was used for the calculation of RI.

\[ RI = \sum E_r^i \]
The toxicity response coefficient for As, Cd, Cr, Ni, Zn and Pb were 10, 30, 2, 6, 1, and 5, respectively (Guo et al., 2010a).

2.4. Geochemical simulation of targeted metal speciation

PHREEQC was a computer software which was used to calculate a variety of low temperature hydrogeochemical reactions. It could offer a more comprehensive range of databases based on geochemical model. Compared with experimental results, it indicated that the results of PHREEQC were scientific (Masindi et al., 2018). PHREEQC can calculate the species of substance formation and the saturation index and simulate the geochemical inversion process. It was also capable of investigating geochemical reactions in a variety of natural and human-affected environments, including acid mine water discharge, radioactive waste isolation, pollutant transport, nutrient enrichment, natural and artificial aquifer restoration, aquifer reserve recovery, potable water treatment, laboratory experiments, and regional aquifer systems. The software of PHREEQC had a powerful thermodynamics database for input and operation. It can be very convenient to obtain the molar concentration and the activity of the component, pH, pE, saturation index, etc (Khoshgoftarmanesh et al., 2006).

2.5. Human health risk assessment model

The human health risk model, which includes an analysis of the average daily dose (ADD), as well as estimation of carcinogenic and non-carcinogenic risks as determined by the US Environmental Protection Agency, had been proved successful and has been successfully adopted globally (Tapia-Gatica et al., 2019). Among the exposures of toxic heavy metal elements to human body through ingestion, inhalation, and dermal contact, the pathway of ingestion was considered in this study to estimate the ADD of targeted metal, owing to that it was the most significant pathway for toxic heavy metals (Giri and Singh, 2015; Chen et al., 2020).

In general, the average daily dose for human health risk assessment was always estimated in terms of total concentration of toxic element, but this tended to ignore the bioavailability and absorption of toxic elements. Heavy metals in nature existed in a variety of ionic forms, and not every kind of ion form with toxicity. Optimized human
health risk assessment through weight analysis could avoid imperfect and uncertainty of traditional risk assessment model. Therefore, the ADD of TM species used for risk assessment were modified according to the following formula:

\[ C_{p,q} = 1000 \times M_{p,q} \times m_p \times n_{p,q} \]  

(8)

\[ w_{p,q} = \frac{C_{p,q} \times r_{p,q}}{\sum (C_{p,q} \times r_{p,q})} \times \frac{A_{p,q}}{\sum A_{p,q}} ; \sum w_{p,q} = 1 \]  

(9)

\[ C'_{p,q} = \sum C_{p,q} \times w_{p,q} \]  

(10)

Where, \( C_{p,q} \) was the concentration of the \( q \) ionic speciation in \( p \) heavy metal element (mg \( .L^{-1} \)), \( M_{p,q} \) was the molar concentration of the \( q \) ionic speciation in \( p \) heavy metal element (mol \( .L^{-1} \)), \( m_p \) represented the relative atomic mass of \( p \) heavy metal, \( n_{p,q} \) was the number of TM from the \( q \) ionic speciation in \( p \) heavy metal element (i.e. \( \text{ZnSO}_4 \), \( n_{p,q} = 1 \)); \( w_{p,q} \) was the weight value of the \( q \) ionic speciation in \( p \) heavy metal element; \( A_{p,q} \) was the activity of the \( q \) ionic speciation in \( p \) heavy metal element; \( C'_{p,q} \) was the modified concentration of the \( q \) ionic speciation in \( p \) heavy metal element.

Herein, \( CR \) and \( HQ \) of TM species were optimized by the relation of the exposure of the target metal species, they could be optimized by weight analysis for accurate health risk assessment. The carcinogenicity risk (\( CR \)) and the hazard quotient (\( HQ \)) of non-carcinogenic risk were calculated by health risk assessment proposed by the US EPA, the evaluation of which can be obtained by the following equations (Dehghani et al., 2017):

\[ \text{ADD}_{pq}' = \frac{c_{pq}' \times IR \times EF \times ED}{AT \times BW} \]  

(11)

\[ \text{HQ}_{pq}' = \frac{\text{ADD}_{pq}'}{RfD} \]  

(12)

\[ HI_p' = \sum \text{HQ}_{pq}' \]  

(13)

\[ THI' = \sum HI_p' \]  

(14)

\[ CR_{pq}' = 1 - e^{(SP_p \times \text{ADD}_{pq}')/m_p} \]  

(15)

\[ TCR_p' = \sum CR_{pq}' \]  

(16)

According to the actual daily situation of the local resident population, the average annual exposure frequency (\( EF \))
of the area was used for 365 days. \( \text{RfD} \) is the reference dose (mg/kg d); \( \text{IR} \) was the water infestation rate (L.day\(^{-1}\)) and \( \text{BW} \) was the body weight (kg); \( \text{AT} \) represented the averaging time (day); \( \text{ED} \) is the exposure duration, where 6 and 30 years was used for children and adults, respectively (Chen et al., 2018; Zhang et al., 2019).

If \( HQ < 1 \), it indicated that the carcinogenic risk can be ignored. If \( HQ > 1 \), it suggested that there are potential non-carcinogenic effects on humans (Mandal and Sengupta, 2006). \( \text{THI} \) represented the total potential hazardous index of the major intake pathways. \( \text{THI} \leq 1 \) demonstrated that non-carcinogenic risk may not occur in the exposure group, when \( \text{THI} > 1 \) showed potential hazardous effects on the group (Siddiqui and Pandey, 2019). The acceptable or tolerable risk range for carcinogenic risk assessment was defined as between \( 10^{-6} \) and \( 10^{-4} \), while if the values of \( CR \) exceed \( 10^{-4} \), the carcinogenic effect was indicated (Zhang et al., 2017).

**Nomenclature**

| Parameter symbol | Parameters | Unit |
|------------------|------------|------|
| \( \text{ADD}_{pq} \) | the modified concentration of the \( q \) speciation in \( p \) metal | mg kg\(^{-1}\) d\(^{-1}\) |
| \( HQ_{pq} \) | the optimized \( HQ \) of \( q \) species in metal \( p \) | - |
| \( HQ_{pq} \) | the \( HQ \) of \( q \) species in metal \( p \) | - |
| \( HI_{pq} \) | the total optimized hazard index in metal \( p \) | - |
| \( THI' \) | the total optimized hazard index | - |
| \( SF_p \) | the slop factor of \( p \) metal element | (kg·d)/mg |
| \( CR_{pq} \) | the optimized \( CR \) of the \( q \) speciation in metal \( p \) | - |
| \( TCR_p \) | the total optimized \( CR \) of metal \( p \) | - |

**2.6. Case study**

**2.6.1. Study area and sampling**

The study area of Suzhou city was located in the middle of the Yangtze river delta, the southeast of Jiangsu province, located at 119°55'E to 121°20'E, 30°47''N to 32°02'N, with the total area of 8657.32 km\(^2\). The city was low-lying and flat, with many rivers and lakes. Most of the water surface of taihu lake were in suzhou. Rivers, lakes and beaches account for 36.6% of the city’s land area. Suzhou was a subtropical monsoon maritime climate, with an average temperature of 17.8℃ and precipitation of 1369.2mm in 2018. The prevailing wind direction was southeast wind. In the shallow layer, the clay soil with slight deformation and high strength was mainly grey, with compact texture.

The study area focused on an abandoned dye factory, which was surrounded by four land uses, such as agricultural,
urban and industrial land, and a mixed zone. The research dyestuff factory was mainly engaged in the production and sales of neutral dyestuff, cationic dyestuff and reactive dyestuff. The factory may have discharged a large amount of heavy metals before being relocated and abandoned. According to the principles of Technical Specifications for Soil Environmental Monitoring, 30 topsoil samples were randomly collected from the target center of the 1km grid in the region on sunny days in September 2019, and the distribution of sampling points were shown in Fig. 2.

2.6.2. Collection and analysis

The soil samples were taken back to the laboratory and naturally dried and ground crushing, first through a 20 mesh sieve for pH analysis, then used for the determination of physical and chemical properties (Papa et al., 2010). The processed soil samples were dissolved in the mixture acid solution (HNO$_3$-HF-HClO$_4$) at a high temperature of 150°C for 4h (Bryanin et al., 2019). Soil pH was determined with a ratio of 2:5 (w/v) soil/water mixture using a pH meter (Cheng et al. 2018). The soil organic matter (SOM) content was determined by the chromic acid titration method. The content of heavy metals Cd, Cr, Zn, Ni and Pb in soil samples were determined by atomic absorption spectrometry (Agilent Technologies 280FS AA). Arsenic concentration was measured by atomic fluorescence spectrometry (AFS) (Gu et al., 2016). Quality assurance and control procedures were carried out via reagent blanks, duplicate samples and standard reference soil samples (GBW07401-07408, China National Reference Materials Centre, Beijing, China.). Each batch of samples was evaluated by reagent blanks to reduce errors for quality assurance (Jiang et al., 2019). The recoveries for each element were controlled in the range of 90-110% and repeat analysis of these recovered materials showed an excellent accuracy of the recovered material with a relative deviation of less than 8% for the treated samples.
3. Results and discussion

3.1. Characteristics of soil heavy metals in statistics

Descriptive summary of concentration characteristics of soil samples were shown in Table 1. The results showed that there was no significant difference in soil physical and chemical properties between soil samples. The average contents of arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb) and zinc (Zn) were 8.09, 0.31, 77.50, 30.22, 23.01 and 93.78 mg/kg, respectively. Under the Chinese soil standard (Class II), the concentrations of Cd and Zn were higher than the background values (BV) for soils in Jiangsu Province and even higher than the mean background for China. The average concentrations of Cd and Zn were 2.46 and 1.5 times of the background values, respectively. This phenomenon preliminarily indicated that the two heavy metal elements were not naturally enriched in the study area, which may be caused by anthropogenic factors (Jiang et al., 2016). The relatively high coefficient of variation (CV) of heavy metal element were Cd, Pb and Zn, with the CV values of 38.70%, 28.56% and 53.09%,
respectively. Among them, Zn and Cd were higher, indicating that they were considered to be affected by more factors. The relatively low total CVs for Ni and Cr were mainly due to their absence of external disturbances, an assumption based on previous studies (Onianwa and Fakayode, 2000). The higher values of As distributed in the farm soil (Fig. 3), indicating that the overuse of fertilizer and pesticide promoted the accumulation of As. Moreover, the research considered that the larger values of Cd were affected by multivariate factors, owing to its broad distributions. Cr was mainly concentrated in the northwest and central areas for bare land and dye factory, suggesting that the existence of industry was a major pollution source for Cr. The relatively larger values of concentrations for Ni, Pb and Zn concentrated on the traffic road, which may directly influenced by vichles and human activities. Meanwhile, the hotspot of Pb, Zn and Ni appeared in the center of the study area. As can be seen from Fig. 2, the main wind direction in the study area was southeast-northwest (CMA, China Meteorological Administration). These similar directions indicated that there was a certain interdependence between prevailing wind direction and metal concentration at the top.

| Element | As   | Cd  | Cr   | Ni   | Pb   | Zn   |
|---------|------|-----|------|------|------|------|
| Min     | 6.52 | 0.14| 46.05| 25.22| 17.95| 89.84|
| Max     | 10.55| 0.56| 83.19| 40.37| 29.21| 96.45|
| Mean    | 8.09 | 0.31| 77.50| 30.22| 23.01| 93.78|
| Median  | 9.18 | 0.29| 71.98| 33.45| 32.92| 92.37|
| GM      | 10.01| 0.34| 60.36| 28.43| 39.16| 74.09|
| SD      | 0.96 | 0.09| 42.09| 6.07 | 7.94 | 77.63|
| CV(%)   | 18.48| 38.70|12.06| 13.47| 28.56| 53.09|
| BVa     | 10.0 | 0.126|77.80| 36.80| 26.20| 62.6 |
| Chinab  | 11.0 | 0.097|61.00| 27.00| 27.00| 74.00|

Table 1

Descriptive statistics of heavy metals in top soil (mg/Kg).

Note: GM- geometric mean; SD-standard deviation; CV- coefficient of variation;
a BV- background value of Jiangsu (Ma et al., 2015);
b Mean value of China (Chen et al., 2020).
3.2. Source apportionment based on spatial interpolation

3.2.1 Pollution sources analysis

For this section, the entire region was analyzed for pollution sources based on a special interpolation model. The A-scale grid content data for the six heavy metals and 121 grids (100 × 100 m) were first introduced into the PMF model to quantify the contribution of potential source categories. The acceptable absolute scale of the residuals suggested a better fit to the model for heavy metals based on a PMF noise ratio range of 3.5 ~ 4 (Uchimiya et al., 2011). From the PMF modelling results, there were four principal factors influencing heavy metal soil contamination in the whole region. As it demonstrated in Fig. 4, four factors were extracted by PMF model, the contribution of

Fig. 3. Spatial distributions of soil heavy metals by the interpolation model of Ordinary Kriging.

Fig. 4.
Factor 1 to the concentration of Cr and Ni was 45.7% and 33.2%, respectively. These elements were easily released by the combustion of fossil dyes and industrial waste water and residue discharge processes such as printing, dyeing and electroplating (Liu et al., 2010). The Factor 2 was loaded mainly by Zn (51.6%) and Pb (39.7%). Zn and Pb were the predominant ingredients in vehicle exhaust from fuel additives and automobiles. Moreover, since the study area covered a dye-stuff plant, the wastewater from the dye industry can also discharge the element of Zn and Pb (Pardyjak et al., 2008; Duan and Tan, 2013). Factor 3 was mainly responsible for the concentration of Cd with a high percentage of 60.6%. Soil cadmium pollution mainly come from the deposition of cadmium in the atmosphere, the use of pesticide, chemical fertilizer and plastic film, sewage irrigation, sludge fertilization, the accumulation of heavy metal-containing wastes, and the pollution of acid wastewater from metal mines (Jia et al., 2017). Factor 4 was characterized for the total concentrations of As (53.8%). As was used largely in the manufacture of pesticides, but also in pigments, dyes and paints (Zheng et al., 2003).

Comparatively speaking, industrial activities occupied the largest contribution to soil heavy metals in the study area; followed by the human activities such as waste emission. The third largest contribution was made by agricultural activities, which were related to the farmland in the study area. Owing to the frequent utilization of vehicle and fuel near the roads, traffic activities accounted for the fourth largest contribution and the followed one was atmospheric deposition. The results were consistent with the current situation of the whole study area, with abandoned factories developed transportation around and frequent agricultural activities, indicating the close relationship between the dye factory and its surrounding soil.
3.2.2 Distribution of soil heavy metals in spatial scales

Ordinary Kriging interpolation was used to investigate the spatial distribution of As, Cd, Cr, Ni, Pb and Zn (Islam et al., 2018). A more accurate spatial visualisation of contamination levels can be achieved by utilising a gridded spatial distribution of soil heavy metal concentrations. This will assist in making more rational decisions on future land rezonings or regional environmental remediation throughout the region. This research presented the distribution of concentration of heavy metal elements in grid A scale, as shown in Fig. 5 (Zhang et al., 2018). It can be intuitively seen from the figure that the heavy metal locations with the highest concentration were all individual, indicating that the distribution of regional pollution sources was complex and different areas are polluted by different element content (Guo et al., 2010b; Song et al., 2017). Due to the gridded processing of the spatial distribution, the distribution map cannot display the same geometry of the study area as presented in Figure 2, but it was still straightforward to identify refinement zones where the soil was heavily contaminated according to the modular division of each zone in Figure 4 by the scale defined previously. The hotspots of Cd and Zn were concentrated around the dye factory, which indicated that the factory had a profound impact on the accumulation of these two soil heavy metals. The highest zinc concentrations were located at grid 7 and 17 in grid space, respectively, in the vicinity of the dyeing plant, indicating reliable analytical results. In addition, higher concentrations of Cr and As were released in the southeastern of the
study area. The grid spatial distribution of As in Figure 4 revealed that the highest concentration of As was at grid 76, which was consistent with the location of the farmland in Figure 2. Zn and Pb had a similar concentration distribution trend, while the high concentration of Pb focused in grid 61 from the center of the region, which mainly near the major traffic artery. The hotspot of Cd was situated in grid 26 near the bareland of the northwest part of the study area, which may be due to the accumulation of household waste in the area (Dong et al., 2018). Different from other soil heavy metals, higher concentrations of Ni were concentrated in grid 96 from residential area with more interference from human activities (Lee et al., 2006). Spatial distributions of soil heavy metals showed that the area with high concentrations of soil trace metals were roughly in the northwest region, which may also be contributed by the dominant wind direction (Li et al., 2017). Therefore, the spatial distribution of soil heavy metal elements can provide significant information for the key remediation of regional pollutant discharge.

![Fig. 5. Spatial distribution of soil heavy metals in grid A scale of the study area (mg/kg).](image)

### 3.3. Screening of TM by potential ecological risk index (PERI)

Potential ecological risks can be used to comprehensively evaluate the concentration effect, toxicity and ecological
sensitivity of toxic heavy metal elements (Li et al., 2017). Four levels of PERI were defined (Islam et al., 2015; Gu et al., 2016), as shown in Table 2. The environmental risk index ($E_i^r$) of Cd and Zn was 14.46 and 72.34, respectively, in which Zn indicating a severe pollution degree. The average $E_i^r$ values of As, Cr, Pb and Ni were 0.89, 1.76, 1.09 and 0.03, respectively. In addition, Zn pollution was the most serious one, with an average PERI value of 326, reaching a severe degree of potential ecological risk level. The maximum PERI value was 232.02 which appeared near the dye plant and heavy metal elements of As, Cd, Cr, Ni and Pb with the average values in the study area showed that each element was in a slight degree of ecological risk. The evaluation results of the potential ecological risk index of various heavy metals showed that the other areas in the study area were at low ecological risk level. In summary, $E_i^r$ values for the studied heavy metals were in the decreased order of Zn > Cd > As > Pb > Cr > Ni. But on the whole, the industrial areas with serious pollution had strong ecological risk. The enrichment of Cd and Zn was obvious in bare land and industrious area. However, the risk level of these two elements was significantly different, which was mainly due to the large difference in toxicity coefficient between the two elements. Nevertheless, the accumulation concentration of Zn heavy metal element was higher, which ultimately led to the higher ecological risk index. The source analysis showed that the heavy metal of Zn in the whole area had an impact on the main pollution sources around the abandoned dye plant. Therefore, it was necessary to strengthen the remediation of Zn element in the study area to further prevent the heavy metal pollution in soil. On the basis of the methodology explored in this paper, Zn was screened out as the TM for further study by means of potential ecological risk assessment. Further research on TM to evaluate the health risks of its metal species and acquaintance with the metal speciation of TM with higher risk levels can achieve targeted pollution control effectively and accurately, which could implement environmental management policies.

Table 2

| Scope of potential ecological risk index ($E_i^r$) | Ecological risk level of single-factor pollution | Slope of potential toxicity index (RI) | General level of potential ecological risk |
|-----------------------------------------------|-----------------------------------------------|--------------------------------------|------------------------------------------|
| $E_i^r < 40$                                   | Low                                           | RI $< 150$                           | Low-grade                               |
3.4. Simulation of Zn (II) speciation

The physical and chemical parameters collected from experimental data for simulation environment were summarized in Table 3. Other parameters, such as pE, pH, basicity, temperature and concentrations of Na⁺, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻, CO₃²⁻, HCO₃⁻, Cl⁻, Mn²⁺, Fe²⁺, Fe³⁺, NO₃⁻ and F⁻ were set according to the experimental data.

The concentrations and activities of TM of Zn species were simulated by the PHREEQC model. Twenty one types of metal species were obtained with the PHREEQC database. The geochemical model was combined with the experimental results, and the PHREEQC results were consistent with the experimental results, which was available for adoption to evaluate health risk assessment of each metal species (Masindi et al., 2018). In addition, the total concentration of 21 ion species obtained by PHREEQC was 5.16 mg/L, which was close to the initial concentration (Khoshgoftarmanesh et al., 2006). The metal species of Zn (II) ionic speciation obtained from geochemical simulation model were Zn(CO₃)²⁻, Zn(NO₃)₂, Zn(OH)₂, Zn(OH)₃⁺, Zn(OH)₄²⁻, Zn₂(OH)³⁺, Zn₂S₃²⁻, Zn₄S₆⁴⁻, ZnCl⁺, ZnCl₂, ZnCl₃⁻, ZnCl₄²⁻, ZnCO₃, ZnF⁺, ZnHCO₃⁺, ZnNO₃⁺, ZnOH⁺, ZnS and ZnSO₄. According to the results shown in Table 4, the highest concentration and activity of Zn (II) ion species were 6.45×10⁻⁵ mol L⁻¹ and 2.68×10⁻⁵ mol L⁻¹ for Zn₂S₃²⁻, respectively. By contrast, the lowest concentration and activity of Zn (II) ion species were 2.14×10⁻¹⁷ mol L⁻¹ and 1.04×10⁻¹⁷ mol L⁻¹ for ZnCl₂, respectively. The simulated concentrations of Zn (II) ion species were decreased in the order Zn₂S₃²⁻ > ZnS > Zn²⁺ > Zn₃S₆⁴⁺ > ZnCO₃ > ZnHCO₃⁺ > ZnSO₄ > ZnF⁺ > ZnOH⁺ > Zn(NO₃)₂ > ZnCl⁺ > Zn(SO₄)₂⁻ > ZnNO₃⁺ > ZnCl₂ > Zn(OH)₃⁺ > Zn(NO₃)₂ > Zn₂(OH)³⁺ > ZnCl₃⁻ > Zn(OH)₄²⁻ > ZnCl₄²⁻. In addition, the simulated concentration of the total Zn (II) species was consistent with that of the detected total one. The distributions of the part of the Zn (II) species with higher concentration were shown in Fig. 6a. it can be seen from the figure that Zn₂S₃²⁻, ZnS and Zn²⁺ were the primary heavy metals in the distribution of Zn (II) species, which occupied 54.94%, 36.71% and 6.98% of the total, respectively. The rest metal species on...
the whole made up for 1.37% owing to the low concentration, which can be ignored. **Fig. 6b** demonstrated the the leading metal species were Zn$_2$S$_3^{2-}$ and ZnS and the two of which accounted for 91.65% of the whole, which may play an important role in the accumulation of concentration of Zn (II) ion. Due to the salinity and their stability, the concentrations of the above heavy metal species will be concentrated, resulting in a high percentage.

### Table 3
The physical and chemical parameters of simulation environment in study area.

| Parameters | Sampling points (n=30) |
|------------|------------------------|
|            | Range(mg L$^{-1}$) | Mean(mg L$^{-1}$) |
| pH         | 6.07-8.85 | 6.58 |
| pE         | 1.18-8.9 | 3.34 |
| Na$^+$     | 109.4-524.06 | 509.50 |
| K$^+$      | 14.8-234.12 | 47.11 |
| Mg$^{2+}$  | 10.91-360.94 | 105.57 |
| Ca$^{2+}$  | 56.49-440.08 | 196.37 |
| SO$_4^{2-}$| 81.95-411.2 | 161.34 |
| HCO$_3^-$  | 395.02-758.2 | 593.05 |
| S$^{2-}$   | 1.92-100.88 | 28.68 |
| Cl$^-$     | 10.87-253.65 | 85.88 |
| CO$_3^{2-}$| 30.45-465.33 | 166.14 |
| Mn$^{2+}$  | 0.438-112.61 | 21.31 |
| Fe$^{2+}$  | 6.87-110.66 | 28.82 |
| Fe$^{3+}$  | 4.65-204.11 | 33.34 |
| NO$_3^-$   | 5.02-104.05 | 20.85 |
| F$^-$      | 1.97-200.13 | 23.39 |
| Zn$^{2+}$  | 0.038-8.56 | 1.39 |

### Table 4
The concentrations and activities of Zn (II) species.

| Zn$^{2+}$ species | Concentration (mol L$^{-1}$) | Activity (mol L$^{-1}$) |
|-------------------|-----------------------------|-------------------------|
| Zn(CO$_3$)$_2^{2-}$| 1.14×10$^{-8}$ | 4.75×10$^{-9}$ |
| Zn(NO$_3$)$_2$    | 3.69×10$^{-14}$ | 3.73×10$^{-14}$ |
| Zn(OH)$_2$       | 1.08×10$^{-8}$ | 1.09×10$^{-8}$ |
| Zn(OH)$_3^{3-}$  | 4.95×10$^{-12}$ | 4.26×10$^{-12}$ |
| Zn(OH)$_4^{-2}$  | 8.65×10$^{-16}$ | 4.75×10$^{-16}$ |
| Zn(SO$_4$)$_2^{2-}$| 1.07×10$^{-9}$ | 5.11×10$^{-10}$ |
| Zn$^{2+}$         | 8.20×10$^{-7}$ | 3.62×10$^{-7}$ |
| Zn$_2$OH$^{3+}$  | 2.59×10$^{-14}$ | 5.65×10$^{-15}$ |
| Zn$_2$S$^{2-}$   | 6.45×10$^{-5}$ | 2.68×10$^{-5}$ |
| Zn$_4$S$_6^{4+}$ | 4.09×10$^{-7}$ | 1.22×10$^{-8}$ |
| ZnCl$^+$          | 2.03×10$^{-9}$ | 1.72×10$^{-9}$ |
| ZnCl$_2$         | 5.03×10$^{-12}$ | 5.11×10$^{-12}$ |
| Species          | $K_f$  | $K_c$  |
|------------------|--------|--------|
| ZnCl$^-$         | $2.43 \times 10^{-14}$ | $1.96 \times 10^{-14}$ |
| ZnCl$^{2-}$      | $2.14 \times 10^{-17}$ | $1.04 \times 10^{-17}$ |
| ZnCO$^3$         | $3.73 \times 10^{-7}$  | $3.76 \times 10^{-7}$  |
| Zn$^{2+}$        | $2.64 \times 10^{-8}$  | $2.12 \times 10^{-8}$  |
| ZnHCO$^4$        | $1.03 \times 10^{-7}$  | $8.59 \times 10^{-8}$  |
| ZnNO$^+$         | $5.06 \times 10^{-10}$ | $4.12 \times 10^{-10}$ |
| ZnOH$^+$         | $2.01 \times 10^{-9}$  | $1.70 \times 10^{-8}$  |
| ZnS              | $4.31 \times 10^{-5}$  | $4.36 \times 10^{-5}$  |
| ZnSO$^4_2$       | $6.48 \times 10^{-8}$  | $6.53 \times 10^{-8}$  |
| Total Zn$^{2+}$  | 8.56   | 3.53   |

Fig. 6. (a) The distribution of the Zn (II) species and (b) the concentration of each Zn metal species by PHREEQC simulation.

### 3.5. Optimized health risk assessment of Zn (II) species

The toxicity of heavy metals affects human health directly or indirectly through the plant or food chain of animals, mainly in the form of metal ions (Wu et al., 2011). Therefore, heavy metal speciation played an important role in human health risks and should be assessed effectively and accurately. On one hand, the TM of Zn with ecological risk level has been screened out for human health risk assessment based on the simulation of metal species. On the other hand, exposure to excessive zinc contamination may result in zinc poisoning with the symptoms of vomiting, diarrhea, death, etc (Wentink et al., 1985; Wang et al., 2008; Board, 2013). Consequently, it was essential to effectively and accurately quantify the health risk of zinc on human.

Potential carcinogenic and non-carcinogenic human health risks of Zn (II) ionic speciation were evaluated through ingestion pathway ($R/D_{Zn}= 3.00E-01$ mg kg$^{-1}$ day$^{-1}$) (IRIS, Cited Pages) according to Eq. (8)-(16). The exposure
parameters used in this study were shown in Table S1. Subsequently, the non-carcinogenic and carcinogenic risk of Zn (II) species were evaluated by optimized ADD of Zn (II) species. Moreover, the non-carcinogenic and carcinogenic risk based on non-modified and modified ADD for adults and children were shown in Table 5. Modified ADD values for metal species were calculated according to Eq. (11) and ADD values for both adults and children decreased in terms of activity of metal speciation, which was consistent with previous reports that metal absorbed by organisms was primarily determined by the dissolved portion and that free ion activity was associated with these processes. The modified ADD values of Zn (II) species were all higher than those of non-modified for both adults and children. Due to the fluidity and resulting bioavailability of neutral ion, the ADD values of Zn(OH)$_2$, ZnS and ZnCO$_3$, were much higher than those of negatively corresponding charged ions, such as Zn(OH)$_3$, Zn$_2$OH$^{3+}$, Zn$_4$S$_6^+$, Zn(CO$_3$)$_2^{2-}$ etc. (Kotas and Stasicka, 2000; Accornero et al., 2010).

In terms of carcinogenic and non-carcinogenic health risk (Table 5), the HI values of Zn (II) species decreased in the order as followed: Zn$_2$S$_3^{2-}$ > ZnS > Zn$^{2+}$ > Zn$_4$S$_6^{4+}$ > ZnCO$_3$ > ZnHCO$_3$ > ZnSO$_4$ > ZnF$^+$ > ZnOH$^+$ > Zn(CO$_3$)$_2^{2-}$ > Zn(OH)$_2$ > ZnCl$^+$ > Zn(SO$_4$)$_2^{2-}$ > ZnNO$_3$ > ZnCl$_2$ > Zn(OH)$_3$ > Zn(NO$_3$)$_2$ > Zn$_2$(OH)$_2^{3+}$ > ZnCl$_3$ > Zn(OH)$_2^{2-}$ > ZnCl$_4^{2-}$. Optimized HQ value of Zn$_2$S$_3^{2-}$ for children was 1.31 surpassing 1 compared with the non-optimized HQ value of 0.40, which exhibited non-carcinogenic risk. In addition, optimized HQ value of Zn$_2$S$_3^{2-}$ for adults was 0.94 approaching to 1. Thus special attention should be paid to this speciation because the potential toxicity of heavy metal species may vary with the accumulation of concentration and change of environment factors. Accordingly, the optimized CR value of Zn$_2$S$_3^{2-}$ for adults was 2.01E-04 and the level of risks surpassing 1E-04 are viewed as unacceptable, therefore it was considered to pose significant hazardous effects on humans. However, the optimized CR value of Zn$_2$S$_3^{2-}$ for children was 1.36E-05, in the range of 10$^{-6}$ - 10$^{-4}$, which was in a tolerable level associated with the exposure and real environment (Granero and Domingo, 2003). Meanwhile, the HQ values of Zn$_4$S$_6^+$ after optimization were changed from 1.65E-06 and 1.11E-06 to 2.83E-05 and 1.74E-05 for adults and children, respectively, as shown in Fig. 7a. The CR values of Zn$^{2+}$ after optimization were changed from 5.17E-07 and 8.53E-
07 and to 4.70E-05 and 1.87E-05 for adults and children, respectively. It was worth noting that the weighted average optimized data were able to assess potential non-carcinogenic risks that were ignored by classical assessment methods. Compared with the traditional evaluation model, using the activity of simulated metal species as a factor to optimize human health risk model was more specific and reliable. The carcinogenic risk for ZnS underwent an acceptable degree for adults after optimization with the CR values of 4.10E-05. However, before modification, the non-carcinogenic risk values of ZnS for adults was 3.62E-06, less than 10^-4, which further underscores the need to modify average daily doses to obtain accurate and effective human health risk assessment, as shown in Fig. 7b. Moreover, the rest of the metal species of Zn (II) ion were all beyond the non-carcinogenic and carcinogenic risk level. The results indicated that Zn_S_3^2-, ZnS, Zn_4S_6^4+ and Zn^{2+} should be converted to other forms to reduce adverse effects on humans.

Traditional risk assessment methods tended to ignore, overestimate or underestimate regional risk level when conducting potential risk assessment. Therefore, when evaluating the relationship between the bioavailability of various metals and health risks, attention should be paid to the absorbability of organisms to different metal ion forms. Hence, it was necessary to assess the level of carcinogenic and non-carcinogenic risk of each metal species for regional management and rehabilitation. A prerequisite for reducing the level of health risks in the region was the screening of high-risk metal forms, which should be converted to non-toxic forms or microbial decomposition for targeted environmental management.
Fig. 7. Non-carcinogenic ($HQ$) and carcinogenic risk ($CR$) of main metal species for adults and children (OP represented optimized human health risk).

Table 5
Estimations of non-optimized and optimized health risk for each metal species of Zn (II) species.

| Metal species | Non-optimized risk | Optimized risk |
|---------------|--------------------|----------------|
|               | HQ                 | CR             | HQ             | CR             |
|               | Adults Children    | Adults Children| Adults Children| Adults Children|
| Zn($CO_3^{2-}$) | 8.25E-05 1.15E-04 | 8.74E-09 7.75E-09 | 1.65E-03 2.31E-03 | 2.34E-07 8.94E-08 |
| Zn(NO$_3^2$)    | 2.68E-10 3.75E-10 | 2.83E-14 2.79E-14 | 5.44E-09 7.62E-09 | 3.76E-13 9.78E-13 |
| Zn(OH)$_2$     | 7.88E-05 1.10E-04 | 8.23E-09 1.24E-09 | 1.59E-03 2.23E-03 | 3.04E-07 3.34E-07 |
| Zn(OH)$_3^-$   | 3.59E-8 5.03E-08  | 4.28E-12 1.54E-11 | 7.20E-07 1.01E-06 | 5.96E-11 8.45E-09 |
| Zn(OH)$_4^{2-}$| 6.28E-12 8.80E-12 | 5.62E-16 8.09E-16 | 1.26E-10 1.76E-10 | 6.67E-15 1.32E-14 |
| Zn(SO$_4^{2-}$) | 7.81E-06 1.09E-05 | 7.92E-10 4.35E-09 | 1.57E-04 2.19E-04 | 5.94E-09 7.76E-08 |
| Zn$_2^+$       | 5.96E-03 8.34E-03 | 5.17E-07 8.53E-07 | 0.12 0.17 | 4.70E-05 1.87E-05 |
| Zn$_2$OH$_3^{3+}$ | 3.76E-10 5.26E-10 | 3.41E-14 3.76E-14 | 7.53E-09 1.05E-08 | 6.04E-13 3.42E-12 |
| Zn$_2$S$_2^{2-}$ | 0.28 0.40     | 5.30E-05 8.96E-05 | 0.94 1.31 | 2.01E-04 1.36E-05 |
| Zn$_2$S$_6^{4-}$ | 1.19E-02 1.66E-02 | 1.65E-06 1.11E-06 | 0.24 0.33 | 2.83E-05 1.74E-05 |
| ZnCl$_4^-$     | 1.47E-05 2.07E-05 | 1.49E-09 2.75E-09 | 2.96E-04 4.15E-04 | 3.14E-08 6.62E-08 |
In this paper, $\text{Zn}_2\text{S}_3^{2-}$, ZnS, $\text{Zn}^{2+}$ and $\text{Zn}_4\text{S}_6^{4-}$ was evaluated as the primary metal species by optimized human health risk assessment. However, this did not mean that other low-risk ion forms can be ignored because the total health risk value of zinc element was shared by each metal species. Changes in the environment, such as pH and alkalinity, will affect ion activity, thus affecting ion concentration and weight distribution, and eventually led to changes in the level of health risks. Therefore, the governance of different regions should be combined with the local actual situation to carry out specific analysis and research.

### 3.6 Uncertainty and limitation of the risk assessment

Uncertainty estimation was an important part of human health risk assessment. Monte Carlo simulation was used to verify that the simulated values were close to those calculated based on human health risk assessment. The results showed that the health risk and output of each factor were stable. However, SOM and pH values can strongly affect soil quality and metal distribution and fraction, further triggering changes in soil bioavailability, exposure dose and toxicity of heavy metals, and finally causing health risks of different degrees. At the same time, the metal speciation may affected by the interaction of metals with humus in soil or soil solution. Other influencing factors, such as sand and clay, should also be considered. In addition, due to the limitation of conditions, the number of sampling points...
was limited, the analysis types of pollutants were not comprehensive enough, and there was a lack of historical
monitoring data of site pollution. Although there was some uncertainty, this study can come up with an unbiased
effective risk index, which could screen out targeted metal by classical ecological risk assessment and optimize the
health risk assessment based on the simulation of morphological evolution of certain heavy metal species.

4. Conclusions

In this study, an optimized methodology for the contribution of metal speciation to health risk was developed by
combining chemical balance modeling with activity correction for average daily doses through exposure pathways.
Primarily, the ecological health risk levels and main pollution sources of six heavy metals (As, Cd, Cr, Ni, Pb and
Zn) in the region were studied. Source apportionment based on PMF spatial scales was conducted and the spatial
distribution of Zn and Cd with high enrichment were mainly in the center of abandoned industrial area, which were
polluted by discharge of Industrial waste water. The optimization simulation of the target heavy metals with high
ecological risk levels was carried out to establish the optimal health risk model. The results showed that the ecological
risk level of zinc was high, which need to be paid more attention, and heavy metals were mainly concentrated near
abandoned factories, which required the government to carry out policy management for soil remediation. The
carcinogenic and non-carcinogenic risk assessment suggested that the health risks of the four metal species of Zn\textsubscript{2}\text{S\textsubscript{3}}\textsuperscript{2-},
ZnS, Zn\textsuperscript{2+} and Zn\textsubscript{4}\text{S\textsubscript{6}}\textsuperscript{4-} need to be paid attention, which can be converted into other harmless substances for effective
degradation and emission. The addition of all forms also indicated carcinogenic and non-carcinogenic risks of
metallic zinc in this region. Moreover, the harm of heavy metals to human health was mainly caused by the forms of
absorbable ions, rather than the total concentration. Traditional risk models may overestimate or underestimate the
actual risk level of heavy metals. In addition, soil pH was a key factor affecting soil heavy metal content, and organic
matter and soil pH value had significant effects on inorganic zinc binding state. Therefore, changing soil conditions
can effectively transform metal speciation with high toxicity.

The method was accurate and reliable and the evaluation results can provide decision-making basis for heavy metal
screening and discharge as well as targeted remediation for site management. Soil pH was found to be a crucial factor affecting soil Zn fraction, and carbonate-bound Zn can be significantly affected by both organic matter and pH of soils.

Authors’ contributions

Fangfang Miao: Writing-original draft, Conceptualization, Methodology, Software, Writing-review & editing. Yimei Zhang: Supervision, Investigation, Methodology. Yu Li, and Qinguo Lin: Investigation, Resources.

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Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

Not applicable

Consent for publication

We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. We affirm that all authors have approved the submission.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could
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