

CHEMICAL SPECIATION AND RISK ASSESSMENT OF TRACE ELEMENTS IN THE SOIL OF THE AGRICULTURAL AREA IN HUAINAN, CHINA

YOU, M.¹ – YAN, Y.² – HU, Y.^{3*}

¹*School of biology engineering, Huainan normal university, Huainan 232001, China*

²*National center for coal chemical products quality supervision and inspection (Anhui), Huainan 232001, China*

³*School of chemistry and materials engineering, Huainan normal university, Huainan 232001, China*

**Corresponding author*
e-mail: huyunhu@ustc.edu.cn

(Received 4th Oct 2023; accepted 16th Nov 2023)

Abstract. In this study, 30 soil samples were collected from the agricultural area of Huainan of Anhui Province, China. The concentrations of six toxic trace elements were determined, the distribution characteristics and chemical speciation were analyzed, the pollution status and potential ecological risk of trace elements were comprehensively evaluated by single factor index, geo-accumulation Index (I_{geo}), the potential ecological risk index and RAC code method. Results showed that the average concentrations of Ni, Cu, Zn, Pb, Cr and Cd in soil were 20.19±8.20, 18.17±4.67, 37.61±10.85, 10.76±3.73, 40.61±15.06, 0.14±0.05 mg/kg, respectively. With increasing soil depth, the concentration of Cr increases while Cd and Pb decrease. It is speculated that Cd and Pb were affected by anthropogenic activities. All the trace elements mainly associate with the residual fraction indicating lower mobility and Cd exists in a relative higher carbonate bound form suggesting it pose a great mobility and bioavailability. The single factor index and the geo-accumulation index (I_{geo}) indicate that pollution caused by Cd to a certain degree of pollution, while pollution caused by other elements belong to the level of uncontaminated. The results of the potential ecological risk index and RAC also shows that Cd has an extremely strong potential ecological risk. Attention should be paid to the pollution caused by Cd. This study provides a theoretical basis for the prevention and control of soil pollution and for agricultural products safety in the study area.

Keywords: *soil pollution, toxic element, source identification, farmland, ecological risk*

Introduction

Soil is the main medium of material cycle and energy transfer in terrestrial ecosystem (Lian et al., 2021), and also an important resource for human survival and agricultural production (Rani Saha et al., 2022). In recent years, various human activities, such as industrial emissions, use of chemical fertilizers and pesticides, sewage irrigation, and transportation, have led to the release of toxic trace elements into the soil (Zhou et al., 2022). Soil pollution is one of the most prominent environmental problems in the world (Zhang et al., 2021).

Trace elements pollution has the characteristic of environmental persistence, toxicity, and irreversible impact on the regional landscape can lead to soil degradation (Hu et al., 2021). Contaminated soil will reduce crop yield by decreasing soil fertility and will lead to trace elements enriched plants and even directly or indirectly threaten human health through the food chain (You et al., 2014; Xie et al., 2022). And the enrichment of toxic trace elements in agricultural soil will affect the safety of agricultural products and bring

potential risks to human, animals, plants, and entire ecosystem (Wu et al., 2022). It is generally believed that the total amount of concentration is an important indicator for evaluating the degree of soil pollution, but it cannot characterize the bioavailability of trace elements accurately (Gao et al., 2018). Some studies have demonstrated that the migration, transformation, and toxicological effects of trace elements in soil are not only related to the total amount of trace elements, but also closely related to their occurrence forms in soil (You et al., 2021, 2023).

The most commonly implemented method for trace element speciation detection is the Tessier sequential extraction (Tessier et al., 1979), and five fractions consisting of exchangeable fraction, carbonate-bound, Fe/Mn oxides-bound, organic matter-bound and residual fraction were separated (Zhang et al., 2017). The exchangeable and carbonate-bound fractions have strong bioavailability, and can be absorbed easily, posing great harm to plants. The Fe/Mn oxides-bound fraction will be released when the soil redox conditions change, and the organic matter-bound fraction absorption is difficult for plants. The residual fraction has stable properties and is not easily absorbed by plants, with low potential risk (Galhardi et al., 2020). Previous research has indicated that the occurrence forms of trace elements in soil can affect their migration and transformation behavior in the soil, as well as their bioavailability and toxicity (Cheng et al., 2018). Therefore, it is of great significance to detect the content and occurrence forms of trace elements in soil accurately, analyze the migration and transformation behavior and evaluate the bioavailability of trace elements.

Huainan mining area has contributed to eastern China's economic and social development as an important coal resource base in China. However, the long-term high-load mining of coal has accumulated dozens of gangue hills with different scales, thus posing a considerable challenge to the safety of surrounding soil agricultural activities and the security of agricultural products (You et al., 2016). Meanwhile, Huainan is also a national food production area in China. Many studies have been conducted on the concentration and quality evaluation of trace elements in the soil of mining and other industrial areas (Chuncao et al., 2014; You et al., 2015; Hu et al., 2021), reclamation areas (Cheng et al., 2018) and subsidence areas (Ouyang et al., 2018; Chen et al., 2019), but a lack of research on the trace elements in the soil of agricultural zone.

In the present study, representative sampling sites were selected to systematically study the trace element pollution in the soil from agricultural area of Huainan, the objectives of this work were to (1) determine the concentrations, distributions and fractionation characteristics of trace metals; (2) evaluate the contamination degree by the single factor index and geo-accumulation index (*I_{geo}*); and (3) assess the potential ecological risk, mobility and availability by trace elements. The results will provide scientific basis for the prevention and control of soil environmental pollution and ecological risk management and control of agricultural area in Huainan.

Materials and methods

Study area

Huainan city is in the middle north of Anhui Province, China. Located between 116° 21' 5"-117° 12' 30" E and 31° 54' 8"-33° 00' 26" N. The study area is in the south of Huainan city (*Fig. 1*), far from the mining area, with latitudes of 116° 55' 7.32"-116° 58' 31.26" E and longitudes of 32° 33' 2.95"-32° 35' 44.92"N, respectively. Which is an important agricultural production base in Huainan city. The terrain is flat, with an altitude

of 21-23 m and an elevation of 18-27 m. Covered by the Quaternary system, with a thickness of 20-60 meters, the lithology mainly consists of clay, sub clay, silt, fine sand, etc. The study area belongs to the warm temperate, semi-humid continental monsoon climate zone, with remarkable climate characteristics, four distinct seasons, and the easterly wind prevails all year-round. The annual average temperature is 15.3 °C, and the annual average precipitation is 926 mm.

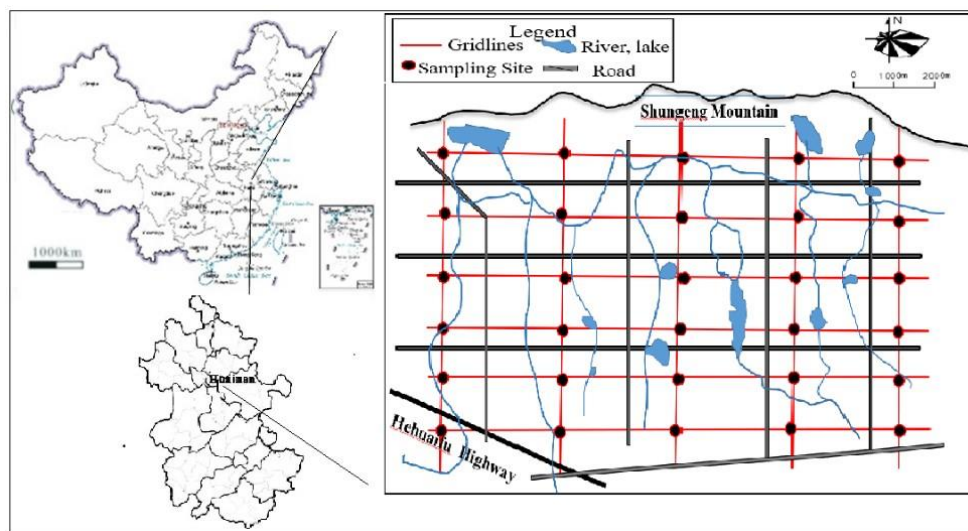


Figure 1. Location of sampling sites

Sample collection and analysis

According to the scale and spatial distribution of agricultural land, a total of 30 soil samples were collected from cultivated land during June to August 2021 using the grid distribution method (Fig. 2). And the sampling sites were in a suburban area dominated by agricultural activities. To ensure the representativeness of the soil samples, four sub samples (vertices of 10 m × 10 m square) were collected at each sampling point and mixed evenly with the quartering method to obtain approximately 1 kg of composite sample. The collection, preparation, testing, and quality control were conducted referring to the Technical Specifications for Soil Environmental Monitoring (Environmental Protection Administration (EPA), 2004).



Figure 2. The photos of the sampling sites

After natural air drying of soil samples, impurities such as roots and gravels were removed from the samples and passed through 100 mesh nylon sieves. The soil pH was determined by the glass electrode method. 2 g soil samples were weighed and digested with HNO₃-HClO₄-HF to be determined. The occurrence forms of trace elements in soil were extracted using the Tessier sequential extraction method (Tessier et al., 1979). The concentrations of Cr, Cu, Zn, and Ni were determined by inductively coupled plasma atomic emission spectrometry (ICP- OES, Optima 5300 DV, PerkinElmer, USA); The concentrations of Cd and Pb were determined by inductively coupled plasma mass spectrometer (ICP-MS, Elan DRC-e, Perkin Elmer, USA). The detection limits of Cr, Ni, and Zn are >1 µg·kg⁻¹, and the detection limits of Cd, Cu, and Pb are >0.1 µg·kg⁻¹. The test set 2% parallel samples, including soil reference material GBW07402 (GSS-2). The recovery rate in the monitoring samples (90% ± 10%), the relative deviation of parallel samples, and the recovery rate of reference materials met the quality control requirements.

Soil pollution assessment

Single factor index

The degree of soil pollution was evaluated by comparing the concentration of trace elements with the related reference standard (Fei et al., 2022). It is the basis of various comprehensive assessment methods of soil pollution and was widely used internationally. The larger the P_i value is, the more serious the soil is polluted, and the calculation formula is:

$$P_i = C_i/S_i \quad (\text{Eq.1})$$

where, P_i is the single factor index of trace element i in soil; C_i is the measured concentration of element i (mg·kg⁻¹), S_i is the reference standard for trace element i , which was the reference background value of Huainan city (Yang et al., 1995). Based on the values of P_i , soil pollution can be grouped into five levels: clean ($P_i \leq 1$), slight pollution ($1 < P_i \leq 2$), mild pollution ($2 < P_i \leq 3$), moderate pollution ($3 < P_i \leq 5$) and severe pollution ($P_i > 5$) (Yan et al., 2022).

Index of geo-accumulation (I_{geo})

The I_{geo} evaluated the soil pollution by comprehensively considering the impact of human pollution factors, environmental geochemical background values (You et al., 2021), and the changes in background values caused by the differences between different regions of rocks. It can be calculated using the equation below.

$$I_{geo} = \log_2 (C_i / 1.5B_i) \quad (\text{Eq.2})$$

where I_{geo} is the geo-accumulation index of trace elements in soil; C_i is the measured concentration of element i (mg·kg⁻¹), B_i is the geochemical background value of the trace elements in Huainan soil (as S_i in *Formula 1*). The constant 1.5 is the potential variation in the baseline data (Yang et al., 1995). Based on the magnitude of I_{geo} , the pollution degree gradually increases from zero to very strong. The I_{geo} values can be classified into seven categories (You et al., 2021): uncontaminated ($I_{geo} < 0$), uncontaminated to moderately contaminated ($0 \leq I_{geo} < 1$), moderately contaminated ($1 \leq I_{geo} < 2$),

moderately to heavily contaminated ($2 \leq I_{\text{geo}} < 3$), heavily contaminated ($3 \leq I_{\text{geo}} < 4$), heavily to extremely contaminated ($4 \leq I_{\text{geo}} < 5$) and extremely contaminated ($I_{\text{geo}} \geq 5$).

Potential ecological risk assessment

Which was proposed by Hakanson (1980) based on the physical and chemical properties of trace elements and their interaction with the environment. It has been widely used for assessing the potential ecological risks of trace elements quantitatively. It considered the biological toxicity and the comprehensive effect of trace elements (Hu et al., 2022) and is calculated using the following equations:

$$E_r^i = T_r^i P_i \quad (\text{Eq.3})$$

$$RI = \sum E_r^i \quad (\text{Eq.4})$$

where, P_i is the single factor index of element i in soil. E_r^i is the potential ecological risk index of element i ; T_r^i is the toxicity coefficient of element i , which were the identified values of 1 for Zn, 2 for Cr, 5 for Ni, Cu and Pb and 30 for Cd (Yi et al., 2019) respectively. RI is the comprehensive potential ecological risk index. The potential ecological risk degrees of trace element i were classed into five grades: Risk level 1(slight), $E_r^i < 30$. Risk level 2 (moderate), $30 \leq E_r^i < 60$. Risk level 3(strong), $60 \leq E_r^i < 120$. Risk level 4(very strong), $120 \leq E_r^i < 240$. Risk level 5(extremely strong), $E_r^i \geq 240$. The comprehensive potential ecological risk index (RI) consists of four classes: Class 1(slight), $RI < 100$; Class 2 (moderate), $100 \leq RI < 200$; Class 3(strong), $200 \leq RI < 400$; Class 4(very strong), $RI \geq 400$ (Zhang et al., 2022).

Mobility and availability of trace elements

The risk assessment code (RAC) method was adopted to evaluate the mobility and availability based on the different occurrence fractions of trace elements (Perin et al., 1985). It considers the exchangeable and carbonate bound fractions as active forms and evaluates their risk level by calculating their ratio to the total amount concentration of trace elements. The higher the proportion of active forms, the greater the risk of environmental harm.

$$\text{RAC} = \text{Exc}\% + \text{Carb}\% \quad (\text{Eq.5})$$

where Exc% is the percentage of exchangeable fraction in the total of the trace element and Carb% represents the percentage of carbonate bound fraction of that. The risk level of mobility and availability are divided into: no risk (<1%); Low risk (1% to 10%); Medium risk (10% to 30%); High risk (30% to 50%); Very high risk (>50%) (Ting et al., 2019).

Data processing and analysis

The data statistics and analysis were completed using Microsoft Excel and SPSS Statistics 19, the chart was prepared using Origin Pro 2021, and the mapping was done in ArcGIS Pro 25.

Results and discussion

Concentration characteristics of trace elements in soil

Descriptive statistics can reflect the distribution characteristics of trace elements in the study area objectively (Hu et al., 2015). The concentration of trace elements is presented in *Table 1*. The average concentrations of Ni, Cu, Zn, Pb, Cr and Cd in soil were 20.19 ± 8.20 , 18.17 ± 4.67 , 37.61 ± 10.85 , 10.76 ± 3.73 , 40.61 ± 15.06 , 0.14 ± 0.05 mg/kg, respectively. The average concentration was in the descending order of $Zn > Cr > Ni > Cu > Pb > Cd$. All the concentrations of elements are lower than those of the corresponding background values in soil of Huainan city and China except for Cd. The National Soil Standard Grade I is to ensure agricultural production and maintain human health, and all the concentrations were below the value of the standard. The variation coefficients (CV) of the elements are $Ni > Cr > Cd = Pb > Zn > Cu$. The CV value of Zn and Cu were < 0.35 , which is medium variation ($15\% < CV < 35\%$), indicating that the distribution of Zn and Cu in the soil is relatively uniform and is less affected by external environment (Eziz et al., 2020). The variation coefficients of other elements were > 0.35 , which is intense variation, indicating that these elements are highly dispersed and unevenly distributed, and the concentrations of trace elements in soil may be affected by human activities, agricultural activities, industrial activities, transportation and other factors.

Table 1. Comparison of concentration of the trace elements in in the soil and that of other previously reported studies (mg/kg)

| Item | Ni | Cu | Zn | Pb | Cr | Cd | Literature |
|---|------------------|------------------|-------------------|------------------|-------------------|-----------------|--------------------|
| Minimum | 0.91 | 10.57 | 13.38 | 0.29 | 14.41 | 0.06 | Present study |
| Maximum | 37.17 | 33.00 | 76.18 | 21.03 | 88.65 | 0.30 | |
| Mean±S. D. | 20.01 ± 8.20 | 18.17 ± 4.67 | 37.61 ± 10.85 | 10.76 ± 3.73 | 40.61 ± 15.06 | 0.11 ± 0.05 | |
| Coefficient of variation | 0.41 | 0.26 | 0.29 | 0.35 | 0.37 | 0.35 | |
| Huainan Soil | 32.0 | 30.7 | 58.4 | 23.5 | 91.5 | 0.06 | (You et al., 2014) |
| Chinese Soil | 26.9 | 22.6 | 74.2 | 26.00 | 61 | 0.09 | (You et al., 2014) |
| National Soil Standard Grade I | 40.00 | 35.00 | 100.00 | 35.00 | 90.00 | 0.20 | |
| Xinzhuangzi mine | 20.78 | 23.08 | 40.96 | 14.31 | 42.59 | 0.11 | (Wei et al., 2017) |
| Panyi mine | 20.45 | 18.60 | 31.10 | 9.40 | 46.52 | 0.14 | |
| Guqiao mine around coal-fired power plant | 20.04 | 18.31 | 28.51 | 8.77 | 43.88 | 0.14 | (Hu et al., 2021) |
| Mining area | | 22.72 | 79.69 | 41.71 | 109.39 | 0.41 | |
| Industrial area | | 21.6 | 39.7 | 12.2 | 44.5 | 0.12 | |
| Agricultural area | | 19.7 | 50.1 | 11.4 | 45.8 | 0.11 | (You et al., 2015) |
| Residential zone | | 17.9 | 36.5 | 12.6 | 39.4 | 0.09 | |
| | | 32.4 | 38.6 | 20.7 | 43.2 | 0.15 | |

Compared with the research reports on the trace elements in the soil from different utilization type area in Huainan city, including mining, industrial and residential areas (Table 1). Except for Cd concentrations was higher than that in previously research of agricultural area, all other elements are lower than the concentrations in mining, industrial and residential areas. Previous studies have confirmed that the duration of mining activities is an important factor affecting the concentration of trace elements in the soil of mining areas. The concentration of Cd in present study is lower than that in reported literatures (You et al., 2015; Hu et al., 2021) of industrial areas and around coal-fired power plants, and higher than that in agricultural areas. Which may be due to the fact that the source of Cd is not only the extensive usage of pesticides and fertilizers containing Cd, but also the emissions from industrial production activities (You et al., 2023).

Variation trend of trace elements with depth. The distribution of trace elements in different depths of soil was shown in Fig. 3. With the increasing of the soil depth, the concentration of Cr correspondingly increases, the variation trend of Ni and Cu concentrations is the same trend and with a maximum concentration at 60-80 cm. The variation trend of Zn, Pb and Cd with soil depth is similar. The concentration of Zn, Pb and Cd in the surface (0-20 cm) soil is significantly higher than that in the deep layer, which indicated that there might be exogenous Cd and Pb input (Rognerud et al., 2000). Some studies demonstrate that Zn in the surface layer of soil moves downward through leaching, while the biological aggregation makes Zn return to the surface layer (Lanlan et al., 2014). Cd has a limited downward mobility in the soil, that is, it is retained in the topsoil layer for a long time, and has a high availability (Kuo, 1990). It is speculated that the topsoil of farmland may contain more organic matter, while Zn, Pb, and Cd in weakly alkaline soil form complexes or chelate with organic matter in the soil easily (Ming et al., 2007). Therefore, the distribution characteristics of trace elements in soil and their respective occurrence and migration properties are also related to soil properties (Ottosen et al., 2009).

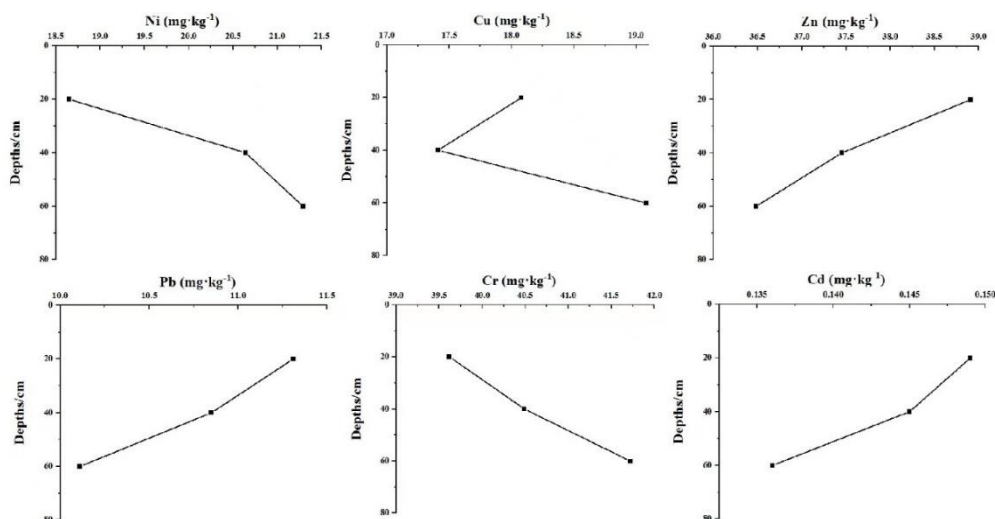


Figure 3. The distribution of trace elements in different depths of soil profile

Fractionation of trace elements

The exchangeable fraction of trace elements can undergo ion exchange and specific adsorption and absorbed by organisms directly in the soil. Carbonate bound fraction refers

to the adsorption or co precipitation onto carbonates (Ribeiro and Flores, 2021). It is easy to migrate and transform in soil and be absorbed by plants when the pH of soil changes (Chunca et al., 2014). Fe/Mn oxides are bound by strong ionic bonds and are difficult to release. Metals are adsorbed or precipitated on the surface of Fe/Mn oxides to form hydroxides or alkali salt. Organic bound state is insoluble in water, formed by combining trace element ions as the central ion and organic matter active groups as ligands. Although the Fe/Mn oxides and organic bound fractions are relatively stable, when the pH changes or the application of complexing agents, trace elements will also be released (Li and Ji, 2017). The residual state is generally referred to as the non-effective state, and elements mainly exist in the mineral lattice and only be released during weathering. Therefore, the residual state is basically not utilized by organisms (You et al., 2023).

The distribution of different chemical fractionations in the soil of the study area is shown in Fig. 4. Percentage distribution of Ni was in the following descending order: residual (68.40%) > organic matter-bound (16.59%) > Fe/Mn oxides-bound (6.58%) > Carbonate-bound (5.83%)>Exchangeable fraction (2.60%). The proportion of Zn association with residual fraction is 63.27 %, followed by organic matter-bound fraction (14.69%), Fe/Mn oxides-bound fraction (11.90%), Carbonate-bound (7.44%) and Exchangeable fraction (2.69%). Apart from the predominant proportion (71.52%) for Pb in the residual form, the amount of Pb in Fe/Mn oxides-bound fraction is 14.20%. Pb is mainly bound to Fe/Mn oxides, which may be due to the strong binding capacity between Fe/Mn oxides and Pb^{2+} . The proportions of different forms for Cu are in the order of residual (71.30%) > Fe/Mn oxides-bound (11.30%) > organic matter-bound (9.72%) > Carbonate-bound (5.44%) > Exchangeable fraction (2.25%). The average proportions of exchangeable, carbonate bound, Fe/Mn oxide bound, organic bound, and residual forms of Cr are 0.86%, 1.10%, 6.11%, 11.02% and 80.91%, indicating low bioavailability of Cr. Cd mainly exists in the form of Residual bound (61.78 %), followed by Carbonate-bound fraction (15.56 %), Organic matter-bound (12.78 %), Exchangeable fraction (5.17 %) and Fe/Mn oxides-bound state 4.72 %). Cd is in a relatively active form in the soil and have potential biological hazards. The soil has a strong adsorption capacity for Cd, especially in soils with more organic matter and clay. The research area belongs to agricultural land, which is prone to the accumulation of Cd (Cheng et al., 2018).

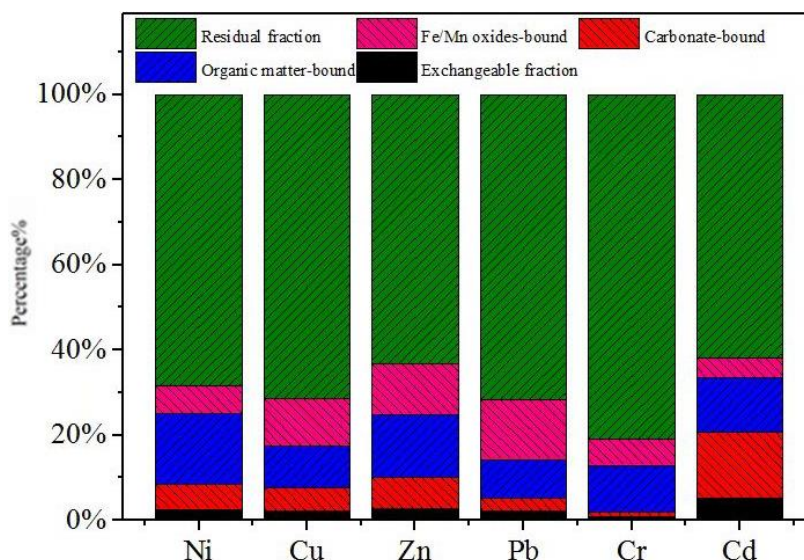


Figure 4. Percentage of trace elements in different fractions

Correlation and source analysis

Correlation analysis is an important basis for identifying the source and migration process of pollutants and a common method for determining the source of soil pollution (Sun et al., 2019). If there is a significant positive correlation between different elements, they are more derived from the same substance or cause of formation (Nakagawa et al., 2022). Pearson correlation analysis was conducted the results are shown in *Table 2*. The correlation coefficients of Ni vs Cu and Ni vs Cu are 0.725 and 0.708, respectively, showing a positive correlation. Cu vs Zn and Cu vs Cr have a positive correlation, and the correlation coefficients are 0.607 and 0.666, respectively. It can be speculated that Cu, Zn and Cr have the same source. Cd and Pb are not related to other elements, and it is inferred that they have different sources from other elements. According to the characteristics of soil content, Cd and Pb are affected by human activities. Cu, Ni and Cr are generally within the range of natural background values and less affected by human activities.

Table 2. Correlation analysis of trace elements in soil of the study area

| Heavy Metals | Ni | Cu | Zn | Pb | Cr | Cd |
|--------------|---------|---------|---------|--------|--------|----|
| Ni | 1 | | | | | |
| Cu | 0.708** | 1 | | | | |
| Zn | 0.725** | 0.607** | 1 | | | |
| Pb | 0.079 | 0.082 | -0.074 | 1 | | |
| Cr | 0.543** | 0.666** | 0.765** | 0.080 | 1 | |
| Cd | -0.049 | -0.016 | 0.175 | -0.134 | -0.007 | 1 |

**Correlation is significant at the 0.01 level (2-tailed)

Assessment of soil pollution

Single factor evaluation

The results of single-factor index were presented in *Table 3*. The average value order of the single factor index is Cd > Zn > Ni > Cu > Pb > Cr. The average single factor index of Cd was 1.89, and the pollution level belongs to slight pollution ($1 < P_i \leq 2$). And single factor index of the other elements were < 1, which belongs to clean ($P_i \leq 1$). The soil pollution in this study primarily concentrated for Cd, and the concentrations in 28 sampling points are exceed the background value in soil of Huainan city (0.06 mg/ kg). The proportion of clean was: Pb (100.00%) = Cr (100.00%) > Cu (90.00%) > Zn (86.67%) > Ni (76.67%) > Cd (10.00%) based on the P_i value.

Table 3. Index of single factor index and geo-accumulation of trace elements in soil of agricultural area

| Item | | Ni | Cu | Zn | Pb | Cr | Cd |
|----------------------|---------|-------|-------|-------|-------|-------|-------|
| Single factor index | Minimum | 0.03 | 0.34 | 0.23 | 0.01 | 0.16 | 1.00 |
| | Maximum | 1.16 | 1.07 | 1.30 | 0.89 | 0.97 | 5.00 |
| | Mean | 0.63 | 0.59 | 0.64 | 0.46 | 0.44 | 1.89 |
| Geo-cumulative index | Minimum | -2.71 | -2.08 | -4.96 | -1.34 | -1.59 | -1.71 |
| | Maximum | -0.17 | -0.47 | -0.37 | -0.14 | -0.31 | 0.58 |
| | Mean | -0.79 | -0.75 | -0.82 | -0.58 | -0.57 | 3.02 |

Results of geo-cumulative index

The results of the geo-accumulation index are also shown in *Table 3*. The order of I_{geo} values is $Cd > Cr > Pb > Cu > Ni > Zn$. The I_{geo} values of Zn, Pb, Ni, Cr and Cu in the soil are negative, indicating uncontaminated ($I_{geo} < 0$). However, the I_{geo} value of Cd is between -1.71 and 0.58, indicating that there is a certain degree of Cd pollution in the soil of the study area, uncontaminated to moderately contaminated ($0 \leq I_{geo} < 1$). The evaluation results of the geo-accumulation index method are consistent with the single factor evaluation results. Hu et al. (2021) reported that the soil around a power plant is polluted by heavy metals, and the degree of pollution is belonged to heavy pollution and moderate pollution in Huainan city.

Potential ecological risk assessment

The average value of pollutant degree (E_r^i) (*Fig. 5*) shows that the average value of E_r^i in the study area is: $Cd > Ni > Cu > Pb > Cr > Zn$, and the average E_r^i values are 56.59, 3.13, 2.96, 2.29, 0.89 and 0.64, respectively. According to the grading standard, Cd and pose a moderate ecological risk ($30 \leq E_r^i < 60$), and the other elements pose a slight ecological risk ($E_r^i < 30$).

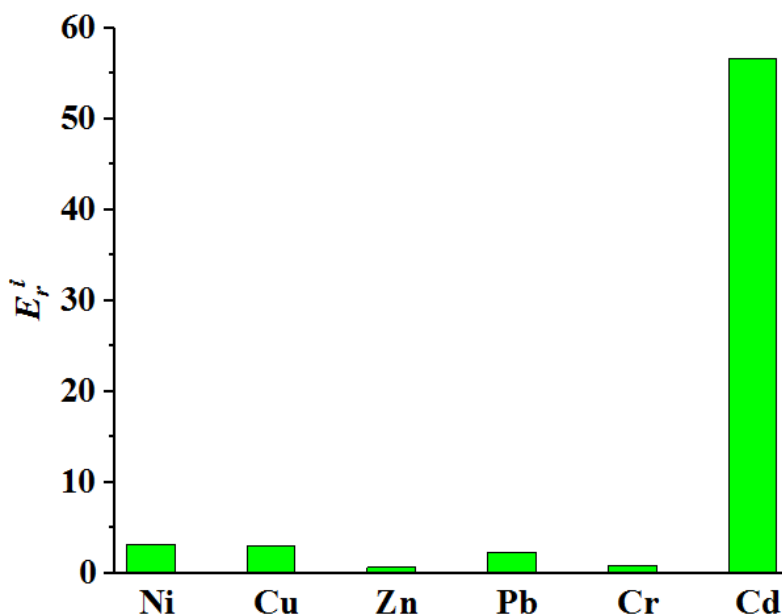


Figure 5. The potential ecological risk assessment results for the trace elements in the soil

According to the distribution of the potential ecological risk index (RI), the sampling points of slight risk and moderate risk in the study area accounted for 63.33% and 36.67%, respectively. The main reason for the high RI is that Cd with a higher value of toxicity coefficient (T_r^i). It can be seen from the integrity of the data that Cd is the main reason affecting the ecological hazard level. Therefore, attention should be paid to the pollution of Cd. The evaluation results are the same as those of the single factor index and geo-accumulation index method, and conclusion was consistent with that of previous study (You et al., 2015, 2016), the degree of soil pollution in agricultural areas is lower than

that in the surrounding soil of mining area (Wei et al., 2017), industrial area (You et al., 2015) and around power plant (Hu et al., 2021) of Huainan city.

Mobility and availability assessment

Based on the exchangeable and carbonate bound fraction, the RAC values was calculated using RAC code method. The larger the proportion of available trace element content to its total amount, the higher its ecological risk (You et al., 2023). As shown in Fig. 6, the RAC average values were in the range of 7.81% for Ni, 4.82% for pb, 1.96% for Cr, 7.35% for Cu, 9.29% for Zn and 20.56% for Cd. According to RAC the RAC average values followed the order of Cd (20.56%) > Zn (9.29%) > Ni (7.81%) > Cu (7.35%) > Pb (4.82%) > Cr (1.96%). The results demonstrated that Cd poses a medium ecological risk (10% ~ 30%), and other elements belong to low risk (1% ~ 10%). Attention should be paid to control Cd in the soil from agricultural area in Huainan city, the results were also similar to that of the potential ecological risk index.

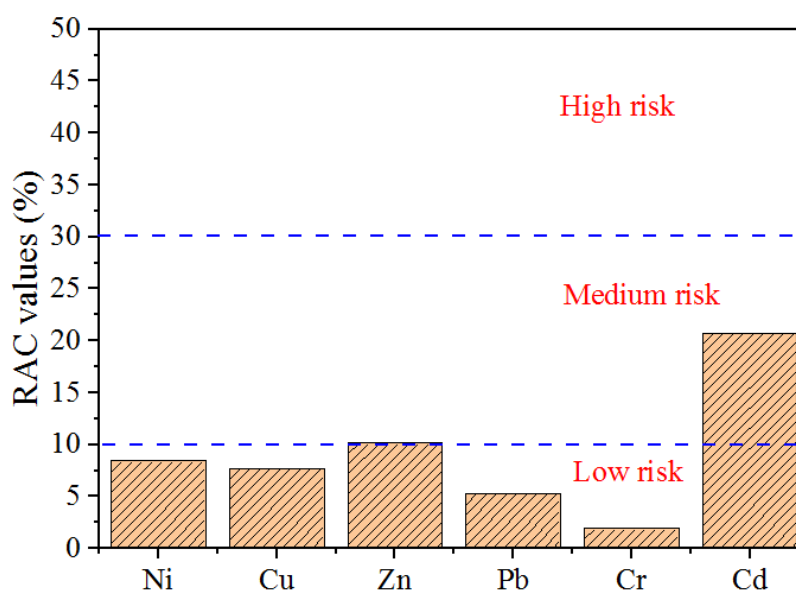


Figure 6. The RAC results for the trace elements in soil samples

Conclusion

In this study, the concentrations of Cr, Ni, Cu, Zn, Cd and Pb in the samples of agricultural soil in Huainan City were determined. The single factor index, geo-accumulation index, and potential ecological risk index were used to evaluate the soil pollution and environmental risk of the study area. The average concentrations of Cr, Ni, Cu, Zn, Cd and Pb in soil were 72.24, 33.23, 23.73, 131.79, 12.10, 0.48, 24.65 and 0.046 $\text{mg}\cdot\text{kg}^{-1}$, respectively. The concentration of Ni and Cu with a maximum concentration at 60-80 cm and Zn, Pb and Cd in the surface (0-20 cm) soil is significantly higher than that in the deep layer. Cd and Pb are affected by human activities, while Cu, Ni and Cr are less affected by human activities. The trace elements mainly appear to associate with the residual fraction, suggesting their lower mobility. Relatively high percentage of Cd exists in carbonate bound fraction, indicating a great degree of mobility and bioavailability. The potential ecological risk of trace elements belonged to slight risk and moderate risk in the

study area, and the results are the same as those of the single factor index and geo-accumulation index method. On basis of the of the potential ecological risk and RAC criteria, Cd poses a medium ecological risk whereas most of the other elements pose low risks, attention should be paid to control Cd in the soil from agricultural area in Huainan city.

Acknowledgements. This work was financially supported by the scientific research project of Anhui Provincial Department of Education (kj2021a0958), the Project of Anhui Province Key Research and Development Plan (No. 2023t07020006), the Postdoctoral Science Foundation of Anhui Province (No. 2020B438). We would like express our gratitude to Zhihui Wang and Wentie Zhang who helped us during the Methodology, review & editing of this thesis. We acknowledge editors and reviewers for polishing the language of the paper and for in-depth discussion.

Author contributions. Mu You: Writing - original draft, Writing - review & editing. Yule Yan: Supervision, Visualization, Methodology. Yunhu Hu: Supervision, Writing - review & editing.

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

Ethics statement. The authors declare that they comply with the IUCN policy statement on Research Involving Species at Risk of Extinction and the Convention on the Trade in Endangered Species of Wild Fauna and Flora.

Competing interests. The authors declare no competing interests.

Additional information. Correspondence and requests for materials should be addressed to the corresponding author.

REFERENCES

- [1] Chen, G., Wang, X., Wang, R., Liu, G. (2019): Health risk assessment of potentially harmful elements in subsidence water bodies using a Monte Carlo approach: An example from the Huainan coal mining area, China. – *Ecotoxicol Environ Saf* 171: 737-745. <http://doi.org/10.1016/j.ecoenv.2018.12.101>.
- [2] Cheng, S., Liu, G., Zhou, C., Sun, R. (2018): Chemical speciation and risk assessment of cadmium in soils around a typical coal mining area of China. – *Ecotoxicol Environ Saf* 160: 67-74. <http://doi.org/10.1016/j.ecoenv.2018.05.022>.
- [3] Chuncai, Z., Gujian, L., Dun, W., Ting, F., Ruwei, W., Xiang, F. (2014): Mobility behavior and environmental implications of trace elements associated with coal gangue: a case study at the Huainan Coalfield in China. – *Chemosphere* 95: 193-199. <http://doi.org/10.1016/j.chemosphere.2013.08.065>.
- [4] Environmental Protection Administration (EPA) (2004): The Technical Specification for soil Environmental monitoring. – Ministry of Ecology and Environment, China. GB HJ/T 166-2004 (in Chinese).
- [5] Eziz, M., Hayrat, A., Xiuyun, Y. (2020): Comparison and Analysis of Estimation Methods for Heavy Metal Pollution of Farmland Soils. – *Journal of Resources and Ecology* 11: 435-442. <http://doi.org/10.5814/j.issn.1674-764x.2020.05.001>.
- [6] Fei, X., Lou, Z., Xiao, R., Ren, Z., Lv, X. (2022): Source analysis and source-oriented risk assessment of heavy metal pollution in agricultural soils of different cultivated land qualities. – *Journal of Cleaner Production* 341: 130942. <http://doi.org/10.1016/j.jclepro.2022.130942>.

- [7] Galhardi, J. A., Leles, B. P., de Mello, J. W. V., Wilkinson, K. J. (2020): Bioavailability of trace metals and rare earth elements (REE) from the tropical soils of a coal mining area. – *Sci Total Environ* 717: 134484. <http://doi.org/10.1016/j.scitotenv.2019.134484>.
- [8] Gao, L., Wang, Z., Li, S., Chen, J. (2018): Bioavailability and toxicity of trace metals (Cd, Cr, Cu, Ni, and Zn) in sediment cores from the Shima River, South China. – *Chemosphere* 192: 31-42. <http://doi.org/10.1016/j.chemosphere.2017.10.110>.
- [9] Hakanson, L. (1980): An ecological risk index for aquatic pollution control. A sedimentological approach. – *Water Research* 14: 975-1001.
- [10] Hu, Y., Fuha, Z., Zhiyuan, N., Zhongbing, D., Guijian, L. (2015): Hydrochemical characteristics of groundwater in centralized drinking water sources and its quality assessment in northern Anhui province. – *Journal of University of Science and Technology* 44(11): 913-920, 925.
- [11] Hu, Y., You, M., Liu, G., Dong, Z. (2021): Characteristics and potential ecological risks of heavy metal pollution in surface soil around coal-fired power plant. – *Environmental Earth Sciences* 80: 566. <http://doi.org/10.1007/s12665-021-09887-x>.
- [12] Hu, Y., You, M., Liu, G., Dong, Z., Wentie, Z. (2022): Distribution and ecological risk assessment of heavy metals in sediment of Huaihe River (Anhui section). – *Fresenius Environmental Bulletin* 31(1): 450-457.
- [13] Kuo, S. (1990): Cadmium Buffering Capacity and Accumulation in Swiss Chard in Some Sludge-Amended Soils. – *Soil Science Society of America Journal* 54: 86-91. <http://doi.org/10.2136/sssaj1990.03615995005400010013x>.
- [14] Lanlan, L., Guijian, L., Xingming, W., Jie, W. (2014): Distribution and ecological risk assessment of trace elements in mining soil in Guqiao coal mine, Huainan coalfield. – *Journal of University of Science and Technology of China* 44: 119-127.
- [15] Li, H., Ji, H. (2017): Chemical speciation, vertical profile and human health risk assessment of heavy metals in soils from coal-mine brownfield, Beijing, China. – *Journal of Geochemical Exploration* 183: 22-32. <http://doi.org/10.1016/j.gexplo.2017.09.012>.
- [16] Lian, Z., Zhao, X., Gu, X., Li, X., Luan, M., Yu, M. (2021): Presence, sources, and risk assessment of heavy metals in the upland soils of northern China using Monte Carlo simulation. – *Ecotoxicol Environ Saf* 230: 113154. <http://doi.org/10.1016/j.ecoenv.2021.113154>.
- [17] Ming, L., Bohan, L., Pufeng, Q. (2007): Fraction distributions and availability of Pb, Cd, Cu, and Zn in contaminated soils around mine. – *Ecology and Environment* 16: 807-811.
- [18] Nakagawa, K., Imura, T., Berndtsson, R. (2022): Distribution of heavy metals and related health risks through soil ingestion in rural areas of western Japan. – *Chemosphere* 290: 133316. <http://doi.org/10.1016/j.chemosphere.2021.133316>.
- [19] Ottosen, L. M., Hansen, H. K., Jensen, P. E. (2009): Relation between pH and desorption of Cu, Cr, Zn, and Pb from industrially polluted soils. – *Water, air, and soil pollution* 201: 295-304. <http://doi.org/10.1007/s11270-008-9945-z>.
- [20] Ouyang, Z., Gao, L., Yang, C. (2018): Distribution, sources, and influence factors of polycyclic aromatic hydrocarbon at different depths of the soil and sediments of two typical coal mining subsidence areas in Huainan, China. – *Ecotoxicol Environ Saf* 163: 255-265. <http://doi.org/10.1016/j.ecoenv.2018.07.024>.
- [21] Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanette, M., Orio, A. (1985): Heavy metal speciation in the sediments of northern Adriatic Sea. – A new approach for environmental toxicity determination. *Heavy metals in the environment* 2: 454-456.
- [22] Rani Saha, T., Abu Rayhan Khan, M., Kundu, R., Naime, J., Md Rezaul Karim, K., Hosna Ara, M. (2022): Heavy metal contaminations of soil in waste dumping and non-dumping sites in Khulna: Human health risk assessment. – *Results in Chemistry* 4. <http://doi.org/10.1016/j.rechem.2022.100434>.
- [23] Ribeiro, J., Flores, D. (2021): Occurrence, leaching, and mobility of major and trace elements in a coal mining waste dump: The case of Douro Coalfield, Portugal. – *Energy Geoscience* 2: 121-128. <http://doi.org/10.1016/j.engeos.2020.09.005>.

- [24] Rognerud, S., Hongve, D., Fjeld, E., Ottesen, R. (2000): Trace metal concentrations in lake and overbank sediments in southern Norway. – *Environmental Geology* 39: 723-732. <http://doi.org/10.1007/s002540050486>.
- [25] Sun, L., Guo, D., Liu, K., Meng, H., Zheng, Y., Yuan, F., Zhu, G. (2019): Levels, sources, and spatial distribution of heavy metals in soils from a typical coal industrial city of Tangshan, China. – *Catena* 175: 101-109. <http://doi.org/10.1016/j.catena.2018.12.014>.
- [26] Tessier, A., Campbell, M. (1979): Sequential extraction procedure for the speciation of particulate trace metals. – *Analytical Chemistry* 51: 844-851.
- [27] Ting, F., Wenxuan, L., Guanjun, H., Kai, C., Xiuxia, Z., Jing, L., Kun, Y., Suofei, J., Yangyang, L., Hui, L. (2019): Fractionation and ecological risk assessment of trace metals in surface sediment from the Huaihe River, Anhui, China. – *Human and Ecological Risk Assessment: An International Journal* 26: 147-161. <http://doi.org/10.1080/10807039.2018.1497476>.
- [28] Wei, Y., Zhou, C., Wang, J., Fan, Z., Liu, G. (2017): Distribution and ecological risk assesment of 6 typical trace elements in mining soils in Huainan coalfield. – *Journal of University of Science and Technology of China* 47(5): 413-420.
- [29] Wu, G., Wang, L., Yang, R., Hou, W., Zhang, S., Guo, X., Zhao, W. (2022): Pollution characteristics and risk assessment of heavy metals in the soil of a construction waste landfill site. – *Ecological Informatics* 70. <http://doi.org/10.1016/j.ecoinf.2022.101700>.
- [30] Xie, N., Kang, C., Ren, D., Zhang, L. (2022): Assessment of the variation of heavy metal pollutants in soil and crop plants through field and laboratory tests. – *Sci Total Environ* 811: 152343. <http://doi.org/10.1016/j.scitotenv.2021.152343>.
- [31] Yan, T., Zhao, W., Yu, X., Li, H., Gao, Z., Ding, M., Yue, J. (2022): Evaluating heavy metal pollution and potential risk of soil around a coal mining region of Tai'an City, China. – *Alexandria Engineering Journal* 61: 2156-2165. <http://doi.org/10.1016/j.aej.2021.08.013>.
- [32] Yang, X., Sun, L., Zhang, Z., Cai, Z. (1995): General study on soil pollution in Huainan area, Anhui Province. – *The Chinese Journal of Geological Hazard and Control* 6: 37-43.
- [33] You, M., Huang, Y., Lu, J., Li, C. (2014): Characterization of Heavy Metals in Soil Near Coal Mines and a Power Plant in Huainan, China. – *Analytical Letters* 48: 726-737. <http://doi.org/10.1080/00032719.2014.940531>.
- [34] You, M., Huang, Y., Lu, J., Li, C. (2015): Environmental Implications of Heavy Metals in Soil from Huainan, China. – *Analytical Letters* 48: 1802-1814. <http://doi.org/10.1080/00032719.2014.999273>.
- [35] You, M., Huang, Y., Lu, J., Li, C. (2016): Fractionation characterizations and environmental implications of heavy metal in soil from coal mine in Huainan, China. – *Environmental Earth Sciences* 75: 78. <http://doi.org/10.1007/s12665-015-4815-7>.
- [36] You, M., Hu, Y., Yan, Y., Yao, J. (2021): Speciation Characteristics and Ecological Risk Assessment of Heavy Metals in Municipal Sludge of Huainan, China. – *Molecules* 26. <http://doi.org/10.3390/molecules26216711>.
- [37] You, M., Hu, Y., Meng, Y. (2023): Chemical speciation and bioavailability of potentially toxic elements in surface sediment from the Huaihe River, Anhui Province, China. – *Mar Pollut Bull* 188: 114616. <http://doi.org/10.1016/j.marpolbul.2023.114616>.
- [38] Yujun, Y., Wenjun, W., Jie, S. (2019): Pollution characteristics, potential ecological risk assessment and source analysis of heavy metals of sediment in the middle and lower reaches of the Yangtze River. – *Water Resources and Hydropower Engineering* 50(544): 4-10.
- [39] Zhang, G., Bai, J., Xiao, R., Zhao, Q., Jia, J., Cui, B., Liu, X. (2017): Heavy metal fractions and ecological risk assessment in sediments from urban, rural, and reclamation-affected rivers of the Pearl River Estuary, China. – *Chemosphere* 184: 278-288. <http://doi.org/10.1016/j.chemosphere.2017.05.155>.

- [40] Zhang, H., Zhang, F., Song, J., Tan, M. L., Kung, H. T., Johnson, V. C. (2021): Pollutant source, ecological and human health risks assessment of heavy metals in soils from coal mining areas in Xinjiang, China. – *Environ Res* 202: 111702. <http://doi.org/10.1016/j.envres.2021.111702>.
- [41] Zhang, B., Jia, T., Peng, S., Yu, X., She, D. (2022): Spatial distribution, source identification, and risk assessment of heavy metals in the cultivated soil of the Qinghai-Tibet Plateau region: Case study on Huzhu County. – *Global Ecology and Conservation* 35. <http://doi.org/10.1016/j.gecco.2022.e02073>.
- [42] Zhou, L., Zhao, X., Meng, Y., Fei, Y., Teng, M., Song, F., Wu, F. (2022): Identification priority source of soil heavy metals pollution based on source-specific ecological and human health risk analysis in a typical smelting and mining region of South China. – *Ecotoxicol. Environ. Saf.* 242: 113864. <http://doi.org/10.1016/j.ecoenv.2022.113864>.