INTEGRATED EXPLORATION OF HEAVY METAL DISTRIBUTION CHARACTERISTICS AND RISK ASSESSMENT OF TYPICAL UNDEVELOPED MINING AREA IN SOUTHWEST CHINA

XU, L.[1] – XIE, W. J.[1*] – DAI, H. P.[2*] – SKUZA, L.[3] – WEI, S. H.[4] – SHI, C. L.[1] – ZHANG, L. C.[1] – XU, J. R.[1]

[1]School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao 266520, China

[2]College of Biological Science & Engineering, Shaanxi University of Technology, Hanzhong 723001, China

[3]Institute of Biology, Centre for Molecular Biology and Biotechnology, University of Szczecin, Szczecin 71-415, Poland

[4]Key Laboratory of Pollution Ecology and Environment Engineering, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China

[*]Corresponding author
e-mail: xwjeric@hotmail.com; daihp72@snut.edu.cn; phone: +86-532-850-71262

(Received 16th Jul 2024; accepted 3rd Dec 2024)

Abstract. Mining process can cause serious heavy metal pollution, so reducing pollution from the source is particularly important. A total of 32 samples were collected from 6 sampling sites in an undeveloped mining area located in Southwest China. In order to reduce the pollution in the mining process, an integrated exploration was conducted based on the spatial, vertical, speciation distribution and correlation coefficient analysis of heavy metals (As, Ni, Cd, Pb, Cr (VI)), as well as pollution level of all soil layers and health risks assessment. In general, the western and south-western parts in the site were heavily polluted, while the eastern part was only slightly polluted. Arsenic pollution was particularly severe in shallow soil, with the mean value of 502.91 mg kg^{-1}, i.e., more than 25-fold higher than the risk screening value. The residual speciation of As, Ni and Cu in almost all samples accounted for more or nearly 70% of the total concentration. Furthermore, Arsenic posed severe pollution and unacceptable health risks (non-carcinogenic and carcinogenic risks) for both adults and children in shallow soil. The study was beneficial to develop clean mineral resources, and thus achieve the goal of reducing pollution at sources and protecting human health.
Keywords: *heavy metal pollution, arsenic, distribution characteristics, environmental assessment, health risk*

Introduction

The problem of soil contamination with heavy metals has become an increasing global concern (Xu et al., 2021; Negahban et al., 2021). Sources of heavy metals in soil are natural and anthropogenic, and the latter mainly involves mining, smelting and other industrial activities (Ran et al., 2021; Zhang et al., 2023a). Among these, mining activities are known to be one of the main sources of heavy metal pollution (Reyes et al., 2021). Mining activities have provided us humans with a large amount of materials and energy, while they have also caused enormous environmental pollution (e.g. heavy metal pollution) from tailings and mining wastewater (Wu et al., 2021). Heavy metals are considered as a unique group of pollutants, which pointed by Wu et al. (2022) and Wang

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

et al. (2021), due to its characterized by long duration and concealment in environment, as well as the accumulation through the food chain and irreversibility for biology (Wang et al., 2018a). This not only poses a threat to the soil and water environment, but also affects the quality of crops, etc., and causes risks to human health through the food chain (Yang et al., 2019; Deng et al., 2020). The close correlation founded indicating that the issue is an urgent problem all over the world, and it deserves special attention in China.

Wenshan is an extremely rich area of high-grade underground mineral resources. There is a variety of black, nonferrous, rare and precious metals as well as non-metallic minerals, and the resources of various minerals in this region rank among the top of the country. The Wenshan Pb-Zn mine, a medium-sized mining area with arsenic, is located in the Southeast Yunnan fold belt of the South China fold system, which is a typical mining area around the world. There are 3 townships around the mining area, with more than 80,000 local residents. Since the severe pollution at the mining process and the enormous amount of time and materials of remediating the contaminated soil, it is particularly important to pay attention to reducing the emission of pollutants at mining process (Ran et al., 2021; Wu et al., 2021). In order to reduce pollution from the source, it was necessary to understand the impact of heavy metals on the local environmental system (Chen et al., 2023), i.e. heavy metal distribution in the soil, pollution level and human health risks. Systematic studies of the spatial distribution of soil heavy metals are essential for pollution assessment and risk control (Cui et al., 2021). Typically, Surfer software (Duan et al., 2020) and geographic information system (GIS) (Cheng et al., 2020) can be used to characterize the spatial distribution of heavy metals. Numerous indices, such as the geo-accumulation index (Igeo) (Zhong et al., 2020), pollution index (PI) (Liu et al., 2021), Nemerow integrated pollution index (NIPI) (Guan et al., 2020) or enrichment factor (EF) (Yu et al., 2021) are applied to evaluate the pollution level and ecological risk. There are also many indices for health risk assessment, e.g. the hazard index (HI) and cancer risk (CR) introduced by U.S. Environmental Protection Agency (USEPA) is one of the most widely applied model to evaluate non-carcinogenic and carcinogenic risks to human body, respectively (Huang et al., 2021). Multivariate statistical methods, e.g. principal component analysis (PCA) and correlation analysis (CA) are often used to qualitatively identify the sources of elements in soil (Wang et al., 2018a; Liu et al., 2021; Ran et al., 2021). In addition, quantitative methods mostly involve receptor models, such as the chemical mass balance (CMB) model (Jiang et al., 2017) or positive matrix factorization (PMF) model (Jiang et al., 2021).

As the commonly known, the mining process has a great impact on the surrounding environment (Chandra et al., 2023). Previous studies have mostly carried out pollution investigations on the mining areas that have been developed and have caused pollution in order to find better remediation strategies. The process not only cost a large amount of consumption and energy, but also caused irreversible hazards and risks to ecology and human health by the contamination. Therefore, understanding the characteristics and distribution of pollutants in mining areas in advance will help reduce pollution at the source when developing mineral resources, thereby reducing the impact and damage to the environment. However, there is little research focus on the undeveloped mining area, i.e., one mining area that has been explored but not yet developed (Ran et al., 2023; Zhang et al., 2023b; Zou et al., 2023; Huang et al., 2024; Zhou et al., 2024; Zhu et al., 2024). Moreover, the previous studies concerning the assessment of heavy metal pollution in soil have mainly focused on the topsoil (Boudia et al., 2019). Actually, in most polluted sites, heavy metals have a relatively obvious downward migration. Only assessing the pollution

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

level of heavy metals in topsoil cannot understand the pollution level of heavy metals migrated downward to each soil layer. Therefore, the current understanding of the whole heavy metal pollution level of the site was one-sided, especially for the undeveloped mining site. In addition, numerous studies have indicated that it is necessary to analyze the speciation of heavy metals, due to the availability of heavy metals were close to the influence of their ecotoxicity (Ye et al., 2015; Zhong et al., 2020). Not only the total concentration of heavy metals, but also heavy metal speciation was essential to determine their risks (Cui et al., 2021). However, previous studies on heavy metal distribution mainly focused on the spatial and/or vertical distribution, fewer studies concerned their speciation distribution and variability with depth (Masri et al., 2021).

In the present study, a typical undeveloped mining area located at Wenshan was selected to systematically and comprehensively analyze the distribution of heavy metals, i.e. spatial, vertical and speciation distribution in the mining area. In addition, correlation coefficient analysis was used to investigate the correlation of heavy metals, as well as pollution assessment in all layers and health risks for both adults and children. Therefore, the study aimed to (1) comprehensively analyze distribution characteristics (including spatial, vertical, and speciation distributions) and the correlation of heavy metals of heavy metals in the mining area; (2) assess the pollution level of heavy metals in shallow soil of each region and the pollution level in each soil layer using the Igeo, PI and NIPI values, so as to evaluated the pollution level of the spatial distribution of heavy metals and their changes with depth; (3) determine the HI and CR values of health risks for local adults and children. This work can provide certain theoretical support and practical basis for more comprehensive research on the distribution of heavy metals in the undeveloped mine, as well as the correlation of heavy metals, in order to control and reduce the pollution in the mining process, then decrease the hazards and risks to the environment and human body, and thus protect the human health.

Materials and methods

Study area, sampling and analysis

Study area

Wenshan Prefecture is located in the southeast of the Yunnan-Guizhou Plateau (*Fig. 1*), between 103°35′-106°12′ east longitude and 22°40′-24°48′ north latitude, the average altitude is between 1000 and 1800 meters. The climate of Wenshan is a tropical monsoon climate, with an average annual temperature of 19℃ and an annual rainfall of 779 mm. The terrain of the site is mainly mountainous, soil type is yellow soil developed by granite with partial sand.

Soil sampling and chemical analysis

The soil samples have been collected through the set-up quadrats, and preliminary analysis has been conducted. After that, six sampling points were reasonably set out on the basis of preliminary experiments and sufficient background studies (*Fig. 1*). The locations of all the sampling points were recorded with a portable Global Positioning System (GPS), and the basic information of the sites had also been documented. However, as it involves the protection of undeveloped mines, and a confidentiality agreement had been signed, the specific coordinate information of the sampling sites in this study cannot be disclosed. Based on the preliminary investigation results, as well as the sampling

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

analysis by X-ray Fluorescence Spectrometry (XRF) and geological conditions at the sampling site, the sampling depth of sample points Y1 and Y4 was 4 m, Y2 and Y6 - 2.5 m, Y5 - 3 m and Y3 - 1 m. One sample was collected every 0.5 m in the upper 3 m, and one sample was collected in the lower 1 m. Thus, there were 7 samples collected at points Y1 and Y4, 5 samples at points Y2 and Y6, 6 samples at point Y5 and 2 samples at point Y3, thus a total of 32 samples was collected, using the sampling drill. All soil samples were collected in plastic zip-lock bags and transported immediately to the laboratory. All soil samples were removed stones, branches, and other materials, then dried at room temperature, ground and sieved through a 0.15-mm nylon sieve, and subsequently stored in plastic zip-lock bags.

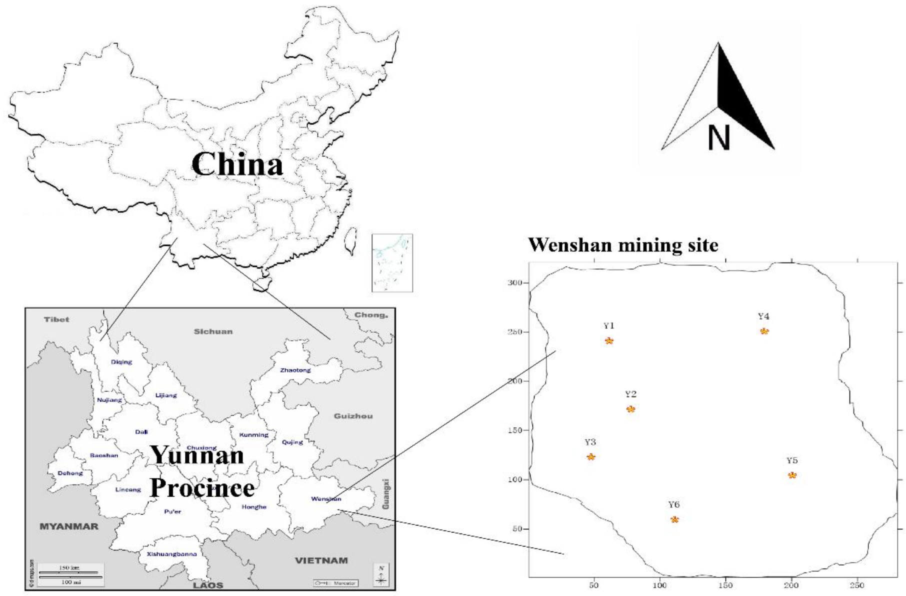

Figure 1. *Geographic information concerning the mining site, including sampling locations and cases*

For the determination of Ni, Pb, Cd, Cu and As total concentrations, the soil samples were digested with the combined acid, i.e., $HCl+HNO_3+HF+HClO_4$ (HJ 832-2017 by National Environmental Protection Standard of the People's Republic of China) and then assayed using inductively-coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5100 SVDV ICP-OES, America Agilent Technologies) (Xu et al., 2021). The Cr(VI) content was pretreated by the method of Soil and sediment-Determination of Cr(VI)-Alkaline digestion/flame atomic absorption Spectrometry (HJ 1082–2019), and also determined using ICP-OES. National first-level standard materials for soil, i.e. GBW07405 (the values of Ni, Pb, Cd, Cu and As were 40 mg kg^{-1}, 552 mg kg^{-1}, 0.45 mg kg^{-1}, 166 mg kg^{-1} and 412 mg kg^{-1}, obtained from the National Standard Detection Research Center, Beijing, China) and GBW(E)070254 (produced by Research Institute NO.240, China National- Nuclear Corporation), as well as reagent blanks, were used to ensure the accuracy of sample digestion procedure and subsequent determinations with respect to the quality assurance and quality control (QA/QC) (Kong et al., 2021). With respect to the recovery of heavy metals, i.e. Ni, Pb, Cd, Cu, As and Cr(VI), the values ranged from 96.8% to 101.7%, indicating that digestion and determination processes of heavy metals in soil were reliable.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

A modified three-step Community Bureau of Reference (BCR) method was used to sequentially extract different speciation of heavy metals from the soil (Ure et al., 1993; Xiao et al., 2019; Zhang et al., 2020). The prepared solution was added to a 50-ml centrifuge tube in sequence, then thorough mixing with the previously added 1 g of the tested soil, so as to the acid-soluble, reducible and oxidizable speciation of heavy metals were obtained (Zhang et al., 2020; Xu et al., 2021). The remaining residue was digested as the method of total concentration measurement to obtain the residual speciation of heavy metals, and subsequently all heavy metal speciation were determined using ICP-OES. All samples were processed in triplicate and the error between the three repetitions was within 5%, indicating reliability of the results.

The Kriging interpolation method and Surfer mapping were applied to graphically and digitally assess the spatial distribution of heavy metal pollution (Kumar, 2015). Ordinary Kriging, as a key method of spatial interpolation, was often used to evaluate spatial data at unsampled locations, boasting high reliability (Ma et al., 2016; Li et al., 2017).

Contamination and risk assessment

Geo-accumulation index

The geo-accumulation (Igeo) index was applied to assess soil contamination by comparing the current concentration with geochemical background values of these elements (Fernández-Martínez et al., 2024; Dong et al., 2024; Huang et al., 2024). The equation was as follows (Zhang et al., 2023a; Yoon et al., 2024):

$$I_{geo} = \log_2 \frac{C_i}{1.5B_i} \quad \text{(Eq.1)}$$

where Ci is the measured concentration of element i in soil, Bi is the geochemical background value of element i obtained from the China National Environmental Monitoring Centre (CNEMC); the background values of Ni, Pb, Cd, Cu and As in Yunnan province were 42.5, 40.6, 0.218, 46.3 and 18.4 mg kg^{-1}, respectively (CNEMC, 1990).

The contamination categories based on Igeo index of heavy metals are divided as (Liu et al., 2021): uncontaminated (<0), uncontaminated to moderately contaminated (0-1), moderately contaminated (1-2), moderately to heavily contaminated (2-3), heavily contaminated (3-4), heavily to extremely contaminated (4-5) and extremely contaminated (≥5) (Khademi et al., 2019; Zou et al., 2023).

Pollution index and Nemerow integrated pollution index

The pollution index (PI) was used to evaluate the pollution risk of a single factor, while the Nemerow integrated pollution index (NIPI) was applied to comprehensively represent the risk of contamination with multiple heavy metals (Nemerow, 1974), taking into account the highest and average values (Chai et al., 2021; Zhang et al., 2023b). PI and NIPI values calculated using Eq. (2-3):

$$PI = \frac{C_i}{S_i} \quad \text{(Eq.2)}$$

where, PI is the pollution index of a single element i; Ci is the concentration of a single element i; Si is the threshold concentration of single element i (*Table 1*).

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

$$NIPI = \sqrt{\frac{{PI_{max}}^2 + {PI_{ave}}^2}{2}} \quad \text{(Eq.3)}$$

where, NIPI is the composite pollution index in soil; PImax and PIave are the maximum and average PI value of all elements. There were five levels distinguished based on the PI and NIPI values: <0.7, 0.7-1, 1-2, 2-3, ≥3, representing no pollution, precautionary pollution, low pollution, moderate pollution and severe pollution, respectively (Liu et al., 2021; Zhang et al., 2023b).

Health risk assessment

The hazard index (HI) and carcinogenic risk (CR) values were used to evaluate the non-carcinogenic and carcinogenic risks based on the USEPA health risk assessment model. Both children (1-17 years old) and adults (over 18 years old) were considered, as well as three exposure routes, i.e. ingestion, dermal contact and inhalation were included in this model for health risk assessment (Khademi et al., 2019; Zhou et al., 2024; Zhu et al., 2024). Average daily doses (ADDs), including ingestion (ADDing), dermal contact (ADDderm) and inhalation (ADDinh) were calculated using Eq. (4-6) from the Exposure Factors Handbook proposed by the United States Environmental Protection Agency (USEPA, 1989, 1997, 2001, 2002; Xu et al., 2021):

$$ADD_{ing} = \frac{C_i \times IngR \times EF \times ED}{\mathrm{BW} \times \mathrm{AT} \times 10^6} \quad \text{(Eq.4)}$$

$$ADD_{derm} = \frac{C_i \times SA \times AF \times ABS \times EF \times ED}{\mathrm{BW} \times \mathrm{AT} \times 10^6} \quad \text{(Eq.5)}$$

$$ADD_{inh} = \frac{C_i \times APM \times InhR \times EF \times ED}{\mathrm{BW} \times \mathrm{AT} \times 10^6} \quad \text{(Eq.6)}$$

Relevant information about the parameters in the formula (e.g. values and units) are listed in *Table S1* of the supplementary material (MEP, 2014; Zhou et al., 2016; Liu et al., 2021; Gui et al., 2023).

The hazard quotient (HQ) was used to evaluate non-carcinogenic risks of by Eq. (7) (USEPA, 1989):

$$HQ = \frac{\mathrm{ADD}}{\mathrm{RfD}} \quad \text{(Eq.7)}$$

The hazard index (HI) was used to comprehensive assess the potential non-carcinogenic risk of multiple heavy metals, according to the following Eq. (8):

$$HI = \sum_{i=1}^{n} HQ_i = \sum_{i=1}^{n} \frac{ADD_i}{RfD_i} \quad \text{(Eq.8)}$$

where, RfD is the reference dose of specific heavy metal and the relevant information were list in *Table S2* of the supplementary material. HQ>1 or HI>1 represent the significant potential non-carcinogenic risk may occur for humans; there is no significant risk otherwise (Xu et al., 2021).

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

The possibility of developing cancer for a person when exposed to multiple heavy metals was calculated based on the CR value according to the following Eq. (9) (USEPA, 1989):

$$CR = ADD \times SF \quad \text{(Eq.9)}$$

where, SF is the carcinogenic slope factor of specific heavy metals and the relevant information were list in *Table S2* of the supplementary material. Three carcinogenic risk levels were listed based on the CR values: $CR<1\times10^{-6}$, $1\times10^{-6} < CR<1\times10^{-4}$, $CR>1\times10^{-4}$, corresponding to no carcinogenic risk; generally acceptable risk; unacceptable risk (Liu et al., 2021; Xu et al., 2022).

Data analysis

The data organization and analysis obtained using Microsoft Office Excel 2010 (Microsoft Corporation, Redmond, WA, USA). The figures of the spatial distribution of heavy metals were created using Surfer 11.0 (Golden Software, Colorado, USA), while the vertical and speciation distribution were determined by Origin 9.0 (OriginLab, Northampton, MA, USA). In addition, SPSS 16.0 (SPSS Inc., Chicago, IL, USA) was applied to analyze the correlation coefficient and R package corrplot (Version 4.0.3) was used to conducted Pearson's correlation matrix (Xu et al., 2021).

Results and discussion

Concentration of heavy metals in soil

Descriptive statistics of heavy metal concentrations in shallow soil

The concentrations of heavy metals were influenced by many factors, including the distribution and release of pollution sources, the characteristics of heavy metals and soil, as well as environmental conditions (Liu et al., 2020). The descriptive statistical concentrations of six heavy metals in shallow soil at the Wenshan site are summarized in *Table 1*. In general, As pollution in shallow soil was particularly severe, the mean As concentration of 502.91 mg kg^{-1} was more than 25-fold higher compared to the risk screening value (20 mg kg^{-1}), while the maximum value (718.94 mg kg^{-1}) exceeded the risk screening value more than 35-fold (GB36600-2018, MEE, 2018). As a type of guest metal, arsenic is found in many kinds of ores (Zhong et al., 2020). Zhang et al. (2023b) reported that the mining process of Pb-Zn mines has led to serious As accumulation in the south of China. The results indicated that the ecological environment and human health could be adversely affected due to the severely exceeded screening value (Cheng et al., 2020). The concentrations of Ni, Pb, Cd, Cu and Cr(VI) were 26.78 mg kg^{-1}, 72.96 mg kg^{-1}, 7.21 mg kg^{-1}, 294.37 mg kg^{-1} and 1.00 mg kg^{-1}, respectively, which were all below the risk screening values. Spatial variability was influenced by natural or extrinsic factors (Zhao et al., 2010). Natural variability was mainly related to the weathering of soil parent materials, while the extrinsic factors included human activities (Li et al., 2017). The coefficient of variation (CV), representing the variability of heavy metal concentrations, was defined as the ratio of standard deviation (SD) to the average of an element (Yu et al., 2021). High CV for heavy metals indicated that their concentrations were affected by the presence of the mine (Cheng et al., 2020). Three levels of the CV were distinguished, i.e. low variation, moderate variation and high

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

variation, with values of ≤16%, 16%<CV≤36% and CV>36%, respectively (Chai et al., 2021). As shown in *Table 1*, the CV values of Ni, Pb, Cd, Cu, As and Cr(VI) were 55.07%, 21.09%, 42.75%, 61.93%, 34.25% and 21.81%, respectively. Among them, Ni, Cd and Cu values constituted more than 36% of the critical value for high variation, considering its lower concentration and the concentration change little with depth, the reason might relate to the natural condition, e.g. the geological evolution and spatial distribution difference of parent material (Zhou et al., 2024). For other heavy metals, i.e. Pb, As and Cr(VI) were moderate variation. This study focused on the soil of undeveloped mines, thus the reasons for the heterogeneity of heavy metal distribution in soil differed from those reported by Zhang et al. (2023b), Zhu et al. (2024), and Zou et al. (2023).

Table 1. *Heavy metal concentrations in shallow soil at the Wenshan mining site*

	Ni (mg kg^{-1})	**Pb (mg kg^{-1})**	**Cd (mg kg^{-1})**	**Cu (mg kg^{-1})**	**As (mg kg^{-1})**	**Cr(VI) (mg kg^{-1})**
Mean	26.78	72.96	7.21	294.37	502.91	1.00
Median	20.60	67.28	6.24	196.87	513.77	1.04
Min	16.26	55.69	3.84	125.17	185.03	0.64
Max	58.61	102.28	13.14	630.03	718.94	1.26
SD	14.75	15.39	3.08	182.31	172.26	0.22
CV (%)	55.07	21.09	42.75	61.93	34.25	21.81
Risk screening value (GB36600-2018)	150	400	20	2000	20	3.0
Risk intervention value (GB36600-2018)	600	800	47	8000	120	30

Risk screening values of Cr(VI), Cu, Ni, Pb, Cd and As were mentioned in the present study

Spatial distribution of heavy metals

The spatial distribution of heavy metals in soil is the basis for the evaluation of pollution risk and decision-making, which was also essential for the understanding the environmental behavior of heavy metals (Liu et al., 2020; Zou et al., 2023). The figure of heavy metal distribution in shallow soil layer was generated in Surfer 11.0 using the Kriging interpolation method (*Fig. 2*). It can be seen that the spatial distribution of heavy metals strongly varied. Ran et al. (2021) pointed out that the spatial distribution of metal in soil was controlled by several factors, including original content of metalloids in the parent materials and rocks, active pedogenesis and various anthropogenic factors. The distribution of Cr(VI) and Ni were quite different from other heavy metals, which indicated that the factors affecting the spatial distribution of Cr(VI) and Ni were different from other heavy metals; Cr(VI) and Ni content were higher in the southeast of the site, where point Y5 was located, and lower in the northwest in the vicinity of points Y1, Y2 and Y3. The distribution of Cd and Pb was relatively similar, with a higher content in the southwest of the site where point Y6 was located, and a lower content in the northeast near point Y4. Cu content was higher in the southwest of the site where point Y3 was established, and it gradually decreased toward the northeast, but none of them exceed the risk screening value. As content strongly exceeded the standard in all the samples collected from the site. Among them, the highest concentrations were recorded in points Y2 and Y6 in the west and southwest of the site, and they exceeded the risk screening value by more than 30-fold. As content at point Y5 in the east of the site, with a lower pollution level, still exceeded the risk value nearly 10-fold (GB36600-2018). Overall, the western and south-western parts of the site were highly polluted, while the eastern parts were less polluted. As was associated with ore, and the spatial distribution of parent material led to As distribution difference (Zhong et al., 2020).

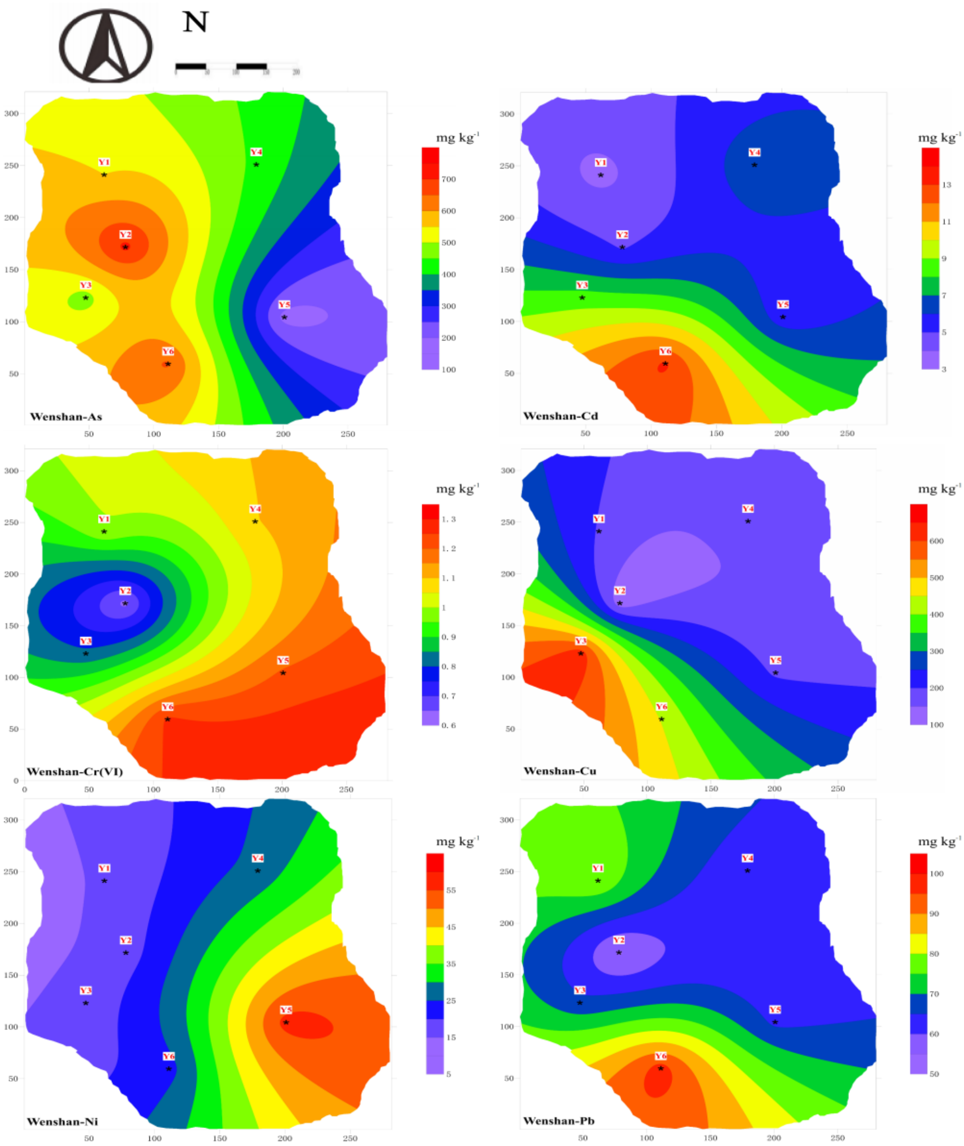

Figure 2. *Spatial maps showing the distribution of heavy metals in shallow soil at the Wenshan mining site*

Vertical distribution of heavy metals

The long-term natural process of the mine, such as leaching process, may cause the migration of heavy metals in soil, thus it was necessary to collect soil samples from a well-developed profile to study downward migration and vertical distribution of heavy metals (Li et al., 2009). *Fig. 3* shows three typical profiles (point Y1, Y4 and Y5) collected to demonstrate the vertical distribution of heavy metals. As content in all layers was higher than the standard risk screening value in the three typical profiles.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

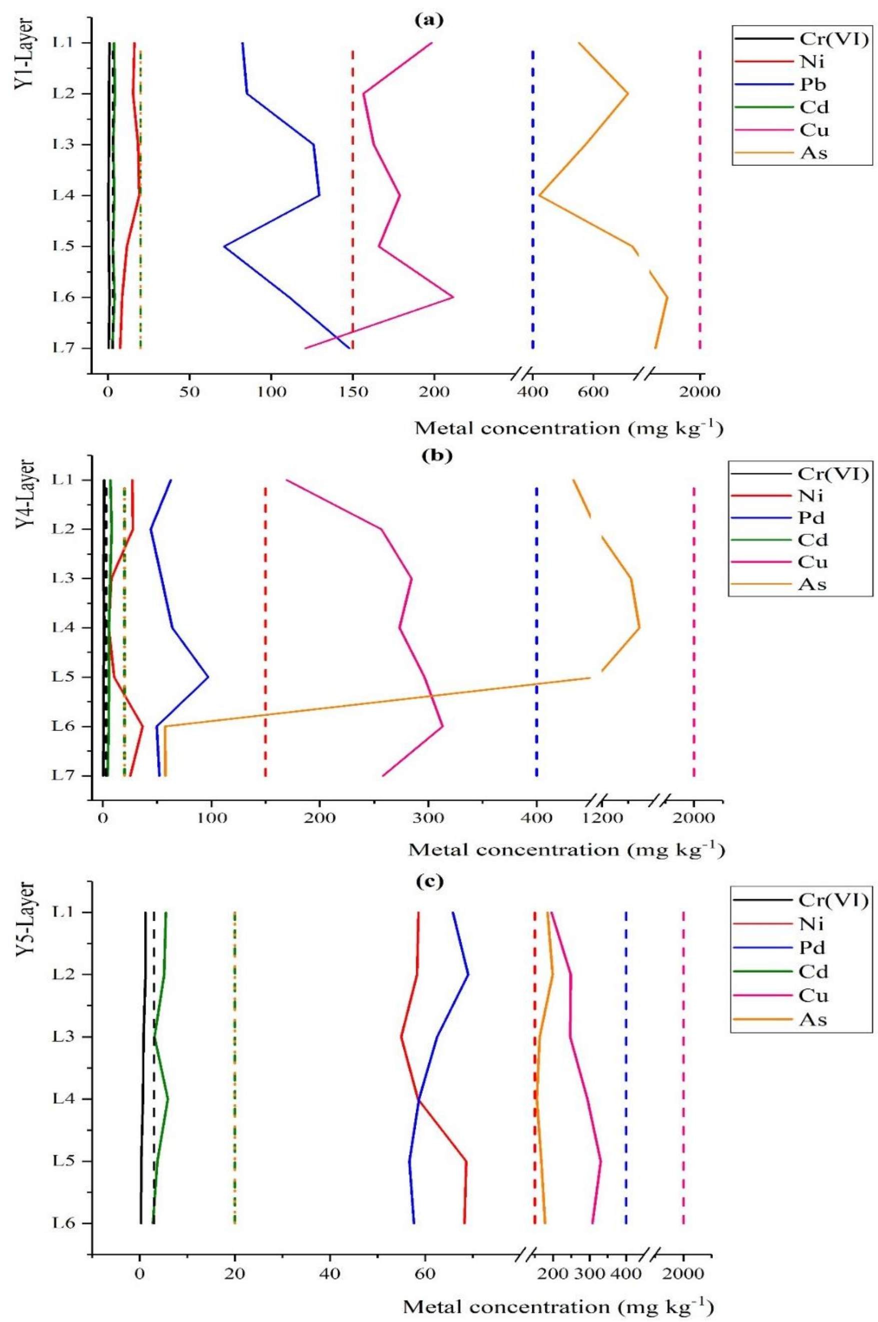

Figure 3. *Vertical distribution of soil heavy metal concentrations at different sampling points (Y1(a), Y4(b) and Y5(c),). The solid line represents the concentration change of heavy metal with depth, and the dotted line represents the risk screening value of the standard (GB36600-2018, MEE, 2018)*

This was mainly related to the fact that the mine ore was associated with arsenic. Especially in point Y1, As concentration in deeper layers (L6 and L7 – 1418.99 mg kg^{-1} and 1208.15 mg kg^{-1}, respectively) was significantly higher than in lower ones (L1 and L2 – 552.86 mg kg^{-1} and 714.28 mg kg^{-1}, respectively) ($p<0.05$), while As content in middle layers (L3 and L4 – 1311.32 mg kg^{-1} and 1342.84 mg kg^{-1}, respectively) was the highest at point Y4. This was consistent with the study by Huang et al. (2009), which

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

reported that the concentrations in deeper layers were higher than in shallow soil at a chromium-containing slag site by ferrochromium production. The higher pollution level and downward migration caused by long-term leaching process, as well as the distribution of parent materials can explain the higher accumulation in the deeper layers (Xu et al., 2021; Li et al., 2020). Moreover, no significant changes of point Y5 with increasing depth were recorded, as shown in *Fig. 3(c)* ($p<0.05$). Li et al. (2020) reported that the content of certain elements changed little with increasing depth at a Pb/Zn smelter aera. This may be attributed to the fact that the distribution of As was mainly affected by the parent material. In addition, the contents of Ni, Pb, Cd, Cu and Cr(VI) were all below the risk screening values, indicating that there would be no major environmental impact in the short term. It should be noted that Ni, Pb, Cd and Cr(VI) concentrations changed only slightly with depth. This might be attributed to the natural distribution (Li et al., 2009). In general, unlike the previous study, the present results were more likely caused by natural factors.

Speciation distribution of heavy metals

Total concentration of heavy metals was important for the assessment of pollution level, but speciation distribution of heavy metals, especially the proportion of active speciation was directly related to the ecological environment and human health, which also requires special attention (Li et al., 2009). Sampling points Y1, Y4 and Y5 were selected to test speciation variation with depth using the BCR sequence (*Fig. 4*). As shown in *Fig. 4(a)*, speciation variation of almost all heavy metals at point Y1 changed little with depth. What is more, the residual (F4) speciation constituted a high percentage (close to or over 70%, except Cd), and the acid soluble (F1) speciation constituted a low proportion in case of all types of heavy metals. Specially, the F1 speciation of all heavy metals was lower than 10%, and the percentages of Pb and Cu were lower than 1%. The results were similar to the study of Chen et al. (2018), who reported that the F1 speciation accounted for a significantly lower percentage of total concentration of heavy metals in typical Pb-Zn mine tailings impoundments in South China. Therefore, these heavy metals exhibited limited migration and transformation ability. *Fig. 4(b)* demonstrates that the acid soluble (F1) proportion of As accounted for 1%-10% in L1-L7 layers, and there were no obvious regularity of As F1 speciation changes with depth. The proportions of acid soluble speciation of Ni, Pb and Cu were lower or close to 1%, while Cd acid soluble speciation was close to 10% at point Y4. Previous studies have shown that heavy metals with strong mobility have a great influence on environmental quality (Sun et al., 2017). Therefore, the Cd pollution at point Y4 should pay more attention. The F4 speciation of Ni, Pb and Cu changed only slightly with increasing depth, while the proportion of Cd F4 speciation increased gradually with depth. In addition, the percentage of the F2 speciation in Pb and Cd accounted for 20-40%, which should be worked on more detail. As shown in *Fig. 4(c)*, the proportion of the F1 speciation of Ni, Pb, and Cu at sampling point Y5 was also lower or close to 1%, similarly as at point Y4. The F1 speciation of Cd and As accounted for 5-15% and 5-10%, respectively, mainly of the total heavy metal concentrations. The reason might relate to the soil parent material, as Cd and As were guest elements in metal ores (Lu et al., 2015). The F4 speciation of Ni, Cu and As changed little with increasing depth, while Pb and Cd were gradually increasing.

It should be pointed out that the F4 speciation of Ni was over 90% at all three points, indicating lower ecological risk. The F1 speciation of Pb changed only slightly with depth at all three points, which could be due to its limited mobility (Yang et al., 2020). The

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

proportion of various speciation of Ni, Cu and As changed little with depth at all three sampling point, meaning that the speciation of these three elements were less affected by human activities and more influenced by natural factors such as parent materials (Li et al., 2020). Unlike numerous previous studies, the geochemical components of heavy metals affected by the physicochemical properties of soil in the present study, thereby altering their bioavailability and mobility in the soil (Dong et al., 2024).

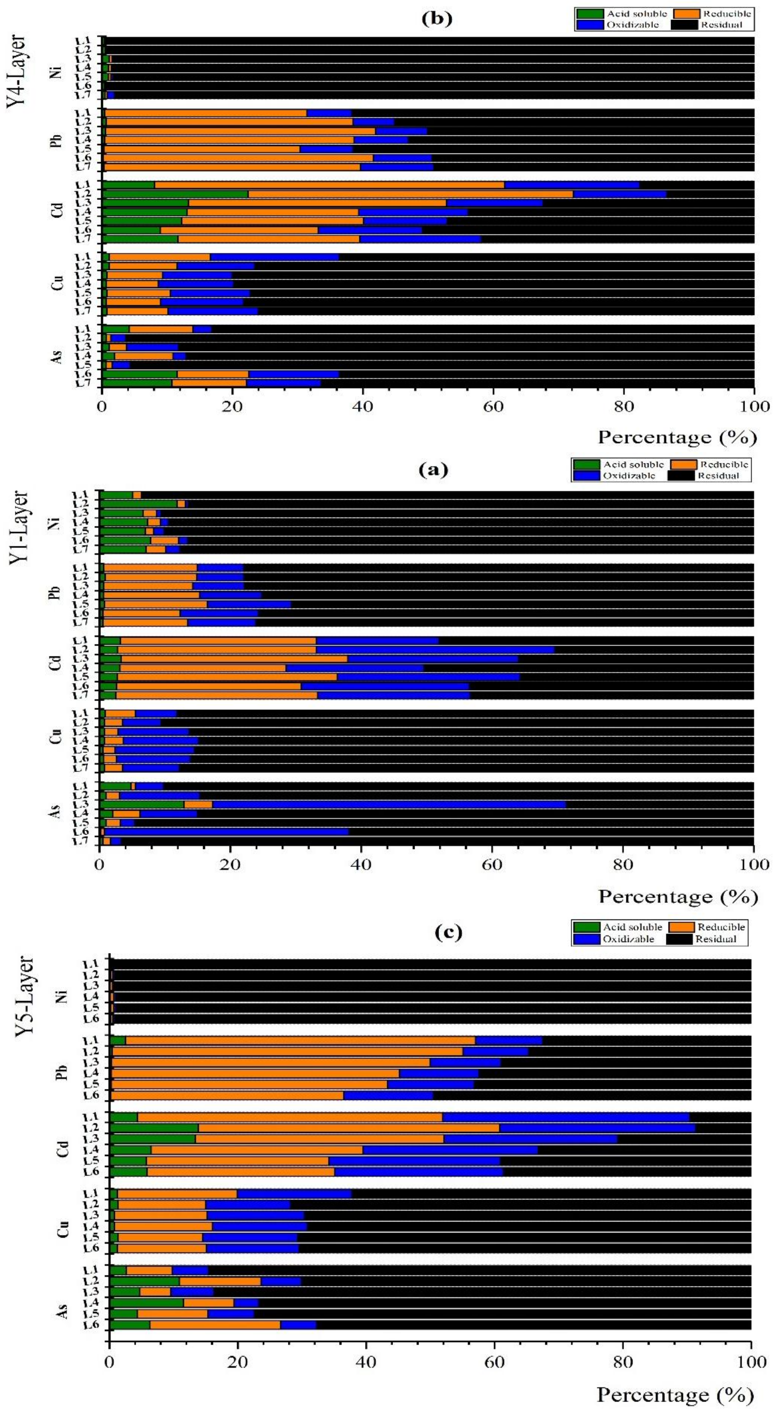

Figure 4. *Speciation distribution of heavy metals in soil with depth at different sampling points (Y1(a), Y4(b), and Y5(c))*

APPLIED ECOLOGY AND ENVIRONMENTAL RESEARCH 23(1):1325-1346.
http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

Correlation coefficient analysis of heavy metals

The assessment of correlation coefficient analysis showed the correlation between all factors (Ran et al., 2021), which was mainly used in the present study to reflect the relationship between heavy metals (Cheng et al., 2020). A higher value of the correlation coefficient between heavy metals in soil samples indicated one or more common sources of origin of these elements (Guo et al., 2012). *Fig. 5* shows Pearson's correlation matrix between all heavy metals in shallow soil.

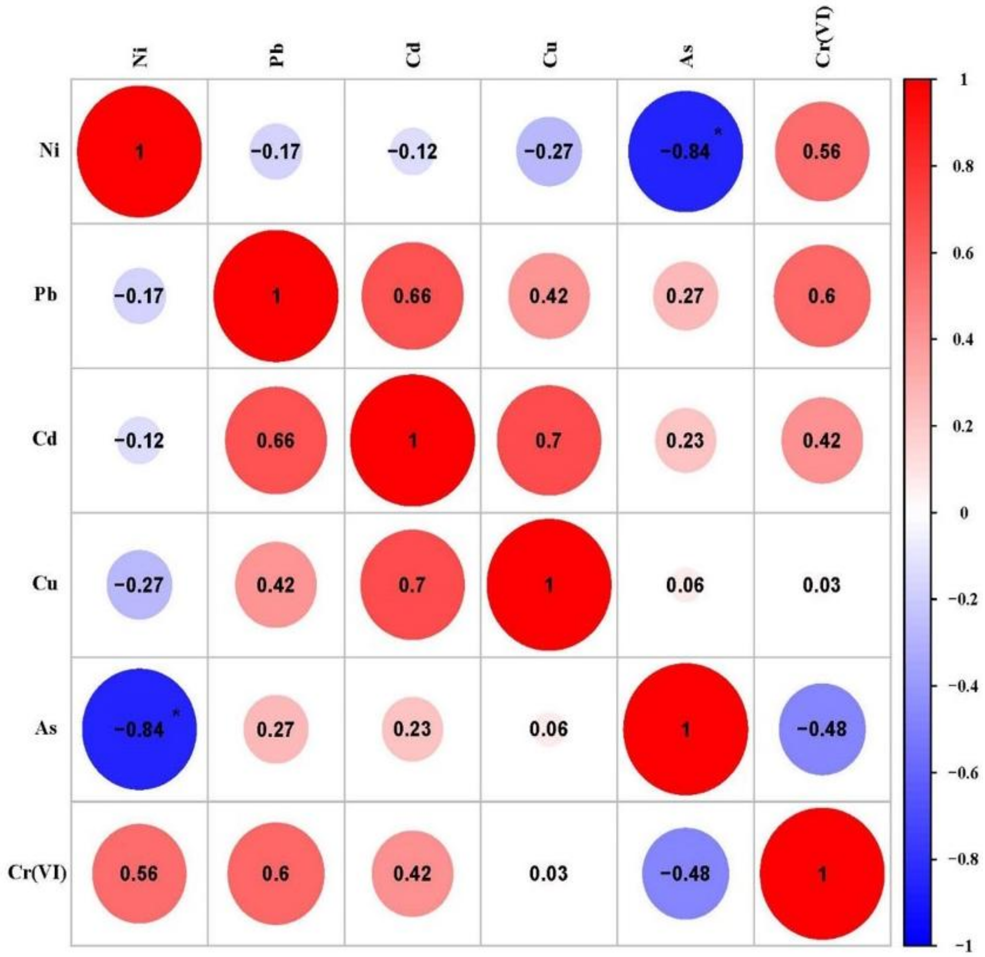

Figure 5. *Pearson's correlation matrix between heavy metals in shallow soil at the Wenshan mining site. (* represents the correlation coefficients significant at p<0.05. The circle size is relevant to the correlation coefficient value and color shows the positive correlation (red) or negative correlation (blue))*

A significantly negative correlation ($p<0.05$) was detected between Ni and As elements (-0.84), indicating a different source of these two elements (Cheng et al., 2018; Chai et al., 2021). In addition, the correlation coefficients of Ni with other heavy metals were negative, e.g. Ni-Pb (-0.17), Ni-Cd (-0.12) and Ni-Cu (-0.27), possibly suggesting a different pathway of Ni and these elements. While the correlation coefficients of Ni and Cr(VI) was 0.56, indicating the higher level correlation of the two elements. Other strong correlations ($r>0.5$) were found between Cd-Pb and Cd-Cu, reaching values of 0.66 and

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

0.7, respectively. Yoon et al. (2024) comprehensive explored the characteristics of soil contamination by potentially toxic elements in mine areas of Mongolia and pointed that the stronger correlations of Pb and Cd, meaning that the higher probability of homology, which was frequently found together in the same deposits, such as Pb-Zn mines. The results indicated that the source of origin of these three elements could be the same. As was present in high concentrations and its correlation coefficients with other elements, i.e. As-Cr(VI) (-0.48), As-Ni (-0.84), As-Pb (0.27), As-Cd (0.23) and As-Cu (0.06) were weak or negative, revealing no obviously common sources between As and others heavy metals, which might relate to the natural condition, i.e. high As concentration in soil parent material (Liu et al., 2021).

Pollution and risk assessment

Pollution assessment

It is necessary to analyze the geographical accumulation and the pollution level of elements to be able to assess the potential risks associated with it (Li et al., 2017). As shown in *Table 2* and *Table 3*, the pollution level of heavy metals in shallow soil layer of each region and the pollution level in each soil layer were studied, respectively.

Table 2. *Pollution assessment of heavy metal contamination in shallow soil layer at the Wenshan mining site*

Site	I_{geo}					PI						NIPI
	Ni	Pb	Cd	Cu	As	Ni	Pb	Cd	Cu	As	Cr(VI)	
Y1	-1.97	0.44	3.55	1.51	4.32	0.11	0.21	0.19	0.10	27.64	0.33	19.83
Y2	-1.84	-0.13	3.93	0.85	4.70	0.12	0.14	0.25	0.06	35.95	0.21	25.78
Y3	-1.88	0.17	4.75	3.18	4.10	0.12	0.17	0.44	0.32	23.73	0.27	17.04
Y4	-1.23	0.04	4.41	1.29	3.97	0.18	0.16	0.35	0.08	21.69	0.37	15.57
Y5	-0.12	0.11	4.08	1.49	2.75	0.39	0.16	0.28	0.10	9.25	0.40	6.66
Y6	-1.45	0.75	5.33	2.69	4.56	0.16	0.26	0.66	0.22	32.61	0.42	23.41
Mean	-1.41	0.23	4.34	1.84	4.07	0.18	0.18	0.36	0.15	25.15	0.33	18.05

Table 3. *Pollution assessment of heavy metals in different layers at the Wenshan mining site*

Site	I_{geo}					PI						NIPI
	Ni	Pb	Cd	Cu	As	Ni	Pb	Cd	Cu	As	Cr(VI)	
L1	-1.25	0.26	4.46	2.08	4.19	0.18	0.18	0.36	0.15	25.15	0.33	18.05
L2	-1.20	-0.01	3.96	2.34	4.46	0.18	0.15	0.26	0.18	30.48	0.33	21.87
L3	-1.53	0.25	3.73	1.81	4.57	0.15	0.18	0.22	0.12	32.88	0.27	23.59
L4	-1.66	0.32	4.12	1.83	4.61	0.13	0.19	0.28	0.12	33.64	0.27	24.13
L5	-1.47	-0.07	3.45	1.80	4.63	0.15	0.14	0.18	0.12	34.23	0.20	24.56
L6	-0.90	0.18	3.61	1.95	4.41	0.23	0.17	0.20	0.13	29.24	0.21	20.98
L7	-0.91	0.42	3.40	1.78	4.20	0.23	0.20	0.17	0.12	25.36	0.15	18.20

Geochemical background values (CNEMC, 1990) were used to calculate the Igeo of heavy metals in shallow soil, and the results are listed in *Table 2*. The order of the Igeo values was as follows: Cd>As>Cu>Pb>Ni. Of all heavy metals, Cd was the most serious pollutant reaching a mean value of 4.34, i.e. heavy to extremely heavy contamination. Not only Cd, but also As constituted heavy to extremely heavy contamination, and the

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

Igeo mean value was 4.07, which also needs more attention. Both Cd and As accumulated to a high level in the southwest of the site, that can seriously affect the quality of the environment (Li et al., 2017). In addition, the level of Cu (1.84) and Pb (0.23) contamination was moderately contaminated and uncontaminated to moderately contaminated, respectively. The Igeo mean value of Ni was -1.41, representing no contamination. The Igeo can evaluate the accumulation level of a single element, but it is not suitable for estimating total pollution. The screening value for soil contamination risk of development land (*Table 1*, GB36600-2018, MEE, 2018) was applied in the present study to calculate the PI and NIPI. As shown in *Table 2*, the PI values of heavy metals in shallow soil were in descending order: As>Cd>Cr(VI)>Pb>Ni>Cu. As was the most serious pollutant according to the PI, reaching the mean value of 25.15, i.e. more than 8-fold higher compared to the critical value (PI=3) of severe pollution. The result must be attributed to the high concentration of As in soil (*Fig. 2*). As for other heavy metals, the PI values were all less than 0.7, i.e. representing no pollution. The NIPI is typically used to comprehensively assess the status of heavy metal pollution (Liu et al., 2021). The NIPI values at all the sampling points were more than 3, and the highest value was measured at point Y2 (25.78), followed by Y6 (23.41) (*Table 2*). The two points, which in the west and southwest of the site, exceeded the critical value more than 8-fold and 7-fold, respectively, indicating critically severe pollution. The main reason was the high PI value of arsenic in these two samples. The mean value of the NIPI was 18.05, i.e. more than 6-fold of the critical value, representing severe pollution.

As the same with the assessment of the pollution in shallow soil layer, the Igeo and NIPI values were also used to assessed the pollution level of different layers in soil profile. The Igeo values of Ni were less than 0 in all soil layers, meaning that the no Ni accumulation in soil. The Pb, Cu, Cd and As accumulation in all soil layers were uncontaminated to moderately contaminated (almost at 0-1), moderately contaminated (almost at 1-2), heavily contaminated (almost at 3-4) and heavily to extremely contaminated (4-5), respectively. The results indicating that the higher accumulation of As, Cd and Cu in soil. Moreover, the I_{geo} values of Cd in L1 and Cu in L2 layers (0-1 m) were significantly higher than deeper layers ($p<0.05$). Li et al. (2020) reported that the heavy metal pollution of upper soil layer was higher at a Pb/Zn smelter aera. The PI values of As (25.15-34.23) in all layers in soil profile were more than 8-times of the severe pollution critical value, with no obvious regularity with depth. For other heavy metals, the PI values were all less than 0.7 in all soil layer, representing no pollution. The NIPI values were used to assess the total pollution level of heavy metals in each soil layers. In all soil layers, the NIPI values were more than 6-times of the severe pollution critical value, which indicated that the NIPI values were mainly affected by the PI value of As. In addition, there was little difference of the heavy metal pollution level between the soil layers.

Health risk assessment

Han et al. (2021) and Zhu et al. (2024) reported that ingestion, dermal contact and inhalation were the main routes that could cause damage to human health. The health risk assessment model designed by the US Environmental Protection Agency is commonly applied, because it includes the exposure route and population factors (Han et al., 2018). *Table 4* lists the HQ, HI and CR values (mean, max and min) of five heavy metals acting on adults and children through three exposure routes.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

Table 4. *Assessment of health risk posed by heavy metals in shallow soil at the Wenshan mining site*

Elements		HQ_{ing}		HQ_{derm}		HQ_{inh}		HI		CR	
		Adults	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**
Cd	mean	1.22E-02	8.69E-02	5.55E-03	9.74E-03	5.54E-02	1.98E-01	7.31E-02	2.95E-01	9.98E-07	3.57E-06
	max	2.22E-02	1.59E-01	1.01E-02	1.78E-02	1.01E-01	3.61E-01	1.33E-01	5.37E-01	1.82E-06	6.50E-06
	min	6.48E-03	4.63E-02	2.96E-03	5.19E-03	2.95E-02	1.05E-01	3.89E-02	1.57E-01	5.32E-07	1.90E-06
As	mean	2.83E+00	2.02E+01	7.87E-02	1.38E-01	2.58E+00	9.20E+00	5.49E+00	2.96E+01	1.45E-03	9.72E-03
	max	4.05E+00	2.89E+01	1.12E-01	1.97E-01	3.68E+00	1.32E+01	7.84E+00	4.23E+01	2.08E-03	1.39E-02
	min	1.04E+00	7.44E+00	2.90E-02	5.08E-02	9.48E-01	3.39E+00	2.02E+00	1.09E+01	5.35E-04	3.58E-03
Ni	mean	2.26E-03	1.61E-02	9.54E-05	1.67E-04			2.36E-03	1.63E-02	9.92E-05	5.89E-04
	max	4.95E-03	3.53E-02	2.09E-04	3.67E-04			5.16E-03	3.57E-02	2.17E-04	1.29E-03
	min	1.37E-03	9.80E-03	5.79E-05	1.02E-04			1.43E-03	9.91E-03	6.03E-05	3.58E-04
Pb	mean	8.80E-02	6.29E-01	2.68E-03	4.70E-03			9.07E-02	6.33E-01	1.11E-06	7.72E-06
	max	1.23E-01	8.81E-01	3.76E-03	6.59E-03			1.27E-01	8.88E-01	1.56E-06	1.08E-05
	min	6.72E-02	4.80E-01	2.05E-03	3.59E-03			6.92E-02	4.83E-01	8.51E-07	5.89E-06
Cu	mean	1.24E-02	8.88E-02	4.72E-04	8.28E-04			1.29E-02	8.96E-02		
	max	2.66E-02	1.90E-01	1.01E-03	1.77E-03			2.76E-02	1.92E-01		
	min	5.28E-03	3.77E-02	2.01E-04	3.52E-04			5.48E-03	3.81E-02		

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

The HQing of Ni, Pb and Cu contributed more than 95% in case of adults and 98% in case of children of the total HQ value. The HQing of As accounted for more than 50% of the total HQ value for both adults and children. Previous study pointed out that ingestion was the major route causing health risks when exposed to heavy metals (Liu et al., 2021). With respect to the HI, only As posed a significant potential non-carcinogenic risk for both adults and children, and the HI values for adults and children were 5.49E+00 and 2.96E+01, respectively. The highest HI values of As for adults and children were 7.84E+00 and 4.23E+01, respectively, i.e. more than 7-fold and 40-fold higher than the critical value (HI=1). The results indicated that heavy metals were more likely to accumulate in children's bodies and posed serious non-carcinogenic risk (Zhu et al., 2024). Numerous studies have reported that high heavy metal concentrations not only in soil but also in dust could cause adverse effects on the health of the body of local residents (He et al., 2019). In the present study, these approaches may pose risks to local residents.

Regarding carcinogenic risks, As was the most serious pollutant with CR values for adults and children of 1.45E-03 and 9.72E-03, i.e. an unacceptable risk (*Table 4*). In addition, children's exposure to Ni could also cause an unacceptable risk (5.89E-04). The CR values of Cd for children, Ni for adults and Pb for both adults and children were all higher than 1E-06 but lower than 1E-04, i.e. representing a generally acceptable risk. *Table 4* shows that both HI and CR values of all heavy metals for children were significantly higher than for adults ($p<0.05$), and these results were consistent with the studies of Liu et al. (2021) and Masri et al. (2021). There were two possible reasons, the first was physiological characteristics, e.g. lower tolerance of body organs; the second was the more direct contact, such as "hand-eating" behavior, etc. Overall, As posed a serious carcinogenic and non-carcinogenic risk for adults and children, which should receive more attention. As is widely known, the mining process easily caused significant accumulation of heavy metals and increased health risks within the area (Zhou et al., 2024). Source-oriented risk assessment established a link between pollution sources and heavy metal risks in soil, and the assessment results were conducive for developing comprehensive risk control strategies to address ecology and health risks associated with mining process.

Conclusions

The present study analyzed the spatial, vertical, and speciation distribution and correlation of heavy metals in soil, as well as assessed pollution in all soil layers and health risks caused by these metals at the undeveloped mining site in Wenshan. The western and south-western parts of the site were highly polluted, while the eastern part was less polluted. As pollution in shallow soil was particularly serious, with the mean value of 502.91 mg kg^{-1} being more than 25-fold higher than the risk screening value. Not only that, As content in all layers was significantly higher than the standard risk screening value in the three typical profiles ($p<0.05$). The proportion of different Ni, Cu and As speciation changed slightly with depth at all three sampling points, and the residual speciation accounted for more than or close to 70% of the total concentration. In addition, a significant negative correlation ($p<0.05$) was detected between Ni and As, indicating a different source of origin of these two elements. The assessment of pollution showed that the pollution level of the mining site was critically high with the most severe level in the west of the site. Among all heavy metals, As was the most influential element. In all layers of soil profile, the pollution far exceeds the level of severe pollution, which was

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

mainly affected by the As. What is more, As also posed a significant potential non-carcinogenic risk and an unacceptable carcinogenic risk for both adults and children. Therefore, a comprehensive understanding of the pollutant characteristics of mining area is conducive to develop mineral resources cleaner, in order to achieve reduce the pollution at the source. It was essential for the protection of the environment and health of more than 80,000 local residents. The present study can provide theoretical support and practical foundations for pollution control and prevention.

Acknowledgements. This work was supported by Sanqin Talents, Shaanxi Provincial First-class Team -- "Contaminated Soil Remediation and Resource Utilization Innovation Team at Shaanxi University of Technology", the project of Foreign Experts Burean of China (G2023041029L, DL2023041006L), Shaanxi Province City-University co-construction Project (SXZJ-2301), Qingdao University of Technology Talent Scheme (JC2022-053, JC2022-003).

REFERENCES

[1] Chai, L., Wang, Y., Wang, X., Ma, L., Cheng, Z., Su, L. (2021): Pollution characteristics, spatial distributions, and source apportionment of heavy metals in cultivated soil in Lanzhou, China. – Ecological Indicators 125: 107507.
[2] Chandra, K., Proshad, R., Islam, M., Idris, A. M. (2023): An integrated overview of metals contamination, source-specific risks investigation in coal mining vicinity soils. – Environmental Geochemistry and Health 45(11): 7425-7458.
[3] Chen, T., Lei, C., Yan, B., Li, L. L., Xu, D. M., Ying, G. G. (2018): Spatial distribution and environmental implications of heavy metals in typical lead (Pb)-zinc (Zn) mine tailings impoundments in Guangdong Province, South China. – Environmental Science and Pollution Research 25: 36702-36711.
[4] Chen, P., Wang, Z., Zhang, Z. (2023): Dynamic characteristics of soil heavy metals and microbial communities under moss cover at different successional stages in a manganese mining area. – Environmental Geochemistry and Health 45(11): 7711-7726.
[5] Cheng, X., Danek, T., Drozdova, J., Huang, Q., Qi, W., Zou, L., Yang, S., Zhao, X., Xiang, Y. (2018): Soil heavy metal pollution and risk assessment associated with the Zn-Pb mining region in Yunnan, Southwest China. – Environ. Monit. Assess. 190: 1-16.
[6] Cheng, W., Lei, S., Bian, Z., Zhao, Y., Li, Y., Gan, Y. (2020): Geographic distribution of heavy metals and identification of their sources in soils near large, open-pit coal mines using positive matrix factorization. – Journal of Hazardous Materials 387: 121666.
[7] Cui, X., Geng, Y., Sun, R., Xie, M., Feng, X., Li, X., Cui, Z. (2021): Distribution, speciation and ecological risk assessment of heavy metals in Jinan Iron & Steel Group soils from China. – Journal of Cleaner Production 295: 126504.
[8] Deng, X., Yang, Y., Zeng, H., Chen, Y., Zeng, Q. (2020): Variations in iron plaque, root morphology and metal bioavailability response to seedling establishment methods and their impacts on Cd and Pb accumulation and translocation in rice (*Oryza sativa* L.). – Journal of Hazardous Materials 384: 121343.
[9] Dong, Y., Lu, H., Lin, H. (2024): Comprehensive study on the spatial distribution of heavy metals and their environmental risks in high-sulfur coal gangue dumps in China. – Journal of Environmental Sciences 136: 486-497.
[10] Duan, Y., Zhang, Y., Li, S., Fang, Q., Miao, F., Lin, Q. (2020): An integrated method of health risk assessment based on spatial interpolation and source apportionment. – J. Clean Prod. 276: 123218.
[11] Fernández-Martínez, R., Corrochano, N., Álvarez-Quintana, J., Ordóñez, A., Álvarez, R., Rucandio, I. (2024): Assessment of the ecological risk and mobility of arsenic and heavy

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

metals in soils and mine tailings from the Carmina mine site (Asturias, NW Spain). – Environmental Geochemistry and Health 46(3): 90.

[12] Guan, Y., Zhang, N., Wang, Y., Rong, B., Ju, M. (2020): Comprehensive assessment of soil risk in a de-industrialized area in China. – Journal of Cleaner Production 262: 121302.

[13] Gui, H., Yang, Q., Lu, X., Wang, H., Gu, Q., Martín, J. D. (2023): Spatial distribution, contamination characteristics and ecological-health risk assessment of toxic heavy metals in soils near a smelting area. – Environmental Research 222: 115328.

[14] Guo, G., Wu, F., Xie, F., Zhang, R. (2012): Spatial distribution and pollution assessment of heavy metals in urban soils from southwest China. – Journal of Environmental Sciences 24(3): 410-418.

[15] Han, W., Gao, G., Geng, J., Li, Y., Wang, Y. (2018): Ecological and health risks assessment and spatial distribution of residual heavy metals in the soil of an e-waste circular economy park in Tianjin, China. – Chemosphere 197: 325-335.

[16] Han, Q., Liu, Y., Feng, X., Mao, P., Sun, A., Wang, M., Wang, M. (2021): Pollution effect assessment of industrial activities on potentially toxic metal distribution in windowsill dust and surface soil in central China. – Science of the Total Environment 759: 144023.

[17] He, M., Shen, H., Li, Z., Wang, L., Wang, F., Zhao, K., Liu, X., Wendroth, O., Xu, J. (2019): Ten-year regional monitoring of soil-rice grain contamination by heavy metals with implications for target remediation and food safety. – Environmental Pollution 244: 431-439.

[18] Huang, S., Peng, B., Yang, Z., Chai, L., Xu, Y., Su, C. (2009): Spatial distribution of chromium in soils contaminated by chromium-containing slag. – Transactions of Nonferrous Metals Society of China 19: 756-764.

[19] Huang, T., Deng, Y., Zhang, X., Wu, D., Wang, X., Huang, S. (2021): Distribution, source identification, and health risk assessment of heavy metals in the soil-rice system of a farmland protection area in Hubei Province, Central China. – Environmental Science and Pollution Research 28: 68897-68908.

[20] Huang, J. L., Li, Z. Y., Mao, J. Y., Chen, Z. M., Liu, H. L., Liang, G. Y., Zhang, D. B., Wen, P. J., Mo, Z. Y., Jiang, Y. M. (2024): Contamination and health risks brought by arsenic, lead and cadmium in a water-soil-plant system nearby a non-ferrous metal mining area. – Ecotoxicology and Environmental Safety 270: 115873.

[21] Jiang, Y., Chao, S., Liu, J., Yang, Y., Chen, Y., Zhang, A., Cao, H. (2017): Source apportionment and health risk assessment of heavy metals in soil for a township in Jiangsu Province, China. – Chemosphere 168: 1658-1668.

[22] Jiang, H. H., Cai, L. M., Hu, G. C., Wen, H. H., Luo, J., Xu, H. Q., Chen, L. G. (2021): An integrated exploration on health risk assessment quantification of potentially hazardous elements in soils from the perspective of sources. – Ecotoxicology and Environmental Safety 208: 111489.

[23] Khademi, H., Gabarrón, M., Abbaspour, A., Martínez-Martínez, S., Faz, A., Acosta, J. A. (2019): Environmental impact assessment of industrial activities on heavy metals distribution in street dust and soil. – Chemosphere 217: 695-705.

[24] Kong, F., Chen, Y., Huang, L., Yang, Z., Zhu, K. (2021): Human health risk visualization of potentially toxic elements in farmland soil: A combined method of source and probability. – Ecotoxicology and Environmental Safety 211: 111922.

[25] Kumar, S. (2015): Estimating spatial distribution of soil organic carbon for the Midwestern United States using historical database. – Chemosphere 127: 49-57.

[26] Li, F. Y., Fan, Z. P., Xiao, P. F., Oh, K., Ma, X. P., Hou, W. (2009): Contamination, chemical speciation and vertical distribution of heavy metals in soils of an old and large industrial zone in Northeast China. – Environmental Geology 57(8): 1815-1823.

[27] Li, X., Yang, H., Zhang, C., Zeng, G., Liu, Y., Xu, W., Wu, Y., Lan, S. (2017): Spatial distribution and transport characteristics of heavy metals around an antimony mine area in central China. – Chemosphere 170: 17-24.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

[28] Li, S. Z., Zhao, B., Jin, M., Hu, L., Zhong, H., He, Z. G. (2020): A comprehensive survey on the horizontal and vertical distribution of heavy metals and microorganisms in soils of a Pb/Zn smelter. – Journal of Hazardous Materials 400: 123255.

[29] Liu, G., Zhou, X., Li, Q., Shi, Y., Guo, G., Zhao, L., Wang, J., Su, Y., Zhang, C. (2020): Spatial distribution prediction of soil As in a large-scale arsenic slag contaminated site based on an integrated model and multi-source environmental data. – Environmental Pollution 267: 115631.

[30] Liu, H. W., Zhang, Y., Yang, J. S., Wang, H. Y., Li, Y. L., Shi, Y., Li, D. C., Holm, P. E., Ou, Q., Hu, W. Y., Hu, W. (2021): Quantitative source apportionment, risk assessment and distribution of heavy metals in agricultural soils from southern Shandong Peninsula of China. – Science of the Total Environment 767: 144879.

[31] Lu, S., Teng, Y., Wang, Y., Wu, J., Wang, J. (2015): Research on the ecological risk of heavy metals in the soil around a Pb–Zn mine in the Huize County, China. – Chinese Journal of Geochemistry 34: 540-549.

[32] Ma, L., Yang, Z., Li, L., Wang, L. (2016): Source identification and risk assessment of heavy metal contaminations in urban soils of Changsha, a mine-impacted city in Southern China. – Environmental Science and Pollution Research 23: 17058-17066.

[33] Masri, S., LeBrón, A. M., Logue, M. D., Valencia, E., Ruiz, A., Reyes, A., Wu, J. (2021): Risk assessment of soil heavy metal contamination at the census tract level in the city of Santa Ana, CA: implications for health and environmental justice. – Environmental Science: Processes & Impacts 23(6): 812-830.

[34] MEE. (2018): Soil Environmental Quality-Risk Control Standard for Soil Contamination of Development Land. – Ministry of Ecology and Environment, PRC. GB36600-2018.

[35] MEP. (2014): Technical guidelines for risk assessment of contaminated sites (HJ 25.3-2014). – Ministry of Environmental Protection, the People's Republic of China, China Environmental Science Press, Beijing (in Chinese).

[36] Negahban, S., Mokarram, M., Pourghasemi, H. R., Zhang, H. (2021): Ecological risk potential assessment of heavy metal contaminated soils in Ophiolitic formations. – Environmental Research 192: 110305.

[37] Nemerow, N. L. (1974): Scientific Stream Pollution Analysis. – McGraw-Hill Book Company, New York.

[38] Ran, H., Guo, Z., Yi, L., Xiao, X., Zhang, L., Hu, Z., Li, C., Zhang, Y. (2021): Pollution characteristics and source identification of soil metal (loid) s at an abandoned arsenic-containing mine, China. – Journal of Hazardous Materials 413: 125382.

[39] Reyes, A., Cuevas, J., Fuentes, B., Fernández, E., Arce, W., Guerrero, M., Letelier, M. V. (2021): Distribution of potentially toxic elements in soils surrounding abandoned mining waste located in Taltal, Northern Chile. – Journal of Geochemical Exploration 220: 106653.

[40] Sun, J., Yu, R., Hu, G., Jiang, S., Zhang, Y., Wang, X. (2017): Bioavailability of heavy metals in soil of the Tieguanyin tea garden, southeastern China. – Acta Geochimica 36: 519-524.

[41] USEPA. (1989): Risk Assessment Guidance for Superfund. – vol. I. Human Health Evaluation Manual (Part a), Washington, DC. EPA/540/1–89/002.

[42] USEPA. (1997): Exposure Factors Handbook, Final Report. – U.S. Environmental Protection Agency, Washington, DC (EPA/600/P-95/002F a-c).

[43] USEPA. (2001): Baseline Human Health Risk Assessment. – Vasquez Boulevard and I-70 superfund site Denver, Denver (Co).

[44] USEPA. (2002): Supplemental guidance for developing soil screening levels for Superfund sites. – Solid Waste and Emergency Response, Washington, DC; [OSWER 9355.4-24].

[45] Wang, Z., Hong, C., Xing, Y., Wang, K., Li, Y., Feng, L., Ma, S. (2018b): Spatial distribution and sources of heavy metals in natural pasture soil around copper-molybdenum mine in Northeast China. – Ecotoxicology and Environmental Safety 154: 329-336.

[46] Wang, Q., Pan, F., Xu, X., Muhammad, T. R., Yang, X., Chen, B., Feng, Y. (2021): Cadmium level and soil type played a selective role in the endophytic bacterial community of hyperaccumulator Sedum alfredii Hance. – Chemosphere 263: 127986.

[47] Wu, B., Peng, H., Sheng, M., Luo, H., Wang, X., Zhang, R., Xu, H. (2021): Evaluation of phytoremediation potential of native dominant plants and spatial distribution of heavy metals in abandoned mining area in Southwest China. – Ecotoxicology and Environmental Safety 220: 112368.

[48] Wu, Y., Santos, S. S., Vestergård, M., González, A. M. M., Ma, L., Feng, Y., Yang, X. (2022): A field study reveals links between hyperaccumulating Sedum plants-associated bacterial communities and Cd/Zn uptake and translocation. – Science of the Total Environment 805: 150400.

[49] Xiao, L., Guan, D., Chen, Y., Dai, J., Ding, W., Peart, M. R., Zhang, C. (2019): Distribution and availability of heavy metals in soils near electroplating factories. – Environmental Science and Pollution Research 26(22): 22596-22610.

[50] Xu, L., Dai, H., Skuza, L., Wei, S. (2021): Comprehensive exploration of heavy metal contamination and risk assessment at two common smelter sites. – Chemosphere 285: 131350.

[51] Xu, L., Dai, H., Skuza, L., Xu, J., Shi, J., Wang, Y., Shentu, J., Wei, S. (2022): Integrated survey on the heavy metal distribution, sources and risk assessment of soil in a commonly developed industrial area. – Ecotoxicology and Environmental Safety 236: 113462.

[52] Yang, Y., Ge, Y., Tu, P., Zeng, H., Zhou, X., Zou, D., Wang, K., Zeng, Q. (2019): Phytoextraction of Cd from a contaminated soil by tobacco and safe use of its metal-enriched biomass. – Journal of Hazardous Materials 363: 385-393.

[53] Yang, S., Gu, S., He, M., Tang, X., Ma, L. Q., Xu, J., Liu, X. (2020): Policy adjustment impacts Cd, Cu, Ni, Pb and Zn contamination in soils around e-waste area: concentrations, sources and health risks. – Science of the Total Environment 741: 140442.

[54] Yoon, S., Kim, D. M., Yu, S., Batsaikhan, B., Kim, T., Yun, S. T. (2024): Characteristics of soil contamination by potentially toxic elements in mine areas of Mongolia. – Environmental Geochemistry and Health 46(1): 1-18.

[55] Yu, B., Lu, X., Fan, X., Fan, P., Zuo, L., Yang, Y., Wang, L. (2021): Analyzing environmental risk, source and spatial distribution of potentially toxic elements in dust of residential area in Xi'an urban area, China. – Ecotoxicology and Environmental Safety 208: 111679.

[56] Zhang, H., Zhang, B. G., Wang, S., Chen, J. L., Jiang, B., Xing, Y. (2020): Spatiotemporal vanadium distribution in soils with microbial community dynamics at vanadium smelting site. – Environmental Pollution 265: 114782.

[57] Zhang, J., Gu, H., Chen, S., Ai, W., Dang, Y., Ai, S., Li, Z. (2023a): Assessment of heavy metal pollution and preschool children health risk in urban street dusts from different functional areas in a typical industrial and mining city, NW China. – Environmental Geochemistry and Health 45(10): 7199-7214.

[58] Zhang, Y., Song, B., Zhou, Z. (2023b): Pollution assessment and source apportionment of heavy metals in soil from lead–Zinc mining areas of south China. – Journal of Environmental Chemical Engineering 11(2): 109320.

[59] Zhao, K., Liu, X., Xu, J., Selim, H. M. (2010): Heavy metal contaminations in a soil–rice system: identification of spatial dependence in relation to soil properties of paddy fields. – Journal of Hazardous Materials 181(1-3): 778-787.

[60] Zhong, X., Chen, Z. W., Li, Y. Y., Ding, K. B., Liu, W. S., Liu, Y., Yuan, Y. Q., Zhang, M. Y., Baker, A. J. M., Yang, W. J., Fei, Y. H., Wang, Y. J., Chao, Y. Q., Qiu, R. L. (2020): Factors influencing heavy metal availability and risk assessment of soils at typical metal mines in Eastern China. – Journal of Hazardous Materials 400: 123289.

[61] Zhou, X., Cao, Z., Ma, Y., Wang, L., Wu, R., Wang, W. (2016): Concentrations, correlations and chemical species of PM2.5/PM10 based on published data in China: Potential implications for the revised particulate standard. – Chemosphere 144: 518-526.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346

[62] Zhou, H., Yue, X., Chen, Y., Liu, Y. (2024): Source-specific probabilistic contamination risk and health risk assessment of soil heavy metals in a typical ancient mining area. – Science of the Total Environment 906: 167772.
[63] Zhu, Y., An, Y., Li, X., Cheng, L., Lv, S. (2024): Geochemical characteristics and health risks of heavy metals in agricultural soils and crops from a coal mining area in Anhui province, China. – Environmental Research 241: 117670.
[64] Zou, H., Ren, B. (2023): Analyzing topsoil heavy metal pollution sources and ecological risks around antimony mine waste sites by a joint methodology. – Ecological Indicators 154: 110761.

APPENDIX

***Table S1.** Relevant parameters to characterize the ADD value*

Parameter	**Unit**	**Description**	**Value**		**Reference**
			Adults	**Children**	
IngR	mg/d	Ingestion rate per unit time	100	200	USEPA, 2001
EF	d/year	Exposure frequency	350	350	MEP, 2014
ED	years	Exposure duration	24	6	USEPA, 2001
BW	kg	Body weight	56.8	15.9	MEP, 2014
AT	d	Average time-non cancer risk	ED×365	ED×365	USEPA, 1989
InhR	m^3 day^{-1}	Inhalation rate of soil	20	20	USEPA, 1997
SA	cm^2	Exposure skin area	5700	2800	USEPA, 2002
AF	mg/(cm^2·day)	Skin adherence factor	0.2	0.2	USEPA, 2002
ABS	(unitless)	Dermal absorption factor	0.001	0.001	USEPA, 2002
APM	mg m^{-3}	ambient particulate matter	0.0651	0.0651	Zhou et al., 2016

***Table S2.** Reference dose (RfD) and carcinogenic slope factor (SF) of heavy metals to characterize the HI and CR values*

Heavy metals	**RfD_{ing} mg kg^{-1} d^{-1}**	**RfD_{derm} mg kg^{-1} d^{-1}**	**RfD_{inh} mg kg^{-1} d^{-1}**	**SF_{ing} 1/ (mg kg^{-1} d^{-1})**	**SF_{derm} 1/ (mg kg^{-1} d^{-1})**	**SF_{inh} 1/ (mg kg^{-1} d^{-1})**
As	3.00E-04	1.23E-04	4.29E-06	1.50E+00 [b]	1.50E+00 [b]	1.51E+01[b]
Cd	1.00E-03	2.50E-05	2.86E-06	NA [a]	NA [a]	6.30E+00
Cu	4.00E-02	1.20E-02	NA [a]	NA [a]	NA [a]	NA [a]
Ni	2.00E-02	5.40E-03	NA [a]	1.70E+00	4.25E+01	8.40 E-01
Pb	1.40E-03	5.24E-04	NA [a]	8.50E-03	NA	4.20E-02[b]

[a] NA represents data not available. [b] The values were obtained from State Environment Protection Administration of China (MEP 2014)

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2301_13251346