Environ Monit Assess (2023) 195:1221
https://doi.org/10.1007/s10661-023-11775-9

RESEARCH

Extraction methods optimization of available heavy metals and the health risk assessment of the suburb soil in China

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Received: 23 June 2023 / Accepted: 24 August 2023 / Published online: 18 September 2023

Abstract Heavy metal pollution has attracted increasing concern due to its high toxicity and persistence. A suitable extraction procedure for available heavy metals in soil is necessary for assessing the ecological risk. In this work, the single extraction methods aided by shaking and microwaves were investigated and analyzed for their ability to extract available heavy metals from soil samples, and a total of 42 soil samples were collected from suburbs of Zhengzhou city in China. The extraction efficiency of Cu, Zn, As, and Cd in the certified fluvo-aquic soil was compared using eight different types of solutions: $CaCl_2$, CH_3COONH_4, NH_4NO_3, CH_3COOH, Na_2EDTA, DTPA, HNO_3, and $NH_4H_2PO_4$. Results indicated that the shaking-assisted method that utilized Na_2EDTA as an extractant demonstrated satisfactory efficiency and was chosen for further optimization and that the optimal conditions were obtained using 0.05 M Na_2EDTA at pH 7, soil-liquid ratio 1:20, and extraction duration 2 h, which gained the perfect extraction efficiency ranging from 85.8 to 109.5%. The proposed approach has been applied to extract available Cu, Zn, As, and Cd in soils of Zhengzhou suburbs, where the mean values varied from 0.129 to 6.881 mg/kg. The bioavailability of different heavy metals in the soil varies greatly, with Cd having the highest activity in the survey region. Significant ($p < 0.01$) positive relationships were observed between the available state and the total amount of all the heavy metals. The assessment of health risks associated with heavy metals indicated that there was no risk for chronic non-carcinogenic effects. Even though the total amount of metal elements in suburban soil of Zhengzhou is 1.6% with high carcinogenic risk, the risk of available elements is still within the acceptable range, which verified that the risk grade obtained by the total amount is higher than the actual risk.

Keywords Heavy metals · Available form · Extractants · Extraction conditions · Health risk assessment

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Introduction

With economic development and urbanization, heavy metal pollution in the soil is increasingly prominent. Heavy metals in the soil that are absorbed by crops not only limit plant growth but also negatively impact human health through the food chain (Hu et al., 2014). The biotoxicity and migration capacity of heavy metals are closely related to their existing forms. The forms of heavy metals tightly bound to soil particles are difficult to be absorbed by plants. On the other hand, the ones that are easily transported in the soil solution and absorbed by plants are usually called the "available state" (Zhang et al., 2023). Compared to the total amount of heavy metals, the available heavy metals can more accurately reflect the toxic effects of heavy metals on plants (Li et al., 2020a, b).

The precise extraction of available heavy metals is a prerequisite for the study of biological toxicity. The rapid urbanization and industrialization in China have severe environmental pollution. Heavy metal concentrations in most Chinese cities are higher than soil background values. According to an assessment of agricultural soils in China, nearly 2000 hm^2 of farmland, or about 20% of the total farmland area, has been considerably polluted by heavy metals (Zhang et al., 2018). There are two primary sources of heavy metals: natural occurrence and anthropogenic contamination; the latter is mainly due to mining activities, sewage irrigation, fertilizer application, atmospheric subsidence, and traffic pollution (Bassetti et al., 2023). Currently, the extraction methods for heavy metals in soil can be divided into single-stage and multistage extraction methods (Ali et al., 2015). In a single-stage extraction method, the available heavy metals are extracted from the soil in a single step using single or mixed extractants. This approach is characterized by simple operation, short retention time, and low reference value. The most commonly used single-stage extraction methods are horizontal oscillation, sulfuric-nitric acid, toxicity characteristic leaching procedure (TCLP), diethylenetriaminepentaacetic acid (DTPA), and $CaCl_2$ extraction methods. The multistage extraction method uses extractants with different extraction abilities to extract all the heavy metals from the soil in several steps, from active to stable. It has strong reference characteristics, but the operation is complicated and time-consuming. European Community Bureau of Reference (BCR) and sequential extraction procedure (SEP) continuous extractions are the widely used extraction methods. The efficiencies of different extraction methods were affected by the target matrices and the dominant species (Ma et al., 2017). Shaking or microwave-assisted solvent extraction has been widely used in the extraction of heavy metals. This study proves that the extraction of heavy metals can be increased by shaking method, and the extraction efficiency of Na_2EDTA was higher than other extractants. Quaghebeur et al. (2003) successfully extracted arsenic from shoot and root material by microwave heating the sample at 90 °C for 20 min. The environmental components and properties of various types of soil are quite diverse, as is the interaction of different heavy metals and soil particles, which results in a significant variation in the extraction results due to various extractants. Li et al. (2012) found that the nitric acid was proven to be effective with respect to Pb, Zn, and Cd, while it was proven to be less effective with respect to As, and the acetic acid was proven to be effective with respect to Zn, while it was proven to be problematic with respect to Pb, Cd, and As. Therefore, it is essential to accurately evaluate the bioavailability of heavy metals in soil in order to select suitable extractants to obtain a stable, reliable, and efficient extraction effect for different types of soil. Even though the single-stage extraction method is a simple process and the use of a single extractant can be applied to different soils, few studies have investigated the effect of the solvent extraction method and extractant type on the bioavailability of heavy metals in soil and how to apply them in cities. At the same time, the heavy metal pollution was assessed by health risk assessment method in order to evaluate soil pollution from multiple angles and contribute to the sustainable development of Zhengzhou suburb. To provide basic data and technical support for soil environmental governance to improve the soil environmental quality in the suburbs of Zhengzhou city.

This study compares the effects of eight widely employed single extractants, namely, $CaCl_2$, CH_3COONH_4, NH_4NO_3, CH_3COOH, Na_2EDTA, DTPA, HNO_3, and $NH_4H_2PO_3$, on the extraction of available Cu, Zn, As, and Cd in order to explore the best extractant and extraction conditions suitable for fluvo-aquic soil (GBW 07442). The best extractant and optimal conditions were then applied to soil samples collected from a city suburb in Zhengzhou, Henan Province.

Materials and methods

Soil sample collection and preparation

In this study, a total of 42 soil samples were collected from a suburb of Zhengzhou. The representative sample from each sampling point is a mixture of five subsamples of topsoil (10–20 cm) with equal weight. The soil specimens that were amassed were stored within polyethylene sacks and categorized numerically. Following a process of organic drying at ambient temperature, any stones, construction rubble, or foliage present in the samples were extracted. The remaining were abraded and passed through a 0.15-mm nylon fiber sieve. All samples were stored in sealed polyethylene bags before further analysis. Certified reference material (CRM) soil (GBW 07442, fluvo-aquic soil) obtained from the CRM/RM information center (Beijing, China) was employed to evaluate extraction efficiency.

Experimental method

Comparison of extractants and methods

Two solvent extraction methods, microwave and shaking, were investigated for the extraction of Cu, Zn, As, and Cd in this study. The extraction efficiencies were calculated by the ratio between the extracted and total heavy metal concentrations. The extraction of Cu, Zn, As, and Cd from the CRM soil (GBW 07442) was compared using eight common extractants, including $CaCl_2$, CH_3COONH_4, NH_4NO_3, CH_3COOH, Na_2EDTA, DTPA, HNO_3, and $NH_4H_2PO_3$. The method and extractant with the highest extraction efficiency were chosen and underwent further optimization. For the shaking method, around 0.5 g of soil samples was precisely measured and deposited into a centrifuge tube made of polyethylene with a capacity of 50 mL, along with a quantity of 20 mL extractant. The tube was agitated within a water bath maintained between the temperatures of 70 to 90 °C at a rate of 150–200 revolutions per minute. Afterward, it was subjected to centrifugation under 9000 rpm for a duration of 30 min. The resulting supernatant was strained through a cellulose acetate membrane with a porosity of 0.22 μm and kept at 4 °C until the point of analysis. For the microwave method, roughly 0.5 g of soil samples was measured and placed into a vessel made from polytetrafluoroethylene (PTFE). Subsequently, 20 mL of extractant was added to the vessel, and it was introduced into the digestion apparatus. Typically, temperatures ranging between 150 and 250 °C are employed. Following the extraction process, the resulting solution was relocated into a centrifuge tube. It underwent centrifugation at a rate of 9000 rpm for a duration of 30 min. The supernatant was then carefully poured into a volumetric flask with a capacity of 50 mL, whereupon it was diluted utilizing deionized water. This is because the supernatant solution obtained contains a high concentration of acids and metal ions; at this time, a certain proportion of deionized water needs to be added for dilution treatment, so as to facilitate subsequent analysis or measurement. At the same time, if there are other impurities or disruptors in the supernatant, adding appropriate amount of deionized water can dilute these disruptors and reduce their impact on the analysis results. The solution, which had undergone dilution, was subjected to filtration through a cellulose acetate membrane possessing a porosity of 0.22 μm. Subsequently, it was stored at a temperature of 4 °C until such time that an analysis could be performed.

Comparison of extraction conditions

To assess the extraction effect of Cu, Zn, As, and Cd from the CRM soil (GBW 07442) by the shaking method, the extraction conditions, including extraction duration, soil-liquid ratio, concentration, and pH of the extractant, were investigated using a univariate method. Extraction durations were 0.5, 1, 2, 4, 8, and 16 h. The soil-liquid ratios were 1:40, 1:20, 1:10, and 1:5. Concentrations of extractant were 0.005, 0.01, 0.05, 0.1, and 0.2 M. The pH values of the extractant were 4, 5, 6, 7, 8, and 9. Finally, the optimal conditions were applied to the soil samples collected from a city suburb in Zhengzhou, Henan Province. The content of the extracted four heavy metals was determined by atomic absorption spectrophotometer. The total heavy metals was determined by ICP-MS.

Health risk assessment

Ecological risk index (RI) was selected to estimate the adverse effect caused by heavy metals on the urban ecosystem, which considers the toxicity and environmental response of different heavy metals based on the toxicity response (Liu et al., 2019). The RI is defined as (Taraneh et al., 2020):

$$C_f^i = \frac{C_i}{B_i} \quad (1)$$

Table 1 Ecological risk index and their grades

Class	Ecological risk index (RI)	Potential ecological hazard
0	RI < 150	Low
1	150 ≤ RI < 300	Moderate
2	300 ≤ RI < 600	High
3	RI ≥ 600	Significantly high

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i C_f^i = \sum_{i=1}^{n} \left[T_r^i\left(C_i/B_i\right)\right] \quad (2)$$

where C_i is the determined content of metal I, B_i represents the geochemical background value of individual elements, C_f^i is the individual pollution index of elements, T_r^i is the biological toxic response factor of each element, and E_r^i represents the potential ecological risk factor for a given substance. According to previous studies, the values of T_r^i for Cu, Zn, As, and Cd are 5, 1, 10, and 30, respectively (Hakanson, 1980). The division of RI is indicated in Table 1 (Tian et al., 2020).

The hazard quotient (HQ) and carcinogenic risk (CR) are widely employed to quantify the potential health risk posed by chemical elements for both children and adults (Gu & Gao, 2018; Islam et al., 2020; Lee et al., 2021). HQ and CR are calculated using the corresponding average daily dose (ADD), reference dose (RfD), and cancer slope factor (SF). Given that the risk generated by heavy metals in soil comes from ingestion (ADD_{ing}), inhalation (ADD_{inh}), and dermal contact (ADD_{derm}), the average daily dose (ADD) could be calculated by Monte Carlo simulation according to the following Eqs. (3)–(5). The optimal probability distributions for the concentration database of exposure heavy metals and exposure parameters used in the method are presented in Tables 2 and 3.

$$ADD_{ing} = \frac{C \times R_{ing} \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (3)$$

$$ADD_{inh} = \frac{C \times R_{inh} \times EF \times ED}{PEF \times BW \times AT} \quad (4)$$

$$ADD_{derm} = \frac{C \times SL \times ABF \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (5)$$

(Here, the software Crystal Ball (11.1.2.4, Oracle, USA) was used to fit the probabilistic distribution of the uncertain concentrations of heavy metals.)

The evaluation indicators of hazard index (HI) and total carcinogenic risk (TCR) for elements could be estimated by the following formulas (Han et al., 2020; Li et al., 2020a, b):

$$HI = \sum_{i=1}^{n} HQ_i = \sum_{i=1}^{n} \left(\frac{ADD_{ing}}{RfD} + \frac{ADD_{inh}}{RfD} + \frac{ADD_{derm}}{RfD} \right) \quad (6)$$

$$TCR = \sum_{i=1}^{n} CR_i = \sum_{i=1}^{n} \left(ADD_{ing} \times SF + ADD_{inh} \times SF + ADD_{derm} \times SF\right)_i \quad (7)$$

When HQ or HI < 1, adverse health effects of heavy metals on the population are unlikely. If HQ or HI > 1, it indicates that soil heavy metals may have negative effects on health (Huang et al., 2021). When CR is less than 1.00E-06, the carcinogenic risk of elements is deemed negligible. The risk to humans is within an acceptable range when CR is between 1.00E-06 and 1.00E-04. When CR is greater than 1.00E-04, the carcinogenic risk produced by pollutants is unacceptable. The corresponding RfD and SF values used in the equations are shown in Table 4.

Results and discussion

Extraction efficiencies of different extractants and methods

In this study, eight extractants were investigated to extract Cu, Zn, As, and Cd from the CRM soil (GBW

Table 2 Uncertain concentrations (mg/kg) of heavy metals in urban soils of Zhengzhou city

Heavy metals	Probabilistic distribution	Parameters (mean, SD)	Reference
As	Normal	N (10.65, 0.18)	(Shen et al., 2023)
Cd	Lognormal	LN (0.19, 0.01)	
Cu	Lognormal	LN (15.28, 0.56)	
Zn	Lognormal	LN (52.36, 2.31)	

Table 3 Parameters for the exposure risk calculations of heavy metals in soil with Mote Carlo simulator

Parameter	Description	Unit	Type	Adult	Reference
EF	Exposure frequency	Day/year	Triangular	TRI (180, 345, 365)	(Huang et al., 2021)
R_{ing}	Ingestion rate of soil	mg/day	Triangular	TRI (4, 30, 52)	(Yang et al., 2019)
SL	Skin adherence factor	mg/cm^2	Lognormal	LN (0.49, 0.54)	(Chen et al., 2019)
R_{inh}	Inhalation rate	m^3/day	Point	14.5	(Han et al., 2020)
ED	Exposure duration	years	Point	24	(Han et al., 2020)
PEF	Particle emission factor	m^3/kg	Point	1.36×10^9	(Huang et al., 2021)
BW	Average body weight	kg	Lognormal	LN (56.84, 1.09)	(Guo et al., 2019)
AT	Average time of exposure to contaminated soils	Day	Point	365 ×ED (non-carcinogenic) 365 ×70 (carcinogenic)	(Han et al., 2020)
SA	Exposed skin area	m^2	Triangular	TRI (0.076, 0.153, 0.382)	(Huang et al., 2018)
ABF	Dermal adsorption factor	-	-	0.001 (non-carcinogenic) 0.01 (carcinogenic)	(Huang et al., 2021)

07442). The extraction efficiency of different extractants and methods is shown in Fig. 1. Typically, an extraction efficiency between 80 and 120% is acceptable (Chen et al., 2005).

The experimental results show the efficiency and feasibility of these two methods, as depicted in Fig. 1. For these two methods (the microwave and shaking methods), the extraction efficiency of the extractants was in the order of $HNO_3 > Na_2EDTA > DPTA > CH_3COOH > CH_3COONH_4 > NH_4H_2PO_4 > NH_4NO_3 > CaCl_2$. As the efficiency of HNO_3 exceeded 120%, it was eliminated. The Na_2EDTA was effective for Cu, Zn, As and Cd extraction, with an efficiency between 80 and 120% in the shaking method, superior to the microwave method, probably because the shaking method ensured a complete mixture of the extractant and soil samples. The capacity of various extractants to unleash metal ions is largely contingent upon their interaction with distinct soil components. Extractants such as weak acids, chelating agents, and electrolytes serve to extract metals from binding sites, while potent acids and other redox agents have the ability to liberate supplementary quantities of metal by virtue of the breakdown of the solid matrix (Wang et al., 2009). Sodium ethylenediaminetetraacetic acid (Na_2EDTA) is a prevalent chelating agent, possessing the capacity to enhance the concentrations of soluble metals within the soil solution. Owing to its efficacy, it has found widespread use in remediation approaches, such as leaching or washing, for soils contaminated with harmful substances (Nowack, 2002; Tandy et al., 2004; Polettini et al., 2007). According to the literature, neutral salt solutions may display a greater degree of effectiveness in the estimation of the availability of metals to plants, compared to other more aggressive extractants, such as DTPA (Gupta & Aten, 1993; Hammer & Keller, 2002). However, there does not exist a consensus regarding which specific neutral salt solution ranks as the most efficacious. Extractants like $CaCl_2$ operate via the exchange of Ca with metals, thereby triggering the liberation of metals that are largely facile to exchange. Other neutral salt extractants, such as $NaNO_3$ (Gupta & Aten, 1993) and NH_4Cl (Krishnamurti et al., 2000) can reduce the pH value of the solution. This is because NH_4Cl and $NaNO_3$ are inorganic acidic salts that can form hydrogen ions and lower the pH value of the solution. At low pH, heavy metal ions are more likely to form complexes without charge or positive charge, and be adsorbed by organic phase extractants, thus improving the extraction

Table 4 The reference doses (*RfD*) for non-carcinogenic metals and slope factors (*SF*) for carcinogenic metals

Heavy metals	*RfD* (mg/kg·d)			*SF* (kg/d·mg)		
	RfD_{ing}	RfD_{inh}	RfD_{derm}	SF_{ing}	SF_{inh}	SF_{derm}
As	3.00E-04[a]	1.23E-04[a]	1.23E-04[a]	1.50E+00[a]	1.51E+01[a]	3.66E+00[a]
Cd	1.00E-03[a]	1.00E-05[a]	1.00E-05[a]	6.10E+00[a]	6.30E+00[a]	3.80E-01[b]
Cu	4.00E-02[a]	4.02E-02[a]	1.20E-02[a]	N/A	N/A	N/A
Zn	3.00E-01[a]	3.00E-01[a]	6.00E-02[a]	N/A	N/A	N/A

N/A, data not available

[a](Huang et al., 2021)

[b](Wang et al., 2017)

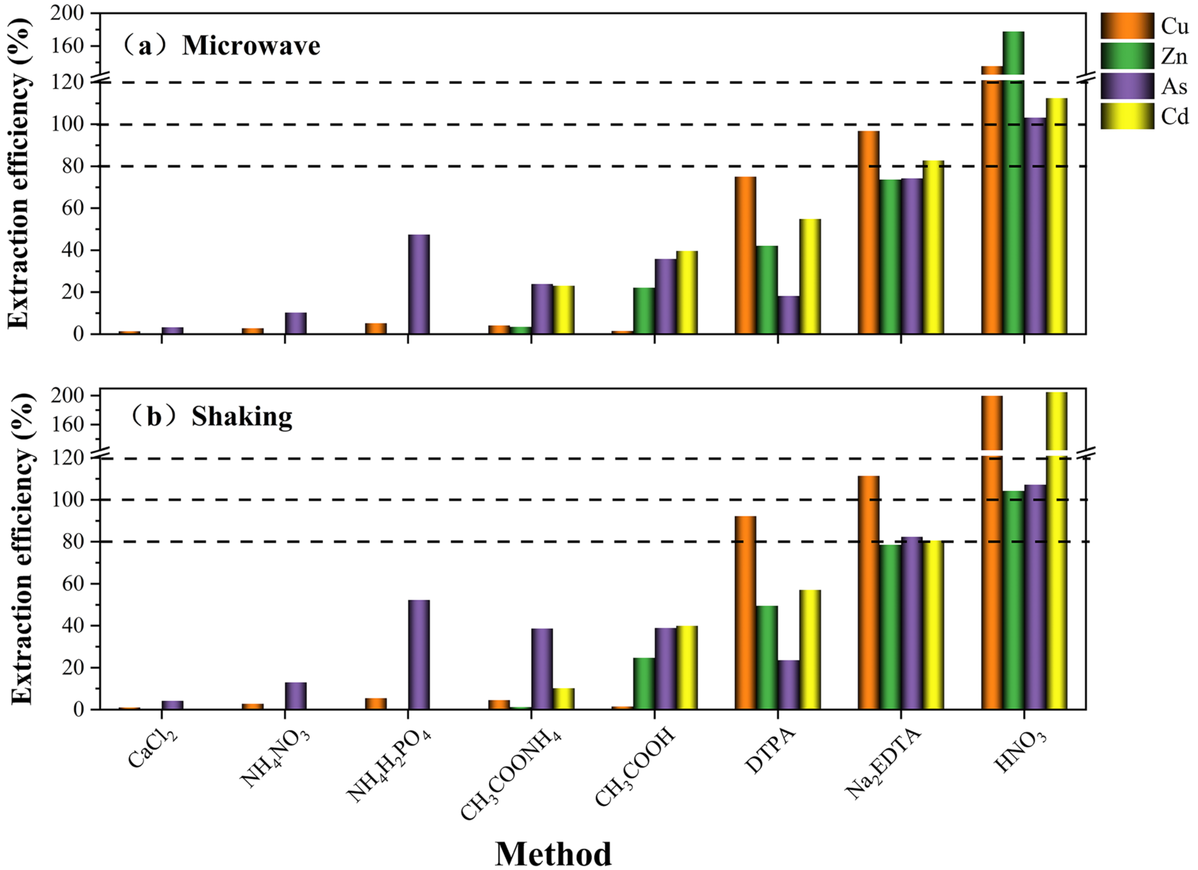

Fig. 1 Extraction efficiency of Cu, Zn, As, and Cd from GBW 07442 using different extractants and solvent extraction methods

efficiency. However, $CaCl_2$ is a neutral salt and cannot change the pH value of the solution. In this case, heavy metal ions exist in a free state, which is difficult to combine with the extractant and be extracted effectively. Therefore, extractants with $NaNO_3$ and NH_4Cl provided a substantially better extraction efficiency than that with $CaCl_2$.

Optimization of Na_2EDTA extraction

The Na_2EDTA which has the best extraction efficiency was selected as the extraction agent for further optimization. The parameters, including extraction time, soil liquid ratio, concentration, and pH of the extractant, were optimized through a univariate approach.

The extraction efficiency determined for the different extraction durations is shown in Fig. 2. The extraction efficiencies of Zn, As, and Cd did not change significantly when the extraction duration ranged from 0.5 to 16 h. The extraction efficiency of Zn at 0.5 and 1 h was below the acceptable limit (< 80%), whereas that of Cu at 8 and 16 h was close to or more than 120%. Generally, the extraction yield increases with extended duration to a certain extent, after which there is basically no change. Feng et al. (2005) used Heilongjiang soil to explore the correlation between extraction duration and the amount of heavy metal extracted and found that the extracted yield initially increased with duration and reached equilibrium after 12 h. Although the extraction rate of Zn did not reach 80% at 2 h but was very close, the optimal extraction duration was selected as 2 h in order to save time.

Figure 3 illustrates the extraction efficiency of different soil-liquid ratios on the release of the four heavy metals from CRM soil (GBW 07442). The extraction efficiencies of the four heavy metals were below the

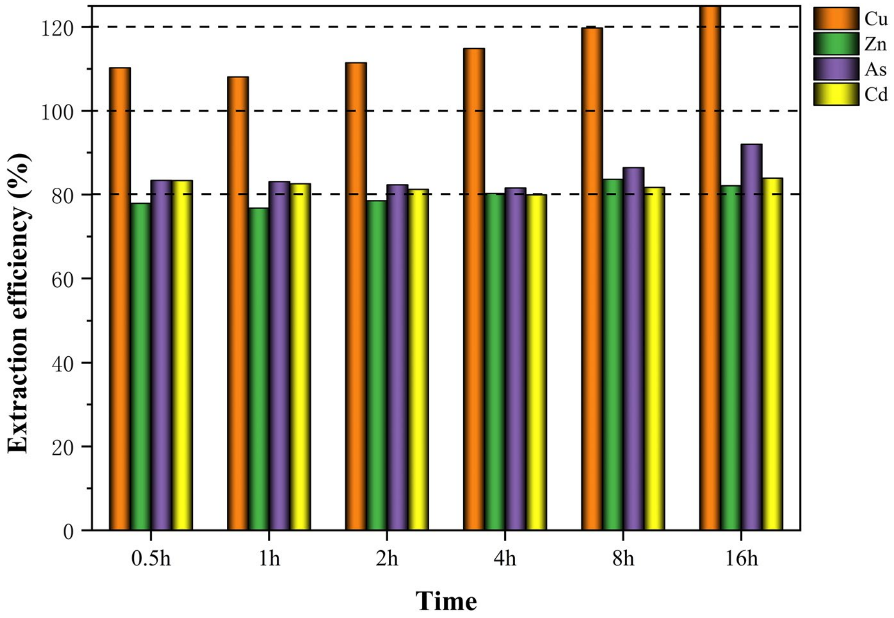

Fig. 2 Effect of duration on extraction efficiency of Cu, Zn, As, and Cd from GBW 07442

acceptable range when the soil-liquid ratio was 1:10 or 1:5. When the soil-liquid ratio was 1:40 or 1:20, the extraction efficiency of Zn did not significantly change. An expansion in the soil-liquid ratio, ranging from 1:40 to 1:5, was found to precipitate a decline in the effectiveness displayed by four heavy metals.

Heavy metal extraction efficiencies generally decrease with an increased soil-liquid ratio (Yin et al., 2000). In a soil heavy metal extraction experiment with 0.05 mol/L Na_2EDTA, Yi Lei et al. discovered that the extraction amounts of Cu and Zn in four tested soils decreased with increasing soil-liquid ratio and reached the maximum at 12.5 (Yi et al., 2012). The soil-liquid ratio of 1:20 was selected to reduce the cost and consumption of reagents.

The extraction efficiency of the four heavy metals during different extractant concentrations is shown in Fig. 4. It showed that the concentrations

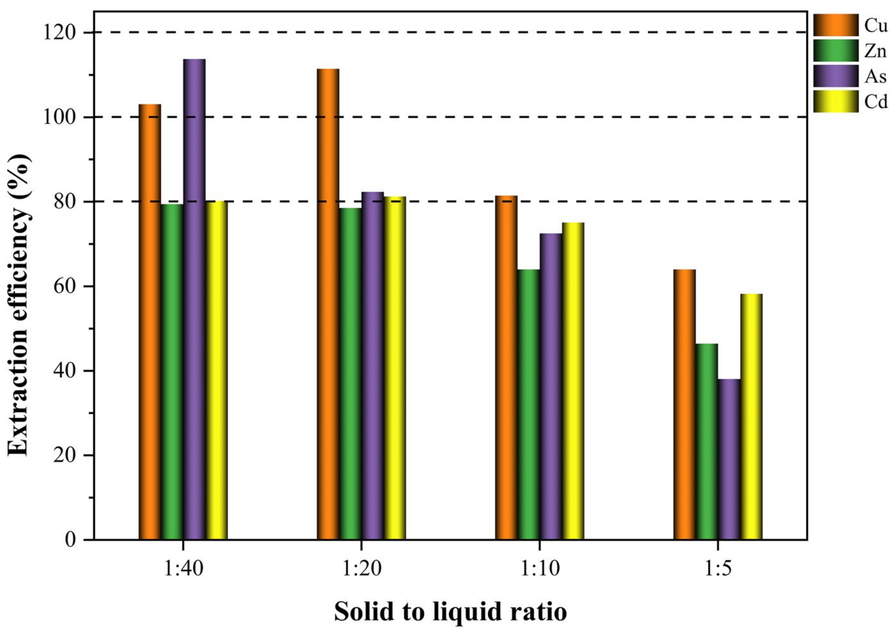

Fig. 3 Effect of solid to liquid ratio on extraction efficiency of Cu, Zn, As, and Cd from GBW 07442

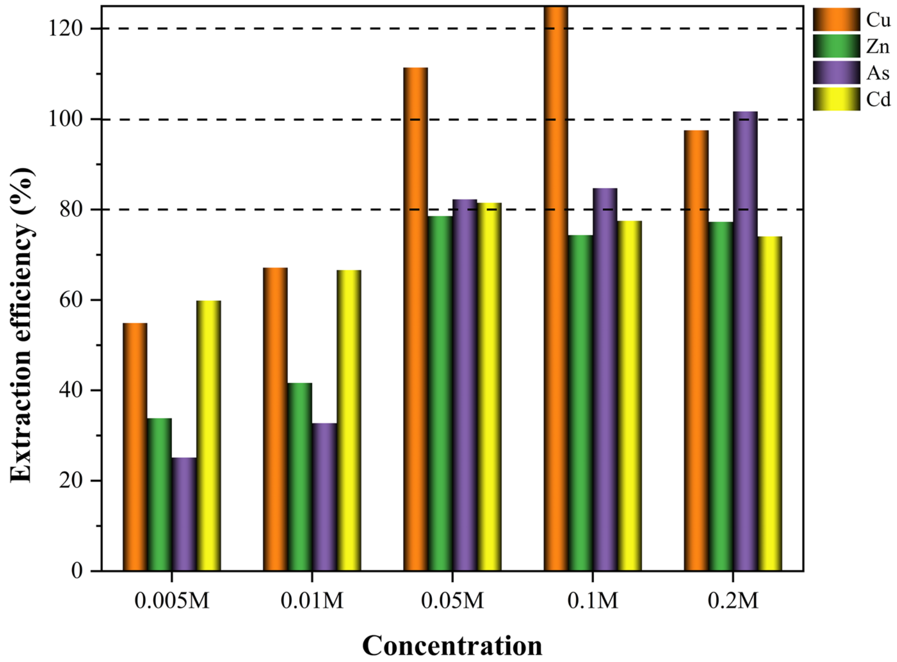

Fig. 4 Effect of Na_2EDTA concentration on extraction efficiency of Cu, Zn, As, and Cd from GBW 07442

of Na_2EDTA (0.005 M, 0.01 M, 0.1 M, 0.2 M) had low extraction efficiencies for the four heavy metals. The efficiency of Cu decreased with increasing the concentration of Na_2EDTA from 0.1 M to 0.2 M. Generally, the extraction efficiency increases with the increase in extractant concentration to a certain extent, after which the change in extraction amount is no longer evident (Yan et al., 2013). For instance, Zeng et al. found that the amount of heavy metals extracted gradually increased with increasing EDTA concentration (0–50 mmol/L); however, after EDTA concentration exceeded 5 mmol/L, the extracted amount was not significant (Zeng et al., 2003). This indicates that a higher concentration of extractant is not always beneficial. Hence, an innovation of extraction methods of available heavy metals in

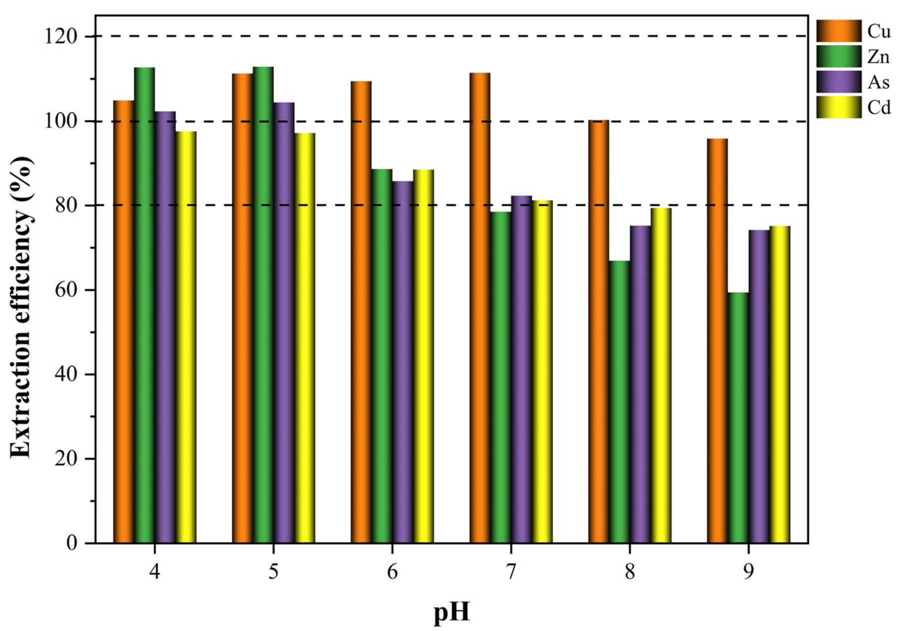

Fig. 5 Effect of Na_2EDTA pH on extraction efficiency of Cu, Zn, As, and Cd from GBW 07442

Table 5 Descriptive statistical analysis of total and available heavy metals in soils from Zhengzhou suburbs

Heavy metals		Min (mg/L)	Max (mg/L)	Mean (mg/L)	Std. deviation (mg/L)	Coefficient of variation (%)
Total heavy metals	tCu	9.62	23.50	14.72	2.66	18.07
	tZn	31.83	94.52	49.71	14.38	28.93
	tAs	6.40	14.19	10.91	1.77	71.22
	tCd	0.08	0.64	0.18	0.11	61.11
Available heavy metals	eCu	0.65	5.80	2.53	1.39	55.01
	eZn	0.49	28.07	6.24	6.03	96.63
	eAs	0.34	1.90	0.97	0.32	32.99
	eCd	0.05	0.48	0.12	0.08	66.67
Activity coefficient	aCu	5.18	37.18	16.55	7.42	44.83
	aZn	1.52	35.53	11.02	7.55	68.51
	aAs	4.50	15.25	8.97	2.98	33.22
	aCd	33.92	87.50	63.80	14.23	22.30

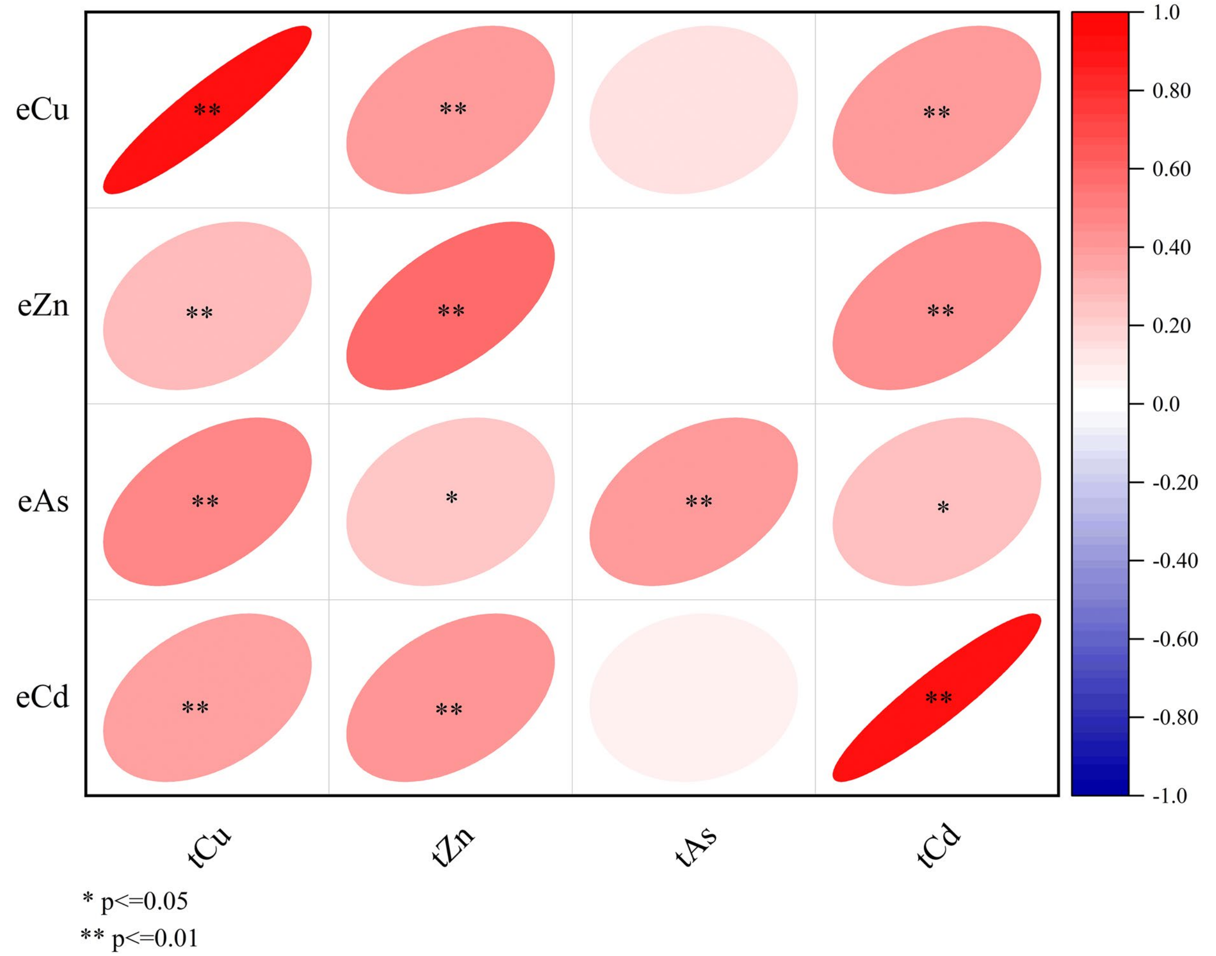

Fig. 6 Correlations of total heavy metals and available heavy metals for the soil samples. The colour of bubble characterizes the correlation coefficient value, with red indicating a positive correlation coefficient and blue representing a negative correlation coefficient. *Correlation is significant at the 0.05 level (two-tailed). **Correlation is significant at the 0.01 level (two-tailed)

soils that 0.05 mol/L Na_2EDTA can synchronously and efficiently extract available Cu, Zn, As, and Cd in fluvo-aquic soils with satisfactory extraction efficiency (85.8–109.5%) has been optimized and verified in the available heavy metals extraction of fluvo-aquic soils collected from the Zhengzhou suburbs of China.

Figure 5 illustrates the extraction efficiencies of Cu, Zn, As, and Cd from CRM soil (GBW 07442) at different extractant pH. It showed that the extraction efficiencies of the four heavy metals reached the acceptable range when the pH was 4, 5, 6, and 7. The extraction efficiencies of Zn, As, and Cd decreased with increasing pH from 7 to 9. This was consistent with the study of Tandy et al. (2004), where heavy metal extraction increased with decreasing pH, but this was offset by an increase in Ca and Fe extraction. Their conclusion was that pH 7 served to deliver the most optimal balance between the efficiency of Cu, Zn, and Pb extraction and the diminution of Ca and Fe levels within the soil. In addition, extracting polluting metals from the soil with a near-neutral pH avoids acidification and minimizes unwanted extraction of major ions (Li et al., 2020a, b). Similarly, Zeng et al. (2011) revealed that the relative value of extractable heavy metals decreased significantly with the increase of soil pH value. However, it is interesting to note that when the soil pH ranged from 5.0 to 7.0, the mean value of extractable Cu was approximately the same, while above pH of 7.0, it decreased significantly. The decrease in pH leads to the dissolution and release of insoluble heavy metals in soil, which increases the content of available metals and improves the extraction efficiency of heavy metals. The pH of the soil in Zhengzhou ranged between 7.7 and 8.95. As a result, the optimal pH selected was 7 in order not to affect the environment.

Application of optimal conditions on fluvo-aquic soil from Zhengzhou suburbs

The total and available heavy metal concentrations in fluvo-aquic soils from Zhengzhou suburbs are shown in Table 5. The average total concentrations (mg/L) of Cu, Zn, As, and Cd in soils were 14.72, 49.71, 10.91, and 0.18, respectively. Averagely, the available heavy metal concentrations (mg/L) in the soils were 2.53, 6.24, 0.97, and 0.12 for Cu, Zn, As, and Cd, respectively. The average activity coefficients (mg/L) of Cu, Zn, As, and Cd

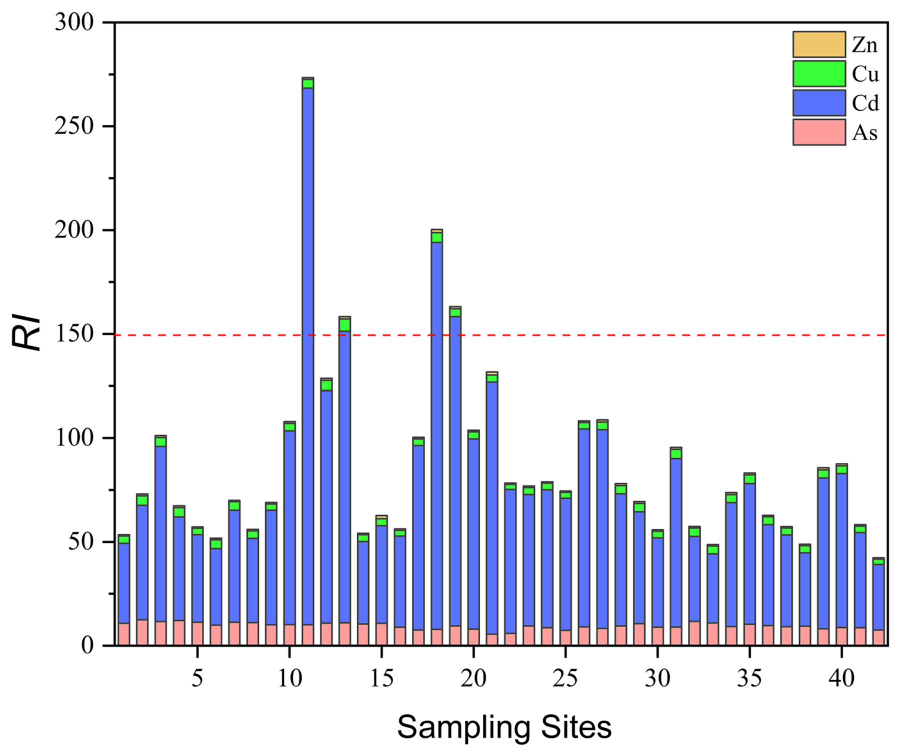

Fig. 7 Potential ecological risk of heavy metals in soil samples

in soils were 16.55, 11.02, 8.97, and 63.80, respectively. The activity coefficients of four heavy metals revealed that the bioavailability of different heavy metals in the same soil condition varies significantly, with Cd having the highest activity in the survey region.

Pearson's correlation analysis was used to study the relationships between total and available heavy metals in the survey area. Significant positive correlations ($p \leq 0.01$) are observed between the total and available heavy metal concentrations, as shown in Fig. 6. This indicates that the concentrations of available heavy metal tested in soil samples increased significantly with increasing total concentrations. Ramos-Miras et al. (2011) discovered that the correlation factors concerned with the complete concentration of heavy metals and the metal portions extractable through EDTA held substantial significance under all circumstances. Similar results were found by García & Millán (1994). The presence of strong correlations among heavy metals seems to indicate that they share a similar source and are inextricably interrelated (Akkajit & Tongcumpou, 2010), thus contaminating the soil at the same time (Gil et al., 2004).

Potential ecological risk of heavy metals and probabilistic healthy risks assessment

The potential ecological risk indices at different sampling sites assessed according to Eq. (2) are depicted in Fig. 7. Referring to the RI category aforementioned, the ecological risks at 38 sampling points were low risk (RI < 150). However, 4 sample sites with 150 ≤ RI < 300 were perceived as moderately risky. The Cd contributed the most to the RI of the four heavy metals, pointing to the imminent need for pollution control in the study area.

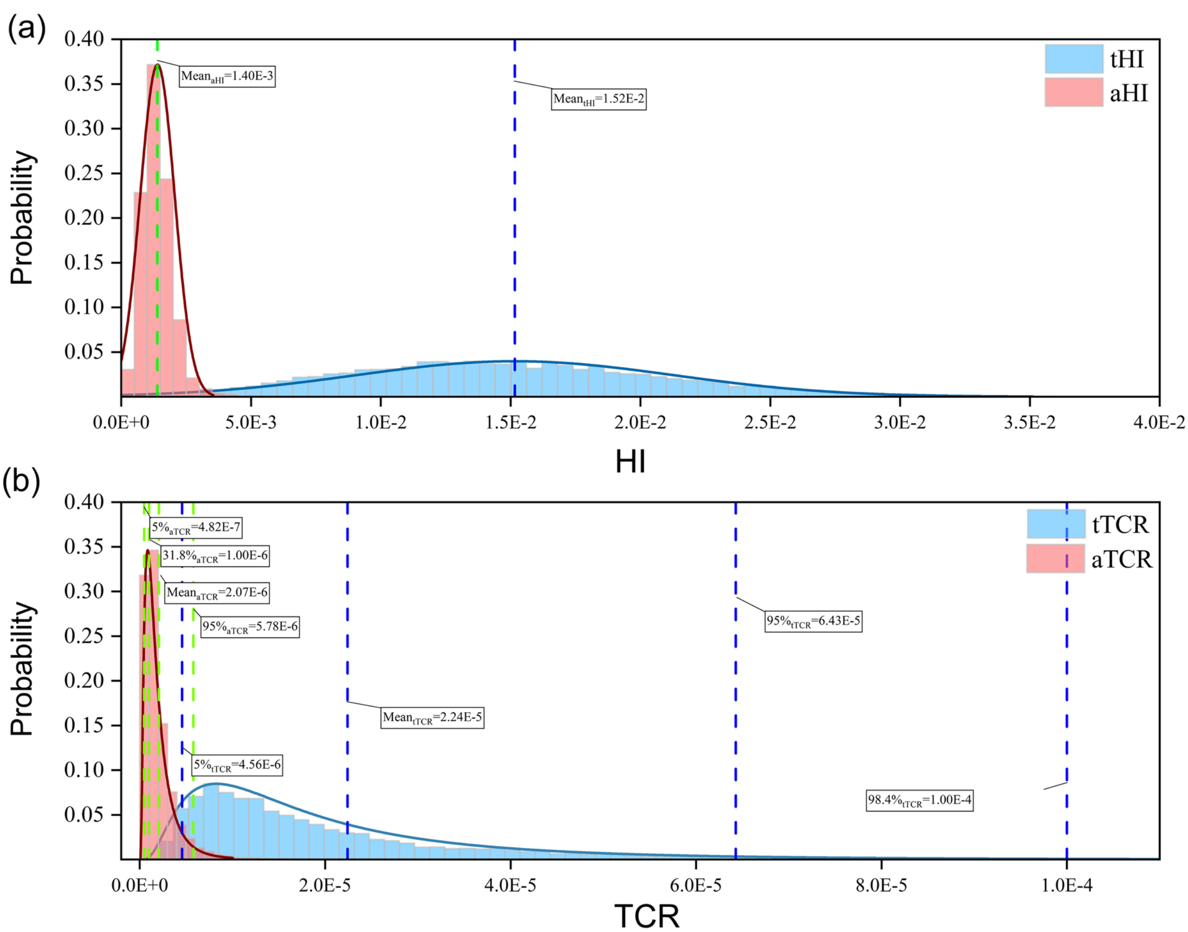

Fig. 8 Estimated distribution patterns of health risks caused by heavy metals: **a** HI and **b** TCR

In order to further clarify the health consequences of pollutants on the residents, the non-carcinogenic and carcinogenic risks based on the heavy metal concentrations are evaluated, as demonstrated in Fig. 8.

As presented in Fig. 8a, the HI is no more than the USEPA's specified value of 1, suggesting that the potential non-carcinogenic risks could be ignored. Additionally, Tong et al. (2019) and Huang et al. (2021) found that although non-carcinogenic risks were negligible, children were more susceptible to non-carcinogenic risks than adults. The probability distribution of TCR in Fig. 8b reveals that the carcinogenic risk in the study area cannot be neglected since the mean values of tTCR and aTCR exceeded the acceptable threshold of carcinogenic risk (1E-06), which were 2.24E-5 and 2.07E-6, respectively. Therefore, everyone should be reminded of the benefits of personal hygiene and proper skin protection when outdoors, especially for developing children.

The total amount of Cu, Zn, As, and Cd in the suburban soil of Zhengzhou has a high carcinogenic risk of 1.6%, while the effective risk of elements is still within the acceptable range, which verified that the risk grade obtained by the total amount is higher than the actual risk assessment.

Conclusion

Solvent extraction methods aided by shaking and microwaves were analyzed for their ability to extract four heavy metals from soil samples. Among the methods tested, the shaking-assisted method that utilized Na_2EDTA as an extractant demonstrated satisfactory efficiency and was chosen for further optimization using a univariate approach. With satisfactory extraction efficiency, the optimum conditions, including Na_2EDTA concentration and pH, solid to liquid ratio, and duration, were determined as 0.05 M, 7, 1:20, and 2 h, respectively. Cd is the predominant species in all the samples investigated due to its extremely high activity coefficient. Significant ($p < 0.01$) positive relationships were observed between the available state and the total amount of all the heavy metals. The assessment of health risks associated with heavy metals indicated that there was no risk for chronic non-carcinogenic effects. However, the total amount of elements Cu, Zn, As, and Cd in suburban soil of Zhengzhou is 1.6% with high carcinogenic risk, while the risk of available elements is still within the acceptable range. This verified that the risk grade obtained by the total amount is higher than the actual risk assessment.

Acknowledgements Mr. Dominic Yellezuome, a Ph.D. student from Shanghai Jiao Tong University, is greatly acknowledged for his proof reading of the manuscript.

Author contribution Ruiqi Zhang**:** Writing–original draft, Formal analysis. Xuejin Zhao**:** Experimental operation, Data curation. **Yanxia He:** Experimental operation, Methodology. **Yifeng He:** Conceptualization, Supervision, Funding acquisition, Writing–review and editing. Li Ma**:** Conceptualization, Resources, Software, Funding acquisition, Supervision, Writing.

Funding This research was funded by the Key Scientific and Technological Project of Henan Province Department of China (Grant no. 222102320396).

Data availability Data can be provided upon request.

Declarations

All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors.

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests The authors declare no competing interests.

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