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Bioaccessibilities and health risk assessment of heavy metals in dust from the Guizhou-Guiyang urban zone, China

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Abstract

To investigate the health risks of heavy metals in dust entering the human body from different exposure pathways. In this study, the old urban area of Guiyang was used as the study area to understand the heavy metals concentrations in surface dust, including recreational plazas, main streets, hospitals, residential areas, and schools in this city, and the bioaccessibility in the simulated lung phase and simulated gastrointestinal phase. The results showed that the concentrations of Cu, Pb, Zn, Cd, Ni, and Cr in the dust were higher than the background values, especially the Zn content exceeded the background value by 9.71 times. The bioaccessibility results indicated that the most soluble heavy metals in the simulated lung phase, simulated gastric phase, and simulated intestinal phase were Zn, Ni, and Cu, respectively, and the bioaccessibility of most heavy metals was significantly higher in the gastric phase than in the intestinal phase, and only Cu was higher in the intestinal phase than in the gastric phase. The linear results fit suggested that the total amount of heavy metals alone could not predict the human intake of heavy metals in the dust. Human health risk assessment based on bioaccessibility showed that children had higher non-carcinogenic and carcinogenic risks than adults for both hand-to-mouth ingestion and respiratory inhalation exposure pathways, but none of them exceeded the limit values.

Keywords: dust; heavy metal; bioaccessibility; health risk

Introduction

Cities are the most active areas for people nowadays, and the rapid development has also triggered a lot of environmental health problems at the same time (Li et al. 2019). As an inorganic pollutant, heavy metals have the characteristics for bioconcentration and difficult degradation and can cause a variety of hazards when they enter the human body through different exposure pathways (Tang et al. 2017). For example, although Cu is an important trace element for the human body, long-term exposure to Cu often causes damage to the human nervous system and blood circulation system (Damian et al. 2007). Pb will accumulate in the bone marrow and spleen after it enters the human body, it has the greatest impact on children, who will suffer

irreversible damage to their intelligence after excessive exposure to Pb, and in serious conditions will cause death (Balamuralikrishnan et al. 2020). Zn, like Cu, is also a common and essential trace element, but excessive intake of Zn will damage the human immune system (Till et al. 2018). Cd is a harmful element to the human body, although the content for Cd is very low in the natural environment. However, due to man-made reasons or special working conditions, a large amount of Cd ingested by the human body will be harmful to the respiratory tract and reproductive system, as well as to the bones (Kobra et al. 2021). Ni is also a trace element, but the body's demand for it is very small and once the body ingests a certain amount of Ni, it can cause inflammation and even affect the body's genetic factors (Michael et al. 2021). Cr itself does not have biotoxicity, but the Cr entering the body will be converted into Cr^{6+} , which is easily adsorbed on the mucous membrane surface for the respiratory tract and can cause various respiratory inflammatory diseases (Nancy et al. 2021).

Urban surface dust is a kind of solid particle deposited on artificial pavement and various buildings due to atmospheric deposition, and dust could act as an important vector for heavy metals and various kinds of pollutants, given that dust is at the different environmental interface and important source-sink effects (Renata et al. 2021). Therefore, many scholars have studied the sources and spatial distribution for heavy metals in dust, and most of the findings show that the sources for heavy metals in dust are mainly related to vehicle exhaust emissions, wear and tear for the vehicle itself and aging for pavement materials, while the spatial distribution is related to the source of pollution (Han et al. 2020; Yu et al. 2021; Jose et al, 2021). Due to heavy metals can be toxic to the human body, some scholars have also conducted health risk evaluations for heavy metals in the dust. However, the heavy metals in dust cannot be completely absorbed by the human body, and the health risk assessment based on total heavy metals may cause errors in the results, so some scholars have introduced bioaccessibility into the health risk assessment (Han et al. 2020; Expósito et al. 2021).

Bioaccessibility refers to the ratio of the number of contaminants released in the gastrointestinal fluid to the total amount after the contaminants in the matrix for soil and food enter the human digestive system, which represents the relative amount of contaminants absorbed by the human body (Yin et al. 2021). Compared with the traditional assessment methods, bioaccessibility can more accurately reflect the release of heavy metals in the human body, which is more scientific and reasonable. There have been a lot of researches on bioaccessibility at domestic and abroad, but the research objects mainly focus on soil heavy metals and metal mining areas, etc (Du et al. 2020; Sultana et al. 2020). Although the bioaccessibility of heavy metals in dust has been reported, the simulated digestion phase is only limited to the gastrointestinal phase, and the bioaccessibility of the simulated respiratory system in vitro is less reported. Human exposure to heavy metals is predominantly through two ways: inhalation and ingestion thus may cause various health problems (Khelifi et al. 2021). Therefore, in this study, we chose in vitro simulated human digestive system and respiratory system to conduct the bioaccessibility study, and it is significant to carry out a health risk assessment for urban populations based on bioaccessible concentration.

Guiyang (the capital city of Guizhou province) is one of the fastest-growing cities

in southwest China, as well as an important regional innovation center and tourist city. With the rapid development of the economy and the continuous expansion of urban transportation, the problem of Guiyang's ecological environment has become increasingly prominent. Therefore, this study selected recreational squares, main streets, hospitals, residential areas, and schools in the old town of Guiyang, where crowds moving more widely, were used as a study area. The main objective of this study was to evaluate the total heavy metals concentrations for these locations. In vitro simulation method was used to simulate the leaching of heavy metals from dust in human lungs and gastrointestinal tract respectively, explore the bioaccessibility of heavy metals. Eventually, according to the bioavailability of heavy metals in different stages, the non-carcinogenic and carcinogenic health risk assessment of heavy metals for the population via different exposure pathways in the urban area was carried out respectively. The results of this study could provide accurate assessment for the population in this urban area, which can serve as a reference for pollution control and environmental planning for heavy metals in urban dust.

Materials and methods

Study area

Guiyang(106°07'-107°17'N, 26°11'-27°22'E), as it is known in Figure 1, is located in the central part of the Guizhou province, and the Yungui Plateau to the east, mainly dominated by hilly terrain and mountainous terrain. The altitude of the study area ranges from around 1100 m, with a humid and mild subtropical climate, average annual temperatures of 15.3°C, average annual relative humidity of 77%, and annual sunshine time is about 1278h, owning annual precipitation of 1200 mm and a frost-free period of 270 days. The old urban areas of Guiyang City were selected for this research: Yunyan District and Nanming District, Yunyan District is located in the northern part of Guiyang City, with an area of 67.5 km², Nanming District is located in the southern part of Guiyang City, with an area of 89.68 km². The old urban areas have a longer development time, and there have been historical residues for heavy metals in the dust on the surface of old urban areas due to the expansion of traffic and the construction of a large number of high-rise buildings during the development process for many years. Therefore, people living in old urban cities are exposed to potential health risks from heavy metals in the dust.

Figure 1. Sampling points and map of the study area

Sampling and sample preparation

A total of 71 dust samples were shown in Figure 1. The sampling sites covered recreational squares, main streets, hospitals, residential areas, schools, and other areas where people mainly concentrated of Yunyan District and Nanming District respectively. The dust samples are collected from April to May in 2021, and it was ensured that the humidity in the city was not high and the weather was clear during the sample collection period. April-May is the flowering period of major flowers in Guiyang, such as Rhododendron and orchids. To avoid large amounts of pollen in the dust, samples were collected mainly from the entrance for schools, air conditioning fans surface, windowsills for residential areas, main streets, and steps, and each dust sample was carefully collected by brush and dustpan and sampling tools were cleaned in sampling sites to avoid cross-contamination. All dust samples were packed in individually labeled polyethylene, sealed plastic bags, and transported back to the laboratory for processing after sampling was completed. Before the experiment, extra materials, such as hairs, sand, grit, and plant residues, were removed from samples through a 1mm nylon screen. Then all samples were dried in an oven at 40°C until constant weight. Finally, samples were sieved through a 200 μ m mesh nylon screen, labeled, and prepared to be tested.

Gamble analysis

In vitro simulated respiratory system is mainly used Gamble analysis method, the method is Zaitos et al. (Zaitos et al.1997) combined with previous research, the proposed method showed qualitatively good correlation with in vivo results, after continuous validation studies, Gamble analysis has become a widely accepted approach for in vitro simulated respiratory system. The simulated lung fluid per liter contained

0.095 g MgCl_2 (Chengdu Jinshan Chemical Reagent Co.), 6.019 g NaCl (Chengdu Jinshan Chemical Reagent Co.), 0.298 g KCl (Tianjin Youpu Chemical Reagent Co.), 0.126 g Na_2HPO_4 (Tianjin Kermel Chemical Reagent Co.), 0.063 g Na_2SO_4 (Tianjin Kermel Chemical Reagent Co.), 0.368 g CaCl_2 (Tianjin Kermel Chemical Reagent Co.), 0.574 g CH_3COONa (Tianjin Kermel Chemical Reagent Co.), 2.604 g NaHCO_3 (Tianjin Kermel Chemical Reagent Co.), 0.067 g $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ (Tianjin Kermel Chemical Reagent Co.), and the final pH for the simulated fluid was adjusted to 7.4. Each reactor was set at 1:1000 solid-to-liquid ratio, experimental temperature simulated normal human temperature at 37°C , it was shaken in a constant-temperature oscillator at $100\text{ r}\cdot\text{min}^{-1}$ for 24 h, the samples were centrifuged at $5000\text{ r}\cdot\text{min}^{-1}$ for 10 min, and filtered through a $0.45\text{ }\mu\text{m}$ filter membrane. Finally, the contents of Cu, Pb, Zn, Cd, Ni, and Cr in the filtrate were measured by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 2000).

Physiologically-based extraction test (PBET) analysis

PBET analytical methods, it had become the most popular method in vitro for simulating the digestive system since it was proposed by Ruby et al. (Ruby *et al* 1993) in 1993 to determine the bioaccessibility for Pb and Cd in soil, which is based on human physiological characteristics simulating the gastric digestion and intestine absorption phases to determine the bioaccessibility for different heavy metals in the matrix, and Ruby et al. (Ruby et al. 1999) also found that the results obtained from the in vitro simulation method showing good correlation when the results were compared with the animal experiments. This analysis method was divided into two phases, and the simulated gastric juice contained 0.5 g sodium malate (Shanghai Aladdin Chemical Reagent Co.), 0.5 g sodium citrate (Shanghai Aladdin Chemical Reagent Co.), 0.42 mL lactic acid (Shanghai Aladdin Chemical Reagent Co.), 0.5 mL glacial acetic acid (Shanghai Aladdin Chemical Reagent Co.), and 1.25 g pepsin (Shanghai Aladdin Chemical Reagent Co.). The pH was adjusted consistently to 1.5 with 1 mol/L HCl (Chengdu Jinshan Chemical Reagent Co.). The simulated gastric juice was added to each reactor at a 1: 100 solid-to-liquid ratio, it was shaken in a constant-temperature oscillator at $100\text{ r}\cdot\text{min}^{-1}$ for 1 h. Argon was injected into the simulated liquid at 1 L/min for serving as an anaerobic environment. After 1 h for oscillation, the supernatant 30 mL was extracted and filtered through a $0.45\text{ }\mu\text{m}$ filter membrane for analysis. In the intestinal phase, saturated NaHCO_3 (Tianjin Kermel Chemical Reagent Co.) solution was added until the pH of the solution was 8.0, and then 0.14 g of bile salt (Shanghai Bowei Bio-Technology Co.) and 0.04 g trypsin (Shanghai Aladdin Chemical Reagent Co.) were added into the constant, and the shaking was continued under the same conditions as the simulated stomach for 4 h. Then the supernatant was collected, centrifuged, and filtered. Gastric and intestinal extracts were stored at 4°C until assayed. Bioaccessibility in the gastric or intestinal stages could be calculated in the following form:

$$BAC(\%) = \frac{C_{IV} \times V_{IV}}{T_s \times M_s} \times 100\% \quad (1)$$

where is the bioaccessibility for heavy metals; is the concentration for heavy metals in the soluble state in the lung dissolution, gastric digestion, and intestinal absorption phases for the simulated experiment (mg/L); is the volume for the reaction solution in each reactor (L); is the total amount for heavy metals in the sample (mg/kg); is the mass for the sample in the reactor (kg).

Human health risk assessment

Health risk assessment is a characterization method for potential threats to the human body due to exposure to toxic or harmful substances. In this research, the health risk assessment model developed by USEPA (USEPA 1989; USEPA 2001) was adopted for the assessment, for which they considered that contamination enters the human body mainly through the following three pathways: (1) direct hand-to-mouth unconscious ingestion for matrix particles; (2) inhalation for suspended particles through the respiratory tract; and (3) entering into the human body through skin contact. Considering that human exposure to heavy metals in the dust is mainly through the two exposure routes for respiratory inhalation and hand-to-mouth ingestion, this study was mainly based on simulated lung and simulated gastrointestinal bioaccessibility to calculate the average daily exposure and the corresponding non-carcinogenic and carcinogenic risks for adults and children under these two routes, and the average daily exposure (ADD) and risk values were mainly calculated in the following form:

$$ADD_{inh} = \frac{C_{dust} \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (2)$$

$$ADD_{ing} = \frac{C_{dust} \times IngR \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

The physical meaning and values of the specific formula parameters are listed in Table 1.

Table 1 Parameter values in average daily intake calculation models of heavy metals

Parameter	Physical meaning	Unit	Child	Adult	Reference
C_{dust}	The concentration of heavy metals in dust	$mg \cdot kg^{-1}$	—	—	This study
$IngR$	Daily intake rate	$mg \cdot kg^{-1}$	100	200	USEPA(2008)
$InhR$	Inhalation rate	$m^3 \cdot d^{-1}$	5.6	16.5	USEPA(2008)
EF	Exposure frequency	$day \cdot year$	180	180	USEPA(2008)
ED	Exposure time	year	6	24	USEPA(2008)
PEF	Dust emission factor	$m^3 \cdot kg^{-1}$	$1.36 \times 10^9 m^3 \cdot kg^{-1}$		USEPA(2008)
CF	Conversion factor	/	1×10^{-6}		USEPA(2008)
BW	Average weight	kg	14.9	58.6	Duan et al. 2012
ABS	Skin absorption factor	/	0.001		USEPA(2008)
SA	Exposed skin surface area	cm^2	4350	1600	Duan et al. 2012
AF	Average exposure time	/	0.2	0.2	USEPA(2008)
AT (non-carcinogens)	Average exposure time	day	365×6	365×24	USEPA(2008)
AT	Average exposure time	day	365×70	365×70	USEPA(2008)

(carcinogens)

heavy metals accumulate in the human body under different exposure pathways and cause chronic non-carcinogenic risks, while Cd, Ni, and Cr are the main elements that cause cancer in people. The human health risks caused by respiratory inhalation, hand-oral ingestion, and dermal exposure in this study are expressed as HI and CR, respectively (USEPA, 2007).

$$HQ = \frac{ADD}{RfD} \quad (4)$$

$$HI = \sum HQ_i \quad (5)$$

$$CR = \sum ADD_i \times SF_i \quad (6)$$

where HQ (Hazard Quotient) is the single non-carcinogenic risk; RfD is the reference dose at different pathways ($\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$). HI represents the total non-carcinogenic risk due to all heavy metals; CR (Cancer Risk) represents the total carcinogenic risk due to all heavy metals; SF is the slope for carcinogenicity ($\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$).

The Environmental Protection Agency (EPA) considers the risk to be low when HQ or $HI < 1$ and some non-carcinogenic risk when HQ or $HI > 1$; the carcinogenic risk is negligible when CR is below 10^{-6} , within the acceptable range when it is between 10^{-6} and 10^{-4} , and above 10^{-4} , it is considered a serious carcinogenic risk. The physical meaning and values of the specific formula parameters are listed in Table

Table 2 Reference doses for non-cancer metals and slope factors for carcinogens metals

Elements	RfD_{ing}	RfD_{inh}	SF_{ing}	SF_{inh}	Reference
Cu	4.00E-02	4.00E-02	-	-	USEPA(2008)
Pb	3.50E-03	3.50E-03	-	-	USEPA(2008)
Zn	0.3	0.3	-	-	USEPA(2008)
Cd	1.00E-03	1.00E-03	6.1	6.30	USEPA(2008)
Ni	2.00E-02	2.06E-02	-	0.84	USEPA(2008)
Cr	3.00E-03	2.86E-05	-	42.0	USEPA(2008)

Sample analysis and data analysis

In this study, dust samples were digested by HCl-HNO₃-HF-HClO₄ four-acid digestion method as detailed in the literature (Xiao et al. 2019), and heavy metals such as Cu, Pb, Zn, Cd, Ni, and Cr were followed by analysis with an inductively coupled plasma mass spectrometer (ICP-MS), and all experimental samples were set as three parallel samples and reagent blanks were added throughout the experiment. The data were compiled by Excel 2016, the spatial distribution for sampling points was performed by ArcGis 10.2. For visualization of the data, results were plotted for using the OrginPro 8.0 program, the fit for the total dust heavy metals to the bioaccessible amount in different simulation phases was performed by SPSS 16.0, and the degree of the fit could reflect the correlation between total amount and bioaccessible amount.

Results and discussion

Total metal concentration

The concentration of Cu, Pb, Zn, Cd, Ni, and Cr in 71 dust samples in this study were shown in Figure 2 and Table 3, which including minimum, maximum, median, mean, standard deviation, coefficient of variation (C.V), background values, and limited levels. From Table 3, all heavy metals concentrations of dust were significantly above the background values, which were 5.16, 1.82, 9.71, 2.92, 3.41, 4.99, and 1.72 times of the background value, respectively. The concentrations were as follows: $Zn > Cu > Cr > Ni > Pb > Cd$, except for Pb, other heavy metals were higher than limited levels. Although the concentration of Pb in this study exceeded the background value, it was significantly reduced compared with previous studies about heavy metals in urban road dust, so it could be inferred that the Pb concentration in this study was less than limited levels probably because of the widespread use of unleaded gasoline, while it was higher than background value probably due to the longer developmental history of old urban areas, and some of the Pb was deposited in the dust may be related to the wear and tear of automobile materials (Zheng et al. 2020). Among the investigated heavy metals, Zn content exceeded the standard significantly more than other heavy metals, and according to our analysis, the main sampling sites in this study were located near the main roads and near the parking lots of residential areas, while some studies suggested that the high concentration of Zn was related to the wear and tear for car parts and tires (Goix et al. 2016). According to the statistical principle, the larger the coefficient of variation (C.V), the greater the degree of dispersion of the pollutant, and the greater the influence of external factors. From Table 3, it could be seen that the coefficient of variation was ranked from high to low as $Pb > Cd > Zn > Cr > Cu > Ni$ so that it could be seen that Pb, Cd, and Zn showed a higher level of variation, indicating that these three heavy metals were more spatially distinct from Cr, Cu, and Ni are not uniformly distributed spatially compared with each other and were more influenced by external factors, while these conclusions in this study were also basically consistent with the results drawn by Fan et al (Fan et al. 2020).

Table 3 Concentrations of heavy metals (mg/kg) in surface dust.

Element	Minimum	Maximum	Median	Mean $\pm$ SD	C.V(%)	Background value	Limited levels
Cu	100.67	315.72	156.98	165.41 $\pm$ 47.37	28.64	32.0	100
Pb	11.24	163.34	45.82	64.41 $\pm$ 44.28	68.76	35.2	120
Zn	157.44	1793.91	996.21	966.61 $\pm$ 373.19	38.61	99.5	250
Cd	0.13	3.62	1.99	1.924 $\pm$ 0.89	46.41	0.659	0.3
Ni	73.72	187.52	127.82	133.26 $\pm$ 26.39	19.81	39.1	100
Cr	54.91	325.86	162.64	164.86 $\pm$ 53.69	32.57	95.9	200

Figure 2. Total heavy metals in dust for this study

In vitro stimulation of the respiratory system

The bioaccessibility of Cu, Pb, Zn, Cd, Ni, and Cr in the simulated lung was shown in Figure 3 and Table 4. Among the six elements involved in this study, Cr had the lowest bioaccessibility (3.81%) and Zn had the highest bioaccessibility (38.97%). It was possible that such a high solubility of Zn in the simulated lung may be related to the speciation characteristic of Zn, which had been proved to be an important source of Zn in dust mainly in the form of ZnO (Adachi et al. 2004), while the low bioaccessibility of Cr may also be related to the speciation characteristic. Some researchers had extracted different forms of Cr by Tessier sequential extraction method and found that Cr was mainly in the insoluble residual fraction and the soluble fraction was relatively low, thus the bioaccessibility of Cr in simulated lung fluid was the smallest. In this study, the bioaccessibility of Cd in simulated lung fluid was similar to that of Cr and showed a lower level (Li et al. 2019). In this study, the bioaccessibility of Cd in simulated lung fluid was similar to that of Cr and showed a lower level. However, some studies had shown that the bioaccessibility of Cd in simulated lung showed a higher level, and the reason for the difference may be related to the components in the simulated lung fluid, pH, extraction time, and the source of Cd (Zhang et al. 2019). The bioaccessibility percentages of the other three heavy metals Cu, Pb, Ni in the simulated lung were 12.99%, 15.51%, 10.54%, respectively.

In vitro stimulation of the digestive system

The bioaccessibilities of heavy metals in the dust for this study in the simulated gastric and intestinal phases were presented in Figure 3 and Table 4. In the Figure and Table, it could be seen that the bioaccessibility of Cu, Pb, Zn, Cd, Ni, and Cr in the stomach and intestine of 71 sample points and an overview of the range, mean, concentration, and median bioaccessibility of heavy metals in dust samples were summarized in Table 2. The heavy metals with high bioaccessibility in the gastric phase were Cu, Zn, Cd, and Ni, which all reached more than 40%, while Cr had the lowest dissolution rate of 4.19%. In the intestinal phase, the average of heavy metals bioaccessibilities was as follows: Cu>Zn>Ni>Cd>Pb>Cr. Compared with the bioaccessibility of the gastric phase, the bioaccessibility in the intestinal phase was significantly lower, Pb bioaccessibility decreased from 23.89% to 13.26%, Zn bioaccessibility from 45.22% to

26.49%, Cd bioaccessibility from 43.07% to 20.17%, and Ni from 46.16% to 25.32%, Cr bioaccessibility did not change much from gastric phase to intestinal phase, while Cu bioaccessibility increased from 41.85% to 53.62%. Overall, the bioaccessibility of most heavy metals was significantly higher in the gastric stage than in the intestinal stage, and some researches showed that heavy metals such as Pb, Zn, Cd, and Ni were more active and easily soluble and digested under acidic conditions in the stomach (Soltani et al. 2021; Zhao et al. 2020), but heavy metals soluble in the gastric stage (acidic) would undergo adsorption- precipitation reactions when they entered the intestinal stage (alkaline) leading to a decrease in heavy metals solubility, while the small degree of change in Cr might be mainly attributed to the Cr was in the form of residue and the dissolution rate was not high in simulated human gastrointestinal fluid (Xing et al. 2019). The reason for Cu bioaccessibility increased was that Cu could complex with trypsin and bile salts, thus showed a higher solubility effect in the intestinal absorption phase (Xu et al. 2018).

Table 4 Bioaccessibility of heavy metals in the lung phase, gastric phase, and intestinal phase of dust.

Heavy metals	Lung(%)			Gastric(%)			Intestinal(%)		
	Range	Median	Mean	Range	Median	Mean	Range	Median	Mean
Cu	6.68-20.36	12.36	12.99	22.77-59.98	41.46	41.85	37.13-75.66	53.26	53.62
Pb	2.26-29.61	15.01	15.51	10.98-43.96	22.11	23.89	4.57-33.14	12.37	13.26
Zn	20.54-57.69	37.67	38.97	24.43-65.69	44.35	45.22	11.25-41.36	26.51	26.49
Cd	0.57-14.03	2.82	3.88	20.26-63.10	42.96	43.07	5.29-35.14	17.46	20.17
Ni	4.99-19.34	10.04	10.54	33.22-57.51	45.91	46.16	13.27-37.46	25.64	25.32
Cr	1.47-9.33	3.39	3.81	1.47-9.51	3.68	4.19	0.27-6.87	3.21	3.09

Figure 3. The percentage for bioaccessibility of each heavy metal at different simulation stages

Relationships between the bioaccessibility and the total concentrations

The linear relationships between total Cu, Pb, Zn, Cd, Ni, and Cr in dust and bioaccessibility in the simulated lung phase, gastric phase, intestinal phase were presented in Figure 3, Figure 4, Figure 5. Linear coefficients (R^2) of the total amount of each heavy metal in the dust and bioaccessibility in the simulated lung phase were 0.0076, 0.8137, 0.8044, 0.0367, 0.0201, and 0.0269, respectively, and only the total amount for Pb ($R^2=0.8137$) and Zn ($R^2=0.8044$) showed a significant correlation with the concentration for the lung extraction stage, while other heavy metals had no significant linear relationship with total concentration. The linear coefficients (R^2) of each heavy metal in the gastric phase were 0.6057, 0.8003, 0.8074, 0.6868, 0.7151, and 0.1168, respectively, and the concentration of Pb, Zn, and Ni in the gastric extraction stage showed good correlations with the total amount in dust, while Cu and Cd showed moderate positive correlation, Cr had no significant correlation. The linear coefficients (R^2) of each heavy metal in the simulated intestinal phase were 0.6279, 0.6276, 0.5085, 0.4501, 0.4135, and 0.1244, respectively, and the total amount of heavy metals showed a moderate positive correlation with the concentration of the intestinal extraction stage except for Cr. It could be seen from the linear fit relationships in different phases that the total Pb and Zn were able to briefly assess the predicted digestive dissolution in the human lung and stomach, but most of the total heavy metals had no significant effect on their bioaccessibility. Since the human intake of heavy metals is mainly absorbed from the intestine, therefore, the previous health risk using total heavy metals had some errors and did not accurately reflect the absorption for heavy metals in the human body and carcinogenic and non-carcinogenic risk values (Sun et al. 2018).

Figure 4. Linear fit of the lung phase

Figure 5. Linear fit of the gastric phase

Figure 6. Linear fit of the intestinal phase

Health risk assessment of heavy metals based on bioaccessibility

Owing to heavy metals in the dust mainly entered the human body through two exposure pathways, respiratory inhalation, and hand-to-mouth ingestion, so the average daily exposure for these two exposure pathways was calculated using the simulated lung and simulated intestinal bioaccessibility instead of the total amount to avoid errors in risk evaluation results. According to Table 5, the average daily non-carcinogenic exposure for children was higher than that for adults in both pathways, and the average daily non-carcinogenic was also higher than that for adults, different heavy metals showed different bioaccessible concentrations in different stages, which led to different average daily non-carcinogenic and carcinogenic exposures for different heavy metals. The average daily exposure of non-carcinogenic heavy metals for hand-to-mouth intake was as follows: Zn>Cu>Ni>Pb>Cr>Cd, Zn was able to reach 8.29E-04, and Cd the smallest was 1.21E-06. Compared with the average daily exposure by respiratory inhalation, each heavy metal also showed the same pattern, but the exposure was much smaller than hand-oral intake. Thus, it could be seen by comparison that the number of heavy metals absorbed in the intestine was higher, and the non-carcinogenic risk by hand-oral intake was also much higher than that by respiratory inhalation (Shahab et al. 2018). However, the non-carcinogenic risks for Cu, Pb, Zn, Cd, Ni, and Cr in both exposure pathways did not exceed 1, which were below the risk threshold, indicating that they did not have non-carcinogenic risks. Although the daily average exposure of Zn to children and adults was the highest under these two pathways, Pb was the non-carcinogenic element with the highest risk value in the non-carcinogenic risk assessment results. As for the three carcinogenic elements, Cd, Cr, and Ni, basing the Table 3 that children had the highest average daily exposure of 4.99E-10 for Ni under the respiratory inhalation pathway, the total carcinogenic risk for children under the two pathways were 6.38E-07, and the total carcinogenic risk value for adults was 8.71E-10, while the carcinogenic risk values of Cd, Ni and Cr for children were 6.35E-07, 1.40E-10 and 2.76E-09, respectively, and it was known from the calculation results that cancer risk in adults was also negligible. According to the carcinogenic risk standard formulated by USEPA, we saw that the carcinogenic risk of children under these three elements was negligible, while the carcinogenic risk values of Cd, Ni, and Cr in adults are 1.46E-11, 4.19E-10 and 8.28E-09 respectively, which the risk of cancer in adults was negligible from the calculation results. Seeing the evaluation results, we could find that although the non-carcinogenic and carcinogenic risks did not reach the risk values, the exposure to heavy metals was highest under the hand-to-mouth pathway of ingestion, so people who need to travel should take protective measures such as wearing

a mask and washing hands regularly.

Table 5 Health risk assessment of heavy metals based on bioaccessibility in dust for adults and children.

Heavy metals	Children					Adults				
	ADD _{ing}	HQ _{ing}	ADD _{inh}	HQ _{inh}	HI	ADD _{ing}	HQ _{ing}	ADD _{inh}	HQ _{inh}	HI
Hazard quotient(HQ) /mg·kg ⁻¹ ·d ⁻¹										
Cu	1.48E-04	3.69E-03	2.72E-09	6.80E-08	3.69E-03	7.51E-05	1.88E-03	2.04E-09	5.09E-08	1.88E-03
Pb	2.51E-05	7.15E-03	1.34E-09	3.84E-07	7.15E-03	1.27E-05	3.64E-03	1.01E-09	2.88E-07	3.64E-03
Zn	8.29E-04	2.76E-03	5.29E-08	1.76E-07	2.76E-03	4.22E-04	1.41E-03	3.96E-08	1.32E-07	1.41E-03
Cd	1.21E-06	1.22E-03	8.77E-12	8.77E-09	1.22E-03	6.17E-07	6.18E-04	6.57E-12	6.57E-09	6.18E-04
Ni	1.12E-04	5.58E-03	1.94E-09	9.43E-08	5.58E-03	5.67E-05	2.84E-03	1.46E-09	7.07E-08	2.84E-03
Cr	1.62E-05	5.41E-03	7.68E-10	2.68E-05	5.44E-03	8.25E-06	2.75E-03	5.75E-10	2.01E-05	2.77E-03
Total	1.13E-03	2.58E-02	5.97E-08	2.75E-05	2.58E-02	5.75E-04	1.31E-02	4.47E-08	2.06E-05	1.32E-02
Cancer risk(CR)/ mg·kg ⁻¹ ·d ⁻¹										
Cd	1.04E-07	6.35E-07	7.52E-13	4.74E-12	6.35E-07	6.01E-14	3.67E-13	2.25E-12	1.42E-11	1.46E-11
Ni	—	—	1.67E-10	1.40E-10	1.40E-10	—	—	4.99E-10	4.19E-10	4.19E-10
Cr	—	—	6.58E-11	2.76E-09	2.76E-09	—	—	1.97E-10	8.28E-09	8.28E-09
Total	1.04E-07	6.35E-07	2.34E-10	2.90E-09	6.38E-07	6.01E-14	3.67E-13	6.98E-10	8.71E-09	8.71E-09

Conclusion

In this study, the total amount for Cu, Pb, Zn, Cd, Ni, and Cr in surface dust in the old urban areas of Guiyang city, including recreational squares, main streets, hospitals, residential areas, and schools, were investigated in terms of their bioaccessibility in different simulated stages and health risk assessment in both respiratory inhalation and hand-to-mouth ingestion exposure pathways. The results indicated that : (1) The total amounts of Cu, Pb, Zn, Cd, Ni, and Cr in surface dust in the old urban area of Guiyang exceeded the background values of Guizhou Province and showing different degrees of pollution, especially the extent of Zn exceeded was more serious, which was 9.71 times of the background value. The coefficient of variation indicated that Pb, Zn, and Cd were mainly disturbed by human activities and external factors. (2) Subsequently, bioaccessibility experiments of heavy metals in dust were conducted in the simulated lung, gastric, and intestinal, the results showed that heavy metals with the highest dissolution in the simulated lung stage, the highest bioaccessibility was Zn (38.97%) and the lowest dissolution was Cr (3.81%). In the gastric phase, the highest bioaccessibility was Ni (46.16%) and the lowest dissolution was Cr (4.19%). In the intestinal phase, the highest bioaccessibility was Cu (53.62%) and the lowest dissolution was Cr (3.09%). (3) Thirdly, a linear fit was performed between the total amount for heavy metals in dust and the bioaccessible amount of Pb and Zn in different simulation stages, finding that there was only the bioavailability of Pb and Zn appearing a better correlation with the total amount in the simulated lung and gastric phases. In the simulated intestine stage, the heavy metals involved in this study had no significant correlation with the total amount, it showed that the total amount of heavy metals alone cannot predict the human intake of heavy metals in the dust. (4) The results of health risk assessment based on bioaccessibility showed that the non-carcinogenic and

carcinogenic risks for children were higher than those of adults under both hand-to-mouth intake and respiratory inhalation exposure pathways, and the non-carcinogenic and carcinogenic risk values for Cu, Pb, Zn, Cd, Ni, and Cr did not exceed the limits, indicating that the health risks of children and adults in this region were within acceptable limits, although the non-carcinogenic and carcinogenic risks did not reach risk values, the risk under the hand-to-mouth pathway was higher than those under the respiratory inhalation pathway so that people living in this urban area need to take certain protective measures. This research suggested that an assessment of the quality of the urban environment is necessary for more rational risk management of heavy metals in the city.

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Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Authors Contributions

Yu Xinjie conceived the research as the first author; Wang Ji , Cai Xiongfei and Zhang Shuai participated in the guidance of the paper; Li Ding verified the correctness of the theoretical analysis and guided the smooth progress of the experiment; Zhao Shuai and Xu Die measured the content of heavy metals in dust and operated in vitro simulation experiment.

Competing Interests

Not applicable

Availability of data and materials

Data available

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