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Original Research

Levels, Risk and Sources of Heavy Metals in Road Dust from University Campus - A Case Study of Xichang, Southwest China

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Abstract

As the place where students live for the longest time, the levels, sources and health risks of heavy metals in road dust from university campuses have not been widely studied. In the present study, 41 road dust samples were collected and analyzed by ICP-MS for Zn, V, Pb, Cr, Ni and Cu. The isotopic composition of Pb was analyzed by MC-ICP MS. These heavy metals were specifically analyzed using enrichment factor, geoaccumulation index, principal component analysis, iso-sources model and health risk assessment model. Zn and Pb pollution levels were high in road dust, and they were defined as moderate enrichment and contaminated. The sources of Pb in road dust from university campus were traffic exhaust, steel smelting, soil, and fly ash, accounting for 59.4%, 23.2%, 12.2%, and 5.2%, respectively. The non-carcinogenic risk of female and male university students is safe, but the carcinogenic risk of Cr needs to be concerned by the authorities.

Keywords: pollution level, Pb isotope, source, health risk, University campus

Introduction

Air pollution, which is one of the environmental problems that most countries in the world need to face. Over the past decade, economic growth in developing countries has been accompanied by worsening air pollution, and high levels of air pollution increase risk of mortality [1]. Dust is not only an important link between the atmosphere, water and soil, but also act as a carrier of heavy metals [2, 3]. Heavy metals in dust are known to be of particular concern because they are toxic and nondegradable, and long-term exposure may have adverse effects on human health. Heavy metals such as lead, mercury, cadmium and arsenic account for 40% of the 10 major chemicals of public health concern, according to the World Health Organization reports (WHO). Men et al. indicated that two heavy metals, nickel and chromium, were classified as Level-1 carcinogens [4]. These heavy metals in dust can be enter the human body via direct inhalation, ingestion and dermal contact absorption [5].

Principal component analysis (PCA), positive matrix factorization (PMF) and multivariate curve resolution-weighted alternating least squares (MCR-WALS) are commonly used for source identification of heavy metals [6]. However, these methods are qualitative

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or semiquantitative analysis of the sources of heavy metals, it is difficult to have a quantitative analysis. Lead isotope tracer technique provides a very useful help to identify the source of lead in environmental media accurately and quantitatively [7, 8].

Considering the environmental risks of heavy metals in dust, many international studies have been conducted in recent years on the levels, distribution characteristics, source identification of heavy metals in dust from urban roads [9, 10], mining roads [11], highways [12], rural highways [13, 14], kindergartens and young pupils roads [15, 16], as well as ecological and human health risk hazards. These studies usually use PCA or PMF, and other methods to analyze the sources of heavy metals in sample dust. For example, Men et al. identified that road dust in Beijing mainly derived from traffic exhaust, fuel combustion, construction, and the use of pesticides and fertilizers [10], but they could not determine the specific sources of typical elements. The inability to provide managers with more detailed sources of pollution has hindered the authorities from implementing pollution prevention and control. As a result, the methods of allocation of these sources remain limited. Recently, an increasing number of studies used Pb isotopic fingerprinting to investigate the pollution sources of dust, $PM_{2.5}$, etc. [17-19]. This is due to the heavier mass of Pb, which undergoes almost no fractionation during the environmental process, retaining the inherited characteristics of their source [20, 21]. Therefore, the Pb isotopic signature has been considered an ideal tool for tracing sources of road dust.

Unfortunately, these studies often ignore a special functional area, that is the university campus. It may be that the public generally believes that university students are already adults, but ignores the fact that their bodies are still growing up. University students spend more than 8 months of the year on university campuses in China. Furthermore, physical and cultural activities further increase the risk of exposure to campus dust. Therefore, the level of heavy metals in dust on university campus is an important environmental issue, and the potential harm caused to university students should be taken seriously.

Xichang, a tourist and mining city, has the only university here. To date, no studies have been conducted on the source and health risks posed by heavy metals in dust at the university. Our study focused on the health risks of heavy metals in road dust on the campus of a local university for male and female students, while precisely quantifying the sources of specific Pb elements by using isotope tracing technology. This will give local officials detailed evidence for Pb pollution control. Therefore, this study aimed to assess: (1) to the concentration levels of six heavy metals, i.e., V, Cr, Ni, Cu, Zn, and Pb; (2) to the pollution level of heavy metals was calculated by calculating different pollution indexes, i.e., enrichment factor, geoaccumulation index, and potential ecological risk; (3) to identify the possible sources of heavy metals by the Principal Component Analysis (PCA) and Pb isotopic fingerprinting; (4) the carcinogenic and non-carcinogenic health risks caused by heavy metals in university dust samples.

Materials and Methods

This research was conducted in Xichang city, Sichuan Province, southwest China. The university campus studied is located in Anning Town, Xichang city, with a total of more than 20,000 students and 1,300 teachers. In November 2021, a total of 41 road dust samples were collected from the university campus (Fig. S1). Road dust of different weights form the road was collected with a brush (sweep area of 1 m^2 per sample), each brush is disposable to avoid cross contamination. All samples were stored in polythene bags and transported to the laboratory immediately where they were air-dried at room temperature and screened with a 200-mesh nylon. Finally, a portion of each sample (0.1000 g) was fully digested by the HNO_3 (UP)-HF (UP) system [8] for the analysis of V, Cr, Ni, Cu, Zn, and Pb. In brief, a mixture of HNO_3 and HF was used to digest the sample, and the second step is to removed HF twice on a heating plate at 120ºC, and then the solution was filtered through a 0.45 μm water system filter, and finally the volume was fixed to 10 mL for testing. An Inductively Coupled Plasma Mass Spectrometry (ICP-MS, PE-2000, USA) analysis device was used to measure the heavy metals. The detection limits for V, Cr, Ni, Cu, Zn and Pb are shown in Table S1. The analysis of Pb isotopes was performed according to the method of Wang et al. [8]. The NBS981 standard was analyzed and obtained the following results $^{206}Pb/^{204}Pb = 16.9400$ (±0.0005 2σ), $^{207}Pb/^{204}Pb = 15.4958$ (±0.0005 2σ), and $^{208}Pb/^{204}Pb = 36.7200$ (±0.0018 2σ).

For the quality control, a representative soil reference standard (GBW07404a), an analytical blank, a reagent blank (Table S2), and 10% duplicate sample were included in each digestion batch of digestion.

The pollution index enrichment factor (*EF*) and geoaccumulation index (I_{geo}) were calculated, which were used to evaluate the enrichment degree and pollution level of the heavy metals in road dust from campus. The *EF* of the elements of the road dust samples was calculated using Mn as the reference element [22]. *EF* and I_{geo} were calculated according to Eq. (1) and Eq. (2), where C and B are the concentrations of the studied element q and the reference element k, in the sample and in the background, respectively. The background value of heavy metals in soil of Panzhihua city was referenced from Zhao et al [23] and listed in Table 1. *EF* and I_{geo} classes [24] are presented in Table S3 and Table S4, respectively.

The potential ecological risk (RI), average daily dose (ADD), hazard quotient (HQ), hazard index (HI), carcinogenic risk (CR) and total carcinogenic risk (TR) of the campus road dust were calculated. RI was calculated according to Eq. (3), where T_q^i is the toxic

Table 1. Descriptive statistics of heavy metal concentration (mg/kg) in road dust (n = 41) of campus and related background values.

Elements	V	Cr	Ni	Cu	Zn	Pb
Min	106.1	30.8	17.4	36.4	64.0	4.8
Max	715.0	374.0	69.0	531.3	2682.8	286.7
Median	340.7	172.3	31.2	94.0	531.6	92.6
Mean	348.4	167.4	31.8	129.2	831.8	105.4
SD	149.7	74.1	10.1	94.4	681.7	71.1
CV (%)	43.0	44.3	31.9	73.1	82.0	67.5
95% UCL	395.7	190.8	35.0	159.0	1047.0	127.8
Background value [23]	179	273	92.8	49.2	165	23.6
Campus dust, Xi'an city [2]	70.9	145.1	35.8	93.5	665.9	158.6
Campus dust, Guiyang city [29]	-	140.4	47.3	68.2	123.8	45.3
Campus dust, Beijing city [30]	-	85.1	34.0	82.4	308.3	54.0
Campus dust, Wuhan city [31]	-	46.0	22.7	70.2	47.2	83.5
Dust, Panzhihua city [32]	4280	1185	79.6	135	4194	170
Dust, Zhuzhou city [33]	-	115	-	98	-	254
Dust, Huainan city [34]	-	61.1	-	36.3	-	42.6
Dust, Guilin city [35]	-	123.3	30.6	149.4	391.3	123.9

SD: standard deviation, CV (%): coefficient of variance, UCL: upper control limit.

response factor. ADD was calculated according to Eq. (4), where C is the sample concentration, which is the upper control limit of 95%, R is the ingestion rate, EF is exposure frequency, ED is the exposure duration, BW is the body weight, and AT is the average lifetime. Inhalation and dermal contact routes are usually lower than ingestion routes [25], so we will only calculate the ingestion routes in this study, namely ADDing. HQ and CR were calculated according to Eq. (5) and Eq. (6), where RfD and SF are reference dose and slope factor, respectively. HI and TR were calculated according to Eq. (7) and Eq. (8), where total noncarcinogenic risk and carcinogenic risk of all heavy metals through the ingestion pathway, respectively. All reference values are shown in Table S5.

$$EF = \frac{\left(\frac{C_q}{C_k}\right)_{sample}}{\left(\frac{B_q}{B_k}\right)_{background}} \quad (1)$$

$$I_{geo} = \log_2\left(\frac{C_q}{C_k \times 1.5}\right) \quad (2)$$

$$RI = \sum_q^7 E_q^i, and\ E_q^i = T_q^i \times \left(\frac{C_q}{B_q}\right) \quad (3)$$

$$ADD_{ing} = \frac{C_q \times R_{ing} \times EF' \times ED \times 10^{-6}}{BW \times AT} \quad (4)$$

$$HQ = \frac{ADD_{ing}}{RfD} \quad (5)$$

$$CR = ADD_{ing} \times SF \quad (6)$$

$$HI = \sum_q^7 HQ \quad (7)$$

$$TR = \sum_q^7 CR \quad (8)$$

The principal component analysis (PCA) is an effective tool for determining the potential sources of heavy metals in road dust [26, 27]. Kaiser-Meyer-Olkin (KMO) checksum significance analysis was performed for the samples, and the result was KMO = 0.73>0.5, p<0.05. In this study, SPSS 21.0, Minitab 19 and Origin 2022 were used for data processing, statistical analysis and mapping.

Results and Discussion

Heavy Metal Concentration and Pollution Characteristics

Table 1 lists the concentration of V, Cr, Ni, Cu, Zn, and Pb in road dust of campus from Xichang University. The mean concentration of Zn in road dust of campus is 831.8 mg/kg, followed by V (348.4 mg/kg), Cr (167.4 mg/kg), Cu (129.2mg/kg), Pb (105.4 mg/kg), while the lowest concentration was Ni (31.8 mg/kg). The median and mean of these heavy metals were 3.22 and 5.04, 1.90 and 1.95, 0.63 and 0.61, 1.92 and 2.63, 3.92 and 4.47, 0.34 and 0.34 times of the soil background [23] values, respectively. According to the coefficient of variation (CV), Han et al. suggested that the variation of CV is proportional to anthropogenic interference, which means that CV≤15% of heavy metals is classified as low variation, while CV>35% is classified as high variation, and 15%-35% is classified as moderate variation [28]. The heavy metals of V (CV:43.0%), Cr (CV:44.3%), Cu (CV: 73.1%), Zn (CV: 82.0%), and Pb (CV: 67.5%) showed high variation, while Ni (CV:31.9%) showed moderate variation.

The concentration of element in road dust from the Xichang campus has been compared with road dust data from 3 other campuses in China (Table 1). It can be seen from this study that the heavy metal composition of campus road dust samples varies significantly among different universities. Specifically, the concentration of Ni was relatively low, while the concentration of other elements was higher than that of universities in Xi'an, Guiyang and Beijing. However, all heavy metal concentrations in this study were higher than those in the Wuhan university cluster. In addition, the concentrations of heavy metals in road dust were compared with those in tourist cities (e.g., Guilin city) and mining cities (e.g., Panzhihua city, Zhuzhou city, and Huainan city). Obviously, the concentration of heavy metals in road dust of this study area was significantly lower than that in Panzhihua city, a mining city adjacent to Xichang city. The concentrations of Cu and Cr of road dust in the study area were higher than the concentrations in other industrial cities, such as Zhuzhou city and Huainan city. For tourist city, the concentrations of Cr, Ni, and Zn of road dust in the study area were significantly higher than the concentrations in Guilin city. This may be attributed to the accumulation of heavy metals caused by local industrial activities and vehicle transport.

The pollution index *EF* and I_{geo} of heavy metals in road dust from campus were calculated to explore whether these elements were caused by natural or anthropogenic sources (Fig. 1). The mean EF values of the elements in descending order were Zn (3.35)>Pb (2.94)>Cu (1.87)>V (1.32)>Cr (0.44)>Ni (0.27). The mean *EF* value of less than 1 for Cr and Ni that means they are from a natural source, while the mean *EF* value of more than 1 for Zn, Pb, Cu, Cd and V that implied influences by human activities. The max *EF* values were for Zn and Pb (9.39 and 8.20, respectively) and have been attributed to anthropogenic sources. The mean of I_{geo} decreased in the order of Zn (1.20)>Pb (1.10)>Cu (0.51)>V (0.23)>Cr (-1.45)>Ni (-2.19). Similar to *EF* index, the mean I_{geo} of Zn and Pb were pointed to moderate pollution (I_{geo}>2), their max I_{geo} values were 3.44 and 3.02, respectively. However, the mean I_{geo} of Cr and Ni were less than 1, which were classified as uncontaminated. According to the calculation of E_q^i, the values of E_q^i in heavy metals are in the following order: Pb (22.33)>Cu (13.13)>Zn (5.04)>V (3.89)>Ni (1.71)>Cr (1.23). Overall, the RI value was 47.33 (RI<140), indicating that the potential ecological risk was low.

Source Identification

Table S6 shows that there are three main factors for road dust cluster analyses that explained 91.4% to the total variance. PC1, explaining 33.1% of the total variance, that dominated by Zn (0.874) and Pb (0.893) with the positive loadings. In this study, Zn and Pb showed high concentrations and pollution levels, and the correlation analysis (Fig. S2) presented that Zn and Pb have an extremely strong correlation (r = 0.918), we concluded that PC1 is an anthropogenic source. Numerous reports suggest that Zn and Pb in road dust come from the vehicle emissions [36-38]. PC2 was dominated by Ni (0.946) and Cu (0.800), explained 29.6% of the total variance. The Cu is often used in coating, paint, pigment, car radiators or lubricants [39, 40]. The field survey shows that the sampling points with higher Cu level are the locations of automobile service engineering and fine arts majors in the university, respectively. However, in the case of

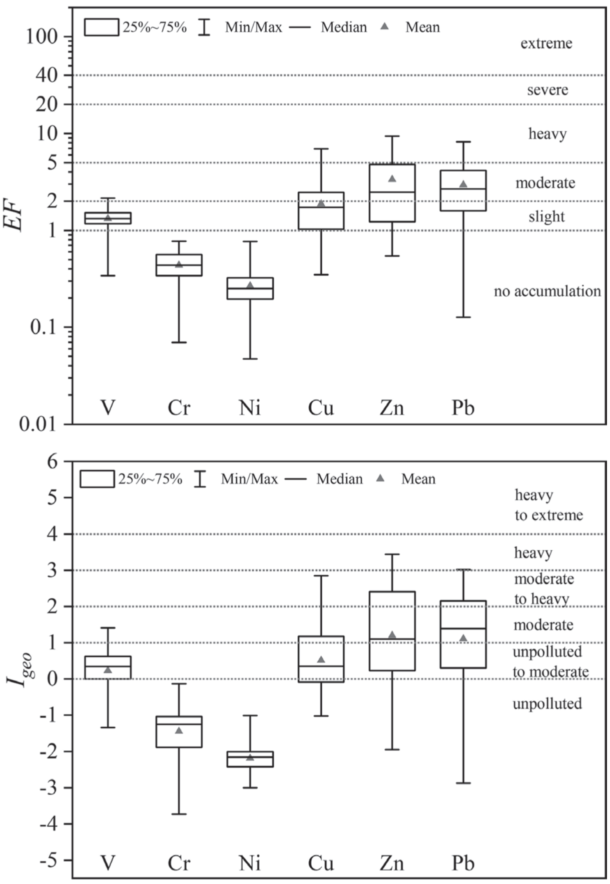

Fig. 1. Box-Whisker plot of *EF* and I_{geo} index for the heavy metal in road dust of campus.

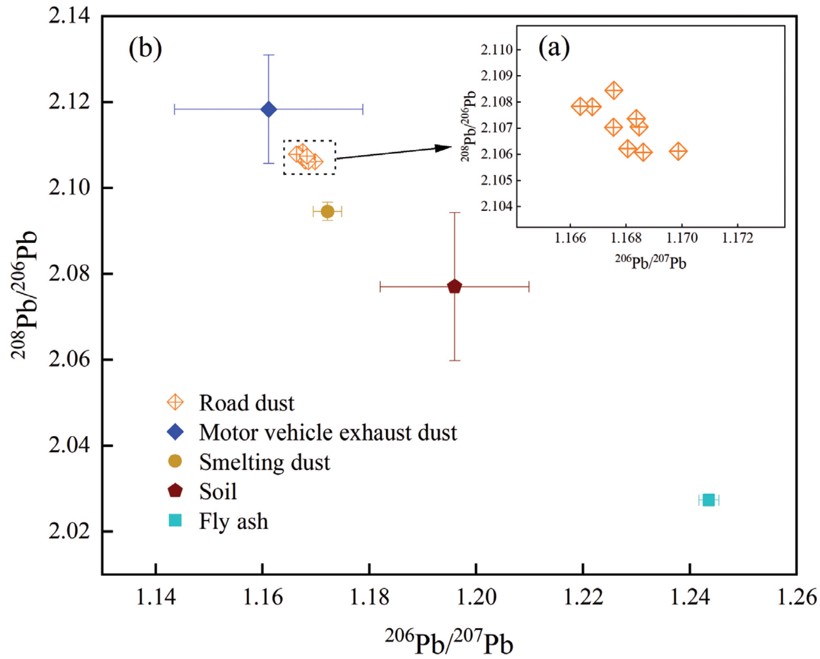

Fig. 2. Lead isotope ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) compositions from road dust and end members. Motor vehicle exhaust dust, Smelting dust, Soil and Fly ash [7].

Ni, it is considered to be from natural sources because it does not reach the level of contamination. Therefore, PC2 should be considered as a mixed source of natural sources and pigments, paints, car repairs, etc. PC3, is mainly loaded by V and Cr, explaining 28.7% of the total variance. This is also evidenced by the positive correlation between V and Cr (0.683). One study has reported that V mainly comes from the local soil [41], which is consistent with this study. Consequently, PC3 was interpreted as a natural source.

Considering that Pb was the only heavy metal with specified concentration limits in ambient air quality standards (AAQS), and the concentration of Pb was high (see Table 1) in this study. Thus, isotope tracing technology was used to quantitatively resolve the potential source of Pb. Fig. 2a) show that the ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ varied between 1.1664 and 1.1699 (average: 1.1680±0.0010) and between 2.1061 and 2.1085 (average: 2.1071±0.0008). In general, natural lead has a high $^{206}Pb/^{207}Pb$ ratio (> 1.2), while artificial lead has a $^{206}Pb/^{207}Pb$ ratio ranging from 0.96 to 1.2 [42]. The lead isotope ratio of the collected campus samples is obviously within the range of artificial factors deposition. As a result, the samples taken were significantly contaminated. In addition, lead isotope ratios of road dust in Panzhihua city and Hangzhou city were compared. In Panzhihua city, the ratio of $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$ (1.165-1.198 vs 2.084-2.110) of road dust has a wider range than the current study, while the ratio $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$ (1.170-1.174 vs 2.087-2.096) ratio of road dust in Hangzhou city is close to the current study [32, 43]. Therefore, this change

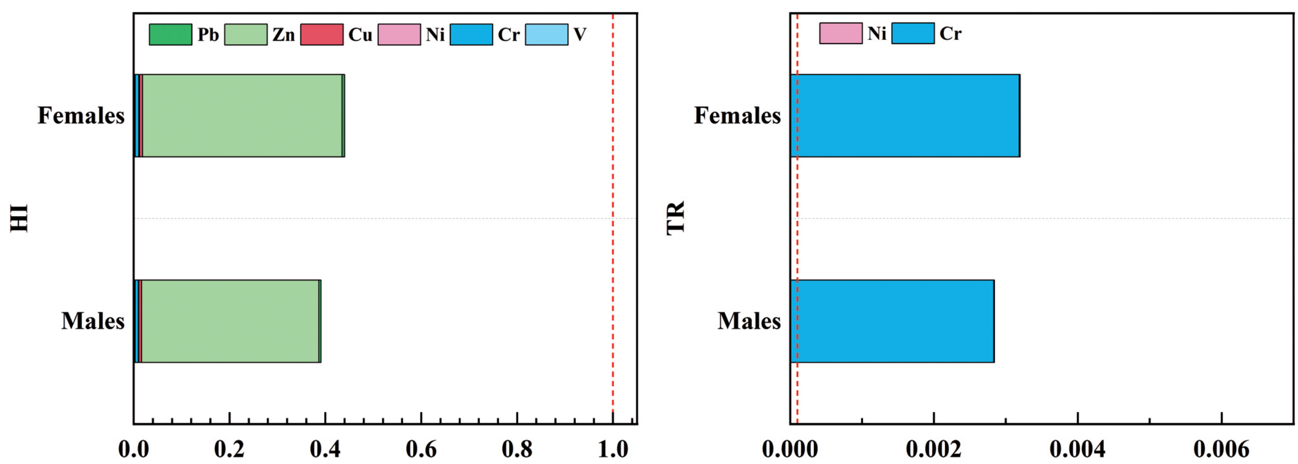

Fig. 3. Health risk assessment of heavy metals in road dust for females and males from university campus.

of lead isotope can effectively trace the source of Pb. Field investigations showed that motor vehicle exhaust dust, smelting dust, soil and fly ash were identified as potential sources of lead. Fig. 2b) show that the road dust samples from campus are relatively closer to motor vehicle exhaust dust, followed by smelting dust. In contrast, it is far away from the fly ash. This trend indicates that automobile exhaust is the domination source of Pb in road dust of campus. Iso source software (EPA. US, 1.3.1 Version) [44] was used to calculate the contribution of potential sources, resulting in 59.4% contribution from motor vehicle exhaust, 23.2% from smelting dust, 12.2% from soil, and 5.2% from fly ash.

Health Risk Assessment

Fig. 3 shows the health risk values of heavy metals for university students (females and males) on campus. For HQ effects of road dust from campus, the order of HQ of heavy metals for both females and males were Zn>Cr>Cu>Pb>V>Ni. The HI values of all heavy metals from road dust for females (HI = 0.44) and males (HI = 0.39) were lower than 1, pointing that the HI of heavy metals in university of Xichang was acceptable. For the CR effects of road dust from university campus, the order of CR of heavy metals for both females and males were Cr>Ni. The TR values of Cr from road dust for females (TR = 3.20E-03) and males (TR = 2.84E-03) were higher than 1E-04, showing that the TR of heavy metals in university of Xichang was unacceptable. It should be noted that the concentration of heavy metals from campus road dust in this study was 95% upper limit, which may lead to uncertainty in the evaluation.

Conclusions

This study focused on the pollution levels, source identification and health risk assessment of students (females and males) of heavy metals in road dust from university campus. Road dust from university campus had higher concentrations of heavy metals (except for Cr and Ni) compared to the local soil background values. Zn (EF = 3.35, I_{geo} = 1.2) and Pb (EF = 2.94, I_{geo} = 1.1) showed moderately enriched and moderately contaminated, which may be hazardous to the campus environment. Based on PCA analysis three sources are identified, namely traffic sources (33.1%), mixed source of pigments, paints, and car repairs (29.6%) and natural sources (28.7%). Lead isotope analysis showed that Pb in road dust of university campus mainly from traffic exhaust (59.4%), steel smelting (23.2%) and soil (12.2%). The non-carcinogenic risk among students (females and males) on university campus is negligible, however the carcinogenic risk of Cr (TR is 3.20E-03 and 2.84E-03 for females and males) require vigilance.

In this study, high-precision isotopic tracing was only carried out for Pb element. Further research is based on the analysis of multiple isotopes (e.g., Zn, Cd, Cu, etc.), which can make the source of pollution clearer. We suggest that local authorities should pay proper attention to changes the concentration in heavy metals from campus road dust and carry out appropriate monitoring. With the rapid development of new energy vehicles (NEVs), we also advocate using NEVs or taking public transportation to commute, which can reduce the accumulation of heavy metals.

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Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Material

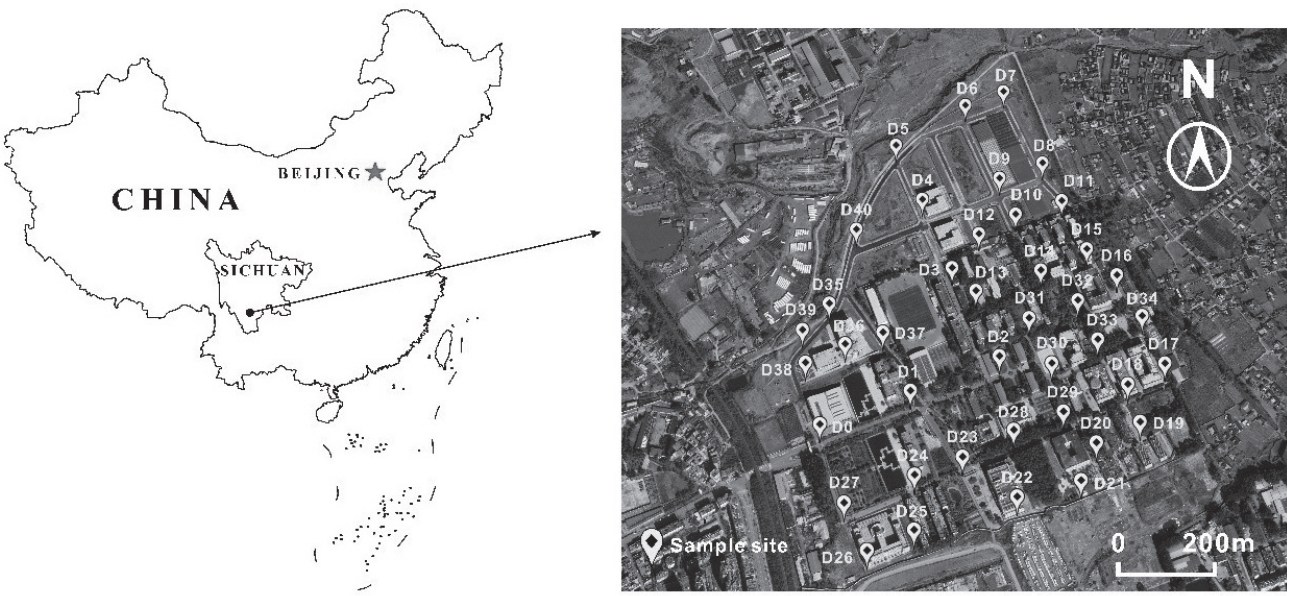

Fig. S1. Location of sampling sites in campus of Xichang city.

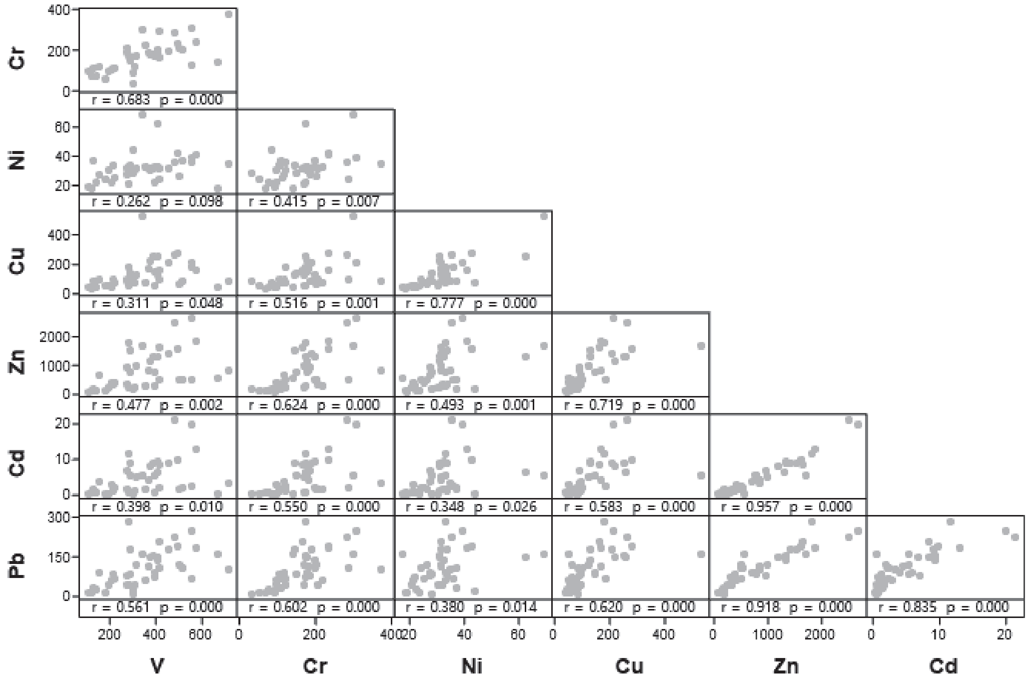

Fig. S2. Matrix map of heavy metals in road dust from campus.

Table S1. The detection limits of heavy metals are shown in Table S1

Element	Detection limit (ppm)
V	0.015
Cr	0.122
Ni	0.106
Cu	0.024
Zn	0.065
Pb	0.010

Table S2. The results of determined certified reference materials GSS-4a and reagent blank (mg/kg).

	V	Cr	Ni	Cu	Zn	Pb
Standard values of GSS-4a	125±6	81±4	36±2	43±2	92±3	37±3
GSS-4a-1	128.639	81.682	37.486	45.506	115.475	36.222
GSS-4a-2	128.076	81.815	37.551	44.480	113.260	35.974
Reagent blank-1	0.174	1.783	0.583	0.528	0.000	0.269
Reagent blank-2	0.110	1.825	0.607	0.522	0.000	0.288

Table S3. The classification of *EF*.

Class	Range	Classification
1	<0	Unpolluted
2	0-1	Unpolluted to moderate
3	1-2	Moderate
4	2-3	Moderate to heavy
5	3-4	Heavy
6	>4	Heavy to extreme

Table S4. The classification of I_{geo}.

Class	Range	Classification
1	<0	Unpolluted
2	0-1	Unpolluted to moderate
3	1-2	Moderate
4	2-3	Moderate to heavy
5	3-4	Heavy
6	>4	Heavy to extreme

Table S5. Parameters used in the health-risk model.

	Unit	Males	Females
IR	mg/day	30	30
EF	day/year	270	270
ED	years	4	4
AT	day	365*ED	
BW	kg	62.8	55.8
RfD	mg/(kg*d)	Ni = 0.01 Cr = 0.01 Pb = 0.01 Cu = 0.01 Zn = 0.001 V = 0.054	
SF	(kg*d)/mg	Ni = 0.84 Cr = 42	

Table S6. Rotation composition matrix of the heavy metals

	Composition		
	1	2	3
V	0.231	0.061	**0.915**
Cr	0.332	0.298	**0.790**
Ni	0.131	**0.946**	0.166
Cu	0.494	**0.800**	0.146
Zn	**0.874**	0.339	0.285
Pb	**0.893**	0.185	0.356
% of variance	33.1	29.6	28.7
Explained % of cumulative	33.1	62.7	91.4