Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Contamination assessment of copper, lead, zinc, manganese and nickel in street dust of Baoji, NW China

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ARTICLE INFO

Article history: Received 30 January 2008 Received in revised form 1 April 2008 Accepted 15 April 2008 Available online 22 April 2008

Keywords: Heavy metal Contamination assessment X-ray fluorescence Street dust

ABSTRACT

Street dusts collected from Baoji, NW China were analyzed for Cu, Pb, Zn, Mn and Ni by using PANalytical PW-2403 wavelength dispersive X-ray fluorescence spectrometry and assessed the contamination level of heavy metals on the basis of geoaccumulation index (I_{geo}), enrichment factor (EF), pollution index (PI) and integrated pollution index (IPI). The results indicate that, in comparison with Chinese soil, street dusts in Baoji have elevated metal concentrations as a whole. The concentrations of heavy metals investigated in this paper are compared with the reported data of other cities. The calculated results of I_{geo} and EF of heavy metals reveal the order of I_{geo} and EF are Pb > Zn > Cu > Ni > Mn. The high I_{geo} and EF for Pb, Zn and Cu in street dusts indicate that there is a considerable Pb, Zn and Cu pollution, which mainly originate from traffic and industry activities. The I_{geo} and EF of Mn and Ni are low and the assessment results indicate an absence of distinct Mn and Ni pollution in street dusts. The assessment results of PI also support Pb, Zn and Cu in street dusts presented serious pollution, and IPI indicates heavy metals of street dust polluted seriously.

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1. Introduction

Street dust, particles deposited on a road, originates from the interaction of solid, liquid and gaseous materials produced from different sources [1]. Components and quantity of street dust are environmental pollution indicators [2]. Street dust receives varying inputs of heavy metals from a variety of mobile or stationary sources [3,4], such as vehicular traffic, industrial plants, power generation facilities, residential oil burning, waste incineration, construction and demolition activities and resuspension of surrounding contaminated soils [4], and makes a significant contribution to the pollution in the urban environment. Therefore, the study of street dust is important for determining the origin, distribution and level of heavy metal in urban surface environments.

Many studies on street dust have focused on trace metal elements concentration, distribution and source identification in the last decades [5–17]. While numerous studies of heavy metal contamination of street dust have been carried out in developed countries [16–19], only limited information is available on heavy metals of street dust for developing countries [1], including China

* Corresponding author at: School of Tourism and Environment, Shaanxi Normal University, Xi'an 710062, PR China. Tel.: +86 29 85310525; fax: +86 29 85303883. *E-mail address:* luxinwei@snnu.edu.cn (X. Lu). [2,13,14]. Elevated levels of trace metal contents are ubiquitous in urban settings as a result of a wide range of human activities [13]. As a consequence, the adverse effects of poor environmental conditions on human health are most evident in urban environments, particularly in developing countries where urbanization, industrialization and rapid population growth are taking place on an unprecedented scale.

Baoji, one important industrial city in Northwest China, has experienced a rapid urbanization and industrialization in the last decades. The rapid growth of industry, population and vehicle exerts a heavy pressure on its urban environment. The main objective of this initial study was to determine the concentration of heavy metals in street dust samples collected from Baoji city and to assess their contaminated level.

2. Materials and methods

2.1. Study area

Baoji $(33^{\circ}34'-35^{\circ}06'N, 106^{\circ}18'-108^{\circ}03'E)$, the second largest city of Shaanxi province in Northwestern China, is situated at the western end of the Guanzhong (Wei River) valley about 150 km west of the provincial capital city Xi'an. The city spans over 1060 km² with the urban population of approximately 760,000 in 2004, compared with about 350,000 in 1980. Baoji city is surrounded by





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Qinling Mountain in its south and west, Loess Plateau over 800 m above sea level in its north. Only the east is open toward the lower reach of the Wei River, a major branch of the Yellow River in Shaanxi province. The Wei River runs through the city from west to east. The city has high vehicular traffic density: more than 30,000 vehicles/day of which 25% is heavy traffic. The climate is a warm temperate zone continental monsoon climate (hot rainy summers and cold dry winters), the annual average temperature is about 7.6-12.9 °C, the annual sunlight is about 2057 h and the annual precipitation is about 600–700 mm. The main soil type in the investigated area is cinnamon soil with a pH from 8 to 9. The texture analysis of the soil shows that it is loam soil, composed of sand (50.2%), silt (37.3%) and clay (12.5%). The prevailing wind direction is from east to west. The city has 35 industries, that is metallurgy, iron and steel mill, chemical industry, ceramics, textile, construction, cement manufacturing plants, paints, beer and alcohol production plant, paper making, machine manufacturing, electric and electronics, coal-fired power plant and so on. The topographic characteristics of Baoji city acts like a natural barrier avoiding the dispersion of air pollutant (such as atmospheric particles) to the north, the west and the south of city.

2.2. Sampling and analytical procedures

Thirty-eight street dust sampling sites were selected in Baoji city, including industrial areas, heavy and low traffic density areas, commercial areas and residential districts. At every sampling site, about 500 g street dust composite sample was collected by sweeping using polyethylene brush and tray from five to eight points of road/pavement edges during the dry season in February 2006. Thirty-eight street dust composite samples were collected. All collected street dust samples were stored in the sealed polyethylene bags, labeled and then transported to the laboratory.

All the samples were air-dried in the laboratory for 2 weeks, and then sieved through a 1.0-mm mesh nylon sieve to remove refuse and small stones before halving. One half was stored, the other one was then ground – with agate mortar and pestle – carefully homogenized and sieved through 75 μ m nylon mesh. After reduction by repeated quartering, the sample was analyzed as outlined below. All procedures of handling were carried out without contact with metals, to avoid potential cross-contamination of the samples.

Weigh 4.0 g of milled street dust sample and 2.0 g of boric acid and place in the mold, and press into a 32-mm diameter pellet under 30 t pressure. The briquettes were stored in a desiccator. Consequently, the concentrations of Pb, Zn, Cu, Mn and Ni in street dust samples were directly measured by wavelength dispersive X-ray fluorescence spectrometry (XRF, PANalytical PW-2403 apparatus), the relative proportions of dust were determined according to methods [20-22]. Meanwhile, a series of soil, sediment and rock standards were used to calibrate the application. These were the GSS-, GRS- and GSD-series geochemical reference materials (Institute of Geophysical and Geochemical Prospecting, PR China), together with NIST-2709, NIST-2710, NIST-2711 (National Institute of Standards and Technology, USA) and soil standards SO-1, SO-2, SO-3 and SO-4 (Canadian Certified Reference Materials Project) were also used. The analytical precision, measured as relative standard deviation, was routinely between 3 and 5%, and never higher than 8%. Accuracy of analyses was checked using standard and duplicate samples. The quality control gave good precision (S.D. <5%) for all samples.

2.3. Contamination assessment methods

A number of calculation methods have been put forward for quantifying the degree of metal enrichment or pollution in soils, sediments and dusts [23–36]. In the study, geoaccumulation index (I_{geo}), enrichment factor (EF), pollution index (PI) and integrated pollution index (IPI) were calculated to assess the heavy metal contamination level in the street dust.

 I_{geo} was originally used with bottom sediments in Ref. [37]. It is computed by the following equation:

$$I_{\text{geo}} = \log_2 \left[\frac{C_n}{1.5B_n} \right]$$

where C_n represents the measured concentration of the element n and B_n is the geochemical background value of the element in fossil argillaceous sediment (average shale). In the study, B_n is the background content of element n in Chinese soil [38]. The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments. The following classification is given for geoaccumulation index [37]: <0=practically unpolluted, 0–1=unpolluted to moderately polluted, 1–2=moderately polluted, 2–3=moderately to strongly polluted, 3–4=strongly polluted, 4–5=strongly to extremely polluted and >5=extremely polluted.

Enrichment factor (EF) of an element in the studied samples was based on the standardization of a measured element against a reference element. A reference element is often the one characterized by low occurrence variability, such as the most commonly used elements: Al, Fe, Ti, Si, Sr, K, etc. [2,32,33,39–42]. The EF calculation is expressed below as

$$EF = \frac{[C_x/C_{ref}]_{Sample}}{[C_x/C_{ref}]_{Background}}$$

where C_x is the concentration of the element of interest and C_{ref} is the concentration of reference element for normalization. EF values less than 5.0 are not considered significant, because such small enrichments may arise from differences in the composition of local soil material and reference soil used in EF calculations [40]. However, there is no accepted pollution ranking system or categorization of degree of pollution on the enrichment ratio and/or factor methodology. Five contamination categories are recognized on the basis of the enrichment factor: EF < 2 states deficiency to minimal enrichment, EF = 2–5 moderate enrichment, EF = 5–20 significant enrichment, EF = 20–40 very high enrichment and EF > 40 extremely high enrichment [2,40].

Pollution index and integrated pollution index are also commonly used to assess the environment quality [43]. The PI was defined as the ratio of element concentration in the study to the background content of the corresponding element of Chinese soil [38]. The PI of each element was calculated and classified as either low (PI \leq 1), middle (1 < PI \leq 3) or high (PI > 3). The IPI of all measured elements for each sample was defined as the mean value of the element's PI, and was then classified as low (IPI \leq 1), middle (1 < IPI \leq 2) or high (IPI > 2) [43].

3. Results and discussion

3.1. Heavy metal concentration in street dust

The descriptive statistic results of heavy metal concentrations investigated in the studied samples, as well as background values of Chinese soils [38], are presented in Table 1. Table 1 shows the concentrations of Cu, Pb, Zn, Mn and Ni in street dusts of Baoji are higher than the background values of Chinese soils. The arithmetic mean of Cu, Pb, Zn, Mn and Ni in street dusts is 123.17, 408.41, 715.10, 804.18 and 48.83 mg kg⁻¹, respectively. The geometric means of all studied metals are less than their arithmetic means, which are

Table 1

Heavy metal concentrations (mg kg⁻¹) in street dust collected from Baoji city

Element	Minimum	Maximum	Mean	S.D.	GM	Median	Skewness	Reference value [38]
Cu	77.90	259.90	123.17	43.25	117.39	113.40	1.77	22.6
Pb	140.60	1846.60	408.41	295.94	355.23	361.45	3.74	26
Zn	384.90	1778.30	715.10	320.08	664.41	610.93	2.00	74.2
Mn	544.50	2335.80	804.18	368.62	754.26	687.70	2.90	583
Ni	33.30	219.30	48.83	29.97	45.28	42.40	5.28	26.9

117.39, 355.23, 664.41, 754.26 and 45.28 mg kg⁻¹, respectively for Cu. Pb. Zn. Mn and Ni. The maximums of Cu and Zn have been found in the sample from heavy traffic site, while their minimums were detected in dust sample from residential site with less traffic density. The source of Cu and Zn in street dust was indicated by research as tyre abrasion, the corrosion of metallic parts of cars, lubricants and industrial and incinerator emissions [7,44,45]. The maximums of Pb and Mn were found in dust sample collected from industry area with iron and steel mill, coke-oven plant, cement manufacturing plants, and coal-fired power plant, but the lowest concentration was detected in sample from residential site with less traffic density. It may be concluded the sources of Pb and Mn in street dusts of Baoji mainly originated from industrial activities and automotive emissions. Concentrations of Ni in most dust samples were found to be in the range of $33.30-58.8 \text{ mg kg}^{-1}$ which are slightly higher than nickel background value of Chinese soils, except two samples with high content (86.10 and 219.30 mg kg⁻¹). This shows Ni in street dusts mainly originated from natural source.

Table 1 shows all the skewness values of heavy metals are big than unit which means all the elements positively skew towards the lower concentrations, as can also be confirmed by the fact that the median concentrations of these metals are lower than their mean concentrations. So, the geometric means of all heavy metals investigated present more probable content data than the arithmetic means.

It is a common practice to compare mean concentrations of heavy metals in road dusts in different urban environments [11,14,18], although there are no universally accepted sampling and analytical procedures for geochemical studies of urban deposits. In Table 2, concentrations of heavy metals measured in street dusts of Baoji are compared with data reported for other cities [2,8,11,14,18,46–51].

The mean concentration of Cu in street dusts sampled in Baoji (this work) is similar to those sampled in Hong Kong and Oslo, higher than those sampled in Ottawa, Calcutta, Luanda, Tokat and Xi'an, and lower than those sampled in Avilés, Guangzhou, Birmingham, Coventry, Amman and Madrid. The mean concentration

Table 2

A comparison of the heavy metal concentrations $(mg kg^{-1})$ in street dusts in Baoji and other selected cities

City	Cu	Pb	Zn	Mn	Ni	Reference
Ottawa	65.84	39.05	112.5	431.5	15.2	[49]
Hong Kong	110	120	3840	594	28.6	[51]
Avilés	183	514	4892	1661	27.5	[48]
Guangzhou	176	240	586	481	23.0	[14]
Calcutta	44	536	159	619	42	[46]
Birmingham	466.9	48.0	534.0	NA ^a	41.1	[18]
Coventry	226.4	47.1	385.7	NA ^a	129.7	[18]
Luanda	42	351	317	258	10	[47]
Amman	177	236	358	NA ^a	88	[8]
Tokat	38	266	98	415	128	[50]
Xi'an	94.9	230.5	421.4	687	NA ^a	[2]
Oslo	123	180	412	830	41	[11]
Madrid	188	1927	476	360	44	[11]
Baoji	123.17	408.41	715.10	804.18	48.83	This work

^a Not available.

of Pb in street dusts of Baoji is high compared with several cites in the world except for Avilés, Calcutta and Madrid (Table 2). The mean concentration of Zn for street dusts in Baoji is higher than other compared cites except for Hong Kong and Avilés. The Mn concentration in street dusts of Baoji is similar to Oslo, while higher than other cities except for Avilés. On the other hand, the mean concentration of Ni in street dusts of Baoji is similar to Calcutta, Birmingham, Oslo and Madrid, while higher than other cites except for Coventry, Amman and Tokat (Table 2). In general, each city has its own characteristics combination of elemental compositions, and the observed similarities as well as variations may not reflect actual natural and anthropogenic diversities among the different urban settings. Therefore, there is an immediate need to establish a standard procedure to represent and analyze urban samples [14].

3.2. Assessment results of the heavy metal contamination in street dusts

The calculated results of I_{geo} of heavy metals in Baoji street dusts are presented in Fig. 1. The I_{geo} ranges from 1.20 to 2.94 with a mean value of 1.79 for Cu, 1.85 to 5.58 with a mean value of 3.19 for Pb, 1.79 to 4.00 with a mean value of 2.58 for Zn, -0.68 to 1.42 with a mean value of -0.21 for Mn and -0.28 to 2.44 with a mean value of 0.17 for Ni. The mean values of I_{geo} decrease in the order of Pb > Zn > Cu > Ni > Mn. The mean I_{geo} and 76% I_{geo} of Cu falling into class 2 indicates moderately polluted, while 24% I_{geo} between 2 and 3 reveals moderately to strongly polluted. The mean I_{geo} obtained for Pb points to strongly polluted. Percentage I_{geo} of Pb mainly falls into class 2 (37%) and class 3 (55%) showing that lead is moderately to strongly polluted and strongly polluted in street dust. The mean I_{geo} and percentage I_{geo} of Zn reveal moderately to strongly polluted

Ni - H · 2.44Mn - H · 1.42Zn - H · 1.42Pb - H · 5.58Cu - H · 5.58Cu - H · 1.2 · 1.42

Fig. 1. Box-plot of Igeo for heavy metals in street dust of Baoji.

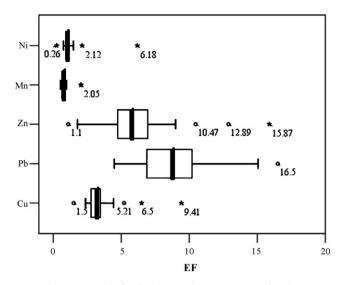


Fig. 2. Box-plot of EF for heavy metals in street dust of Baoji.

and strongly polluted of Zn in street dust, while the mean I_{geo} and percentage of Mn and Ni show that most street dust samples were practically unpolluted and unpolluted to moderately polluted with Mn and Ni.

Enrichment factors of heavy metals were calculated for each street dust sample relative to the background value of the elements in Chinese soil [38], choosing Fe as the reference element. The EF of Cu, Pb, Zn, Mn and Ni is in the range of 1.503–9.410, 4.486-16.500, 1.105-15.873, 0.477-2.050 and 0.257-6.178, with an average of 3.509, 9.025, 6.198, 0.855 and 1.201, respectively (Fig. 2). The mean EF of Cu, Pb and Zn is higher than 3, while the mean EF of Mn and Ni is less than or close to unity. On the other hand, maximum EF of Cu, Pb and Zn is close to or higher than 10, which shows that Cu. Pb and Zn in street dusts mainly originate from anthropogenic sources [52]. It seems, therefore, that EF can also be an effective tool to differentiate a natural origin from anthropogenic sources in the study. The order of mean EF values are Pb > Zn > Cu > Ni > Mn, similar to the order of I_{geo} , which can also be seen as the decreasing order of their overall contamination degrees of street dusts in Baoji. The mean EF (3.509) and 84% EF of Cu in 2-5 indicates Cu of street dusts is mainly moderate contamination, while about 11% sample belongs to significant contamination. Lead has 97% EF between 5 and 20, with mean EF higher than 5, reflecting Pb is significant contamination. Zn has 37% EF and 58% EF in 2–5, and 5–20 respectively, with mean EF higher than 5, indicating significant contamination. Mn and Ni have 95% EF less than 2, revealing the lack of contamination with Mn and Ni as a whole. The analytical results of EF of heavy metals are same as the analytical results of Igeo.

The PIs, calculated according to the background concentration of heavy metals in Chinese soil, vary greatly across the different metals (Fig. 3). Nickel and Mn exhibit lower values, ranging from 1.24 to 8.15 and from 0.93 to 4.01, respectively. For Mn, the mean PI is 1.38 and all of the samples have low- or mid-level PIs except for one sample, indicating that the concentration of Mn in the street dust samples are comparable with the background concentration of Chinese soil and there is no pollution of Mn in Baoji street dust samples. The mean PI for Ni is 1.82, and only two samples is classified as high PI and thirty-six samples are classified as middle PI, indicating an absence of problematic Ni pollution of street dusts in Baoji.

The PIs of Cu, Pb and Zn are much higher since all dust samples contained high PIs, ranging from 3.45 to 11.50, 5.41 to 71.72 and 5.19

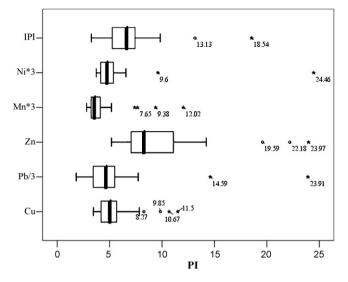


Fig. 3. Box-plot of Pl and IPI for heavy metals in street dust of Baoji.

to 23.97, with mean value of 5.45, 15.72 and 9.64 for Cu, Pb and Zn, respectively. These data indicate that Cu, Pb and Zn of street dust presented serious pollution in Baoji. The IPIs of street dust samples vary from 3.26 to 18.54 with an average of 6.80, indicating that all samples studied presented heavy metal pollution.

4. Conclusion

The concentrations of heavy metal Cu, Pb, Zn, Mn and Ni and their contamination level in street dust collected from Baoji, NW China have been studied in the work. The concentration of Cu, Pb, Zn, Mn and Ni in street dust ranges from 77.90 to 259.90, 140.60 to 1846.60, 384.90 to 1778.30, 544.50 to 2335.80 and 33.30 to 219.30 mg kg⁻¹, with an arithmetic mean of 123.17, 408.41, 715.10, 804.18 and 48.83 mg kg⁻¹, respectively. The concentrations of heavy metals investigated in the work are compared with the reported data of other cities and with the background values of elements in Chinese soil. The results indicate that street dusts in Baoji have elevated metal concentrations as a whole.

The calculated results of I_{geo} and EF of heavy metals reveal the order of I_{geo} and EF are Pb > Zn > Cu > Ni > Mn. The high I_{geo} and EF for Pb, Zn and Cu in street dusts indicate that there is a considerable Pb, Zn and Cu pollution, which mainly originate from traffic and industry activities. The I_{geo} and EF of Mn and Ni are low and the assessment results indicate an absence of distinct Mn and Ni pollution in street dust present serious pollution, and IPI indicates heavy metals of street dusts polluted seriously. These findings indicate that more attention should be paid to heavy metal contamination of street dust in Baoji, especially Pb.

Acknowledgments

The research was supported by the Program for New Century Excellent Talents in University under Grant NCET-05-0861 and the Provincial Natural Sciences Foundation of Shaanxi Province under Grant 2006D14. Appreciation is expressed to Editor Dr. Tay and the anonymous reviewers for their insightful suggestions and critical reviews of the manuscript. Opinions in the paper do not constitute an endorsement or approval by the funding agencies and only reflect the personal views of the authors.

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