Grain-Size Distribution and Chemical Speciation of Heavy Metals in Chinese Street Dust

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Abstract

In order to assess the grain-size distribution and chemical speciation of heavy metals, 34 dust samples were collected in the city of Wuhu. Heavy metals concentrations in street dust of different districts varied greatly. Zn concentration in the traffic district, for example, is more than two times that of other districts, and Cu concentration in the industrial district is more than three times that of other districts. Zn mainly comes from traffic sources, and Cu mainly comes from industrial emissions sources. The highest concentrations of Cu and Cd appeared in the particle size of < 75 μm, and the other heavy metals appeared in the particle size of 96-75 μm. Heavy metals concentrations for different speciation appeared in an increasing trend with a reduction in particle size. Zn and Cd were mainly bound to acid-extractable state. Cr, V, Ni, and Co elements were mainly bound to a residual state. Cu and Pb were mainly bound to an organic state. The grain size fraction loads (GSF_{Load}) of different chemical speciation were mainly high in fine particles. The biological mobility of heavy metals in street dust decreased in the order of Pb (91%) > Cu (85.6%) > Zn (85.24%) > Cd (78.3%) > Co (49.3%) > Ni (39.3%) > V (23.7%) > Cr (20.19%). Bioavailability of Cu emitted from industrial sources was high.

Keywords: surface dust, heavy metals, chemical speciation, grain-size distribution, Wuhu

Introduction

Over the last several decades, heavy metals content in urban street dust has received increasing attention because of the associated health hazards and risks [1-3]. The spatial distribution, accumulation, and environmental effects of heavy metals in dust have been researched [4-9].

The particle size fractions of dust will influence the mobility of heavy metals. The amount of dust inhaled and ingested by humans is usually dependent on grain size. Studies of the particle size fractions of street dust have been conducted since the 1980s [7, 10-14]. Deletic and Orr [12] reported that the max concentrations of heavy metals in Arab street dust appeared in the particle size of 2-63 μm. McKenzie et al. [15] reported that Cr, Ni, Cu, Zn, and Pb were mainly enriched in the fine particle dust of <1.5 μm. But Co and Vi, which come from natural sources, were mainly enriched in coarse sizes of 500-1,000 μm [5-6].

The chemical speciation of heavy metals in street dust decided their activity and bioavailability in the environment. Most metals existed in the speciation of non-residual state, such as organic-sulfide combining and Fe-Mn oxide state [12, 16-17]. Studies mainly focused on the chemical speciation research of heavy

metals in street dust, while little information is available on heavy metals concentration and geometrical shape of the proportion in the different particles. Chang et al. [18] studied particle effect and bioavailability of heavy metals in street dust of Shanghai, and their results showed that the grain-size distribution had little influence on exchange state concentrations of Zn, Pb, Cd, Ni, Cu, and Cr. But the carbonate, Fe-Mn oxide combination, and organic combination concentrations of Cd and Pb were significantly influenced by particle size distribution.

Fang et al. [19] reported that high concentrations of heavy metals appeared on street dust in the city of Wuhu. The main objectives of this study are: 1) to determine the concentrations of acid-extractable, reducible, oxidizable, and residual state of heavy metals in street dust with the BCR sequential extraction procedure by the European Community Bureau of Reference and 2) to discuss grain size distribution and biological activity of heavy metals in Wuhu street dust. The above objectives are useful for both helping the government establish protective measures and to alleviate heavy metals pollution of non-point control.

Materials and Methods

Study Area

Wuhu (118°46′E, 31°20′N) is the subcenter city of Anhui province in the southeast of China, located in the south of the Yangtze River. In order to better study the relationship between human activity and heavy metal distribution characteristic in street dust, the study region was divided into industrial district, business district, traffic district and residential district according to industry layout, traffic flow, human activities and other characteristics in Wuhu city.

Samples Acquisition and Processing

Details of the study area and sampling method can be seen in Fang et al. [19]. Dust samples were collected using a brush and white plastic collection pan. Each brush and pan was used only once or cleaned using acetone. At each sampling site, four sub-samples were collected randomly and then mixed thoroughly to obtain a bulk sample.

Thirty-four street dust samples were collected from four functional districts in Wuhu, including 10 in an industrial district, eight in a residential district, seven in a business district, and nine in a traffic district. Samples were air-dried naturally in the laboratory, debris and small stones were removed using stainless steel tweezers, and then the samples were sieved through 830 μm nylon mesh. Half was used for particle size analysis. Another part of the 250 μm samples was ground with an agate mortar, then carefully homogenized and sieved through 150 μm nylon mesh. The milled samples were used for heavy metals concentration determination by BCR extract steps. Eleven samples were chosen (including traffic district 2, business district 3, residential district 3, industrial district 3) and sieved through 830 μm, 250 μm, 150 μm, 96 μm, and 75 μm nylon mesh, respectively, then the samples were divided into five particle-size levels, including 830-250 μm, 250-150 μm, 150-96 μm, 96-75 μm, and <75 μm. 830-250 μm and 250-150 μm samples were sieved through 150 μm nylon mesh with an agate mortar.

Experimental Analysis

In order to measure the total amount of heavy metals, about 0.2 g of the prepared dust sample was digested with a concentrated HNO_3-$HClO_4$-HF mixture and diluted with 2% HNO_3 to 50 mL. Sequential extraction was performed using a three-stage modified procedure recommended by BCR, which has been used for several studies [20]. The elements chemical speciation were divided into four types: acid-extractable state, reducible state, oxidizable state, and residual state (Table 1). Subsequently, the concentrations of Zn, Pb, Cr, Cu, Ni, Cd, V, and Co were determined by using an inductively coupled plasma-optical emission spectrometer (ICP-OES).

Quality Control

All the containers used during sample analysis were washed with detergent, acid-soaked (10% nitric acid), and then rinsed thoroughly with deionized water. GBW07401 (GSS-1) and GBW07403 (GSS-3) certified reference materials were used to analyze the precise and accurate measurements. The average recoveries of heavy metals in the GSS materials were between 90.6 and 114.1%. Reagent

Table 1. Extracting and analyzing flow of the modified BCR.

Step	Extractant	Sample: solution/g mL^{-1}	Extraction Time	Speciation
1	0.11 mol/L CH_3COOH HOAc	1:40	Oscillate 16 h	Acid-extractable
2	0.l mol/L $NH_2OH·HCL$	1:40	Oscillate 16 h	Reducible
3	8.8 mol/L H_2O_2, pH2-3, 85ºC	1:10	1h, Occasionally oscillate	Oxidizable
	8.8 mol/L H_2O_2, pH2-3, 85ºC	1:10	1h, Occasionally oscillate	
	1 mol/L NH_4OAc, pH = 2	1:50	Oscillate 16 h	
4	HCl-HNO_3-$HCLO_4$	1:10		Residual

blanks and analytical duplicate samples were included to ensure the accuracy and precision of analysis. All chemicals used for metals measurement were guaranteed reagents.

Results and Discussion

Heavy Metals Concentrations in Street Dust

The mean concentrations of heavy metals for 34 street dust samples of Zn (365.25 mg/kg), Cd (2.23 mg/kg), Pb (82.3 mg/kg), Co (9.00 mg/kg), Ni (22.82 mg/kg), Cr (55.19 mg/kg), V (59.92 mg/kg), and Cu (196.83 mg/kg) of Wuhu were low compared with some large and medium-sized cities in China. Zn, Pb, and Cr concentrations affected by traffic activity were lower than those in Shanghai, Beijing, and Baoji [18, 21]. The reason is because the city scale, population density, and traffic flow of Beijing and Shanghai far exceed those of Wuhu. Baoji is a heavy industry city and transportation hub. Heavy metals from traffic and industrial emissions were discharged into an urban environment with particulate matter. Cu concentration in urban street dust in Wuhu was close to the level in Shanghai, and far higher than the level in Baoji and Beijing [18, 21-22], which can be explained by the fact that the automobile industry is the leading industry of Wuhu. Cd concentration in Wuhu dust was obviously higher than the level in Shanghai, caused by the high soil background value of Cd in Wuhu. Therefore, population scale, traffic flow, leading industry, and background value can affect the heavy metals concentrations in urban dust.

Heavy Metals Concentrations in Street Dust from Different Functional Districts

Heavy metal concentrations in street dust from different functional districts in Wuhu are presented in Fig. 1. Zn concentration decreased in the order of traffic district (614.54 mg/kg) > industrial district
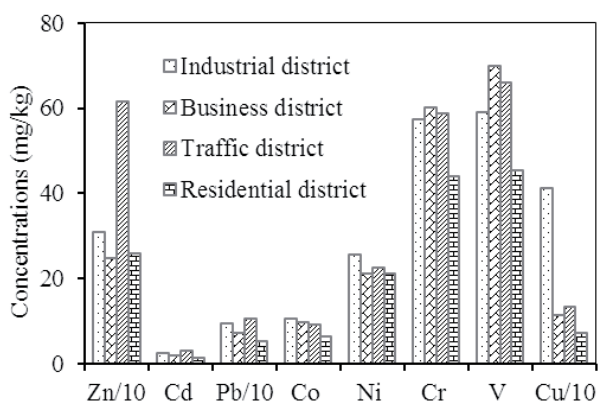
(307.87 mg/kg) > residential district (260.21 mg/kg) > business district (246.72 mg/kg). Zn concentration in the traffic district was more than two times the concentration in other functional districts. The results showed that Zn concentration is mainly affected by traffic activities. Cd and Pb concentrations decreased in the order of traffic district > industrial district > business district > residential district. Pb and Cd concentrations in the traffic district are two times more than those in the residential district. Pb and Cd were also affected by fuel burning release, in addition to traffic emissions. The Cu concentration decreased in the order of industrial district (413.24 mg/kg) > traffic district (134.14 mg/kg) > business district (112.46 mg/kg) > residential district (70.67 mg/kg). Cu concentration in the industrial district was three times more than those in other districts due to Cu released by the process of auto industry production, and meanwhile Cu concentration in industrial district soil was high [23]. Concentrations of Co, Ni, Cr, and V were not significantly different in different functional districts. Cr and V concentrations decreased in the order of business district > industrial district > traffic district > residential district. In addition to Zn, the lowest concentrations of Cd, Pb, Cu, V, Ni, and Co appeared in the residential district, therefore heavy metals concentrations in street dust of the residential district was less affected by human activities. The spatial difference of heavy metals (such as Zn and Pb) affected by traffic source was not significantly different from that of Cu affected by industrial pollution, which is explained by the clear boundary of the centered industrial distribution. With the development of traffic, traffic emissions affect all areas of the city. On the whole, Zn, Pb, Cu, V, and Cr concentrations varied greatly in different functional districts, and Ni, Cd, and Co concentrations have no obvious difference in different functional districts.

Heavy Metal Loadings in Different Particle Size Fractions in Street Dust

The results of grain-size distribution of heavy metals are presented in Table 2. The highest concentrations of Cu and Cd appeared in the particle size of <75 μm, and the highest concentrations of other heavy metals appeared in the particle size of 96-75 μm (Table 2). Variance analysis showed that Co, Zn, and V concentrations in each particle size have no obvious difference in the 5% confidence level. Cd and Cu concentrations in particle sizes of 150-96 μm, 96-75 μm, and < 75 μm were higher than the levels in particle sizes of > 150 μm. Cr, Pb, and Co concentrations in particle sizes of 830-250 μm were obvious difference compared with the other particles. Ni concentration in the particle size of 96-75μm was obviously higher than that in other particle sizes. Overall, the results of grain-size distribution of heavy metals indicated that metals tend to be associated with fine particles. Han et al. [5] reported that heavy metals in the dusts of Baotou were largely accumulated in the particles of <50 μm. Chang et al. [18] reported that heavy metals in street dust of

Fig. 1. Concentrations of heavy metals in street dust in different functional districts of Wuhu city.

Table 2. Concentrations of heavy metals in different particle sizes of street dust (mg/kg).

Particle size	Zn	Cd	Pb	Co	Ni	Cr	V	Cu
830-250 μm	177.03	2.71	66.82	10.00	12.82	26.29	38.28	119.67
250-150 μm	179.87	2.96	77.52	11.04	19.34	32.26	51.35	142.75
150-96 μm	250.08	5.30	100.19	14.30	24.39	50.62	68.68	260.31
96-75 μm	284.12	6.86	110.62	14.28	31.22	56.65	71.57	299.92
<75 μm	282.04	7.27	92.58	13.74	25.55	52.94	64.64	302.15

Shanghai were enriched in particle sizes of 150 μm and 75 μm. Manno et al. [17] reported that most heavy metals in street dust were enrichment in the particle size of 63-125 μm. Different metals have different sources, which lead to different distribution rules in different particle sizes.

The concentrations of Co, Ni, and Cu for industrial sources in different particle sizes were maximum in the industrial district, and have no obvious difference with other districts. Zn concentration in each particle size dust had obvious difference in the traffic district. Zn concentration in fine particles was obviously higher than that in coarse particles in the traffic district, and Zn concentration in the fine particles in traffic district was obviously higher than those in other districts. Zn concentration in different particle sizes had no obvious difference in the residential district and was a little high in coarse particles. Therefore, Zn in the fine particle dust mainly comes from traffic activities, and Zn in coarse particle dust mainly comes from soil weathering. High concentrations of Pb, Cd, and Cr in the particle size of <75 μm appeared in the industrial district, and high concentrations of Pb, Cd, and Cr in other particle sizes appeared in the residential district. The high value of Cr in the particle size of 150-96 μm and 830-250 μm appeared in the traffic district. The metals from transportation sources may easily be loaded in fine particles. Different heavy metals concentrations in the different particles in different functional districts of Wuhu had different distribution characteristics due to their different sources. Cd concentration in different functional districts had obvious differences, which increased with the decrease of particle size. The concentration of Cd in the particle size of 96-75 μm and <75 μm was significantly higher than those in the other particle sizes, and the difference was especially obvious in the traffic and industrial districts. The max concentration of Pb in different particle sizes appeared in the residential district, which indicated that Pb maybe have a complex source, for example car emissions, heating, fuel burning, and other emissions. Cars often drive slowly in residential districts, emitting high amounts of Pb in the process. In addition to the industrial district, the highest levels of all heavy metals appeared in the particle size 95-75 μm. The peak concentrations of heavy metals in the industrial district appeared in the particle size of <75 μm. The difference of Co and V in each particle size was not significant.

Chemical Speciation of Heavy Metals in Street Dust of Wuhu

Chemical speciation of heavy metals in street dust in Wuhu city, calculated by the average of 34 samples, are shown in Fig. 2. Zn and Cd were given priority to an acid-extractable state, with the average concentrations of 168.07 mg/kg and 0.71 mg/kg, accounting for 46.72% and 32.1% to the total, respectively. Reducible concentrations of the two elements were 40%, and the residual concentration was relatively low. Zn speciation distribution decreased in the order of acid-extractable (46.72%) > reducible (21.20%) > oxidizable (17.32%) > residual (14.76%). The speciation distribution of Cd decreased in the order of acid-extractable (32.1%) > oxidizable (24.9%) > residual (21.7%) > reducible (21.3%). Cd distribution in street dust of Wuhu was relatively uniform in different speciation, which may be explained by the fact that Cd has different sources. The residual state of Cd in street dust mainly comes from the earth's crust weathering. The other state may come from coal combustion and tire wear. Cd in the street dust was given priority to oxidizable state (43%). But in Chongqing, Cd in street dust was given priority to exchange state and carbonate combination state [24]. These results showed that the chemical form distribution of the same element have obvious differences because of various sources.

The elements of Cr, V, Ni, and Co from natural sources were given priority to residual state, and a
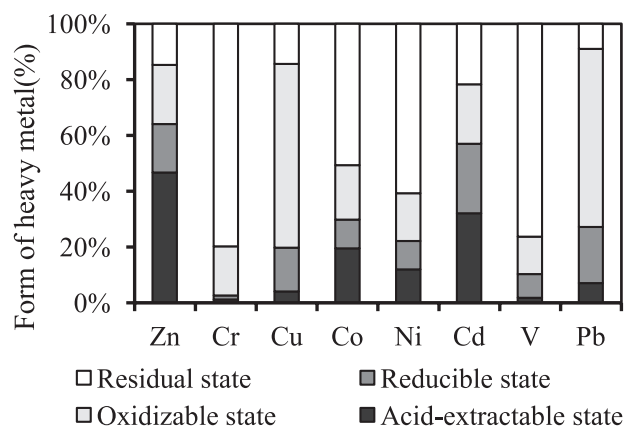

Fig. 2. Heavy metals speciation distribution in urban street dust from Wuhu city.

verage concentrations were 43.69 mg/kg, 44.78 mg/kg, 13.6 mg/kg, and 4.45 mg/kg, respectively. And the ratios to the total were 79.81%, 76.3%, 60.7%, and 50.7%, respectively (Table 3). The distribution trend of Cr and V decreased in the order of residual > oxidizable > reducible > acid-extractable. The distribution trend of Ni and Co decreased in the order of residual > oxidizable > acid-extractable > reducible. Cr was given priority to a residual state belonging to kiss rock elements, easy to form a stable oxygen acid anion, then mainly existing with oxide speciation and usually complexed with silicon dioxide, ferric oxide, and magnesium oxide [25].

Cu and Pb were given priority to oxidizable state, and the average levels were 124.42 mg/kg and 51.68 mg/kg, with the ratios of 65.9% and 63.8% of the total, respectively. The reducible ratios of the total were 15.6% and 20.2%, respectively. The speciation distribution of Cu and Pb decreased in the order of oxidizable > reducible > residual > acid-extractable. Oxidizable had strong ability chelating metal ions, and attached to the surface of the mineral grains with the speciation of oxidizable membrane, which changed the surface properties of mineral grains, then can enhance the adsorbtion ability of heavy metals. Meanwhile, Cu had a strong combination ability with organic matter [26]. The oxidizable state of Cu and Pb were influenced by the emissions of oxidizable clastic, coal, oil, and natural gas incomplete combustion and human activity. Iron and manganese oxide and exchange state of Cu and Pb were influenced by emissions of mechanical processing, electrical power, and the electrical and electronics industries.

Heavy Metals Bioavailability in Street Dust

The activity and bioavailability of heavy metals had a relationship with its soluble and chemical speciation. The residual state is a "stable fraction." The high proportion of the residual state leads to less migration and bioavailability, and a little influence on the environment. Acid-extractable, reducible, and oxidizable states were "labile fraction," and when the labile fraction is high, the migration and bioavailability parts of heavy metals are high, which have a great impact on the environment. The bioavailability coefficient (k) can be calculated by the ratio of the sum of acid-extractable, reducible, and oxidizable states to the total heavy metals concentration.

k in Wuhu street dust decreased in the order of Pb (91%) > Cu (85.6%) > Zn (85.24%) > Cd (78.3%) > Co (49.3%) > Ni (39.3) > V (23.7%) > Cr (20.19%). According to bioavailability coefficients [26], when k < 0.2, heavy metal has stable status. When 0.2 < k < 0.8, heavy metal is relatively stable, but had potential risk, which may pose a threat to human health when the environmental conditions change. When k > 0.8, heavy metal is active for biology. By this standard, Pb, Cu, and Zn were biologically available elements, and Cd (78.3%),

Table 3. Chemical speciation concentrations of heavy metals in street dust of Wuhu (mg/kg; n = 34).

Element	Acid-extractable			Reducible			Oxidizable			Residual			Total	
	Average	Range	Scale (%)	Average	Range	Scale (%)	Average	Range	Scale (%)	Average	Range	Scale (%)	Average	Range
Zn	168.07	1.53-586	46.6	62.39	1.74-291.26	17.3	76.25	24.09-263	21.1	53.21	1.89-156.8	15.0	360.46	132.9-1269
Cr	0.63	0.0032-4.1	1.1	0.76	0.046-2.71	1.4	9.66	3.85-21.86	17.7	43.69	1.26-98.4	79.8	54.74	17.71-102.2
Cu	7.73	0.0096-129.6	4.1	29.50	0.038-654.7	15.6	124.42	13.54-827	65.9	26.95	0.086-31.5	14.4	188.6	28.25-1619.9
Co	1.71	0.017-14.03	19.5	0.90	0.027-2.77	10.3	1.71	0.30-4.15	19.5	4.45	0.0056-9.79	50.70	8.77	2.67-16.6
Ni	2.66	0.033-10.67	11.9	2.28	0.047-13.8	10.2	3.86	1.11-9.89	17.2	13.6	3.76-21.5	60.7	22.4	11.05-46.01
Cd	0.71	0.0019-3.38	32.1	0.55	0.049-2.75	24.9	0.47	0.18-2.84	21.3	0.48	0.0014-1.78	21.7	2.21	0.18-7.78
V	1.09	0.0043-2.2	1.8	4.99	0.22-13.70	8.5	7.84	1.69-21.47	13.4	44.78	1.38-51.6	76.3	58.7	19.1-109.4
Pb	5.70	0.08-37.23	7.0	16.33	0.02-100.60	20.2	51.68	11.26-105	63.8	7.31	0.06-67.4	9.0	81.02	20.2-155.8

Table 4. Average concentrations (AC) and GSF$_{Load}$ of heavy metals speciation in different particle sizes of street dust (mg/kg; n = 11).

Element	Speciation	830-250 μm AC/GSF$_{Load}$	250-150 μm AC/GSF$_{Load}$	150-96 μm AC/GSF$_{Load}$	96-75 μm AC/GSF$_{Load}$	< 75 μm AC/GSF$_{Load}$
Zn	Acid-extractable	45.60/7.25	49.62/12.73	60.55/10.16	51.18/12.74	86.28/57.12
	Reducible	29.66/6.90	36.28/12.32	51.88/10.88	61.07/18.56	58.42/51.34
	Oxidizable	49.92/13.03	39.23/12.37	51.36/11.27	64.28/21.31	59.18/42.02
	Residual	42.86/8.68	37.90/10.95	60.60/12.76	66.33/15.56	76.82/52.05
Cr	Acid-extractable	0.41/15.31	0.46/28.81	0.27/10.81	0.18/9.07	0.25/36.00
	Reducible	1.17/9.18	1.63/28.25	1.08/11.63	1.55/13.57	1.10/37.37
	Oxidizable	10.24/13.73	8.30/14.47	10.49/12.20	11.38/18.86	9.72/40.74
	Residual	14.55/5.88	22.05/11.17	38.62/12.74	43.95/19.15	42.05/51.05
Cu	Acid-extractable	5.46/13.70	8.39/15.11	4.99/18.19	6.28/11.43	0.80/41.57
	Reducible	27.15/15.34	23.32/28.49	0.77/10.74	89.04/17.94	0.92/27.48
	Oxidizable	67.48/9.57	74.67/11.24	136.42/12.98	123.26/18.98	122.90/47.23
	Residual	22.78/6.91	39.57/11.34	121.81/9.74	160.13/18.60	203.60/53.42
Co	Acid-extractable	3.65/12.93	1.74/18.05	1.39/12.27	1.05/13.08	0.94/43.68
	Reducible	1.19/7.59	1.00/17.23	1.10/11.91	1.59/17.85	1.19/45.41
	Oxidizable	1.27/9.40	1.24/12.70	1.96/12.60	2.07/19.17	2.00/46.12
	Residual	4.34/6.27	7.22/15.38	9.90/12.88	10.17/18.00	9.98/47.48
Ni	Acid-extractable	1.46/10.86	1.32/16.27	1.67/13.66	1.40/14.57	1.47/44.64
	Reducible	1.64/6.83	2.71/19.68	2.29/14.89	4.12/17.92	2.54/40.68
	Oxidizable	2.32/9.76	3.99/18.93	3.15/10.82	3.52/18.16	3.14/42.33
	Residual	7.69/5.81	11.24/13.88	17.01/12.09	22.34/19.83	18.73/48.39
Cd	Acid-extractable	0.27/9.19	0.31/12.16	0.40/10.12	0.53/16.14	0.56/52.39
	Reducible	0.29/10.40	0.31/11.72	0.40/10.89	0.55/15.49	0.52/51.50
	Oxidizable	0.53/13.24	0.47/11.85	0.67/11.26	0.79/19.22	0.74/44.43
	Residual	1.51/27.15	1.56/4.30	3.43/6.93	4.55/9.75	5.19/51.87
V	Acid-extractable	0.32/5.98	0.43/9.60	1.32/17.68	0.53/13.10	1.33/53.65
	Reducible	6.36/14.13	6.90/23.19	5.85/10.24	6.82/15.54	4.94/36.91
	Oxidizable	8.99/14.66	7.37/16.96	8.13/11.27	8.74/18.27	7.21/38.85
	Residual	23.40/6.49	37.26/14.77	54.27/13.23	56.67/18.44	52.56/47.08
Pb	Acid-extractable	1.89/10.77	6.44/20.87	2.90/12.17	1.60/10.08	3.20/46.10
	Reducible	19.35/11.25	32.65/22.61	6.35/4.08	19.87/17.05	15.52/45.01
	Oxidizable	37.32/12.69	30.43/11.44	59.73/13.16	63.00/20.91	44.51/41.80
	Residual	17.68/9.68	10.40/7.56	32.97/13.83	32.37/17.72	36.02/51.21

Co (49.3%), and Ni (39.3%) were potential biologically available elements.

Wang et al. [22] reported the overall migration order of heavy metals in street dust of Baoji as: Cd (90.11%) > Pb (82.33%) > Zn (79.32%) > Cu (62.35%) > Co (29.02%) > Ni (23.62%) > Cr (18.68%). The bioavailability of heavy metals in street dust of Kayseri decreased in the order of Cd (93.3%) > Zn (83.8%) > Pb (77.2%) > Co (75.9%) > Ni (60.1%) > Cu (59.0%) > Cr (58.6%) [27]. Therefore, the bioavailability of heavy metals in different urban street dust varied greatly, which is relevant to the differences of regional geochemical background values, industry, energy structure, traffic flow, atmospheric environment, and so on. Although the results of different cities varied,

generally Pb, Cu, Zn, and Cd are prone to migration, easy to use by living beings. We should pay attention to the high health risks from Pb, Cu, Zn, and Cd.

The bioavailability of Cu in street dust of Wuhu was higher than those of other cities, mainly because of industrial emissions sources. Compared with other cities, the bioavailability of Cd in Wuhu street dust was low, mainly because of its soil parent material, which is relatively stable. In general, elements emitted from natural sources mainly existed in a residual state. The bioavailability of elements emitted from traffic and industrial sources was relatively high.

Different Speciation of Heavy Metals Loadings in Different Particle Size Fractions

In order to determine how particles of different grain size contributed to the overall metals loads of the bulk sample, the metals load percentage was computed for each individual sample by combining the concentration data for the grain-size fractions and their mass-size percentages. The grain-size fraction load (GSF$_{Load}$) was calculated using the following formula [28-29]:

$$\mathrm{GSF_{Load}} = \frac{C_i \times GS_i}{\sum\limits_{i=1}^{m} C_i \times GS_i}$$

…where C_i is the heavy metal concentration in an individual grain size fraction in mg/kg, CS_i is the mass percentage by mass of the size fraction i in the total sample, and m is the number of grain-size fractions.

The highest concentrations of acid-extractable, reducible, residual state of Zn appeared in street dust of the particle size of <75 μm, and the GSF$_{Load}$ reaches more than 50% (Table 4). The peak concentrations of oxidizable state appeared in the particle size of 96-75 μm, and the GSF$_{Load}$ of oxidizable state was 21.31%. The highest concentrations of acid-extractable, oxidizable, reducible, residual state of Cu appeared in the particle sizes of 250-150 μm, 150-96 μm, 96-75 μm, and <75 μm, respectively. The source of Cu in different particle sizes is complex. The distribution differences of reducible state and residual state of Cu in different particle sizes was obvious. The GSF$_{Load}$ of Cu residual state in fine particle dust was more than 50%. The GSF$_{Load}$ of Cu oxidizable state in the fine particles was 47.23%.

The highest concentration of acid-extractable state Co appeared in particle sizes of 830-250 μm, and the peak concentrations of other speciation appeared in particle sizes of 95-75 μm. Except for the oxidizable state, the GSF$_{Load}$ values of other speciations were less than 50% in particle sizes of <75 μm. The highest concentrations of acid-extractable Ni appeared in the 150-96 μm particle size. The difference between particle sizes was not obvious. The peak concentrations of reducible and residual state appeared in particle sizes of 95-75 μm. The highest Ni concentrations of oxidizable state appeared in particle sizes of 250-150 μm. The GSF$_{Load}$ of all speciation was less than 50% in particle sizes of <75 μm.

The highest concentrations of acid-extractable state and residual state of Cd appeared in the <75μm particle size. The peak concentration of reducible state and oxidizable state appeared in the particle size of 96-75 μm. In addition to the oxidizable state, the GSF$_{Load}$ of other speciation was more than 50% in the particle size of <75 μm. The highest concentrations of acid-extractable state and reducible state of Cr appeared in the particle size of 250-150 μm. The highest concentrations of oxidizable state and residual state appeared in the 250-150 μm particle size. The distribution difference of residual state on the coarse particles and fine particles was big. The highest concentrations of acid-extractable and reducible state of Pb appeared in the 250-150 μm particle size. The residual state mainly was enriched in street dust of particle size <75 μm.

Overall, the grain size fraction loads (GSF$_{Load}$) of different chemical speciation were mainly high in fine particles. The particle size of street dust is more fine, the contributions of heavy metals of different sizes are more vulnerable to the influence of human activity and produce disturbance. Fine particles have larger available surface area and surface energy, and they have a high adsorption rate for metals compared to larger particles [30]. The fine particles concentrate a lot of heavy metals into the atmosphere and cause potential harm to human health.

Conclusion

The concentrations of Zn, Cd, Pb, and Cu in urban street dust of Wuhu were higher than the background values of Wuhu soil. There existed obvious enrichment and pollution. Concentrations distribution of heavy metals in street dust of different functional districts were obviously different. The Zn concentration in the traffic district were more than two times that in other districts, Cu concentration in street dust in the industrial district was more than three times that in other districts. Zn mainly comes from traffic sources, and Cu mainly comes from industrial emissions sources. Different metals had different sources, leading to different distributions in different particles. Overall, the concentrations of heavy metals were high in the fine particles. The more fine a particle, the more vulnerable it is to the influence of human activity and the more likely to produce a disturbance. Fine particle dust concentrates a lot of heavy metals that can enter the atmosphere and cause potentially harm to human health.

The heavy metal concentrations in different particle dust had different functions in different districts, due to the different sources of coarse and fine particles of each district.

Zn and Cd were given priority to acid-extractable state, respectively for 46.6% and 32.1% of the total amount, low-residual state. The elements of Cr, V, Ni, and Co, which

come from natural sources, were given priority to residual state for 50% above. Cu and Pb were given priority to oxidizable states, respectively for 65.9% and 63.8% of the total amount. The chemicals from different elements are related to the nature and source of the elements. The grain size fraction loads (GSF_{Load}) of different chemical forms were mainly high in fine particles.

The biological mobility of heavy metals in Wuhu street dust decreased in the order of Pb (91%) > Cu (85.6%) > Zn (85.24%) > Cd (78.3%) > Co (49.3%) > Ni (39.3%) > V (23.7%) > Cr (20.19%). Pb, Cu, and Zn were biologically available elements, and the biological mobility of Cu was much higher than those in other reports due to Cu emitted from the industry source in Wuhu. A partition difference of combined speciation of different elements was different. The different form distribution of V, Zn, and Cr in different functional districts had no obvious difference. The proportions of an ecologically effective state of most elements in industrial and residential districts were big. In the residential district the metals can harm human health, which should be a cause for serious concern.

Acknowledgements

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