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ORIGINAL ARTICLE

Contamination assessment of copper, lead, zinc and chromium in dust fall of Jinan, NE China

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Abstract To assess the pollution of heavy metal in dust fall, nine dust fall samples were collected during the heating period and non-heating period from Jinan, a city in northeastern China. The samples were analyzed for Cu, Pb, Zn and Cr and the contamination level of heavy metals was assessed on the basis of the geo-accumulation index (I_{geo}). The results indicated that all of the four investigated metals accumulated significantly in the dust fall of Jinan, and the metal concentrations were much higher than background values. During the heating period, the mean values for Cu, Pb, Zn and Cr in the dust fall were 354.9, 688.5, 2,585.5 and 478.6 mg kg^{-1}. During the non-heating period, the mean values for Cu, Pb, Zn and Cr in the dust fall were 228.2, 518.2, 1,933.9 and 96.3 mg kg^{-1}, respectively. The I_{geo} values calculated based on background values revealed that the contamination level of heavy metal in the dust fall ranges from moderately contaminated to heavily contaminated, and it mainly originates from traffic and industry. In this work, the dust fall residue compared to the standard reference was also chosen as the background value to calculate the I_{geo} value. This method is useful for situations in which the background value is difficult to obtain.

Keywords Contamination assessment · Dust fall · Heavy metal · Geo-accumulation index

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Introduction

Soil, sediment and dust are the three materials which originate primarily from the Earth's crust. Among them, dust fall is the most pervasive and important factor affecting human health and well-being. Non-exhaust particulate emissions resuspended by traffic often represent an important source of atmospheric particulate matter in urban environments (Thorpe and Harrison 2008; Norman and Johansson 2006). Consequently, resuspension of dust fall can lead to high human exposures to heavy metals, metalloids and mineral matter.

Dust fall is one of the most complex and hazardous pollutants in the atmospheric environment (Joshi et al. 2009); its trace heavy metals are one of the largest pollution sources (Var et al. 2000). In general, heavy metals are found in the atmospheric environment at low natural concentrations. However, human activities like transportation, industrial discharges, domestic heating and waste incineration make a significant contribution to the high contents of toxic metals in dust fall (Gibson and Farmer 1986; Harrison et al. 1981). These elements get distributed among soils, air, surface dust and water. As a result, dust fall often contains elevated concentrations of a range of heavy metals and concerns have been expressed about the consequences for both environmental quality and human health (Banerjee 2003; Imperato et al. 2003). Vehicle emission is another main source of the trace metals in dust fall, especially the traffic-related metals, such as Pb, Cu and Zn (Akhter and Madany 1993; Omar et al. 2007). Although the use of leaded gasoline has been prohibited for decades, Pb and the associated metals continue to accumulate in dust fall because of their non-biodegradability and long residence time (Duong and Lee 2011; Wei et al. 2009). In addition, a variety of other sources, including coal combustion, metal smelting, etc., are important contributors of metals as well (Christoforidis and Stamatis 2009). Thereby, dust fall plays the role of a metal-sink in cities.

In recent years, methods of analyzing and determining the concentration of heavy metal in the sediment samples to assess the degree of heavy metal pollution and potential ecological risk have become quite accurate and dependable. The content of trace heavy metals of Cu, Pb, Zn, Cr in different forms in dust fall is determined by Tessier's (Tessier et al. 1979) method of conformation taxonomy and graphite furnace atomic absorption spectrometry (Saygi et al. 2007), but the degree of pollution was not quantitatively researched.

The vast majority of studies on the contents of heavy metals in dust fall have been carried out in developed countries but very few in China, and systematic studies of large regions in China have only been done in important cities such as Beijing or Dalian (Wei and Yang 2010; Shi et al. 2010; Lu et al. 2009). Organic and inorganic constituents of dust fall in some areas have also been reported (Boonyatumanond et al. 2007; Joshi et al. 2009; Li and Feng 2010).

Based on the aforementioned facts, the aims of this research were to (1) determine the concentrations of selected metals from sampled dust fall collected from urban areas of Jinan, (2) map the metal distribution through geo-statistical analysis to identify their spatial patterns in the region, and (3) identify the main sources of individual metals in the dust fall using geo-statistical analyses. The results of this research may be useful for the city government in alleviating metal contamination in the course of Jinan's development.

Materials and methods

Sample collection

Six dust fall sampling sites were selected in Jinan, including the campus of Shandong University, the provincial seed station, a fertilizer plant, a plastic factory, the Jinan steel industrial complex and the biotechnology park in the Jinan high-tech development zone. Sampling stations (1 m^2) 1.5 m above the ground were placed at each site and dust fall samples were collected after about 1 day. Samples S1 to S9 represent the three samples taken during the non-heating period and six samples taken during the heating period. In order to collect comparable samples, all the dust fall samples were collected under similar weather conditions. All the collected samples were kept in sealed polyethylene (PE) packages to avoid contamination; subsequently the samples were transported to the laboratory and preserved in a refrigerator.

Sample processing

All of the samples were dried in an oven at 353 K for 24 h, and then the dried samples were milled and sieved to retain the 20–40 mesh fractions for analysis. To determine the total metal contents of the dust fall, 0.5 g samples were placed in polytetrafluoroethylene vessels and digested with HNO_3, HF and $HClO_4$ in a microwave oven (MDS-2002AT), according to the method described by Sandroni et al. (2003). Then the solutions were dissolved with distilled water to a final volume of 50 ml. The contents of elements Cu, Pb, Zn and Cr were analyzed by graphite furnace atomic absorption spectrophotometer (GF-AAS) (180-80, Polarized Zeeman, HITACHI).

To obtain the contents of heavy metals in the residual of dust fall samples, the samples were treated with different solvent-extractions; this sequential extraction includes: Step 1 exchangeable (magnesium chloride, pH 7); Step 2 bound to carbonates: (sodium acetate/acetic acid, pH 5); Step 3 bound to Fe/Mn oxides: (hydroxylammonium chloride, pH 2); Step 4 bound to organic material and sulfides: (hydrogen peroxide, pH 2, ammonium acetate); Step 5 residual: digestion; for more details refer to Tessier et al. (1979). In this study, the contents of heavy metals in residual of the sequential extraction were used as the background values of the dust fall to calculate the I_{geo} values. All the extractions except the residual fraction were carried out in 50 ml polypropylene centrifugation tubes with tight lids. When continuous agitation was required, samples were shaken lengthwise on an end-to-end mechanical shaker. After each successive extraction, separation was done by centrifugation (800-Electric centrifugal precipitators) at 5,000 rpm for 30 min at 298 K. The concentrations of heavy metals in the residual material were obtained by the same method described by Sandroni et al. (2003) as the background values compared to the standard background values.

Choice of the elemental types of heavy metals

In this paper, Cu, Pb, Zn and Cr were the main research objects. The levels of the toxic metals Hg and As are very low in the atmosphere and particulate matter of Jinan, and the content of Cd was far below the limit of pollution emission required by state. Therefore, these metals were not considered. The four tested metals have standard methods to determine their contents, and their distributions in particulate matter have been widely reported. Therefore, Cu, Pb, Zn and Cr were chosen for evaluation.

Contamination assessment methods

Numerous calculation methods have been put forward to quantify the degree of metal enrichment or pollution in soil, sediments and dusts (Upadhyay et al. 2006, 2007). In this study, the geo-accumulation index (I_{geo}) put forward by Muller (1969) was calculated to assess the heavy metal contamination level in the dust fall.

I_{geo} was originally used with bottom sediments (Muller 1969; Ji et al. 2008) and has been successfully applied to the measurement of soil contamination (Loska et al. 2003). It is computed by the following equation:

$$I\text{geo} = \log_2 \frac{C^n}{1.5B^n}$$

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 this study, B_n is the standard reference value from data provided by the Jinan Municipal Environmental Protection Bureau as the background content of element n. The constant factor 1.5 was introduced to analyze natural fluctuations in the contents of a given substance in the environment and very small anthropogenic influence (Loska et al. 2004). According to different I_{geo} values, Muller (1981) proposed seven classes of the geo-accumulation index, as shown in Table 1.

The choice of background reference value in geo-accumulation index (I_{geo})

The assessment results rely on the concentrations of the samples and the choice of geochemical background value. Different geochemical background values would distinctly affect the geological accumulation index (I_{geo}), therefore the choice of geochemical background value to calculate the geo-accumulation index should be the background value of sediment in the researched region. If the geochemical background value of researched region could not be ascertained, the sedimentary features, granularity and substance constitution of the sediment should be considered sufficiently, and the background value should be chosen from the geochemical background value approaching the sediment geochemical features and environmental features of the region. In this paper, the background values for the calculation of the geo-accumulation index were chosen from the dust fall residue of the collecting samples and standard reference values from data provided by the Jinan Municipal Environmental Protection Bureau, separately. The different reference values are listed in Table 2.

Table 1 Seven classes of the geo-accumulation index

Class	I_{geo} value	Dust fall quality
0	$I_{geo} \leq 0$	Practically uncontaminated
1	$0 \leq I_{geo} \leq 1$	Uncontaminated to moderately contaminated
2	$1 \leq I_{geo} \leq 2$	Moderately contaminated
3	$2 \leq I_{geo} \leq 3$	Moderately to heavily contaminated
4	$3 \leq I_{geo} \leq 4$	Heavily contaminated
5	$4 \leq I_{geo} \leq 5$	Heavily to extremely contaminated
6	$5 \leq I_{geo}$	Extremely contaminated

Results and discussion

Metal levels of dust fall and source analysis

The concentration of metals (geometric, maximum, minimum) and the sampling period are shown in Table 3. The average levels of the four observed metals in dust fall samples during the heating period were higher than the samples during the non-heating period. However, both periods' metal levels were much higher than the standard background values which were provided by the Jinan Municipal Environmental Protection Bureau and the dust fall residue. During the heating period, the concentration of Cu, Pb, Zn and Cr in the dust fall ranges from 218 to 568, 328.5 to 1,037.5, 1,095 to 4,492 and 335 to 570 mg kg^{-1} with the geometric mean is 354.9, 688.5, 2,585.5 and 478.6 mg kg^{-1}, respectively. During the non-heating period, the contents of Cu, Pb, Zn and Cr in the dust fall ranges from 107 to 364, 505 to 1,041.5, 985 to 3,080 and

Table 2 Different reference values of the analyzed metal elements (mg/kg)

Source	Cu	Pb	Zn	Cr
Standard reference value	50	70	175	90
Dust fall residue	47.2	50.2	154	61.8

Table 3 Heavy metal concentrations (mg kg^{-1}) in dust fall collected from Jinan city

Parameter	Cu	Pb	Zn	Cr
Heating period				
S1	501	853.5	2,400	522
S2	414	966.5	1,935	472
S3	568	1,037.5	3,225	570
S4	218	328.5	1,095	539
S5	331	630	4,492	335
S6	235	601.5	4,055	474
Geometric	354.9	688.5	2,585.5	478.6
Non-heating period				
S7	364	1,041.5	3,080	265
S8	107	264.5	985	27.2
S9	305	505	2,384	124
Geometric	228.2	518.2	1,933.9	96.3

Table 4 I_{geo} values calculated based on the different background value

Parameter	S1	S2	S3	S4	S5	S6	Average
Based on standard value							
Cu	2.74	2.46	2.92	1.54	2.14	1.65	2.24
Pb	3.02	3.20	3.30	1.65	2.58	2.52	2.71
Zn	3.19	2.88	3.62	2.06	4.10	3.95	3.30
Cr	1.95	1.81	4.32	2.00	1.31	1.81	2.20
Based on dust fall residue value							
Cu	2.82	2.55	3.00	1.62	2.23	1.73	2.33
Pb	3.50	3.68	3.78	2.13	3.06	3.00	3.19
Zn	3.38	3.07	3.80	2.24	4.28	4.13	3.48
Cr	2.49	2.35	4.87	2.54	1.85	2.35	2.74

27.2 to 265 mg kg^{-1} with the geometric mean is 228.2, 518.2, 1,933.9 and 96.3 mg kg^{-1}, respectively. Therefore, we can conclude that coal burning for heating increases the levels of metals in dust fall to a certain extent. The maximum values of Cu and Zn were found in the sample from a site 100 m from a heavily trafficked road, while their minimum values were detected in a dust sample from a residential site with less traffic density. The source of Cu and Zn in street dust has been shown to be tire abrasion, the corrosion of metallic parts of cars, lubricants and industrial and incinerator emissions (Al-Khashman 2004; Jiries et al. 2001). The maximum amounts of Pb and Cr were found in the dust sample collected from an industry area with an iron and steel mill, coke-oven plant, cement manufacturing plants, and a coal-fired power plant, while the lowest concentration was detected in the sample from a residential site with less traffic density. It may be concluded the sources of Pb and Cr in street dusts of Jinan mainly originated from industrial activities and automotive emissions. The dust fall has similar compositions to the road dusts and sediments. It is a common practice to compare mean concentrations of heavy metals in road dusts in different urban environments (Miguel et al. 1997; Duzgoren-Aydin et al. 2006), although there are no universally accepted sampling and analytical procedures for geochemical studies of dust fall.

From the above results, it was concluded that there are different main sources of metals in various areas of a city. Higher population density did not always result in heavier pollution. Both the levels of environmental management and the living habits of residents could influence the environmental quality.

Metal pollution assessment based on I_{geo}

The contents of heavy metal in standard background value and dust fall residue were separately selected as the reference in the assessment of toxic metal pollution. The geo-accumulation method I_{geo} was used to calculate the degree of metal contamination in dust fall. The I_{geo} results are summarized in Table 4. The I_{geo} based on standard reference values ranges from 1.54 to 2.74 with a mean value of

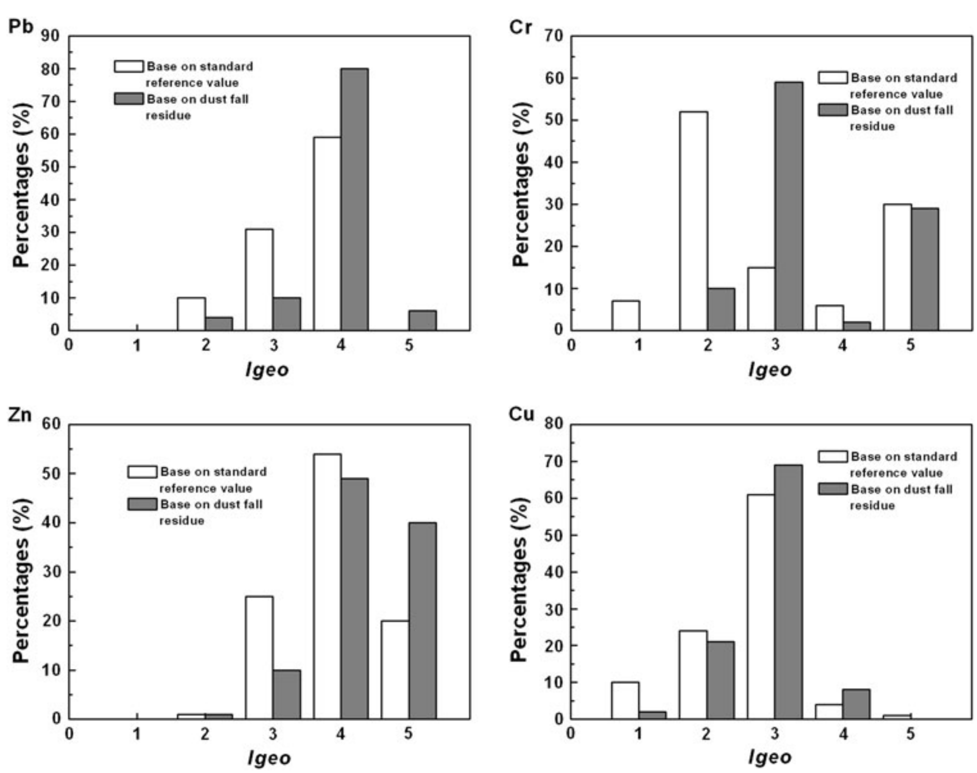

Fig. 1 Percentages of samples in varied I_{geo} classes

2.24 for Cu, 1.65 to 3.30 with a mean value of 2.71 for Pb, 2.06 to 4.10 with a mean value of 3.30 for Zn, 1.31 to 4.32 with a mean value of 2.20 for Cr. The mean values of I_{geo} decreased in the order of Zn > Pb > Cu > Cr. Figure 1 shows the percentages of sample in varied I_{geo} classes. The mean I_{geo} value and 69% I_{geo} of Cu fall into class 3, indicating moderately to heavily contaminated, while 21% I_{geo} falls into class 2, indicating moderately polluted. The mean I_{geo} and percentage I_{geo} of Cr showed the samples were moderately to heavily contaminated. The mean I_{geo} obtained for Pb and Zn pointed to heavy pollution. In Fig. 1, the results calculated with standard reference value as background were close to those found using dust fall residue.

Conclusions

All four investigated metals were accumulated significantly in the dust fall of Jinan, and the metal concentrations were much higher than background values. Moreover the contents of the metal in the dust fall during the heating period were a little higher than during the non-heating period. The choice of background reference value is important. If samples of some areas were special or the standard background reference value was inappropriate, it was suggested that the residue value of the area be chosen as the background reference value.

The calculated I_{geo} of the analyzed heavy metals was in the order Zn > Pb > Cu > Cr. The high I_{geo} values for Zn, Pb, Cu and Cr in dust fall indicate that there was considerable Zn, Pb, Cu and Cr pollution, which mainly originated from traffic and industrial activities. With the increasing control of point-source pollution (e.g., industry), non-point source contaminants have become an international concern. However, the non-point pollution is difficult to characterize and monitor. More attention should be paid by both governments and scientists to the reckless and unconscious pollution of the environment in dust fall.

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