Mercury and arsenic contamination assessment of roadway dust from Baoji, NW China

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ABSTRACT
Mercury and arsenic contents in roadway dust from Baoji, NW China were determined by an Atomic Fluorescence Spectrophotometer. Contamination levels were assessed on the basis of the geoaccumulation index and the enrichment factor. The results show that mercury concentration ranged from 0.48 to 2.32 μg g^{-1}, with a mean value of 1.11 μg g^{-1}, 17.1 times the Chinese soil mercury background value (0.065 μg g^{-1}). The arsenic concentration ranged from 9.0 to 42.8 μg g^{-1}, with a mean value of 19.8 μg g^{-1}, 1.8 times the Chinese soil arsenic background value (11.2 μg $g^{-1)}$. Assessment of the geoaccumulation index and enrichment factor indicate that mercury in the dust mainly originated from anthropogenic sources with ratings of "strongly polluted" and "strongly to extremely polluted", whereas arsenic in dust originated from both natural and anthropogenic sources, with a ratings of "moderately to strongly polluted" and "strongly polluted". Industrial activities, such as a coal-fired power station, coke-oven plant, and cement manufacturing plant, augmented by vehicular traffic, are the anthropogenic sources of mercury and arsenic in the roadway dust of Baoji.

RÉSUMÉ
Le contenu en mercure et arsenic des poussières des axes routiers de Baoji, NW China, a été déterminé par Spectromètre à Fluorescence Atomique. Les niveaux de contamination ont été évalués sur la base de l'index de géo-accumulation et du facteur d'enrichissement. Les résultats montrent que les concentrations en mercure varient de 0.48 à 2.32 μg g^{-1}, avec pour médiane 1.11 μg g^{-1}, soit 17.1 fois plus que les valeurs de fond du sol Chinois (0.065 μg g^{-1}). Les concentrations en arsenic varient de 9.0 à 42.8 μg g^{-1}, avec une valeur médiane de 19.8 μg g^{-1}, soit 1.8 fois plus que les valeurs de fond du sol Chinois (11.2 μg g^{-1}). L'évaluation du facteur d'enrichissement et de l'index de géo-accumulation indiquent que le mercure présent dans les poussières a principalement provenu des sources anthropiques avec des estimations « fortement pollué » et « fortement à extrêmement pollué », tandis que l'arsenic contenue dans les poussières provient de sources naturelles et anthropiques, avec des estimations de « modérément à fortement pollué » et « fortement pollué ». Le trafic routier avec les activités industrielles, telles que des centrales à charbon, usines de fours à coke, et usines de ciments ont les principales sources anthropiques du mercure et de l'arsenic dans la poussière de chaussée de Baoji.

1 INTRODUCTION

Atmospheric pollution is a major source of metal contamination. Fine particulate (dust) is an important pathway for the dispersed of pollutants to the urban environment and for deposition on roadways. The chemical components and quantities of roadway dust in urban centre can be taken as an important environmental pollution indicator (Yongming et al., 2006). Although there have been numerous studies of the extent of heavy metal contamination (Pb, Cu and Zn) of roadway dust and source identification in western countries in recent decades (Ahmed and Ishiga, 2006; Akhter and Madany, 1993; Al-Khashman, 2004, 2007a, 2007b; Azimi et al., 2005; Bilos et al., 2001; Charlesworth et al., 2003; Imperato et al., 2003; Li et al., 2001; Sezgin et al., 2003), very limited information is available for other countries, including China. Moreover, limited attention has been focused on other trace metals, such as As and Hg.

In most major cities of China, rainfall or snowmelt runoffs discharge directly into streams or rivers without treatment. There is a lack of recorded data for air, water and sediment quality. Baoji, an important industrial city in Northwest China, has experienced rapid urbanization and industrialization in recent decades. Surface runoff discharges directly into the Wei River, the major tributary of the Yellow River. This temperate semiarid industrial city provides an excellent location for the study of metal contamination in air, dust and soils. The objective of this study was to determine and assess the concentration of mercury and arsenic in roadway dust samples from Baoji.

2 MATERIALS AND METHOD

2.1 Study Area

Baoji, the second largest city of Shaanxi province in Northwestern China, is situated at the western end of the

Guanzhong (Wei River) valley (33°34′-35°06′ N, 106°18′-108°03′ E) about 150 km west of the provincial capital, Xi'an (Fig. 1). The city covers an area of over 1060 km^2 with an urban population of approximately 760, 000 in 2004, compared with about 350, 000 in 1980. Baoji city is bounded by Qinling Mountain in the south and west and by Loess Plateau, over 800 m above sea level, at the north. Only the east is open toward the lower reach of the Wei River, which traverses the city from west to east. The city has high vehicular traffic density, more than 30,000 vehicles a day, 25% of this being transportation trucks. Baoji is subject to a temperate zone continental monsoon climate (hot rainy summers, cold dry winters) with an annual average temperature of 7.6 to 12.9℃, annual sunlight of about 2057 h and annual precipitation of 600-700 mm. The main soil type in the area investigated is cinnamon soil with a pH of 8 to 9. Texture analysis of the

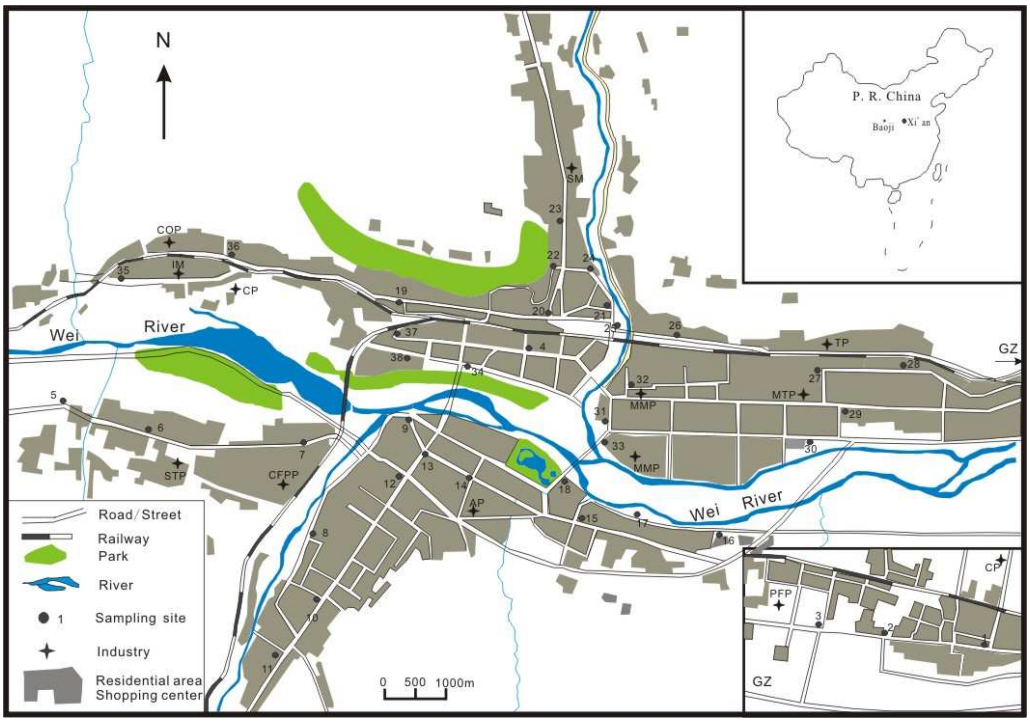

Figure.1. Study area and sampling sites
CFPP: coal-fired power plant; CP: cement plant; COP: coke-oven plant; STP: steel tube plant; AP: accumulator plant; MM: machine manufacturing; MTP: machine tool plant; TP: textile plant; IM: iron mill; SM: steel mill; PFP: phosphate fertilizer plant.

soil shows that it is loam, composed of sand (50.2%), silt (37.3%) and clay (12.5%). The prevailing wind direction is from east to west. The main industries are an iron and steel mill, chemical industry, ceramics, textile, construction, cement manufacturing plants, paints, beer and alcohol production, paper making, machine manufacturing, electric and electronics, and a coal-fired power plant.

2.2 Sampling and analytical procedures

Thirty-eight roadway dust sampling sites were selected in Baoji city, including industrial areas, heavy and low traffic density areas, commercial areas and residential districts (Fig. 1). At every sampling site, a roadway dust composite sample of ~500 g was collected by sweeping using a polyethylene brush and tray from five to eight points of the road or pavement edges during the dry season in February 2006. Thirty-eight composite dust samples were collected. All collected samples were stored in sealed polyethylene bags, labeled and then transported to the laboratory. Samples were air-dried in the laboratory for two 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 was then ground with an agate mortar and pestle, then carefully homogenized and sieved through a 75 μm nylon mesh. After reduction by repeated quartering, the sample was analyzed for mercury and arsenic concentration as outlined below. All handling were carried out without contact with metals, to avoid possible cross contamination.

Dry weights of mercury and arsenic in the roadway dust samples were determined by AFS-810 double channel atomic fluorescence spectrometry with two hollow cathode lamps, one for each of mercury and arsenic (AFS-810 and hollow cathode lamps are produced by Beijing Titan Instrument Corporation) and high-purity argon (Cai 2005). The analysis process was as follows: a 0.300 g sample was weighed and put into a

50 ml volumetric flask. 10 ml of a freshly prepared mixed acid (1 ml high concentration HNO_3:1 ml high concentration HCl) was added. The bottle was the covered and the contents mixed. The volumetric flask was then uncovered and placed on boiling water for 2 h, shaking every 30 min. After cooling, 5 ml of 5% thiocarbamide-5% ascorbic acid solution were added and the solution was diluted to 50 ml. Mercury was determined in the 5% HCl with 20 g/L natrium borohydride ($NaBH_4$) as the reducing agent, at the same time as the blank and standard substances were determined.

A standard reference GSS1 (geochemical standard reference sample soil in China) was used to examine the precision and accuracy of determination. The certified values of arsenic and mercury were 34±4 μg g^{-1} and 0.032±0.004 μg g^{-1}, respectively, whereas the measured values in the experiment were 35 and 0.036 μg g^{-1},

Table 1. Mercury and arsenic concentrations in roadway dust of Baoji and other cities reported in literatures (μg g^{-1})

	Mean	SD	Median	Min	Max	CV	Skewness	Location/ Source
Hg	1.11	0.41	1.02	0.48	2.32	0.367	1.18	Baoji, China/This study
	0.638	0.723	0.429	0.108	5.212	1.13	4.42	Xi'an,China/Yongming et al., 2006
	0.11			0.03	0.33			Chongqing, China/Li et al., 2006
	0.34							Beijing, China/Liu and Cen, 2007
	0.13	0.09	0.11	0.03	0.57	0.69		Luanda, Angola/Ferreira-Baptista and De Miguel, 2005
	2.56[a]	1.38[b]		1.20	10.8	0.99		Avilés, Spain/Ordóñez et al., 2003
As	19.8	7.6	18.2	9.0	42.8	0.382	1.4	Baoji, China/This study
	10.62	3.46	9.78	5.95	20	0.32	0.94	Xi'an, China/Yongming et al., 2006
	6.82			2.30	15.49			Chongqing, China/Li et al., 2006
	6.2							Beijing, China/Liu and Cen, 2007
	5	0.92	4.9	3.5	7.8	0.18		Luanda, Angola/Ferreira-Baptista and De Miguel, 2005
	17.5[a]	1.15[b]		11.0	26.0	0.30		Avilés, Spain/Ordóñez et al., 2003

a: geometric mean; b: geometric SD; CV=SD/mean

respectively. High-purity concentrated nitric acid and hydrochloric acid were used throughout the study. All other chemicals were of analytical grade. Deionized water was used exclusively for sample preparation. All glass containers utilized in the experiments were soaked in 5% v/v nitric acid for at least 24 hours and then rinsed with distilled water and deionized water to ensure that there was no cross contamination.

2.3 Contamination assessment methods

Contamination levels of mercury and arsenic in the dusts were assessed by means of the geoaccumulation index (I_{geo}) and enrichment factor (EF), commonly applied in the literature (Lim et al., 2006; Meza-Figueroa et al., 2007; Tasdemir and Kural, 2005; Tumer and Simmonds, 2006; Varrica et al., 2003; Yongming et al., 2006). The former is given by

$$I_{geo}=\log_2 [C_n/1.5B_n] \quad (1)$$

where C_n represents the measured concentration of element n, and B_n is the geochemical background value of the element in fossil argillaceous sediment (average shale). B_n is the background content of element n in the continental crust (Taylor and McLennan, 1995; Wedepohl, 1995).

The enrichment factor is calculated from

$$EF=[C_x/C_{ref}]_{Sample}/[C_x/C_{ref}]_{Background} \quad (2)$$

where C_x is the concentration of the element of interest and C_{ref} is the concentration of the reference element for normalization. EF can assist in differentiating an anthropogenic source from a natural origin. A value of EF close to 1 indicates a crustal origin, whereas values >10 are considered to denote a non-crustal source (Liu et al., 2003). EF can also assist in determining the degree of metal contamination.

3 RESULTS AND DISCUSSION

Table 1 shows statistical results for mercury and arsenic concentrations in the roadway dust of Baoji. The mercury concentrations in roadway dust of Baoji ranged from 0.48 to 2.32 with an average of 1.11 μg g^{-1}, which is consistent with mercury concentration in surface soil around the Baoji coal-fired power plant (0.2-2.1 μg g^{-1}) (Lu et al., 2008). Fig. 2 shows that mercury concentrations in all dust samples are higher than the mercury background value of Chinese soil (0.065 μg g^{-1}) (State Environmental Protection Administration of China, 1993), 7.4 to 35.7 times the Chinese soil mercury background level. Higher mercury concentrations (in excess of the mean) were found in dust samples from the industrial area, in particular near the coal-fired power plant, coke-oven plant, cement manufacturing plant and heavy traffic sites. Dust samples collected from residential area with less traffic density contained lower concentrations.

Arsenic concentrations in roadway dust ranged from 9.0 to 42.8 μg g^{-1}, with an average of 19.8 μg g^{-1} (Table 1). Most concentrations are higher then the Chinese soil arsenic background level (11.2 μg g^{-1}) (Fig. 2) (State Environmental Protection Administration of China 1993), with a range of 0.8 to 3.8 times the Chinese soil arsenic background value. Higher arsenic concentrations (>20 μg g^{-1}) were measured in dust samples collected from the power plant / industrial area and from heavy traffic sites. Arsenic is positively correlative with mercury (r=0.31).

This indicates that coal-fired industries and automotive emissions are the main contributors to the mercury and arsenic of Baoji roadway dust. As shown in Table 1, mercury and arsenic concentrations in roadway dust of Baoji are higher than for comparable cities, except for Avilés.

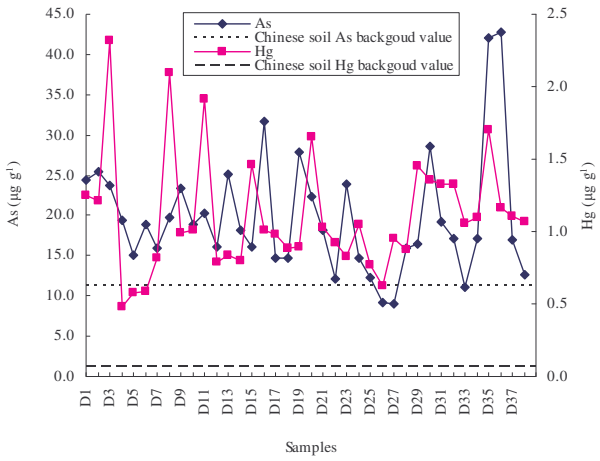

Figure 2. Mercury and arsenic concentrations in roadway dust of Baoji compared with Chinese soil background values

The I_{geo} results for mercury and arsenic in Baoji roadway dust are presented in Fig.3. I_{geo} ranged from 3.01 to 5.27 with a mean value of 4.13 for mercury, and from 2.00 to 4.25 with a mean value of 3.04 for arsenic. Table 2 shows that 55.2% of the dust samples can be classified as "strongly to extremely" mercury polluted, while 39.5% of the dust samples were "strongly" mercury polluted. The mean I_{geo} and 50.0% of I_{geo} value of arsenic were between 3 and 4 corresponding to "strong" arsenic pollution in street dust, while 44.7% of I_{geo} value were between 2 and 3 revealing "moderately to strongly" polluted.

Mercury and arsenic enrichment factors in roadway dust samples were calculated with respect to their natural abundance in the continent crust, with Al as the reference element. EF for mercury and arsenic were from 8.0 to 41.4 and 4.8 to 26.7, with averages of 20.7 and 9.8, respectively (Fig. 4). EF of mercury in 94.7% dust samples and in 36.8% samples exceeded 10, indicating that the mercury mainly originated from anthropogenic activities, whereas the arsenic in the dust originated from both natural and anthropogenic sources. As shown in Table 3, the mean EF of 9.80, with 89.5% EF of arsenic falling between 5 and 20 indicates that the arsenic in the roadway dust is significant contamination. Mercury has a mean EF >20.7 and 55.3% of the values 5 and 20, and 39.5% between 20 and 40, indicating significant and very high contamination, respectively. The contamination assessment results of EF are consistent with those of I_{geo}.

4 CONCLUSIONS

Mercury and arsenic concentrations and their contamination levels in roadway dust from Baoji, NW China have been determined. The concentration of mercury and arsenic in roadway dust ranged from 0.48 to 2.32, and 9.0 to 42.8 μg g^{-1}, with averages of 1.11 and 19.8 μg g^{-1}, respectively. Higher mercury and arsenic concentrations were found in dust from an industrial area and heavy traffic sites. The mean mercury and arsenic concentrations in roadway dust of Baoji are higher than reported for other cites, and are respectively 17.1 and 1.8 times the respective Chinese soil background values.

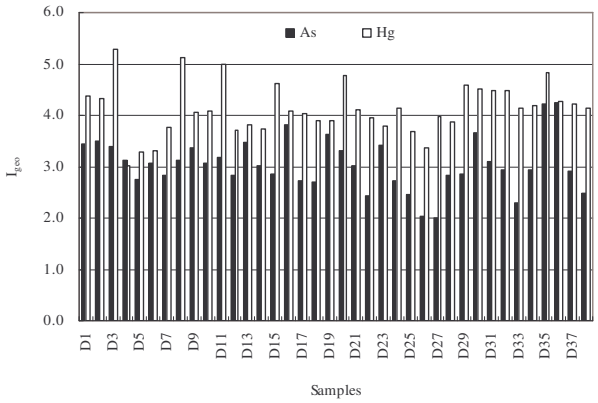

Figure 3. Geoaccumulation index of mercury and arsenic in roadway dust of Baoji

Table 2. Percentage Igeo of Hg and As (%) in roadway dust of Baoji

Class	Value	Street dust quality	Hg	As
0	$I_{geo}<0$	Practically unpolluted	0	0
1	$0<I_{geo}<1$	Unpolluted to moderately polluted	0	0
2	$1<I_{geo}<2$	Moderately polluted	0	0
3	$2<I_{geo}<3$	Moderately to strongly polluted	0	44.7
4	$3<I_{geo}<4$	Strongly polluted	39.5	50.0
5	$4<I_{geo}<5$	Strongly to extremely polluted	55.2	5.3
6	$5<I_{geo}$	Extremely polluted	5.3	0

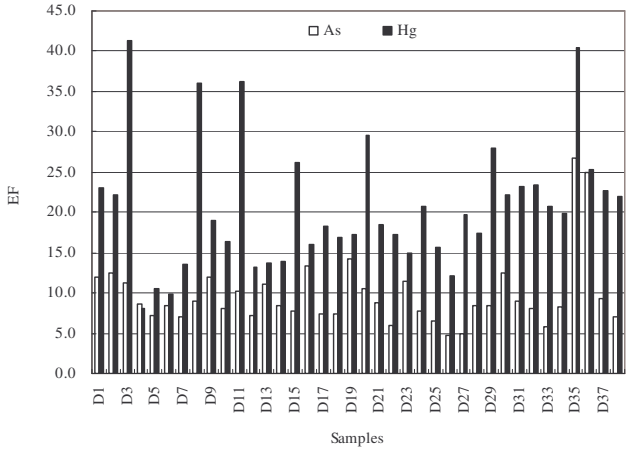

Figure 4. Enrichment factor of mercury and arsenic in roadway dust of Baoji

Table 3. Percentage EF of Hg and As (%) in roadway dust of Baoji

Class	Street dust quality	Hg	As
EF<2	Deficiency to minimal enrichment	0	0
EF=2-5	Moderate enrichment	0	5.2
EF=5-20	Significant enrichment	55.2	89.5
EF=20-40	Very high enrichment	39.5	5.3
EF>40	Extremely high enrichment	5.3	0

Contamination assessments based on geoaccumulation index and enrichment factor classes mercury as “strongly polluted” and “strongly to extremely polluted”, whereas arsenic in dust revealed “moderately to strongly polluted” and “strongly polluted”. Mercury in roadway dust appears to have mainly originated from anthropogenic sources, whereas the indicators suggest that arsenic in roadway dust originated from both natural and anthropogenic sources. Coal-fired industrial activities and traffic vehicles are likely to be the anthropogenic sources of mercury and arsenic in the roadway dust of Baoji.

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