International Journal of Environmental Engineering– IJEE
Volume 1 : Issue 4 [ISSN 2374-1724]
Publication Date : 27 December,2014

Concentration, speciation and environmental risk of heavy metal in dusts collected from the different functional areas of a medium-size city in China

Xinwei Lu, Loretta Y. Li, Ni Zhao, Dan Shang, Ranran Li

***Abstract*—Concentrations of Cd, Cr, Co, Mn, Ni, Pb and Zn in urban dust samples from different functional areas of a medium-size city in China were determined by atomic absorption spectrophotometry. The speciation of these heavy metals was determined by the three-stage sequential extraction procedure suggested by European Community Bureau of Reference (BCR), and their environmental risks were evaluated based on the potential ecological risk index method. The results show that the concentrations of Cd, Co, Ni, Pb and Zn in the dust, but not Cr or Mn, are higher than their corresponding background values of local soil. The analyzed heavy metals in the dusts from different urban functional areas presented distinct accumulation. Speciation analysis results indicate that Cd and Zn were mainly in acid soluble form (45.1% and 36.1% respectively); Pb was mainly in reducible form (53.9%); Co and Cr were mainly in the form of residual state (43.1% and 65.6%, respectively); Mn was mainly in the residual state and oxidizable form (33.4% and 29.8%, respectively), whereas Ni was mainly in oxidizable and residual form (36.1% and 35.2%, respectively). Cd presented considerable ecological risk to very high ecological risk in the dusts, while the other metals examined presented low ecological risk. The total ecological risks of all analyzed metals in the dust corresponded to high ecological risk.**

***Keywords*—concentration, speciation, risk assessment, dust, China**

I. Introduction

Cities are the highly concentrated centres of anthropogenic activities. Because of accelerated urbanization and industrialization, nearly half of the world's population now lives in cities [1] where dense population, traffic, industry and economic activities cause increasing amounts of pollutants to be discharged to the urban environment. Consequently, a variety of environmental issues are emerging, e.g. air pollution, soil pollution and water pollution. Heavy metal pollution is a major issue, especially in atmospheric particles, soil and dust [2].

Xinwei Lu, Ni Zhao, Dan Shang, Ranran Li
School of Tourism and Environment, Shaanxi Normal University
Xi'an 710062, P. R. China

Loretta Y. Li
Department of Civil Engineering, University of British Columbia
Vancouver, V6T 1Z4 Canada

Urban dust, one important environmental medium with complicated composition in urban regions [3], refers to solid particles that deposit on the impermeable surface of urban area, e.g. hard pavement or cement roads, etc [4]. It easily enters the atmosphere, soil and water by re-suspension, deposition and precipitation runoff. Therefore, urban dust is the cause of significant linkages among urban environmental media: atmosphere, soil and water. As sinks and sources of contaminants, urban dust often contains elevated concentrations of organic and inorganic contaminants, such as heavy metals, polychlorinated biphenyls and polycyclic aromatic hydrocarbons [5-7]. Urban dust contamination by heavy metals has caused increased concern in recent decades owning to toxicity, non-biodegradability and long residence times [1]. Research on heavy metal contamination in urban dust has mainly focused on concentration, distribution, source, pollution level, ecological and health risk assessment [8-13]. However, most previous studies were done in large and/or industrial cities in western countries, with little data available for rapidly industrializing and urbanizing areas of other countries, including China [14]. The medium and small cities of western China are of particular interest, as urban construction and development have been very fast in this region since implementation of the Chinese Western Great Development policy in 1990s. This has especially affected medium and small cities. At same time, urban environmental pollution is becoming more serious with city construction and economical development in these areas. However, information about heavy metal pollution in these urban areas is lacking in the literature.

Shangluo, situated in the southeast of Shaanxi province, China, is a medium-sized industrial and tourist city. It has a warm semi-humid continental monsoon climate, with an annual precipitation of 710-930 mm, annual sunlight of 1860-2130 h and annual average temperature of 7.8 - 13.9°C. The prevailing wind direction is southeast and east. The annual average wind velocity is 1.3-2.7 m/s. The main soil type in this area is cinnamon soil. The topography deceases from northwest to southeast. The urban area of Shangluo is 2670 km^2, and the population is 540,000. The number of motor vehicles was about 140,000 in 2013. The main industries are the chemical industry, cement-making, construction, paper-making, Zn-smelting, and a coal-based power plant. The chief objectives of this study were to determine the concentrations of Cd, Cr, Co, Mn, Ni, Pb and Zn in dust collected from the different functional areas of Shangluo, to analyze the speciation of measured heavy metals in the dusts and to evaluate their environmental risk. The results could help local environmental planning, management and protection.

International Journal of Environmental Engineering– IJEE
Volume 1 : Issue 4 [ISSN 2374-1724]
Publication Date : 27 December,2014

II. Materials and Methods

A. Sampling and Experiments

Urban dust samples were collected from six main functional areas of Shangluo, i.e. traffic area (TA), commercial area (CA), residential area (RA), industrial area (IA), educational area (EA) and park area (PA). Five different sampling locations were selected in each functional area. At every sampling site, one composite dust samples (200-300 g) was collected by sweeping using a polyethylene brush and tray from three to five points of road/pavement edges during the cold and dry season in January, 2014. The dust samples collected from these five locations were mixed together to yield a single sample representing that functional area. All dust samples were air-dried in the laboratory for more than 2 weeks, and then sieved through a 1.0 mm mesh nylon sieve to remove extraneous matter such as small stones and other debris. Half of the dust samples was ground with an agate mortar and pestle, then homogenized and sieved through a 75 µm nylon mesh.

A small portion of each sample, about 0.50 g, was collected and placed in a polytetralfuoroethylene vessel. Then the samples were digested with concentrated HNO_3, HF and $HClO_4$. The total concentrations of heavy metals were determined by a Analytik Jena AG ZEEnit700 atomic adsorption spectrophotometer analyzer, with flame law for measurement of Pb, Zn, Mn, Ni, Cr and Co, and graphite stove method for Cd [2]. At the same time, soil standard material (GSS-1) and sediment standard material (GSD-12), obtained from the National Research Center for Certified Reference Materials of China, were analyzed as part of the quality assurance and quality control (QA/QC) procedures. Good agreement was achieved between the data from the present work and the certified values, with recoveries between 92 and 108%. Analysis of the samples, including dust samples and blanks, was performed in triplicate. The standard deviation was within ±5% of the mean value.

Heavy metal speciation in the dust was determined by based on the modified BCR (the European Community Bureau of Reference) sequential extraction procedure [15, 16]. This method includes four steps. Step 1: acid soluble/exchangeable fraction (F1, exchangeable metal and carbonate-associated fractions). Acetic acid (20 ml of 0.11 M solution) was added to 0.5 g of dust samples in 50 ml polyethylene centrifuge tubes, and mechanically shaken for 16 h at room temperature. The extracts were then separated from the residues by centrifuging for 20 min at 4000 rpm. Subsequently, the supernatant was decanted and the residues rinsed with 10 ml of de-ionized water by shaking for 15 min, and then centrifuged. Step 2: reducible fraction (F2, fraction associated with Fe and Mn oxides). Hydroxyl ammonium chloride (20 ml of 0.1 M solution, adjusted to pH 2.0 with nitric acid) was added to residues from step 1, and re-suspended by mechanical shaking for 16 h at room temperature. The procedures for separation of the extract, collection of the supernatant, and rinsing of residues were the same as described in Step 1. Step 3: oxidizable fraction (F3, fraction bound to organic matter). H_2O_2 (5 ml of 8.8 M H_2O_2 solution, pH 2.0-3.0) was added to the residues from Step 2. The tubes were then covered and the contents digested for 1 h at room temperature. The contents were next heated on a hot plate at 85°C for 1 h and evaporated to near dryness. Step 3 was performed twice. Finally, ammonium acetate was added to the cool residues, and the extraction procedure was performed as described in Step 1. Step 4: residual fraction (R). The residue from step 3 was treated by the procedure used for determination of heavy metal contents in the dust sample.

B. Environmental Risk Assessment

The potential ecological risk index (*RI*), proposed by Håkanson in 1980 and then widely used in pollution assessment of sediment, soil and dust [17-19], was used to evaluate the environmental risk of heavy metals in dust from Shangluo city. *RI* is expressed as

$$RI = \sum_{i=1}^{n} E_i = \sum_{i=1}^{n} T_i \times C_f^i = \sum_{i=1}^{n} T_i \times \frac{C_s^i}{C_b^i} \quad (1)$$

where E_i is the potential ecological risk factor of heavy metal *i*. T_i is the toxic-response factor of heavy metal *i*, i.e. Cd=30, Pb=Ni=Co=5, Cr=2, Zn=Mn=1. C^i_f, the pollution index of heavy metal *i*, is equal to the concentration of heavy metal *i* in the sample (C^i_s) divided by its background value (C^i_b) in local soil [20]. The ecological risk degree was classified as low ecological risk (E_i < 40, *RI* < 150), moderate (40 ≤ E_{i+} <80, 150 ≤*RI* <300), considerable (80 ≤E_i <160, 300 ≤*RI* < 600), high (160 ≤ E_i <320, *RI* ≥ 600) or very high (E_i ≥ 320).

III. Results and Discussion

A. Heavy Metal Concentrations in Dust

Heavy metal concentrations in the dust samples are listed in Table 1. It can be seen from this table that the concentrations of Cd, Co, Cr, Mn, Ni, Pb and Zn in dust from Shangluo city ranged from 0.35 to 3.78, 34.6 to 41.5, 23.1 to 73.9, 311.7 to 569.6, 53. to 77.0, 51.3 to 147.6 and 148.5 to 308.5 mg/kg, with average values of 2.4, 37.2, 49.4, 443.5, 65.0, 104.8 and 257.0 mg/kg, respectively. Their mean values are 25.1, 3.5, 0.8, 0.8, 2.3, 4.5 and 3.6 times the corresponding background values of local soil, respectively. The Cd, Co, Ni, Pb and Zn concentrations in the dusts collected from all functional areas of Shangluo are higher than their background values in local soil. The concentrations of Cr in the dusts from CA and RA are slightly above, whereas in the dusts from other functional areas they are less than its background value. The concentrations of Mn in the dusts from all functional areas are below or close to its background value. The dusts of different functional areas have various accumulations of heavy metals. The concentrations of heavy metals in dusts from PA are relatively low, compared to the other functional areas. Heavy metal concentrations in dusts from Xian [13], Baoji [14], Xianyang [21] and Tongchuan [22], the main cities in central Shaanxi, are compared with the present work in Table 1. Cr concentrations in the dusts from Shangluo are less than for the other four cities, while the concentrations of Cr, Mn, Ni, Pb and Zn in the present work are comparable to other cities. The diversities of heavy metal concentrations among the compared cities may relate to their surrounding environment and human activities, such as topography, population density, traffic volume and degree of industrialization.

TABLE I. HEAVY METAL CONCENTRATIONS IN DUST

Location	Metal concentration (mg/kg)						
	Cd	Co	Cr	Mn	Ni	Pb	Zn
IA	2.48	37.6	53.0	569.6	60.4	147.6	292.1
CA	3.78	34.6	69.1	485.9	53.1	141.2	308.5
TA	1.37	37.8	23.1	346.0	77.0	63.8	206.5
RA	3.62	36.2	73.9	471.0	66.4	124.4	305.3
PA	0.35	35.4	23.3	311.7	57.0	51.3	148.5
EA	2.68	41.5	53.9	476.4	76.2	100.7	281.1
Xi'an [13]			167.4	687		230.5	421.5
Baoji [14]		15.9	126.7	804.2	48.8	433.2	715.3
Xianyang [21]			135.6	604.4	69.5	77.3	375.4
Tongchuan [22]		34.0	106.4	361.9	25.3	75.2	141.8
Reference[20]	0.09	10.6	62.5	557.0	28.8	21.4	69.4

IA=industrial area; CA=commercial area; TA=traffic area; RA=residential area; PA=park area; EA=educational area

B. *Chemical Speciation of Heavy Metal*

Chemical speciation of all analyzed heavy metals in the studies dusts obtained by the BCR sequential extraction procedure are shown in Figures 1 to 7. The analyzed heavy metals were present in different chemical speciation in dust from Shangluo. Figure 1 shows that Cd in the dust was mainly present in the acid soluble/exchangeable fraction, with a proportion of 36.0 to 63.5%. The acid soluble/exchangeable fraction of Cd in the dust from the traffic area (TA) was highest (63.5%).

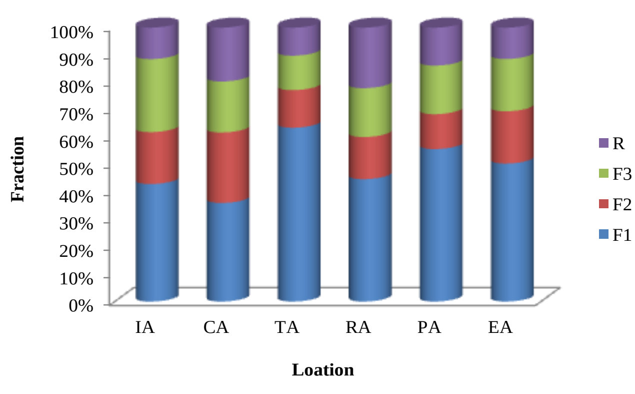

Figure 1. Chemical fractions of Cd in dusts from six main functional areas of Shangluo including exchangeable metal and carbonate-associated fractions (F1); fraction associated with Fe and Mn oxides (F2); fraction bound to organic matter (F3); and residual fraction (R).

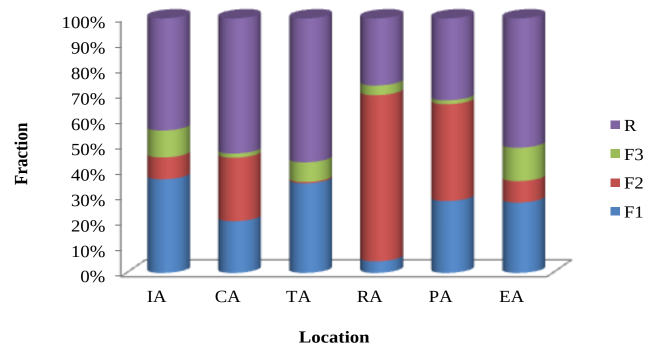

Figure 2. Chemical fractions of Co in dusts from from six main functional areas of Shangluo including exchangeable metal and carbonate-associated fractions (F1); fraction associated with Fe and Mn oxides (F2); fraction bound to organic matter (F3); and residual fraction (R).

The chemical speciation of Co in dusts from the residential area (RA) and the park area (PA) was mainly present in the reducible fraction (65.3% and 38.1%, respectively), while in the dusts from other functional areas it was mainly in the residual fraction (Figure 2). From Figure 3, it can be found that Cr mainly existed in the residual fraction (58.4–73.4%) in Shangluo dust.

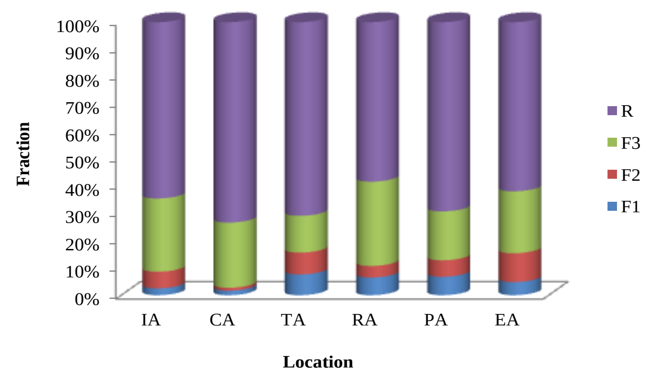

Figure 3. Chemical fraction of Cr in dusts from six main functional areas of Shangluo including exchangeable metal and carbonate-associated fractions (F1); fraction associated with Fe and Mn oxides (F2); fraction bound to organic matter (F3); and residual fraction (R).

Mn in dusts from the traffic area, park area and educational area was mostly in the oxidizable fraction, while in dust from the industrial area it was mainly in acid soluble/exchangeable fraction and in dusts from the commercial and residential areas, it was mostly in the residual fraction (Figure 4).

Figure 5 shows that Ni in the dust from the residential area was primarily in the residual fraction, whereas in the dusts from other areas it was mainly in the oxidizable fraction. Pb and Zn in the dusts from different areas of Shangluo were mostly in reducible fraction and acid soluble/exchangeable fraction, respectively (see Figures 6 and 7).

International Journal of Environmental Engineering– IJEE
Volume 1 : Issue 4 [ISSN 2374-1724]
Publication Date : 27 December,2014

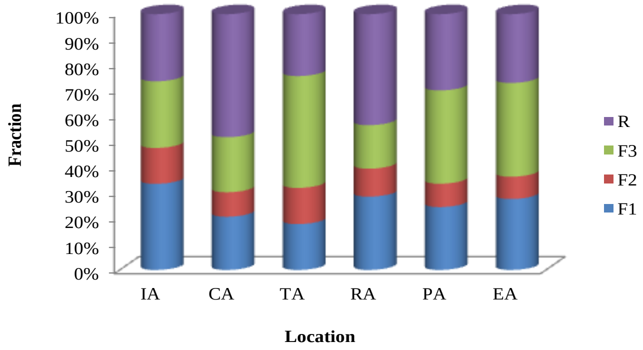

Figure 4. Chemical fraction of Mn in dusts from six main functional areas of Shangluo including exchangeable metal and carbonate-associated fractions (F1); fraction associated with Fe and Mn oxides (F2); fraction bound to organic matter (F3); and residual fraction (R).

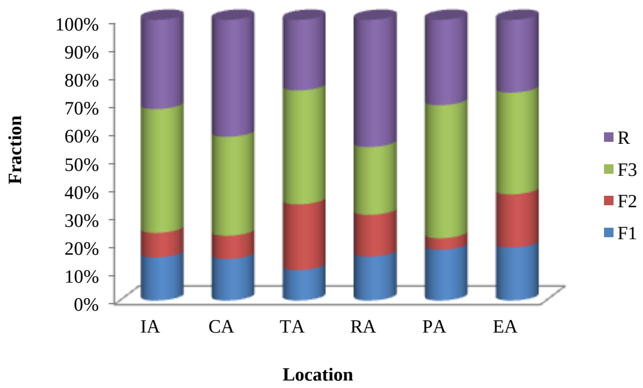

Figure 5. Chemical fraction of Ni in dusts from six main functional areas of Shangluo including exchangeable metal and carbonate-associated fractions (F1); fraction associated with Fe and Mn oxides (F2); fraction bound to organic matter (F3); and residual fraction (R).

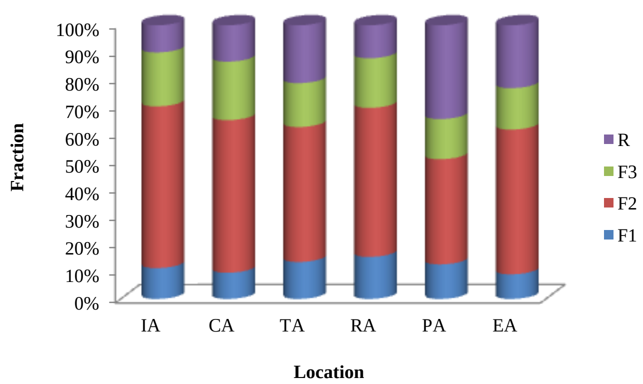

Figure 6. Chemical fraction of Pb in dusts from six main functional areas of Shangluo including exchangeable metal and carbonate-associated fractions (F1); fraction associated with Fe and Mn oxides (F2); fraction bound to organic matter (F3); and residual fraction (R).

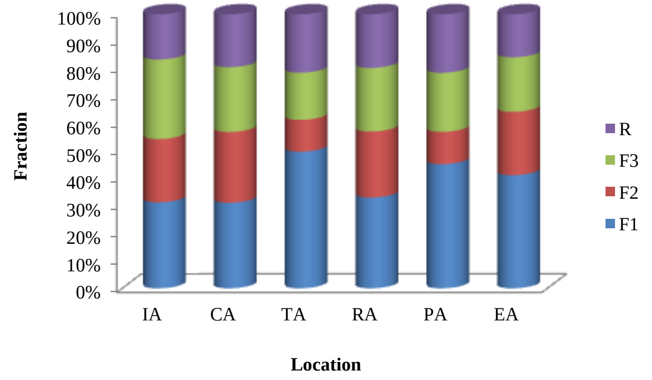

Figure 7. Chemical fraction of Zn in dusts from six main functional areas of Shangluo including exchangeable metal and carbonate-associated fractions (F1); fraction associated with Fe and Mn oxides (F2); fraction bound to organic matter (F3); and residual fraction (R).

In the BCR sequential extraction procedure, the former three chemical forms are easily movable under natural environmental conditions. Figures 1 to 7 show that the easily movable forms (sum of F1, F2 and F3) for Cd, Co, Cr, Mn, Ni, Pb and Zn in the dust studied were in range of 77.9–89.8%, 43.5–73.7%, 26.6–41.6%, 51.9–73.8%, 54.7–74.1%, 66.0–90.1% and 78.7–84.3% with averages of 85.2%, 56.2%, 33.6%, 66.9%, 66.6%, 81.1% and 81.0%, respectively, indicating that all heavy metals in the dust are easily movable and, except for Cr, represent major environmental hazards.

C. *Environmental Risk of Heavy Metals*

The potential ecological risk assessment results for the heavy metals analyzed in the dust from the different functional areas of Shangluo are presented in Table 2. It is seen that the E_i values of Co, Cr, Mn, Ni, Pb and Zn in the dusts from the six functional areas of Shangluo were all <40, showing low ecological risk. The E_i values of Cd in the dusts from all functional areas, except the park area (PA), were, on the other hand, >320, indicating very high ecological risk. The potential ecological risk index (*RI*) values of heavy metals in the dusts from the industrial area (IA), commercial area (CA), residential area (RA) and educational area (EA) were >600, corresponding to high ecological risk. The *RI* values for heavy metals in the dust from the traffic area and park area were in the ranges 300-600 and 150-300, respectively, corresponding to considerable ecological risk and moderate ecological risk, respectively. Cd is the main contributor of potential ecological risk, with its ecological risk accounting for 73-95% of the total ecological risk.

TABLE II. ASSESSMENT RESULTS OF ECOLOGICAL RISK FOR HEAVY METALS IN DUST FROM SHANGLUO

Location	**Ecologial risk factor (E_i)**							*RI*
	Cd	**Co**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**	
IA	791.5	17.7	1.7	1.0	10.5	34.5	4.2	861
CA	1206.4	16.3	2.2	0.9	9.2	33.0	4.4	1272
TA	437.2	17.8	0.7	0.6	13.4	14.9	3.0	488
RA	1155.3	17.1	2.4	0.8	11.5	29.1	4.4	1221
PA	111.7	16.7	0.7	0.6	9.9	12.0	2.1	154
EA	855.3	19.6	1.7	0.9	13.2	23.5	4.1	918

IV. Conclusions

The concentration, speciation and environmental ecological risk of Cd, Co, Cr, Mn, Ni , Pb and Zn in the dusts from urban different functional areas of Shangluo were determined. Urban dusts of Shangluo had elevated concentrations of all of these heavy metals except Mn and Cr. Dusts sampled from different functional areas had diverse heavy metal accumulation levels. The dust from the park area had lower concentrations of heavy metals compared to the other functional areas. Cd and Zn in the dust were mainly in acid-soluble form, while Pb was mostly in reducible form, Co and Cr primarily in residual form, and Ni mainly in oxidizable and residual form. The chemical speciation of Mn had larger diversity in dusts from different functional areas. Environmental risk assessment results indicate that Cd presented considerable to very high ecological risk, while other metals displayed low ecological risk. The total ecological risks of all determined metals in the dust were present in the high ecological risk category. The heavy metals analyzed are poisonous to human health. The high concentrations of Cd, Co, Ni, Pb and Zn, and their high mobility, in particular those of Cd, are of particular concern,

Acknowledgments

All experimental analysis were carried out in the Environmental Laboratory of Shaanxi Normal University. The authors sincerely thank X. Ding and Q. Ji for their assistance with the sample analysis.

References

[1] R.L.Tang, K.M. Ma, Y.X. Zhang, Q.Z. Mao, “The spatial characteristics and pollution levels of metals in urban street dust of Beijing, China” Appl. Geochem. vol. 35, pp. 88–98, 2013.

[2] G.T. Shi, Z.L. Chen, S.Y. Xu, J. Zhang, L. Wang, C.J. Bi, J.Y. Teng, “Potential toxic metal contamination of urban soils and roadside dust in Shanghai, China” Environ. Pollut. vol. 156, pp. 251–260, 2008.

[3] G.T. Shi, Z.L. Chen, C.J. Bi, L. Wang, J.Y. Teng, Y.S. Li, S.Y. Xu, “A comparative study of health risk of potential metals in urban and suburban road dust in the most populated city of China” Atmos. Environ. vol. 45, pp. 764–771, 2011.

[4] O.A. Al-Khashman, “The investigation of metal concentrations in street dust samples in Aqaba city Jordan” Environ. Geochem. Health vol. 29, pp. 197–207, 2007.

[5] L.J. Wang, X.W. Lu, C.H. Ren, X.X. Li, C.C. Chen, “Contamination assessment and health risk of heavy metals in dust from Changqing industrial park of Baoji, NW China” Environ. Earth Sci. vol. 71, pp. 2095–2104, 2014.

[6] R. Boonyatumanond, M. Murakmi, G. Wattayakorn, A. Togo, H. Takada, “Sources of polycyclic arometic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkon, Thailand” Sci. Total Environ. vol. 384, pp. 420–432.

[7] S. Harrad, C. Ibarra, M. Robson, L. Melymuk, X.M. Zhang, M. Diamond, J. Douwes, “Polychlorinated biphenyls in domestic dust from Canada, New Zealand, United Kingdom and United States: implications for human exposure” Chemosphere vol. 76, pp. 232–238, 2009.

[8] F. Ahmed, H. Ishiga, “Trace metal concentrations in street dusts of Dhaka city, Bangladesh” Atmos. Environ. vol. 40, pp. 3835–3844, 2006.

[9] M.S. Atiemo, G.F. Ofosu, H. Kuranchie-Mensah, A.O. Tutu, L. Palm, S.A. Blankson, “Contamination assessment of heavy metals in road dust from selected roads in Accra, Ghana” Res. J. Environ. Earth Sci. vol. 3, pp. 473–480, 2011.

[10] E. De Miguel, I. Iribarren, E. Chacón, A. Ordoñez, S. Charlesworth, “Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain)” Chemosphere vol. 66, pp. 505–513, 2007.

[11] N.S. Duzgoren-Aydin, C.S.C. Wong, A. Aydin, Z. Song, M. You, X.D. Li, “Heavy metal contamination and distribution in the urban environment of Guangzhou, SE China” Enviorn. Geochem. Health vol. 28, pp. 375–391, 2006.

[12] L. Ferreira-Baptista, E. De Miguel, “Geochemistry and risk assessment of street dust in Luanda, Angola: a tropical urban environment” Atmos. Environ. vol. 39, pp. 4501–4512, 2005.

[13] Y.M. Han, P.X. Du, J.J. Cao, E.S. Posmentier, “Multivariate analysis of heavy metal contamination in urban dusts of Xi’an, Central China” Sci. Total Environ. vol. 355, pp. 176–186, 2006.

[14] X.W. Lu, L.J. Wang, L.Y. Li, K. Lei, J. Huang, D. Kang, “Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China” J. Hazard. Mater. vol. 173, 744–749, 2010.

[15] Ş. Tokalıǧlu, Ş. Kartal, “Multivariate analysis of the data and speciation of heavy metals in street dust samples from the Organized Industrial District in Kayseri (Turkey)” Atmos. Environ. vol. 40, pp. 2797–2805, 2006.

[16] H.M. Li, X. Qian, W. Hu, Y.L. Wang, H.L. Gao, “Chemical speciation and human health risk of trace metsls in urban street dusts froma metropolitan city, Nanjing, SE China” Sci. Total Environ. vol. 456-457, pp. 212–221, 2013

[17] Y.B. Sun, Q.X. Zhou, X.K. Xie, R. Liu, “Spatial, sources and risk assessment of heavy metal contamination of urban souls in typical regions of Shenyang, China” J. Hazard. Mater. vol. 174, pp. 455–462, 2010.

[18] G.L. Yuan, T.H. Sun, P. Han, J. Li, X.X. Lang, “Source identification and ecological risk assessment of heavy metals in topsoil using environmental geochemical mapping: Typical urban renewal area in Beijing, China” J. Geochem. Exp. vol. 136, pp. 40–47, 2014.

[19] H.T. Zhao, X.Y. Li, “Risk assessment of metals in road-deposited sediment along an urban-rural gradient” Environ. Pollut. vol. 174, pp. 297–304, 2013.

[20] CNEMC (China National Environmental Monitoring Centre), The background values of Elements in Chinese soils, 1st ed., Beijing: Environmental Science Press of China, 1990, pp. 30–180 (in Chinese).

[21] X.M. Shi, L.X. Chen, J.H. Wang, “Multivariate analysis of heavy metal pollution in street dusts of Xianyang city, NW China” Environ. Earth Sci. vol. 69, pp. 1973–1979, 2013.

[22] X.W. Lu, X. Wu, Y.W. Wang, H. Chen, P.P. Gao, Y. Fu, “Risk assessment of toxic metals in street dust from a medium-sized industrial city of China” Ecotoxi. Environ. Safty vol. 106, pp. 154–163, 2014.