

The Chemical Speciation of Trace-Metals in Street Dusts of Irbid, Jordan

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Received on May 31, 2012

Accepted on Nov. 12, 2012

Abstract

Street dust samples were collected from different locations in Irbid city, Jordan. The concentrations of Pb, Cu, Zn, Cd, Ni, Mn, Cr and Al in these samples were determined using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) after chemical fractionation according to the modified Community Bureau of Reference (BCR) sequential extraction procedure. The street dusts were sequentially extracted into three operationally defined fractions; exchangeable and bound to carbonates, bound to Fe-Mn oxides and residual. The order of bioavailability of measured elements (exchangeable and bound to carbonates) is found to follow the order: Zn > Cu > Mn > Cd > Pb > Ni > Cr > Al. However, the relative abundance of the metals in mobile phases of the samples based on the sum of acid-extractable and oxidizable fractions are in the following sequence: Pb (96.2%) > Mn (92.9%) > Zn (77.2%) > Cu (76.3%) > Cd (65.7%) > Ni (44.5%) > Cr (33.4%) > Al (28.4%). Enrichment factor calculations indicated that Zn, Cu, Pb and Cd are highly enriched (EF values > 100), which indicates a widespread contamination of these elements by human sources. However, enrichments of other elements were moderate and show large variability. The highest EF values for Cr and Ni are found in the residential areas followed by the main roads.

Keyword: Street dust; Heavy metals; ICP-OES; Sequential extraction; Enrichment factors; Jordan.

Introduction

Among all environmental compartments, soil could be the most important one because it receives heavy metals coming from many sources simultaneously and controls the movement of these metals to another compartment ^[1]. Heavy metals can accumulate on topsoil from atmospheric deposition by sedimentation, impaction and interception. The dust emitted into the atmosphere from different industrial activities and traffic represents some anthropogenic origins of soil contamination with heavy metals. For instance, one of the most important heavy metal sources in urban areas is vehicle emission. Car components and corrosion are also believed to be the sources of

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some metals in street dust. Waste materials applied to soil, residual of sewage sludge, fertilizers and some crop protection chemicals are also important sources of soil pollution by different heavy metals ^[1,2].

Thus, from an environmental point of view, urban areas can be considered as risk areas with regard to trace metals. The importance of street dust investigation comes from the fact that street's dust is being inhaled by those who live within the vicinity of the streets. Hence, the higher the levels of heavy metals in the dusts, the more people are subjected to the health hazards associated with these metals. Metals are non-degradable and can accumulate in the fatty tissues of the human body and affect the central nervous system. Consequently, the normal function of the internal organs could be disrupted ^[3]. Other health problems associated with heavy metals include reduced intelligence, attention deficit and contribution to cardiovascular disease in adults ^[4]. Some metals (i.e., Pb, As, Hg and Cd) are toxic even at extremely low concentrations. These metals play as potential cofactors, initiators or promoters in many diseases and cancer ^[5, 6]. The digestion system in children has a much higher absorption rate of heavy metals than that in adults. In addition, sensitivity of hemoglobin towards heavy metals in children is higher than in adults ^[7].

It is well documented that metals from anthropogenic sources tend to be more mobile than pedogenic or lithogenic ones ^[8, 9]. Therefore, there is a need to improve the understanding about pollutant behavior in soils in general and in soils in urban environments in particular. Speciation of the metals can help assess how strongly they are retained in soil and how easily they may be released into soil solution. Different sequential extraction techniques are commonly applied to evaluate the potential mobility of metals in the environment ^[10-12]. The main objectives of the present study are: (a) to estimate the average concentrations of some heavy metals (Cu, Cd, Cr, Al, Mn, Ni, Pb and Zn) in street dust samples collected from various areas in Irbid city, (b) to ascertain their mobility and hence bioavailability by solid phase speciation using sequential extraction.

Experimental

Materials

All reagents employed were analytical grade purity, HF assay 40% (Union LAR. Supplies), and high purity HNO₃ assay 69-71 % (BDH Limited, England). All solutions were prepared using deionized water (18.2 MΩ). Acetic acid and hydroxyl amine hydrochloride were obtained from Merck.

Sampling and pretreatment

Polyethylene bottles and glassware used for sample handling were soaked in 10% HNO₃ for 48 h followed by thorough rinsing in de-ionized water. A total of 29 road dust samples were collected in the pre-cleaned polyethylene bottles from different sites in Irbid city, Jordan. Sample collection was carried out at the end of the dry summer season to avoid rain washing out of the heavy metals. The sampling of dust was

achieved by sweeping an area of about 1 m² of the road using a plastic dustpan and brushes. Collected samples were dried at 105 °C in a drying oven for 18 hours. Samples were ground using pestle and mortar, and sieved through a mesh of 1mm pore size to remove extraneous material.

Sequential Extraction

Soil samples were extracted with the modified version of the Community Bureau of Reference BCR-three step sequential extraction procedure. This procedure can be described as follows^[13, 14]: First step (Exchangeable and weak acid soluble fraction): 1 g soil sample was extracted with 40 mL of 0.11 M acetic acid solution at room temperature using a mechanical shaker for 16 h. The extract was separated by centrifugation at 3000 rpm for 20 min, collected in polyethylene bottles and stored until analysis. The residue was washed by shaking for 15 min with 20 mL of deionized water and then centrifuged, discarding the supernatant. Second step (Reducible fraction): 40 mL of 0.50 mol L⁻¹ hydroxyl amine hydrochloride solution was added to the residue from the first step, and the mixture was shaken at room temperature for 16 h. The extract was separated and the residue was washed as in the first step.

According to the BCR procedure^[13, 14], residue from the second step should be extracted by a mixture of H₂O₂ and ammonium acetate (pH 2-3) in order to evaluate the oxidizable fraction. However, the organic carbon content in the study area soil is low^[15] due to the small area covered by plants and the arid climate in Jordan. Therefore, residue from the second step was digested with a mixture of HNO₃ and HF. About 15 mL of high purity concentrated HNO₃ and 4 mL HF were added and left overnight at ambient temperature. Hydrofluoric acid was added to dissolve siliceous materials. Samples were then refluxed (the beaker is covered) for about 6 hours until complete digestion of the solid particles. When the mixture became clear, the cover was removed and the acids were slowly evaporated to near dryness. At this stage, 2 mL of the concentrated nitric acid were added and the solutions were re-evaporated again to about 1.0 mL. The digest was cooled and diluted with deionized water up to 50 ml and stored in plastic bottles.

Analysis of samples

The concentration of each of the measured elements in the extracts was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). A Varian, VISTA-MPX, ICP-OES system coupled with a CCD-Simultaneous detector was used in this study. The recommended manufacturer procedure was followed for the analysis of the digested samples.

Laboratory blanks were routinely prepared and analyzed to detect the possibility of sample contamination during digestion and subsequent analysis. Accuracy of measurements was checked by regular analysis of synthetic standards and standard

reference materials NIST, SRM 1646 (Estuarine sediment). A good agreement was observed between the obtained and the certified values for the metals analyzed.

Results and Discussion

Descriptive statistical results are reported in table 1, including the average, standard deviation, minimum, maximum and geometric mean. Mean values were used when heavy metal concentrations had normal distributions, and geometric mean values were used when heavy metal concentrations had lognormal distributions. Therefore, both values are presented in the table to facilitate comparisons with literature data. The total concentration of every sample was obtained by the summation of carbonate fraction, Fe-Mn oxides fraction, and residuals. The high standard deviation values indicate high variation within the transect. The soil pH was generally above 7.0, with a minimum of 7.29 and a maximum of 8.31, indicating that the soil is neutral or slightly alkaline. The high pH of the soils suggests that the soil contains lime.

Comparison of the obtained data with the literature is one of the essential steps in order to know the extent of contamination by these metals. Observed concentrations of elements are compared with those found by others in other cities and presented in the last four columns in table 1. The data reveals that mean concentration of Cd in soils of this study (3.31 mg/kg) is higher than those reported for Greece and Turkey and about 2 times lower than those observed in central Jordan and South Jordan. Similarly, levels of Zn and Cu are among the highest as compared to those in table 1. These observations indicate a fairly wide-scale contamination by these elements. Copper and Zn are usually used in the production of the brass alloy itself, Cd was used to protect the surface of the brass from corrosion. However, the close matching in the levels of these elements to that of Pb in the different sub-regions indicate that the distribution of Cd, Cu, Zn and Pb across the city can be explained by their association with traffic and other industrial activities.

Levels of the remaining elements are either close to or less than those reported in table 1. Both Cr and Ni have shown similar distribution patterns; high levels of Cr are almost associated with high levels of Ni. These elements have both anthropogenic and crustal sources. High concentrations of these two elements in residential areas are probably anthropogenic. The widespread uses of these two elements in the production of office furniture, stainless steel, metal plating for prevention of corrosion, coloring agents for emerald green glass, chemical analysis, leather tanning and textile color pigments are among the common sources for these two elements in residential areas ^[16].

Table 1: Comparison of total metal concentrations in urban soils with literature data (mg/Kg).

	This Study			Central Jordan ^[17]	South Jordan ^[18]	Greece Kavala ^[19]	Turkey Kayseri ^[20]
	Average	SD	GM	Average	Average	Average	Average
Al	4909	8404	2483				
Cd	3.31	2.25	2.70	4.98	5.00	0.2	2.53
Cr	37.44	29.72	28.30	83.93	22.18	232.2	29.0
Cu	107.26	181.57	55.66	-	2.89	172.4	36.9
Mn	150.19	198.98	95.11				237
Ni	37.56	15.27	32.44			67.9	44.9
Pb	46.27	47.49	33.91	62.17	55.00	386.9	74.8
Zn	372.98	187.28	304.59	146.94	44.51	354.8	112
pH	7.92	0.17	7.92				

Partitioning of metals

Soil has long been regarded as a repository for society's wastes. Gradually mobilized by biogeochemical processes, soil contaminants can pollute water supplies and impact food chains. Heavy metals, such as Pb, Cd, Cu, Cr, Ni, and Zn, are all potential soil pollutants. Soils consist of heterogeneous mixtures of organic and inorganic solid components as well as a variety of soluble substances. Therefore, metal distribution among specific forms varies widely based on the metal's chemical properties and soil characteristics ^[21]. Thus, it is important to evaluate the availability and mobility of heavy metals to establish environmental guidelines for potential toxic hazards and to understand chemical behavior and fate of heavy metal contaminants in soils ^[22].

Generally metals are most toxic in the ionic un-complexed form. The bioavailable fraction can be defined as the fraction of the total amount of a chemical present in a specific environmental compartment that, within a given time span, is either available or can be made available for uptake by organisms or plants, from either the direct surrounding of the organism or the plant or by ingestion of food.

The average fractionation pattern of the metals in the street dust samples are given in figure 1. As it can be seen, the contents of the metals as relative abundance in exchangeable and carbonate phase of the samples are in the following sequence: Zn (24.5%) > Cu (24.1%) > Mn (21.1%) > Cd (20.1%) > Pb (17.5%) > Ni (8.2%) > Cr (4.0%) > Al (1.1%). However, the relative abundance of the metals in mobile phases of the samples based on the sum of acid-extractable and oxidizable fractions are in the following sequence: Pb (96.2%) > Mn (92.9%) > Zn (77.2%) > Cu (76.3%) > Cd (65.7%) > Ni (44.5%) > Cr (33.4%) > Al (28.4%).

Most of lead is associated with the Fe-Mn oxide phase, followed by the carbonate and residual fractions. The percentage of Pb associated with the Fe-Mn

oxide phase was 78.7%. The predominance of Pb in the Fe–Mn oxide fraction is in broad agreement with the fractionation of Pb in sediments^[23, 24], soils^[25, 26] and street dusts^[28-30]. The adsorption of Pb cations on the hydrous (amorphous) oxides of iron and Mn is considered as a reasonably universal fixation mechanism. The association of lead with the Fe-Mn oxide fraction of dusts gives rise to a pool of lead which, though relatively immobile, may create long term contamination problems. The percentage of Pb in the carbonate phase is 17.5% followed by 3.8% for the residual fraction. Similar behavior is observed for the association of Mn with different phases. Most of the Mn (71.8%) is tied up with Fe-Mn phase followed by the carbonate phase (21.1%).

The distribution of Zn pattern in each fraction followed the order: Fe-Mn oxide >> carbonate > residual. The majority of Zn was associated with the Fe-Mn oxide fraction (52.7%). Earlier studies on soils, sediments and street dusts indicated that larger fractions of Zn were associated with the Fe-Mn oxide fraction^[23, 25, 29]. They suggested that Fe and Mn oxides may occlude Zn in the lattice structures. The speciation pattern obtained for Cu is similar to Zn and followed the order; Fe-Mn oxide >> carbonate > residual. Similarly, the largest fraction for Cd is observed in the Fe-Mn oxide phase (45.7%) followed by the residual fraction (34.3%). Cadmium is associated with motor traffic emissions as a constituent of motor alloys or with the electronic components and batteries of cars. Because of cadmium impurities in zinc materials, cadmium also accompanies zinc oxides used in tire manufacture^[30]. This may explain the relatively high fractions of Cd found in the Fe-Mn oxide phase. About 20% of the Cd is tied up with the carbonate phase, which is consistent with the findings of Stone and Marsalek^[29]. Enhanced significance of carbonate fraction in the present study is probably a consequence of the more alkaline and calcareous nature of the soil and dust in Jordan^[31]. At higher pH, the substitution of Cd²⁺ for Ca²⁺ in the calcite and precipitation of CdCO₃ is expected^[32].

The distribution patterns for Ni and Cr in different fractions followed the order: residual > Fe–Mn oxide > carbonate. The relative occurrences of these elements in the residual fraction are 66.6% and 55.4% for Cr and Ni, respectively. However, relatively small amounts of Cr and Ni have occurred in the carbonate fraction, 4.0% and 8.0%, respectively. These findings are in good agreement with results reported by Stone and Marsalek^[29] and Sutherland and Tolosa^[33] in street dust. In all samples, Al is associated mainly with the residual fraction. Its content in the residual fraction ranged from 67 to 95%. These finding are in good agreement with most of the literature, in which residual fraction contains most of the Al^[34].

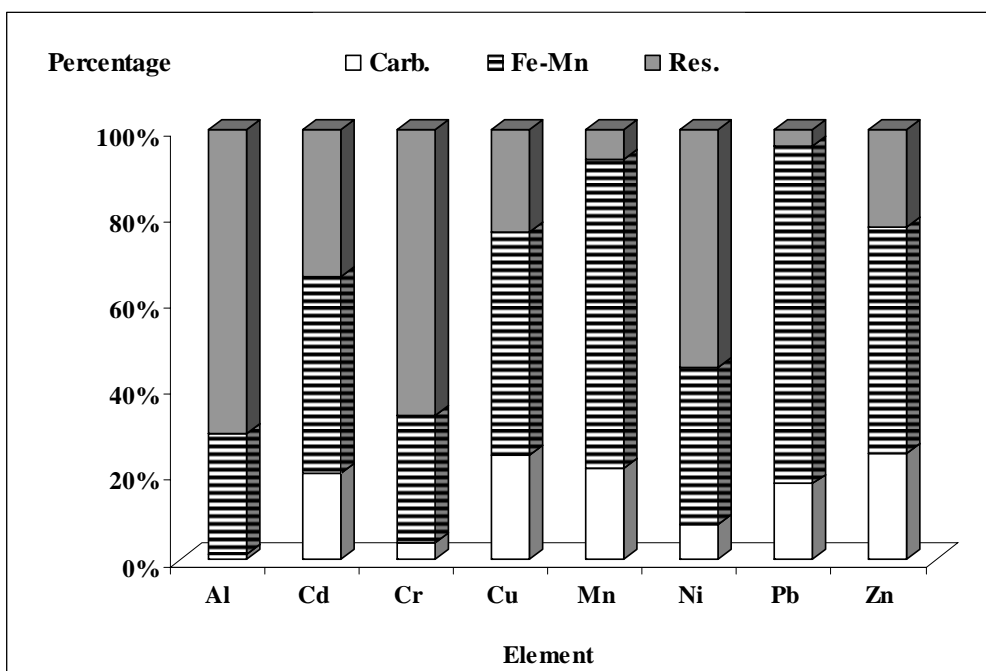


Figure 1: The chemical fractionation patterns of Al, Cd, Cr, Cu, Mn, Ni, Pb and Zn in the street dust samples.

Enrichment of measured elements

The main component of elements in sediments is the aluminosilicate material. If there were no anthropogenic sources, concentrations of elements should be explained by this source. However, the composition of sediment is modified by contributions from various man-made sources. The degree of the modification of chemical composition of sediments may be different at each sampling point due to different magnitude of source contributions at each station. Crustal enrichment factors (EF_c) of elements are frequently used in studies of atmospheric aerosols^[35, 36] to determine the degree of modification in the soil composition. Aluminum was used as a reference element because it is the crust-dominated element^[37].

The EF_c is given by:

$$EF_c = \frac{(C_x / C_{Al})_{sample}}{(C_x / C_{Al})_{crust}}$$

where $(C_x / C_{Al})_{sample}$ is the ratio of concentration of an element X in $\mu\text{g/g}$ to that in the sample and $(C_x / C_{Al})_{crust}$ is the same ratio in crustal material obtained from compilation for trace elements in earth's crust^[38]. Elements which have other sources than crustal dust have enrichment factors higher than unity. Generally, EF values less than 5.0 are not considered significant, because such small enrichments may arise from differences in the composition of local soil material and reference soil used in EF calculations.

Figure 2 shows the crustal enrichment factors of measured elements in soil samples. These data place the urban data into the context of natural background concentrations in Irbid, indicating that, Zn, Cu, Pb and Cd are highly enriched (EF

values > 100). These data suggest widespread contamination by human sources. Cadmium was highly enriched in all samples, which must be considered to be indicative of gross contamination.

Manganese is slightly enriched (EF values < 20) in all dust samples, however, Ni and Cr are moderately enriched and their EF values showed large variability. The highest EF values for Cr and Ni are found in the residential areas followed by the main roads. The relatively higher enrichment for these metals in the residential areas could be attributed to the use of different tools that are plated by these metals. It may also be expected that the rehabilitation and construction work is likely to mobilize these metals from these tools.

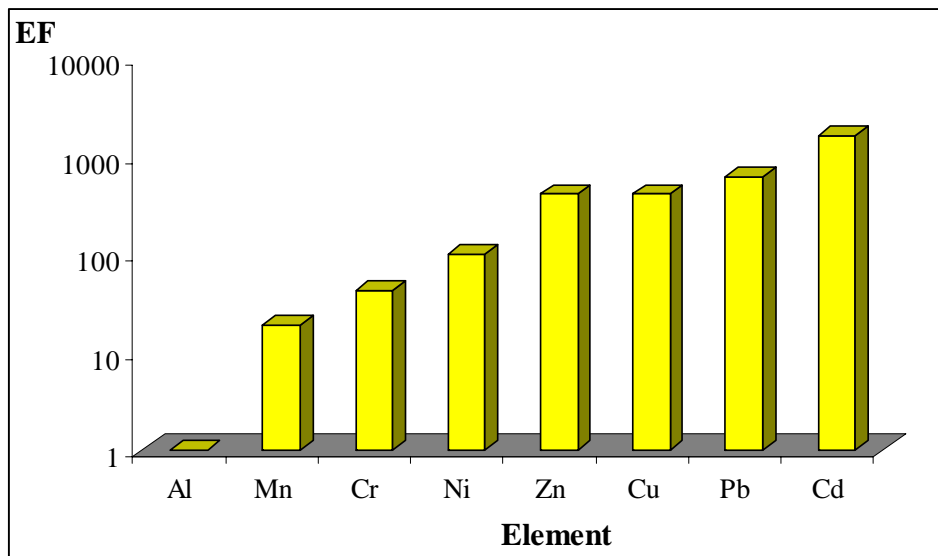


Figure 2: Enrichment factors of measured elements in soil samples.

Conclusions

The street dust samples collected from Irbid city show significant contamination by Cu, Cd and Zn. However, the contamination is relatively similar or lower than that of other cities in Jordan or worldwide. The sequential extraction method is used to assess the potential mobility and bioavailability of the metals in the street dusts. The mobility of these metals is related to their solubility and geochemical forms, and it decreases in the order of extraction sequence, i.e., exchangeable and carbonate > Fe–Mn oxide bound > residual. Accordingly, the order of bioavailability of measured elements is: Zn > Cu > Mn > Cd > Pb > Ni > Cr > Al. However, the relative abundance of the metals in mobile phases of the samples based on the sum of acid-extractable and oxidizable fractions are in the following sequence: Pb (96.2%) > Mn (92.9%) > Zn (77.2%) > Cu (76.3%) > Cd (65.7%) > Ni (44.5%) > Cr (33.4%) > Al (28.4%).

Enrichment factor calculations indicated that Zn, Cu, Pb and Cd are highly enriched (EF values > 100). These data suggest widespread contamination by human sources. Cadmium was highly enriched in all samples which must be considered to be

indicative of gross contamination. Enrichments of other elements were moderate and show large variability. The highest EF values for Cr and Ni are found in the residential areas followed by the main roads.

Acknowledgments

The financial support from Yarmouk University is gratefully acknowledged.

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