Pak. J. Sci. Ind. Res. 2010 **53** (6) 323-329

Estimation of Heavy Metals in Dust Fall Samples from Three Different Industrial Areas of Karachi

Durdana Rais Hashmi*, Farooq Ahmad Khan, Akhtar Shareef and Alia Bano Munshi
Center for Environmental Studies, PCSIR Laboratories Complex, Shahrah-e-Dr. Salimuzzaman Siddiqui, Karachi-75280, Pakistan

(received July 22, 2009; revised July 7, 2010; accepted July 21, 2010)

Abstract. The study of accumulation of heavy metals, Fe, Cu, Mn, Zn, Pb and Cd, in the dust fall samples, collected from three selected industrial areas of Karachi, showed the level of heavy metals to decrease gradually from sites of high activity to those of low activity such as from roundabouts to main roads to side roads. Concentration of heavy metal showed a variation of the order Fe>Zn>Pb>Mn>Cu>Cd. Iron had the highest concentration in all the sampling areas in the range of 1.947 ± 0.00 to 30.039 ± 0.01 mg/g. Lower values were observed for Cd with respective ranges of 0.001 ± 0.00 to 0.009 ± 0.01 mg/g. The results suggested that heavy metal pollution in the dust fall samples of industrial areas may be due to automobile and industrial exhaust from different industrial units.

Keywords: dust fall, heavy metals, industrial areas, automobile emission, industrial emission, air pollution

Introduction

Pollution due to heavy metals is now a worldwide phenomenon, these metals are discharged into the environment through industrial activity. In industrial areas, vehicular emission is the greatest source of atmospheric pollution contributing about 60% of the total load. Pollutants discharged from automobiles are CO, SO_2, NO_x, particulate matter and hydrocarbons. Many heavy metals including lead, cadmium, copper, manganese, nickel and zinc are also discharged into the atmosphere through the automobile exhaust.

Metals such as Fe, Cu, Zn and Cd are essential components of many alloys, wires and many industrial processes and may be released into the environment as a result of mechanical abrasion and normal wear (Jaradat and Momani, 1999).

Heavy metal analysis is important part of environmental pollution studies (Buszewski *et al.*, 2000; Chibowski 2000; Momani *et al.*, 2000). Determination of heavy metal contents in various environmental materials such as soil, natural water, plants, dust etc have been continuously performed by researchers (Krolak, 2000; Soylak *et al.*, 2000).

Modernization and enhanced industrial activities have led to increase the use of fossil fuels and their derivates, particularly in metropolitan cities. Karachi is one of the thickly populated cities of the world with the population of more then 14 million, spread over 3580 km^2. It is congested with a large number of motor vehicles, including both public and private transport. It has also a well defined industrial base; there are about 20,000 small and large industrial units working in various industrial areas of Karachi city. Vehicular emission, biomass burning for cooking, brick kilns and industrial emissions around the Karachi city are the main contributor to heavy metal pollution.

Dust fall is an indicator of heavy metal pollution in the atmosphere and is a major means of ingress of heavy metals into the soil and subsequently living tissues of plants and human beings. A range of metals and chemical compounds found in the atmospheric dust environment results in health hazards. Pollutants can attack specific sites or organs of the body and disease can develop as a consequence of such exposure (Shinggu *et al.*, 2007). Several epidemiological studies have indicated a strong association between elevated concentrations of inhaleable particles and increased mortality and morbidity (Mahmud *et al.*, 2008).

The aim of this study was to investigate the present status of air-borne heavy metal concentration of iron, zinc, lead, manganese, copper and cadmium in the environment of different industrial sites of Karachi city, so as to create a database that could help to develop future control strategies towards creating a pollution- free environment in Karachi.

Materials and Methods

Sampling map. Seventeen (17) locations were selected in three different industrial areas of Karachi metropolis along major roads, side roads and round-abouts as shown in the location map (Fig. 1).

Sampling. Dust samples were collected by deposited gauge method (Sami *et al.*, 2006). Deposited gauge units were setup

*Autor for correspondece; E-mail: drhpak@yahoo.com

Fig. 1. Sample collection location.

with collecting bowls and bottles at 17 identified locations in the industrial areas of Karachi. The deposit gauge units were placed about 3 m above the ground level to avoid interference from animals and public. Samples of dust were collected from Sindh Industrial Trading Estate (SITE), Korangi Industrial Area (KIA), Landhi Industrial Trading Estate (LITE) and from the control site. After one month, the deposited gauge units were collected and the samples were prepared and analyzed for heavy metals.

Reagents. All the experiments were performed with analytical reagent grade chemicals. All the glassware were extensively soaked with dilute HNO_3 and rinsed twice with distilled water. All the reagents were ultra pure or analytical reagent (A.R) grade. Distilled and de-ionized water was used for dilution and preparation of reagents and standards. Reference standards were used from ACCU.

Sample preparation. Dust samples (5.0 g) were oven dried at 105 °C to remove the moisture. The digested samples were dissolved in an acid mixture containing 10 mL of 65% HNO_3 and 60% $HClO_4$. The mixture was then filtered through Whatman # 42 filter paper, into a volumetric flask and made up to the mark by adding deionized water.

Apparatus. Analysis was performed on atomic absorption spectrophotometer (Hitachi Z-8000), with Zeeman effect background correction. The spectrophotometer was equipped with a graphite furnace, a microprocessor and a built-in printer. Determination of Fe, Zn, Mn and Cu was carried out by flame atomic absorption Spectrometry (FAAS) whereas Pb and Cd were carried out by electro-thermal atomic absorption spectrometry (ETAAS) on atomic absorption spectrophotometer, employing the standard addition technique. Measurements were takes using hollow cathode lamp for the metals Fe, Zn, Pb, Mn, Cu and Cd.

Analysis of dust samples. Solution samples of Fe, Zn, Pb, Mn, Cu and Cd were analyzed by the method of direct calibration curve using flame atomic absorption spectrometry (FAAS) whereas Pb and Cd, by elector-thermal atomic absorption spectrometry (ETAAS). Triplicate readings were taken on each sample by AAS, and mean values of these figures were used to calculate the results. Working conditions for detecting various elements by atomic absorption spectrophotometer are presented in Table 1.

Results and Discussion

Samples of dust fall were collected from seventeen identified locations in industrial areas of Karachi during the year 2008. The stations selected for this study were on the main roads, side roads and junctions. Results of analysis of iron, zinc, lead, manganese, copper and cadmium are presented in Table 2-5. Quantities of all the ions investigated in dust samples were determined at mg/g level.

Sindh industrial trading estate (SITE) of Karachi is one of the largest and oldest industrial estates of Pakistan. It was established in 1953 and is located at latitude 24° 54′ and longitude 67°10′ in the district south of Karachi. Nearly 2000 various types of industries are located in this area. Approximately 60 % of these industries are textile mills while others deal with pharmaceuticals, chemicals, detergents, iron and steel, vegetable oils, beverages and food products etc. Codes S1, S2 and S3 are used here to indicate the stations selected in SITE, Karachi. Results (Table 2) suggested that Fe had the highest concentration followed by Zn, Pb, Mn, Cu and Cd, in the order. Maximum average concentration of Fe in SITE was 30.039 mg /g at station S3 followed by S1 (23.33 mg/g) and S2 (23.11mg/g). All the three stations selected were roundabouts, which were surrounded by different industries like pharmaceuticals, chemicals, iron and steel, foods beverages; these are also the busiest intersections with reference to high traffic density. Concentrations of other metals like Zn, Pb, Mn, Cu and Cd followed the similar pattern (Table 2).

Table 3 shows the level of Fe, Zn, Pb, Mn, Cu and Cd determined in dust fall samples of the Korangi Industrial area (KIA) of Karachi, which is the second largest industrial area of Karachi. It is located in the East of Karachi at latitude

Table 1. Working condition for the detecting elements by atomic absorption spectrophotometer

Parameters	Fe	Zn	Pb	Mn	Cu	Cd
Slit	0.2	1.3	1.3	0.4	1.3	1.3
Wave length (nm)	248.3	213.9	283.3	279.3	324.8	228.8
Drying temperature (°C)	-	-	80-120	-	-	80-120
Ashing temperature (°C)	-	-	400	-	-	300
Atomisation temperature (°C)	2300	2300	2000	2300	2300	1500

Table 2. Level of heavy metals in dust samples of SITE

Code for	Locations	Fe mg/g	Zn mg/g	Pb mg/g	Mn mg/g	Cu mg/g	Cd mg/g
S1	Roundabout	23.333	1.487	1.143	0.631	0.167	0.004
S2	Roundabout	23.108	1.232	0.563	0.616	0.156	0.003
S3	Roundabout	30.039	1.625	1.851	0.712	0.184	0.004
Average	–	25.493	1.448	1.186	0.653	0.169	0.004
Maximum	–	30.039	1.625	1.851	0.712	0.184	0.004
Minimum	–	23.108	1.232	0.563	0.616	0.156	0.003

24°51′ and longitude 67°11′. Approximately 2000 various types of industries are located in this area, which include tanneries (more than 100 units), pharmaceuticals, textile, chemicals and refineries etc. Code No K1 to K7 are used for the selected stations of KIA of Karachi. K1, K2 and K3 are the roundabouts whereas K4 to K7 are the side roads and the link roads. Maximum level of Fe here was 24.82 mg/g at station K3 followed by K1, 21.26 mg/g and K2 19.39 mg/g. These three stations of KIA are the roundabouts surrounded by heavy industries with traffic congestion. Levels of other metals followed the same pattern with K3>K1>K2 and the concentrations of metals as Zn>Pb>Mn>Cu>Cd (Table 3). Stations K4 to K7 were side roads or link roads with the minimum level of Fe followed by K1, K2 and K3. Level at K7 was 2.95 mg/g followed by K4, 2.47 mg/g, K5, 2.00 mg/g and K6, 1.94 mg/g. Level of other metals at K4 to K7 followed the same pattern as K7>K4>K5>K6, with concentration of metals as Zn>Mn>Pb>Cu>Cd (Table 3). Low value obtained here may be due to the fact that these stations are side roads having low traffic density and low influence of industrial emissions showing the pattern of heavy metals as Fe>Zn>Mn>Pb>Cu>Cd.

Table 4 presents the levels of heavy metals at Landhi industrial trading estate (LITE). This industrial estate was established in 1958 and is located in the east of Karachi at latitude 24° 08′ and longitude 67° 03′. There are three hundred industrial units of different categories located in this estate which include textile, foods, chemicals, pharmaceutical and engineering. Codes L1 to L6 indicate the stations in LITE. L1 and L2 are the main roads, whereas L4 to L6 are side roads. Maximum average concentration of Fe was 20.0 mg/g at L1 and 15.34 mg/g at L2 which are the main roads, followed by L6, L3, L5 and L4, selected as side roads. Level of other metals followed the same pattern as L1>L2>L6>L3>L5>L4 and heavy metals were in the order of Zn>Mn>Pb>Cu>Cd (Table 4).

Table 5 presents the level of heavy metals at control site, C1, selected for this study. Station C1, is at some distance away from the main source of pollution and is, therefore, more representative of air pollution of general background of exposure. This station is located at latitude 24°71′ and longitude 67°08′. It is about 20 km down wind from the city centre and about one km from the main Super Highway. Its surrounding areas are sparsely populated and there is no industrial zone

Table 3. Level of heavy metals in dust samples of KIA

Code no.	Locations	Fe mg/g	Zn mg/g	Pb mg/g	Mn mg/g	Cu mg/g	Cd mg/g
K1	Roundabout	21.267	1.286	0.375	0.614	0.091	0.003
K2	Roundabout	19.398	0.755	0.346	0.339	0.076	0.02
K3	Roundabout	24.818	1.613	1.258	0.673	0.128	0.005
K4	Side road	2.474	1.276	0.026	0.244	0.028	0.006
K5	Side road	2.002	0.862	0.021	0.228	0.026	0.005
K6	Link road	1.947	0.851	0.019	0.219	0.018	0.005
K7	Link road	2.955	1.321	0.027	0.262	0.032	0.007
Average		10.694	1.138	0.296	0.368	0.057	0.007
Maximum		24.818	1.613	1.258	0.673	0.128	0.020
Minimum		1.947	0.755	0.019	0.219	0.018	0.003

within and around 2 km. Air masses reach the sampling site, generally from Super Highway, where the traffic density is very high. At the control site, the highest concentration of Fe was 7.03 mg/g which may be due to the influence of heavy duty vehicles and the mechanical workshops. Same trend of all metal pollutants i.e., Fe>Zn>Pb>Mn>Cu>Cd may be seen in Table 5.

The highest concentration of iron in the dust samples in all the three industrial areas of Karachi may be attributed to the metal used in construction work, iron bending and welding of metal, which is a common practice along the streets in industrial areas of Karachi. Virtually at every round-about, there is a mechanical workshop having various sections that deal with either, filling of metals, welding and panelling of vehicular bodies etc. Chronic exposure to Fe can cause benign pneumonia-conuisis and can enhance harmful effects of various carcinogens. Ingestion of Fe in excessive quantity inhibits the activity of many vital enzymes (Mahmud *et al.,* 2008). Iron filling from metal works, exhaust emissions from vehicles, spillage of gasoline, diesel, engine oil and lubricating oils, coupled with rusting of non-coated metals have all collectively contributed to the high concentration of the elements Fe, Zn, Pb, Mn, Cu and Cd.

Lead, cadmium, copper, manganese and zinc are the major metal pollutants of the road-side environment. High concentration of these metals in dust fall may be due to their release from fuel burning, wear out of tyres, leakage of oils and corrosion of batteries and metallic parts such as radiators etc (Akber *et al.,* 2006).

Lead is the most significant element in environmental heavy metal pollution. The most probable sources of its emission are gasoline vehicles, pesticides, gasoline additives, lead pipes and other materials. Even a very small amount of Pb becomes physiologically active and results in its accumulation in the food chain. Its adverse effects on humans, particularly on infant central nervous system (CNS), are well established (Berlizov *et al.,* 2007).

The sources of Cd are much less well defined than those of lead, but metal plating and tyres enforced with metals are considered the likely common anthropogenic sources of cadmium in dust fall through burning of tyres and bad conditions of roads. Other sources of cadmium and zinc are found in lubricating oil as parts of many additives. It was reported that the cadmium level in car tyres is in the range of 20-90 µg/g as Cd is associated with the process of vulcanisation (YU *et al.,* 2003). Uses of cadmium in plating and galvanised equipment in food processing industry, cadmium containing enamel for pottery glazes and cadmium based pigments or stabilizers in plastics may also be significant sources of cadmium.

Figure 2 shows variations in the trend of heavy metals at SITE, KIA, LITE and control sites. Concentrations of all the metals in the air were higher at SITE, nearly same at KIA and LITE and lower at the control site. The locations selected in SITE

Table 4. Level of heavy metals in dust samples of LITE

Code no.	Locations	Fe mg/g	Zn mg/g	Pb mg/g	Mn mg/g	Cu mg/g	Cd mg/g
L1	Main road	20.008	1.688	0.598	0.617	0.068	0.002
L2	Main road	15.338	1.5	0.197	0.503	0.054	0.001
L3	Side road	4.053	1.044	0.058	0.236	0.042	0.008
L4	Side road	2.313	0.997	0.031	0.205	0.021	0.003
L5	Side road	2.881	1.002	0.039	0.233	0.025	0.007
L6	Side road	5.157	1.224	0.066	0.243	0.045	0.006
Average		8.292	1.243	0.165	0.340	0.043	0.005
Maximum		20.008	1.688	0.598	0.617	0.068	0.008
Minimum		2.313	0.997	0.031	0.205	0.021	0.001

Table 5. Level of heavy metals in control dust samples

Code no.	Location	Fe mg/g	Zn mg/g	Pb mg/g	Mn mg/g	Cu mg/g	Cd mg/g
C1	Main Gate	7.031	0.421	0.077	0.215	0.032	0.004

were roundabouts and surrounded by industries, mechanical workshops and automobile stands; traffic is also held up at traffic signals. Hence, the higher values of heavy metals at this site may be due to the industrial and vehicular emissions. KIA and LITE are the neighboring industrial areas. The locations selected in KIA and LITE are roundabouts, main roads and side road where nearly the same trend of the concentrations of heavy metals was observed. The low values found here may be due to the selection of the round abouts in KIA and LITE at relatively open places and situated on the intersection of very wide roads with large open areas.

Figure 3 shows the distribution pattern of trace metals in dust fall samples of industrial areas of Karachi. The distribution pattern of the total average concentration of Fe, Zn, Pb, Mn, Cu and Cd indicates their relatively high concentration stations S1, S2, S3, K1, K2, K3, L1 and L2. These stations are roundabouts having high traffic density and under influence of industries. Same pattern for other metals Zn>Pb>Mn> Cu>Cd can also be seen in Fig. 3. The lowest concentrations of metals were found at station L4 which is the side road under less influence of industrial emissions and with low traffic density. The level of heavy metals compared with the control site (PCSIR Labs Complex, Karachi) shows that all the pollution (70%) is generated by vehicular emissions.

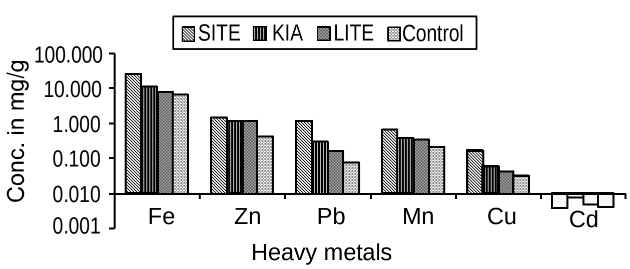

Fig. 2. Total average concentration of heavy metals in industrial site and control site environments of Karachi.

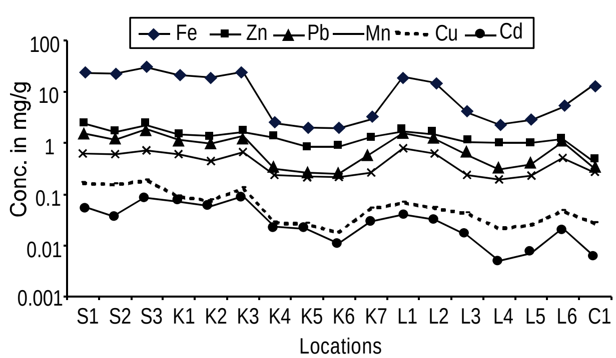

Fig. 3. Distribution pattern of heavy metals (Fe, Zn, Pb, Mn, Cu and Cd) in dust fall samples of Karachi.

The health implication of this ugly trend is quite obvious. Both children and adults are highly vulnerable to cough through inhalation of dust with its high heavy metal content. It has been observed that inhalation of some mineral particles can produce diseases in persons working in quarry sites. These mainly affect the lungs and the major anthropogenic effect is the formation of fibrotic tissues in the lungs. The loss of operational capacity of the lungs is dependent on the amount and type of mineral dust inhaled. This response of lungs to mineral dust with the formation of fibrotic tissue is commonly referred to as pneumo-nomosis (Nsi and Shallsuku, 2002).

Apart from this, effects of dust are also felt indirectly. It settles on dried food-stuff such as rice, maize, ground nut, yam flour and dried cassava. When the moisture contents of these foods are still high, the dust dissolves in the moisture and becomes absorbed and thereby contaminates the food stuff. Dust also settles on buildings, walls, roofs, window panes and doors causing mechanical abrasion and aesthetic blight.

References

Akber, K.F., Hale, W.H.G., Headley, A.D., Athar, M. 2006. Heavy metal contamination of roadside soils of northern England. *Soil and Water Research*, **1:** 158-163.

Berlizov, A.N., Blum, O.B., Filby, R.H., Malyuk, I.A., Tryshyn, V.V. 2007. Testing applicability of black poplar (*Populous nigra* L.) bark to heavy metal air pollution monitoring in urban and industrial regions. *The Science of the Total Environment*, **372:** 693-706.

Buszewski, B., Lastrzebska, A., Kowalkowski, T., Gornabinkul, A. 2000. Monitoring of selected heavy metal uptake by plants and soils in the area of Torun, Poland. *Polish Journal of Environmental Studies*, **9:** 511- 515.

Chibowski, S. 2000. Studies of radioactive contaminations and heavy metal contents in vegetables and fruits from Lublin, Poland. *Polish Journal of Environmental Studies*, **9:** 249-253.

Jaradat, Q.M., Momani, K.A. 1999. Contamination of road side soils, plants and air with heavy metals in Jordan, a comparative study. *Turkish Journal of Chemistry*, **23:** 209-220.

Krolak, E. 2000. Heavy metals in falling dust in Eastern Mzazowieckie Province. *Polish Journal of Environmental Studies*, **9:** 517-522.

Mahmud, T.A., Siddiqui, M.N.A., Salam, A., Alam, A.M.S. 2008. Temporal Variation of atmospheric aerosol particulate matters and heavy metals concentration in Dhaka, Bangladesh. *Pakistan Journal of Analytical and Environmental Chemistry*, **9:** 26-31.

Momani, K.A., Jiries, A.G., Jaradat, M.Q. 2000. Atmospheric deposition of Pb, Zn, Cu and Cd in Amman, Jordan. *Turkish Journal of Chemistry,* **24:** 231-237.

Nsi, E.W., Shallsuku, P. 2002. Industrial pollution: a case study of dust pollution from a cement industry. *Journal of Chemical Society of Nigeria,* **27:** 85-87.

Sami, M., Amir, W., Akbar, S. 2006. Quantitative estimation of dust fall and smoke particles in Quetta valley. *Journal of Zhejiang University of Science B,* **7:** 542-547.

Shinggu, D., Ogugbuaja, V., Barminas, J., Toma, I. 2007. Analysis of streetdust for heavy metal polltants in Mubi, Adamawa State, Nigeria. *International Journal of Physical Science,* **2:** 290-293.

Soylak, M., Narin, I., lci, L., Dogan, M. 2000. Lead concentration of dust samples from Nigda city, Turkey. *Fresenius Environmental Bulletin,* **9:** 36-39.

YU, K.N., Yeung, Z.L., Kwok, R.C.W. 2003. Determination of multi element profiles of soils using energy depressive X-ray fluorescence (EDXRF). *Applied Radiation and Isotopes,* **58:** 339-346.