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Determination of Total Suspended Particulate Matter and Heavy Metals in Ambient Air of Four Cities of Pakistan

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Abstract: Total suspended particulates (TSPs) in ambient air of four cities of Pakistan were collected using a high volume sampling technique for subsequent heavy metal analysis. The sampling was conducted for 24 hours and the concentration of TSPs ranged 568-2074, 1191-3976, 1133-4400 and 112-280 µg/m^3 for Islamabad, Gujranwala, Faisalabad and Bahwalnagar, respectively. The level of TSP contamination was very high in ambient air of two big industrial cities, Gujranwala and Faisalabad. TSPs were also analyzed for Cd, Pb and Zn using flame atomic absorption spectrometry (FAAS) following digestion using a mixture of analytical grade nitric acid and hydrochloric acid. Compared to other metals, concentration of Cd was slightly high (around 325 ng/m^3) in the samples of Gujranwala and Faisalabad. Overall, the order of metal concentrations were Cd > Pb > Zn.

Key words: Total suspended particles % Particulate heavy metals % Cadmium % Lead % Zinc

INTRODUCTION

The quality of air that we breathe in is determined by the amount of gaseous pollutants and particulate matter present in the air. Among all air pollutants, particulate matter (PM) which can be inhaled into the human respiratory system [1] is related to the most serious health effects including pulmonary and cardiovascular illnesses [2]. Besides its effects on health, PM also impairs visibility, plays an important role in the formation of acid rain, affects the amount of sunlight reaching the ground and in turn interferes with a variety of environmental processes. The main sources of air borne particulates include natural and anthropogenic processes. The most noteworthy anthropogenic sources with regard to quantity stem from incomplete combustion processes, such as fossil fuel and biomass burning [3]. The composition of ambient air PM is complex and differs depending on source and location. The occurrence of toxic heavy metals in the respirable fraction of PM is assumed to contribute to substantial health effects [2, 4]. Some of the particulate heavy metals are strong triggers for carcinogenesis, teratogenesis and mutagenesis [5, 6].

The studies conducted by Pakistan Environment Protection Agency (Pak-EPA) in collaboration with the Japan International Cooperation Agency (JICA) revealed that concentration of PM in major cities of Pakistan are 4.4 to 7.5 times higher than WHO Guidelines [7]. In another study, Pak-EPA/JICA investigated the quality of ambient air in Gujranwala and Faisalabad [8]. In Gujranwala, TSP concentration (24 hour average) reached to 5,190 ìg/m^3 which is 30 times higher than WHO Guidelines. An environmental assessment report recognized PM pollution as a serious environmental and health concern in Pakistan and responsible for 22,000 premature deaths among adults and 700 deaths among children [9]. The report declares vehicular emissions, industrial pollution and burning of municipal waste as principal sources of particulate pollution.

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Present study was conducted to investigate levels of TSP and some environmentally significant heavy metals in ambient air particulates of four cities of Pakistan (Islamabad, Gujranwala, Faisalabad and Bahawalnagar). This preliminary research may help researchers and policy makers in preventing and managing air pollution. A conventional analytical technique, atomic absorption spectroscopy is used for the analysis because of its selectivity, sensitivity, reproducibility and wide dynamic concentration range [10, 11].

MATERIAL AND METHODS

Total Suspended Particulate (TSP) Matter: The ambient air sampling was performed at 5 sites; 2 sites in Islamabad, 1 in Gujranwala, 1 in Faisalabad and 1 in Bahawalnagar. In total, 48 samples were collected from these sites using high volume air sampler (FandJ specialty Inc. DH-504EV.2, USA using FandJ filter discs, FP-4.0M). The DH-504EV.2 air sampling system is designed to provide continuous air sampling. It maintains the flow rate of air sample constant at a selectable value - typically 25 to 70 CFM (Cubic Feet per Minute) through the filter medium. The sampler comprised of a suction sub-system, an inlet sub-system, a filter assembly and the associated instrumentation and control sub-system. The sampling was conducted for 24 hours at all sites and the mass of TSPs was determined by weighing the filter, before and after sampling.

Analysis for Selected Heavy Metals: The qualitative analysis of filtered samples for selected heavy metals was carried out by energy dispersive X-ray fluorescence spectrometer (JEOL JSX-3202-M, Japan). The filter discs containing samples were cut into 4 cm^2 pieces. These small pieces were directly analyzed by XRF without any sample preparation. The instrument software allowed simultaneous multi-element spectral measurement and qualitative elemental analysis.

The concentrations of metals in ambient air particulates were determined by flame atomic absorption spectrometer (Varian AA 240, USA) with air/acetylene burner. Each filter disc (containing TSP) was extracted using digestion reagents; hydrogen peroxide 35%, hydrochloric acid 37% and nitric acid 65% (Merck, Germany) following similar open acid digestion approaches reported in literature [12, 13]. Each filter was divided into four equal pieces using a clean paper cutter. One portion of the divided filter was further torn into small pieces and transferred to beaker to which 30 ml of HCl (1+1) and 5 ml of H_2O_2 were added. The beaker was covered with a watch glass and heated on a hot plate at 120°C for 1 hour. After cooling, the solution was separated using a filter paper (Whatman 41). Another 20 mL of HCl (1+1) was added to the residual in the beaker and heated for 15 minutes for complete metal extraction. The beaker content was filtered again and the filtrate was added to the filtrate of the previous step. This solution was concentrated on a hot plate till small amount of liquid left in the beaker. Then, HNO_3 (2+98) mixture was added to the beaker. The beaker content then transferred to a 25 mL volumetric flask and filled up to the mark with HNO_3 mixture. The prepared sample was transferred to a polyethylene bottle and was analyzed on FAAS. Blank filters were prepared by digesting clean filter discs with the same digestion method for the samples. The concentrations of analyte metals (Cd, Pb and Zn) were corrected against filter blanks.

RESULTS AND DISCUSSION

Total Suspended Particulate (TSP) Matter: The values of TSPs at all sampling sites were considerably high as demonstrated in Table 1. The TSP values in Islamabad samples agree with the reported values [14]. The TSP concentrations at Margalla Road (Islamabad) were relatively high as compared to the concentrations at Sector H-12 (Islamabad) because of high vehicular emissions and wind-blown dust. Other probable source of high TSP values in Islamabad is the emissions from small industries present in the city. The TSP levels at Faisalabad and Gujranwala are very high due to the high vehicular and industrial activities. Both Faisalabad and Gujranwala rank largest industrial centers in Pakistan. Faisalabad has a strong industrial base including textiles, jewellery, home furniture and pharmaceuticals whereas Gujranwala's industrial areas have numerous textile mills, cutlery manufacturing and large agricultural processing plants, ceramics industries, electronic equipments and auto industry [15]. In these cities, sources of high TSP values include wind-blown dust, emissions from stationary fuel combustion, industrial processes, heavy transport, solid waste disposal, power plants, etc. Such emissions result in gas to particle conversion in the atmosphere. The concentrations of TSPs in Bahwalnagar samples were relatively low because this site is located away from the vehicular and industrial sources. According to WHO Guidelines the reference value for particulate matter (PM_{10}) is 150 μg/m^3 [16] and most samples examined in the present study had values higher than the reference value.

Table 1: Concentrations of TSPs in µg/m^3 in 48 ambient air samples

		TSP concentration (µg/m^3)			
Sampling Sites	No. of samples	Min.	Max.	Average	> 150 µg/m^3 (%)
Islamabad: Margalla Road	13	1275	2074	1614	100
Gujranwala: Shaikhupura Road	08	1191	3975	2756	100
Faisalabad: Abdullahpur Crossing Junction	11	1133	4400	3074	100
Bahwalnagar: Male Declaration monitoring site	10	112	280	214	80
Islamabad: Sector H-12	06	568	703	634	100

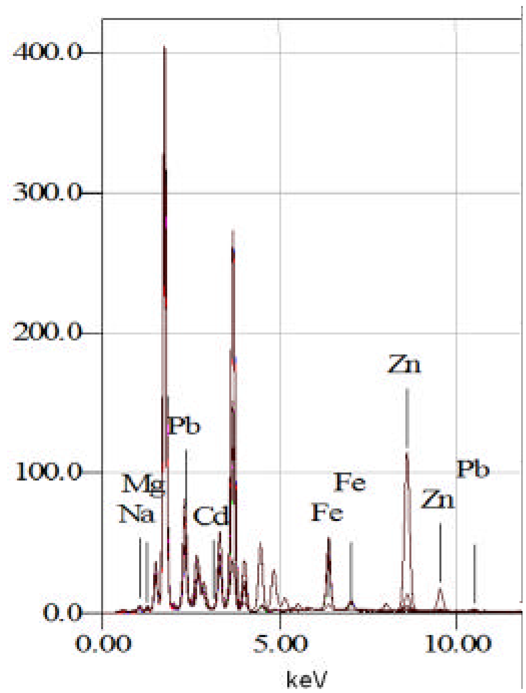

Fig. 1: XRF spectrum showing Pb, Zn and Cd lines in Margalla Road (Islamabad) sample

Flame Atomic Absorption Spectroscopy (FAAS): The qualitative analysis of ambient air samples was carried out by XRF in order to assess the presence of selected heavy metals (Cd, Pb, Zn) in the ambient air TSPs of three highly populated (Faisalabad, Gujranwala, Islamabad) and one comparatively less populated (Bahwalnagar) cities of Pakistan. The qualitative analysis of selected samples was also carried out by XRF prior to their quantification by FAAS. The XRF analyses demonstrated the presence of Cd, Pb and Zn in all TSP samples. XRF spectrum of one such sample is shown in Figure 1.

The concentration of particulate metals (Cd, Pb and Zn) at each sampling site was determined by flame atomic absorption spectrometry (FAAS). The calibration curves for all three metals demonstrated good linearity over the concentration range (0.1 to 10.0 mg/L) with correlation coefficients, R^2 in the range of 0.996 to 0.999. The precision among the values of each calibration data point (replicate analysis) was calculated with the help of 95% confidence intervals based on triplicate measurements. The determination of the LOD is very important for metals under investigation. LOD here means the lowest concentration that can be detected with FAAS. In this study the LODs of all metals were determined by using the calibration data; y-intercept and standard deviation of the regression [17]. The values of LOD for each metal are shown in Table 2.

The units of metal concentrations were converted from mg/L to ng/m^3 using the following equation, where (C) is the concentration of heavy metals in µg/m^3:

$$C = \frac{(c_1 - c_b) \times v \times S/s}{V_0}$$

Here

c_1 is metal concentration in the solution of sample (mg/L)

c_b is metal concentration in the solution of blank filter (mg/L)

v is sample solution volume (25mL)

S/s is Ratio of divided (=4)

S is sampled filter area

s is analyzed filter area

V_o is sampling air volume (m^3) at standard conditions

$V_o = V \times 298/T$

V is sampling air volume at ambient conditions (m^3)

T is average temperature during sampling (K)

Concentrations of Cd, Pb and Zn were measured in all 48 ambient air TSP samples; the mean values of the metal concentrations are given in Table 3.

The analysis showed that Cd concentrations in Bahawalnagar samples were relatively low as compared to Cd levels in the samples of two big cities (Faisalabad and Gujranwala). The high Cd concentrations in these cities

Table 2: Calibration curves; correlation coefficient (R^2) of linear trend lines along with their LODs

Metal	R^2	LOD µg/L
Cd	0.999	22
Pb	0.999	10
Zn	0.996	18

Table 3: Concentration of Cd, Pb and Zn (ng/m^3) in ambient air samples along with standard deviation (S.D.)

	Mean Concentration (ng/m^3) ± S.D.		
Sampling Site	Cd	Pb	Zn
Islamabad: Margalla Road	26.0 ± 8.6	5.1 ± 1.8	13.5 ± 3.2
Gujranwala: Shaikhupura Road	326.5 ± 53.3	91.9 ± 19.7	35.2 ± 7.1
Faisalabad: Abdullahpur Crossing Junction	320.8 ± 47.2	88.6 ± 14.4	25.5 ± 6.6
Bahawalnagar: Male Declaration monitoring site	2.7 ± 0.8	12.4 ± 3.7	56.1 ± 13.4
Islamabad: Sector H-12	8.2 ± 2.2	71.3 ± 11.3	Not detected

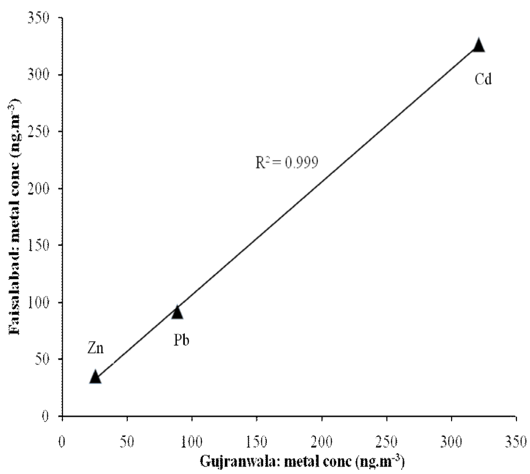

Fig. 2: Comparison of the concentrations of metals (mean values) determined in two big cities; Faisalabad and Gujranwala

may be associated with industrial emissions especially from steel production units because a large amount of Cd-plated steel scrap is recycled in these industries. Other possible sources include open burning of municipal wastes containing discarded Ni-Cd batteries and plastics containing Cd pigments; vehicular emissions including tyre abrasions and cigarette smoking. Because of such industrial and vehicular emissions, the average Cd levels in Faisalabad and Gujranwala (around 320 ng/m^3) were approximately 80 times and 4.2 times higher than the reported Cd concentrations in Islamabad [18] and Lahore [19], respectively. On the other hand, levels of Cd in Bahawalnagar and Islamabad (sector H-12) samples were close to the reported concentration, 4 ng/m^3 [18].

Pb is ubiquitous in industrialized regions. The presence of Pb in ambient air of Faisalabad, Gujranwala and Islamabad (sector H-12) may be associated with the manufacturing of automobile batteries, pigments and cable sheathing. Such usage of Pb in plumbing, solders, paints, ceramic-ware, plastics and ammunition pose a significant environmental risk [20].

Zn occurs naturally in soil and ambient air particulate matter. In industrial zones (Faisalabad and Gujranwala), Zn containing particles might have been released by metallurgical plants and brass/zinc production facilities [21]. The presence of Zn in the atmosphere of Bahwalnagar might be due to wind-blown soil and road dust. The concentrations (mean) of metals determined in present study has same order of magnitude as were reported in a study conducted in Islamabad [22].

There was significant correlation between Cd, Pb and Zn concentrations, in the air samples of Faisalabad and Gujranwala. Figure 2 presents comparison of the concentrations of metals (mean values) determined in two big cities, Faisalabad and Gujranwala.

The value of correlation coefficient (0.999) indicates that the heavy metals were emitted from the industrial and crustal sources with the same rate. This deduction also gets support by considering the high and similar values of TSPs present in the ambient air samples of Faisalabad and Gujranwala.

CONCLUSION

This study reveals that ambient air of main cites of Pakistan are heavily contaminated with TSPs and the constituents of particulate matter contains toxic heavy metals especially Cd in considerable concentrations that may pose threat to human health and the environment. Efforts should be made to keep the levels of metal contamination low, especially with industrial growth continuing in the studied areas.

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