Study of Particle Size and Trace Metal Distribution in Atmospheric Aerosols of Islamabad

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(Received 4th November 2008, accepted in revised form 26th January 2009)

Summary: Atmospheric aerosol samples were collected on glass fibre filters using high volume air samplers. Half of each aerosol sample was solubilized in nitric acid/hydrochloric acid based wet digestion method and the concentration of trace metals was determined through flame atomic absorption spectrophotometer. Among the eight trace metals analyzed, mean concentration recorded for Zn (844 ng/m^3), Fe (642 ng/m^3) and Pb (253 ng/m^3), was found to be higher than mean levels of Mn, Cr and Co. The size distribution of the collected particulate samples was carried out on mastersizer, which revealed PM_{10-100} as the major fraction (55 %) followed by $PM_{2.5-10}$ (28 %). The correlation study evidenced a strong tendency of trace metals to be associated with fine particulate fractions. The atmospheric trace metal levels showed that the mean metal concentrations in the atmosphere of Islamabad are far higher than background and European urban sites mainly due to the anthropogenic emissions.

Introduction

Particulate pollution has been considered as an emerging atmospheric problem particularly due to overwhelming anthropogenic activities, such as, industrialisation, urbanization and automobile emissions [1, 2]. Numerous health effects have been reported due to atmospheric particulates which are mainly due to their smaller aerodynamic size and toxic chemical species associated with these particulates [3, 4]. Trace metals are among the chemical species considered as 'air toxics' and health implication associated with the atmospheric trace metals have been reported for many regions of the world [5, 6]. The particulate size and its chemical composition particularly trace metals are the major contributors towards atmospheric toxicity [7, 8]. To assess the human health effects, the particulate size distribution and their relationship with the trace metals in rural and urban atmosphere should be scrutinized on continuous basis [9, 10]. Major sources of fine particulates in the atmosphere are combustion/industrial processes, automobile emissions, mining and excavation activities [11]. Anthropogenic trace metals have been reported to be mainly associated with fine particulates, whereas, the natural sources mostly contribute to coarse and large particulates [12].

Recent industrial development and urbanization in Islamabad have not gone in pace with environmental safety, resulting in numerous problems arising from atmospheric pollution. Over the years the transportation flux has also increased tremendously, consequently, the local urban population is now facing typical adverse health effects of air pollutants [13]. Some previous studies conducted in the city evidenced that the local atmosphere was overburdened with airborne particulates comprising toxic trace metals, in far excess to those in background air [14-16]. These studies indicated significant anthropogenic enhancement of trace metal concentrations in road side deposited soil and in water and air.

Keeping in view the environmental significance of the potential influence of trace metals in aerosols and their continued contribution of high levels in the local atmosphere, the present investigation was carried out to assess, in the first place, the current status of the atmospheric trace metal burden in the urban atmosphere and then to examine its relationship with the size of airborne particulates. It is anticipated that this study would provide baseline data that could help evolve a health related pollution abatement programme and could motivate further studies on the trends of atmospheric trace metal distribution, size fractionation, mass loading and enhancement relative to clean background.

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Results and Discussion

The data on the mean trace metal levels (ng/m^3) estimated in 74 aerosol samples collected from residential/urban areas of Islamabad are given in Table-1, along with the statistical distribution parameters, which reveal that Zn has highest mean concentration of 844 ng/m^3, followed by Fe, at 642 ng/m^3 and Pb at 253 ng/m^3. These results are quite expected since Zn and Pb are well known to be associated with industrial and automobile emissions, respectively, while, Fe in the atmosphere is normally considered as soil derived [17-19]. In the absence of well known anthropogenic sources of Fe such as, steel industry, mostly it is conceived to be associated with wind blown soil dust and hence predominantly contributed by natural sources as reported in earlier studies [2, 7, 15, 18, 20-25]. Of the remaining metals, Mn, Cr and Co showed mean levels of 69, 26 and 15 ng/m^3, respectively. These levels could be attributed to industrial emissions in the area, as these metals find their way into the atmosphere mostly from industrial sources, such as, metallurgical units, garbage incineration and metal pickling units etc. [20-23]. Average levels of Ni and Cd were estimated to be 10 and 5 ng/m^3, respectively. The overall increasing order of metal concentrations was Zn > Fe > Pb > Mn > Cr > Co > Ni > Cd. Their relative contribution is shown in Fig. 1. By far the most dominant metal in the local atmospheric aerosols is Zn (45.3 %), followed by Fe (34.4 %) and Pb (13.6 %). Of the remaining fractions, Mn (3.7 %) and Cr (1.4 %) emerge as minor contributors, because of their low contribution from natural sources.

Table-1: Statistical distribution parameters for trace metal levels (ng/m^3)* in the aerosol samples (n = 74).

	Zn	Fe	Pb	Mn	Cr	Co	Ni	Cd
Minimum	27	37	16	23	4	3	4	2
Maximum	2350	2950	2013	314	94	59	65	17
Mean	844	642	253	69	26	15	10	5
Median	793	536	133	60	9	8	8	4
Standard Deviation	578	450	396	43	23	17	14	2
Standard Error	67	52	46	5.0	2.7	2.0	1.6	0.2
Kurtosis	-0.7	9.1	9.6	14.5	-0.1	0.4	7.2	8.4
Skewness	0.3	2.4	3.1	3.0	0.7	1.4	2.9	4.7

*where applicable

A comparison of mean and median concentrations of the various metals on one hand and their standard deviation and standard error on the other hand, indicates an almost normal distribution of Cd, Ni and Mn. However, marginal differences between these parameters in case of Pb, Zn, Fe and Cr indicate that their distribution pattern is predominantly random and both industrial and vehicular sources could be considered to this effect. Asymmetry and lop-sidedness of the data measured in terms of skewness and kurtosis are very high for Cd, Mn, Pb, Fe and Ni, however, Cr, Co and Zn exhibit lowest skewness and kurtosis and hence more regularity in their distribution.

The data on particulate size fractionation are given in Table-2 which lists the volume % fractions of particles found in the aerosol samples. Particle size fractionation was obtained for four size categories;

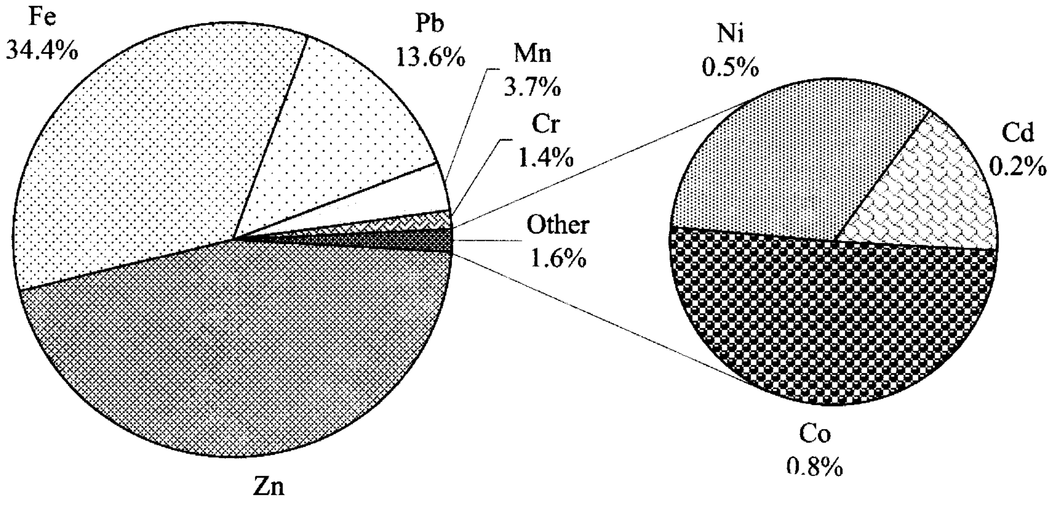

Fig. 1: Comparison of average metal contents in the atmospheric aerosol samples (n = 74).

Table-2: Statistical distribution parameters for particle size fractions (volume %)* in the aerosol samples (n = 74).

	$PM_{<2.5}$	$PM_{2.5-10}$	PM_{10-100}	$PM_{>100}$
Minimum	2.69	13.64	28.89	1.05
Maximum	11.42	41.48	75.12	45.66
Mean	7.64	27.98	55.76	8.60
Median	7.77	28.69	57.31	4.91
Standard Deviation	1.90	6.03	9.29	10.64
Standard Error	0.22	0.70	1.08	1.24
Kurtosis	-0.15	-0.29	0.90	4.48
Skewness	-0.19	-0.21	-0.76	2.23

*where applicable

$PM_{<2.5}$ (<2.5 μm, representing the respirable fraction), $PM_{2.5-10}$ (2.5-10 μm, representing the fine/medium fraction), PM_{10-100} (10-100 μm, representing the coarse fraction) and $PM_{>100}$ (>100 μm, representing the giant particles). These data indicate the PM_{10-100} fraction as the largest, at 55.76 volume %, followed by $PM_{2.5-10}$ fraction, at 27.98 volume %. On to the extreme, both $PM_{<2.5}$ and $PM_{>100}$ fractions are found to be present at 7.64 volume % and 8.60 volume %, respectively. Again, a comparison of mean and median values along with standard deviation and standard error demonstrate that the respirable particulates ($PM_{<2.5}$) are most consistent in the local atmosphere with highest symmetry. However, the highest value of standard deviation (10.64) is associated with $PM_{>100}$ fraction which shows that giant particulates are most divergently distributed. The remaining two fractions ($PM_{2.5-10}$ and PM_{10-100}) also reveal random distribution in the urban atmosphere of Islamabad. On the comparative scale, PM_{10-100} has largest contribution to particulate pollution followed by $PM_{2.5-10}$, as shown in Fig. 2. About 55 % of the local particulate matter is constituted by PM_{10-100} fraction (Fig. 2); 28 % by $PM_{2.5-10}$ and these two fractions account for more than 80 % of the total atmospheric particulates. Although giant particulates and respirable fraction have similar % contributions, but most consistent are the respirable particulates.

Table-3 outlines the linear correlation matrix for trace metals and particulate fractions. An examination of the table shows that particle-to-particle size correlation has strong positive relationship between $PM_{<2.5}$ and $PM_{2.5-10}$ with r = 0.673, at $p < 0.01$. No other pair of particulate fractions shows a positive correlation; rather all are negatively correlated with each other. This indicates

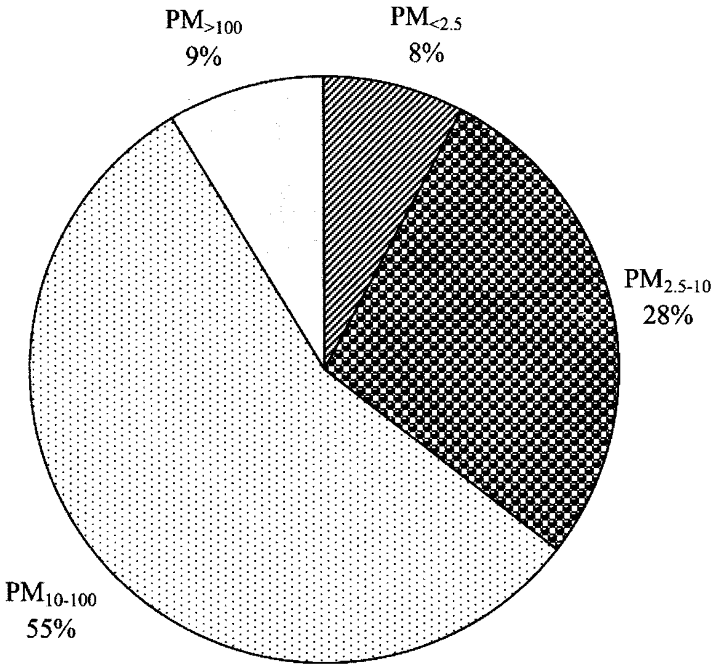

Fig. 2: Comparison of average particle size gradation in the atmospheric aerosol samples (n = 74).

Table-3: Correlation coefficient* matrix for trace metals and particulate fractions in aerosol samples (n = 74).

	Zn	Fe	Pb	Mn	Cr	Co	Ni	Cd	$PM_{<2.5}$	$PM_{2.5\text{-}10}$	$PM_{10\text{-}100}$
Fe	0.462										
Pb	0.214	0.335									
Mn	0.573	0.671	0.304								
Cr	0.124	0.255	0.011	0.135							
Co	0.259	-0.019	0.030	0.092	0.029						
Ni	-0.109	-0.007	-0.004	-0.031	0.106	-0.078					
Cd	0.281	0.182	0.297	0.327	-0.213	0.209	0.008				
$PM_{<2.5}$	0.265	0.213	-0.094	0.279	0.070	0.153	0.034	-0.082			
$PM_{2.5\text{-}10}$	0.264	0.252	0.190	0.325	-0.113	0.195	-0.099	-0.016	0.673		
$PM_{10\text{-}100}$	-0.332	-0.277	-0.132	-0.315	0.307	-0.026	0.066	-0.348	-0.222	-0.184	
$PM_{>100}$	0.092	0.059	0.018	0.039	-0.217	-0.116	-0.008	0.327	-0.366	-0.528	-0.728

*values of r >0.270 or < -0.270 are significant at $p < 0.01$

that $PM_{<2.5}$ fraction is heavily drawn from the $PM_{2.5\text{-}10}$ fraction and as such, this accounts for its presence due to the $PM_{2.5\text{-}10}$ fraction. The data in the table also evidence that Mn is positively correlated with $PM_{<2.5}$ and $PM_{2.5\text{-}10}$ fractions with r values equal to 0.279 and 0.325 respectively; followed in the same way by Fe and Zn and only feebly by Co. The study thus shows that while Mn, Fe, Zn and Co have shown correlations with a specific size of particulates, Pb exhibits only a weak positive correlation with $PM_{2.5\text{-}10}$ fraction. The coarse and giant particulates predominantly reveal negative relationships with trace metals. A fraction of atmospheric Cd and Cr may be considered to originate from natural sources as evident by their correlation with $PM_{>100}$ (r = 0.327) and $PM_{10\text{-}100}$ (r = 0.307), respectively.

As for the metal to metal correlation, Zn is found to be correlated with Mn (r = 0.573) and Fe (r = 0.462). Similarly, Fe is strongly correlated with Mn (r = 0.671), thus Fe, Mn and Zn follow a similar pattern. Pb is positively correlated with Mn, Fe, Cd and Zn and this analysis suggests that these metals find their way through multiple sources, which could be either industrial emissions, automobile exhaust, soil-derived or based on a severe weathering process arising from heavy quarrying and mining activity in search of good quality construction material from the Margalla Hills.

The mean levels of atmospheric trace metals are compared with the permissible levels laid down by regulatory agencies and counterpart data from the other background, rural and urban regions around the world and the results are given in Table-4. Present mean levels of Pb, Mn, Cr and Cd are found to be within the permissible limits laid down by WHO [33] and USEPA [34], whereas, average concentration of Ni is much higher than permissible levels as shown in the table. The mean metal levels are also compared with the background concentrations reported for Antarctica [35] to estimate the degree of contamination due to anthropogenic activities and it is revealed that the selected metals in the urban atmosphere of Islamabad are highly enriched. On the average, the trace metal concentrations in the urban atmosphere of Islamabad are 120 to 8800 times higher than the background levels.

In comparison to the previously reported metal levels from the urban atmosphere of Islamabad [14, 15], present Pb, Zn and Cd levels were fairly high, however, Fe, Mn, Cr, Co and Ni levels were found to be almost comparable. It is also observed from the comparison that the trace metal levels in the urban atmosphere of Islamabad are extremely higher than the reported rural concentrations [7, 17]. Even when compared with European urban and industrial sites like Deberecen, Hungary [18], Birmingham, UK [19], La Coruna, Spain [20] and Poland [21] where strict actions have been employed for environmental safety, the metal levels are found to be higher by many folds (except Fe) in the local atmosphere of the city. However, the airborne metal levels are found to be slightly higher compared with some industrial and urban sites of Italy [22] and Argentina [23]. Compared with other South Asian mega cities, the estimated concentration of trace metals exhibit typically much lower levels than reported for Tehran [2], Lahore [24], Delhi [25] and Mumbai [26]. With some exceptions, the airborne trace metal levels demonstrate a similar trend to that of Dhaka [27], Taejon, Korea [28], Beijing, China and Yamaguchi, Japan [29]. Among the selected trace metals, Cd exhibit almost background levels [30-31], while all other metals are found enriched in atmospheric aerosols.

Table-4: Mean metal concentrations (ng/m^3) in aerosols versus counterpart data for other sites around the world.

Site/*Nature*	Zn	Fe	Pb	Mn	Cr	Co	Ni	Cd
Islamabad, Pakistan/urban*	844	642	253	69	26	15	10	5
Regulatory Agencies								
WHO [33]	-	-	500	150	1100	-	0.38	5
USEPA [34]	-	-	1500	500	100	-	0.24	6.37
Background								
King Sejong, Antarctica [35]	0.130	-	0.041	-	0.114	0.0017	0.083	0.0013
Rural								
Vienna, Austria [7]	18	189	17	33	20	-	9	-
Brownfields, UK [17]	63	260	30	6	-	0.1	2	1
Urban								
Islamabad, Pakistan [14]	-	-	185	-	-	-	-	-
Islamababad, Pakistan [15]	674	606	228	61	19	12	7	2
Deberecen, Hungary [18]	56	911	72	23	18	-	5	-
La Plata, Argentina [23]	273	1183	65	26	4	-	3	0.4
Tehran, Iran [2]	327	2230	1020	78	48	8	37	-
Lahore, Pakistan [24]	2770	9930	3920	-	-	-	-	43
Delhi, India [25]	-	5220	380	-	104	-	97	7
Mumbai, India [26]	350	2950	550	-	40	-	40	40
Dhaka, Bangladesh [27]	801	2480	279	-	-	-	-	3
Beijing, China [29]	274	5100	46	1210	-	26	51	-
Yamaguchi, Japan [29]	309	9000	173	210	-	5	16	-
Roadside/Industrial								
Birmingham, UK [19]	30	204	27	6	-	-	2	0.5
Poland [21]	137	1303	95	29	-	-	-	-
La Coruna, Spain [20]	8	850	32	13	-	-	-	1
Tito Scalo [22]	304	521	60	27	13	-	5	2
Taejon, Korea [28]	240	1633	243	50	25	1	38	3

*present study

In conclusion, the present study brings out the marked difference between the levels of trace metals in the local urban atmosphere. The relatively higher levels of the trace metals in Islamabad are indicative of the fact that the local atmosphere is undergoing some significant anthropogenic translocations, possibly through the process of colloidal particulate transport and/or preferential flow of air masses. During the period of present study, the met office data indicated that WE winds mostly carried the anthropogenic particulate burden towards central locations in Islamabad, a fact that supports higher influx of trace metals in the urban area. On the whole, the major particulate contributors are Zn, Fe and Pb, while the minor contributions come from Mn, Cr, Co, Ni and Cd. The trace metals are mostly contributed by automobile emissions and industrial emissions along with some contribution from natural sources. Most of the metals reveal positive correlations with smaller size particles ($PM_{<2.5}$ and $PM_{2.5-10}$), which are detrimental to human health. The comparison study presents an alarming situation of airborne metals and it is high time to evolve an air pollution abatement strategy to ward off people against the hazardous effects arising from elevated trace metal levels and to reduce the atmospheric emission responsible for the trace metals in the aerosols.

Experimental

A high volume air sampler (Model GMWL-2000H, USA) was used to trap atmospheric aerosols on glass fibre fillers (8″×10″). The flow rate on the sampler was adjusted at 43 CFM, with an automatic compensation for the flow rate loss. The sampling was conducted on 8-12 hours daytime basis. An axial air sampler (Gallenkamp, FV series) was also used periodically as a parallel check for the same sampling duration. In all, 74 aerosol samples were collected at sector H-8, representing the typical residential/urban area and stored in a desiccator at constant humidity. After sampling, each filter containing aerosol particulates was cut into two halves, one was digested in concentrated HNO_3/HCl (1:3, v/v) for Atomic Absorption Spectrophotometric (AAS) based quantification [32] of the eight trace metals (Zn, Fe, Pb, Mn, Cr, Co, Ni and Cd) and the other for particle size determination using a mastersizer (Hydro 2000MU, USA) [14-15]. Blanks were prepared simultaneously for a routine check for estimation of each metal in solvent, acids and blank filters. The

AAS analysis of the digested samples was done under optimum analytical conditions established on the Shimadzu AAS system (Model AA-670, Japan). Particle size fractionation was obtained for four size categories; $PM_{<2.5}$, $PM_{2.5-10}$, PM_{10-100} and $PM_{>100}$, on volume % basis.

All reagents used were of AAS grade (certified purity >99.99 %) procured from either E-Merck, or BDH. The metals stock solutions (1000 ppm) were used to prepare working standards. Doubly distilled water was used throughout the present work. Standard Reference Material (OL-96) procured from National Institute of Health, was routinely employed to ensure reliability of the metal data. Frequent inter-laboratory comparison of the data was also carried out and normally, the two results agreed within ± 1.0 – 1.5 % for triplicate runs of the sub-samples.

Acknowledgements

We are thankful to Chief, Public Health Department, National Institute of Health, Islamabad, for provision of SRM and collaborative work on inter-laboratory comparison. We are also grateful to Department of Chemistry, Quaid-i-Azam University for the award of research fellowship to carry out this investigation.

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