Statistical analysis of atmospheric trace metals and particulate fractions in Islamabad, Pakistan

Munir H. Shah *, N. Shaheen

Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

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Abstract

Airborne suspended particulate matter was collected on glass fibre filters in urban atmosphere of Islamabad, Pakistan, using high volume sampler. The particulate samples were analysed for 10 selected metals (Fe, Na, Zn, K, Pb, Mn, Cr, Ni, Co and Cd) by FAAS method. Maximum mean contribution was noted for Fe ($1.761\,\mu g/m^3$), followed by Na ($1.661\,\mu g/m^3$), Zn ($1.021\,\mu g/m^3$), K ($0.488\,\mu g/m^3$) and Pb ($0.128\,\mu g/m^3$). The particle size determination on vol.% basis for nine fractions ($PM_{<1.0}$, $PM_{1.0-2.5}$, $PM_{2.5-5}$, PM_{5-10}, PM_{10-15}, PM_{15-25}, PM_{25-50}, PM_{50-100} and $PM_{>100}$) was carried out using Mastersizer. $PM_{5.0-10}$ were found to be most abundant in the local atmosphere followed by $PM_{2.5-5.0}$ and PM_{15-25} while coarse/giant particles (PM_{50-100} and $PM_{>100}$) showed lower contribution. The trace metals were found to be mainly associated with smaller particulate fractions up to PM_{10-15}. Among the climatic parameters temperature has significant relationship with fine particles and airborne metal levels while relative humidity showed negative correlation. The source identification was carried out by principal component analysis and cluster analysis. Five metal sources were identified: industrial, vehicular emissions, metallurgical operations, garbage incineration and soil derived dust. The metal levels were also compared with those reported for other rural and urban parts around the world.
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Keywords: Trace metals; Particulate matter; Size distribution; Multivariate analysis; AAS

1. Introduction

Atmospheric trace metal levels have been reported to exhibit great variations due to the increased anthropogenic emissions of suspended particulates in both urban and rural areas [1]. Airborne suspended particulate matter may affect the distribution of trace metals in other segments of the environment, such as, water and soil [2,3]. Among anthropogenic sources, automobile exhaust and industrial emissions contribute to a larger extent in this respect [4,5]. Particulates ranging from fine to giant fractions are contributed by large number of processes, such as, fuel combustion, industrial processes, automobile emissions, mining and quarrying activities [6]. Generally, toxic metals are found to be mainly associated with fine particulates compared to the coarse ones and the average airborne metal concentrations are also time dependent [7]. With these facts in view, the atmospheric partic-

ulate size distribution and their metallic composition have been given due consideration with respect to the ill effects on human health and environment [8,9].

The distribution of trace metals in atmospheric particulates has been found to be dependent on climatic conditions [10]. It has been reported that metal contents exhibited a positive correlation with temperature [11] and an inverse relationship with precipitation [12]. Wind speed and direction have also been affecting the trace metal distribution in fine and coarse particle fractions [13,14]. Moreover, in the absence of other atmospheric pollutants trace metal concentrations are considered as a useful index of air quality of the local atmosphere [15,16].

A number of statistical models have been suggested for better characterization of atmospheric particulates [17,18]. The multivariate statistical methods, principal component analysis (PCA) and cluster analysis (CA) are considered a strong tool to identify the sources and to understand the distribution of trace metals in the atmosphere [19,20].

Recently, trace metal particulates are causing nuisance of air pollution in mega cities of the world [15,21,22]. In fast growing cities like Islamabad, heavy transportation flux has gone

* Corresponding author. Tel.: +92 51 9219811; fax: +92 51 2873869.
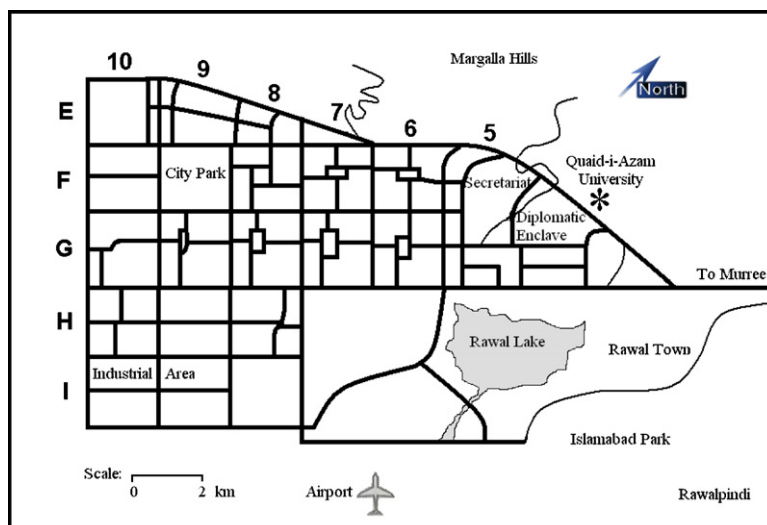*E-mail addresses:* munir_qau@yahoo.com, mhshahg@qau.edu.pk
(M.H. Shah).

Fig. 1. Location of sampling site (*) and residential sectors of Islamabad, Pakistan.

up tremendously in last decade, with a lot of industrial activities across the city (Fig. 1). It is high time to characterize the chemical composition of atmospheric particulate matter and its contribution from various sources in order to minimize the health impact associated with it [23]. It has been reported that the roadside deposited soil, water and air in urban areas of Islamabad are enriched in trace metal contents, thus rendering the city to a grossly polluted city of the world [24].

The present study is carried out to investigate the relationship among atmospheric concentration of trace metals (Fe, Na, Zn, K, Pb, Mn, Cr, Ni, Co and Cd), particulate fractions ($PM_{<1.0}$, $PM_{1.0–2.5}$, $PM_{2.5–5}$, $PM_{5–10}$, $PM_{10–15}$, $PM_{15–25}$, $PM_{25–50}$, $PM_{50–100}$ and $PM_{>100}$) and climatic parameters measured during the monitoring period. PCA along with CA is used for the source identification for airborne trace metals following the course of action reported in literature [25,26]. The metal contents are then compared with those reported from other parts of the world. It is anticipated that the current study will provide an apportionment process to identify the sources of trace metals in atmospheric particulates, to further investigate the contribution of anthropogenic sources to this effect and to analyse the mutual relationship among pollutant levels and climatic parameters giving their distribution.

2. Experimental

2.1. Site description

Islamabad, the capital city of Pakistan, is situated at an elevation of about 500 m above sea level (latitude $33°49'N$; longitude $72°24'N$) and is 14 km northeast of its twin city Rawalpindi. It is flanked by Margalla Hills in its north and plains of Punjab and water bodies on other sides (Fig. 1). The city extends over $906 km^2$ with a present population of about one million. The climate is tropical with two distinct seasons, viz., winter (October–February) and summer (March–September). The city is divided into eight basic zones some of which are shown in

Fig. 1E–I. The industrial sectors, I-9/10 and Kahuta Triangle to the south of I-10, not shown in figure, have high vehicular traffic density which is the main source of city's air pollution. The main industries located in these sectors are: steel mills, marble factories, flour mills, oil and ghee units, soap/chemical factories, ceramics, paints, pigments, pharmaceutical manufacturing plants, and several other small industrial units.

2.2. Sampling and analytical procedures

Sampling of suspended particulate matter was carried out using a high volume air sampler (Model GMWL-2000H, USA). The sampler was installed on the top-roof of Department of Chemistry, building-II, approximately 15 m above the ground level, and well cleared from other tall buildings around (Fig. 1). Glass fibre fillers (8 in. × 10 in.) were used for collecting SPM samples for 12–24 h [22,25]. The flow rate on the sampler was adjustable between 20 and 60 cubic feet per minute (CFM), with an automatic compensation for the flow rate loss. An axial air sampler (Gallenkamp, FV series) was also used periodically as a parallel check for the same sampling duration. In all, 181 particulate samples were collected, during September 2003–March 2004, a period marked by a usual 'dry spell' (no precipitation) with almost 50% or less relative humidity and stagnant atmospheric conditions prevailing all through.

After sampling, each filter containing particulate matter was cut into two halves, one was digested in 4:1 (v/v) $HNO_3/HClO_4$ mixture [27] for Atomic Absorption Spectrophotometric (AAS) based quantification of the 10 selected trace metals (Fe, Na, Zn, K, Pb, Mn, Cr, Ni, Co and Cd), and the other for particle size determination using Mastersizer 2000 (Malvern, Ver. 3.01, UK) [28]. Blanks were prepared simultaneously for a routine check for estimation of each metal in the acids and blank filters. For all measured elements, the blank values were approximately <10% of the estimated values. The AAS analysis of the digested samples was done under optimum analytical conditions established on the Shimadzu AAS system (Model

Table 1
Basic statistical parameters for selected metal levels ($\mu g/m^3$) and particle size fractions (vol.%) in airborne particulate samples ($n = 181$)

	Range	Mean	Median	S.E.	S.D.	Skewness
Fe	0.037–5.979	1.761	1.720	0.058	0.784	0.949
Na	0.016–3.554	1.661	1.655	0.059	0.787	0.164
Zn	0.023–2.076	1.021	1.067	0.046	0.619	−0.263
K	0.018–1.524	0.488	0.534	0.018	0.245	0.047
Pb	0.013–0.360	0.128	0.131	0.006	0.081	0.419
Mn	0.008–0.089	0.055	0.058	0.001	0.019	−0.696
Cr	0.009–0.318	0.059	0.046	0.004	0.048	2.433
Ni	0.006–0.157	0.017	0.015	0.001	0.015	5.209
Co	0.004–0.108	0.020	0.018	0.001	0.018	2.414
Cd	0.003–0.019	0.006	0.005	0.001	0.004	0.923
$PM_{<1.0}$	1.07–7.10	4.67	2.67	0.05	0.60	−0.01
$PM_{1.0-2.5}$	4.72–13.62	8.09	7.82	0.11	1.52	0.32
$PM_{2.5-5.0}$	7.31–18.16	15.96	14.48	0.10	1.39	−0.61
$PM_{5.0-10}$	12.76–25.78	19.16	18.87	0.24	3.17	0.13
PM_{10-15}	9.25–26.54	13.95	13.42	0.22	2.98	0.70
PM_{15-25}	13.04–19.74	14.64	14.49	0.09	1.21	0.69
PM_{25-50}	0.10–20.16	11.96	13.47	0.28	3.74	−0.41
PM_{50-100}	0.05–17.05	6.83	8.79	0.36	4.79	−0.29
$PM_{>100}$	0.03–15.68	5.35	6.45	0.21	2.78	0.08

AA-670, Japan). Particle size fractionation was obtained for nine size categories: $PM_{<1.0}$, $PM_{1.0-2.5}$, $PM_{2.5-5}$, PM_{5-10}, PM_{10-15}, PM_{15-25}, PM_{25-50}, PM_{50-100} and $PM_{>100}$, on vol.% basis. The climatic data was obtained from Pakistan Agriculture Research Council (PARC) on regular daily basis. All the climatic parameters were recorded for the particulate sampling matched duration using standard procedures [24,48]. Statistical analysis of the data was performed with STATISTICA software [29]. Multivariate statistical methods based on standard procedure were used for metal source identification [19].

All reagents used were of AAS grade (certified purity >99.99%) procured from E-Merck. Standard metal stock solutions (1000 ppm) were used to prepare working standards. Doubly distilled water was used throughout the present investigation. Standard Reference Material (NIST SRM, 1573a, TL) was routinely employed to ensure reliability of the finished metal data. Frequent inter-laboratory comparison of the data was made at the Nutrition Division, National Institute of Health, Islamabad. Normally, the two results agreed within ±2.0% for triplicate runs of the sub-samples.

3. Results and discussion

3.1. Trace metal concentration levels

The data on the average levels of selected trace metals in $\mu g/m^3$ estimated in 181 airborne particulate samples are given in Table 1, along with some statistical parameters. The data reveal that Fe has a maximum mean concentration of 1.761 $\mu g/m^3$, followed by Na, at 1.661 $\mu g/m^3$. Of the remaining metals, both Zn and K showed mean levels of 1.021 and 0.488 $\mu g/m^3$, respectively. These metal levels may find their way into the atmosphere from soil derived dust [21], vehicular and industrial sources [3,30]. Lead was the next metal that showed up higher concentration level, approaching 0.128 $\mu g/m^3$. The over-

all decreasing order of metal concentrations was as follow: Fe > Na > Zn > K > Pb > Cr > Mn > Co > Ni > Cd. The levels of Cr, Mn, Co, Ni and Cd were found to be comparatively lower while those of Fe, Na, Zn, K and Pb emerged as dominant air pollutants in the local atmosphere. The enhanced levels of Pb in the local atmosphere could be attributed to vehicular emissions, as the number of transport heavy vehicles has increased tremendously during the last decade [7,28].

A comparison of mean and median values of metals indicated almost equivalent levels of Fe, Na, Pb, Mn, Ni, Co and Cd. However, standard error and standard deviation parameters were noted to be higher for Fe, Na, Zn, K, Pb and Cr, indicating that their distribution does not follow a normal distribution pattern. Hence, some sources other than the natural sources could be operative to give rise to their higher levels in the atmosphere. Large skewness values for Cr, Ni, Co, Cd and Fe reveal that their distribution in the atmosphere is random, a fact that supports the observation cited above.

3.2. Particle size distribution

The data on particulate size distribution are also given in Table 1, which lists the vol.% fractions of particles found in 181 airborne particulate samples. These data indicate that on the average, the $PM_{5.0-10}$ fraction is the largest, at 19.16 vol.%, followed by $PM_{2.5-5.0}$ and PM_{15-25}, at 15.96 and 14.64 vol.%, respectively. The particulate fractions, PM_{10-15} and PM_{25-50} also exhibit significant contributions at 13.95 and 11.96 vol.%. The fine fractions, $PM_{<1.0}$ and $PM_{1.0-2.5}$ show up 4.67 and 8.09 vol.% mean contribution while the giant particulates, PM_{50-100} and $PM_{>100}$ are found to be present at 6.83 and 5.35 vol.%, respectively. Again, a comparison of mean and median values show that the four fractions ($PM_{2.5-5.0}$, PM_{10-15}, PM_{15-25} and $PM_{>100}$) are almost equally poised for a close match towards normal distribution. However, the least value of

Table 2
Statistical summary of climatic parameters prevailing during the study period ($n = 181$)

	Range	Mean	Median	S.D.
Maximum T (°C)	10.0–39.0	24.2	24.0	7.0
Minium T (°C)	−1.0–23.0	8.9	7.5	6.3
RH 8:00 (%)	61.0–100.0	86.9	88.0	8.4
RH 14:00 (%)	21.0–100.0	45.1	41.0	17.6
Sunshine (h/day)	0.0–11.2	7.1	8.1	2.8
Wind Speed (m/s)	0.1–2.0	0.5	0.4	0.3

standard error (0.05) and standard deviation (0.60) is associated with $PM_{<1.0}$ which shows that this fraction has consistent particle size distribution in its class; most divergently distributed particle size, on the other hand, is PM_{50-100}, with a standard deviation value of 4.79, associated with negative skewness.

3.3. Climatic parameters

Table 2 provides the details for the climatic parameters for all 181 samples. The average maximum temperature stands at 24.2 °C while the minimum at 8.9 °C. The relative humidity (RH) recorded at two peak hours (08:00 and 14:00 h) shows the average values of 86.9 and 45.1%, respectively. The mean sunshine duration during the study period is 7.1 h/day with an average wind speed of 0.5 m/s. Among the parameters, temperature and sunshine show relatively lower variations, while RH and wind speed exhibit substantial variations during the study period.

3.4. Correlation statistics

Table 3 outlines the Pearson correlation matrix for various metal levels and particulate fractions, where r values >0.25 or <-0.25 are significant at $p < 0.001$. An examination of the table shows that Fe is significantly correlated with Mn (0.55) and Ni (0.30) thus indicating a common source of these metals as also manifested by positive correlations of Mn–Zn (0.46), Mn–K (0.49) and K–Zn (0.36). Lead is notably correlated with Cd (0.37), again a case of common source. Sodium is found to be positively correlated with Zn (0.26) and K (0.27) while significant negative correlations are observed with Co (−0.25) and Cd (−0.27). Another significant correlation is observed between Cr–Co (0.33); both are negatively correlated with Na, Zn, K, Pb and Mn. Although very complex in its nature, this analysis suggests that Fe, Mn, Zn and K find their way through a common source while Pb and Cd are contributed by the other source.

In case of particulate size fractions, smaller particles, $PM_{<1.0}$ to PM_{10-15} exhibit strong mutual correlations ($p < 0.001$) whereas these particulate fractions show highly negative correlations with coarse and giant particulates, PM_{15-25} to $PM_{>100}$. The coarse particle fractions, PM_{25-50} and PM_{50-100} reveal highly positive correlation (0.94). This indicates that the PM_{25-50} fraction is heavily drawn from the PM_{50-100} fraction and as such, this accounts for its presence due to the PM_{50-100} fraction. The data in Table 3 also evidence strong correlations of Fe, Mn, K and

Table 3
Pearson correlation coefficient matrix for selected metal levels and particle size fractions in airborne particulate samples ($n = 181$)

	Fe	Na	Zn	K	Pb	Mn	Cr	Ni	Co	Cd	$PM_{<1.0}$	$PM_{1.0-2.5}$	$PM_{2.5-5.0}$	$PM_{5.0-10}$	PM_{10-15}	PM_{15-25}	PM_{25-50}	PM_{50-100}
Na	−0.10																	
Zn	0.14	**0.26**																
K	0.20	**0.27**	**0.36**															
Pb	−0.11	0.07	0.24	0.12														
Mn	**0.55**	0.13	**0.46**	**0.49**	0.11													
Cr	0.04	−0.05	**−0.61**	**−0.35**	**−0.28**	−0.18												
Ni	**0.30**	−0.22	−0.04	0.10	0.06	0.04	0.06											
Co	−0.16	−0.25	**−0.42**	−0.18	−0.04	**−0.33**	**0.33**	0.19										
Cd	−0.05	**−0.27**	**0.39**	−0.07	**0.37**	0.01	−0.23	0.24	0.23									
$PM_{<1.0}$	**0.66**	−0.14	0.23	**0.26**	−0.11	**0.74**	0.04	0.05	**−0.27**	−0.09								
$PM_{1.0-2.5}$	**0.70**	**−0.36**	0.20	0.21	−0.18	**0.60**	0.04	0.24	−0.16	0.02	**0.91**							
$PM_{2.5-5.0}$	**0.74**	0.10	**0.45**	**0.27**	−0.07	**0.75**	−0.03	0.12	−0.16	0.08	**0.78**	**0.72**						
$PM_{5.0-10}$	**0.75**	−0.22	**0.40**	**0.39**	−0.04	**0.73**	**−0.34**	0.10	**−0.33**	0.03	**0.86**	**0.86**	**0.78**					
PM_{10-15}	**0.55**	**−0.45**	0.12	0.24	−0.13	**0.49**	−0.21	0.14	**−0.31**	−0.05	**0.76**	**0.84**	**0.41**	**0.82**				
PM_{15-25}	−0.06	**−0.39**	**−0.33**	0.02	**0.26**	**−0.36**	−0.14	0.23	0.13	0.04	**−0.35**	−0.11	**−0.45**	−0.09	0.15			
PM_{25-50}	**−0.63**	**0.38**	−0.25	**−0.29**	0.06	**−0.60**	0.21	−0.10	0.20	0.01	**−0.87**	**−0.89**	**−0.63**	**−0.90**	**−0.88**	0.15		
PM_{50-100}	**−0.69**	**0.41**	**−0.32**	**−0.35**	0.01	**−0.59**	**0.36**	−0.18	0.22	−0.10	**−0.78**	**−0.86**	**−0.61**	**−0.94**	**−0.89**	−0.07	**0.94**	
$PM_{>100}$	**−0.26**	−0.14	0.08	−0.02	−0.05	−0.24	−0.25	**0.27**	0.22	0.13	−0.23	−0.25	**−0.31**	−0.20	−0.21	**−0.29**	−0.07	0.01

Bold values are significant at $p < 0.001$.

Table 4
Pearson correlation coefficient matrix for selected metals/particulate fractions vs. climatic parameters prevailing during study period ($n = 181$)

	Maximum T	Minium T	RH 8:00	RH 14:00	Sunshine	Wind speed
Fe	**0.41**	**0.44**	−0.19	0.02	0.09	**−0.32**
Na	**−0.31**	**−0.55**	−0.08	**−0.28**	**−0.43**	**−0.39**
Zn	0.14	**0.31**	0.06	0.11	−0.04	**−0.30**
K	0.17	**0.28**	**−0.34**	−0.01	−0.07	−0.07
Pb	−0.07	0.03	−0.28.	0.04	0.14	−0.18
Mn	**0.53**	**0.42**	**−0.42**	**−0.34**	0.07	**−0.35**
Cr	−0.03	**−0.36**	0.06	**−0.26**	0.19	0.08
Ni	0.07	0.17	0.13	0.14	0.22	−0.08
Co	−0.19	−0.24	0.15	−0.05	0.21	0.13
Cd	−0.03	0.16	**0.27**	0.22	0.20	−0.11
$PM_{<1.0}$	**0.84**	**0.63**	**−0.41**	**−0.32**	0.20	−0.22
$PM_{1.0–2.5}$	**0.81**	**0.77**	−0.20	−0.03	0.21	−0.07
$PM_{2.5–5.0}$	**0.46**	**0.39**	−0.18	**−0.27**	0.01	**−0.58**
$PM_{5.0–10}$	**0.69**	**0.79**	**−0.28**	−0.02	0.05	**−0.25**
$PM_{10–15}$	**0.85**	**0.84**	−0.22	0.12	0.18	0.13
$PM_{15–25}$	−0.19	0.24	**0.26**	**0.74**	−0.15	**0.40**
$PM_{25–50}$	**−0.86**	**−0.81**	**0.31**	0.10	**−0.29**	0.06
$PM_{50–100}$	**−0.75**	**−0.87**	**0.25**	−0.12	−0.22	0.07
$PM_{>100}$	−0.02	−0.08	−0.11	−0.14	**0.41**	0.15

Bold values are significant at $p < 0.001$.

Zn with fine particle size fractions ($PM_{<1.0}$ to $PM_{10–15}$), while inverse relationships are observed with coarse and giant particulate fractions. Sodium is positively correlated with $PM_{25–50}$ and $PM_{50–100}$ fractions, followed by similar but weak correlations of Cr and Co with these fractions. The study thus shows that while Fe, Mn, K and Zn have shown significant correlations with a specific size of particles [30], Pb shows only weak correlations with $PM_{15–25}$ size fraction and Ni and Cd revealed only weak correlations with all particulate fractions.

Table 4 shows the linear correlation coefficients for various metal levels and particulate fractions versus climatic parameters. An examination of the table reveals that most of the metals show a negative correlation with relative humidity, sunshine and wind speed, of which relative humidity and wind speed exhibit some significant values. The temperature shows significant positive correlation with some metals like Fe (0.41 and 0.44), Mn (0.53 and 0.42), Zn (0.31) and K (0.28) at $p < 0.001$. Wind speed reveals significant negative correlations with Fe, Na, Zn and Mn. The case of Na is different as it exhibits significant negative correlation with all climatic parameters, which suggest that Na levels are arising from randomized sources and thus their distribution in the atmosphere is not dependent on a regular time scale basis.

In case of particulate fractions, two distinctly different correlation patterns are observed in Table 4; the smaller particulate fractions ($PM_{<1.0}$ to $PM_{10–15}$) exhibit strong positive correlations with temperature, and significant negative relationship with relative humidity and wind speed while coarse particulate fractions ($PM_{25–50}$ and $PM_{50–100}$) show an opposite behaviour. The particulate fraction, $PM_{15–25}$ shows significant positive correlations with relative humidity and wind speed, whereas $PM_{>100}$ is positively correlated with sunshine parameter. This means that temperature favours the re-suspension of fine particulate matter; in comparison relative humidity exhibits a washing effect as shown by its negative correlation with fine particle fractions [11]. The coarse and giant particles are found to be carried by high wind speeds under humid conditions.

3.5. Multivariate statistics

The multivariate methods are normally used to identify the combined effect of several measured variables and the influence of external parameters on given distribution [19]. In the present study, two multivariate techniques have been applied;

Table 5
Principal component loadings (varimax normalized) of selected metals and particle size fractions in airborne particulate samples ($n = 181$)

	PC 1	PC 2	PC 3	PC 4	PC 5
Fe	**0.75**	0.12	0.05	−0.01	0.37
Na	−0.41	**0.61**	−0.21	0.41	0.30
Zn	0.21	0.34	0.34	**0.71**	−0.10
K	0.22	0.04	0.06	**0.61**	0.21
Pb	−0.14	0.08	**0.55**	0.32	−0.19
Mn	**0.65**	0.40	0.03	0.38	0.21
Cr	0.07	−0.23	0.22	**0.80**	−0.30
Ni	0.17	−0.24	**0.55**	−0.17	0.48
Co	0.17	0.07	−0.40	**0.65**	0.06
Cd	0.02	−0.03	**0.85**	0.04	−0.11
$PM_{<1.0}$	**0.92**	0.27	−0.13	0.04	0.08
$PM_{1.0–2.5}$	**0.96**	0.02	0.01	−0.05	0.13
$PM_{2.5–5.0}$	**0.73**	0.51	0.12	0.11	0.29
$PM_{5.0–10}$	**0.92**	0.02	0.01	0.31	0.08
$PM_{10–15}$	**0.87**	−0.36	−0.14	0.16	0.01
$PM_{15–25}$	0.13	−0.03	**0.92**	−0.04	−0.27
$PM_{25–50}$	−0.03	**0.96**	−0.02	0.11	−0.19
$PM_{50–100}$	−0.19	**0.93**	0.10	0.24	−0.08
$PM_{>100}$	0.12	−0.07	−0.24	0.03	**0.84**
Eigen value	5.52	3.92	2.86	1.53	1.37
%Variance	33.61	17.80	13.38	8.08	7.20
%Cumulative variance	33.61	51.41	64.79	72.87	80.07

Higher loadings are shown in bold.

Table 6
Mean trace metal concentration levels ($\mu g/m^3$) in SPM vs. counterpart data for other sites around the world

Site/nature	Fe	Na	Zn	K	Pb	Mn	Cr	Ni	Co	Cd
Islamabad, Pakistan/urban[a]	1.761	1.661	1.021	0.488	0.128	0.055	0.059	0.017	0.020	0.006
Changlagali, Pakistan/rural [36]	3.950		0.122	3.980	0.069	0.0964	0.015		0.0017	0.0005
Vienna, Austria/rural [30]	0.189	–	0.018	–	0.017	0.033	0.020	0.009	–	–
Brownfield, UK/rural [32]	0.260	–	0.063	–	0.030	0.006	–	0.002	0.0001	0.0006
Frankfurt, Germany/rural [37]	–	–	0.0287	–	0.0116	0.0097	0.0038	0.0026	0.0002	0.0002
Lahore, Pakistan/urban [21]	9.930	2.740	27.70	3.300	3.920	–	–	–	–	0.0435
Karachi, Pakistan/urban [38]	4.200	8.700	0.100	–	0.070	0.080	0.030	0.020	–	–
Delhi, India/urban [22]	5.220	–	–	–	0.380	–	0.104	0.097	–	0.0067
Mumbai, India/urban [35]	2.950	–	0.350	–	0.550	–	0.040	0.040	–	0.040
Calcutta, India/urban [39]	26.40	–	3.04	11.65	6.630	0.430	0.11	–	–	–
Tehran, Iran/urban [40]	2.230	1.680	0.327	2.150	1.020	0.078	0.048	0.037	0.008	–
Dhaka, Bangladesh/urban [16]	24.80	1.270	0.801	1.550	0.279	–	–	–	–	0.0025
Beijing, China/urban [41]	6.42	5.55	0.154		0.0418	0.29	0.00641	0.007	0.049	0.00044
Tokyo, Japan/urban [42]	0.6769	0.637	0.2987	–	0.1247	0.0401	0.0061	0.0056	–	–
Frankfurt, Germany/urban [37]	–	–	0.1056	–	0.0326	0.0353	0.0163	0.0073	0.0008	0.0003
Deberecen, Hungary/urban [1]	0.911	–	0.056	–	0.072	0.023	0.018	0.005	–	–
Milan, Italy/urban [43]	2.700	–	0.239	0.934	0.861	0.078	0.065	0.038	0.0043	0.0076
La Plata, Argentina/urban [33]	1.183	–	0.273	–	0.0645	0.026	0.0043	0.00315	–	0.00041
Ho Chi Minh City, Viet Nam/urban [44]	2.904	0.770	0.203	0.789	0.146	0.038	0.0086	–	0.0011	–
Rio de Janeiro, Brazil/urban [45]	1.2128	2.546	0.6283	0.6103	0.0149	0.0241	0.0021	0.0031	0.0004	0.0003
New York, USA/urban [46]	0.177	–	0.015	–	0.003	0.008	–	0.0009	0.0001	–
Detriot, USA/urban [3]	0.003–1.00	–	0.030–0.180	–	0.040–0.100	–	0.007–0.015	0.005–0.016	–	0.001–0.003
Birmingham, UK/roadside [15]	0.204	–	0.030	–	0.027	0.006	–	0.002	–	0.0005
Krakow, Poland/heavy traffic [5]	1.303	–	0.137	–	0.095	0.029	–	–	–	–
Taiwan/industrial [34]	0.721–1.415	–	0.225–0.333	–	0.079–0.112	0.049–0.119	0.003–0.014	0.007–0.023	0.008–0.037	0.003–0.013
Tito Scalo, Italy/industrial [10]	0.521	–	0.304	–	0.060	0.027	0.013	0.005	–	0.002
Taejon, Korea/industrial [47]	1.633	–	0.240	–	0.243	0.0503	0.0251	0.0379	0.00153	0.00324
Rio de Janeiro, Brazil/industrial [48]	38.903	0.175	2.120	0.048	0.101	1.216	0.421	0.0005	0.0011	0.0009
La Coruna, Spain/industrial [49]	0.850	–	0.008	–	0.032	0.013	–	–	–	0.00092

[a] Present study.

the principal component analysis (PCA) and the cluster analysis (CA). PCA defines the quantitative relationships among the variables in the form of groups within the data, which reduces the number of variables/dimensionality in a dataset using a smaller number of linearly independent new variables. These new variables are principal components (PCs), each of which is a linear combination of originally correlated variables, which are metals and particulate fractions in the present study. CA organizes a set of variables into two or more mutually exclusive unknown groups/clusters based on combination of internal variables. The purpose of CA is to discover a system of organizing variables where each groups/cluster share properties in common. Thus, it is cognitively easier to predict properties/sources based on group membership all of which share similar properties [31]. These help to define source profiles and their interpretation in terms of measured variables [19,25].

PCA with varimax normalized rotation on the dataset of selected metals and particle size fractions is performed for the source identification. Table 5 presents the PC loadings with Eigen values >1, embodying and explaining more than 80% of total variance. It turns out that the first PC explaining most of the variance (33.61%) has maximum loadings for Fe, Mn, $PM_{<1.0}$, $PM_{1.0-2.5}$, $PM_{2.5-5.0}$, $PM_{5.0-10}$ and PM_{10-15}. It represents the contribution of these metal particulates emitted from different industries and other anthropogenic sources, duly supported by the CA [3,10,21,30,32,33]. The second PC showed the higher loadings for the Na, PM_{25-50} and PM_{50-100}, which is mainly conceived to be contributed by wind blown soil dust caused by the quarrying activity taking place round the clock at Margalla Hills (Fig. 1) [21,30]. The CA also supports this observation. The third PC reveals maximum loadings for Pb, Cd, Ni and PM_{15-25} and it is believed to originate from vehicular emissions/residual oil combustion, which mainly have source from internal combustion engines in urban areas with high traffic density (13.38%) [1,22,25,30]. The fourth PC which presents the high loadings for Zn, K, Cr and Co, is traced from the biomass burning, municipal garbage incineration and metallurgical operations [3,22,30,34]. Finally, the last PC exhibiting higher loadings in favour of $PM_{>100}$ is contributed by occasional stormy conditions. The corresponding dendrogram obtained through CA is shown in Fig. 2, evidencing that anthropogenic metals such as Fe, Zn, Mn and K are mainly associated with fine particulates while Na is contributed by large wind blown dust particles.

The source identification of this study is in agreement with the majority of the reported data on this subject [19,22,25,26] and shows that the major anthropogenic contribution of toxic metals in the airborne particulate matter comes from traffic emissions/oil combustion along with industrial emissions as recently proposed by different workers in various parts of world [25,26,33,35].

3.6. Comparison with counterpart data of other sites around the world

The levels of airborne trace metals are compared with the counterpart data from the other background/rural, urban and industrial sites around the world and the results are given in
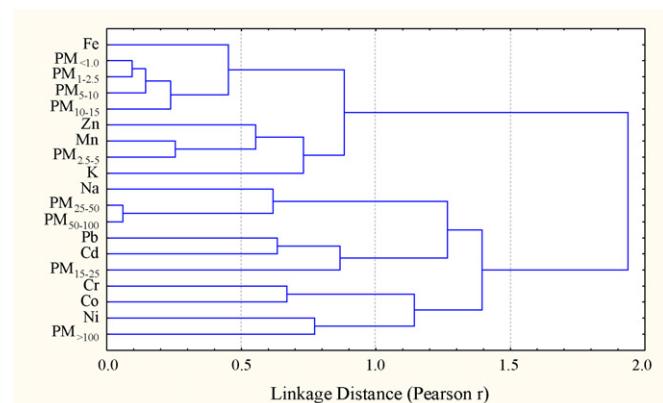

Fig. 2. Dendrogram (complete linkage) showing the clustering pattern of trace metals and particulate fractions ($n = 181$).

Table 6. In comparison with background metal levels reported for Changlagali [36], a remote location situated 50 km north of Islamabad; the concentration levels of Zn, Pb, Cr, Co and Cd are significantly higher in urban atmosphere of Islamabad. Likewise, the present airborne trace metals levels are also many folds higher than those found in rural areas of Vienna (Austria) [30], Brownfield (UK) [32] and Frankfurt (Germany) [37].

In comparison with other urban sites, such as Detriot (USA) [3], Deberecen (Hungary) [1], Frankfurt (Germany) [37], La Plata (Argentina) [33], Birmingham (UK) [15], Krakow (Poland) [5] and New York (USA) [46], where strict actions have been employed for environmental safety, most of the metal levels are found to be considerably higher in local atmosphere of the city. However, some of the particulate metal levels are found to be comparable with urban sites of Milan (Italy) [43], Ho Chi Minh City (Viet Nam) [44] and Rio de Janeiro (Brazil) [45]. When compared with industrial sites of Taiwan [34], La Coruna (Spain) [49] and Tito Scalo (Italy) [10], the local atmospheric metal levels in Islamabad are markedly higher but they are almost similar to the reported levels for industrial site of Taejon (Korea) [47] and lower than those found for industrial district of Rio de Janeiro (Brazil) [48].

Compared with other Asian mega cities, the estimated concentration of trace metals exhibit typically much lower levels than observed in Lahore [21], Delhi [22], Mumbai [35], Calcutta [39], Tehran [40], Dhaka [16] and Beijing [41]. With some exceptions, the airborne trace metal levels show a similar trend to that of Karachi [38] and Tokyo, Japan [42]. All the trace metals were found enriched in airborne particulate samples as revealed by the comparison with rural/background sites.

4. Conclusions

In conclusion, present study brings out the clear difference between the levels of trace metals in local urban atmosphere. The most dominant metals in local atmosphere are Fe, Na, Zn, K and Pb. Of the remaining fractions Mn, Cr, Co, Cd and Ni emerge as minor contributors. $PM_{5.0-10}$ carries largest fraction of particulate matter, followed by $PM_{2.5-5.0}$ while $PM_{<1.0}$ and $PM_{1.0-2.5}$ also exhibited significant contributions. The relatively

higher levels of selected trace metals in Islamabad are indicative of the fact that the local atmosphere is undergoing some remarkable anthropogenic translocations. Industrial metals like Fe, Zn, Mn and K showed viable correlations while Pb is correlated with Cd because of their common source. Most of the metals are significantly correlated with smaller particulate fractions while exhibiting negative relationships with coarse fractions. Among the climatic parameters, temperature shows some significant influence on metal distribution in atmosphere, whereas all other parameters show inverse or weak relationship with metals. Source apportionment study through PCA and CA enabled to identify five sources of trace metals and particulate fractions in the local atmosphere; industrial activities, automobile emission, metallurgical operations, garbage incineration and soil derived dust. The comparison study presents an alarming situation of airborne trace 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.

Acknowledgments

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