Atmospheric Pollution Research

www.atmospolres.com

Assessment of the trace elements level in urban atmospheric particulate matter and source apportionment in Islamabad, Pakistan

Munir H. Shah, Nazia Shaheen, Rashida Nazir

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

ABSTRACT

The present study was conducted to investigate the distribution, correlation, source apportionment and enrichment of trace elements (Cd, Co, Cr, Cu, Fe, Mn, Pb, Sb and Zn) in the urban atmospheric particulate matter. The total suspended particulate matter samples were extracted in nitric acid and hydrochloric acid mixture, followed by the quantification of the trace elements on flame atomic absorption spectrophotometer. The estimated elemental data were then evaluated for their mutual variations in the urban particles. Average 24–h concentrations of Fe and Zn were dominant in the atmospheric particles followed by Cu, Pb, Co, Cr, and Sb, while lowest concentrations were observed for Mn and Cd. The present TSP and elemental levels were also compared with those reported from other areas around the world. The correlation study showed strong relationships between TSP–Fe, Mn–Fe, TSP–Mn, Pb–Mn, Cd–Pb, and Co–Zn. Principal component and cluster analyses revealed automobile emissions, industrial activities, combustion processes and mineral dust as the major pollution sources in the atmospheric particles. Among the trace elements, Sb, Cd, Zn and Pb showed very high enrichment by the anthropogenic activities, while Co and Cu were also significantly enriched in the particulate samples. Most of the trace elements exhibited random distribution with diverse correlations in the atmospheric particles. Comparison of the present elemental levels with those reported from other areas around the world showed relatively elevated concentrations of the elements in the atmospheric particulates. Different anthropogenic activities were found to be mainly responsible for the trace element pollution duly supported by the enrichment factors.

Keywords:
Particulate matter
Urban atmosphere
Trace elements
Source apportionment
PCA

Article History:
Received: 26 May 2011
Revised: 24 August 2011
Accepted: 27 August 2011

Corresponding Author:
Munir H. Shah
Tel: +92-51-90642137
Fax: +92-51-90642241
E-mail: mhshahg@qau.edu.pk

doi: 10.5094/APR.2012.003

1. Introduction

Suspended particulates are introduced into the atmosphere from a variety of natural and anthropogenic sources, although the latter are predominant in the urban and industrial areas (Borbely–Kiss et al., 1999; Pakkanen et al., 2001). Some of the well known anthropogenic processes contributing to the airborne particulate pollution include transportation, industrial activities, biomass burning and agricultural activities (Harrison et al., 1997; Hien et al., 2001; Arditsoglou and Samara, 2005; Valavanidis et al., 2006). There is an increasing concern about the hazardous effects of atmospheric pollutants on humans and other living organisms in populated areas (Freitas et al., 2010; Garcia et al., 2011). However, recently epidemiological studies have pointed out that airborne particulates containing toxic components, such as heavy metals, are of special concern due to numerous health effects (Andersen et al., 2006; Sarnat et al., 2006; Liu et al., 2009; Mavroidis and Chaloulakou, 2010). The urban population is exposed to the airborne toxic metals that often are well above natural background levels (Hadad et al., 2003; Salam et al., 2003; Samura et al., 2003; Zereini et al., 2005; Shridhar et al., 2010). Many monitoring programs on atmospheric particulate matter have been conducted in several parts of the world which showed diverse fluctuations and disparities among the trace element constituents (Sohrabpour et al., 1999; Bilos et al., 2001; Rizzio et al., 2001a; Wang et al., 2001; Ragosta et al., 2002; Quiterio et al., 2004a; Gupta et al., 2007; Hao et al., 2007; Ayrault et al., 2010).

The present study was undertaken in order to assess the atmospheric particulate pollution in Islamabad, the capital city of Pakistan, situated at an elevation of about 500 m above sea level (Latitude 33°49′N; Longitude 72°24′N). It is 14 km northeast of its twin city Rawalpindi, flanked by Margalla Hills on its north and plains of Punjab and water bodies on other sides. The city extends over 906 km^2 with a present population of more than one million (Pakistan Bureau of Statistics, 2004). The urban area of the city is divided into residential, commercial, industrial and diplomatic zones. A number of industrial units housed in sectors, I–9/10 and Kahuta Triangle, along with the ever–increasing automobile emissions that are the main sources of city's air pollution. Steel mills, marble factories, flour mills, oil and ghee units, soap/chemical factories, paints, pigments and pharmaceuticals manufacturing plants are the main industries located in these sectors. This study is based on the analysis of urban airborne particulate samples collected during an intensive sampling campaign originally aimed at elucidating the role of trace elements to air quality deterioration in Islamabad and to explore the mutual variations among the trace elements in terms of their source apportionment. Anthropogenic enrichment of trace elements in atmospheric particulates were also envisaged along with the comparative evaluation of the estimated elemental levels with those reported from other areas around the world.

2. Materials and Methods

Sampling of atmospheric particulates was carried out using a high volume air sampler (Thermo–Andersen, GMWL–2000H, USA) in a typical urban area of Islamabad (Figure 1). The sampler was installed at the roof–top approximately 15 m above the ground level, and well cleared from other tall buildings around. The

sampling was performed on regular 24–h basis (excluding public holidays), starting at 08:00 h, during September 2008–March 2009. A total of 153 total suspended particulate (TSP) samples were collected on cellulose and glass fiber filters (20.4 cm x 25.4 cm) at a stipulated flow rate of 1.13 m^3/min (Method IO–2.1, 1999).

TSP mass was determined gravimetrically prior to analysis (Method IO–2.1, 1999). For the estimation of selected elements, each filter was extracted by a nitric acid (Merck Suprapure, 65%) and hydrochloric acid (37%) mixture (Method IO–3.1, 1999). The extracted solution was filtered with washing by doubly distilled water and refrigerated in pre–cleaned strong polyethylene bottle until analyzed. Filter and reagent blanks were also processed following the above procedure for sample treatment. Selected elements were determined by atomic absorption spectrophotometer (Shimadzu, AA–670, Japan) following standard method (Method IO–3.2, 1999). The elements estimated in blanks were <5% of the sample average contents. The accuracy of the method was evaluated using a standard reference material (OL–96). Inter–laboratory comparison of the data was also exercised at an independent laboratory and normally, a maximum of $\pm 5\%$ deviation was observed in the results of the two laboratories. The results obtained were comparable within $\pm 2\%$ in the range of the standard reference material used. Along with the basic statistical parameters and correlation analysis, multivariate methods comprising of principal component analysis (PCA) and cluster analysis (CA) were performed on the dataset using the STATISTICA software (StatSoft, 1999). The PCA was conducted using Varimax normalized rotation on the dataset and the CA was applied to the standardized matrix of samples, using Ward's method and the results are reported in the form of dendrogram.

A more comprehensive understanding of the origin of trace elements in atmospheric particulate matter demands developing relationships between airborne TSP and soil, through the Enrichment Factors (EFs). Estimation of EFs is a measure to find out the anthropogenic origin of atmospheric trace elements. The results of EF can provide useful evidence for the human intrusion of the elements in TSP by using measured element concentrations in particulates (Bilos et al., 2001; Arditsoglou and Samara, 2005; Zereini et al., 2005; Shah and Shaheen, 2008; Shridhar et al., 2010). The EF value close to unity suggests that the element is dominantly contributed by natural soil dust or the contribution of anthropogenic sources is not significant. The values much higher than 1 may imply sources other than crustal dust. These sources include human activities (e.g., combustion, automobile and industrial emissions, agricultural activities etc.) and other processes (e.g., forest fires, volcanoes, sea salt).

EFs are usually taken as double ratios of the target element and a reference element in aerosols and earth crust. The reference element must be one that is overwhelmingly derived from a natural source. Usually, Na, K, Al, Mg, Ca, Mn and Fe are used as the reference. In the present study, EFs were calculated using Fe as the reference element, using the relationship;

$$EF = \frac{[X/Fe]_{TSP}}{[X/Fe]_{crust}} \quad (1)$$

where $[X/Fe]_{TSP}$ and $[X/Fe]_{crust}$ refers, respectively, to the ratios of mean concentration of the target element and Fe in atmospheric particulate matter and continental crust. The EFs are calculated on the basis of earth crust mean abundance of the elements given in CRC handbook (Lide, 2005).

3. Results and Discussion

Statistical parameters pertaining to the distribution of TSP and trace elements for the atmospheric particulate samples are given in Table 1. The 24–h TSP levels in urban particulate matter exhibited a mean concentration of 119 μg/m^3, showing predominantly a random distribution. Among the trace elements in atmospheric particulate samples, major contribution was noted for Zn and Fe. Overall, the decreasing trend of average trace element concentrations (24–h) in the particulates revealed the following order: Zn > Fe > Pb > Sb > Mn > Cu > Co > Cr > Cd. Almost a similar pattern was observed for the median trace element concentrations. Most of the trace elements showed a random distribution pattern manifested by higher standard deviation (SD) and standard error (SE) values on one hand and considerable skewness values on the other hand. Maximum dispersion was noted for Zn, Fe, Pb and Sb, thus supporting their variable distribution in the urban particulates. All the atmospheric particulate elements were found to spread over several orders of magnitude, as shown by their respective ranges.

The present data on airborne TSP and trace elements are also compared with the international guidelines as well as with the counterpart data from other sites around the world as shown in Table 1. The 24–h TSP levels measured during the current study were found to be significantly higher than WHO and USEPA standard values (WHO, 2000; ATSDR, 2002). Among the atmospheric trace elements, Cr, Mn and Pb levels (24–h) in the present study are within the permissible limits laid down by WHO and USEPA but the Cd levels in some cases are fairly higher compared with the guideline values. A number of health related problems may thus be associated with elevated TSP and Cd concentrations in the atmosphere. Average TSP levels in the atmosphere of Islamabad were significantly higher than those reported from Yokohama (Khan et al., 2010), Delft (Wang et al., 2001), Tito Scalo (Ragosta et al., 2002), Ho Chi Minh City (Hien et al., 2001) and Santa Cruz (Quiterio et al., 2004a) while, the present levels were substantially lower than those reported from Lahore (Harrison et al., 1997), Faisalabad (Qadir and Zaidi, 2006), Delhi (Shridhar et al., 2010), Beijing (Wang et al., 2001), Cartagena (Moreno–Grau et al., 2000), Bilbao (Aranguiz et al., 2002) and previously reported levels from Islamabad (Shah and Shaheen 2008). However, the TSP levels reported from Mumbai (Tripathi et al., 2004), Athens (Valavanidis et al., 2006), Pristina (Arditsoglou and Samara, 2005) and Rio de Janerio (Quiterio et al., 2004b) were almost comparable with the levels measured in the present study.

Average concentrations of the elements in the atmospheric particulate matter in comparison with the worldwide reported levels from different urban areas showed that most of the present trace element levels were comparatively lower than those found in highly polluted metropolitan cities such as, Lahore (Harrison et al., 1997), Karachi (Parekh et al., 1987), Calcutta (Gupta et al., 2007), Delhi (Shridhar et al., 2010), Dhaka (Salam et al., 2003), Tehran (Sohrabpour et al., 1999), Shiraz (Hadad et al., 2003), Beijing (Wang et al., 2001), Bursa (Samura et al., 2003), Bilbao (Aranguiz et al., 2002), Athens (Valavanidis et al., 2006), and Santa Cruz (Quiterio et al., 2004a). The mean Cd concentration in the urban particulates estimated in the present study was found to be higher than most of the reported levels in Table 1 except Lahore (Harrison et al., 1997), Faisalabad (Qadir and Zaidi, 2006), Kolkata (Gupta et al., 2007), Delhi (Shridhar et al., 2010), Cartagena (Moreno–Grau et al., 2000), and Bilbao (Aranguiz et al., 2002). The atmospheric Co levels pertaining to the present study were also found to be higher than those reported for most of the cities, being only lower than previously reported levels from Islamabad (Shah and Shaheen, 2008). The average levels of Cr in the atmospheric particulates of Islamabad were lower compared with most of the cities, however, these levels were comparable with those reported from Mumbai (Tripathi et al., 2004), Ponzone (Rizzio et al., 2001b), Ispra (Rizzio et al., 1999), Ho Chi Minh City (Hien et al., 2001), and Pristina (Arditsoglou and Samara, 2005). Mean levels of airborne Cu and Mn were comparable to most of the European cities but lower than most of the Asian cities. Present Fe levels in the particulates were found to be comparable with those reported from Kolkata (Gupta et al., 2007), Mumbai (Tripathi et al., 2004), Won Ju City

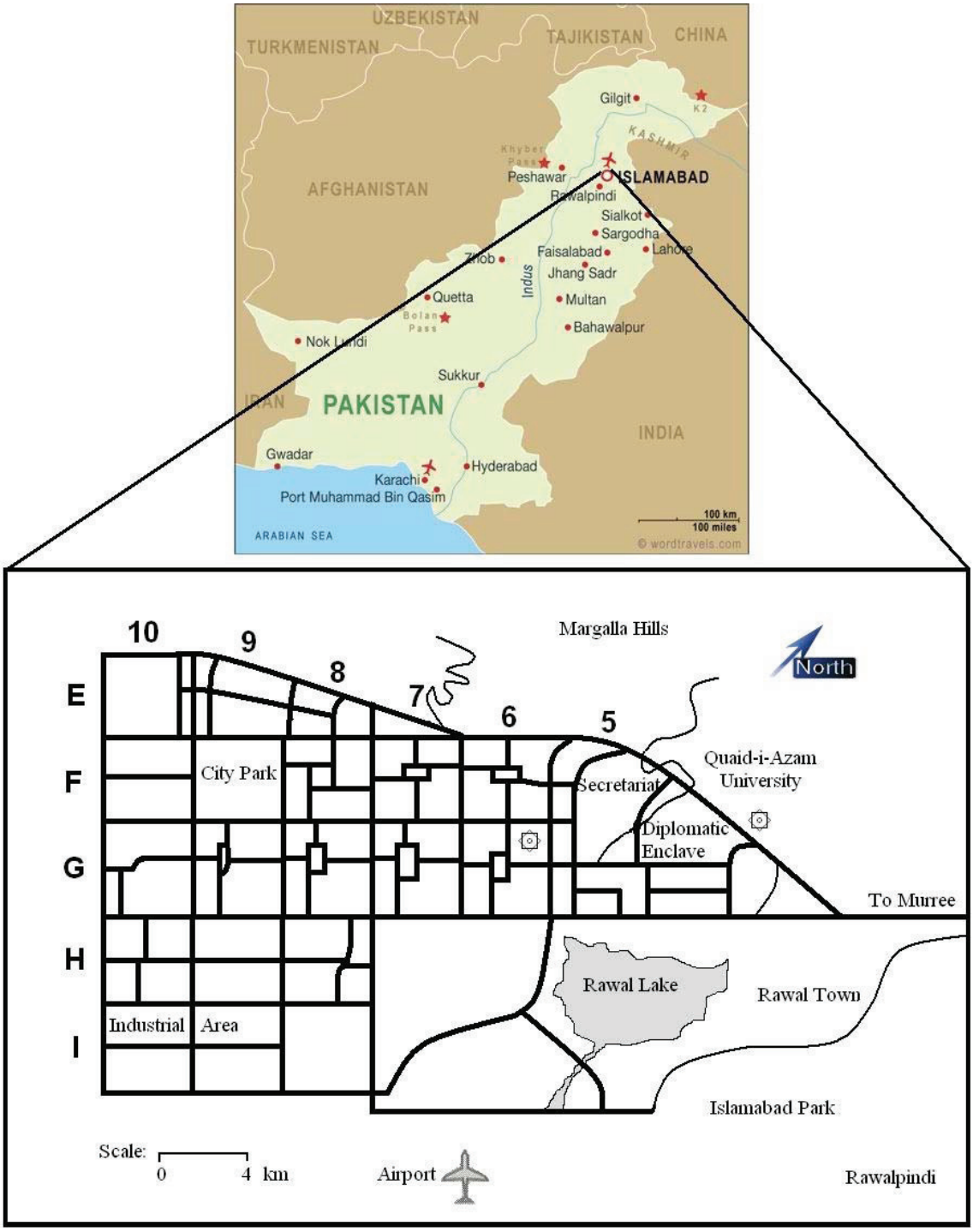

***Figure 1**. Location of sampling site (⌬) in Islamabad, Pakistan.*

(Kim, 2004), La Plata (Bilos et al., 2001) and Rio de Janerio (Quiterio et al., 2004b), but higher than those reported from Faisalabad (Qadir and Zaidi, 2006), Paris (Ayrault et al., 2010), Debrecen (Borbely–Kiss et al., 1999), Ponzone (Rizzio et al., 2001b), Ispra (Rizzio et al., 1999), and Tito Scalo (Ragosta et al., 2002). Mean Pb levels estimated in the present study were comparable to those found in Karachi (Parekh et al., 1987), Won Ju City (Kim, 2004), Bursa (Samura et al., 2003), Debrecen (Borbely–Kiss et al., 1999), Tito Scalo (Ragosta et al., 2002), and La Plata (Bilos et al., 2001), nonetheless, these levels were lower in comparison with the grossly polluted cities of the world, such as Lahore (Harrison et al., 1997), Faisalabad (Qadir and Zaidi, 2006), Kolkata (Gupta et al., 2007), Delhi (Shridhar et al., 2010), Dhaka (Salam et al., 2003), Tehran (Sohrabpour et al., 1999), Shiraz (Hadad et al., 2003), Qingdao (Hao et al., 2007), Beijing (Wang et al., 2001), Cartagena (Moreno–Grau et al., 2000), Bilbao (Aranguiz et al., 2002), Athens (Valavanidis et al., 2006), Pavia (Rizzio et al., 2001a), and Santa Cruz (Quiterio et al., 2004a). The average Sb and Zn levels in the particulates were estimated at elevated levels compared with most of the locations reported in Table 1. In conclusion, the trace element levels in the urban atmosphere of Islamabad in comparison with some European urban sites were many times higher; however, these particulate trace element levels were found to be comparable with few urban sites in the world. Nonetheless, the estimated elemental levels in the present study were lower than those reported for large metropolitan cities (Lahore, Karachi, Calcutta, Delhi, Dhaka, Tehran, Shiraz, Beijing, Bursa, Bilbao, Athens, and Santa Cruz).

Table 1. *Statistical summary of TSP (μg/m^3) and trace element levels (ng/m^3) in the airborne particulate matter (n = 153) and their comparison with other urban areas around the world and guidelines of regulatory agencies*

	TSP	Cd	Co	Cr	Cu	Fe	Mn	Pb	Sb	Zn
Minimum	29.1	0.27	1.05	0.25	5.17	72.5	14.1	4.17	0.75	376
Maximum	226	15.5	35.1	20.1	87.8	2 693	83.7	296	150	6 926
Mean	119	3.43	12.2	7.18	38.1	1 343	38.8	63.5	43.9	3 325
SD	42.8	2.67	8.35	5.19	15.3	554	14.4	56.3	35.3	2 001
SE	6.45	0.40	1.26	0.82	2.31	83.6	2.17	9.02	5.80	343
Skewness	0.12	2.41	0.95	0.73	0.86	0.27	1.03	2.41	1.31	0.45
Regulatory Agencies										
WHO (WHO, 2000)	80	5		1 100			150	500		
USEPA (ATSDR, 2002)	60	6.37		100			500	1 500		
Urban Areas										
Islamabad, Pakistan (Shah and Shaheen, 2008)	164	4	33	10	306	2 464	79	144	157	2 311
Lahore, Pakistan (Harrison et al., 1997)	607	43.4		113	420	9 930	350	3 920		27 700
Karachi, Pakistan (Parekh et al., 1987)				30		4 200	80	70		100
Faisalabad, Pakistan (Qadir and Zaidi, 2006)	550	20.5	5.6	30.9		14.5		549	4.9	16.1
Kolkata, India (Gupta et al., 2007)		39.6		56.0		1 100	28.1	159		607
Delhi, India (Shridhar et al., 2010)	546	10		350	3 690	16 430	740	440		4 670
Mumbai, India (Tripathi et al., 2004)	134	0.7		5.0	15.8	1 620	40.39	101		260
Dhaka, Bangladesh (Salam et al., 2003)		2.5			54	24 800		279		801
Tehran, Iran (Sohrabpour et al., 1999)			8	48		2 230	78	1 020		327
Shiraz, Iran (Hadad et al., 2003)				15	122	2 621	53	545		85
Yokohama, Japan (Khan et al., 2010)	34.2	1.2		4.1	47.7		32.5	27.2		130
Qingdao, China (Hao et al., 2007)		5.1			38.2	3 788	134	315		452
Beijing, China (Wang et al., 2001)	496	4.44	7.09		154			404		454
Delft, Netherlands (Wang et al., 2001)	56	0.458	0.147		139			16.64		21.35
Won Ju City, Korea (Kim, 2004)		2.1		14.7		1 486	33.3	84		
Bursa, Turkey (Samura et al., 2003)		1.8		92		41 400	992	53		311
Cartagena, Spain (Moreno-Grau et al., 2000)	200	9.23			50			690		2 100
Bilbao, Spain (Aranguiz et al., 2002)	171	8			200	4 480	260	1 570		12
Athens, Greece (Valavanidis et al., 2006)	133	4.5		370	700	10 200		2 700		3 500
Frankfurt, Germany (Zereini et al., 2005)		0.3	0.8	16.3	102		35.3	32.6	23.5	106
Paris, France (Ayrault et al., 2010)		0.393	0.208	4.12	18.4	483	6.95	15.37	4.53	45.8
Debrecen, Hungary (Borbely-Kiss et al., 1999)				4.5	10.6	598	14.7	61.9		50
Pavia, Italy (Rizzio et al., 2001a)		1.3	2.1	59	54	2 828	56	185	14	258
Ponzone, Italy (Rizzio et al., 2001b)		0.75	1.15	7.0	21.4	807	23	36	4.9	98
Ispra, Italy (Rizzio et al., 1999)		0.51	0.75	6.5	10.5	511	14	98	4.5	119
Tito Scalo, Italy (Ragosta et al., 2002)	60	2		13	58	521	27	60		304
Pristina, Kosovo (Arditsoglou and Samara, 2005)	109	3.6	6	11	179	1 725	49	25	6.6	42
Ho Chi Minh City, Viet Nam (Hien et al., 2001)	74		1.14	8.63	1.28	2 904	38	146	2.5	203
La Plata, Argentina (Bilos et al., 2001)		0.41		4.32	29.5	1 183	25.5	64.5		273
Santa Cruz, Brazil (Quiterio et al., 2004a)	87	0.9	1.1	421	335	38 903	1 216	101		2 120
Rio de Janerio, Brazil (Quiterio et al., 2004b)	133	0.3	0.4	2.1	70.7	1 213	24.1	14.9		628

The Spearman correlation coefficient matrix pertaining to the TSP and trace elements in the urban particulate matter is given in Table 2. TSP was found to be very strongly correlated with Fe (r = 0.770) and Mn (r = 0.694), a significant correlation was observed for Pb (r = 0.443). The data in Table 2 manifested a significant role of Fe and Mn in TSP, while rest of the elements did not show strong correlation with TSP. It may be assumed from this correlation pattern that Fe and Mn are mostly derived from the windblown soil particles and hence mainly natural origin. Some of the element pairs revealed very strong correlations in the urban particulate samples. Fe and Mn showed a strong relationship with r = 0.734, followed by Mn–Pb (r = 0.548), Cd–Pb (r = 0.520) and Co–Zn (r = 0.520). A couple of other significant correlations were observed between Cd–Cr and Cr–Zn. Based on the correlation study, it may be concluded that Fe and Mn were contributed by some common sources, probably by natural processes, whereas, Cd, Cr, Pb and Zn were contributed by various anthropogenic activities. Among all the trace elements, Cu and Sb did not show significant association with any other element; hence manifesting their independent variations as well as multisource origin in the urban particulate matter.

Multivariate techniques of principle component analysis and cluster analysis were used for the source apportionment of TSP and trace elements in the urban particulate samples (Harrison et al., 1997; Bilos et al., 2001; Hien et al., 2001; Ragosta et al., 2002; Quiterio et al., 2004a; Arditsoglou and Samara, 2005; Shah and Shaheen, 2008). The cluster analysis related to TSP and trace element data for the airborne particulates is presented in the form of dendrogram in Figure 2. The strongest cluster was observed among Fe–Mn–TSP, followed by another strong cluster among Pb–Cd–Cu. Co–Sb and Cr–Zn also constitute two clusters although they are very weak. Table 3 presents the principal component loadings for the TSP and trace element data pertaining to the urban particulates, with corresponding eigenvalues and variances.

Three PCs with eigenvalues greater than 1.0 were extracted, representing 71.35 % cumulative variance. An examination of the data (Table 3) showed maximum variance (35.75%) was contributed by PC 1 which had higher principal component loadings for TSP, Fe, and Mn. This revealed close association of Fe, and Mn in TSP in the urban atmosphere, mainly contributed by the wind–blown mineral dust (Borbely–Kiss et al., 1999; Pakkanen et al., 2001; Hao et al., 2007; Shah and Shaheen, 2008). Thus, PC 1 mainly shows the natural contribution of particulate element pollution in the urban atmosphere. Second PC exhibited higher loadings for Pb, Cd, Cu and Zn, along with considerable contributions from Cr and Mn. These elements are believed to be originated from automobile

***Table 2**. Spearman correlation coefficient (r) [a] matrix for TSP and selected elements in the airborne particulate matter (n = 153)*

	TSP	Cd	Co	Cr	Cu	Fe	Mn	Pb	Sb	Zn
TSP	1.000									
Cd	0.286	1.000								
Co	0.185	0.152	1.000							
Cr	0.058	**0.455**	0.280	1.000						
Cu	0.348	0.209	0.207	0.215	1.000					
Fe	**0.770**	0.249	0.236	0.122	0.184	1.000				
Mn	**0.694**	0.221	0.038	0.175	0.204	**0.734**	1.000			
Pb	**0.443**	**0.520**	0.142	0.273	0.374	0.339	**0.548**	1.000		
Sb	0.173	0.182	0.397	0.060	0.059	0.236	0.170	0.171	1.000	
Zn	-0.078	0.221	**0.520**	**0.402**	0.200	0.069	0.040	0.260	0.055	1.000

[a] *r-values shown in bold are significant at p≤0.001*

***Table 3**. Principal component loadings of TSP and selected elements in the airborne particulate matter*

	PC 1	PC 2	PC 3
Eigen values	3.575	2.169	1.391
% Total variance	35.75	21.69	13.91
% Cumulative variance	35.75	57.45	71.35
TSP	0.904	0.101	0.044
Cd	0.215	0.811	0.217
Co	-0.079	0.178	0.864
Cr	-0.056	0.478	0.362
Cu	0.126	0.679	-0.164
Fe	0.905	0.087	0.160
Mn	0.892	0.363	-0.072
Pb	0.342	0.824	0.065
Sb	0.235	-0.051	0.818
Zn	-0.430	0.526	0.357

emissions together with industrial emissions, especially, the metallurgical/electroplating units located in the industrial area of the city (Parekh et al., 1987; Wang et al., 2001; Ragosta et al., 2002; Quiterio et al., 2004a; Zereini et al., 2005; Shah and Shaheen, 2008). Third PC showed higher loadings for Sb, and Co with significant contributions from Zn and Cr, originating from industrial emissions, as pointed out earlier (Harrison et al., 1997; Arditsoglou and Samara, 2005; Zereini et al., 2005; Shah and Shaheen, 2008). During the present study, wind direction was observed to be predominantly north–east as shown in Figure 3. Consequently, most of the industrial emissions from sectors I–9 & I–10 (industrial area) were carried to the adjoining residential areas of the city and thus exposing the urban population of Islamabad to elevated atmospheric pollution released from the industries. Another interesting finding of the present study is that Cr and Zn have several sources in the urban atmosphere of Islamabad, as these elements revealed strong/significant loadings to almost all the PCs. The cluster of Cr and Zn is also fairly weak, supporting the above statement. The PCA findings are in agreement with the CA results (Figure 2).

The EFs of individual elements are shown in Figure 4. According to the degree of enrichment, the elements were grouped as follows:

- Highly enriched (EF > 100) included Cd, Pb, Sb, and Zn.
- Moderately enriched (EF between 10 and 100) included Co and Cu.
- Less enriched (EF less than 10) included Cr and Mn.

On comparative basis, most of the trace elements were highly enriched in the urban particulate matter. As reported, the highly enriched elements were relatively volatile elements which can be readily transported from industrial to residential and urban areas. The wind direction during the study period also supported this assumption. In the present study, large variations of EF values were found for different elements in the particulates. Amongst these, EFs of Sb and Zn are the highest, followed by those of Cd and Pb. The higher EF values of these elements showed that anthropogenic sources (industrial and automobile emissions) contributed a substantial amount of the elements in atmospheric particulates, which otherwise were difficult to justify on the basis of normal crustal weathering processes. Automobile emissions

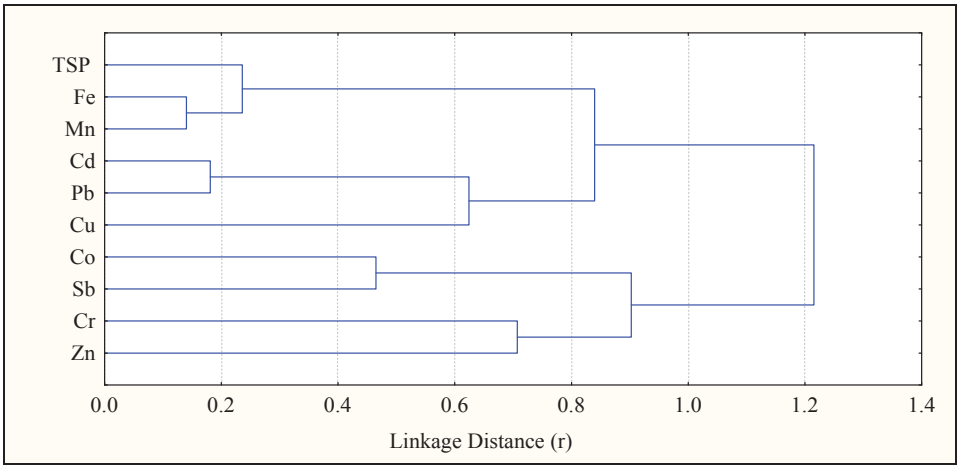

***Figure 2**. Cluster analysis of TSP and selected elements in the airborne particulate matter.*

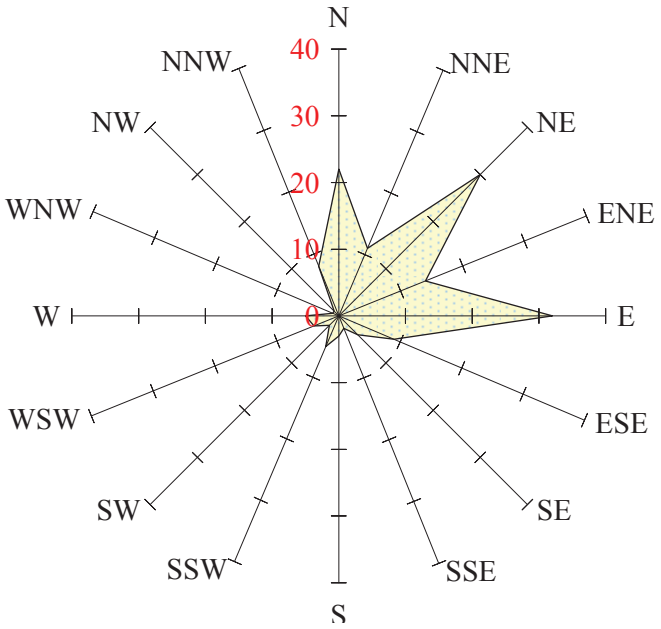

***Figure 3**. Mean wind directions during the study period.*

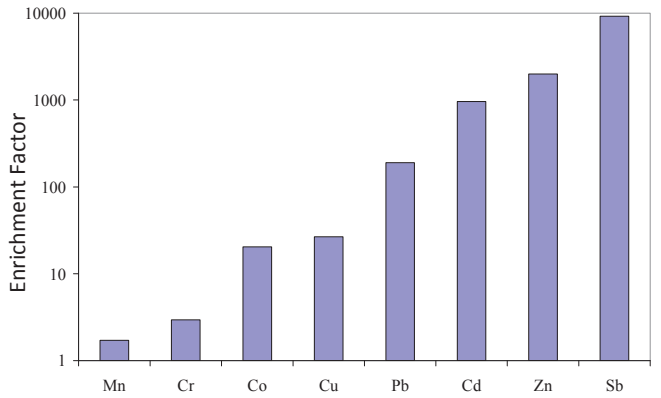

***Figure 4**. Enrichment factors (EFs) of the trace elements in the airborne particulate matter.*

were major contributors of Pb, Cd, and Zn which were consistent with their dominant presence in the particulate matter. However, Sb was reported to be derived from the industrial emissions. Similarly, Co, Cr and Cu with comparable magnitude of EF, indicated their emissions from metal industries. In contrast, the less enriched elements were dominantly derived from earth crust, and re–suspension of soil dust. On the whole, all elements revealed EF greater than unity, thus predominantly contributed by the anthropogenic sources.

4. Conclusions

In conclusion, present study revealed elevated 24–h TSP concentrations which were significantly higher than the regulatory agencies levels. Among the selected trace metals, highest concentration was noted for Zn and Fe, followed by Pb in the urban atmospheric particulates. The estimated airborne metal concentrations in the present study were higher than in the most of the European studies; however, these metal contents were lower than large metropolitan cities of the world. Correlation study along with multivariate PCA and CA evidenced significant anthropogenic contribution of the measured pollutants in the urban atmosphere of Islamabad. Major atmospheric pollution sources were industrial emissions, automobile emissions and wind blown soil dust. Some of the metals (Cd, Pb, Sb and Zn) were found to be highly enriched by anthropogenic activities in the local atmosphere, which may be associated with adverse health effects to the inhabitants of the city. Thus it is high time to control the atmospheric pollution in order to protect the urban population from hazardous health effects of these potentially toxic pollutants.

Acknowledgements

The research fellowship awarded by Quaid–i–Azam University, Islamabad to carry out this project is thankfully acknowledged.

References

Andersen, Z.J., Wahlin, P., Raaschou-Nielsen, O., Scheike, T., Sloft, 2006. Ambient particle source apportionment and daily hospital admissions among children and elderly in Copenhagen. *Epidemiology* 17, S200-S201.

ATSDR, 2002. Regulations and Guidelines Applicable. Agency for Toxic Substances and Disease Registry. Retrieved from http://www.atsdr.cdc.gov/toxprofiles/tp11-c8.pdf

Aranguiz, I., Barona, A., Gurtubai, L., 2002. Chemical analyses after consecutive extraction of inorganic components in suspended particulate matter in Bilbao (Spain). *Water Air and Soil Pollution* 134, 41-55.

Arditsoglou, A., Samara, C., 2005. Levels of total suspended particulate matter and major trace elements in Kosovo: A source identification and apportionment study. *Chemosphere* 59, 669-678.

Ayrault, S., Senhou, A., Moskura, M., Gaudry, A., 2010. Atmospheric trace element concentrations in total suspended particles near Paris, France. *Atmospheric Environment* 44, 3700-3707.

Bilos, C., Colombo, J.C., Skorupka, C.N., Presa, M.J.R., 2001. Sources, distribution and variability of airborne trace metals in La Plata city area, Argentina. *Environmental Pollution* 111, 149-158.

Borbely-Kiss, I., Koltay, E., Szabo, G.Y., Bozo, L., Tar, K., 1999. Composition and sources of urban and rural atmospheric aerosol in eastern Hungary. *Journal of Aerosol Science* 30, 369-391.

Freitas, M.C., Pacheco, A.M.G., Verburg, T.G., Wolterbeek, H.T., 2010. Effect of particulate matter, atmospheric gases, temperature, and humidity on respiratory and circulatory diseases' trends in Lisbon, Portugal. *Environmental Monitoring and Assessment* 162, 113-121.

Garcia, V.C., Gego, E., Lin, S., Pantea, C., Rappazzo, K., Wootten, A., Rao, S.T., 2011. An evaluation of transported pollution and respiratory–related hospital admissions in the state of New York. *Atmospheric Pollution Research* 2, 9-15.

Gupta, A.K., Karar, K., Srivastava, A., 2007. Chemical mass balance source apportionment of PM_{10} and TSP in residential and industrial sites of an urban region of Kolkata, India. *Journal of Hazardous Materials* 142, 279-287.

Hadad, K., Mehdizadeh, S., Sohrabpour, M., 2003. Impact of different pollutant sources on Shiraz air pollution using SPM elemental analysis. *Environment International* 29, 39-43.

Hao, Y.C., Guo, Z.G., Yang, Z.S., Fang, M., Feng, J.L., 2007. Seasonal variations and sources of various elements in the atmospheric aerosols in Qingdao, China. *Atmospheric Research* 85, 27-37.

Harrison, R.M., Smith, D.J.T., Pio, C.A., Castro, L.M., 1997. Comparative receptor modelling study of airborne particulate pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan). *Atmospheric Environment* 31, 3309-3321.

Hien, P.D., Binh, N.T., Truong, Y., Ngo, N.T., Sieu, L.N., 2001. Comparative receptor modelling study of TSP, PM_2 and $PM_{2\text{-}10}$ in Ho Chi Minh City. *Atmospheric Environment* 35, 2669-2678.

Khan, M.F., Hirano, K., Masunaga, S., 2010. Quantifying the sources of hazardous elements of suspended particulate matter aerosol collected in Yokohama, Japan. *Atmospheric Environment* 44, 2646-2657.

Kim, K.H., 2004. Relationships between spatial and temporal variabilities in airborne metal distributions in Won Ju City, Korea. *Environment International* 29, 901-906.

Lide, D.R., 2005. *CRC Handbook of Chemistry and Physics. Section 14: Geophysics, Astronomy and Acoustics; Abundance of elements in the earth's crust and in the sea*. 85th edition, CRC Press, Boca Raton, Florida.

Liu, L., Ruddy, T., Dalipaj, M., Poon, R., Szyszkowicz, M., You, H.Y., Dales, R.E., Wheeler, A.J., 2009. Effects of indoor, outdoor, and personal exposure to particulate air pollution on cardiovascular physiology and systemic mediators in seniors. *Journal of Occupational and Environmental Medicine* 51, 1088-1098.

Mavroidis, I., Chaloulakou, A., 2010. Characteristics and expected health implications of annual PM_{10} concentrations in Athens, Greece. *International Journal for Environment and Pollution* 41, 124-139.

Method IO-2.1, 1999. Sampling of ambient air for total suspended particulate matter and PM_{10} using high volume sampler. In: Compendium of methods for the determination of inorganic compounds in ambient air. US-EPA, Cincinnati, OH.

Method IO-3.1, 1999. Selection, preparation and extraction of filter material. In: Compendium of methods for the determination of inorganic compounds in ambient air. US-EPA, Cincinnati, OH.

Method IO-3.2, 1999. Determination of metals in ambient particulate matter using Atomic Absorption (AA) spectroscopy. In: Compendium of methods for the determination of inorganic compounds in ambient air. US-EPA, Cincinnati, OH.

Moreno-Grau, S., Perez-Tornell, A., Bayo, J., Moreno, J., Angosto, J.M., Moreno-Clavel, J., 2000. Particulate matter and heavy metals in the atmospheric aerosol from Cartagena, Spain. *Atmospheric Environment* 34, 5161-5167.

Pakistan Bureau of Statistics, 2004. Statistical Year Book. Government of Pakistan, Islamabad.

Pakkanen, T.A., Loukkola, K., Korhonen, C.H., Aurela, M., Makela, T., Hillamo, R.E., Aarnio, P., Koskentalo, T., Kousa, A., Maenhaut, W., 2001. Sources and chemical composition of atmospheric fine and coarse particles in the Helsinki area. *Atmospheric Environment* 35, 5381-5391.

Parekh, P.P., Ghauri, B., Siddiqi, Z.R., Husain, L., 1987. The use of chemical and statistical methods to identify sources of selected elements in ambient air aerosols in Karachi, Pakistan. *Atmospheric Environment* 21, 1267-1274.

Qadir, M.A., Zaidi, J.H., 2006. Characteristics of the aerosol particulates in the atmosphere in an urban environment at Faisalabad, Pakistan. *Journal of Radioanalytical and Nuclear Chemistry* 267, 545-550.

Quiterio, S.L., da Silva, C.R.S., Arbilla, G., Escaleira, V., 2004a. Metals in airborne particulate matter in the industrial district of Santa Cruz, Rio de Janeiro, in an annual period. *Atmospheric Environment* 38, 321-331.

Quiterio, S.L., Escaleira, V., Sousa, C.R.S., Maia, L.F.P.G., Arbilla, G., 2004b. Metals in airborne particulate matter in downtown Rio de Janeiro, Brazil. *Bulletin of Environmental Contamination and Toxicology* 72, 916-922.

Ragosta, M., Caggiano, R., D'Emilio, M., Macchiato, M., 2002. Source origin and parameters influencing levels of heavy metals in TSP, in an industrial background area of southern Italy. *Atmospheric Environment* 36, 3071-3087.

Rizzio, E., Bergamaschi, G., Profumo, A., Gallorini, M., 2001a. The use of neutron activation analysis for particle size fractionation and chemical characterization of trace elements in urban air particulate matter. *Journal of Radioanalytical and Nuclear Chemistry* 248, 21-28.

Rizzio, E., Bergamaschi, L., Valcuvia, M.G., Profumo, A., Gallorini, M., 2001b. Trace elements determination in lichens and in the airborne particulate matter for the evaluation of the atmospheric pollution in a region of northern Italy. *Environment International* 26, 543-549.

Rizzio, E., Giaveri, G., Arginelli, D., Gini, L., Profumo, A., Gallorini, M., 1999. Trace elements total content and particle sizes distribution in the air particulate matter of a rural-residential area in north Italy investigated by instrumental neutron activation analysis. *Science of the Total Environment* 226, 47-56.

Salam, A., Bauer, H., Kassin, K., Ullah, S.M., Puxbaum, H., 2003. Aerosol chemical characteristics of a mega-city in Southeast Asia (Dhaka-Bangladesh). *Atmospheric Environment* 37, 2517-2528.

Samura, A., Al-Agha, O., Tuncel, S.G., 2003. Study of trace and heavy metals in rural and urban aerosols of Uludağ and Bursa (Turkey). *Water, Air and Soil Pollution: Focus* 3, 111-129.

Sarnat, J.A., Marmur, A., Klein, M., Kim, E., Russell, A.G., Mulholland, J.A., Hopke, P.K., Sarnat, S.E., Peel, J.L., Tolbert, P.E., 2006. Associations between source-resolved particulate matter and cardiorespiratory emergency department visits. *Epidemiology* 17, S267-S268.

Shah, M.H., Shaheen, N., 2008. Annual and seasonal variations of trace metals in atmospheric suspended particulate matter in Islamabad, Pakistan. *Water Air and Soil Pollution* 190, 13-25.

Shridhar, V., Khillare, P.S., Agarwal, T., Ray, S., 2010. Metallic species in ambient particulate matter at rural and urban location of Delhi. *Journal of Hazardous Materials* 175, 600-607.

Sohrabpour, M., Mirzaee, H., Rostami, S., Athari, M., 1999. Elemental concentration of the suspended particulate matter in the air of Tehran. *Environment International* 25, 75-81.

StatSoft, 1999. STATISTICA for Windows. Computer program manual. StatSoft, Tulsa, OK.

Tripathi, R.M., Kumar, A.V., Manikandan, S.T., Bhalke, S., Mahadevan, T.N., Puranik, V.D., 2004. Vertical distribution of atmospheric trace metals and their sources at Mumbai, India. *Atmospheric Environment* 38, 135-146.

Valavanidis, A., Fiotakis, K., Vlahogianni, T., Bakeas, E.B., Triantafillaki, S., Paraskevopoulou, V., Dassenakis, M., 2006. Characterization of atmospheric particulates, particle-bound transition metals and polycyclic aromatic hydrocarbons of urban air in the centre of Athens (Greece). *Chemosphere* 65, 760-768.

Wang, C.X., Zhu, W., Peng, A., Guichreit, R., 2001. Comparative studies on the concentration of rare earth elements and heavy metals in the atmospheric particulate matter in Beijing, China, and in Delft, the Netherlands. *Environment International* 26, 309-313.

WHO, 2000. Guidelines for Air Quality. World Health Organization, Geneva. Retrieved from http://www.who.int/environmentalinformation/Air/Guidelines/aqguide7.pdf

Zereini, F., Alt, F., Messerschmidt, J., Wiseman, C., Feldmann, I., Von Bohlen, A., Muller, J., Liebl, K., Puttmann, W., 2005. Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am Main, Germany. *Environmental Science and Technology* 39, 2983-2989.