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Metallic species in ambient particulate matter at rural and urban location of Delhi

Vijay Shridhar*, P.S. Khillare, Tripti Agarwal, Sharmila Ray

School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, 110 067, India

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ABSTRACT

In the present study 14 metallic species (six crustal and eight trace metals) were quantified in the suspended particulate matter (SPM) at a rural and urban location of Delhi, India. Particulate matter was collected on glass fiber filters for a period of one year (from September 2003 to August 2004). Rank sum test revealed that the TSP concentration at the urban site was significantly ($P = 0.47$) higher as compared to the rural site. Urban site showed highest SPM concentration during winter while rural site during summer. Enrichment factor (EF) and coefficient of variation (CV) were calculated to assess the variability of elemental concentration data. Trace metals viz. Pb, Cd, Cu and Zn were observed to be highly enriched at both the sites, but EF for Zn and Cu was 2–3 times higher at the urban site as compared to the rural site. Trace and crustal metal concentration displayed less variability at the urban site. In the urban area, metals were mainly found to come from construction and industrial activities in surrounding. At the rural site, re-suspended and wind-blown dust appeared to be the source of observed elemental concentration.

1. Introduction

Impacts of atmospheric particulate matter on human health and environment have been recognized world wide. High air pollution condition is a cause of multiple ailments to human health, climate change, ecological imbalance, visibility impairment, and low agricultural productivity. Various health problems include aggravating asthma, heart attack, irritation, cancer, coughing and sneezing etc which may be acute or chronic in nature. Overall high air pollution enhances the burden on society and public exchequer in terms of monetary expenditure on development of health care infrastructure.

There is substantial evidence from developed countries showing strong correlation between exposure to ambient air pollution and human health [1–8]. Exposure to pollutants such as airborne particulate matter has been associated with increase in hospital admissions due to respiratory and cardiovascular disease and mortality [9]. Many authors from India showed concern for higher SPM and RSPM concentration in Indian cities [10,11]. Health risks (HR) study conducted by Pandey et al. [12] in Delhi showed that Health Risk (HR) due to SPM is 16.13 times more than of SO_2.

Air pollution is one of the major causes of concern for deterioration of environmental conditions, particularly in developing countries such as India. Scenario in other parts of Asia is not far better and various studies caution the increasing anthropogenic emission in North-eastern Asia [13,14]. Prevalence of high atmospheric particulate matter load in most of the metropolitan areas of India indicates grim situation in terms of security of public health. Various researchers observed disparity between developed and developing countries with respect to air quality criteria and mass concentration, especially SPM and PM_{10} [15,16]. Concentration of SPM, arising from human activities as well as from natural sources is a valuable index of air pollution. Aerosols found in urban areas represent a mixture of primary particles emitted from several sources such as vehicle, coal fired power plant, domestic/biomass burning, industrial combustion, municipal services, re-suspended dust and secondary particles formed from aerosols.

Airborne particles are important carriers of metals, some of which possess toxic properties. Consequently, it has been proposed that the toxic properties of particles in part may be due to the biochemical activity of metals [17,18]. The focus has often been on transition metals such as iron (Fe), vanadium (V), nickel (Ni), chromium (Cr), copper (Cu), and zinc (Zn) due to their ability to generate reactive oxygen species (ROS) in biological tissues. Most of the evidences pointing to the biological effects of metals have come from studies involving exposures to laboratory animals *in vivo*, or to cells *in vitro* [19,20]. Urban populations are exposed to metals in suspended particles and these are often well above nat-

* Corresponding author. Present address: School of Environment and Natural Resources Doon University, Kedarpur, Dehradun 248001 Uttarakhand India. Tel.: +91 135 2533108.
E-mail address: vijayshridhar@gmail.com (V. Shridhar).

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ural background levels owing to mainly anthropogenic processes [21]. Elevated metal concentrations can pose an important risk to human health. Understanding emissions from various urban activities includes identification of the sources, which is also crucial for designing control measures. A detailed perceptive of the concentration distribution of toxic trace metals is considered to be one of the essential elements in investigations of particle geochemistry and related air quality change [22,23].

Delhi, the capital of India was once rated by W.H.O. [24] as the fourth most polluted city in the world. Various national and international agencies [24,25] have established a link between higher rate of respiratory illnesses and the higher values of particulate matter in Delhi. Delhi has been declared as the most cancer prone area by the National cancer registry programme. A detailed characterization of suspended particulate matter is most urgently required step in the direction of particulate pollution control in Delhi. The present study was mainly aimed at establishing a link between metal concentration in SPM and their possible sources. A comparison was done between a rural and urban site in terms of following criteria: (1) particulate mass concentrations; (2) concentration of crustal and trace metals; (3) relative patterns of temporal variations; (4) coefficient of variation (CV) of metal concentrations; (5) relative abundance of strong correlations; and (6) enrichment factor (EF) values and the sources of the analyzed metals.

2. Study area

2.1. Delhi and its environment

Delhi, the capital city of India, is situated in North India, 160 km of south of Himalayas (28′25″ latitude and 76′50″ longitude) at an altitude of between 213.3 and 305.4 m above mean sea level. It is surrounded by the Thar Desert of Rajasthan in the west and hot plains of central India to the south. Delhi is a rapidly growing city extending over 1483 km^2. The climate of Delhi is subtropical with hot summers and moderately cold winters. The monthly mean temperature varies between 14.3 °C (min. 2 °C) in January and about 34.5 °C (max. 48 °C) in June.

Delhi is often categorized as a service town with governmental office complexes and medical, agriculture and educational institutions. However, Delhi has experienced a phenomenal growth in industries and vehicular numbers. There have been a many fold increase in industrial units from 18,500 in 1961 to 126,218 in 1996 [26] while motor vehicle registration increased to 5.13 million in March 2007 from 1.81 million in 1991 [27]. Emissions from these large number of industries and motor vehicles, as well as four power stations located in the eastern site of city, are the main sources of pollution in the atmosphere of Delhi. These power plants are based on coal and gas fuel and combined capacity remains around 1300 MW. Generally low wind speed (average 3 m/s) and frequent temperature inversion conditions (mixing height as low as 100 m) lead to an accumulation of airborne pollutants over the city particularly in winter months, while in summer the situation is exacerbated by the dust storms [28,29]. In recent years, vertical temperature inversions in winter months have been reported [30].

2.2. Sampling sites

Two sampling sites, one near the city centre and another one in rural area were selected to study the air quality. These two sampling sites were with varying traffic densities, surrounding industrial setups, and land use pattern shown in Fig. 1. Distance between the two sampling sites was more than 12 km. Urban site was located in PadamNagar (PN), a typical urban residential site located close to the city centre. It is a congested area with high traffic density. There are several small scale industries e.g. hosiery, plastic product manufacturing units, electrical and metal product manufacturing units in the surrounding area of the site. Small dairy units are also located within residential colony. Many industrial areas are also located in a periphery of 3–4 km (Anand Parvat, Shahjada Bagh, Bharat Nagar). Kanhaiya Nagar is a railway station and commodity storage centre. Sarai Rohilla another railway centre is not far away. Rural site was taken in Natthhupura (NP), a site with open agricultural fields in vicinity. Horticulture, floriculture and animal husbandry are other prevalent activities in the area. Samaipur Badli industrial area, Bhalswa waste dumpsite and NH-1 highway are located at a distance of 3–4 km from the site. Small shops for motor repairing can be seen along the road in Natthhupura. This site was under indirect influence of various activities in the neighborhood.

3. Methodology

3.1. Sample collection

The sampling was carried out from September 2003 to August 2004 by High volume samplers for SPM (Envirotech APM 415). The average flow rate of suction pump was maintained at 1.2 m^3 min^{-1}. The sampling was carried out for 24 h. Power failure during sampling hours was added for additional sampling time period. Total 30 samples were collected simultaneously at two sites. The sampling substrate used was 10×8 glass fiber filters. The 24 h desiccated filter papers were weighed twice on the balance (AE163, Metler; sensitivity 0.0001 g). The conditioned and weighed filter papers were taken to the field for sampling in closed envelops to avoid contamination of the filter papers on the way. Before starting the sampling, initial volume, timer and the manometer readings for high volume sampler were recorded in field monitoring sheet. After sampling, the filter paper was again desiccated for 24 h and weighed. Before and after each set of sampling, data was entered in the field data sheet in the predefined format and concentrations of SPM were calculated gravimetrically. The sampled filter papers were stored in desiccators until further chemical analysis was undertaken.

3.2. Chemical analysis

All the reagents used were of analytical grade procured from Merck. Standard metal stock solutions (1000 ppm) were used to prepare working standards. MilliQ water was used for dilution and other preparatory work throughout the study. Metals were analyzed using Atomic Absorption Spectrophotometer (AAS) model SHIMADZU AA6800 with Carrier gas (acetylene and Nitrous oxide) of 95% purity.

For the metal analysis of particulate matter one punch of 2′ diameter taken out from each filter paper. These samples were digested separately on the hot plate in acidic condition. The sampled glass fiber filter paper was first treated with 7.5 ml of boiling concentrated HNO_3. Then, 5 ml of $HClO_4$ were added and heating was continued until the solution was clear and colorless. The excess acid was boiled off and the dry material was redissolved in 2.5 ml of HNO_3 and 10 ml of double distilled water by gentle heating. The solution obtained was cooled and diluted to 25 ml in a graduated flask [31]. A blank filter paper was similarly digested and the same procedure was carried out. Standard solutions of metals were prepared as described in APHA [32]. All the reagents used were of analytical grade. Metals were analyzed using Atomic Absorption Spectrophotometer (AAS) model SHIMADZU AA6800. Concentration was calculated by comparing the absorbance of the sample solution with that of the standard metal solution.

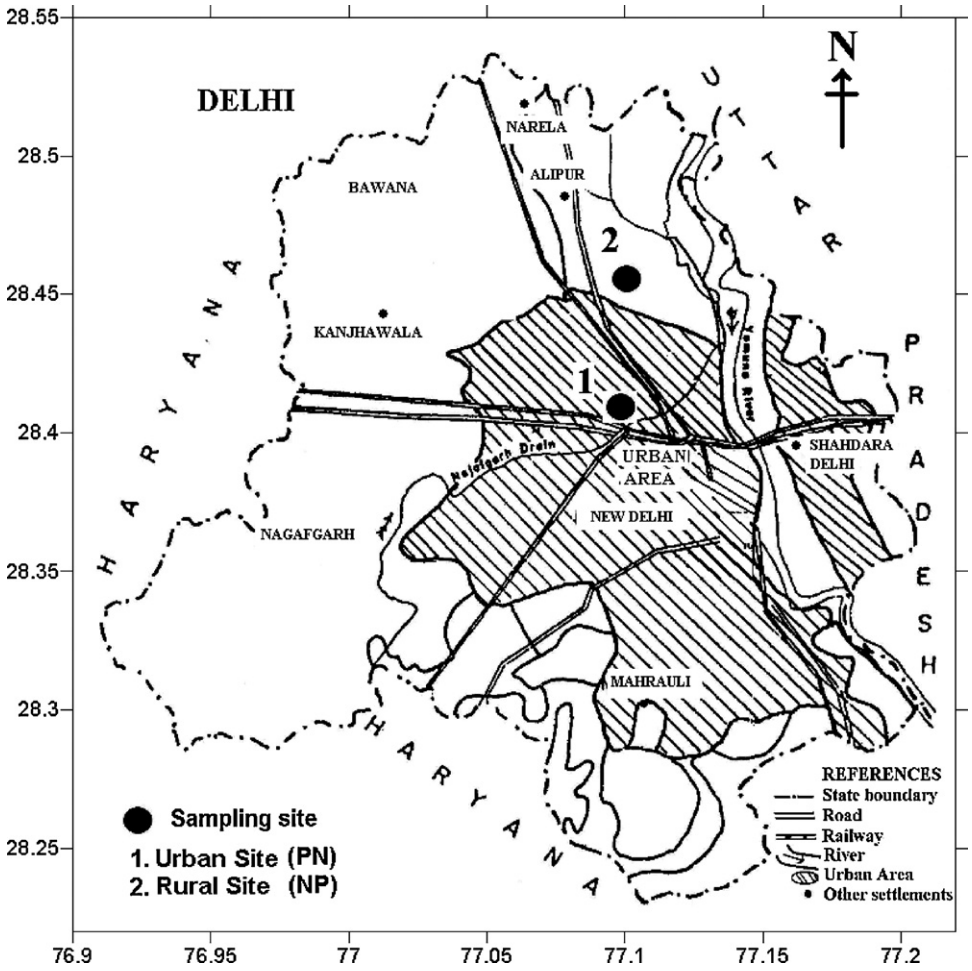

Fig. 1. Map of Delhi showing the location of sampling sites.

3.3. QA/QC

One tenth of the samples were analyzed in duplicates. Reproducibility tests demonstrated the stability/precision of instruments. The deviation was within the range of 5% of observed value. Otherwise standard calibration process was performed. Routinely blank sample was run after 10 samples of analyses.

3.4. Statistical analysis

General statistical tools were applied on particulate mass concentration data and elemental mass concentration data at rural and urban site of Delhi. Rank sum test, correlation coefficient, coefficient of variation were used to compare the data at two sites. Principal component analysis was used for the data reduction and factor identification of these elements at both the sites.

4. Results and discussion

4.1. Particulate mass concentration

Annual average concentration of total suspended particulate matter (SPM) at the urban (PN) and rural (NP) site was $545.84 \pm 174.52\ \mu g\,m^{-3}$ and $479.08 \pm 276.90\ \mu g\,m^{-3}$ respectively (Table 1). Rank sum test was used to compare SPM concentration at the two sites because data was not following the normal distribution. Result of the test revealed that the SPM concentrations at the urban site was significantly ($P = 0.47$) higher as compared to the rural site.

Observed concentrations were three to four times higher as compared to the air quality standard for SPM ($140\ \mu g\,m^{-3}$) prescribed by Central Pollution Control Board for residential areas [33] in India. On the basis of this standard, SPM concentration at the urban site revealed the pollution level in critical condition ($>540\ \mu g\,m^{-3}$) and the rural site in high pollution level ($360–540\ \mu g\,m^{-3}$). High SPM concentrations in the range of $200–400\ \mu g\,m^{-3}$ have also been reported from other Asian cities particularly big cities of China, but even higher concentration ($>500\ \mu g\,m^{-3}$) in Delhi is an indication of prevailing alarming condition [34–36]. Though, government has taken various measures for pollution control in Delhi, the SPM levels found in the present study are at the higher side as compared to the levels reported in earlier studies from Delhi [33,37,38]. High SPM concentrations in Delhi could be attributed to the uncontrolled anthropogenic activities which may includes high rate of construction activities without any preventive measures, refuse dust, biomass combustion, mechanical erosion from paved and unpaved roads and soil dust.

4.2. Temporal variation of particulate matter

SPM concentration displayed different seasonal trend at the urban and rural site as displayed in Fig. 2. Urban site showed highest SPM concentration during winter while rural site during summer. At both the sites lowest SPM concentrations were observed during monsoon. The urban site (PN) was located close to the city center in a closed and congested area with multistory buildings.

Table 1
Mass concentration ($\mu g\,m^{-3}$), coefficient of variation (CV) and enrichment factor (EF) of analyzed species in SPM at the urban and rural site.

	Urban site					Rural site				
	Mass concentration		CV	EF		Mass concentration		CV	EF	
	Average	SD		Average	SD	Average	SD		Average	SD
SPM	545.84	174.52				479.08	276.90			
Ni	0.15	0.07	0.48	13.02	7.67	0.07	0.15	2.20	5.71	12.14
Cr	0.35	0.20	0.56	22.78	11.78	0.10	0.05	0.49	6.63	3.49
Pb	0.44	0.21	0.48	220.58	98.81	0.25	0.25	0.98	136.50	129.00
Mn	0.74	0.37	0.50	4.93	2.46	0.36	0.52	1.43	2.25	3.25
Cd	0.01	0.01	0.70	379.26	290.20	0.00	0.01	1.86	148.95	264.62
V	0.53	0.36	0.69	24.63	17.72	0.31	0.17	0.56	15.57	8.17
Cu	3.69	1.90	0.52	462.69	346.51	1.01	1.30	1.30	110.13	132.73
Zn	4.67	3.30	0.70	480.85	431.28	1.85	2.30	1.25	171.52	228.14
Na	3.81	2.59	0.68	0.90	0.73	3.21	1.34	0.42	0.86	0.46
K	4.73	1.13	0.24	1.21	0.48	4.43	1.53	0.34	1.22	0.56
Ca	18.32	4.68	0.26	3.41	0.85	14.74	8.40	0.57	2.58	0.77
Mg	6.34	1.50	0.24	1.94	0.52	4.92	2.22	0.45	1.63	0.82
Fe	16.43	4.65	0.28	2.11	0.65	10.49	4.46	0.43	1.42	0.56
Al	13.34	4.15	0.31			12.83	6.52	0.51		

These site characteristics in addition to the low wind speed in winter might have helped in the accumulation of particles from local sources. So, at the urban site, highest concentration of SPM in winter months may be due to lower dispersion rate of pollutants and low level ground based inversions during winter [39]. On the other hand, the rural site (NP) was located in an open and sparse area which was surrounded by agricultural land and more prone to be knocked by dust laden wind. This is being reflected in the highest SPM concentration in summer months at this site. Moreover, during post harvest season in summer months, open fields get exposed to strong winds and low soil moisture make particles more prone to wind dislodgement which contribute additional quantities of air borne dust. This could be another reason of very high particulate load during summer months at the rural site. Urban and rural particulate load indicates boundary layer effects around the National capital region.

Average lowest particulate concentrations were observed during the month of July, August and February. Low concentrations during the month of July and August could be due to wash out effect during monsoon rainy season while for the month of February ventilation effect of high wind movements could be the possible reason. Many other studies also indicate similar trend in these months [40,41]

4.3. Elemental concentration

Average mass of analyzed metals constitute 13.5% at urban site and 11.4% at rural site of total suspended particulate matter. Total mass concentration of trace metals contributed ~2% at urban site but its contribution was less than 1% at rural site.

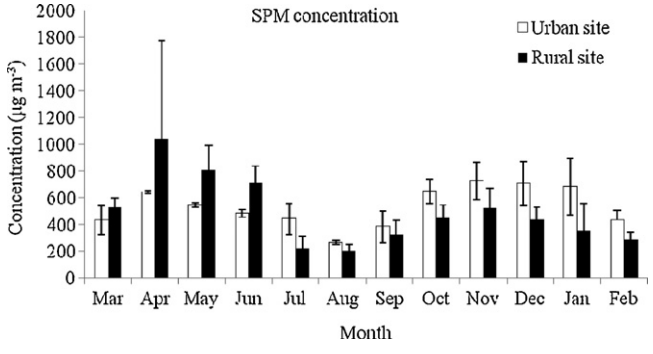

Fig. 2. Monthly average concentrations ($\mu g\,m^{-3}$) of SPM at the urban and rural site.

Average mass concentrations of all analyzed metals at urban and rural sites are given in Table 1. Higher mean concentration values were observed at the urban site for all the analyzed metal species. The mean values of the metals analyzed followed the order: Ca > Fe > Al > Mg > K > Na > Zn > Cu > Mn > V > Pb > Cr > Ni > Cd at both sites. However, at the rural site, Al concentration was higher than Fe concentration. Mass concentration of most of the trace metals at urban site was found to be two times or more high than rural site. Relatively higher trace metals concentrations at the urban site could be due to higher traffic density, small scale industries and commodity railway station in adjacent areas. Observed difference in mass concentration of crustal metal at two sites was very low. A Study of SPM bound metals from Korea also reported similar trend of mass concentration (Fe ≫ Cu > Mn ~ Pb > Ni ~ Cr > Cd) for limited analyzed metals, but concentration of metals was ~5times lower than present study [42]. Central pollution control board (CPCB) has prescribed national ambient air quality standard only for Pb. The annual average concentration of Pb in present study did not exceed the national standard of 0.75 $\mu g\,m^{-3}$. In comparison to earlier study, trace metal concentrations in the present study were 1.5–3 times higher for Cr, Cd, Ni and Fe (Table 2). Lead concentration was observed to be comparable with earlier study [37]. Metal concentration in present study was found very high in comparison to other studies reported from Asian cities. These concentrations were found comparable for some metals with study reported metal concentration in traffic junction of Mumbai and Gandhinagar [43].

4.4. Correlation between particulate matter and individual analyzed species

Correlation exercise was done to establish the relationship between suspended particulate matter and analyzed species at both the sampling sites. Correlation coefficients are given in Table 3. Significant value of correlation coefficient ($r > 0.5$) between SPM and analyzed species indicates towards common source of correlated species. At the urban site (PN) SPM fraction was found significantly correlated with Ca, Mg and Al. These three metals are considered of crustal origin and crustal metals have high input to decide SPM concentration. This is also shown from inter elemental correlation between these three metals apart from SPM. Correlation between two variables is understandable on the basis of same (crustal) origin. Other crustal metals at this site seem to have some local contributing processes other than the natural but the contribution to SPM might not be proportionate from these activities. This may be due to different mechanical processes, high rise build-

Table 2
Metal concentration levels (ng m^{-3}) in SPM around the world (numbers in the parentheses are the reference list numbers).

Site/type	Ni	Cr	Pb	Mn	Cd	V	Cu	Zn	Na	K	Ca	Mg	Fe	Al
Present study/urban	148	351	441	745	11	526	3691	4675	3812	4726	18325	6337	16435	13340
Present study/rural	70	96	254	362	4	308	1005	1845	3210	4434	14735	4919	10490	12834
Northern France/urban [51]	–	–	26–56	56–64	–	–	6–16.5	41–164	981–1561	219–389	839–1121	191–253	729–963	234–275
Islamabad, Pakistan/urban [52]	1–64.0	1–398	3.0–4000	11–314	2.0–7	–	–	3.0–2350	3–11650	8.1–2600	–	–	37–2950	–
Thailand/urban [53]	–	34	40	34	–	–	78	90	–	–	–	119	386	–
Kanazawa, Japan/urban [54]	–	–	6	35	0.45	37	18	1386	–	–	1073	380	869	–
New York, USA/urban [55]	0.9	–	3	8	–	–	–	15	–	–	–	–	177	–
Coimbatore, India/urban [56]	160–220	5–880	210–620	–	–	–	700–770	11330–20700	–	–	–	–	2200–6000	–
La Plata, Argentina/urban [57]	3	4	65	26	0	–	30	273	–	–	5343	1472	1183	–
Northern France/rural [51]	–	–	18–31	24–38	–	–	4–6.0	49–90	845–1053	216–237	370–542	164–176	297–435	134–187
Islamabad, Pakistan/rural [52]	1.0–65	1.0–42	2.0–4075	2–400	1.0–17	–	–	11–1790	36–5045	23–2348	–	–	2.0–1990	–
Brownfield, UK/rural [58]	2	–	30	6	0.6	–	–	63	–	–	–	–	260	–
Frankfurt, Germany/rural [59]	3	4	12	10	0	–	–	29	–	–	–	–	–	–
Beijing, China/rural [60]	7	6	42	290	0.44	–	–	154	5550	–	–	–	6420	–
Dhaka, Bangladesh/urban [61]	–	–	279	–	3	–	–	801	1270	1550	–	–	24800	–
Beijing, China/urban [62]	51	–	46	1210	–	–	–	274	14700	28000	–	–	51000	–
Won Ju City, Korea/urban [23]	15	15	84	33	2	–	–	–	–	–	–	–	1486	–
Tehran, Iran/urban [63]	37	48	1020	78	–	–	–	327	1680	2150	–	–	2230	–
Uludag, Turkey/rural [64]	4	3	7	14	2	–	–	33	293	205	–	–	486	–
Cadrezzate, Italy/rural [65]	10	7	98	14	0.51	4	11	149	–	413	–	275	511	–
Seoul, Korea/urban [42]	19	15	77	80	3	–	208	–	–	–	–	–	2397	–
Mexico/urban [67]	6–220	5–900	170	20–700	20	0–240	1000	–	–	–	–	–	–	–

ing in surrounding areas and congestion within locality. At the rural Site (NP) analyzed species viz, Ni, Cr, Mn, K, Ca, Fe, Al displayed significant correlation with SPM. These elements include three trace metals which indicate their source common to other crustal metals. This source can be inferred as soil. Enrichment of these trace metals also found near unity at rural site, which support their crustal origin. Rural site was with adjoining open, agricultural land where from soil as source of these compounds can dislodge with the wind movements.

4.5. Coefficient of variation (CV)

To learn more about the factors affecting the spatial variability of airborne metals, we compared the "Standard deviation (SD)/mean" ratio (coefficient of variation: CV) of a given metal for each study site (Table 1). It may be reasonable to assume that the ratio of above unity is indicative of more variability than that of below unity. When these ratios were examined from all 28 matching pairs (14 metals by two sites), 23 of these exhibited values below unity. The results of this simple comparison thus suggest that the cases with less variability are more dominant than their counterparts.

The CV values of all analyzed metals at the urban site (PN) were found below the unity. Five trace metals at the rural site (NP) were found to be highly variable in comparison of other metals. It is computed that the CV values of the crustal metals at both sites are more homogenous than trace metals. This indicates the presence of same activity responsible for generation of crustal metals at both sites. Consequently, this comparative analysis indicates that the strong homogeneity exists in spatial distribution of K, Na, Fe, Mg, Cr, Al, V, Ca, Pb. Kim et al [42] also reported strong homogeneity of Pb and Fe in spatial distribution in Korean aerosols.

5. Source identification

5.1. Enrichment factor

Enrichment factor (EF) is used to calculate the contribution of anthropogenic emission to the atmospheric elemental levels. This relation is standardized with the use of information on concentration of certain reference metals, such on Al, Si, Ti or Sc. Thus, the enrichment factor of the element X can be estimated through the formula. EF(X) = (X/Ref) aerosol/(X/Ref) reference material, where (X/Ref) is the concentration ratio of element X to a reference metal. For this study, aluminum metal was taken as reference metal and average metal concentration in continental soil as reference material [44]. As a reference metal for calculating enrichment factor, aluminum was the best choice assuming its low anthropogenic emissions. Values of EF near unity suggest that crustal erosion is the primary source of element X and that its geochemical cycle has not been altered by emissions from anthropogenic sources. Metals showing enrichment factor in the range of 10–100 are considered as moderately enriched. Metals/trace metals having enrichment factor more than 100 are considered as highly enriched metals.

Enrichment factors calculated for the analyzed species in SPM, at two sampling sites are given in Table 1. All crustal metals at two sampling sites showed EF values between 1 and 10 except Na for which it was less than unity. This implies that concentration of Na in aerosols of Delhi was less than natural concentration and hence depleted along moving through air mass coming from sea coast.

Among the trace metals, Ni, Cr, V at the urban site and V metal at the rural site was observed moderately enriched. Four trace metals viz, Pb, Cu, Zn, and Cd were found highly enriched at both sampling sites with higher value at the urban site (PN) than rural site (NP). Other metals, mainly Mn was found to have lesser enrichment at both sites. Earlier study which were limited to few trace

Table 3
Correlation matrix of SPM and analyzed metallic species at (a) the urban and (b) rural site.

(a)

Urban	SPM	Ni	Cr	Pb	Mn	Cd	V	Cu	Zn	Na	K	Ca	Mg	Fe	Al
SPM	1.00														
Ni	0.32	1.00													
Cr	−0.04	0.21	1.00												
Pb	0.37*	0.23	0.18	1.00											
Mn	0.43*	0.45*	0.45*	0.17	1.00										
Cd	−0.15	0.12	−0.04	0.28	−0.15	1.00									
V	0.30	−0.09	−0.18	0.01	−0.09	0.25	1.00								
Cu	−0.16	0.31	0.21	0.15	0.30	0.28	−0.18	1.00							
Zn	−0.43	0.33	0.31	−0.18	0.03	0.35	−0.24	0.33	1.00						
Na	0.16	−0.12	−0.08	0.38*	0.21	−0.11	−0.21	0.01	−0.52	1.00					
K	0.23	0.26	0.14	−0.05	0.18	0.00	−0.18	−0.08	0.40*	−0.38	1.00				
Ca	0.64**	0.28	−0.06	0.07	0.49**	−0.32	−0.10	0.08	−0.27	0.35	0.14	1.00			
Mg	0.67**	−0.01	0.13	0.04	0.34	−0.46	0.00	−0.27	−0.38	0.32	0.25	0.58**	1.00		
Fe	0.48**	0.17	0.25	0.20	0.29	−0.13	0.03	0.23	−0.10	0.04	0.24	0.31	0.38*	1.00	
Al	0.81**	0.14	0.03	0.22	0.40*	−0.34	0.16	−0.01	−0.38	0.09	0.08	0.70**	0.56**	0.44*	1.00

(b)

Rural	SPM	Ni	Cr	Pb	Mn	Cd	V	Cu	Zn	Na	K	Ca	Mg	Fe	Al
SPM	1.00														
Ni	0.54**	1.00													
Cr	0.55**	0.78**	1.00												
Pb	0.41*	0.59**	0.36	1.00											
Mn	0.82**	0.68**	0.64**	0.54**	1.00										
Cd	−0.13	−0.06	−0.16	0.25	−0.12	1.00									
V	0.47**	0.56**	0.49**	0.29	0.51**	−0.02	1.00								
Cu	0.26	0.05	0.06	0.05	0.20	−0.02	0.20	1.00							
Zn	0.28	0.28	0.41*	0.01	0.34	−0.25	0.06	0.31	1.00						
Na	−0.30	−0.22	−0.26	0.09	−0.31	0.41*	−0.04	−0.06	−0.22	1.00					
K	0.51**	0.49**	0.50**	0.31	0.61**	0.02	0.67**	0.12	0.13	−0.23	1.00				
Ca	0.69**	0.30	0.45*	0.08	0.46**	−0.24	0.38*	0.23	0.20	−0.08	0.41*	1.00			
Mg	0.36	0.00	0.04	−0.25	0.14	−0.21	0.13	0.45*	−0.24	−0.05	0.17	0.50**	1.00		
Fe	0.72**	0.31	0.48**	0.07	0.55**	−0.10	0.37*	0.46**	0.25	−0.43	0.44*	0.72**	0.49**	1.00	
Al	0.65**	0.52**	0.48**	0.33	0.78**	−0.07	0.37*	0.26	0.44*	−0.13	0.42*	0.57**	0.23	0.51**	1.00

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

metals analysis in urban Delhi before CNG regime implementation [37] also reported high enrichment of Pb and Cd. High degree of enrichment of Pb, Cu and Cd metals in Korea has been reported by Kim et al [42] but level was higher for Cu and Cd metal while Pb metal was observed on lower end.

5.2. Principal component analysis

Principal component analysis (PCA) was used to identify possible sources of SPM and metals. PCA was executed by the rotated factor matrix method in SPSS version 11. Factor loading scores for both the sites are given in Table 4. At the urban site (PN) more than 75% variance extracted in the form of five component factors, which have eigen value greater than 1. First factor, having ~25% variance, extracted with four crustal metals (Ca, Mg, Fe, Al) and Mn. This indicates the source of these metals as construction activities and re-suspended dust [43,45]. Second factor was extracted with ~20% variance with high component score for five trace metals (viz, Ni, Cr, Mn, Cu, Zn) which might have originated from industrial activities in surrounding areas. Last three factors have comparable variance

Table 4
Varimax rotated factor loading matrix for the elemental concentrations in SPM at the urban and rural site (factor loading >0.5 are made bold).

	Urban site					Rural site				
Factors	1	2	3	4	5	1	2	3	4	5
Ni	0.13	**0.74**	0.23	−0.01	0.07	−0.16	**0.80**	0.07	0.05	−0.04
Cr	0.19	**0.60**	0.24	−0.04	−0.12	0.49	0.40	0.50	0.15	−0.02
Pb	0.10	−0.05	−0.09	**0.89**	−0.08	−0.14	0.11	**0.72**	−0.14	0.06
Mn	**0.62**	**0.69**	−0.02	−0.06	−0.10	0.21	0.14	**0.76**	0.11	−0.12
Cd	−0.41	0.13	0.14	**0.70**	0.36	−0.10	0.12	−0.17	0.05	**0.83**
V	0.09	−0.13	−0.08	0.04	**0.90**	0.41	**0.69**	0.31	−0.19	0.23
Cu	−0.22	**0.76**	−0.34	0.16	−0.04	**0.71**	−0.13	−0.09	0.33	−0.07
Zn	−0.51	**0.59**	0.44	−0.17	−0.07	0.23	0.01	−0.02	**0.92**	−0.09
Na	0.31	−0.06	−0.67	0.43	−0.39	−0.08	−0.39	0.25	−0.30	**0.69**
K	0.15	0.17	**0.86**	0.10	−0.20	0.38	**0.67**	0.24	0.05	−0.15
Ca	**0.82**	0.18	−0.17	−0.08	−0.07	**0.88**	0.13	0.20	0.10	0.04
Mg	**0.83**	−0.19	0.09	0.05	−0.26	**0.83**	−0.08	−0.20	−0.34	−0.19
Fe	**0.61**	0.23	0.30	0.14	0.23	**0.80**	0.24	0.05	0.17	−0.23
Al	**0.87**	0.08	0.03	−0.10	0.27	**0.77**	0.28	0.29	0.33	0.06
Eigen Values	3.63	2.76	1.75	1.45	1.19	4.93	2.10	1.43	1.08	1.00
% of variance	25.94	19.72	12.49	10.39	8.48	35.25	15.02	10.24	7.72	7.18
Cumulative %	25.94	45.66	58.15	68.54	77.01	35.25	50.27	60.51	68.22	75.40

of ~10% each with K, Pb, Cd and V as elements in three factors respectively. Source could be identified as biomass combustion, battery repair and refuse oil burning respectively [43,45].

At rural site (PN), first factor was extracted with variance ~35% accounted for four crustal metals (Ca, Mg, Fe, Al) and Cu. The source can be inferred as re-suspended dust/soil. Second factor extracted with only 15% variance having good component score of Ni, V and K metals. Source could be recognized as burning of low grade coal, biomass with the help of petroleum products in rural areas for domestic and commercial purposes. Third factor having good loading of three metals (Cr, Pb, Mn) but enrichment of these metals at this site was very low except for Pb. So source could be inferred as vehicular emission which is in the form of re-suspended road dust. Manganese (Mn) based additives in gasoline are used to increase gasoline octane, and Mn and Cr are emitted by vehicles as brake-dust [46,47]. Fourth factor which has good factor loading of Zn element with low loadings of Cu, Al metal could be ascertained to wind-blown dust as a source in this region. This factor represented wind assisted transport of pollutants arising from the mining areas located 100 km away from the receptor site. Fifth factor having good loadings of Cd and Na might have originated from Samaipur Badli industrial area by air mass body traversed from south-western and west direction. In Samaipur Badli industrial area, plastics (PVC and acrylics), rubber and metal factories are predominant [48]. Most of Cd comes from anthropogenic sources [49]. The important uses of Cd are as alloys, in electroplating industry, in pigments, as stabilizers in polyvinyl plastics and in Ni–Cd batteries [50].

6. Conclusion

High particulate load was observed at both, the urban and rural site. Observed concentrations were 3–4 times higher as compared to the air quality standard for SPM (140 $\mu g\,m^{-3}$) prescribed by Central Pollution Control Board for residential areas in India. Annual average concentration of SPM and analyzed metals was observed higher at urban site than rural site. Correlation analysis, enrichment factor and principal component analysis cumulatively indicated presence of anthropogenic driven dust as a major source of crustal and some trace metals at both the sites. High CV for certain trace metals having high enrichment factor at rural site indicates irregular anthropogenic source of these metals. Policy maker should take note that ongoing efforts are not sufficient to prevent alarming particulate load in atmosphere of Delhi. Uncontrolled construction activities without preventive measures, presence of debris and road dust along the unpaved road seems to be a potent source of particulate matter in atmosphere of Delhi.

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References

[1] C.A. Pope, M. Thun, J. Namboodira, D.W. Dockery, J.S. Evans, F.W. Speizer, C.W. Heath Jr., Particulate air pollution as a predictor of mortality in prospective study of US adults, Am. J. Respir. Crit. Care 151 (1995) 669–674.
[2] D. Dockery, C.A. Pope, X. Xiping, J. Spengler, J. Ware, M. Fay, B. Ferris, F. Spiezer, An association between air pollution and mortality in six US cities, N Engl. J. Med. 329 (24) (1993) 1753–1759.
[3] J. Schwartz, The effects of particulate air pollution on daily deaths: a multi-city case crossover study, Occup. Environ. Med. 61 (2004) 956–961.
[4] World Health Organization, WHO air quality guidelines global update 2005, Report on a Working Group meeting, Bonn, Germany, October 18–20, 2005. www.euro.who.int/Document/E87950.pdf.
[5] B. Brunekreef, S.T. Holgate, Air pollut. Health, Lancet 360 (2002) 1233–1242.
[6] L. Curtis, W. Rea, P. Smith-Willis, E. Fenyves, Y. Pan, Adverse health effects of outdoor air pollutants, Environ. Int. 32 (2006) 815–830.
[7] M. Kampa, E. Castanas, Human health effects of air pollution, Environ. Pollut. 151 (2008) 362–367.
[8] Y. Chen, L. Craig, D. Krewski, Air quality risk assessment and management, J. Toxicol. Environ. Health Part A 71 (2008) 24–39.
[9] B.D. Ostro, G.S. Eskeland, J.M. Sanchez, T. Feyzioglu, Air pollution and health effects: a study of medical visits among children in Santiago, Chile, Environ. Health Perspect. 107 (1999) 69–73.
[10] A.D. Bhanarkar, D.G. Gajghate, M.Z. Hasan, Air pollution concentration in Haryana sub-region, India, Bull. Environ. Contam. Toxicol. 69 (2002) 690–695.
[11] A.P. Mitra, C. Sharma, Indian aerosols: present status, Chemosphere 49 (2002) 1175–1190.
[12] J.S. Pandey, R. Kumar, S. Devotta, Health risks of NO_2, SPM, and SO_2 in Delhi (India), Atmos. Environ. 39 (2005) 6868–6874.
[13] J.H. Lee, Y.P. Kim, K.C. Moon, H.K. Kim, C.B. Lee, Fine particle measurements at two background sites in Korea between 1996 and 1997, Atmos. Environ. 35 (4) (2001) 635–643.
[14] X. Querol, A. Alastuey, S. Rodriguez, F. Plana, E. Mantilla, C.R. Ruiz, Monitoring of PM10 and PM2.5 around primary particulate anthropogenic emission sources, Atmos. Environ. 35 (2001) 845–858.
[15] B. Sivertsen, Presenting air quality data. NILU-F 6/2002, National Training Course on Air Quality Monitoring and Management, Norwegian Institute for Air Research, Kjeller, Norway.
[16] M. Sharma, S. Maloo, Assessment of ambient air PM10 and PM2.5 and characterization of PM10 in the city of Kanpur, India, Atmos. Environ. 39 (2005) 6015–6026.
[17] K.R. Smith, A.E. Aust, Mobilization of iron from urban particulates leads to generation of reactive oxygen species in vitro and induction of ferritin synthesis in human lung epithelial cells, Chem. Res. Toxicol. 10 (1997) 828–834.
[18] J.S. Lighty, J.M. Veranth, A.F. Sarofim, Combustion aerosols: factors governing their size and composition and implications to human health, J. Air Waste Manage. Assoc. 50 (2000) 1565–1618.
[19] K. Donaldson, D.M. Brown, C. Mitchell, M. Dineva, P.H. Beswick, P. Gilmour, W. MacNee, Free radical activity of PM10: iron mediated generation of hydroxyl radicals, Environ. Health Perspect. 105 (1997) 1285–1289.
[20] L. Shao, Z. Shi, T.P. Jones, J. Li, A.G. Whittaker, K.A. BéruBé, Bioreactivity of particulate matter in Beijing air: results from plasmid DNA assay, Sci. Total Environ. 367 (2006) 261–272.
[21] A.J.F. Espinosa, M.T. Rodrıǧuez, F.J.B.D.L. Rosa, J.C.J. Saǐ nchez, A chemical speciation of trace metals for fine urban particles, Atmos. Environ. 36 (2002) 773–780.
[22] D.S. Lee, J.A. Garland, A.A. Fox, Atmospheric concentrations of trace elements in urban areas of the United Kingdom, Atmos. Environ. 28 (16) (1994) 2691–2713.
[23] K.H. Kim, J.-H. Lee, M.-S. Jang, Metals in airborne particulate matters in the Taejon industrial complex area of Korea, Environ. Pollut. 118 (1) (2002) 41–51.
[24] WHO, Air Quality in mega cities of world. World health organization publication, 1992.
[25] Indoor air pollution: Energy and health for the poor, World Bank, ESMAP, 7, 2002.
[26] Delhi Economic survey, 2001-2002, Govt of Delhi.
[27] Transport dept, Delhi Govt, 2007. http://transport.delhigovt.nic.in/info/info8.html.
[28] Indian Metrological Department, (IMD), http://www.imd.ernet.in/section/nhac/dynamic/decr10.htm.
[29] P. Goyal, T.V.B.P.S. Rama Krishna, Dispersion of pollutants in convective low wind: a case study of Delhi, Atmos. Environ. 36 (2002) 2071–2079.
[30] B.P. Murthy, Meteorological potential for urban air pollution in India, Mousam 35 (1984) 237–239.
[31] P. Geladi, S.F. Adams, The determination of Cd, Cu, Fe > Pb and Zn in aerosols by atomic absorption spectrophotometer, Anal. Chim. Acta 96 (1978) 229–241.
[32] APHA, Standard methods for the examination of water and waste water. 17th ed. Wasington, DC, 1989.
[33] CPCB, Parivesh 1995, http://www.cpcb.nic.in/as.htm.
[34] S.K. Mittal, S. Goyal, SPM levels of an urban area (Patiala city) and its relation to automobile exhaust, Clean Technol. Environ. Policy 6 (2004) 263–267, doi:10.1007/s10098-003-0238-3.
[35] T. Okuda, J. Kato, J. Mori, M. Tenmoku, Y. Suda, S. Tanaka, K. He, Y. Ma, F. Yang, X. Yu, F. Duan, Yu Lei, Daily concentrations of trace metals in aerosols in Beijing, China, determined by using inductively coupled plasma mass spectrometry equipped with laser ablation analysis, and source identification of aerosols, Sci. Total Environ. 330 (2004) 145–158.
[36] P.C. Chu, Y. Chen, S. Lu, Z. Li, Y. Lu, Particulate air pollution in Lanzhou China, Environ. Int. 34 (2008) 698–713.
[37] P.S. Khillare, S. Balachandran, B.R. Meena, Spatial and temporal variation of heavy metals in atmospheric aerosol of Delhi, Environ. Monit. Assess. 90 (2004) 1–21.
[38] DPCC., Towards cleaner Air. Department of Environment, Government of NCT of Delhi and Delhi Pollution Control Committee. http://dpcc.delhigovt.nic.in/down/cleanerair.pdf.
[39] P. Goyal, Sidhartha, Effects of winds on SO_2 and SPM concentrations in Delhi, Atmos. Environ. 36 (17) (2002) 2925–2930.
[40] I. Gupta, R. Kumar, Trends of particulate matter in four cities in India, Atmos. Environ. 40 (2006) 2552–2566.
[41] K. Ravindra, S. Mor, Ameena, J.S Kamyotra, C.P. Kaushik, Variation in spatial pattern of criteria pollution before and during initial rain of Monsoon, Environ. Monit. Asses. 87 (2003) 145–153.

[42] K.-H. Kim, B.-J. Choib, S.-T. Yunc, S.-J. Hwang, Studies of spatial and temporal distribution characteristics of TSP-bound trace metals in Seoul, Korea, Environ. Pollut. 127 (2004) 323–333.
[43] G. Fang, Y. Wu, S. Huang, J. Rau, Review of atmospheric metallic elements in Asia during 2000–2004, Atmos. Environ. 39 (2005) 3003–3013.
[44] B. Mason, Principles of Geochemistry, third edition, John Wiley &sons, Inc., 1996.
[45] G. Fang, Y. Wu, C. Wen, S. Huang, J. Rau, Ambient air particulate concentrations and metallic elements principal component analysis at Taichung Harbor (TH) and WuChi Traffic (WT) near Taiwan Strait during 2004–2005, J. Hazard. Mater. 137 (2006) 314–323.
[46] A.V. Kumar, R.S. Patil, K.S.V. Nambi, Source apportionment of suspended particulate matter at two traffic junctions in Mumbai, India, Atmos. Environ. 35 (2001) 4245–4251.
[47] A. Tandon, S. Yadav, A.K. Attri, City-wide sweeping a source for respirable particulate matter in the atmosphere, Atmos. Environ. 42 (2008) 1064–1069.
[48] http://dissertations.ub.rug.nl/FILES/faculties/rw/2000/j.v.bentinck/c6.pdf
[49] J.M. Pacyna, Source inventories for atmospheric trace metals, in: R.M. Harrison, R. Van Grieken (Eds.), Atmospheric Particles, John Wiley and Sons Ltd., 1998.
[50] J.M. Pacyna, Emission factors of atmospheric elements, in: J.O. Nriagu, C.I. Davidson (Eds.), Toxic Metals In The Atmosphere, Advances in Environmental Science and Technology, vol. 17, Jolm Wiley & Sons, Inc., New York, 1986.
[51] F. Ledoux, L. Courcot, D. Courcot, A. Aboukaïs, E. Puskaric, A summer and winter apportionment of particulate matter at urban and rural areas in northern France, Atmos. Res. 82 (2006) 633–642.
[52] M.H. Shah, N. Shaheen, M. Jaffar, A. Khalique, S.R. Tariq, S. Manzoor, Spatial variations in selected metal contents and particle size distribution in an urban and rural atmosphere of Islamabad, Pakistan, J. Environ. Manage. 78 (2006) 128–137.
[53] G. Fang, Y. Wu, W. Lee, T. Chou, I. Lin, Ambient air particulates, metallic elements, dry deposition and concentrations at Taichung Airport Taiwan, Atmos. Res. 84 (2007) 280–289.
[54] X. Wang, S. Tsutomu, B. Xing, T. Shuji, S. Tao, Source identification, size distribution and indicator screening of airborne trace metals in Kanazawa, Japan, J. Aerosol Sci. 36 (2005) 197–210.
[55] K.X. Yang, K. Swami, L. Husain, Determination of trace metals in atmospheric aerosols with a heavy matrix of cellulose by microwave digestion-inductively coupled plasma mass spectroscopy, Spectrochim. Acta Part B: At. Spectrosc. 57 (2002) 73–84.
[56] C. Vijayanand, P. Rajaguru, K. Kalaiselvi, K Panneer Selvam, M. Palanivel, Assessment of heavy metal contents in the ambient air of the Coimbatore city, Tamilnadu, India, J. Hazard. Mater. 160 (2008) 548–553.
[57] C. Bilos, J.C. Colombo, C.N. Skorupka, M.J. Rodriguez Presa, Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina, Environ. Pollut. 111 (2001) 149–158.
[58] A.G. Allen, E. Nemitz, J.P. Shi, R.M. Harrison, J.C. Greenwood, Size distributions of trace metals in atmospheric aerosols in the United Kingdom, Atmos. Environ. 35 (2001) 581–4591.
[59] F. Zereini, F. Alt, J. Messerschmidt, C. Wiseman, I. Feldmann, A. Bohlen, J. Muller, K. Liebl, W. Puttmann, Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am main, Germany, Environ. Sci. Technol. 39 (2005) 2983–2989.
[60] Z. Guoshun, G. Jinghua, Y. Hui, Z. Chengyi, The composition, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment, Chin. Sci. Bull. 46 (2001) 895–901.
[61] A. Salam, H. Bauer, K. Kassin, S. Mohammad Ullah, H. Puxbaum, Aerosol chemical characteristics of a mega-city in South-east Asia (Dhaka-Bangladesh), Atmos. Environ. 37 (2003) 2517–2528.
[62] I. Mori, M. Nishikawa, T. Tanimura, H. Quan, Change in size distribution and chemical composition of kosa (Asian dust) aerosol during long range transport, Atmos. Environ. 37 (2003) 4253–4263.
[63] M. Sohrabpour, H. Mirzaee, S. Rostami, M. Athari, Elemental concentration of the suspended particulate matter in air of Tehran, Environ. Int. 25 (1999) 75–81.
[64] A. Samura, O. Al-Agha, S.G. Tuncel, Study of trace metals in rural and urban aerosols of Uludag and Bursa (Turkey), Water, Air Soil Pollut.: Focus 3 (2003) 109–126.
[65] E. Rizzio, G. Giaveri, D. Arginelli, L. Gini, A. Profumo, M. Gallorini, 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, Sci. Total Environ. 226 (1999) 47–56.
[67] V. Mugica, M. Mauberta, M. Torresa, J. Munoza, E. Rico, Temporal and spatial variations of metal content in TSP and PM10 in Mexico City during 1996–1998, Aerosol Sci. 33 (2002) 91–102.