

## Particulate Matter (PM<sub>2.5</sub>) Concentration and Source Apportionment in Lahore

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Neste trabalho foram estudadas as concentrações das PM<sub>2.5</sub> (partículas com diâmetro aerodinâmico de 2,5 µm ou menos) e das fontes de incremento das PM<sub>2.5</sub>, monitoradas numa área urbana residencial de Lahore, Pasquidão. Amostras de PM<sub>2.5</sub> em aerosol foram coletadas 2 dias por semana, num intervalo de 12 h por dia, nas estações seca e húmida, usando um filtro de papel Zefluor™ contendo um amostrador de ar ambiente termo-elétrico (Thermo-Electron Corporation Reference Ambient Air Sampler, RAAS). No total 310 amostras foram coletadas durante o período de estudo, ou seja, de novembro de 2005 a dezembro de 2007. Altas concentrações de PM<sub>2.5</sub> foram encontradas no inverno, sendo aproximadamente 4 vezes maiores que nos períodos de verão, primavera, outono e época das monções. A análise das fontes de incremento foram feitas a partir de resultados de curta duração, de novembro de 2005 a março de 2006, usando o modelo fatorial de matrix positiva (Positive Matrix Factorization, PMF). Os resultados derivados do modelo PMF indicam que os maiores contribuintes a PM<sub>2.5</sub>, em Lahore, são: poeira de solos e rodovias, emissões industriais, emissões veiculares e aerossóis secundários. Verificou-se também que além das emissões veiculares e industriais locais, a cidade é também afetada por poluentes aéreos de fronteira, particularmente por aerossóis secundários (especialmente SO<sub>4</sub><sup>2-</sup>) durante o inverno, os quais aumentam a concentração total de PM<sub>2.5</sub> quando, relativamente, menos dispersão aérea existe. As partículas de sulfato também aumentam a formação de neblina/nevoeiro em condições calma e humidade, reduzindo a visibilidade e aumentando a incidência de doenças respiratórias na cidade ao longo do ano.

The work reported in this paper was carried out to study the trends of PM<sub>2.5</sub> (particles with an aerodynamic diameter of 2.5 µm or less) concentrations and source apportionment of PM<sub>2.5</sub> monitored at an urban residential site in Lahore, Pakistan. PM<sub>2.5</sub> aerosol samples were collected for 2 days in a week at 12 h interval in a day, both in dry and wet seasons, on Zefluor™ filter papers using Thermo-Electron Corporation Reference Ambient Air Sampler (RAAS). Total 310 samples were collected during the period under study, *i.e.*, from November 2005 to December 2007. High PM<sub>2.5</sub> loads were observed in winter, which were approximately 4 times greater than those observed in the summer, spring, fall and monsoon seasons in the yearlong measurements. Source apportionment was performed on short duration analysis results of November 2005 to March 2006 using Positive Matrix Factorization (PMF) model. The results derived from PMF model indicated that the major contributors to PM<sub>2.5</sub> in Lahore are: soil/road dust, industrial emissions, vehicular emissions and secondary aerosols. It is, therefore, concluded that in addition to local vehicular and industrial emissions, the city is also affected from trans-boundary air pollutants particularly due to secondary aerosols (especially SO<sub>4</sub><sup>2-</sup>) during winter which increase PM<sub>2.5</sub> concentrations manifold when relatively less mixing height exists. The sulfate particles also facilitate in haze/fog formation during calm highly humid conditions, thus reduce visibility and increase the incidents of respiratory diseases encountered in the city every year.

**Keywords:** airborne particulate matter, source apportionment, PM<sub>2.5</sub>, Lahore

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## Introduction

Urban atmosphere, in general, is highly convoluted and assorted because of the wide variability in the type, intensity, density and spatial distribution of emission sources. Aerosol particles, due to their relatively small size may remain airborne for several days so transported over large distances and are, therefore, ubiquitous in the atmosphere. Air pollution primarily affects urban areas, where the density of buildings, existence of industries and presence of a large number of vehicles prevent dispersion of pollutants. Thus, the studies on air quality date back to the point of extensive awareness about the present and the future hazards of air pollution. The detrimental effects of particulates on human health have been studied in various urban centers across Europe, United States of America and many other countries. Even for polar region, Turpin and Huntzicker reported a range of species, such as SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, produced by photochemical oxidation of gases which are of both anthropogenic and biogenic origin.<sup>1</sup> Pope *et al.*<sup>2</sup> reported the association between increased air pollution and human health deterioration. Dockery *et al.*<sup>3</sup> and Anderson<sup>4</sup> carried out studies relating air pollution, mortality and hospital admissions for asthma. There are many reports on the negative impact of PM<sub>2.5</sub> on respiratory tract.<sup>5-7</sup> WHO estimated premature deaths caused by urban polluted air to be over 750,000 globally including more than 530,000 in Asia.<sup>8</sup> In USA, peak adverse health effects occur among people of age 65 and older while in Delhi (India), peak effects occur even at relatively much younger age (15 to 44).<sup>9</sup> The Indian Ocean Experiment (INDOEX) documented that every year, from December to April, anthropogenic haze spreads over most of the North Indian Ocean and South and South East Asia.<sup>10</sup>

It is well understood that aerosols also have serious regional climatic implications. They can modify the climate forcing by altering the radiative heating of the planet and cloud properties. Therefore, long term study of PM<sub>2.5</sub> and identification of local and distant sources are imperative for control policy recommendations.

A bad ambient air quality in terms of higher TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, CO and hydrocarbon (methane) has been reported in Lahore as compared to those in the other major cities of Pakistan.<sup>11</sup> The major emission sources in Karachi and Lahore, the two biggest cities of Pakistan, are vehicles, industries and fossil fuel based thermal power plants.<sup>12,13</sup>

In order to monitor air quality in the country, Pakistan Space and Upper Atmosphere Research Commission (SUPARCO) carried out a number of short term winter studies in Lahore over the years 1998-99,<sup>14</sup> 2000,<sup>15</sup> 2001<sup>16</sup> and 2005-2006.<sup>17</sup> In these studies, exceptionally high

SO<sub>4</sub><sup>2-</sup> concentrations were reported during the foggy days. SO<sub>4</sub><sup>2-</sup>/Se tracer technique was applied to quantify the in-cloud oxidation of sulfur dioxide.<sup>18</sup> The SO<sub>4</sub><sup>2-</sup>/Se tracer technique was also applied to delineate the origin of the sulfate aerosol.<sup>14-16</sup> A study conducted by Hameed *et al.*<sup>14</sup> reported high SO<sub>4</sub><sup>2-</sup>/Se ratios (from 2,873 up to 12,903) which suggested that the distant fossil fuel combustion, about 400 to 933 km away from Lahore, contributed significantly towards high SO<sub>4</sub><sup>2-</sup> levels. Another study<sup>17</sup> reported comparatively low SO<sub>4</sub><sup>2-</sup>/Se ratio, from 910 up to 2,534, which led to the conclusion that the local as well as remote sources contributed to the elevated sulfate levels.

The work undertaken by SUPARCO is still in progress and on the basis of the reports highlighted above, less polluting energy sources are being explored, e.g., attempts are being made to gradually replace the coal and gasoline with natural gas in domestic and industrial usage.

The present study is aimed at studying diurnal and seasonal concentration of PM<sub>2.5</sub>, estimating contribution of various sources.

## Experimental

### Study site

For the purpose of monitoring fine particulate matter (PM<sub>2.5</sub>) in Lahore (Lat. 31.470 N and Long. 74.253 E), Jauhar Town, a residential area located in the South of the city was selected (Figure 1). Lahore is the second largest city of the country bordering India. The study site should represent the local and distant sources of air pollution. Therefore the selected site for this study is ideal because it is downwind to the city. The well planned canal road is at distance of one km from the sampling site for this study. Different industrial activities in the vicinity (2 to 6 km) of the sampling site are taking place in "Hanjarwal", "Multan Road", "Township" and "Kot Lakhpat" (Figure 1).

### PM<sub>2.5</sub> monitoring

PM<sub>2.5</sub> samples were collected using Thermo Electron Corporation PM<sub>2.5</sub> Reference Ambient Air Sampler (RAAS) during the time period, one from November 22, 2005 to March 10, 2006 and the other from November 29, 2006 to December 17, 2007 at "Jauhar Town". The sampling was performed at a height of 10 meter from the ground level. From November 22, 2005 to December 23, 2005, the 12 h daytime sampling was divided into two intervals: 'morning' from 9:00 to 15:00 h and 'evening' from 15:00 to 21:00 h, whereas the 'night' samples were collected for 12 h from

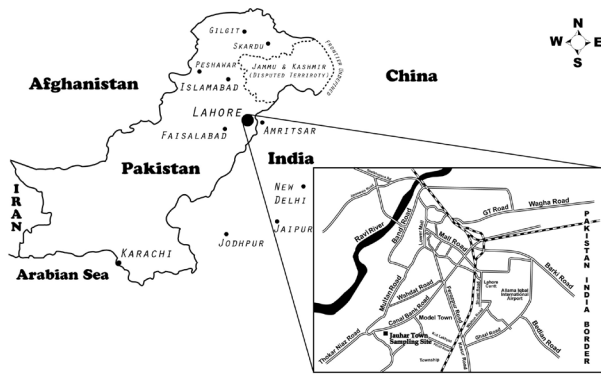


Figure 1. Location of the sampling site.

21:00 to 9:00 h. From December 24, 2005 to March 10, 2006 the ‘morning’ and ‘evening’ sampling times were shifted to 8:00 to 14:00 h and 14:00 to 20:00 h, respectively while the nighttime samples were collected for 12 h from 20:00 to 8:00 h. For the yearlong data from November 29, 2006 to December 17, 2007 sampling was done at 12 h intervals. The samples were collected on 47 mm pre-weighed Zeffluor™ filter papers at constant air flow rate of 16.67 l min<sup>-1</sup>.

#### Chemical analysis

The filter papers were kept in controlled environmental conditions at a temperature of 20-23 °C and relative humidity of 30-40% for 24 h, as per USEPA standard, prior to and after the collection of PM<sub>2.5</sub> mass. PM<sub>2.5</sub> mass was determined gravimetrically by the difference of weight of filter paper before and after collecting PM<sub>2.5</sub>. The samples collected from November 2005 to March 2006 were analyzed for ions and trace metals. Analysis of extracts for ions of interest was done by DIONEX (Model DX 500) equipped with Peaknet software.<sup>19</sup> The filters were digested in a microwave oven and analyzed for 25 trace metals by inductively coupled plasma mass spectrometry (ICP-MS).<sup>20</sup> Some samples analysis was also done at SUPARCO Lab., using Metrohm’s ion chromatograph and ICP.

#### Model based data analysis

Backward air trajectories were used to assess the origin of the pollutants collected at the receptor site. Backward trajectory of 72 h accessed *via* the NOAA (National Oceanic and Atmospheric Administration) Air Resources Laboratory, READY (Real-time Environmental Applications and Display sYstem) website with the HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model.<sup>21, 22</sup>

Positive Matrix Factorization (PMF), a multivariate receptor based model developed by Paatero *et al.*,<sup>23-25</sup>

was applied to the analytical results of the PM<sub>2.5</sub> samples collected at the receptor site during the winters of 2005 and 2006 to identify sources and their contributions to the receptor site airborne fine particulate matter. Receptor based multivariate source apportionment models use chemical composition of fine particulate matter measured at receptor site(s) to determine correlation among them assuming that highly correlated species come from a common source. EPA PMF version 1.1, a software tool based on PMF model, was used for PM<sub>2.5</sub> source apportionment in the current study. Further, the quantitative contribution of each species to each source obtained from the PMF results was utilized to quantify the contribution of each source to PM<sub>2.5</sub> mass.

#### Model description

A general receptor model assumes there are  $p$  sources contributing to a receptor site. This can be mathematically stated as

$$X_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

where,

$X_{ij}$  = concentration of species  $j$  in  $i^{\text{th}}$  sample

$g_{ik}$  = contribution of  $k^{\text{th}}$  factor to the  $i^{\text{th}}$  sample

$f_{kj}$  = fraction of  $k^{\text{th}}$  factor that is species  $j$

$e_{ij}$  = residual for the  $j^{\text{th}}$  species in  $i^{\text{th}}$  sample

To estimate the contributions ( $g_{ik}$ ) and source profiles ( $f_{kj}$ ), PMF uses constrained, weighted, least squares method. The task of EPA PMF is to minimize the sum of squares of standardized (residual divided by corresponding uncertainty value) residuals ( $Q$ ):

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{e_{ij}}{s_{ij}} \right)^2 \quad (2)$$

where,

$n$  = total No. of samples

$m$  = total No. of species

$s_{ij}$  = uncertainty for  $j^{\text{th}}$  species in  $i^{\text{th}}$  sample

Equation (1) can also be written in matrix form as

$$X = GF + E \quad (3)$$

where,

$X$  = matrix of measured data with dimension “No. of samples” × “No. of species”

$G$  = contributions matrix with dimension “No. of samples” × “No. of factors”

$F$  = source profiles matrix with dimension “No. of species” × “No. of factors”

$E$  = matrix of residuals with dimension “No. of samples” × “No. of species”

Matrix of the measured concentrations ‘X’ and uncertainty matrix ‘S’ are the inputs for the PMF model whereas the matrices ‘G’, ‘F’ and ‘E’ are obtained as output data.

The source contribution matrix “G” was further utilized for source apportionment by taking into account the measured PM<sub>2.5</sub> mass. To perform the quantitative source apportionment, a scaling coefficient,  $y_k$ , is introduced in the model equation (1) so that

$$X_{ij} = \sum_{k=1}^p g_{ik} f_{kj}$$

$$X_{ij} = \sum_{k=1}^p g_{ik} \cdot \frac{y_k}{y_k} f_{kj}$$

$y_k$  was determined by multi-linear regression of computed source contribution against measured PM<sub>2.5</sub> mass. Constant of linear regression was assumed to be zero.

$$m_i = \sum_{k=1}^p y_k g_{ik}$$

After determination of  $y_k$  values, the final scaled source contributions were determined. PM<sub>2.5</sub> mass was again calculated from scaled source contribution.

EPA-PMF 1.1, after several runs, revealed five most interpretable sources with a minimum Q value (Figure 4).

## Results and Discussion

The results are reported at two levels. At the first level, the seasonal variation of PM<sub>2.5</sub> concentration with standard deviation is discussed, whereas, at the second level the PMF model results with grouping of species from the same possible sources are discussed along with the diurnal variations of the elemental concentrations. The contribution of various sources is also discussed.

### Seasonal PM<sub>2.5</sub> concentration variations

PM<sub>2.5</sub> concentration during November 2005 to January 2006 ranged from 53 μg m<sup>-3</sup> to 476 μg m<sup>-3</sup> with the mean value of 191 ± 90 μg m<sup>-3</sup>. During February 2006 to March 2006, PM<sub>2.5</sub> level ranged from 32 to 400 μg m<sup>-3</sup> with the mean value of 143 ± 100 μg m<sup>-3</sup>. After a gap of seven months the PM<sub>2.5</sub> monitoring was restarted on continuous basis. PM<sub>2.5</sub> concentration variation from November 2005 to December 2007 is demonstrated in Figure 2. The particulate concentration showed marked seasonal variations. Comparatively high and alarming levels

were recorded in winter (December-February). These levels varied from 49.9 to 447 μg m<sup>-3</sup> with the mean of 175 ± 88.52 μg m<sup>-3</sup> (November 2006 to February 2007). Some higher levels ranging from 24.95 to 432 μg m<sup>-3</sup> with mean of 136 ± 114.81 μg m<sup>-3</sup> were also observed on some days of spring (March-April). However, a sharp decrease in particles (PM<sub>2.5</sub>) level was observed in summer (May-June) when concentrations varied from 34.52 to 273.62 μg m<sup>-3</sup> (mean 93.35 ± 64.77 μg m<sup>-3</sup>), during monsoon (July-August), these levels varied from 17 to 66.34 μg m<sup>-3</sup> with an average of 36.78 ± 12.06 μg m<sup>-3</sup> and in post monsoon (September-October) these varied from 12 to 185.72 μg m<sup>-3</sup> having an average of 47.61 ± 36.55 μg m<sup>-3</sup>.

The observed PM<sub>2.5</sub> concentrations in winter and spring were 2 to 14 times greater than the prescribed limits of the USEPA, *i.e.*, 35 μg m<sup>-3</sup>. A 2 to 8 times excess from the standard limit was observed in summer. Annual arithmetic mean of PM<sub>2.5</sub> for the year 2007 was 103 μg m<sup>-3</sup> which exceeded seven fold from USEPA annual standard for PM<sub>2.5</sub> (15 μg m<sup>-3</sup>).

Alarming high PM<sub>2.5</sub> concentrations were recorded in dry winter (November-January) in the densely populated areas. The visibility in Lahore and its adjoining areas during winter is often as low as 50 meters. PM<sub>2.5</sub> concentrations also showed a sudden rise which was many-fold during foggy days when secondary aerosols especially sulfate also contribute to total aerosol load (Table 1). Luckily, during heavy monsoon seasons in Lahore, the suspended particulates are washed away in the rainy days. Therefore, a steeper decline in PM<sub>2.5</sub> concentration was observed from late June to September.

Backward air trajectories, produced with HYSPLIT from the NOAA ARL<sup>21,22</sup> are presented in Figure 3 (a, b, c and d) for the days when maximum concentration was observed. Each air trajectory was computed 72 h back in time at a height of 1000 m. On 21<sup>st</sup> and 23<sup>rd</sup> December, 2005 (Figure 3 a and b), when high PM<sub>2.5</sub> concentration was measured (476, 308 μg m<sup>-3</sup> respectively), the air trajectories revealed air parcels transported from south-east of Lahore (India). This trend may be explained on the assumption that the wind direction from east and south-east has strong influence on fine particulate pollution load especially due to increased concentration of sulfate during foggy days. In the air parcel coming from east and north on December 20, 2006, the PM<sub>2.5</sub> concentration was 400 μg m<sup>-3</sup> while on December 06, 2007, the air parcels received from the north-west and north had PM<sub>2.5</sub> concentration of 422 μg m<sup>-3</sup>. It appears that apart from the distant sources, the local industrial and vehicular emissions, emissions from brick kilns and indiscriminate burning of agricultural and solid waste also contribute to the PM<sub>2.5</sub> concentration especially

through the emission of trace metals, Elemental Carbon (EC) / Black Carbon (BC) and Organic Carbon (OC).

NH<sub>4</sub><sup>+</sup>, Be, V, Cr, Ni, Mo, Mg, Al, Na, K, Ca, Mn, Co, Zn, As, Se, Sr, Cd, Sn, Sb, Ba, Fe, Ti and Pb are presented in Tables 1 and 2.

Analytical results of PM<sub>2.5</sub> winter samples (November 2005 to March 2006)

Source apportionment

The analytical results of PM<sub>2.5</sub> aerosol samples of November 2005 to March 2006 analyzed for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>,

The analytical results distributed in five factors (sources) displayed by Positive Matrix Factorization (EPA PMF 1.1)

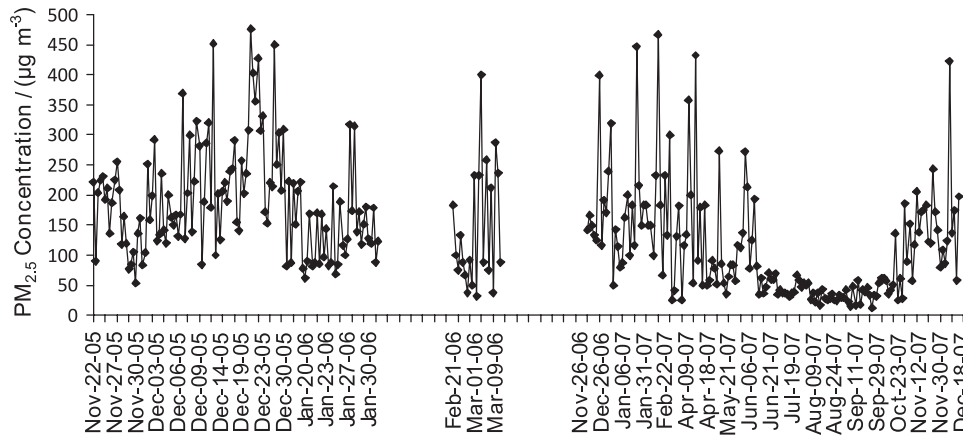


Figure 2. PM<sub>2.5</sub> concentrations variation from November, 2005 to December, 2007.

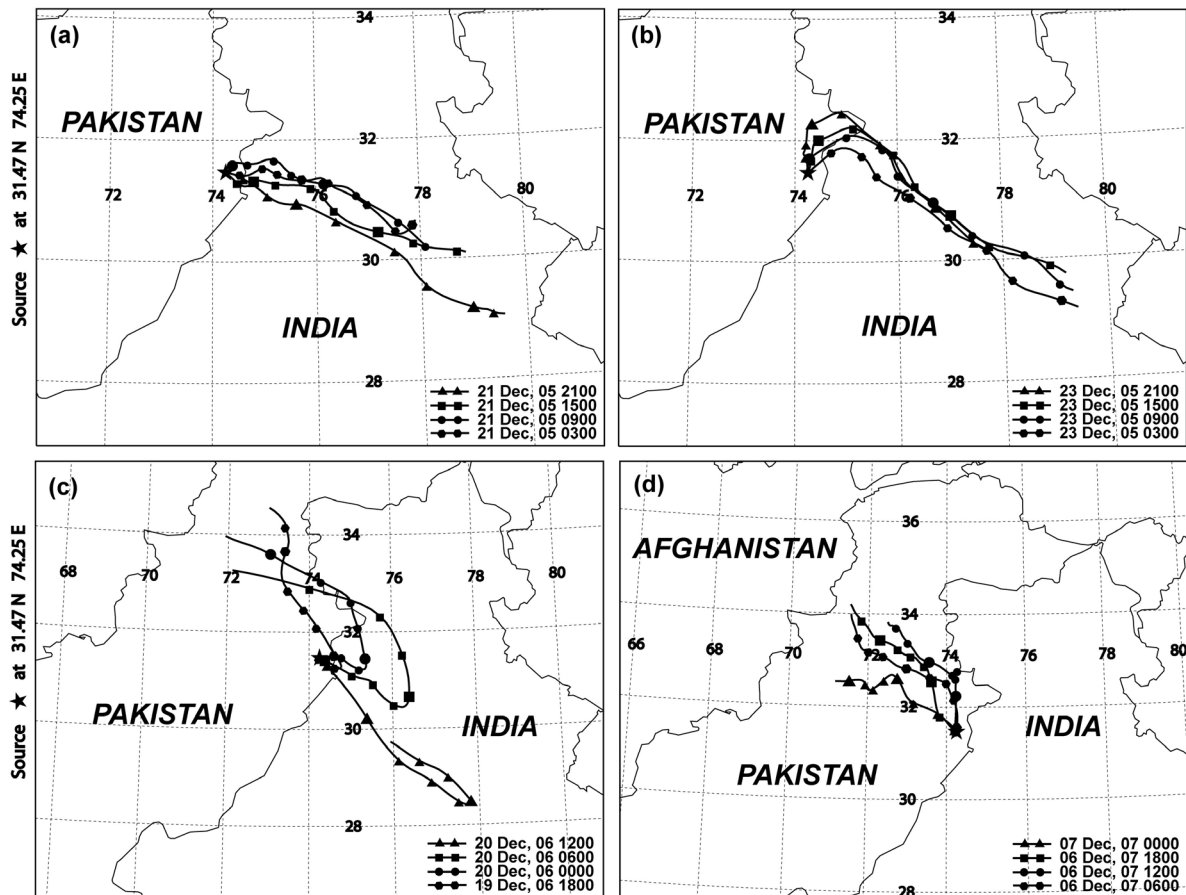


Figure 3. 72 h backward air trajectories produced with HYSPLIT4 from the NOAA ARL.



**Table 1.** PM<sub>2.5</sub> and elements and ions concentration in PM<sub>2.5</sub> measured from November 22, 2005 to March 10, 2006 (Lahore, Pakistan)

Period	PM <sub>2.5</sub>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Be	V	Cr	Ni	Mo	Mg	Al	Na	K	Ca
	Concentration/(µg m <sup>-3</sup> )				Concentration/(ng m <sup>-3</sup> )									
Range (Day)	53-476	3.33-59	2.10-73	1.98-54	0.04-2.33	0.34-17.9	0.32-2514	1.13-1857	0.17-269	100-1357	28-1908	61-928	243-2954	183-3467
Range (Evening)	84-403	3.63-52	0.42-44	3.43-46	0.04-0.71	1-14.5	1.71-1794	0.44-1411	0.12-205	45-1058	179-2118	51-1482	589-5087	176-3040
Range (Night)	105-452	4-66	4.16-37	4.57-60	0.02-0.47	0.23-14.3	0.18-2902	2.27-2002	0.08-294	99-773	52-2146	132-2194	259-5660	289-1489
Average (Day)	161.4	12.64	21.83	14.53	0.52	6.36	479.6	349.2	45.74	319.0	559.9	296.3	1358	715.1
Average (Evening)	186.0	11.50	16.51	12.10	0.32	4.91	403.6	286.6	37.97	467.5	1039	346.1	1781	941.6
Average (Night)	228.8	15.70	20.95	15.79	0.22	5.70	278.4	179.6	24.22	397.5	964.9	405.5	2083	730.6

**Table 2.** Elements concentration in PM<sub>2.5</sub> mass measured from November 22, 2005 to March 10, 2006 (Lahore, Pakistan)

Period	Mn	Co	Zn	As	Se	Sr	Cd	Sn	Sb	Ba	Fe	Ti	Pb
	Concentration/(ng m <sup>-3</sup> )												
Range (Day)	11.7-438	0.26-31.4	39-47864	2.4-23.4	0.99-24.2	0.79-11.4	0.34-27.7	0.75-315	1.39-66	1-22.5	141-11112	8.94-141	11.17-6948
Range (Evening)	16.3-490	0.32-138	10-31543	0.25-135	1.26-20.9	0.96-84	0.13-93	8-988	0.26-157	0.08-99.7	194-9661	15.9-116	20.8-11617
Range (Night)	16.9-1646	0.13-34.6	42-41046	0.97-50	2.29-24.3	1.01-7.1	0.37-57	0.19-553	2.16-97	2.48-21	221-13125	3.92-135	47.6-9095
Average (Day)	106.9	6.20	4439	9.58	10.53	3.58	7.02	97.82	15.80	7.37	2996	38.46	953.3
Average (Evening)	128.1	10.12	2831	11.09	9.18	6.24	9.83	133.9	18.60	13.27	3025	57.61	820.6
Average (Night)	155.6	3.27	4195	8.65	10.08	3.84	7.52	96.28	12.47	10.93	2382	48.06	778.7

model application on the short term data of daytime, evening and nighttime (November 2005-March 2006) are shown in Figure 4. Factor 1 includes Al, Ca, K which refer to soil and road side dust (Figure 4). The average evening (1039 ng m<sup>-3</sup>) and nighttime (964.9 ng m<sup>-3</sup>) concentrations of Al were higher than the daytime concentration (559.9 ng m<sup>-3</sup>). Calcium concentration in the evening (941.6 ng m<sup>-3</sup>) was higher than the nighttime (730.6 ng m<sup>-3</sup>) and daytime (715.1 ng m<sup>-3</sup>) concentrations. Higher K concentration was recorded at night (2083 ng m<sup>-3</sup>) as compared to the evening (1781 ng m<sup>-3</sup>) and daytime (1358 ng m<sup>-3</sup>) concentrations. Soil contains characteristic elements Al, Si, Ca, Mg, Ti and K. The road dust contribution (18%) may be from unpaved and grass free belts.

Factor 2 comprises Co, Cr, Fe, Mo, Ni, and Sn referring to industrial emissions originating principally from ferrous metal sources. Factor 2 has high loading percentage for Cr, Mo and Ni. The average concentrations of Cr, Mo and Ni were highest in daytime, *i.e.*, 479.6,

45.74 and 349.2 ng m<sup>-3</sup>, respectively whereas the lowest concentrations were observed at night (278.4, 24.22 and 179.6 ng m<sup>-3</sup>, respectively). The possible source for Factor 2 may be industrial emissions from iron and steel industry or ferrous smelters. A relatively higher contribution of Factor 2 in PM<sub>2.5</sub> mass was found in weekdays as compared to that in the weekends (Figure 5).

PMF displays a separate factor designated as Factor 3, for Cd, Pb, Sb, and Zn indicating vehicular/traffic emission as their common source. This group has higher loading percentage that is more than 80% Zn and Pb. The concentrations of Zn and Pb were higher (4439 and 953.3 ng m<sup>-3</sup>, respectively) in the 1<sup>st</sup> half of the day as compared to the evening (2831 and 820.6 ng m<sup>-3</sup>, respectively) and nighttime (4195 and 778.7 ng m<sup>-3</sup>, respectively) concentrations. Factor 3 represents vehicular emissions especially those from two stroke engines. Vehicular emissions and battery manufacturing are two major sources of airborne lead. Zn, Cd, Sb, Ba and Pb are

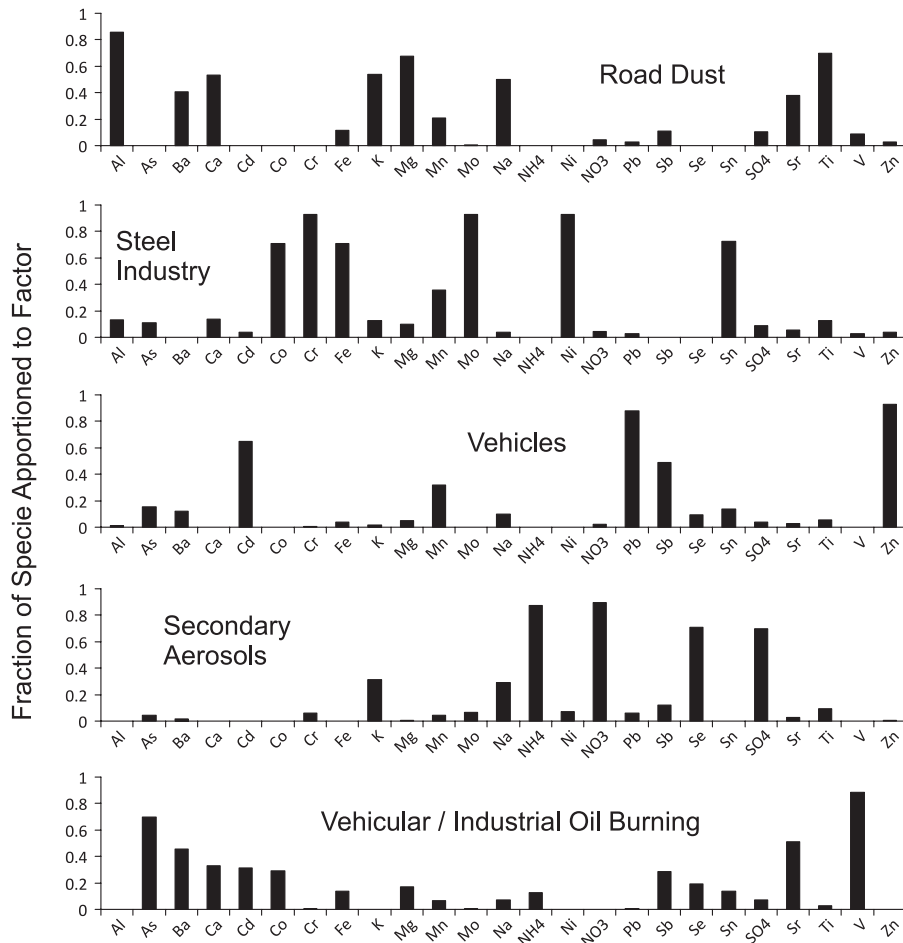


Figure 4. Source profiles resolved from  $PM_{2.5}$  mass.

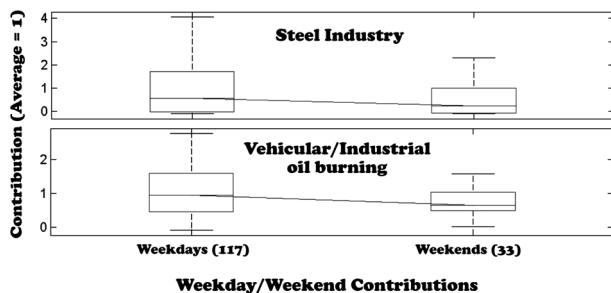


Figure 5. Weekday/weekend contributions of Factors towards  $PM_{2.5}$  mass.

emitted from road traffic in considerable quantities. Zn is emitted from lubrication oil, brake linings and tyres, whereas, metal wear particles from Cd-bearing alloys are also emitted. Pb plates used in battery manufacturing usually contain about 4-5% Sb.<sup>12</sup> Unleaded gasoline has been introduced in most of the refineries of Pakistan and the ratio of vehicle engine conversion from gasoline to compressed natural gas (CNG) due to low price is also on increase. Therefore, a rapid decrease in Pb level was expected to be observed. On the contrary, a high Pb

concentration was recorded. This is likely to be due to rapid increase in private car ownership because of bank leasing facilities, use of adulterated fuel, traffic jams and soil deposited Pb etc. The day time mean Pb level ( $953.3 \text{ ng m}^{-3}$ ) is higher than that observed in 2002 ( $856 \text{ ng m}^{-3}$ ).<sup>15</sup> However, vehicular exhaust derived lead is reduced to 67% in day and night and to 55% in the evening as compared to the earlier reported value of 70%,<sup>15</sup> while aerosol Pb from large battery manufacturing has increased to 33% and 45% in day and evening samples respectively as compared to the earlier reported value of 30%. It was found that Cd and Sb, despite their short history as traffic-emitted metals, have increased more than eight times in roadside soils as compared to background levels.

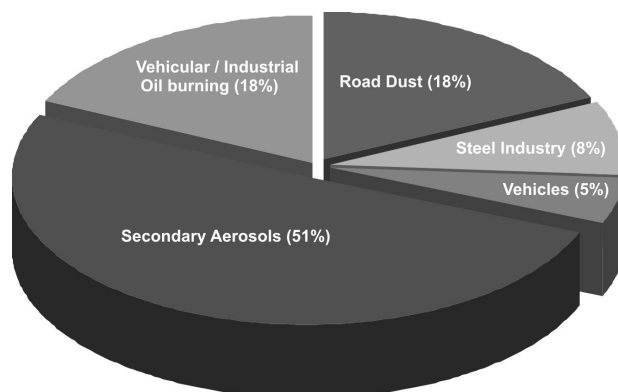
Factor 4 with high percentage of  $SO_4^{2-}$ ,  $NO_3^-$  and  $NH_4^+$  refers to secondary aerosols. Secondary sulfates have been identified and characterized by a high concentration. These secondary aerosol particulate could be largely from coal and biomass combustion in the rural areas of Lahore. The precursor gas of nitrate,  $NO_x$  is emitted by vehicles and stationary sources such as thermal electricity

generating plants. The percentages of secondary sulfates, secondary nitrates and Se were 75, 60 and 60%, respectively (Figure 4). Factor 5, containing high percentage of V, As, Sr and Ba, refers to mixed urban source of Oil/Coal burning probably in industries, vehicles and brick kilns. The contribution of this factor, in PM<sub>2.5</sub> mass, during weekdays was found higher than that in the weekends (Figure 5).

#### Source contribution to PM<sub>2.5</sub> mass

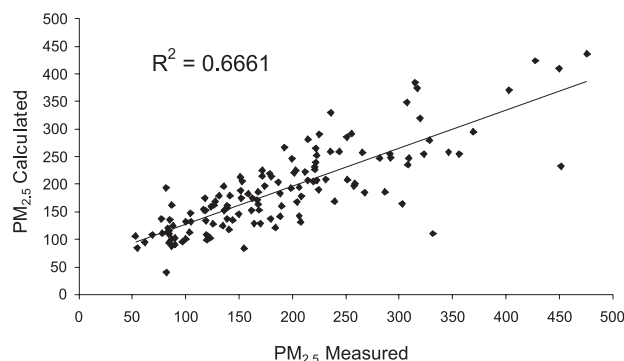
The PM<sub>2.5</sub> mass calculated from scaled source contribution of PMF and the results of multi-linear regression is applied to estimate the contribution of each source to PM<sub>2.5</sub> mass.

Source apportionment results shown in Figure 6 display the high contribution of secondary aerosols, crustal elements and industrial emissions towards PM<sub>2.5</sub> mass. The overall contribution of road dust to PM<sub>2.5</sub> was 18%, whereas, industrial emissions (Industrial oil burning, smelting, steel industry) contributed up to 26%. The source apportionment results show that the secondary products were the dominant (51%). City is also affected from distant sources of air pollution. Every winter a dense belt of fog occurs over northeastern India extending to northwestern India and to eastern Pakistan. The visibility impairment in the form of brown cloud, fog and haze/smog also is experienced in Asia round the year. Indian Ocean Experiment (INDOEX) also reported substantial amounts of inorganic, organic and secondary aerosol pollutants over the entire northern Indian Ocean.<sup>26</sup> The intensity of fog episode is greater in India as compared to the eastern part of Pakistan. These episodes and low dispersion are often experienced in India extending to the border areas of Pakistan. Therefore pollutants contribution from distant sources under similar meteorological conditions should be evaluated. The SO<sub>2</sub> emissions in India are much higher than those in Pakistan, as coal is extensively used in India for electricity generation (thermal power plants). In India, the dominant share of sulfur dioxide load (tones/day) by different categories is 89% of the total load.<sup>27</sup> SO<sub>2</sub> emissions from China and India increased by approximately 60% and 150% respectively between 1980 and 2000<sup>28</sup> and are expected to increase further.<sup>28,29</sup> Stationary sources are major contributors to aerosol sulfur pollution.<sup>30</sup> The higher sulfur content in diesel fuel being used in Pakistan<sup>31</sup> is also one of the major local sources of SO<sub>2</sub> and sulfate in urban Lahore. Similarly, there is a contribution of SO<sub>2</sub>/H<sub>2</sub>S from open sewage drains in Lahore. In addition, there are many brick kilns operating in and around Lahore. The low quality and/or adulterated fuel used in some of these may also contribute to overall SO<sub>2</sub>.



**Figure 6.** Contributions of identified sources to PM<sub>2.5</sub> mass at Lahore, Pakistan.

A good correlation, with an R<sup>2</sup> value of 0.666 (Figure 7) was observed between the measured (gravimetrically measured mass collected on filter paper used in sampler) and the calculated mass of PM<sub>2.5</sub> from PMF when the analytical data of trace and toxic metals and anions were used as input matrix. The correlation between measured and calculated PM<sub>2.5</sub> mass is a reasonably significant value, *i.e.*, 66% (more than 50%). The unexplained 34% of the correlation may account for the carbonaceous aerosol (EC and OC), which were not included in this source apportionment study.



**Figure 7.** Correlation between measured and calculated PM<sub>2.5</sub> mass.

## Conclusions

It was observed that, during the study period, the PM<sub>2.5</sub> concentrations measured in Lahore ranged from 2 to 14 times higher than the prescribed limits of USEPA, *i.e.*, 35 µg m<sup>-3</sup> in winter and spring. The excess from standard limit in summer was observed ranging from 2 to 8 times while steeper decline from late June to September was observed. The alarmingly high levels of PM<sub>2.5</sub> must be affecting the health of local dwellers. Therefore, a well thought health study needs to be undertaken. The source apportionment results of winter 2005 and 2006 indicate that the major contributors of PM<sub>2.5</sub> during winter in Lahore are: secondary aerosols, industrial emissions, soil/road



dust and vehicular emissions. The high secondary aerosol contribution shows that in addition to local vehicular and industrial emissions, the city is also affected by trans-boundary air pollution sources. However, the prominent contribution from local vehicular and industrial emissions cannot be neglected. The trace metals Cr, Mo and Ni from industrial source profile showed higher concentrations in daytime as compared to that in the evening and night. Zn and Pb concentrations were also recorded higher in the daytime. Although the Pb concentration was higher than that observed in 2000, however, there was a decrease in vehicular Pb concentration as compared to that reported earlier. The concentrations of soil/road dust characteristic elements Al, Ca and K were found minimum in the daytime while higher in the evening and nighttime samples. It implies that soil/dust remains suspended in evening and night due to activities in the 2<sup>nd</sup> half of the day. To alleviate air pollution problem, the mass transport system should be in place to curtail ever-increasing demand of private cars and the use of fossil fuels should be reduced in industry.

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