Source Apportionment of PM\textsubscript{10} at an Urban Site of a South Asian Mega City

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ABSTRACT

In the present study, analysis and source apportionment of the elemental composition of PM\textsubscript{10} was conducted in the urban atmosphere of Karachi. Trace elements such as Ni, Ba, Cd, Ca, Mg, Cr, Mn, Fe, Co, Cu, Sr and Ti were measured. The PM\textsubscript{10} concentration ranged from 255 \(\mu\text{g m}^{-3}\) to 793 \(\mu\text{g m}^{-3}\), with an average of 438 \(\pm 161 \mu\text{g m}^{-3}\). Among the various elements analyzed, concentrations of Ca, Al and Fe were the highest (> 10000 ng m\(^{-3}\)), followed by Mg and S (> 1000 ng m\(^{-3}\)). Elements such as Zn, P, Cu, Pb, Mn, Ti, Sr and Ba demonstrated medium concentrations (> 100 ng m\(^{-3}\)), whereas the lowest concentrations were found for elements such as Cr, Ni and Se (> 10 ng m\(^{-3}\)). The Positive Matrix Factorization (PMF) model identified five possible factors that contributed to PM\textsubscript{10}, namely, biomass burning, coal combustion, resuspended road/soil dust, vehicular emissions and industrial dust. Industrial dust was the highest contributor (23.2%) to PM\textsubscript{10} followed by Biomass burning (23%), Vehicular emissions (22.2%), Coal combustion (21.7%) and Re-suspended dust (9.9%). A strong positive correlation (\(R^2 = 0.98\)) was observed between the model predicted PM\textsubscript{10} mass and the gravimetrically measured mass collected on filters.

Keywords: Particulate matter; Air pollution; Urban air quality; Elemental analysis; Source apportionment; Positive Matrix Factorization.

INTRODUCTION

Air pollutants is turning out to be highly problematic in developing countries like China, India and Pakistan, especially in mega cities like Beijing, Shanghai, Mumbai, Calcutta, Delhi, Lahore and Karachi. There has been a growing concern on almost all levels regarding airborne Particulate Matter (PM) in recent years. Anthropogenic sources which contribute to PM consist mainly of fossil fuel and biomass burning, industries and construction activities (Parekh et al., 2001). PM not only influences global climate change, but also has been associated with adverse health and environmetal impacts as reported in previous studies (Gwynn et al., 2000; Husain et al., 2007; Lodhi et al., 2009; Khan et al., 2010; Stone et al., 2010; Kaushar et al., 2013; Kim et al., 2015; Pope et al., 2015). Ghude et al. (2016) has reported premature mortality rate due to exposure of PM\textsubscript{2.5} and ozone concentration in India and Chate et al. (2013) has assessed the population exposure in India due to air pollutants during Common Wealth games in 2010. Atmospheric PM that has aerodynamic diameter less than or equal to 10 \(\mu\text{m}\) (PM\textsubscript{10}) has been studied intensively over the past few decades, because this size fraction is respirable is trapped by the alveoli of the lungs (Perez et al., 2008).

According to the reports of World Health Organization (WHO), there is a strong association between air pollution and cardiovascular and cancerous diseases, beyond respiratory diseases. Some regional festivals like new year Diwali also deteriorate the air quality in South Asian cities. Parkhi et al. (2016) and Beig et al. (2013) has reported the large variation in air quality during Diwali festivals and also estimate population exposure during these festivals. Trace elemental profiles have been studied extensively due to the numerous adverse effects of elements on human health (Sarnat et al., 2006; Liu et al., 2009; Freitas et al., 2010; Mavroidis and Chaloulakou, 2010; Anderson and Thundiyil, 2012). Like other developing countries, there has been a deep concern on airborne particulate matter levels in Pakistan. There are limited number studies that have discussed air

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quality in Karachi and some of these have been summarized as follows:

According to Husain et al. (2007) and Lodhi et al. (2009) some key anthropogenic activities such as transportation, agricultural activities, industries, biomass burning for cooking and construction activities are progressively deteriorating air quality in Karachi due to rapid and excessive contributions of particulate matter. Khwaja et al. (2012) have described the impact of bad air quality on the morbidity rate in the metropolitan city of an estimated population of 15 million. Another study by Khwaja et al. (2009) features measurements of the composition of urban aerosol using electron microscopy. They report that seven different types of sources namely, sea salt, cement, steel mill, fossil fuel, soil, biological, and mobile sources contributed to ambient air, whereas vehicular traffic emission was the major contributor. Shahid et al. (2016) have reported PM$_{2.5}$ concentration of 75 µg m$^{-3}$ in Karachi. Mansha et al. (2012) has described PM$_{2.5}$ concentration and corresponding source apportionment using PMF model at an urban site in Karachi and showed that the sea salt originated from the Arabian Sea while road dust, transport and industrial emissions are major contributors to secondary aerosols. Parekh et al. (2001) reported TSP loading in the ambient air of Karachi and observed an averaged TSP concentration of 668 µg m$^{-3}$. Ghauri et al. (2007) has established baseline levels in major urban cities including Karachi and reported TSP concentration at 410 µg m$^{-3}$ in Karachi. Yakub and Iqbal (2010) studied the risk of hyperhomocysteinemia due to lead (Pb) level in blood of a low income urban population in Karachi. Shahid et al. (2016) reported chemical characterization of PM$_{10}$ and PM$_{2.5}$ that included Elemental Carbon (EC), Organic Carbon (OC), soluble ions, anyhdro sugars and mass closure. All the studies mentioned above reported PM$_{10}$ and TSP concentrations only one Mansha et al. (2012) has used PMF model for PM$_{2.5}$ This study is an attempt to estimate the contribution of five different sectors in PM$_{10}$ mass using trace metals concentrations in PMF model.

MATERIALS AND METHODS

Study Area

Karachi is situated on coast of Arbaín Sea in south of Pakistan with geographic coordinates 24°51′N 67°02′E. The sampling site for this study is situated on the northwestern region of Karachi airport i.e., SUPARCO Headquarters as shown in Fig. 1. There are four different seasons in the region which includes pre-monsoon usually from April–June, monsoon from July to September, post-monsoon from October to December and winter from January–March. The annual average rainfall in Karachi is about 170 mm, and approximately 80% of the precipitation occurring between July to September. The air is usually hot and humid and dew point temperatures are usually above 21°C. Daytime temperatures can exceed 27°C throughout the year. The monthly mean wind magnitude and vectors (m s$^{-1}$) from

![Fig. 1. Location map.](image-url)
MERRA 2 satellite data at 10 m height during the study period i.e., March and April of year 2010 are provided in Fig. 2(a). According to Dutkiewicz et al. (2009) in Karachi, winds are comparatively calm in winter, but there is a strong influence of northeasterly continental air. The daily mean temperature at 2 m height over Karachi, during March and April of 2010 have been given in Fig. 2(b).

**Sampling**

PM samples were collected on Quartz fiber filters (Pall Corporation) at an urban site in Karachi as shown in Fig. 1 using a PM$_{10}$ high volume sampler. The sampling was done during the pre-monsoon season in the months of March–April 2009. The field blanks samples were also collected and considered for calculation procedures. In order to reduce the losses due to evaporation and volatization, the filter samples were kept in refrigeration prior to chemical analysis.

**Chemical Analysis**

Trace metals Ni, Ba, Cd, Ca, Mg, Cr, Mn, Fe, Co, Cu, Sr, and Ti were measured using 5% HNO$_3$ standard solution and Al, Pb, Zn, Se, P and S, 1000 mg L$^{-1}$ in 1%

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**Fig. 2(a).** Monthly mean wind magnitude and vectors (m s$^{-1}$) from MERRA 2 satellite data at 10 m height during March and April of 2010.

**Fig. 2(b).** Daily mean Temperature at 2 m height over Karachi, during March and April of 2010.
HNO₃ standard solution using Inductively coupled plasma atomic emission spectroscopy (ICP-AES), spectrometer. The method was described by Mukhtar and Limbeck (2012). The used methods were assessed for accuracy and the applicability by investigation of the certified reference material SRM 2709b (San Joaquin Soil) from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) which was processed and analyzed in the same way as the collected aerosol samples. The uncertainty in chemical analysis has been described in detail by Mukhtar and Limbeck (2012).

**Source Apportionment and Data Analysis**

Receptor models are widely used in various research areas because of their capability to handle large datasets. These models are applied so as to reduce the original datasets into lower dimensions, in order to analyze hidden information and to clarify the inconsistency of the measured variables. Particularly, in the field of environmental studies, the goals of receptor modelling are to estimate the number and composition of sources, to highlight any trends and/or correlations among observations and to identify potential tracer/indicator for pollutant sources. The positive matrix factorization (PMF) is a mathematical approach developed by Paatero and Tapper in (1994), and used for quantification of source contributions to the samples based on the composition or markers of the sources. PMF is a non data-sensitive method that can resolve inhomogeneous datasets without any univariate analysis. An error estimates (or weight) related to the data can be introduced in PMF e.g., in difficult data sets outliers or below-detection limit can be introduced in the model with some weight. The composition is determined by analytical techniques suitable for the particular medium and important species that are required to separate impacts. A speciated data set can be used as a data matrix X of i by j dimensions, where i is number of samples and j is chemical species that are measured with certain uncertainties s_j. The aim of this receptor model is to resolve the chemical mass balance (CMB) between source profiles and measured species concentrations, (Eq. (1)), with number of factors p, the species profile f_j of each source, and the amount of mass g_i contributed by each factor to each sample.

\[ x_j = \sum_{k=1}^{p} g_{ia} f_{kj} + e_j \]  

(1)

To analyze source profiles \( f_{kj} \) and contributions \( g_{ia} \), PMF uses a least squares method. The purpose of EPA PMF is to minimizes the sum of squares of standardized (residual divided by corresponding uncertainty value) residuals (Q).

\[ Q = \sum_{i=1}^{a} \sum_{j=1}^{b} \left( \frac{e_{ij}}{x_j} \right)^2 \]  

(2)

where, \( a = \) Total number of samples, \( b = \) Total number of species and \( s_j = \) Uncertainty for \( f_j \) species in the \( j \)th sample.

Eq. (1) can be defined as

\[ X = GF + E \]  

(3)

where \( X \) is Matrix of Measured data with dimension “no. of samples” \( M = \) “no. of species”.

\( G \) is Contributions Matrix with dimension “no. of samples” \( M \times \) “no. of factors”.

\( F \) is Source profiles Matrix with dimension “no. of species” \( \times \) “no. of factors”.

\( E \) is Matrix of residuals with dimension “no. of samples” \( M \times \) “no. of species”.

The uncertainty matrix ' \( S \)' and Matrix of the measured concentrations ' \( M \)' are inputs for PMF model, matrices ' \( G \)', ' \( F \)’ and ‘ \( E \)' are attained as output data. The source contribution matrix “ \( G \)’ was applied for source apportionment by considering the measured PM10 mass. For quantitative source apportionment, a scaling coefficient, \( y_i \), is presented in the model Eq. (1) as follows,

\[ x_j = \sum_{i=1}^{p} g_{ia} \frac{y_i}{y_j} f_{kj} + e_j \]  

(4)

so that \( y_i \) was measured by multi-linear regression of calculated source contribution against measured particulate matter mass. The constant of linear regression was assumed to be zero. Moreover,

\[ m_i = \sum_{j=1}^{b} y_j g_{ia} \]  

(5)

This approach was implemented in the EPA-PMF version 3.1.1, and applied to the analytical results of the collected PM10 samples to classify their sources and contributions to the receptor's site. After several runs, EPA-PMF 3.1.1 revealed the five most appropriate sources that have a minimum Q value.

**RESULTS AND DISCUSSION**

**Particulate Matter**

The average PM₁₀ concentration at the sampling site varied from 255 µg m⁻³ to 793 µg m⁻³ with an average of 438 ± 161 µg m⁻³. The minimum value of PM₁₀ is much higher than WHO limits (150 µg m⁻³) and also prescribed by Pakistan National Environmental Quality Standards (NEQS) for Ambient Air (Pak-EPA). The PM₁₀ concentrations at Karachi has been shown in Fig. 3. The observed PM₁₀ concentration of this study is quite high as compared to the studies conducted in most of the European cities. In Milan-Italy PM₁₀ levels of 81.4 µg m⁻³ and 91.9 µg m⁻³ were observed during day and night times respectively (Vecchi et al., 2007). Limbeck et al. (2009) reported PM₁₀ levels in Vienna-Austria at three different sites of Schaltberg (20.4 µg m⁻³), Kendlerstraße (27.7 µg m⁻³) and Rinnbockstraße (32.5 µg m⁻³). A mean PM₁₀ concentration of 34.4 µg m⁻³ was observed in an urban environment of Zaragoza city of Spain by Callen et al. (2013). In Ulsan-Korea PM₁₀ concentration of
50.5 µg m⁻³ was reported by Hieu and Lee (2010). Similarly, from Istanbul-Turkey the annual mean concentration of PM₁₀ of 39.1 µg m⁻³ was noted by Theodosi et al. (2010). The measured PM₁₀ level of 438 µg m⁻³ at the sampling site is comparable to the other reports from the Asian countries. Duan et al. (2007) reported PM₁₀ at an urban location of Guangzhou that ranged from 80 µg m⁻³ to 397 µg m⁻³. Karar and Gupta (2007) measured PM₁₀ mass concentrations ranged from 68.2 µg m⁻³ to 280.6 µg m⁻³ and 62.4 µg m⁻³ to 401 µg m⁻³ at the residential and industrial sites of Kolkata respectively. The PM₁₀ concentration levels measured in other cities of Pakistan (including Karachi) were also in the range of observation mentioned in the present study. Alam et al. (2015) reported PM₁₀ mean concentration of of 480 µg m⁻³ in the Peshawar city that is very close to PM₁₀ concentration in presented study. At Lahore, Pakistan an annual average PM₁₀ mass concentration of 340 µg m⁻³ was observed by Schneidemesser et al. (2010). Similarly, respirable PM₁₀ annual average concentration of 336 µg m⁻³ were reported by Stone et al. (2010). Likewise Alam et al. (2014) reported that PM₁₀ concentration at an urban site in Lahore varied from 254 µg m⁻³ to 555 µg m⁻³ with an average of 406 µg m⁻³. In Faisalabad city average PM₁₀ concentrations of 372 µg m⁻³, 283 µg m⁻³, 223 µg m⁻³ and 150 µg m⁻³ were observed at designated sites by Zafar et al. (2015). In a comparative study; PM₁₀ concentrations were assessed from four large cities (Karachi, Lahore, Rawalpindi and Peshawar) in Pakistan. From all these above cited studies it is obvious that PM₁₀ concentration in Karachi is comparable to other cities in the region but far higher than WHO limits and European cities.

**Trace Elements**

The total eighteen elements were analyzed in PM₁₀ samples collected from an urban area of Karachi. According to the observed concentration ranges elements have been divided into four groups as summarized in Table 1. In the first group three elements: Ca, Al and Fe have been place. Among this group, the concentration of Ca was highest with an average amount of 57260 ng m⁻³. It may originate from soil sources and sea salt spray. After Ca, Al and Fe have the highest average concentrations of 14280 ng m⁻³ and 13730 ng m⁻³ respectively. Both these elements are the dominant constituent of mineral dust. Apart from that, these elements can come from vehicular emissions, constructional activities and industrial emissions. Limbeck et al. (2009) has reported trace metals concentrations in Vienna that has less than 0.1 ng m⁻³ (Cd), approximately 200 ng m⁻³ (Zn), and mineral components ranging from 0.01 ng m⁻³ (Ca) to 16.3 ng m⁻³ (Si). Hieu et al. (2010) has reported Ca (3025 ng m⁻³) followed by Al (166 ng m⁻³) and Na (1523 ng m⁻³) in Ulsan, South Korea. Venkataraman et al. (2002) reported the size and chemical characteristics of aerosols measured at Mumbai and measured concentration of various elements like Al (3330 ng m⁻³), Si (70 ng m⁻³), Fe (1920 ng m⁻³), Mn (40 ng m⁻³) and Zn (770 ng m⁻³). Mansha et al. (2012) examined the source apportionment of PM in Karachi. The chemical analysis of these samples indicated that Al (31440 ng m⁻³), Ca (43910 ng m⁻³) and K (51360 ng m⁻³) as the major components of the samples during the summer season (Mansha et al., 2012).

Mg and S constitute the second group of elements with concentrations of 7350 ng m⁻³ and 6390 ng m⁻³, respectively. Mg may have its origin from earth crest, sea salt spray and industrial activities, whereas S may come from vehicular emissions and burning of fossil fuels.

Elements like Zn, P, Cu, Pb, Mn, Ti, Sr and Ba have been placed in the third group. The average concentrations of
Table 1. Summary of trace element levels (ng m\(^{-3}\)) in the airborne particulate matter (PM\(_{10}\)).

<table>
<thead>
<tr>
<th>Element</th>
<th>PM(_{10}) ((\mu g) m(^{-3}))</th>
<th>Minimum (ng m(^{-3}))</th>
<th>Maximum (ng m(^{-3}))</th>
<th>Average (ng m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>7050</td>
<td>7050</td>
<td>32200</td>
<td>14280</td>
</tr>
<tr>
<td>Ba</td>
<td>50</td>
<td>50</td>
<td>190</td>
<td>220</td>
</tr>
<tr>
<td>Ca</td>
<td>28200</td>
<td>&lt; LOD</td>
<td>91360</td>
<td>57260</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>Co</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>Cr</td>
<td>20</td>
<td>20</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Cu</td>
<td>190</td>
<td>190</td>
<td>540</td>
<td>420</td>
</tr>
<tr>
<td>Fe</td>
<td>4930</td>
<td>4930</td>
<td>31160</td>
<td>13730</td>
</tr>
<tr>
<td>Mg</td>
<td>3320</td>
<td>3320</td>
<td>14980</td>
<td>7350</td>
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<tr>
<td>Mn</td>
<td>130</td>
<td>130</td>
<td>730</td>
<td>370</td>
</tr>
<tr>
<td>Ni</td>
<td>10</td>
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<td>50</td>
<td>20</td>
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<tr>
<td>P</td>
<td>270</td>
<td>270</td>
<td>730</td>
<td>570</td>
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<tr>
<td>Pb</td>
<td>120</td>
<td>120</td>
<td>1160</td>
<td>410</td>
</tr>
<tr>
<td>S</td>
<td>3760</td>
<td>3760</td>
<td>10650</td>
<td>6390</td>
</tr>
<tr>
<td>Se</td>
<td>10</td>
<td>10</td>
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<td>10</td>
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<td>Sr</td>
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<td>110</td>
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<tr>
<td>Ti</td>
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<td>640</td>
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</tr>
<tr>
<td>Zn</td>
<td>180</td>
<td>180</td>
<td>1870</td>
<td>830</td>
</tr>
</tbody>
</table>

these elements were comparable and found to be: Zn (830 ng m\(^{-3}\)), P (570 ng m\(^{-3}\)), Cu (420 ng m\(^{-3}\)), Pb (410 ng m\(^{-3}\)), Mn (370 ng m\(^{-3}\)), Ti (260 ng m\(^{-3}\)), Sr (220 ng m\(^{-3}\)) and Ba (220 ng m\(^{-3}\)). These heavy elements affect the human health the most and are usually attributed to anthropogenic sources. Salam et al. (2003) determined trace elements in Dhaka Bangladesh and found that Fe (24800 ng m\(^{-3}\)), As (9.8 ng m\(^{-3}\)), Cd (2.5 ng m\(^{-3}\)), Cu (54 ng m\(^{-3}\)), Pb (280 ng m\(^{-3}\)), Zn (800 ng m\(^{-3}\)), Na (1300 ng m\(^{-3}\)), K (1600 ng m\(^{-3}\)), Ca (6800 ng m\(^{-3}\)) and Mg (42 ng m\(^{-3}\)) concentration in aerosol samples collected under pre-monsoon conditions. Alam et al. (2015) investigated the elemental profile in the aerosol samples collected from Peshawar. Elements analyzed were crustal Al (7590 ng m\(^{-3}\)), Si (3060 ng m\(^{-3}\)), Mg (4050 ng m\(^{-3}\)), Fe (8630 ng m\(^{-3}\)), traffic related Cu (1750 ng m\(^{-3}\)), Mn (190 ng m\(^{-3}\)), Pb (2200 ng m\(^{-3}\)), Zn (1420 ng m\(^{-3}\)), Ba (60 ng m\(^{-3}\)) and mixed sources of soils and pollution like Sr (1110 ng m\(^{-3}\)), Cr (550 ng m\(^{-3}\)), K (2570 ng m\(^{-3}\)) and Na (5280 ng m\(^{-3}\)). Alam et al. (2014) described the characterization of crustal Al (12000 ng m\(^{-3}\)), Ca (18000 ng m\(^{-3}\)), Mg (5690 ng m\(^{-3}\)), Fe (10200 ng m\(^{-3}\)), S (5600 ng m\(^{-3}\)), and Ti (210 ng m\(^{-3}\)) and trace metals As (5 ng m\(^{-3}\)), Ba (111 ng m\(^{-3}\)), Cd (40 ng m\(^{-3}\)), Cr (30 ng m\(^{-3}\)), Cu (230 ng m\(^{-3}\)), Mn (290 ng m\(^{-3}\)), Ni (10 ng m\(^{-3}\)), Pb (920 ng m\(^{-3}\)), Sn (10 ng m\(^{-3}\)) and Zn (3020 ng m\(^{-3}\)) in PM\(_{10}\) samples collected from an urban site in Lahore. Ali and Athar (2010) monitored the ambient air quality of Lahore and determined PM10 and Pb levels. The concentration of Pb at different locations of the city was found in the range of 1900 to 7200 ng m\(^{-3}\). Niaz et al. (2012) evaluated the air pollutant Lead (Pb) in the Faisalabad city. The Pb contents of 4330 ng m\(^{-3}\) were recorded during whole study period Ghauri et al. (2007) determined lead contents from various sites in the urban area of Karachi with concentrations which ranged from 3030–5870 ng m\(^{-3}\).

The least concentrations were measured for elements placed in the fourth group. This included heavy metals like Cr, Ni, Se and found to be 50 ng m\(^{-3}\), 20 ng m\(^{-3}\) and 10 ng m\(^{-3}\) respectively. The trace concentration of these metals were observed due to their lowest crustal abundance, while concentration of both Co and Cd were lower than the detection limit. Das et al. (2015) measured elemental composition of particulate matter from 16 locations in Greater Kolkata. In PM\(_{10}\) size fractions Fe (11242 ng m\(^{-3}\)), Na (2393 ng m\(^{-3}\)), Al (5223 ng m\(^{-3}\)), K (3486 ng m\(^{-3}\)), Ca (7610 ng m\(^{-3}\)) were present in high concentrations, Mn (249 ng m\(^{-3}\)), Zn (761 ng m\(^{-3}\)) and Pb (394 ng m\(^{-3}\)) demonstrated medium concentrations, while V (18 ng m\(^{-3}\)), Co (4.1 ng m\(^{-3}\)), Ni (48 ng m\(^{-3}\)), Mo (15 ng m\(^{-3}\)), Cd (8.6 ng m\(^{-3}\)), Sn (21 ng m\(^{-3}\)) and Sb (10 ng m\(^{-3}\)) had low concentrations (Das et al., 2015).

Qadir et al. (2012) monitored geological and anthropogenic contributions to the urban air of Rawalpindi/Islamabad by trace elemental analysis. The presence of Yb, Cs, Sc, Rb, Co, Eu, La, Ba, Zn and Hf indicated their geological origin, while Se was considered to be arising from coal burning. The presence of Cr, Fe, Ce, Pb and Cd was attributed to anthropogenic activities (Qadir et al., 2012). Schneidemesser et al. (2010) measured detailed elemental composition in monthly composites from Lahore. Elemental analysis revealed extremely high concentrations of Pb (4400 ng m\(^{-3}\)), Zn (12000 ng m\(^{-3}\)), Cd (77 ng m\(^{-3}\)) and several other toxic metals (Schneidemesser et al., 2010). It is obvious from all above cited studies that elemental concentration at Karachi is much higher than European cities but comparable to region South Asian cities like Lahore, Peshawar, Mumbai. As most of the mega cities in South Asia experience worst air quality Gulia et al. (2015).

**Source Apportionment**

The Positive Matrix Factorization model (EPA PMF 3.1.1) was used for source apportionment. The analytical results of the PM\(_{10}\) samples collected during this study were used in the PMF model in order to identify sources
and their contributions to the total PM$_{10}$ mass. Based on the analytical results of the present study, five (05) factors were identified by PMF. The major sources of PM$_{10}$ were identified as biomass burning, coal combustion, re-suspension road/soil dust, vehicular emission, and industrial dust as shown in Fig. 4.

Lim et al. (2010) measured PM$_{10}$ concentration at Daejeon, Korea and identified nine different sources using PMF model that includes vehicle exhaust, soil, road dust, cement/construction, fossil fuel combustion and field burning, secondary aerosol, incineration/Pb related industry and metal smelting. Xie et al. (2008) determined source contributions to ambient PM$_{10}$ in Beijing, China with PMF model. Results indicated various sources of ambient PM$_{10}$ which were urban fugitive dust, crustal soil, coal combustion, secondary sulfate and nitrate, biomass burning with municipal incineration and vehicle emissions. Chueinta et al. (2000) reported fine and coarse fractions of airborne particulate matter in an urban residential area of metropolitan Bangkok. PMF revealed soil as the major source of airborne particulate matter for all data sets while other sources were motor vehicles, sea-salt spray, charcoal/wood burning and incineration contributions. Gu et al. (2011) used PMF method in order to identify the sources of ambient particles (PM$_{10}$) in Augsburg. For particulate chemical composition data, six factors were identified and associated with NaCl, secondary sulfate, biomass burning, secondary nitrate, traffic emission and re-suspended dust. Chan et al. (2008) collected PM samples from Melbourne, Sydney, Brisbane and Adelaide. Chan et al. (2008) reported eight different factors for the fine particle samples that includes combustion sources, crustal/soil dust, ammonium sulphates, nitrates, motor vehicles, marine aerosols, chloride depleted marine aerosols, and industry. While for the coarse particle four facts were recognized including marine aerosols, crustal/soil dust, nitrates and road side). Gupta et al. (2012) reported the PM sources of various sites within Mumbai city using PMF. Industrial area of Mahul showed sources such as residual oil combustion and paved road dust, traffic, coal fired boiler and nitrate sources. On the basis of the previous studies, as described earlier five factors were designed for source apportionment in PMF. These factors covers almost all aspects of available sources in the region and these factors includes biomass burning, coal combustion, re-suspended soil dust, vehicular emission and industrial combustion. The uncertainties values for chemical analysis used in PMF has been given in Table S1 as (Supplementary Material).

Factor-1 corresponds to biomass burning, and it has a major contribution from Cu, Co, Cd, Mg, and Ca, which results in 23% average mass of PM$_{10}$ as shown in Fig. 5. Recently, Alam et al. (2015) reported that household combustion emission in Peshawar contained biomass burning, which
contributed 12.8% of the total mass of PM$_{10}$. Secondary aerosol formation in rural areas of Lahore and Karachi could be largely from coal and biomass combustion (Lodhi et al., 2009; Mansha et al., 2012). Secondary aerosols contain nitrates and sulfates, which are emitted directly from natural as well as anthropogenic sources. Gugamsetty et al. (2012)
reported that biomass burning, wood burning, and vegetative burning produces high concentration of potassium and sulphate.

Factor-2 is identified as coal combustion, which has a major contribution from Zn, Sn, Cd, and Co. Coal combustion contributed 21.7% of the total mass of PM$_{10}$.

Factor-3, re-suspended road/soil dust contributed 9.9% of the total mass of PM$_{10}$. Re-suspended road/soil dust includes Ba, Al, Mg, Cu, Fe, Ca, Cr and Mn. Recent studies reported that re-suspended road/soil dust includes high concentration of Al, Ca, Fe, Mg, Mn, Sr, Ti, and Zn (Gugamsetty et al., 2012; Alam et al., 2014).

Factor-4 is responsible for vehicular emission, and has a major contribution from Pb, Sb, Zn, Sn, S, As and Cd, which results in 22.2% average mass of PM$_{10}$.

Factor-5 was identified as industrial dust, which contributed 23.2% of the total mass of PM$_{10}$. Industrial dust has a major contribution from Ni, Ti, Fe, Al, As and Mn. The PMF model result appears to be significantly good for the elemental data of particulate matter utilized. A strong positive correlation was observed between predicted and calculated mass of PM$_{10}$. The correlation ($R^2$) between the measured (gravimetrically measured mass collected on filter) and the model predicted PM$_{10}$ mass was 0.98 as shown in Fig. 6.

**CONCLUSION**

During the last few decades, there has been a rapid increase in population, urbanization, industrialization, transportation and other human activities, especially in developing countries. As a result, a sharp increase has occurred in both the variety and the quantity of air pollutants and their corresponding sources. The ambient air quality of Karachi is getting worse day by day due to a large number of factors, including industrialization, inefficient energy usage, tremendously high vehicular population, unobstructed solid waste burning, and utilization of ozone depleting species. The average PM$_{10}$ concentration measured at an urban site in Karachi was found to be many folds higher than the maximum daily and annual average concentrations of PM$_{10}$ prescribed as ambient-air guidelines by Pakistan NEQS and WHO. This measured value was also significantly higher than the limits given by European and United States ambient air quality standards. The observed and predicted values of PM$_{10}$ by PMF showed excellent correlation, with $R^2 = 0.98$, a mean bias of 0.22 and an RMSE value of 17.3 µg m$^{-3}$, demonstrating the accuracy of the model. The PMF study revealed that industrial dust is a major contributor (23.2%) to PM$_{10}$ followed by biomass burning (23%), Vehicular emissions (22.2%), Coal combustion (21.7%) and Re-suspended dust (9.9%).

![Fig. 6. Correlation between observed and predicted PM$_{10}$ concentration. The RMSE value is in µg m$^{-3}$.](image)
The extreme heat wave in June 2015 killed more than 1500 people in Karachi, and air pollution may have increased its impact in urban areas. In order to improve the air quality to safe levels, it is indeed high time for the establishment of continuous air monitoring stations, the complete characterization and source identification of pollutants, and the revision and implementation of air quality standards and legislation along with development of future strategies and effective planning.

**SUPPLEMENTARY MATERIAL**

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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