Particulate Matter and Its Source Apportionment in Peshawar, Northern Pakistan

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ABSTRACT

The present work is undertaken to investigate the aerosol volume and mass size distribution, concentration of Particulate Matter (PM) and its source apportionment by using GRIMM spectrometer data in the city of Peshawar, Northern Pakistan. In Peshawar, the concentration of Particulate matter (PM_{2.5} and PM_{10}) was noticed to increase day by day due to rapid urbanization and industrialization. The use of several transportation activities, construction of buildings, roads and overhead bridges has badly affected the atmosphere of this region. Positive Matrix Factorization (PMF) Model has been used to find out different sources of PM in Peshawar. The data were collected for twenty days in April 2011 for both morning and afternoon periods. It has been observed that the values of aerosol volume size distribution were almost high during morning and afternoon rush hours. The mean concentrations of PM_{10} and PM_{2.5} were determined to be 480 µg/m^{3} and 172 µg/m^{3}, respectively. A reasonably significant correlation (R^{2} = 0.65) was also found between observed and expected PM mass. The PMF result revealed five (05) sources in Peshawar, which were re-suspended road/soil dust, vehicular, industrial, brick kiln emission and household combustion emission.

Keywords: PM_{10}; Size distribution; Mass concentration; PMF; Peshawar.

INTRODUCTION

Aerosols can be defined as the solid particles or liquid droplets suspended in gas (air) (Reist, 1993; Hinds, 1999; Baron, 2001; Rodriguez et al., 2007; Alam et al., 2011b). They are roughly classified as smoke, smog, fume, mist, clouds, haze, fog, etc. (Hinds, 1999) and its classification is based on their chemical and physical properties, formation mechanism, size, shape, volume and intensity. The variation of aerosol’s diameter is of the order of a few nanometers to several micrometers (Alam et al., 2011b), and strongly depends on (a) sources (b) formation mechanism and (c) age of the particles (Rodriguez et al., 2007). The stability of aerosol particles depends on the particle size and its concentrations. Their life time may vary from a few seconds to a year and sometimes more. For example bigger particles remain suspended in the atmosphere for a few seconds and smaller particles may stay in the atmosphere for a year or more (Hinds, 1999). Due to their smaller size the aerosols ubiquity is high in the atmosphere and can be transferred over long distances (Lodhi et al., 2009). Two types of aerosol particles are of important concern; i.e., mono-disperse which consists of particles of the same size and polydisperse which consists of particles of different sizes. When aerosols are formed, they are usually polydisperse in nature (Reist, 1993). Aerosol particles are not always the same; they have some variations in shape, chemical composition and optical properties (Alam et al., 2011b). The equivalent diameter is referred as the diameter of a sphere having the same properties as the properties being measured for irregularly shaped particle (Baron, 2001). There are different shapes of aerosol particles, e.g., Isometric particles, Platelets, and fibers, but for convenience the spherical shape of aerosol is used (Reist, 1993).

To distinguish between anthropogenic and natural aerosols, it is crucial to analyze particle size distributions (Yang and Wenig, 2009; Alam et al., 2011b). Aerosol particles can be formed by natural sources (the particles present in the atmosphere without involving human activities) or anthropogenic (man-made) sources (Seinfeld and Pandis, 1998). The natural sources include suspended windblown dust particles, sea salt, volcanic emission, coniferous forest burning, soil dust, botanical debris, gas-to-particle conversion, photochemical etc. The anthropogenic sources include vehicular emission (i.e., bus, truck, car), Petroleum refineries, energy power plants, industrial emission (building, mining,
manufacture of cement, ceramic and bricks, and smelting), biomass burning, etc. (Hinds, 1999).

The aerosol particles, especially particulate matters play a very important role in changing the atmosphere both globally as well as regionally (Tian et al., 2005; IPCC, 2007; Alam et al., 2012; Gugamsetty et al., 2012). In recent years, tremendous damage to the environment in the world has caused because of the rapid population growth (Ilyas, 2005), increased industrial emission, vehicular emission, Ozone depletion (Hinds, 1999), deforestation, municipal wastes, etc. (Ilyas, 2007). Particulate matters appear to be responsible for severe rainfall in the southern parts of China at one hand and for the drought situation in its northern parts on the other hand (Sarkar et al., 2005; Alam et al., 2011a).

Beside the atmospheric variation, aerosols have some hazardous effect on human health, their ecosystems and other living organisms (Han et al., 2006; Begum et al., 2007; Brook et al., 2010; Liang et al., 2013).

Particulate matters (PM_{10} and PM_{2.5}) are inhalable, and are among the most critical and harmful pollutants in almost all urban areas of the world and their impacts on human health and ecology are the largest (Yadav et al., 2014).

The increased emissions of various pollutants, including carbonaceous species from the megacities of Asia deteriorated air quality and can impact climate on regional and global scales (Sahu et al., 2011).

The particulate matter, arising from their sources, may cover very long distances by wind, when these particles penetrate inside respirable duct and may cause severe breathing problems. Asthma and malfunctioning of Human lungs is caused by the excessive inhalation of particulate matter (Reponen et al., 2003). Some metallic particulate matter e.g., Mercury (Hg), zinc (Zn), and lead (Pb) can cause other chronic illnesses (Hopke et al., 2003). The effects of pollutants emitted from natural sources are very much smaller when compared to that caused by anthropogenic sources. One of these sources in the province of KPK is the Brick kilns where the intensive use of coal is made. Burning of coal increases the level of particulate matter considerably. Alam et al. (2011b) has stated that high concentrations of particulate matter can result in secondary effects that include heart failure, aggravation of diabetes, neurodegenerative diseases, skin problems, and can obviously also cause lung diseases. The inhalable particulate matter can affect the health and is of particular concern (Hinds, 1999). The short term (hours, days) exposure and long term (months, years) exposure to particulate matter adversely affect human health. The black carbon soot can damage human body cells and cause cancer (Lewtas, 2007).

The main purpose of the present study is to find the aerosol particle size distribution, mass size distribution and concentration of particulate matter by using their optical and physical properties and also to find the source apportionment of these particles for Peshawar city. To the best of author knowledge, aerosol source apportionment is reported for the first time in Peshawar, Northern, Pakistan. This may fill a geographic gap in our present knowledge pertaining to the size and nature of aerosols existing in the said region.

### DATA AND METHOD

#### Site Description

The capital city of the Khyber Pakhtunkhwa Province, Peshawar, is located in the northern part of Pakistan (34°02'N; 71°37'E) as shown in Fig. 1. The western side of Peshawar is flanked by hills. Its climate is tropical i.e., the mean maximum temperature of Peshawar is 40°C in summer (May–August) and 10°C in winter (November–March), while the relative humidity changes from 46% to 76% in June and August respectively. The average wind speed per year is 5 knots in December and 24 knots in June. In winter the northern areas which are about 245 km from Peshawar receive more precipitation as heavy snowfall. Most precipitation comes in some areas of Peshawar with the summer monsoons during July and August. The population of Peshawar has been greatly increased in the last three decades because of migration of people in search of jobs, education and better services. Peshawar has population from 3.5 to 4.0 million people, covered an area of around 1257 km². Peshawar is a big industrial city that includes food processing and the manufacture of cigarettes, firearms, cardboard, textiles, pharmaceuticals, furniture and paper. It is also a major center of the steel industry in Pakistan (Alam et al., 2011b).

The sampling was carried out in Gul Bahar at a height of 2 m from the ground. Gulbahar is situated on the eastern part of the city. The major industries are located at a distance of 8 km to the west of the sampling site.

#### Instrumentation

In the present study the GRIMM model 1.109 has been used to measure the aerosol concentration near the surface. The GRIMM is a compact and portable device which has been built for continuous measurement of airborne particles as well as for measuring the particle count distribution. This device can also be used for the measurement of aerosol particle number concentrations. The GRIMM possesses an integrated gravimetric filter on which all particles are collected after the optical measurement and thus are available for further analysis. The data can be displayed as particle concentration in the unit particle/liter and also as mass concentration in the unit µg/m³. The standardized dust mass fraction is in terms of occupational health respirable, thoracic and alveolic. A second dust mass fraction is named as PM_{10}, PM_{2.5} and PM_{1}. Inside the measuring cell the scattering light is being led directly and via a mirror with a wide opening angle onto the detector.

At the beginning of every measurement the device makes a self-test. Here all optical, pneumatical, and electronic components are being checked. The self-test lasts about 30 seconds. Afterwards the actual measurement starts and the Liquid Crystal Display (LCD) shows the data continuously after every six seconds. This enables real-time measurements of the dust concentration. At the same time all measuring results will be transmitted in certain, adjustable storage intervals to the storage card if one was inserted into the device. Via the built-in RS-232 interface data can be transmitted to an external PC or printer. Data output can
happen in intervals from 6 seconds up to 60 minutes. With online PC connection even intervals of 1, 2, or 3 seconds are possible.

The detector is positioned at the right angle of the incident laser beam. This setup of the detector is denominated as 90° scattering light detection. This optical alignment increases the scattering light collected by the detector and optimizes the signal-to-noise ratio. Therefore, even very small particles down to 0.25 µm can be detected. If a particle crosses the laser beam, it creates a light pulse. The signal of the detector diode will be classified into different size channels after accordant amplification. The GRIMM model 1.109 consists of 31 size channels which differentiate the particles within a potential diameter range between 0.25 µm to 32 µm. The comprehensive explanation of GRIMM was discussed by Alam et al. (2011b).

In the present study, the data were collected from 1st to 20th April, 2011. Before starting the measurements, the GRIMM was calibrated for particle size detection with reference unit whereby the observed deviation was less than 1%.

Elemental Analysis

By using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AMS by Thermo Scientific, USA) various metals like S, Si, Sr, Ti, Al, Cd, Cr, Cu, Fe, K, Mg, Na, Mn, Ni, P, Pb, Zn, B, Ba, Ca and Zr were determined in the PM10 samples. The collected samples were completely mineralized by using hydrofluoric acid, aqua regia, and a microwave digestion procedure carried out in a Multiwave 3000 digestion system (Anton Paar, Austria). The Multiwave 3000 digestion system (Anton Paar, Austria) was equipped with a 16MF100 Rotor and MF 100 digestion vessels. Until the final analysis, PM10 samples were diluted to about 30 mL. After the dilution of the sample, it was then stored in a refrigerator at 4°C. Introduction of the sample was performed by using a Thermo Scientific hydrofluoric acid resistant kit which consists of a torch with a ceramic center tube, polymeric Burgener Mira Mist nebulizer and polymeric cyclonic spray chamber. In a quartz apparatus ultra-pure water was obtained from de-ionized water. The auxiliary and cooling gas flow rates, nebulisation sample flow rate, and radio-frequency induction are the optimized instrumental
parameters, and these parameters were used for the analysis of the samples. In a quartz apparatus Ultra pure water was obtained through the distillation of the water. The chemicals like hydrochloric acid, nitric acid, perchloric acid, and hydrofluoric acid satisfied the quality requirements (Merck, Darmstadt, Germany). Merck provided standard solutions for the investigated metals and diluted from stock solutions. The Analysis of Certified Reference Material (NIST SRM 2709—San Joaquin Soil) evaluated the accuracy and applicability of the procedure, which was digested and analyzed in the same way as the aerosol samples were collected. The accuracy of procedure used was confirmed because there was a good agreement between certified contents and derived results from the investigated reference material (Alam et al., 2011b).

RESULTS AND DISCUSSION

This section deals with the discussion pertaining to aerosol size distribution, mass concentration, particulate matter concentration and source apportionment in Peshawar. The details of these are delineated in the following lines.

Aerosol Volume Size Distribution

Aerosol volume size distribution describes the physical properties of particle behavior. The behavior and atmospheric effects caused by aerosol particles strongly depend on the size of aerosol particles (More et al., 2013). The aerosol volume size distribution is a very important characteristic in understanding its effect on the environment.

From the particle physical properties, we can then differentiate between fine and coarse particle size. In the present study, aerosol volume size distribution of particles vs. diameter (µm) of the aerosol particles is shown in Figs. 2 to 3 for Peshawar city. The measurement of the number concentrations of aerosol particles was conceded out by using the GRIMM 1.109 model aerosol spectrometer.

The data shown in the Figures on abscissa represent the diameter of aerosol particles (in µm) by using lognormal scale and the data on the ordinate represented the particle volume size concentration (µm³/µm²) for 2nd and 17th April 2011 both in the morning and afternoon. The variation in volume size distribution shows a similar trend in the morning and afternoon data for April 2nd and 17th except the order of magnitude. Similar variation in volume size distribution occurred for other days (not shown here).

In the graph of 2nd April morning, Fig. 2, the volume size distribution increases from around 0.06 µm³/µm² at a diameter of 0.29 µm, shows a clear peak, passing through a trough followed by a sudden increase till 0.01 µm³/µm² for diameter of 0.54 µm. The next peak is observed for 0.192 µm³/µm² at a diameter 5.75 µm. The fourth and fifth peaks are observed for 0.203 µm³/µm² and 0.212 µm³/µm² at diameters of 11.25 µm and 18.75 µm respectively. Fig. 3 show the similar behaviour with different values of diameter and peaks which are tabulated in Table 1.

Peshawar is a very busy city where the main sources of aerosol particles are re-suspension road dust due to heavy traffic, vehicular emission, burning of fossil and diesel fuel in small factories and for the production of domestic and sport goods. The highest peaks in the graphs for volume size distribution are because of the road dust and vehicular emission in Peshawar. Cheung et al. (2013) concluded from his study that the volume size distribution was almost higher every day because of the industrial emission near the area under consideration for study i.e., Taipei, Taiwan.

In the present study there are actually four modes or peaks of volume size distribution, i.e., the first peak lies in the fine mode while the rest are displayed in coarse mode. The fine mode is for those aerosol particles whose diameter range is less than 2.5 µm whereas the coarse mode is attributed for those particles whose diameter range is 10 µm or greater than 10 µm. The sources of fine mode of aerosol particles are anthropogenic aerosol consisting of black carbon emission while the coarse mode contains re-suspension road dust, mineral dust and vehicular emission (Kanai et al., 2005).

Fig. 2. Aerosol volume size distribution in the Morning and Afternoon on 2nd April, 2011.
A detailed analysis of these graphs shows certain peaks. The summary of the magnitude of these peaks and the corresponding values of particle diameter (µm) have been depicted in Table 1. It can be seen from the Figures that the values of volume size distribution are increasing slowly and then decreases for both morning and afternoon. In all these graphs the values of aerosol volume size distribution were almost high during morning rush hours and afternoon because of the solar radiation which can evaporate the moisture from the aerosol particles especially from the soil dust particles. The similar result was explained for Taipei, Taiwan, by (Young et al., 2012).

The wind speed and direction may also cause the high concentration of aerosol volume size distribution in Peshawar. The meteorology variations such as wind direction and its speed are responsible for dilution and dispersion of pollutants in the air (Begum et al., 2013). The volume size distribution was observed very high in the morning rush hour periods i.e., 8:00 to 11:00 PKT (Pakistan standard time) and afternoon from 13:00 to 15:00 PKT. Similar results were reported by Kanai et al. (2005) who concluded from the study that there was an increase in coarse particles in spring because of a dust storm. It was also concluded that the volume size distribution was larger for the East Asia in 2002 as compared with the variation in 2001, 2003 and 2004.

In order to understand the origin of air masses and to assess the transport of aerosol in the measured area, we used Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003). Both Lagrangian as well as Eulerian approach calculations are carried out through this model. For the frame of reference in motion this model utilizes the Lagrangian approach and for three dimensional stationary frames, Eulerian approach is used. Detailed information about this model was discussed by Alam et al. (2010).

Six-day back trajectories were computed at several altitudes (1500 m, 1000 m, and 500 m) during the study period as shown in Fig. 4. These trajectories showed that air masses arrived in Peshawar from Turkey, Rostov, Sochi, Greece, Azarbaijan, and Iran. Some of these trajectories arrived from Afghanistan and entered the northern areas of Pakistan, then again travelled back to Noristan (Afghanistan) and finally reached Peshawar. Alam et al. (2011b) analyzed that air masses reached Peshawer from Afghanistan, carrying desert dust that contributed to local pollution, resulted high aerosol concentrations. Air masses that arrived in different cities of Pakistan were from the Arabian Sea, Dasht (Iran), Thar (India), Sahara desert, and Afghanistan (Alam et al., 2010, 2011c, 2014b). Alam et al. (2014b) reported that air masses from Afghanistan transported biomass burning...
aerosol to Swat, Pakistan, consequently amalgamate aerosol concentrations. Therefore, both local and external sources may be the possible reason of high aerosol concentrations in Peshawar.

**Aerosol Mass Size Distribution**

Aerosol mass concentration is one of the most important methods to explain the concentrations of aerosol particles. The aerosol mass distribution (also called number concentration) is also an important function of aerosol particle size (Hinds, 1999). The Figs. 5 to 6 shows the graphs of mass concentration ($\mu g/m^3$) vs. particle diameter ($\mu m$) for three days i.e., 2nd April, and 17th April, 2011 for Peshawar city. In all the graphs the particle diameter is taken on abscissa whereas the aerosol mass concentration is shown on the ordinate.

In all these graphs the first few low peaks reveal the concentration of fine particles whereas the remaining higher peaks show the concentration of coarse particles. The aerosol mass size distribution is depicted in Fig. 5 for 2nd April morning and afternoon, and the values of its peaks versus diameter are tabulated in Table 2. In Fig. 3 the first peak of mass size distribution is observed for 13.62 $\mu g/m^3$ at a diameter of 0.27 $\mu m$. Dubovik et al. (2002) reported the two different modes of aerosol particles, i.e., the fine particles with a diameter less than 0.6 $\mu m$ and the coarse mode with a diameter range greater than 0.6 $\mu m$. 

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![Six-day back trajectories for Peshawar, Pakistan during the study period.](image_url)
In the present study it is observed that the first peak lies in the fine mode whose particle range is 0.27–2.5 μm. In that fine mode there is a long trough after the first peak with very small fluctuations of mass size distribution. The second peak is observed at 4.17 μg/m³ at a diameter of 0.64 μm. The next peak of aerosol mass distribution is observed in coarse mode 2.5–10 μm at 51.10 μg/m³ for particle diameter of 5.75 μm. The fourth and fifth peaks are depicted as 51.59 μg/m³ and 41.57 μg/m³ against their diameters as 11.25 μm and 27.50 μm respectively. Similarly the detailed analysis of the
remaining graphs and their peak values against their diameter shows certain peaks. The magnitude of these peaks and the corresponding values of particle diameter, in µm, have been summarized in Table 2. All the other graphs (not shown here) have the similar behavior as discussed for Figs. 5 and 6.

It has been concluded that the high values of aerosol mass concentration in morning and late afternoon rush time in Peshawar city are due to the re-suspension road dust particles, industrial emission, brick kiln emission, vehicular emission etc. Similar result is reported by Alam et al. (2011b) who calculated the day time variation in mass concentration on 15th, 20th, 22nd, and 25th of March 2010 for fine and coarse particles and observed that “the hourly averaged mass concentrations for the fine mode showed fluctuations throughout the 24 hours of the day, with high concentrations during morning and late afternoon rush hours at all the selected sites.” It has also been observed during the study that the mass concentration was highest for Peshawar city when compared with other cities.

The high peaks in the graphs of aerosol mass size distribution for Peshawar indicate that the concentration in mass is very high during morning and late afternoon rush hours periods. Alam et al. (2011a) concluded from his study that the higher values of aerosol mass distribution are due to dust emission in summer and also because of some metrological parameters i.e., wind speed, wind direction, temperature, relative humidity and pressure. The same mass size distribution was calculated (Kanai et al., 2005) in which were employed the high volume air sampler to obtain the mass concentration of East Asia and concluded from the study that mass size distribution was very high followed by decrease for first intensive observation periods owing to the different meteorological conditions in China. Jain et al. (2007) also calculated the mass concentration on 6th, 9th, 13th July 2003 for three different cities i.e., Lei, Hanle, and Delhi in India. It was reported that the increased value in mass concentrations for the three cities during the morning were because of peak traffic time. The second highest value of mass concentration was noted during evening hours due to busy traffic flow followed by strong inversion.

**Particulate Matter (PM) Concentration**

The atmospheric particulate matters sometimes known as particulates or particulate matter (PM) consist of very tiny pieces of solid or liquid matter associated with the Earth’s atmosphere (Reist, 1993; Hinds, 1999; Baron, 2001). The composition of PM strongly depends on its sources, i.e., natural or anthropogenic (Hinds, 1999).

Fig. 7 revealed daily variations of PM for twenty days, i.e., from 1st April to 20th April 2011 for Peshawar city. The local time and PM concentration are taken respectively on x-axis and y-axes. The WHO permissible limit for PM$_{10}$ and PM$_{2.5}$ is 50 µg/m$^3$ and 25 µg/m$^3$ sequentially.

In Fig. 7, the PM concentrations of PM$_{10}$ and PM$_{2.5}$ were noticed to be very much higher during the morning and late afternoon rush hour period, and relatively low during early in the morning and night time. When compared with the WHO permissible limits for PM$_{10}$ and PM$_{2.5}$, it has been concluded that the air quality of Peshawar city is alarming. The values of PM$_{10}$ concentration for 1st April varied from 94 µg/m$^3$ to 811 µg/m$^3$ with an average of 485 ± 109 µg/m$^3$. Similarly the PM$_{2.5}$ concentration range is 261–36.9 µg/m$^3$ with a mean value of 168 ± 32 µg/m$^3$. The mean concentration of PM$_{10}$ and PM$_{2.5}$ for Peshawar city during the study period has been figured out to be respectively 480 ± 83 µg/m$^3$ and 172 ± 68 µg/m$^3$. The remaining values of mean PM concentrations for all days with standard deviations are tabulated in Table 3, also shown in Fig. 7.

Similar to the results reported by Alam et al. (2011b) for Peshawar city and it was reported that the mean PM$_{10}$ and PM$_{2.5}$ concentrations were 540 ± 120 µg/m$^3$ and 160 ± 55 µg/m$^3$, respectively. Khodeir et al. (2012) calculated the

![Fig. 7. PM$_{10}$ and PM$_{2.5}$ variations for Peshawar during the study period.](image-url)
elemental composition of PM$_{10}$ and PM$_{2.5}$ in Jeddah (Saudi Arabia) and concluded that at all study sites the mean PM concentration was 28.4 ± 25.4 µg/m$^3$ for PM$_{2.5}$ and 87.3 ± 47.3 µg/m$^3$ for PM$_{10}$ that exceeded the WHO permissible limit by 10 and 20 µg/m$^3$ respectively. Husain et al. (2007) observed the similar high PM concentration at Lahore, Pakistan and concluded that the mean PM$_{2.5}$ mass was 190 µg/m$^3$, and varied from 89 to 476 µg/m$^3$, far in excess of US proposed air quality standard of annual average of 15 µg/m$^3$. Yadav et al. (2014) found higher values of PM in Udaipur, India and reported that PM$_{10}$ and PM$_{2.5}$ concentrations were 121 ± 12 and 32 ± 6, respectively during April, 2010.

Fig. 7 evidences daily mean PM$_{10}$ and PM$_{2.5}$ variations during April, 2011. The highest concentrations noticed for PM$_{10}$ and PM$_{2.5}$ were 550.23 µg/m$^3$ and 187.602 µg/m$^3$ respectively on 2nd April 2011. The possible reason of high PM concentration in Peshawar city is attributed to traffic emission, soil dust, re-suspension of road dust, emission from small industries nearby the city, oil and gas burning for domestic chores. Similar reasons for high PM concentration were found by Alam et al. (2011b) who reported that the PM concentrations was very high at different sites of Pakistan during the morning and late afternoon due to the emission from heavy traffic, nearby industries. Pipal et al. (2011) reported very high PM concentration at Semi rural site of Agra, India, the PM$_{10}$ and PM$_{2.5}$ concentrations were reported to be 278 and 90 µg/m$^3$ respectively. Gugamsetty et al. (2012) calculated the PM concentration for Shinjung, Taiwan, and reported that the maximum values of PM$_{10}$ and PM$_{2.5}$ were 39.45 µg/m$^3$ and 21.82 µg/m$^3$ respectively.

Various elements like S, Si, Sr, Ti, Al, Cd, Cr, Cu, Fe, K, Mg, Na, Mn, Ni, P, Pb, Zn, Ba, Ca and Zr were determined in the PM$_{10}$ samples. The elemental concentrations of each element are presented in Table 4. Elements include crustal elements (Al, Si, Mg, Fe), traffic related elements (Cu, Fe, Mn, Pb, Zn, Ba), mixed sources of soils and pollution (Sr, Cr, K, Na) and secondary sulfate source (S) (Alam et al., 2011b). The average concentrations (µg/m$^3$) of Fe, Ca, Al, and Mg were 8.63 ± 0.27, 34.6 ± 0.92, 7.9 ± 0.77, and 4.05 ± 0.03, respectively. Similarly, the average concentrations (µg/m$^3$) of Pb, S, and Na were 2.20 ± 0.18, 2.63 ± 0.05, and 5.28 ± 0.11, respectively. Alam et al. (2011b) reported that average concentrations (µg/m$^3$) of Al, Ca, Fe, Pb, S in Peshawar were 7.38 ± 2.18, 43.5 ± 7.26, 8.56 ± 2.26, and 2.65 ± 0.67, respectively. Schneidemesser et al. (2010) found that Pb concentration in Lahore was 4.4 µg/m$^3$, which is higher than the values reported in the present study. Mansha et al. (2012) found higher concentrations (µg/m$^3$) of Al, Ca, K, and N during summer season in Karachi, these concentrations were 51.44 ± 22.69, 43.91 ± 19.05, 51.36 ± 32.32, and 60.22 ± 223.78, respectively. Concentrations of crustal elements (Al, Ca, Mg, Fe, S, and Ti) were recently reported by Alam et al. (2014a) in Lahore, Pakistan. The highest concentrations among the crustal elements were found for Ca, varying from 11.5 µg/m$^3$ to 32.4 µg/m$^3$.

### Table 3. Mean PM (PM$_{2.5}$ and PM$_{10}$) Concentrations with their Standard Deviation for all days in Peshawar.

| Days   | PM$_{10}$ (µg/m$^3$) with SD | PM$_{2.5}$ (µg/m$^3$) with SD |
|--------|-------------------------------|-------------------------------|
| 01/04/2011 | 485 ± 109 | 168 ± 32 |
| 02/04/2011 | 553 ± 101 | 169 ± 18 |
| 03/04/2011 | 512 ± 70 | 187 ± 19 |
| 04/04/2011 | 480 ± 83 | 176 ± 18 |
| 05/04/2011 | 510 ± 77 | 167 ± 18 |
| 06/04/2011 | 482 ± 67 | 176 ± 17 |
| 07/04/2011 | 510 ± 71 | 159 ± 18 |
| 08/04/2011 | 500 ± 86 | 180 ± 17 |
| 09/04/2011 | 496 ± 70 | 168 ± 16 |
| 10/04/2011 | 488 ± 98 | 168 ± 18 |
| 11/04/2011 | 520 ± 68 | 184 ± 19 |
| 12/04/2011 | 489 ± 103 | 177 ± 20 |
| 13/04/2011 | 450 ± 96 | 169 ± 19 |
| 14/04/2011 | 430 ± 106 | 171 ± 17 |
| 15/04/2011 | 479 ± 85 | 165 ± 19 |
| 16/04/2011 | 490 ± 81 | 181 ± 17 |
| 17/04/2011 | 410 ± 95 | 175 ± 17 |
| 18/04/2011 | 417 ± 101 | 170 ± 18 |
| 19/04/2011 | 447 ± 93 | 163 ± 19 |
| 20/04/2011 | 460 ± 81 | 166 ± 16 |

* SD = Standard deviation.

### Table 4. Average Elemental Concentrations of each element.

| Elements | Max (µg/m$^3$) | Min (µg/m$^3$) | Mean ± SD (µg/m$^3$) |
|----------|---------------|---------------|----------------------|
| Al       | 8.80          | 6.40          | 7.59 ± 0.77          |
| K        | 2.89          | 1.12          | 2.57 ± 0.25          |
| Ba       | 0.40          | 0.03          | 0.06 ± 0.08          |
| Ca       | 36.7          | 32.8          | 34.6 ± 0.92          |
| Cr       | 0.56          | 0.54          | 0.55 ± 0.00          |
| Cu       | 8.54          | 0.61          | 1.75 ± 1.06          |
| Fe       | 9.12          | 8.12          | 8.63 ± 0.27          |
| Mg       | 4.12          | 4.01          | 4.05 ± 0.03          |
| Mn       | 0.20          | 0.19          | 0.19 ± 0.00          |
| Si       | 3.12          | 3.01          | 3.06 ± 0.03          |
| P        | 0.39          | 0.32          | 0.36 ± 0.01          |
| Pb       | 2.91          | 2.09          | 2.20 ± 0.18          |
| S        | 2.71          | 2.47          | 2.63 ± 0.05          |
| Sr       | 0.13          | 0.10          | 1.11 ± 0.00          |
| Ti       | 0.23          | 0.20          | 0.20 ± 0.00          |
| Zn       | 1.55          | 1.29          | 1.42 ± 0.06          |
| Na       | 5.51          | 5.15          | 5.28 ± 0.11          |
| Ni       | 0.64          | 0.51          | 0.54 ± 0.03          |
| B        | 0.05          | 0.01          | 0.01 ± 0.00          |
Fig. 8. Source composition profiles for the particulate matter.

**SOURCE 1**

The first source, i.e., emission from small industries is considered as a big problem in Peshawar for so many years. This source is mainly characterized by CO$_2$ and some portion of smelting emission also contain Al, Ca, Cr, Zn, Fe, Mg, Pb, Sr, Ti, Zn, and Ni etc. (Begum *et al.*, 2013). In Peshawar the manufacturing of brass (petal) utensils, ploughing tools, machines spear parts and some other small industries requires coal, gas, rubber, dung cakes, for metal smelting (Hopke *et al.*, 2003; Mansha, 2012; Begum *et al.*, 2013). Beside the metal smelters there are small factories of white sugar and brown sugar (locally known as gur) production around Peshawar. The burning of coal, wood, rubber, plastic material, gas, petrol etc. produces large amount of smoke (Gordon, 1988) and bad smell which results in air pollution and visibility reduction. The percentage contribution is 12.9% of the total mass of PM concentration (see Fig. 9).

**SOURCE 2**

Household combustion emission in Peshawar city largely contains biomass burning for cooking and heating purposes for many years. This source is enriched mainly in Ca, Fe, Pb, S, Sr, Ti, Zn, Ni, and small concentrations of Al and Cu (Hailin *et al.*, 2008). This source, in our investigations, contributed 12.8% of the total mass of PM concentration (see Fig. 9). Coal combustion increases the concentration of BC and S in atmosphere. The shortage of natural gas supply for the last 5 years has increased the use of biomass burning as a fuel. This vigorous increase of biomass burning
in the region has increased the concentration of S and Pb. Saolapurkar and Sharma, (2006) showed that coal combustion has increased the concentration of Pb, Sr and Zn in the air.

**SOURCE 3**

Vehicular emission is characterized by Mn, Pb, Sr, Ti, and Zn. Vehicular emission contributed 27.4% of the total mass of PM$_{10}$. The crustal elements, Mg, Si, Fe and Al are also mixed with this source (Begum et al., 2007). The ambient air pollution is greatly caused by vehicular emission (Mansha et al., 2012). The highest concentration of elemental and organic carbon is caused by the frequent use of diesel engines in Peshawar city. Traffic in Peshawar is very heavy and congested, and most car driving is usually slow and jammed which emits continuous smoke and soot. These soot particles may cause the absorbing and scattering of the solar radiation (Begum et al., 2013). Emissions from incomplete combustion of fossil fuels and biomass burning are the major sources of black carbon in the atmosphere (Sahu et al., 2012).

The diesel combustion inside heavy duty vehicles increased the concentration of S and Pb in the atmosphere which is highly hazardous to human health and living organisms. The incessant use of motorbikes and motorcycles in Peshawar largely produces Zn from the combustion of lubricating oil (Begum et al., 2013). The combustion of substandard fuel (oil, petroleum, gas, coal etc.) used in vehicles of Peshawar may emit high concentration of Pb (Mansha et al., 2012) that causes chronic illness in human and animal health. The higher concentration of Zinc in Peshawar atmosphere is greatly caused by the sub standard tire wear and fuel burning (Klimaszewska et al., 2007) used in cars, buses, trucks, rickshaws, motorcycles etc. The average concentration of vehicular emission in Shinjung station, Taiwan was reported as 24.92% by Balakrishna et al. (2009).

**SOURCE 4**

Kiln emission is also an important source of PM concentration. This source has characteristics of Al, Ca, Cr, Fe, Mg, Pb, S, Zn, Ni and trace amount of crustal elements (Watson et al., 2001). In the operation of brick kiln waste materials like plastic, coal and wood are burnt and can cause the emission of Zn and Pb (Begum et al., 2013). The biomass burning inside kilns causes the emission of K in large quantity (Azad et al., 1998). There are a large number of brick kilns in the region of Peshawar in which a considerable amount of wood, rubber and coal is burnt. The production of bricks in Peshawar is usually done during the dry season and causes higher PM concentration and air pollution (Gordon, 1988). The emission from kiln contributes 11% of the total fine mass. The coal that is burnt in kiln contains 4 to 6% sulphur (Begum et al., 2013).

**SOURCE 5**

Re-suspended road/soil dust includes very high concentrations of Al, Ca, Fe, Mg, Mn, Sr, Ti, and Zn (Gugamsetty et al., 2012; Watson et al., 2001). The average contribution of re-suspended road/soil dust was calculated as 35.9% of the total PM$_{10}$ mass. These concentrations may be from broken and muddy roads, under construction road side buildings, unpaved and grass free belts (Lodhi et al., 2009). Alam et al. (2014a) reported that industrial dust contributed 18.2% of the total PM$_{10}$ mass in Lahore. Mansha et al. (2012) found that the dust contribution was 16.1% of the total PM$_{2.5}$ mass in Karachi. The rigorous construction of houses, buildings and roads may produce Ca (Lough et al., 2005) in Peshawar city. The concentration of soil dust and road dust is usually higher in the dry season and minimum during rainy days (Begum et al., 2007). Bhave et al. (2001) and Ho et al. (2003) investigated that soil dust...
and road dust contain S and BC in addition to other soil constituent particles. The concentration of Pb in the urban regions was found to be almost 20 times higher than the rural sites. The soil/road re-suspended dust elements such as Al, Ca, Ti, Mg and Fe are the main constituent of air born fugitive and soil dust. Lough et al. (2005) showed that Al, Ca, Ti, Mg and Fe metals are the main contributors to coarse particle fraction. Very small contribution from Pb was also reported in the re-suspended road/soil dust source.

Source Contribution to PM Mass

The results of source apportionment are displayed in Figs. 8 and 9 indicating the high contribution of vehicular emission, road/soil re-suspended aerosols, brick kiln emission, small industrial emission and household combustion emission towards PM mass.

The total contributions of vehicular emission was 27.4%, whereas, re-suspended road/soil dust contributed up to 35.9%, followed by kiln emission which was 11%, small industrial emission (coal burning, smelting, etc.) contributed 12.9% and 12.8% contribution from the combustion emission (Gas, coal, biomass, etc.) inside houses. The source apportionment results evidence that the re-suspended road/soil dust emissions were dominant among all sources. The distant particulate aerosols from distant sources also affected Peshawar city.

Fig. 10 showed the value of R², 0.65, between observed and expected PM masses. It is a reasonably significant (more than 50%) correlation. The remaining unexplained 35% correlation value may consist of secondary and carbonaceous (OC & EC) that were not included in the present source apportionment study.

CONCLUSION

In Peshawar, Pakistan, the concentration of Particulate Matter (PM₂.₅ and PM₁₀) is increasing day by day due to rapid urbanization and industrialization. The use of numerous transportation activities, construction of buildings, construction of roads and overhead bridges in Peshawar has badly affected the atmosphere. These PM pollutants are mostly emitted from anthropogenic sources and predominantly from transportation activities. This air pollutant is very harmful to public health and environment when it is compared to other pollutants.

The work presented in this research was carried out to find out the aerosol volume size distribution, aerosol mass size distribution, concentration of PM and finally its source apportionment. The data has been taken by using GRIMM spectrometer instrument in Peshawar, northern Pakistan. Positive Matrix Factorization (PMF) Model has been used to find out different sources of PM in Peshawar.

It has been observed that the values of aerosol volume size distribution were almost high during morning rush hours and afternoon because of the solar radiation which can evaporate the moisture from the aerosol particles especially from the soil dust particles. The high values of aerosol mass concentration in morning and late afternoon rush time in Peshawar city are due to the re-suspension road dust particles, industrial emission, brick kiln emission, vehicular emission and household combustion emissions.

The maximum and minimum values of PM₁₀ were found to be 553 ± 101 µg/m³ and 410 ± 95 µg/m³ respectively. Similarly the maximum and minimum values for PM₂.₅ were reported to be 187 ± 19 µg/m³ and 159 ± 18 µg/m³ respectively. The air quality in Peshawar city is found to be alarming, when compared with the WHO permissible limits for PM₁₀ and PM₂.₅. The 24-h averaged PM₂.₅ and PM₁₀ concentrations measured in Peshawar were 6 to 9 times higher than the existing WHO thresholds. Therefore, regular monitoring is needed, but even more urgent is the quest for actions to mitigate the high levels of air pollution (Alam et al., 2011b). The PMF result revealed five (05) sources in Peshawar, which were re-suspended road/soil dust (35.9% of PM), vehicular emission (27.4% of PM), industrial emission (12.9% of PM), brick kiln emission (11% of PM) and household combustion emission (12.8% of the total PM₁₀ mass). Long-term datasets for this region will be used in future studies in order to better understand the impacts of aerosol size distribution on local and regional climate system of Pakistan.

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