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Study of chemical characteristics of particulate matter concentrations in Riyadh, Saudi Arabia

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ABSTRACT

Particulate matter samples were collected from several locations during September 2011 and September 2012 in Riyadh, Saudi Arabia. In addition to determining particulate matter (as PM_{10}) concentrations, the samples were analyzed for several metals and ions. PM concentration was approximately 3 times higher than the Country's ambient air quality standards respectively. Metals and ions contributed to about 21.5% and 16.2% of the PM concentrations respectively. Summer vs. winter comparison showed that PM concentrations were approximately 84% higher in summer and the crustal matter species such as Fe, Mn, Ti, Ca^{+2}, Mg^{+2} increased several folds in summer, primarily attributed to dust storms. The weekdays PM concentrations were 17% more than the weekend concentrations, indicating weekday activities contribute to the concentrations. The dust storms lead to over 200% increase in the PM and some elements primarily Al, Fe, Mg and Ca. Spatial comparison at industrial and residential locations revealed about 60% increase in PM concentrations and substantial increase in Zn, Mn, B, Mg, Fe, and Al and the ions K^+, SO_4^{--}, and Cl^- at industrial locations. Bivariate correlations among the metals and ions demonstrated that strong correlation existed between Al, Fe, Mg, K and Mn suggesting a common origin for these species i.e. the crustal mineral aerosols. The correlations among cations and anions implied the presence of compounds in the atmosphere such as $CaSO_4$, $(NH_4)_2SO_4$, KCl, KSO_4, and also to some extent $MgSO_4$. An investigation of ionic ratios revealed that ratios SO_4^{-2}/NO_3^-, Ca^{+2}/K^+, and Ca^{+2}/Na^+ could be possible indicators to identify scenarios industrial over residential locations, storm days over no storm days and summer over winter periods respectively.

Keywords: *PM_{10}, metals and ionic composition, spatial and temporal indicators, Riyadh*

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1. Introduction

The importance of air pollution research further increases as International Agency for Research on Cancer (IARC), an agency of World Health Organization (WHO) has classified it as carcinogenic. While air pollution is a complex mixture of many gases and compounds, Particulate Matter (PM) in the air has been particularly identified as the main component causing the cancer (IARC, 2013). Many studies have revealed an increasing risk of lung cancer, morbidity, mortality and other diseases with increasing levels of exposure to outdoor air pollution and particulate matter (Dockery, 2001; Lin et al., 2002; Pope et al., 2002; Brunekreef and Forsberg, 2005; Sioutas et al., 2005; Nieuwenhuijsen et al., 2007; Perez et al., 2012; Fossati et al., 2014; Tao et al., 2014). The presence of particulate matters in atmosphere also impacts the environment by the reduction of visibility, formation of clouds, effecting heat transfer in the atmosphere, thereby contributing to the climate change (Furuta et al., 2005; Wang et al., 2013).

Understanding the ionic chemistry of the atmospheric PM is important to study its relative effects on human health and environment (Horvath, 1996; Tsai and Cheng, 1999; Schichtel et al., 2001; Tsai et al., 2003; Yadav et al., 2003; Lee et al., 2005). Several studies have focused on the detailed analysis of atmospheric aerosols for metals and water soluble ions (Kadowaki, 1976; Wall et al., 1988; Kim and Fergusson, 1994; Kerminen et al., 2001; Venkataraman et al., 2001; Hsu et al., 2008; Shen et al., 2008) and it has been shown that the compositions show significant spatial and temporal variation (Prospero et al., 2002; Reid et al., 2005; Wang et al., 2005; Shen et al., 2009).

Riyadh is the capital and largest city of Saudi Arabia with a population of over 5 million. In recent years, due to strong economic growth, initiation of massive construction projects, expansion of industries, and increase in traffic flow, severely affected the atmospheric environment, particularly contamination by atmospheric particulate matter. The hot and arid climate in the city with events of severe summer dust storms increases enormously the PM concentration in the atmosphere. While the adverse health effects of the PM are evident, it has been particularly shown that the exposure to the dust caused general health illness, sleep and psychological disturbances in the Riyadh city (Meo et al., 2013). Two earlier studies have also identified that the presence of heavy metal Pb in the atmosphere and was attributed to the traffic density in the city (El–Shobokshy, 1984; Al–Saleh and Taylor, 1994). The impact of dust storms on aerosol optical properties was studied for Saudi Arabia and it was found that the dust storm events significantly changes the optical properties of the aerosol (Maghrabi et al., 2011; Alharbi et al., 2013). A relatively detailed study was undertaken by Rushdi et al. (2013), PM samples were collected from June 2006 to May 2007 for determining its chemical composition. The results showed that the PM concentrations were higher for PM_{10} compared to $PM_{2.5}$, indicating that the major PM source was local dust. The enrichment factor approach was used to characterize the chemical composition and it was shown that sulfur and nickel were both enriched in PM. The concentration of PM was found higher in year 2007 when compared to the year 2006.

In order to further comprehend the current state of air pollution and determine the levels of PM and analyze its chemistry, a comprehensive monitoring program was undertaken. Riyadh city was divided into 16 grids and the necessary in–situ data and PM samples (as PM_{10}) were collected for about a year (September 2011 to September 2012). The samples were analyzed for twenty metals (As, Co, Te, Mo, V, Ni, Cr, Cu, Cd, Li, Pb, Zn, Mn, B, K, Na, Mg, Fe, Al), five cations (NH_4^+, Ca^{+2}, Mg^{+2}, Na^+, K^+) and three anions (Cl^-, NO_3^-, SO_4^{-2}). The objectives of this paper are (1) to present the results of the analysis of metal and ions of the PM samples, (2) to study the temporal and spatial variation i.e. summer vs. winter, weekdays vs. weekends and storm days vs. normal days and industrial locations vs. residential locations, (3) to identify possible chemical forms that might exist in the atmosphere using bivariate correlation analysis among the metals and ions, and (4) to investigate the ratios of the ions and correlate to the various scenarios.

2. Materials and Methods

2.1. Sampling

To capture the complete scenario, Riyadh city was divided into 16 grids as shown in Figure S1 (see the Supporting Material, SM). Table S1 describes each grid and its classification. The grids were mainly classified as industrial (predominantly industries in the area) and residential (largely residential areas). Two mobile stations were employed to collect the samples from various locations at different times. Each sampling was performed at each grid for 24 hours at a flow rate of 16.67 Lpm (1 m^3/h) on quartz microfiber filter discs (47 mm) using PQ–100 particulate samplers with PM_{10} inlet (BGI Incorp. USA) and the air inlet was located 2.5 m above the ground level. Prior to sampling, the filters were baked at 300–550 °C for at least 4 h to remove any traces of organics. After sampling, the filters were packed in petri dishes covered with aluminum foil to protect them from sunlight. Filters were conditioned in a desiccator at constant temperature (23–25 °C) and relative humidity (40–50%) before and after sampling and the initial and final weight of each filter disks was recorded to determine particulate mass collected over the sampling period and stored in a refrigerator (–1 °C).

Apart from PQ–100 Particulate samplers, both mobile stations equipped with TEOM–1400a (Thermo Fisher Scientific, Inc.) ambient Particulate Monitor equipped with Automatic Cartridge Collection Unit (ACCU) for particulate collection on quartz microfiber filter discs (47 mm). In one station, the monitor has fitted with PM_{10} inlet while in the other station the monitor has fitted with $PM_{2.5}$ inlet. The total flow rate in the system was 16.67 Lpm and this flow has been bifurcated in two channels. The channel which goes to TEOM unit maintains 3.0 Lpm and the other channel to ACCU unit maintains 13.67 Lpm. The $PM_{2.5}$ samples collected from ACCU unit were utilized for the analysis of ionic concentrations in addition to samples collected with PQ–100 particulate samplers. For the analysis of elemental concentrations, only PM_{10} samples collected with PQ–100 particulate samplers were utilized.

2.2. Chemical analysis

Sample extraction. Water soluble ionic components (NH_4^+, Ca^{+2}, Mg^{+2}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{-2} and Silica) associated with sampled particulate were determined by aqueous extraction method. Each sample filter disc was cut into pieces and taken into polypropylene tube (50 mL) separately containing 20 mL of deionized water. The tubes containing samples were sonicated for one hour, and left for 1 hour to settle down the filter fragments, then sonication continued for another 30 minutes. After sonication the samples were subjected to centrifugation at 3 000 rpm in order to settle the particles and the supernatant extract finally filtered through Acrodisc (0.45 µm) with disposable syringe.

Ionic analysis. Anions (Cl^-, NO_3^- and SO_4^{-2}) were analyzed using Shimadzu Ion–Chromatography system with CDD–6A conductivity detector and Shim pack IC– A1 column. Mobile phase containing 2.5 mM phthalic acid and 2.4 mM tris– (hydroxymethyl) aminomethane was used with a flow rate of 1.5 mL/min at 40 °C. The instrument was calibrated with Dionex anion standard (Dionex Seven Anion standard, no. 057590, Thermo Fisher Sci., USA). Each sample analyzed in triplicate and average concentration was recorded.

For cations (NH_4^+, K^+, Mg^{+2}, Na^+ and Ca^{+2}), Shim pack IC–C3 (100 mm x 4.6 mm ID) column was used and oxalic acid (3.0 mM) mobile phase with a flow rate of 1.0 mL/min at 40 °C was applied. Calibration was done with Dionex six cation standard (no. 046070, Thermo Fisher Sci, USA).

Analysis of silica. Analysis of Silica was performed utilizing 5 mL of same aqueous extract which was prepared for ionic analysis following Silicomolybdate method (no. 8185) by DR/4000 Spectrophotometer (Program no. 3350) as recommended by HACH Co. USA.

Elemental analysis. Microwave assisted acid extraction was performed following the USEPA Compendium Method IO–3.1 using advanced composite vessels in MDS 2100 microwave digestion system (CEM Crop, UK). Extracting acid was prepared in a 1 L volumetric flask, combining in order and mixing 500 mL of deionized distilled water, 55.5 mL of concentrated nitric acid and 167.5 mL of concentrated hydrochloric acid, cooled and diluted to 1 L with deionized distilled water. After cutting the filter papers into small pieces, 20 mL of extracting acid was added. The microwave digestion system was programmed to 50% power, 30 psi pressure for 30 minutes for digestion. Aliquot of digested samples was filtered by Acrodisc syringe filters (0.2 µm). Blank samples were also run simultaneously. Analysis of elements was carried out following Compendium Method IO–3.4. Targeted elemental analysis was finally performed by using ICP–OES (Optima–2000DV, Perkin Elmer, USA). Calibrations of elements were performed using ICP Multi Elemental Standard solution VI CertiPUR (Merck Co.) as the reference material. Every sample was analyzed in triplicate and the mean concentration of each metal was calculated.

2.3. Climate

During summer the climate conditions in Riyadh city are predominantly hot and dry while winters are cold. During the sampling period, the maximum temperature reached as high as 50 °C recorded during July and minimum temperature was about 3 °C during December. The average temperature in summer and winter was 24.5 °C and 14.1 °C respectively. Highest relative humidity (about 47%) occurred in December while the lowest value of 12% was observed in July. Seasonal variation of wind speed is slight, the average summer wind speed occurred in June was 4.4 m/s and the month of October recorded as 2.5 m/s. Winds were mainly West–South–Westerly (WSW) during summer and Westerly (W) in winter.

3. Results and Discussion

3.1. PM concentration and chemical composition

A total of 185 PM samples were collected over a period of one year, these samples were analyzed for various metals and ions. Table S2 (see the SM) presents the summary statistics of PM, metals and ions for summer (April and September), winter (October to March), and the average for the whole year. Annual PM concentrations were in the range of 39.7–1 803 µg/m^3 with a mean and standard deviation of 289.24±228.5 µg/m^3. The average monthly variation of PM and annual average are shown in Figure 1. The annual average PM concentration was over 3 times higher than the ambient air quality limits (80 µg/m^3) recommended by the country's environmental standards (PME, 2011). The average PM