Air quality and elemental enrichment factors of aerosol particulate matter in Riyadh City, Saudi Arabia

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Abstract:

Air particulate matter (PM) samples were collected from June 2006 to May 2007 for determination chemical elements. PM samples were taken in two size fractions ($PM_{2.5}$ and PM_{10}) with MiniVolume air samplers on rooftops of various buildings (15-25 m above ground) in the city of Riyadh. The samples were subjected to XRF analysis to measure major (Na, Mg, Al, K, Ca, Si, P, S and Fe) and trace elements (Mn, Ni, Cu, Zn, and Ba). 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. Also the spatial distribution with high PM concentrations was observed in the south and southeast of the city and the lowest levels were in the center and northeast of the city. This spatial distribution was attributed to different factors such as wind direction and velocity, emission from cement factories, presence of buildings, trees and paved streets that reduce the amount of dust resuspended into the atmosphere. The air quality of the city was found to range from good to hazardous based on $PM_{2.5}$ and from good to very hazardous based on PM_{10}. The element enrichment factors revealed two element groups according to their changing spatial behavior. The first group showed no significant spatial changes indicating they have the same common source. The second group (mainly S and Ni) exhibited significant changes as expected from anthropogenic inputs. The origin of S is possibly a combination of minerals ($CaSO_4$) and fossil fuel combustion. The source of Ni is probably from fossil fuel combustion.

Keywords: $PM_{2.5}$, PM_{10}, Riyadh, Air quality, Major and trace elements

1. Introduction

The occurrence of aerosol particulate matter (PM) in the atmosphere is a result of anthropogenic (e.g. traffic emissions, urban activities, construction activities, industries, etc.) and natural (e.g. resuspension, wild fires and direct abrasion of agricultural soil) inputs and secondary PM formation by atmospheric chemical reactions (e.g. ozonization) (Capri, 2004; Dunnivant and Anders, 2006; Fellenberg, 2000; Newton, 2004; Prospero et al., 2002; Seinfeld and Pandis, 1998; Sodhi, 2005). Atmospheric transport of dust advected from desert and semi-arid regions is another source of aerosol PM (Chiapello et al., 1995, 1997; Ellis and Merrill, 1995; Koelemeijer et al., 2006; Mochida et al., 2003; Prospero et al., 1995, Simoneit and Elias, 2000; Swap et al., 1992). Moreover, the atmospheric dust and fine particle loadings often change rapidly over space and time (Prospero et al., 1996; Reid et al., 2005). During a desert storm event, dust and fine particle mass loadings can change by orders-of-magnitude in a matter of hours (Reid et al., 2005; Tindale and Pease, 1999). The loading variations also change the chemical components of the dusts and fine particles. These changes are due to the transit of the dust plumes over developed regions, which can add pollutants and other atmospheric constituents (Ashbaugh et al., 2003; El-Shobokshy and Al-Saedi, 1993; Hindy and Baghdady, 1996; Pilcher 1999; Reid et al., 2005; Sabba Rao and Al-Yamani, 1999; Savoie et al., 1987). Transport of mineral dust and particulate matter from the Arabian Peninsula not only affects climate change over a large region (El-Shobokshy and Al-Saedi, 1993; Harrison et al., 2001; Prospero and Lamb, 2003; Prospero et al., 1996; Reid et al., 2005), but also biodiversity and human health (Barnard, 1998; Batjargal et al., 2006).

Epidemiological research indicates that there is an increase in human morbidity and mortality with exposure to inhaled airborne PM (Brunekreef and

Forsberg, 2005; Dockery et al., 1993; Samet et al., 2000; Schwartz et al., 1996; Sioutas et al., 2005). Inhaled PM (< 2.5μm) can be deposited in the lung and migrate from there by systemic circulation to the heart, as well as to more distal organs (Nemmar et al., 2002). Coarser PM (< 10 μm) has also been shown to be mutagenic (Buschini et al., 2001; Pagano et al., 1996; Shi et al., 2006) and has been linked to abnormal fluctuations in heart rate in older adults (Gong et al., 2004; Lipsett et al., 2006). In addition, coarse PM generated from burning agricultural waste has been associated with increases in respiratory problems in children and the elderly (Cançado et al., 2006), as well as farmers (McCurdy et al., 1996). A recent investigation of children living in Toronto revealed significantly elevated rates of hospitalizations from respiratory infections associated with ambient $PM_{10-2.5}$ compared with any other measured pollutant or meteorological condition (Lin et al., 2002). Similarly, the strongest association between air pollutants and respiratory symptoms in school children from cities in China was for levels of $PM_{10-2.5}$ (Zhang et al., 2002). In another urban study, hospitalization rates for asthma in children 6-12 years old were significantly associated with $PM_{10-2.5}$ after adjustment for confounders (Lin et al., 2002).

Data on the distribution and chemical composition of both coarse (PM_{10}) and fine ($PM_{2.5}$) aerosol particles generated from the same urban and rural areas and within a specific geographic region is very limited. Therefore, the purpose of this work is to investigate the levels, distribution and enrichment factors as indications for the element sources of $PM_{2.5}$ and PM_{10} in the city of Riyadh, capital of Saudi Arabia.

2. Methodology

2.1. Sampling

Aerosol PM samples were collected in June 2006 and then every three months from November 2006 to May 2007 on rooftops (approximately 15-25 m above ground) of different buildings in Riyadh. MiniVol portable air samplers (Airmetrics, Eugene, OR, USA), using the cascade impactor principle to collect two sizes (PM_{10} and $PM_{2.5}$) were employed to acquire the aerosol samples. The sampling sites were selected to cover the entire area of the city as shown in Figure 1 and included the northwest (sites AM and AQ), west (DR), southwest (OR), south (SH), North (AZ), city center (AL), northeast (NZ), and southeast (JZ and MN). The descriptions of the site locales are given in Table 1. The PM samples were collected on Teflon fiber film filters (0.45 µm pore size for coarse particles and 0.22 µm pore size for fine particles) for this study. Sampling was performed at a total flow rate of 5L min^{-1} for a 24 hour period.

2.2. Analysis

The chemical analysis was performed by X-ray fluorescence (XRF) (XEPOS; Spectro ED-XRF, Germany) to determine the major (Na, Mg, Al, K, Si, P, S, Ca and Fe) and trace elements (Mn, Ni, Cu, Zn, Ba, Co, As, Se, Mo, Cd, Sn, and Sb).

3. Results and Discussion

The concentration levels and the spatial and temporal variations of PM_{10} and $PM_{2.5}$ for June 2006 to May 2007 are given in Table 2 and shown in Figure 2.

3.1. Concentration and distribution of aerosol $PM_{2.5}$ and PM_{10}

The data show that the concentrations of $PM_{2.5}$ were mostly lower than those of PM_{10} (Fig. 2), in agreement with other studies in the region (Kubilay et al., 2000; Ganor et al., 2000, 2009; Saliba et al., 2007; Shaka' and Saliba, 2004). The

concentrations of coarse particulate matter (PM_{10}) were approximately 1.0 to 4.0 (1.9±0.8) times higher than fine ($PM_{2.5}$) (Fig. 3a) indicating that the dominant PM component was coarse. Two factors can be attributed to these spatial and seasonal changes: (1) the seasonal wind direction and speed and (2) local development and human activities in the city.

The concentration of $PM_{2.5}$ ranged from 55.6 to 219.5 µg m^{-3} with a mean value of 104.0±61.4 µg m^{-3} in June 2006, where the lowest concentration was in the northwest of the city (AM site) and the highest in the southeast (MN site). In November 2006, the average concentration (76.3±66.1 µg m^{-3}) was lower than in June 2006, with the low (13.9 µg m^{-3}) in the northwest (AM site) and high (226.7 µg m^{-3}) in the northwest (AQ site). In February 2007, the average concentration was 124.5±69.6 µg m^{-3} with the low (26.7 µg m^{-3}) in the south (SH site) and high (213.3 µg m^{-3}) again in the southeast (MN site). In May 2007, the average concentration was higher (189.4±81.6 µg m^{-3}) with minimum (110.7 µg m^{-3}) in the northeast (AZ site) and maximum (257.6 µg m^{-3}) in the southwest (MN site). Apparently, the spatial and seasonal variations in the PM concentrations were mainly due to changes in the wind direction and speed as well as the concurrent construction activities around the city (Table 1).

For PM_{10}, the average concentration was 180.1±124.8 µg m^{-3} in June 2006 with a minimum (58.0 µg m^{-3}) in the city center (AM site) and maximum (478.2 µg m^{-3}) in the southwest (MN site). In November 2006, the average concentration (146.0±112.1 µg m^{-3}) was lower than in June also with a minimum (28.6 µg m^{-3}) in the northeast (AM site) and maximum (318.8 µg m^{-3}) in the southwest (MN site). The February average concentration was 268.1±164.6 µg m^{-3}, with a low (62.0 and 56.3 µg m^{-3}) in the northeast and southeast (AM and SH sites, respectively) and a high

(504.5 µg m^{-3}) in the southwest (MN site). For May 2007, the mean value was 312.2±146.8 µg m^{-3} with a minimum (145.8 µg m^{-3}) in northwest (AQ site) and maximum (597.2 µg m^{-3}) in the southeast (MN site). The results also show that the PM levels were higher in 2007 than 2006 (Fig. 3b) likely due to an increase in local construction activities around the city.

3.2. Air quality of aerosol $PM_{2.5}$ and PM_{10}

To assess the temporal and spatial air quality of Riyadh we used the air quality index (AQI) standard by EPA (1999). The cut-off-points of the AQI are: good (0-15.4 µg m^{-3} for $PM_{2.5}$; 0-54 µg m^{-3} for PM_{10}), moderate (15.5-40.4 µg m^{-3} for $PM_{2.5}$; 55-154 µg m^{-3} for PM_{10}), unhealthy for sensitive groups (40.5-65.4 µg m^{-3} for $PM_{2.5}$; 155-254 µg m^{-3} for PM_{10}), unhealthy (65.5-150.4 µg m^{-3} for $PM_{2.5}$; 255-354 µg m^{-3} for PM_{10}), very unhealthy (150.5-250.4 µg m^{-3} for $PM_{2.5}$; 355-424 µg m^{-3} for PM_{10}), hazardous (250-350.4 µg m^{-3} for $PM_{2.5}$; 425-504 µg m^{-3} for PM_{10}), and very hazardous (350.5-500.4 µg m^{-3} for $PM_{2.5}$; 505-604 µg m^{-3} for PM_{10}). Based on the overall PM concentrations, the air quality of Riyadh ranged from good to hazardous for $PM_{2.5}$ and from good to very hazardous for PM_{10} (Figs. 4 and 5). In summer (June 2006) the air quality ranged from good to very unhealthy for both $PM_{2.5}$ and PM_{10}; whereas in fall (November), it was good to very unhealthy for $PM_{2.5}$ and good to unhealthy for PM_{10}. In winter (February 2007), the AQI ranged from good to very unhealthy for both $PM_{2.5}$ and PM_{10}, and in spring (May 2007), good to hazardous for $PM_{2.5}$ and good to very hazardous for PM_{10}.

Regionally, the AQI was similar for most of the sectors of metropolitan Riyadh. The northwest had AQI ranging from good to unhealthy, whereas the northeast was slightly better with AQI of good to unhealthy for sensitive groups

(except in February it ranged from unhealthy to sensitive people to unhealthy). The southwest AQI varied from good to unhealthy (except in May it ranged from unhealthy to hazardous) and the southeast from moderate to very hazardous. The city centre had AQIs from good to very unhealthy. These assessments cover both particle size samples.

To evaluate the overall PM air quality in Riyadh we categorized the AQI into 7 numerical levels (i.e., 1 = good, 2 = moderate, 3 = unhealthy for sensitive groups, 4 = unhealthy, 5 = very unhealthy, 6 = hazardous, and 7 = very hazardous) following the same concentration cut-offs given by the EPA (1999). Then we used Figures 4 and 5 to estimate the air quality levels (AQL) in the city. The AQLs for Riyadh are given in Table 3 and illustrated in Figure 6. During the sampling period, the average AQLs were higher for $PM_{2.5}$ than for PM_{10} at all sites except MN. The best air quality was found in the city center (AL site) as moderate (standard range) and the worst condition was in the southeast (MN site) at very unhealthy. The AQLs were higher in 2007 than in 2006 and the minimum value was found in November 2006.

3.3. Concentrations and enrichment factors of elements

The major and trace elements in the PM were determined for the sites in Riyadh, and the spatial and temporal variations of the concentrations and the enrichment factor of each element can be examined. Co, As, Se, Mo, Cd, Sn and Sb were below the detection limits of the instrument. The major elements showed similar variations, and it was assumed that similar element behavior indicates a similar source of origin (Bellis et al., 2001; Chester et al., 1999; Furuta et al., 2005; Saliba et al., 2007). The element concentrations for this study are summarized in Table 4. Spatial variations of elemental concentrations were observed around the city with the highest

concentrations in the outskirts away from the center (AQ, NZ, MN Sites; Fig. 7). The total concentrations of the elements were higher in the coarser particulate matter as summarized in Figure 7. The elevated concentrations of major and trace elements in the city center (site AL) in February 2007 were mainly due to the building and road construction activity in the area. Based on these results, the major and trace elements were classified into two groups according to the similarity of their temporal and spatial variation, where Group 1 includes Na, Mg, Al, K, Ca, Si, P and Fe and Group 2 S and Ni. The concentration of Ni was high in the city center and lower in the perimeter, while S had high concentrations for all sites.

The enrichment factor, EF, is an approach to characterize the chemical composition of airborne particulate matter. It relates the concentration of an element (X) to that of a crustal element (such as Al, Ti or Fe) in the air, normalized to the ratio of these elements in the average continental crust (Hoffmann et al., 1972; Wedepohl, 1971; Zoller et al., 1983):

$$EF = (X/Al)_{(air)}/(X/Al)_{(crust)}$$

Therefore, an EF of about unity indicates that the dominant source is natural crustal PM and an EF value > 1 indicates an anthropogenic input to the PM. Al was used as the normalizing crustal element in calculating the EFs, assuming that its anthropogenic input was minor and negligible.

Generally, an element is assumed to originate from natural sources when its enrichment factor is less than 10 (Chester et al., 1999; Finlayson-Pitts and Pitts, 2000; Saliba et al., 2007; Torfs and Van Grieken, 1997). The mean enrichment factors of the major and trace elements found at high levels in both coarse (PM_{10}) and fine particles ($PM_{2.5}$) are listed in Table 4. The enrichment factors of most elements were < 5 for

both PM sizes, and are termed Group 1 with a likely origin from natural sources. The EFs of Group 2 are relatively higher (> 5) and include sulfur and nickel. The EFs at different seasons for S ranged from 91±40 to 279±203 for $PM_{2.5}$ and from 125±45 to 441±391 for PM_{10}. The EFs at different seasons for Ni ranged from 7±6 to 14±9 for $PM_{2.5}$ and from 10±4 to 35±62 for PM_{10} (Table 4 and Fig. 8). Both S and Ni have higher values for PM_{10} than $PM_{2.5}$ and their enrichment factors are higher for coarse PM. The high EFs for S of 91-441 indicate that the atmosphere is heavily polluted by S, probably from anthropogenic sources such as construction dust (e.g. gypsum) and fugitive SO_2 emissions. The high EFs for Ni indicate release from the combustion of fossil fuel (e.g. traffic).

The computed EF values in Riyadh were lower than those reported in other cities in the region (Chen et al., 2008; Herut et al., 2001; Kubilay and Saydam, 1995), suggesting that regional and local crustal sources influence the element/Al ratios in the EF calculation. The general EF variation for the major elements in Riyadh was observed to be similar to the variation trend in other regional areas (Chen et al., 2008; Saliba et al., 2007), indicating that the local surface crust is the major source of these elements in aerosol dust. Obviously, the estimation of the EF is affected by the regional and local crustal components, thus it is more precise to utilize regional crust in estimating the EF values.

4. Conclusion

This monitoring program of atmospheric PM in metropolitan Riyadh revealed several facts. It was found that PM_{10} was more abundant than $PM_{2.5}$ in the city. PM was at higher concentrations in 2007 than 2006, probably as a result of increased development activities in the city. The highest PM levels occur in the southeast sector

where industrial activities, mainly cement, ceramic and stone cutting factories, are the major local dust sources for the region. The lowest PM concentrations were in the city center, where only traffic and limited resuspension of soil dust are the major source of PM. The air quality of the city ranged from good to hazardous for $PM_{2.5}$ and from good to very hazardous for PM_{10}. The enrichment factors (EFs) of each element showed spatial variations, where each group of elements is likely to have similar sources. The EFs of the elements over the crustal means showed that only sulfur and nickel were enriched in both $PM_{2.5}$ and PM_{10}, indicating that they are from anthropogenic sources. It is apparent that the atmosphere of Riyadh was seriously polluted by sulfur.

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