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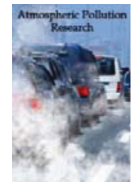

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Characterization of size–fractionated PM_{10} and associated heavy metals at two semi–arid holy sites during Hajj in Saudi Arabia

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ABSTRACT

The size–fractionation of inhalable particles and their heavy metal content during the Hajj season have yet to be explored. The principal objective of this study is to evaluate the concentration of heavy metals associated with six different PM_{10} fractions to which pilgrims are exposed during Hajj. Two holy sites (Mina and Arafat) characterized by the simultaneous obligatory stay of all pilgrims and concomitant intense vehicular emissions were selected for sampling. Characterization of inhalable PM, their fractional size distribution and concentration of heavy metals were investigated. The sum of total fractions (coarse+fine) as PM_{10} was recorded at an average of 181.3 µg/m³ at Mina and 289.6 µg/m³ at Arafat during peak days of the Hajj period, corresponding to Arabic (8–12 Dhu Al–Hijjah). The average concentration (µg/m³) of coarse (3.0 to 10.0 µm) and fine fractions (3.0 to ≤0.49 µm), and their relative percentages were recorded [Mina: 62.2, 34.2% (fine), 119.1, 65.8% (coarse); Arafat: 114.5, 35.9% (fine), 175.1, and 64.1% (coarse)]. The metal concentrations associated with these fractions, their enrichment factor, and possible adverse effects on pilgrims were assessed. Cd and Se were highly enriched, followed by Cr, Pb, Cu, Ni and Co, indicating vehicular emissions as the likely anthropogenic source. Air Quality indices were calculated based on PM_{10} and $PM_{2.5}$ particulate concentrations in ambient air during the Hajj period, and the days were categorized in relation to health impacts. This work provides crucial information and alerts about the possible impact of PM on ambient air quality, and data suggests pilgrims, particularly susceptible groups, should adopt suitable precautionary preventive measures during the Hajj period.

Keywords: *Particulate matter, metals, Hajj, AQI*

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1. Introduction

Air borne particulate matter (PM) consists of a complex mixture of particles of varying size and chemical composition. The behavior of PM in the atmosphere and its potential to affect human health and atmospheric visibility are dependent on its physical and chemical characteristics (Boueres and Orsini, 1981; de Miranda et al., 2002; Toledo et al., 2008). These characteristics are dependent on the source type and on the formation processes that particles undergo at the sources or in the atmosphere (Willeke and Whitby, 1975; Sweet et al., 1993; Pacyna, 1998; Spurny, 1998; CEPA, 1999). The hazardous effects of particulates on human health are usually associated with the presence of inhalable particulates in the range of ≤10 µm at high concentration levels in the ambient air. Several epidemiological studies have indicated that short– and long–term exposure to fine PM have associated adverse health effects, including excess instances of respiratory and cardiovascular diseases (NRC, 2001; Pope et al., 2002; HEI, 2010). Inhalable PM in the atmosphere can be categorized in three modes based on formation (size) and source: nuclei (Aitken) mode, accumulation mode, and coarse mode. Nuclei mode (ultrafine) particles <0.1 µm are principally formed from the condensation of hot vapors during high temperature combustion processes and result in the nucleation of atmospheric species and formation of new particles that contribute little to overall particle mass loading. Nuclei mode particles are subject to random motion and collide quickly in coagulation processes to yield larger particles with short atmospheric residence times. Accumulation mode particles (0.1 to 2.0 µm) result from the coagulation of particles in the nuclei mode and condensation of vapors on existing particles, which subsequently grow to this size range (Clark and Whitby, 1967; CEPA, 1999; Weckwerth, 2001; de Kok et al., 2006). These particles account for most of the surface area and much of the particle mass in the atmosphere and can remain in the atmosphere for days to weeks. Particles >2.5 µm in size are considered as coarse mode and are typically associated with mechanical processes such as wind erosion, grinding operations, and wind–blown soil. These particles are efficiently removed by gravitational settling and remain in the atmosphere for periods of hours to a few days (Willeke et al., 1974; Willeke and Whitby, 1975; Danielsson et al., 1999; Shu et al., 2001; Vassilakos et al., 2007; Fang et al., 2010; Zheng et al., 2010).

The Hajj pilgrimage is the world's largest Muslim religious ritual, where approximately 2–3 million pilgrims from various parts of the world visit and perform a sequence of rituals at two holy sites, Mina and Arafat in the province of Makkah Al Mukarramah in Saudi Arabia. The Hajj pilgrimage is held between 8–12 Dhual–Hijjah according to the Arabic calendar annually. Among these rituals, the Day of Arafat (9^{th} Dhual–Hijjah) is the most significant event, where all pilgrims stay together from sunrise to sunset within the defined area at Arafat. On day 1 of the pilgrimage (8^{th} of Dhul–Hijjah) millions of pilgrims gather at Mina and spend the day and night in tents, and typically depart on day 2 (9^{th} of Dhul–Hijjah) just after dawn to travel to the ground of Arafat by various forms of motor vehicles (as well as on foot). The pilgrims spend the entire day at Arafat and after sunset they depart for the nearby open place (Muzdalifah) situated between Arafat and Mina, where they perform an obligatory night stay. In the following three days (from 10–12 of Dhul–Hijjah), pilgrims remain at Mina to complete all rituals. Due to enormous vehicular and pedestrian movements during the activities of Hajj, pilgrim's exposure to various gaseous and particulate pollutants is inevitable. Determining the load of inhalable PM of aerodynamic diameter ≤10 µm (PM_{10}) in the ambient air, and its chemical characterization, are important aspects of potential health impacts on pilgrims during the event. The PM under 2.5 µm diameter ($PM_{2.5}$) is of great concern and earlier studies demonstrated that $PM_{2.5}$ can efficiently penetrate into the lungs (Wilson and Spengler, 1996). Furthermore, particles coated with first row transition metals play a significant role in creating inflammatory responses in the lungs (Amdur, 1996; Utell and Samet, 1996). Dockery and Pope (1994) and Pope et al. (1995) illustrated the health effects associated with short–term exposure to 10 µg/m³ increases in PM_{10} concentration, such as cardio-vascular, respiratory morbidity, hospital admission for respiratory problems and symptom exacerbation among asthmatics. Epidemiological studies are considered useful for recognizing the possible health effects of particulate exposure. However, accurate identification of ambient fine PM in toxicological studies is a challenge, as they commonly consist of a mixture of different components with wide toxicological characteristics. Various studies have revealed that diesel exhaust and other vehicular emissions cause lung function deficiencies in humans and animals (Scheepers and Bos, 1992a; Scheepers and Bos, 1992b; Mauderly, 1994). Fine particles from vehicular sources had a higher mutagenic effect than samples from other sources (Stevens et al., 1990; Bronzetti et al., 1997). The increases in cardiovascular deaths were found to be more relevant and frequent (Samet et al., 2000; Wichmann et al., 2000; U.S. EPA, 2003). Kappos et al. (2004) reported that short–term exposure to PM had associated health repercussions, such as hospital admissions, and that these were associated with asthma, chronic obstructive pulmonary disease, pneumonia, cardiovascular and other respiratory causes. In pre–existing asthmatics, a small impairment of lung function and an increase of respiratory symptoms (cough, phlegm, shortness of breath) are found in association with particulate exposure. Reduced heart rate variability (HRV) in patients with cardiovascular complications and diabetics also seem to be affected by exposure to ambient PM (Peters et al., 1996; Peters et al., 1997; Schwela and Zali, 1999). There is growing concern over the environmental and health effects on pilgrims as a result of contaminants release and exposures. PM_{10} load, fractionations and toxic chemical content and associated potential health impacts during Hajj, have yet to be investigated. The findings reported here is part of an air quality monitoring study characterizing the inhalable PM and its fractions as well as the associated concentrations of selected heavy metals.

2. Material and Methods

2.1. Study locations

Makkah (21°25'19" and 39°49'46") is a great holy city approximately 80 km inland from the Red Sea and at an elevation of 277 m above sea level. Sources of PM in the area are mostly high volume of traffic, construction and minor industrial activities, re–suspension of particulates and geographical conditions. Mina (21°41'33" and 39°89'33") and Arafat (18°79'14" and 42°89'37") are located in Makkah Province in Western Saudi Arabia, and are separated by 22.1 km (Figure 1).

2.2. Sample collection

PM samplings were performed at the premises of King Fahad Hajj Research Institute, on the top of a metallic shed at Arafat, and over the roof of a Health Care Center in Mina simultaneously. Samplings were done using a volumetric flow controlled (VFC) High Volume Air sampler (Model: TE–6070V) equipped with a PM_{10} size selective inlet and a cascade impactor, model: SE–230 (Tisch Environmental, Inc.USA,) particle size cutoffs (µm) at 50% collection efficiency for spherical particles with unit mass density at 25 °C 760 mm Hg comprised of 5 stages which separate 7.2–10; 3.0–7.2; 1.5–3.0; 0.95–1.5; and 0.49–0.95 µm size particles. The sampler was placed at a height of 3.0 m above ground level and samplings were carried out between the 5th and 14th of Dhul–Hijjah, 1425H (January 15–24, 2005). Five fractions of PM was collected over pre–weighed slotted Quartz fiber filter substrate (SAC–230–QZ) and Whatman QM–A micro–quartz fiber filter (8"x 10" size) used for back–up (<0.49 µm) filter to capture all finest particles. Each sampling was performed continuously for 24 hours; from midnight 0:00 to 0:00 next day at a flow rate of between 67.8–70.2 m³/hr. Meteorological data were simultaneously recorded during sampling days. The samples were preserved separately in polyethylene bags until delivery to the laboratory. Final weights of each sample, including from the various filters size fractions, were taken and particulate concentrations in the ambient air were calculated.

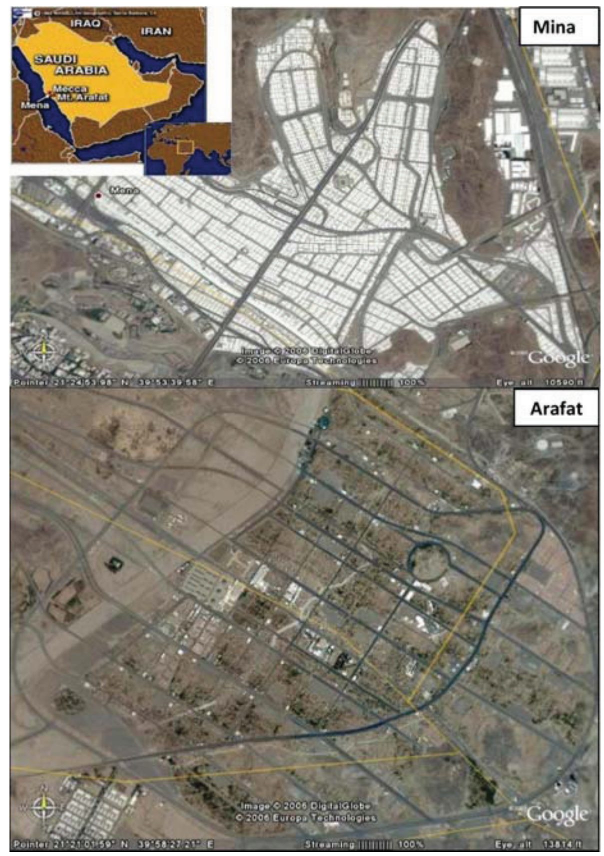

Figure 1. *Location of Mina area where pilgrims stay in tents for five days and Arafat area where pilgrims performs obligatory stay from sunrise to sunset on the 9th day of Hajj.*

2.3. Metal analysis

The particulate filter samples obtained from the cascade impactor. Five different size fractions and a back–up filter (2.54 cm × 20.32 cm size strip) were digested separately with concentrated nitric acid (15 mL) following acid extraction of method for metalic elements (Compendium Method IO–3.1, EPA/625/R–96/010a, U.S. EPA, 1999a) using advanced composite vessels in an MDS–2100 microwave digestion system. Aliquots of digested samples were initially filtered through filter paper (Whatman 42) followed by Gelman Acrodisk (0.45 µm) filters and the volume of the aliquot were made up to 25 mL as a final extract volume with deionized water. The digested samples were finally analyzed for Pb, Cd, Se, V, Ni, Co, Cu, Cr and Mn using ICP–OES (Optima 2000 DV, Perkin Elmer, USA), and the blank contents duly subtracted from the analysis (Davidowski and Grosser, 2000). Each sample was analyzed in triplicate and the mean concentrations were calculated. For the back–up filter substrate, the concentration was calculated following