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Measurements and source apportionment of particle-associated polycyclic aromatic hydrocarbons in ambient air in Riyadh, Saudi Arabia

Qijing Bian [a], Badr Alharbi [b], Jeffrey Collett Jr. [a], Sonia Kreidenweis [a, *], Mohammad J. Pasha [b]

[a] Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80526, USA
[b] National Center for Environmental Technology, King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia

HIGHLIGHTS

- One year of particle-phase PAH concentration measurements in Riyadh are reported.
- High concentrations of low-molecular-weight (LMW) PAH were observed.
- LMW PAH were attributed to evaporative and oil combustion sources.
- A unique source profile was associated with energy production from oil combustion.
- High-molecular-weight PAH were associated with traffic and solid fuel combustion.

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ABSTRACT

Ambient air samples were obtained in Riyadh, the capital and largest city of Saudi Arabia, during two measurement campaigns spanning September 2011 to September 2012. Sixteen particle-phase polycyclic aromatic hydrocarbons (PAH) were quantified in 167 samples. Pyrene and fluoranthene were the most abundant PAH, with average of 3.37 ± 14.01 ng m^{-3} and 8.00 ± 44.09 ng m^{-3}, respectively. A dominant contribution from low molecular weight (LMW) PAH (MW < 228) suggested a large influence of industrial emissions on PAH concentrations. Monte Carlo source apportionment using diagnostic ratios showed that 80 ± 10% of the average LMW PAH concentrations were contributed by petroleum vapor emissions, while 53 ± 19% of high molecular weight (HMW) PAH were from solid fuel combustion emissions. The positive matrix factorization model estimated that oil combustion emissions dominated total PAH concentrations, accounting for on average 96%, likely due to widespread use of oil fuels in energy production (power plants and industries). Our results demonstrate the significant influence of petroleum product production and consumption on particulate-phase PAH concentrations in Riyadh, but also point to the importance of traffic and solid fuel burning, including coke burning and seasonal biomass burning, especially as they contribute to the ambient levels of HMW PAH.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are aromatic species with at least 2 benzene rings, widely distributed in the atmosphere due to their myriad sources and potentially long atmospheric lifetimes. This class of compounds has received a great deal of attention due to their known or suspected detrimental effects on human and environmental health (Hoffman and Wynder, 1971; IARC, 2013; Grimmer, 1983; Perera, 1997). PAH, with benzo(*a*)pyrene (BaP) designated as a representative compound, have been classified as probable human carcinogens by both the United States Environmental Protection Agency (ATSDR, 1995) and the International Agency for Research on Cancer (IARC, 2013). Considering their probable carcinogenic and mutagenic effects, and the need for new strategies aimed at broad reductions in their emissions, the guideline values for equivalent BaP concentrations have been set between 0.1 and 1.3 ng m^{-3} for many agencies worldwide (Kim et al., 2013).

* Corresponding author.
E-mail address: sonia@atmos.colostate.edu (S. Kreidenweis).

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PAH are emitted into the atmosphere from natural as well as anthropogenic sources. Natural sources include forest fires and volcanic eruptions, while anthropogenic sources include meat cooking, motor vehicles, road dust (including particles generated by tire wear and brake lining erosion), natural gas home appliances, tobacco smoke, asphalt, boilers, wood burning (Seinfeld and Pandis, 2006), solid waste incineration, petroleum spills and discharge (Haritash and Kaushik, 2009) and aluminum production (vanLoon and Duffy, 2005). After emission into the atmosphere, PAH partition between the gas phase and aerosol particles. The PAH with smaller molar masses (less than 4 rings) are volatile and found mainly in the gas phase, whereas the larger species (PAH with 4 or more rings) are mainly associated with fine particulate matter via adsorption of the PAH onto surfaces of particle types that likely include soot and soil dusts (vanLoon and Duffy, 2005; Akyüz and Cabuk, 2008 and references therein). The atmospheric fate of PAH is mainly controlled by their distribution between the gas and particulate phases which influences their rates of dry and wet deposition, reaction with oxidant species (HO, O_3, NO_2, N_2O_5, and HNO_3), and degradation via photolysis (Manahan, 2005).

Since anthropogenic emissions associated with industrial processes, energy production, and transportation are major sources of PAH, the levels of PAH in ambient air are of increasing concern worldwide with the rapid growth of urban areas and of energy usage. The sources include vaporization and incomplete combustion during production, transport, and consumption of petroleum and petroleum products. The magnitude and prevalence of potential sources related to these activities pose environmental and health risks. As home to a large fraction of the world's known oil and gas reserves and a major global producer and consumer of petroleum and its products, with nearly 60% of the country's energy consumption supplied by petroleum combustion, Saudi Arabia has extensive potential PAH sources from extraction, refining, and energy production activities that do not exist to the same extent in many other regions. Further, the persistent dust aerosols over the Arabian Peninsula may provide surfaces for adsorption of PAH, favoring their partitioning to the particle phase despite the warm year-round temperatures. To date only a few studies of particulate matter properties and concentrations in Saudi Arabian cities have been published, most of them focused on Jeddah, a port city on the Red Sea having the second largest population among Saudi Arabian cities after the capital city Riyadh. Jeddah was reported to be susceptible to Los Angeles-type photochemical pollution (Nasralla, 1983); data for an annual cycle of the chemical composition of dustfall showed secondary sulfate dominated among the soluble components of the dust. Previously published Saudi Arabian measurement studies, with most particulate matter data having been obtained in Makkah, have been compiled (Munir et al., 2013); their analyses suggested meteorological variables are the main controlling factor for PM_{10} concentrations in the region, rather than traffic emissions. Of particular interest to the present work is a study that reported $PM_{2.5}$ and PM_{10} composition data for June–September at seven sites in Jeddah, and conducted a source apportionment using factor analysis (Khodeir et al., 2012). The study attributed 69% of $PM_{2.5}$ mass and 18% of PM_{10} mass to heavy oil combustion, whereas soil sources represented 8.2% and 64% of $PM_{2.5}$ and PM_{10}, respectively. Only three prior studies examined ambient levels of particle-phase PAH in Saudi Arabia. In 2004, 16 PAH in extractable organic matter in eleven 24-h PM_{10} samples from urban sites in Jeddah were quantified; the focus of that study was on characterizing the genotoxicity of the extracts (ElAssouli et al., 2007). El-Mubarak et al. (2014) measured PM_{10} PAH concentrations in ambient air in Riyadh in December 2010 and concluded that emissions from traffic were the major source of PAH, particularly diesel emissions. Both vapor and particulate phase PAH were measured in Jeddah in 2013 by Alghamdi et al. (2015). They found the major sources of total gas + particulate PAH to be gasoline vehicles, industrial sources and diesel/fuel oil combustion. Other studies have documented PAH levels in the larger region. Characterization of particle-phase PAH, Ni and V in emissions from the burning of oil fields in Bahrain, Kuwait were reported by Madany and Raveendran (1992). PAH observations in Tehran, Iran in 2005 were used to estimate health effect in the study of Halek et al. (2008). In a later study in the same city, diesel emissions were estimated to be the dominant source of PAH (Halek et al., 2010). Studies in other cities worldwide, some of which are summarized below, have measured and reported concentrations of PAH for various seasons, contributing to the growing body of information on the ambient levels and distributions of these compounds.

We report here the first long-term measurements of ambient particulate-phase PAH concentrations in Riyadh, the capital and most populous city of Saudi Arabia and one of its major industrial centers. As with other large cities in Saudi Arabia, Riyadh has experienced high growth rates in recent decades and has a heavy vehicular traffic load, as well as multiple heavy and light industries within or close to the city boundaries, including an oil refinery, multiple power plants, a cement plant, multiple steel production plants, and several sewage treatment plants. The goals of this work are to report concentration levels of PAH in Riyadh ambient air; to evaluate the spatial distributions of PAH; and to conduct a source apportionment study. The findings from these measurements represent vital reference information for future urban development and health risk assessment studies in Riyadh and other cities with similar characteristics.

2. Materials and methods

2.1. Site description and sampling procedure

Fig. 1 shows an image of Riyadh city and its immediate surroundings, indicating the locations of major emissions sources. The study region was divided into 16 12 km × 12 km sampling cells as shown in Fig. 1 to represent the whole urban environment of the city, including different sectors with different characteristics, and sampling was performed from a mobile laboratory located approximately at the centre of each cell. Ambient air was sampled using PQ-100 portable samplers (BGI Incorp., USA) through a PM_{10} inlet located 2.5 m above ground level. Aerosol was sampled onto quartz microfiber filter discs (47 mm) over a 24 h period at a flow rate of 16.67 lpm (1 m^3 h^{-1}); samples were obtained on alternate days over a total 6-day period in each cell, and then sampling was moved to the next grid. This 6-day period of alternate days of sampling was repeated four times during the study period for a total of 167 filter samples (Table S1). 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 was recorded to determine total particulate mass collected. Filters were stored in a refrigerator at −1 °C before extraction to limit volatilization of the low molecular weight compounds.

2.2. Sample extraction

Filter samples were placed in 50 ml EPA glass vials and 20 ml of 10% acetonitrile in dichloromethane were added. Each sample was sonicated in an ultrasonic bath for 30 min, held for 1 h, and then sonicated for another 30 min. After sonication the extract was