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Atmospheric polycyclic aromatic hydrocarbons (PAHs) from post-harvest biomass burning emissions in the Indo-Gangetic Plain: Isomer ratios and temporal trends

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ABSTRACT

Atmospheric concentrations of particulate polycyclic aromatic hydrocarbons (PAHs) and their isomer ratios have been studied for two distinct biomass burning emissions (post-harvest burning of paddy-residue in Oct–Nov and wheat-residue burning during April–May) in the Indo-Gangetic Plain (IGP). The mass concentrations of $PM_{2.5}$ (Av: 246 μg m^{-3}), OC (92 μg m^{-3}), EC (7 μg m^{-3}) and ΣPAHs (40 ng m^{-3}) are significantly higher from the paddy-residue burning. In contrast, for wheat-residue burning emissions, concentrations of $PM_{2.5}$ (53 μg m^{-3}), OC (15 μg m^{-3}), EC (4 μg m^{-3}) and ΣPAHs (7 ng m^{-3}) are about 4–5 times lower. The large temporal variability in the concentrations of particulate species and OC/EC ratio (range: 1.9–25.7) is attributed to differences in the two biomass burning emissions and their relative source strength. The mass fraction of EC (Av: 3.1%), associated with the poor combustion efficiency of moist paddy-residue, is significantly lower than that from the wheat-residue burning ($EC/PM_{2.5}$ = 7.6%) during dry weather conditions. Furthermore, OC mass fractions from paddy- and wheat-residue burning emissions are 37% and 28% respectively; whereas ΣPAHs/EC ratios are significantly different, 5.7 and 1.6 mg g^{-1}, from the two emission sources. The particulate concentrations of 5- and 6-ring isomers (normalized to EC) from paddy-residue burning are about 3–5 times higher than those from the wheat-residue burning emissions. The cross plots of PAHs show distinct differences in isomer ratios from agricultural-waste burning emissions vis-à-vis fossil-fuel combustion.

1. Introduction

The chemical characteristics of atmospheric aerosols from fossil-fuel combustion and biomass burning emissions have been reasonably well studied and represented in the literature (Bond et al., 2004; Fine et al., 2002; Fon et al., 2007; Fraser et al., 2002; Harrison et al., 1996; Rengarajan et al., 2007; Rogge et al., 1998; Schauer et al., 2002; Simoneit, 2002; Venkataraman et al., 2005; Wang et al., 2009). However, detailed information on the chemical composition of aerosols particularly from agricultural-waste burning emissions is rather lacking (Andreae and Merlet, 2001; Hays et al., 2005; Jenkins et al., 1996). Recently, attempts have been made to study the particle-size distribution in the controlled combustion experiments conducted for rice- and wheat-straw (Hays et al., 2005; Li et al., 2007; Zhang et al., 2011). These laboratory based experiments have reported a unimodal size peaking at less than 0.5 μm, with the exception of one set of results on bimodal-size distribution of particles from rice-straw combustion (Keshtkar and Ashbaugh, 2007). More recently, study based on freshly emitted particles from rice- and wheat-straw burning has reported a unimodal size distribution at 0.10 μm and 0.15 μm respectively (Zhang et al., 2011).

The significance of large-scale biomass burning emissions on the atmospheric chemistry, climate and bio-geochemical cycles has been widely emphasized (Crutzen and Andreae, 1990; Das et al., 2008; Dey and Tripathi, 2007; Gustafsson et al., 2009; Menon et al., 2002; Ram et al., 2010; Ramanathan et al., 2007). Several studies with top-down approach have been carried out from the South Asian region, suggesting that 50–90% of the black carbon (BC) is derived from the fossil-fuel combustion sources (Mayol-Bracero et al., 2002; Novakov et al., 2000; Ramanathan et al., 2007; Stone et al., 2007). In contrast, bottom-up approach based on emission inventories suggest that biomass burning is a dominant source in the South Asia and accounts for nearly 70% of the BC (Gustafsson et al., 2009; Rengarajan et al., 2007; Venkataraman et al., 2005). However, these inferences are derived mainly from OC/EC ratios, and can be biased to some degree by fractionation of carbonaceous

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aerosols during chemical processing in the atmosphere and can, thus, have misleading conclusions drawn on their source characterization (Cabada et al., 2004; Castro et al., 1999; Gustafsson et al., 2009; Ram and Sarin, 2010; Schauer et al., 1996). These diverging views on the sources of carbonaceous aerosols require a comprehensive data set for EC and OC from biomass burning emissions, as well as for some of the diagnostic tracers such as polycyclic aromatic hydrocarbons (PAHs) (Mandalakis et al., 2005; Li et al., 2009a,b; Sheesley et al., 2009; Tham et al., 2008; Thornhill et al., 2008; Yunker et al., 2002).

This manuscript presents a first comprehensive data set on airborne PAHs (and isomer ratios), OC and EC in $PM_{2.5}$ (particles with aerodynamic diameter $\leq$ 2.5 μm) collected during two distinct agricultural-waste burning practices followed in the Punjab and Haryana regions of the Indo-Gangetic Plain (IGP). Our primary objective is to assess the relative impact of emissions from post-harvest burning of paddy-residue during Oct–Nov and wheat-residue burning emissions during April–May. Detailed information on concentrations of PAHs and their isomer ratios from agricultural-waste burning emissions is lacking in the literature for this dominant source of carbonaceous aerosols in the IGP. The post-harvest burning of paddy-residue in Punjab region (during Oct–Nov) is estimated to be around 100 million tons of rice-straw (Badarinath et al., 2006; Gupta et al., 2004; Punia et al., 2008). The emission strength from wheat-residue burning is about a factor of 2–3 lower during April–May. The time period of December–March is characterized by emissions from bio-fuels (Babool, Cowdung cake, Eucalyptus, Jujube and Shisham) and fossil-fuel combustion sources.

2. Aerosol sampling and methodology

2.1. Site description & meteorology

The sampling site at Patiala (30.2 N, 76.3 E; 250 m amsl) is located upwind of the major industrial pollution sources in the Indo-Gangetic Plain (IGP), Fig. 1. The site is mainly influenced by the downwind transport of carbonaceous aerosols from two distinct and seasonal post-harvest biomass burning emissions in Oct–Nov and April–May. In order to characterize the chemical constituents from agricultural-waste burning emissions, $PM_{2.5}$ samples were collected during drier months (from Oct 2008 to May 2009). The sampling during the wet period (south-west monsoon; July–Sept) is not relevant due to wash-out of the atmosphere by frequent rain events. During summer months (May–June), transport of mineral dust from western India and northwest Desert regions is a conspicuous feature (Jethva et al., 2005). The entire study period from Oct–May is sub-divided into three phases: Oct–Nov, referred to as post-monsoon, is influenced by emissions from post-harvest burning of paddy-residue; Dec–Mar (wintertime) is dominated by bio-fuel (Babool, Cowdung cake, Eucalyptus, Jujube and Shisham) and fossil-fuel combustion, with occasional fog events. The time period of April–May is influenced by emissions from post-harvest burning of wheat-residue. The daily temperature varied from 19 to 33 °C during Oct–Nov, 11–31 °C during Dec–Mar and 22–41 °C during April–May, with corresponding relative humidity of 61 ± 15%, 62 ± 15% and 37 ± 12% respectively. The winds were north-westerly and weak (1 m s^{-1}) during the Oct–Nov, changing to moderate intensity (4 m s^{-1}) during Dec–Mar from north-westerly

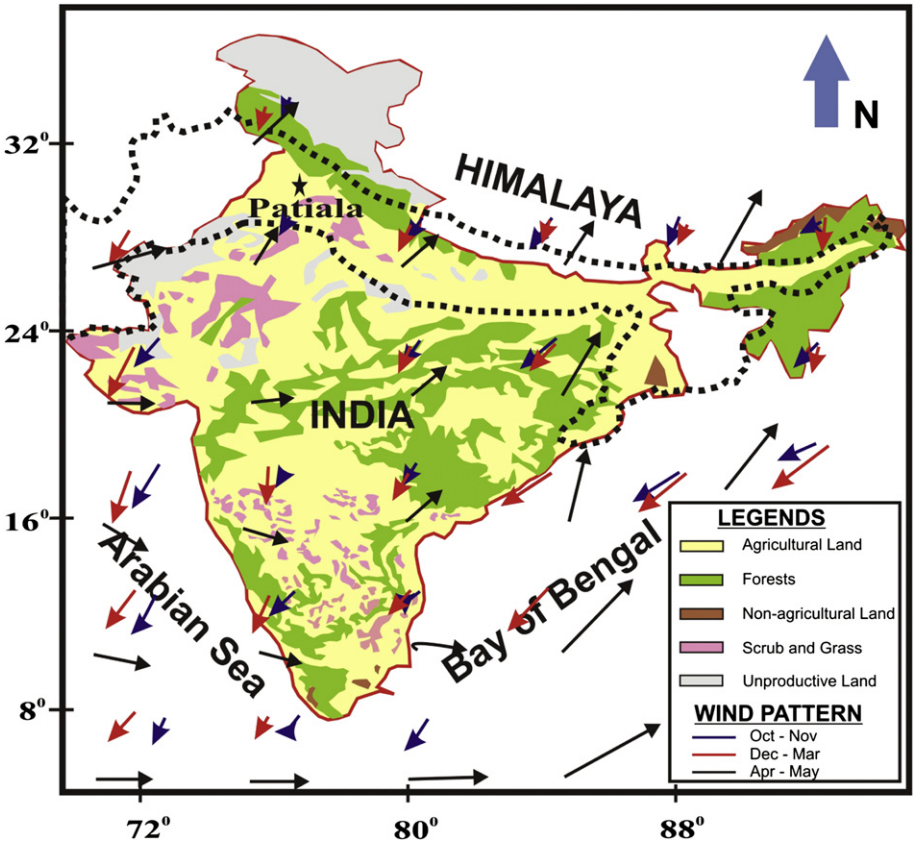

Fig. 1. Aerosol sampling site at Patiala (shown by star) in the Indo-Gangetic Plain (area marked by dotted line). Typical wind-fields (during the sampling period) and major land use patterns in India are also shown (adapted from maps of India.com).