Measurements of polycyclic aromatic hydrocarbons at an industrial site in India

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Abstract Polycyclic Aromatic Hydrocarbon (PAH) concentrations were measured in Total Suspended Particulate Matter (TSPM) from December 2005 to August 2006 at Nunhai, an industrial site in Agra (India). Particulate matter samples were collected on glass fibre filters using High Volume Sampler (HVS-430) and were extracted using dichloromethane with ultrasonication and analyzed by GC. Total PAH concentration varies between 0.04 to 2.5 μg m⁻³ accounting only 1.6×10⁻³% of TSPM. The mass distribution in air was dominated by high molecular weight DbA, BghiP, BaP, BkF and IP. Combustion PAH (CPAH) except BeP represents 58% of the total PAH mass and IARC classified total carcinogenic PAH accounting 63% of TPAH concentration. Correlation studies between PAH revealed the contribution of low molecular weight PAH was mainly due to primary emission from diesel exhaust while high molecular weight PAH were formed during combustion. The presence of specific tracers and calculation of characteristic molecular diagnostic ratios Fla/(Fla + Pyr), BaP/(BaA + Chy), BaA/(BaA + Chy), IP/(IP + BghiP), BaP/BghiP and IP/BghiP were used to identify the sources of the emissions of PAHs in the atmospheric samples. Seasonal variation in atmospheric PAH showed four fold increase in winter concentration than summer. The BaP and relative BaP amount calculated from the measurements suggested that photo-oxidation may also be responsible for the variation in PAH concentrations during winter and summer. Seasonal trends in atmospheric PAH concentration in the study area were influenced by fossil fuel usage for domestic heating, boundary height and temperature.

Keywords Particulate matter • Polycyclic aromatic hydrocarbons • Urban pollution • Photochemical oxidation • Ambient air

Introduction

PAHs are one of the major groups of organic atmospheric constituents. Recent investigations in the field of air pollution, as well as a large set of collected data, have consistently shown that polycyclic aromatic hydrocarbons (PAHs) remain as a concern, due to their adverse effects on human health. They are formed during the incomplete combustion of organic matter such as petroleum, oil, coal, and wood (Golomb et al. 2001; Halsall et al. 2001; Garban et al. 2002). Benzo(a)Pyrene, Benzo(b)Fluoranthene, Benzo(k)Fluoranthene, and a number of other aromatic hydrocarbons are formed by the pyrolysis of simple hydrocarbons such as acetylene, butadiene,
ethylbenzene, styrene, n-butylbenzene and tetralin at 700°C (Knize et al. 1999). At the temperature of pyrolysis (about 700°C) aromatic ring systems are the most stable among the structural type present, while aliphatic C-C bond and C-H bonds readily break down to yield molecular fragments of free radical character which then undergo recombination (Golomb et al. 2001; Hwang et al. 2003).

More than 30 PAH compounds and several 100 PAH derivatives have been identified, that have carcinogenic and mutagenic effects, making them the largest single class of chemical carcinogens known (Bjorseth and Ramdahl 1985). The physico-chemical properties of the PAHs largely determine their environmental behaviour. They are semi-volatile substances at atmospheric conditions and frequently occur both in the vapour-phase and as attached to particles depending on the vapor pressure of each PAH (Wingfors et al. 2001; Basheer et al. 2003). Low molecular weight PAHs, containing two or three fused rings are more water soluble and volatile and are found predominantly in vapour phase. High molecular weight PAH containing more than three fused rings, which are primarily associated with particles are found mainly adsorbed on particulate material.

PAHs can persist in the environment and they have ability to be transported over long distances (Aamot et al. 1996; Halsall et al. 2001) they are mainly concentrated to urban and industrial zones, but can also be found in rural areas (Gevao et al. 2000; Garban et al. 2002) or even in remote regions (Kallenborn et al. 1998; Migaszewski 1999). Elevated levels of site specific PAHs are generally found near emission sources and they have been measured extensively during the last few decades in environmental samples, especially in atmospheric particles (Halsall et al. 1994; Smith and Harrison 1996). It is known that some of these PAHs are mutagenic and carcinogenic and some of them are associated with acute and chronic health problems and therefore may have a potential health impact on human (IARC 1984; Menzie et al. 1992; Nielson et al. 1996; Fang et al. 2004). In the last decade, more and more data on airborne concentrations of PAH have become available from many industrialized countries around the world such as Brazil (84.5 ng m $^{-3}$; Tavares et al. 2004), China (170–490 ng m $^{-3}$; Simoneit et al. 1991), UK (20–164 ng m $^{-3}$; Coleman et al. 1997; Gardner et al. 1995), USA (48.3–58.3 ng m $^{-3}$; Simick et al. 1997), Urban Malaysia (7–9 ng m $^{-3}$; Fang et al. 1999; Omar et al. 2002), Urban Heraclion (21.4–59 ng m $^{-3}$; Gogou et al. 1996). However, for less developed nations, the availability of data is far less.

Investigations in the field of measurements of PAH concentration in urban atmospheres in India include the studies carried out in Mumbai (Mohan Rao et al. 1982; Kulkarni and Venkataraman 2000), Lucknow (Bhargava et al. 2004), Ahmedabad (Aggarwal et al. 1982; Raiyani et al. 1993) and Nagpur (Vaishali et al. 1997) conducted with a view to evaluate the carcinogenic risk from PAH exposure. Studies carried out by Raiyani et al. (1993) in Ahmedabad showed total PAH concentration of 90–195 ng m $^{-3}$ in an industrial area and between 23–66 ng m $^{-3}$ in a residential area. Concentration of four PAHs in an industrial area in Mumbai ranged between 20–95 ng m $^{-3}$ (Pandit et al. 1996). PAH concentration in residential, commercial and industrial areas in Nagpur were 125–190 ng m $^{-3}$ with over 70% of the mass in particles less than 10 μm diameter (Vaishali et al. 1997). PAH concentrations in indoor studies from Lucknow were found high for cow dung cake combustion ranging from 2.23–46.07 μg m $^{-3}$ and lowest for LPG combustion ranging from 0.86–4.76 μg m $^{-3}$ (Bhargava et al. 2004). Studies carried out at Mumbai revealed higher concentrations of PAHs in the breathing zones and maximum concentrations in winter compared to summer (Kulkarni and Venkataraman 2000). Bimodal size distributions were obtained with a predominance of non-volatile PAH species in the fine mode and semi-volatile PAH species in the coarse mode with automobile emissions being the primary PAH contributor along with cooking fuel combustion and industrial oil burning.

Agra (India) has experienced rapid urbanization and industrial expansion resulting in increased utilization of fossil fuels in automobiles, trucks and public transportation. It observes an arid climate that may further aggravate pollution levels resulting in enormous levels of suspended particulate matter, which have been reported to vary between 130–190 μg m $^{-3}$ (Parmar et al. 2001). Studies on characterization of wet deposition, dry deposition, aerosols, fog and dew have been carried out at Agra particularly with reference to their inorganic constituents (Saxena 1992, 1996; Kulshrestha et al. 1995, 1998; Kumar et al. 1996; Parmar et al. 2001). However, no data on PAHs and other organic compounds are available.