Characterization of particulate-bound polycyclic aromatic hydrocarbons and trace metals composition of urban air in Delhi, India

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ABSTRACT

The concentrations of sixteen polycyclic aromatic hydrocarbons (PAHs) and trace metals adsorbed to respirable particulate matter (PM $\leq$ 10 μm) and the fine fraction of particulate matter (PM $\leq$ 2.5 μm) were determined at a site in Delhi (India) during the winter and summer periods in 2007–2008. The annual mean concentrations for PM_{10} and $PM_{2.5}$ were 138.5 ± 40.4 μg m^{-3} and 50.6 ± 20.4 μg m^{-3}, respectively, with higher concentrations during winter than summer period. Concentrations of PM_{10} and $PM_{2.5}$ have been found that were higher than the prescribed limits of the WHO and the NAAQS given by CPCB, India. The trace metals detected in the PM_{10} and $PM_{2.5}$ were Al, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn and their concentrations were similar to those observed in heavily polluted urban areas from local traffic and other anthropogenic emissions. Total PAH concentrations for PM_{10} and $PM_{2.5}$ were much higher in winter (81.5 and 96 ng m^{-3}, respectively) compared to summer (33.1 and 45.8 ng m^{-3}, respectively) with high molecular weight homologues (4–6 ring PAHs), which account for 80–95.8% of total PAHs. In general, the $PM_{2.5}$ PAH concentrations were higher than PM_{10} particles. The results of diagnostic ratio and enrichment factor analyses showed that vehicular and anthropogenic emissions related to combustion, industrial processes as well as natural sources associated with the transport of dust from the roadside area were the main pollutant sources for PAHs and trace metals.

1. Introduction

Airborne particulate matter (PM) within most urban areas of developing countries derives from a wide variety of sources such as road traffic emissions, secondary particles and coarse particles (deriving mainly from marine aerosol), resuspension of soils and road dusts (APEG, 1999). Recent studies in urban atmospheres showed that the concentrations of PM_{10} and $PM_{2.5}$ aerosols exhibit good agreement with traffic-related pollutants (both diesel and gasoline vehicles) and their health effects through respiratory and cardiac diseases (Lee et al., 2006).

Ambient particulate matter consists of various organic compounds, which includes volatile or semi-volatile organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) compounds, which are formed due to incomplete combustion of organic materials and these, are carcinogenic and/or mutagenic in nature (Larsen and Larsen, 1998). Some studies in India have examined PAHs associated with Total Suspended Particulate (TSP) and PM_{10} aerosols in urban and remote areas (Sharma et al., 2007;

Khillare et al., 2008) but study on determination of PAHs associated with $PM_{2.5}$ has not been done so far in India.

Heavy metals constituting the PM, arising from different environmental sources are an important group to be considered due to their toxic characters. Many studies have been done in India addressing the problem of pollution by heavy metals either based on short-term studies of coarse suspended particulates or TSP (Tripathi et al., 2004; Srivastava et al., 2009; Sridhar et al., 2010) and on metal composition of PM_{10} (Karar and Gupta, 2006; Nair et al., 2006; Kulshrestha et al., 2009) but there are very few studies on metal composition of $PM_{2.5}$ (Kulshrestha et al., 2009).

Large amount of data on concentration levels of SPM, NO_x, SO_2, CO and PAHs associated with TSP are available for prominent urban areas in India; studies on the simultaneous measurements of trace metals and PAHs from PM_{10} and $PM_{2.5}$ in ambient air of major cities are rather limited. In the present study, the seasonal variations of particle associated PAHs and trace metals in Delhi is evaluated in order to assess the behaviour of these compounds and their risk for human health. The seasonal distribution of the PM fraction in selected major cities of various countries has also been compared with ones in Delhi. Diagnostic ratios and Enrichment factors are also determined to evaluate the different pollution sources contributing to the trace metals and PAHs.

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2. Experiments

2.1. Study area and site description

Delhi, the capital of India, has a geographic area of 1483 km^2 and is situated at latitude of 28°24′17″N–28°53′N and the longitude of 76°20′37″E–77°20′37″E with an altitude of 216 m above mean sea level. Delhi is surrounded by four different climatic zones i.e., the Himalayas in the north, central hot plains in the south, the Thar Desert in west and the Gangetic plain in the east. Delhi lies in the semi-arid zone of India. The summers and winters are extreme with maximum and minimum temperatures as 45.6 °C and 27.6 °C in summers (March–June) and 22.2 °C and 2 °C in winters (November–February), respectively. The air over Delhi is dry during the greater part of the year with April and May being the driest months. The monitoring site (G.G.S.I.P University campus) located in the eastern part of Delhi is just 50 m away from the busy road with unique transportation which includes buses, gasoline passenger vehicles, taxis and trucks fuelled by diesel. Around 100 m from the sampling site, many local roads interweave together and have a large amount of motor vehicles. The traffic density at the sampling site was approximately 500–600 vehicles per hour during the sampling period. There are no other large combustion sources nearby besides vehicular emissions. The map of Delhi showing the sampling site is given in supplementary information; Fig. S1.

2.2. Ambient sampling

The samples for particulate matter were collected by Respirable Dust Sampler APM 460 BL, (flow rate: 1.2 Lpm) and Fine Particulate Sampler APM 550 (flow rate: 16.6 Lpm) (both supplied by Envirotech Instruments Pvt. Ltd., Okhla, Delhi) for PM_{10} and $PM_{2.5}$ respectively. Whatman GF/A glass-fibre filters were used for collection of PM_{10} and $PM_{2.5}$ (size 8″ × 10″ and 47 mm, respectively). The instruments were kept at 15 m above the ground level. Collection for PM was performed in two periods: winter (22nd November 2007–26th February 2008) and summer (2nd April–25th June 2008), with 16 and 14 samples for winter and summer, respectively. Glass-fibre filters (GFFs) used for the particulate matter sampling were pre-cleaned by baking at 550 °C for 10 h before use to minimize PAH and trace metals blank in the GFFs.

Before and after sampling the filters were kept in a Secador desiccator (Tarson) under controlled temperature (5–30 °C; with automatic controller) and 35–40% relative humidity for at least 24 h to prevent hydration of the filter surface. The filters were weighed twice before and after sampling using four digit microbalance with 0.010 μg sensitivity (Sartorius, Model: GC1603S-OCE) to obtain PM_{10} and $PM_{2.5}$ concentration respectively. After weighing, the filter papers were packed in aluminium foil to protect them from sunlight and they were stored under refrigeration (−16 °C) to prevent volatilization of PAHs of lower molecular weight, until extraction and analysis could be completed. It is pertinent to mention here that only the particulate PAHs associated with PM_{10} and $PM_{2.5}$ may be trapped on the glass-fibre filter. Since, in the present study no collection media (sorbent) was used down-stream of the filters to collect the gaseous component of PAHs; the measured values of PAHs would have in all probability a low bias (USEPA, Method TO-13A).

2.3. Extraction of PAHs and analysis by GC–MS

The PAHs were extracted from the PM collected on the filter paper using appropriate solvents. For extracting the PAHs, a quarter of the filter paper was taken (both in PM_{10} and $PM_{2.5}$) and further cut into strips and was extracted with 30 mL of HPLC-grade dichloromethane (DCM) using ultrasonic agitation for 30 min, the extraction procedure was repeated two times more to attain maximum extraction. The extract was evaporated to small volume (∼5 mL) using a rotary evaporator at a temperature between 30–40 °C and then under flow of ultra pure nitrogen gas, it was further reduced and finally adjusted to exactly 1 mL by DCM after filtering through membrane filter (PVDF 0.5 μm micro syringe). The extract was then injected into GC–MS for analysis. 0.5 ng of semi-volatile internal standard supplied by Supelco was added to all extracts prior to chromatographic analysis. The particulate PAHs were quantified by Hewlett–Packard 5890 Gas Chromatograph-5971A Mass selective Detector (GC–MS) system equipped with a fused silica capillary DB-5 column (30 × 0.25 mm i.d., 0.25 μm film thickness). The Carrier gas was helium (0.5 ml min^{-1}). The ionization was carried out in the electron impact mode at 70 eV and the mass range scanned was from 50 to 550 amu under full scan acquisition mode. The temperature program was as follows: initial temperature of 50 °C was held for 2 min, increased at rate of 4 °C min^{-1}–280 °C, then held for 20 min. 1 microlitre volume of each sample was injected in the splitless mode and the purge time was 1 min. Identification and quantification of 16 PAHs compounds were based on matching their retention time with a mixture of PAH standard (Supelco-EPA 610 PAH mix, Supelco, USA). The 16 PAHs compounds were Naphthalene (Naph), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Flt), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Dibenzo[a,h]anthracene (DahA), Benzo[ghi]perylene (BghiP), and Indeno[123-cd]pyrene (IcdP).

Blank samples (including two GFFs) were prepared, treated and analyzed in the same manner as the real samples to evaluate analytical bias and precision. The method detection limit (MDL) was used to determine the lowest concentration level that can be detected which is statistically different from a blank. The MDL was determined by selecting the concentration slightly higher than the lowest concentration of the standard line. This blank concentration was repeated several times to estimate the standard deviation. Then, the MDL was based on three times the standard deviation of the blank concentration. Method detection limits were between 0.039 ng and 0.531 ng for BghiP and Chr, respectively. Recoveries of PAHs were calculated by spiking a standard PAH solution containing the 16 PAHs (16PAH-mix, Supelco, U.S.A) in a quarter piece of a blank filter and following the same experimental procedure used for the sample treatment. For the 16 spiked individual PAHs, the recoveries from Naph to BghiP were from 60 to 115% for the GFF. Reproducibility was calculated on replicate analyses giving an error of about ±12%.

2.4. Analysis of heavy metals

Another quarter of the filter was taken for the estimation of heavy metals by Wavelength Dispersive X-Ray Fluorescence Spectrometer (WD-XRF), S4 Pioneer (Bruker AXS) equipped with Rh X-Ray tube, a 2.7 kW generator, an eight-position automatic crystal changer, a gas flow-proportional counter and a scintillation detector. The spectral data were processed with Spectra^{Plus} software. The following metals were quantified: Al, Ca, Cr, Cu, Fe, Mn, V, Ni, Pb, Cd and Zn. Minimum detection limits (MDL) for most of the elements varied from 4 to 35 ng m^{-3}. Some of the other elements (Co, Zr, As, Mo and Sn), although principally