

## **Profiles, Carcinogenic Potencies, Sources and Association of Black Carbon and Polycyclic Aromatic Hydrocarbons in Size-fractionated Urban and Forest Soils of Delhi, India**

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### **Abstract**

Polycyclic aromatic hydrocarbons (PAHs) belong to a group of hazardous pollutants with strong carcinogenic and toxic properties. Black carbon (BC) has attracted considerable interest from environmental chemists because of its enhanced sorption capacity for some hydrophobic organic compounds. The study focused on two key components of PAH chemistry in the soil environment. First, the distribution of PAHs, BC, and total organic carbon (TOC) in size-segregated soil was evaluated to help explore an interaction between soil grain size and pollutant fractionation. Second, the relationship between PAHs and carbonaceous species in soil layer was investigated as the controlling factor of PAH pollution cycling. This work can thus be represented as the first effort to concurrently measure the distribution of PAH, BC, and TOC in Indian soil.

New Delhi, the capital of India, is also one of the most polluted cities in the country. Soil samples were collected over a year-long period from Bawana forest and R. K. Puram urban area in Delhi, India. Analysis of 16 USEPA priority PAHs, black carbon (BC), and total organic carbon (TOC) in five grain size fractions,  $x$ , in  $\mu\text{m}$  of  $0 \leq x < 53$  (I),  $53 \leq x < 250$  (II),  $250 \leq x < 500$  (III),  $500 \leq x < 2000$  (IV), and their sum (total: T) were conducted. The PAHs were detected by HPLC using a UV detector at a wavelength of 254 nm. BC was

determined by Chemo-Thermal Oxidation method for soils at 375°C (CTO 375) and subsequent analysis on CHNS-O Analyzer.

**Keywords:** Soil, Delhi, Polycyclic Aromatic Hydrocarbon, Black carbon, size fraction.

## 1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) belong to a group of hazardous pollutants with strong carcinogenic and toxic properties (IARC, 1983). Several PAH species have been classified as probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer (IARC, 1987). In addition, benzo[a]pyrene is now classified by IARC as a Group 1 carcinogen—known to cause cancer in humans. The major source of PAHs in the environment is incomplete combustion of fossil fuels (Lima et al., 2005). It has been estimated that more than 90% of the total environmental burden of PAHs reside in surface soils (Wild and Jones, 1995). PAHs in soils, once accumulated, lead to contamination of vegetables and other crops to enter the food chain as one of the key human exposure routes (Khan and Cao, 2011). Black carbon (BC) has attracted considerable interest from environmental chemists because of its enhanced sorption capacity for some hydrophobic organic compounds (e.g., at least 10–100 times) relative to amorphous organic matter (AOM). The objectives of the study were: 1) to determine the distribution of PAHs, BC, and total organic carbon (TOC) in size-segregated soil, 2) to evaluate the association of PAHs, BC, and total organic carbon (TOC) and 3) to determine the sources of carbonaceous species. This work can thus be represented as the first effort to concurrently measure the distribution of PAH, BC, and TOC in soil.

## 2. Methodology

Delhi has a population of approximately 18 million with a geographic area of 1,483 sq km and lies in the semi-arid zone over the sub-tropical belt with an altitude of 216 m above mean sea level. Climatic conditions of Delhi are extreme in terms of temperature with maximum (46°- 47°C) in May-June (summer) and minimum (1°- 2°C) in December-January (winter). Its mean annual rainfall is 612 mm, around 80% of which is received during the monsoon months (July-September). Winds are predominantly northwesterly except in the monsoon season when easterly and southeasterly winds are most common (Agarwal et al., 2009). However, relatively little is known about their distributions along with various land-use patterns and partitioning in the soil layer, especially with respect to soil grain size. In order to understand the influence of urbanization as a diffuse anthropogenic source on the surrounding environment (Jensen et al., 2007), we carried out the study for PAHs by exploring the mobilization and equilibrium status of PAH concentrations in various soil fractions across urban and forest areas.

Forest soil samples (BG) were collected from Bawana City Forest situated in the northern part of Delhi. The vegetation in this forest was of arid nature, mainly consisting of Babool (*Acacia nilotica*) and Cactus (*Opuntia ficus indica*). These BG sampling sites were located 100 metres away from the Bawana Road. There were no industries nearby and a fairly low vehicular traffic density. The urban site (UB) was located in R. K. Puram in the southern part of Delhi. Samples at the UB site were collected from a small park inside a residential complex of Sector 12, R. K. Puram. The UB site is likely to be impacted upon by pollution from adjacent roads with heavy traffic and from residential/domestic heating.

Soil samples were collected over a year-long period from Bawana forest and R.K. Puram, urban site in Delhi, India for the analysis of 16 priority polycyclic aromatic hydrocarbons, black carbon (BC) and total organic carbon (TOC) in five grain size fractions. The five grain sizes that were analyzed were (in  $\mu\text{m}$ ) 0- 53, 53 - 250, 250 - 500, 500 – 2000, and their bulk samples. PAHs were determined by HPLC using UV detector at 254 nm. BC was determined by Chemo-Thermal Oxidation method for soils at 375°C (CTO – 375) method using Carbon Analyzer. Seasonal variation showed maximum pollutant concentration during winter.

### **3. Results and Discussions**

Maximum concentrations of PAH, BC and TOC were observed in the smallest size fraction (0 - 53  $\mu\text{m}$ ) comprising silt and clay, irrespective of site or season. It is possible to infer that PAHs in macro-porous fractions are more prone to volatilization or degradation relative to micro-porous fractions.

The mean TPAH concentration at the BG site varied from 511 to 694  $\mu\text{g}/\text{kg}$ . The PAH pattern at BG site was dominated by LPAH (> 70% of TPAHs; Fig. 3). This finding suggests that the BG site, being upwind of the city, is less significantly affected by anthropogenic emission. Among the individual PAHs, naphthalene (NAP) showed the maximum concentration, followed by acenaphthylene (ACN) and acenaphthene.

The mean TPAH concentration at the UB site varied between 991 and 2241  $\mu\text{g}/\text{kg}$  across the various fractions. The PAH concentration pattern at the UB site was dominated by high molecular weight four-ring PAHs. The PAH concentration pattern at the UB site was dominated by four-ring PAHs such as pyrene (PYR), fluoranthene (FLT), and phenanthrene (PHN). These three PAHs are commonly considered tracers of vehicular emissions (Wan et al., 2006). The mean PAH concentration at the urban (UB) site was 1794  $\mu\text{g kg}^{-1}$ , three times higher than forest (BG) soil (619  $\mu\text{g kg}^{-1}$ ).

Carcinogenic PAHs at the UB site were 11 times higher than those at the BG site. The mean BC levels measured at the background and urban sites were 0.47 and 0.82  $\text{mg g}^{-1}$  respectively. Correlation analyses of PAH and BC shows significant correlations ( $p < 0.001$ ) at the background and urban sites. ANOVA shows significant differences in PAH, BC, and TOC concentrations at both the sites.

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Results of the molecular diagnostic ratios and principal component analysis (PCA) identified biomass burning, and vehicular emissions as major sources of PAHs at the two sites, while BC/TOC ratios pointed toward biomass combustion as the chief source of carbonaceous species. Results of the molecular diagnostic ratios and principal component analysis (PCA) identified biomass combustion as the major source of PAHs at the forest site and vehicular emissions at the urban site.

#### 4. Conclusion

This study is first of its kind considering PAH, BC, and TOC in size – segregated Indian soils. Based on this study, we can conclude that both BC and TOC are important geosorbents for PAHs. Both of these geosorbents, especially black carbon can be harnessed for sequestering PAHs by limiting their transport and retarding their bioavailability.

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