

ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) and heavy metals are the two major groups of pollutants in terms of effects on human health and ecosystem, emitted from anthropogenic sources. The United States Environmental Protection Agency (USEPA) has prioritized a list of 16 PAHs for monitoring in the environment for protecting human health. Recent researches have documented occurrence of PAHs in soil, aquatic and atmospheric environments worldwide. The fate and toxic effects of PAHs in soil are strongly affected by organic carbon (OC). The environmental behavior, distribution and bioavailability of PAHs were also affected by black carbon (BC) due to their similar source of origin. Colloids, including both organic and inorganic, have a great ability affecting transport of metals and PAHs.

Assessment of heavy metals in surface soil and groundwater is important due to their toxicity. Since both heavy metals and PAHs are emitted from similar sources they could be used together for source apportionment study.

This study explores all attributes of PAHs and heavy metals in soils and groundwater of two oilfields of upper Assam with the following objectives:

1. To understand the spatial and seasonal distributions of PAHs and some heavy metals in surface soil and groundwater around oilfields of upper Assam.
2. To understand the nature of the sources of PAHs in oilfield areas.
3. To evaluate the ecological risk of PAHs and heavy metals.
4. To establish association of PAHs signatures in surface soil to PAHs signature in groundwater to understand the mode of transport of PAHs from surface soil to groundwater.

The study was conducted around two oilfields of Assam-Arakan Basin located in Jorhat and Golaghat district of upper Assam namely Borholla and Nambar oilfield. Surface soil and groundwater sampling was carried out in 15 different sites around Borholla oilfield and 21 different sites around Nambar oilfield based on various land use pattern (oilfield sites, roadside sites and residential sites). Soil and water samples were collected for three successive seasons viz. pre-monsoon, monsoon and post-

monsoon for two years i.e. 2011 and 2013 around Borholla oilfield and for one year i.e. 2013 around Nambar oilfield.

The extraction of PAHs in surface soil samples was carried out by ultrasonic extraction and extraction of water samples was done by liquid-liquid extraction (LLE) method as per APHA (American Public Health Association). The purification and fractionation of concentrated sample was achieved by silica gel column chromatography by following the USEPA method 3630C. Finally, analysis of PAHs was performed using a High Performance Liquid Chromatography (HPLC) system equipped with UV detector.

The organic carbon (OC) in surface soil sample was determined by Walkley and Black Method. The OC content of the water sample was estimated in TOC analyzer (Elementer, Liqui TOC II, Germany). Black carbon present in soil samples was quantified by TOC analyzer (Analytik Jena, HT1300). Heavy metal analysis was done in ICP-OES (Inductive coupled plasma- optical emission spectroscopy; Perkin Elmer Optima 2100DV). All the major cations and anions in water samples were analysed as per standard procedure given by the APHA and similar procedure was adopted for soil sample, which was performed in soil solution (1:5; soil: distilled water).

Strict quality control measures were employed throughout the analysis. Triplicate sample analyses were done to achieve precision and accuracy of measurements.

All the statistical analyses were performed using the SPSS (Statistical Package for Social Sciences, version 16.0). Back trajectories were figured from the archive data of Global Data Assimilation System model using NOAA Air Resource Laboratory's (ARL) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model.

Seasonal variation in PAHs concentration was observed in both the oilfields, with maximum concentration during post-monsoon followed by pre-monsoon and monsoon season. In Borholla oilfield, soil mean Σ PAHs concentrations were 2840 ± 1770 , 534 ± 298 and 3920 ± 2810 ng g⁻¹ during pre-monsoon, monsoon and post-monsoon seasons of 2011 respectively. In 2013, soil mean Σ PAHs concentrations were 2800 ± 1870 , 549 ± 570 and 3910 ± 2980 ng g⁻¹ during pre-monsoon, monsoon and post-monsoon seasons respectively. In Nambar oilfield, soil mean Σ PAHs concentration was 996 ± 555 during pre-monsoon, mean 346 ± 187 during monsoon and

1330 \pm 729 ng g⁻¹ during post-monsoon season. Maximum concentration of BaP was recorded in roadside soil, BS15 (2150 ng g⁻¹) in Borholla and NS2 (84.6 ng g⁻¹) in Nambar oilfield. Minimum rainfall and temperature increase scavenging rate of PAHs along with enhanced biomass burning activities lead to higher deposition on soil surface during post-monsoon. On the other hand heavy rainfall during monsoon results in runoff and lower soil PAHs concentration. Prevailing atmospheric condition with thermal inversion and long range atmospheric transport are attributed as the possible cause for high PAHs accumulation in post-monsoon period.

Roadside sampling sites showed maximum total PAHs concentration in both the study areas, mostly attributed to vehicular emission sources. Soil PAH profiles in both the oilfields were dominated with LMWPAHs (Low molecular weight PAHs). During monsoon period lowest abundance of carcinogenic PAHs was observed in both the oilfields.

Source apportionment studies based on diagnostic ratio of marker species revealed the dominance of pyrogenic input of PAHs in surface soil as well as groundwater of both the oilfields; however some ratios also indicate petrogenic input of PAHs. Biomass, wood and coal combustion, traffic related diesel emission were the main sources of pyrogenic PAHs. Principle component analysis along with multiple linear regression (PCA-MLR) also indicated the dominance of pyrogenic sources of PAHs with <26% of contribution from petrogenic sources in Borholla oilfield and <18% in Nambar oilfield. PAHs dissipation in surface soil, specifically the LMWPAHs was controlled by both BC and OC, indicating that PAHs were mostly from combustion derived sources.

Concentration of heavy metals in surface soil was also showed seasonal variation with higher values during post-monsoon period. Heavy metal toxicity in soil as per various pollution indices revealed low to moderate toxicity. Relationship of PAHs with heavy metals and major ions signified there co-emission sources.

Despite their hydrophobicity the presence of PAHs in groundwater is due to the colloid facilitated transport of these compounds. Seasonal variation in PAHs concentration was also observed in groundwater samples with maximum concentration during post-monsoon period and minimum during monsoon period in both the oilfields. Lowering of the water table during post-monsoon period results in

increased concentration of PAHs, whereas dilution of PAHs compounds due to rise of water table during monsoon caused decreased concentration of PAHs.

Dominance of LMWPAHs in PAHs profile of groundwater could be due to their high water solubility. Sources of both petrogenic and pyrogenic input of PAHs in groundwater was identified by using diagnostic ratio. TOC showed positive correlation with total PAHs in all seasons which suggested that organic carbon could have played a significant role in the transport of PAHs in groundwater. Heavy metal and major ions also showed positive relationship with some PAHs, signifying that PAHs enter into groundwater through inorganic and organic colloids.

PAHs signature of surface soil was correlated significantly with signature of groundwater in all three sampling seasons which suggest that colloidal transport of PAHs from soil is the main contributor of PAHs in groundwater.

Key words: PAHs; oilfield soil; colloidal transport; source apportionment; diagnostic ratios; PCA-MLR.