

Understanding Levels and Sources of PAHs in Water of Bharalu Tributary of the Brahmaputra River

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Abstract: Polycyclic Aromatic Hydrocarbons (PAHs) were assessed in Bharalu River water of Guwahati city area during two seasons of 2012-2013. Water samples of seven representative locations were analysed for USEPA's priority 16 PAHs. PAHs were extracted from water samples by organic-aqueous partitioning and were cleaned up by a silica column. Qualitative and quantitative analysis of the PAHs were performed by HPLC. Concentrations of \sum_{16} PAHs were found to be in the range 3.351-72.893 ng/ml. When compared with other studies elsewhere, levels of the present study were found to be on higher side. Profiles of PAHs were dominated by 3-, 4- and 5-ring compounds. Flan, Pyr, BaA, Chry, BkF, IP and \sum_{16} PAHs showed good correlations with OC and TC. Sources of PAHs were empirically explored on the basis of diagnostic ratios, which indicated for pyrogenic sources mainly from diesel, gasoline, coal and wood combustion. Petrogenic signature ratios of PAHs were also found.

Key words: PAHs, river water, BC, OC.

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) make an important class of ubiquitous and persistent organic pollutants. Due to carcinogenic, mutagenic and genotoxic effects PAHs have attracted much attention around the world (Thyssen et al., 1981; Clean Water Act, 1993; Matsumoto et al., 2007; Claxton and Woodall, 2007; Zanieri et al., 2007; Liang et al., 2007) PAHs are widely detected in environmental matrices and living organisms (Li et al., 2010).

One of the chief goals of environmental quality studies is to interpret the impacts of anthropogenic micropollutants such as PAHs on ecosystems in order to prevent and minimize their effects (Yu et al., 2009). Despite efforts to ensure water quality by aiming at point sources of major contaminants, many rivers and streams experience environmental quality below environmental standards (Beasley and Kneale, 2004). In general anthropogenic sources of PAHs in aquatic

environment can be both pyrogenic and petrogenic. Pyrogenic sources of PAHs include combustion of organic matter like petroleum fuel, coal and biomass. Petrogenic PAHs are from crude and refined petroleum products which can enter aquatic environments through accidental oil spills, municipality and urban runoff and industrial processes.

Surface water and sediment consists important information regarding anthropogenic activities adjacent to bank. Primary pathways of PAHs entering aquatic environments include direct wet or dry deposition from atmosphere, runoff from land, roads, pavements, roofs, guttering and industries (Marsalek et al., 1999; van Metre et al., 2000) and direct water outlet (Maliszewaska-Kordybach, 1999). Stormwater is a major delivery route of PAHs to the receiving water bodies irrespective of types of sources of PAHs in urban areas. Therefore, to address effective control and remediation of these pollutants their source and sink have to comprehended well (O'Reilly et al., 2010).

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In urban soils non-homogenous distributions of PAHs is observed (Müller et al., 2000). Upon entering aquatic systems, PAHs preferably tend to settle, partition or adsorb onto non-aqueous phase such as soil or sediment due to their hydrophobicity (Cornelissen et al., 2006) and high octanol/water partition coefficients. Adsorption to solid particles makes them less susceptible to degradation (Guzzella and Depaolis, 1994). So, the presence of PAHs in water system of a river can also be used as an indicator of their presence in sediment.

Due to their mutagenic and carcinogenic effects to land and water organisms (Connel et al., 1997), distribution and sources of PAHs in aquatic environment near urban centres have received much attention. Potentially hazardous and persistent nature of PAHs in the environment encouraged the USEPA to include 16 of them (Appendix A) into priority list of pollutants (Manoli et al., 2000). The Water Framework directive 2000/60/EC considered them as priority substances due to their environmental behaviour and their toxic effects. High toxicity, high stability in the environment and lipophilic nature of PAHs enable them to transport through food chains with human being as final destination (IARC, 1983; Okay et al., 2000; Vagi et al., 2005). The EU Directive 98/83/EC, relevant to drinking water, has set a limit of 0.10 µg/L for the sum concentration of BbF, BkF, BgP and IP and 0.010 µg/L for BaP (European Communities (Drinking Water) Regulations, 2007). Thus, monitoring of these compounds in surface water can provide inputs for potential toxic effect assessment of these pollutants in addition to decision-making for management authorities (Nikolaou et al., 2009).

India is a land of great rivers. However, after so many years of industrialization studies on PAHs of river water are limited. Assam, a state in the Northeast India, is also blessed with two large rivers namely Brahmaputra and Barak with several tributaries covering the entire state.

Bharalu river, once comforted thousands of people living on its bank with fish and many aquatic flora and fauna in addition to potable water a few decades ago, has become the carrier of city's wastes over the years. With continuous deposition of all types of urban wastes and discharge by drains to the river made it more or less a stagnant water body with shallow bed. During the monsoon, stormwater carries huge load of sediments from the city's catchment areas and during this rainy season one can see the river flow. So, the polluted Bharalu water may also meet the aquifers and contaminate the groundwater, which is a source of drinking water of large population of the city.

In this paper, levels of USEPA's priority 16 PAHs, total carbon (TC), organic carbon (OC) and inorganic carbon (IC) concentration trends of surface water of Bharalu river during two sampling seasons have been presented. Spatial and temporal variations of PAHs in water together with the composition profile on the basis of number of rings of the compounds have been discussed. Toxic Equivalency Factors (TEFs) of the PAHs which indicate the potential toxicological risk have been presented as BaP equivalents. Source identification of PAHs has been addressed empirically on the basis of diagnostic ratios of marker species. As the river discharges into Brahmaputra river, the unknown risk can be ascertained from this study.

Methodology

Study Area

Bharalu originates in Meghalaya hills, runs through entire stretch of Guwahati city and finally meets Brahmaputra. Guwahati is situated between the bank of Brahmaputra river and foothills of Shillong plateau spread around 26.1° N and 91.8° E. The monsoon brings heavy rainfall to Guwahati. Temperature fluctuates between 35° and 10° C during summer and winter months respectively.

The city has a dense human population with heavy concentration of vehicular traffic. As per the 2011 Government of India census Guwahati recorded population of ~1.0 million at a decadal growth rate of 8%. Over the last decade Guwahati witnessed a vehicular growth (both light and heavy motor vehicle) of ~87% with 58,638 numbers of vehicles plying on road in the first quarter of 2013.

Description of Sampling Sites

Sampling locations are shown in Figure 1. Seven sampling locations were chosen from the entire stretch of Bharalu river within the city area based on local activities and effluent discharge. Local characteristics of the sampling locations are illustrated in Table 1.

Sample Collection

Surface water samples were collected during the post-monsoon (October-November 2012) and pre-monsoon (February-March 2013) seasons. Samples were collected with an amber colour bottle of one litre volume. Bottles were pre-washed with acetone and oven dried to avoid contamination. Samples were carried to the laboratory within 24 hours, filtered to remove debris and preserved at 4°C till further processing.

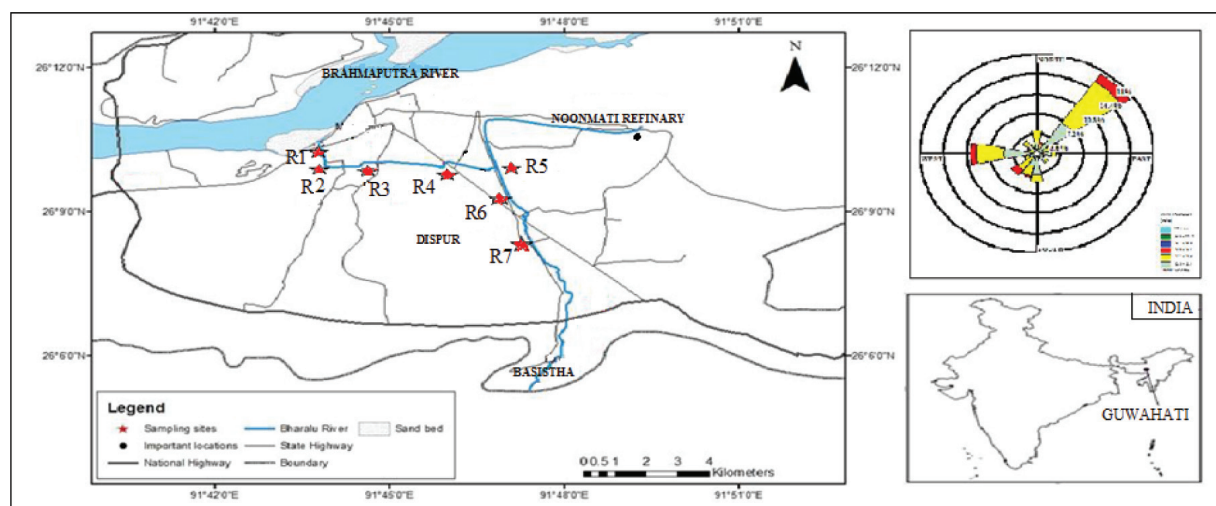


Figure 1: Sampling sites shown in map of Guwahati (inset: prevailing wind condition and location of Guwahati in India).

Table 1: Description of sampling sites

Sites	Coordinates	Prevailing activities
R 1: Bharalumukh	91°44.798' E 26°8.49' N	Confluence of Bharalu to Brahmaputra. A commercial and residential area with heavy traffic.
R 2: Kumarpara	91°73.555' E 26°14.713' N	Market place with residential apartments with high traffic density with 2–3 wheeler motor vehicles.
R 3: Athgaon	91°44.345' E 26°10.27' N	An important commercial area and large business houses are built here.
R 4: Rajgarh	91°46.231' E 26°10.48' N	A place with thick vehicular traffic. Many commercial complexes are set up here.
R 5: Zoo Road	91°46.453' E 26°10.113' N	A mixed commercial and residential area and heart of the city.
R 6: Sundarpur	91°46.586' E 26°9.34' N	A completely residential area.
R 7: Dispur	91°47.424' E 26°8.519' N	The capital region of Assam state, a busy commercial and thickly populated area. The location is surrounded by residential complexes, industrial estates, office buildings, schools, automobile workshops and business houses. Lots of vehicular movement is common here with frequent traffic blockage.

Chemicals

Standard mixture of 16 PAHs (specified in EPA method 610) was procured from Sigma-Aldrich (Germany). The four internal standard mixture naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene- d_{10} and chrysene- d_{12} were obtained from Supelco (Bellefonte, PA, USA). All solvents (acetonitrile, cyclohexane, dichloromethane, hexane and pentane) of HPLC and analytical grade were used for sample processing and analysis. High purity deionised water from Milli-Q system was used for the HPLC runs.

Sample Extraction

Each 1000 ml filtered water sample was extracted by liquid-liquid extraction (organic-aqueous partitioning) in a separating funnel according to the method described by APHA (1998). Organic phase mixture of 100 ml *n*-hexane and dichloromethane (1:1 v/v) was used to extract the PAHs with a separating funnel. Every sample was considered for three repeated extractions, which were combined and reduced to about 2 ml in a rotary evaporator.

Clean Up

Clean up of samples were done as per USEPA method.* PAHs in the extracts were separated by a silica column of 10 mm internal diameter. Ten gm of activated silica (130° C for 12 hours) of 100-200 mesh (Merck) was made to slurry with dichloromethane and packed into column. The column was capped with sodium sulphate and prewashed with 40 ml pentane at 2 ml min⁻¹ and the eluent was discarded. The sample was then loaded into the column in 4 ml cyclohexane and eluted with 25 ml pentane and discarded. Finally for desired PAHs in the sample, the column was eluted with 25 ml mixture of dichloromethane and pentane in 2:3 ratio (v/v). This time, the eluent was taken and evaporated to reduce volume for analysis.

Analysis

Sample analysis was done in HPLC (Waters) equipped with UV detector (254 nm) and Waters PAH C18 column (4.6 mm × 250 mm, 5 µm particle size. Acetonitrile and water was used as the carrier in a gradient mode (Agarwal, 2009). The quantitative estimation was done with external and internal calibration standards by calculating relative response factor (RRF). Compound concentration was calculated using both peak area response and mean RRF for both internal and external standard. Appendix A illustrates the retention times of the PAHs together with their LOD and solubilities.

Determination of Carbon

Total carbon (TC), organic carbon (OC) and inorganic carbon (IC) content was quantified in TOC analyser (Analytikjena, multi N/C HT1300) equipped with a Non-dispersive Infrared Detector. Measurement calibrations were done with sodium carbonate graduated standard solutions.

Quality Control

All samples and laboratory blanks were spiked with internal standard mixtures prior to extraction to determine analytical recovery efficiencies. The average recoveries for water samples spiked with 40 ppm of internal standard were found to be 78±34% for naphthalene-d₈, 82.44±36.26% for phenanthrene-d₁₀ and 73.65±29.22% for chrysene-d₁₂.

The limit of detection (LOD) was found to be between 1.4 and 32.9 ppb from Naph to IP (Appendix A). LOD was calculated as two times the standard deviation of the replicate analysis of extremely low concentration

of external standards ($n = 5$). For statistical analysis of the data below detection limit (BDL) values were replaced by half of LOD. Periodically blank samples were performed to avoid contamination.

Result and Discussion

PAHs

Concentration of PAHs with their mean and range are shown in Table 2. The concentration of total detected PAHs in Bharalu river ranged 3.351-72.893 ng/ml with mean value of 29.8±21.7. The highest Σ_{16} PAHs was found at R5 during pre-monsoon and lowest at R1

Table 2: Mean concentration (ng/ml) with range of individual PAHs, Σ PAHs and their mean BaPq concentration in Bharalu river

Compound	Mean (Range)	BaPq mean
Naph	2.0±2.1 (BDL-6.6)	0.002±0.002
Acy	1.2±2.3 (BDL-7.2)	0.001±0.002
Acen	0.5±0.5 (BDL-1.8)	0.0004±0.0005
Flu	1±1.2 (BDL-3.9)	0.001±0.001
Phen	8.0±4.2 (BDL-13.7)	0.008±0.004
Anth	1.1±1.5 (BDL-4.9)	0.011±0.015
Flan	1.9±1.6 (BDL-5.6)	0.002±0.002
Pyr	7.1±7.9 (BDL-16.9)	0.007±0.008
BaA	0.40±0.5 (BDL-1.2)	0.036±0.021
Chry	3.2±2.1 (BDL-8.3)	0.032±0.021
BbF	8.3±15.3 (BDL-44.5)	0.827±1.531
BkF	2.8±5.1 (BDL-14.6)	0.283±0.507
BaP	0.4±0.7 (BDL-2.6)	0.372±0.719
DBA	1.9±3.2 (BDL-7.7)	1.903±3.237
BgP	0.1±0.1 (BDL-0.1)	0.0006±0.0006
IP	5.9±10.2 (BDL-23.9)	0.591±1.022
Σ PAHs	29.8±21.7 (3.4-72.9)	2.274±3.234

*Method 3630C, EPA USA manual.

during post-monsoon. The BaP concentrations were found between BDL and 2.608 ng/ml. The highest BaP was detected during pre-monsoon at R5. R1 is the snout of the tributary. As Bharalu flows the distance through the city it probably gathers more pollutants before it finally meets the Brahmaputra river.

It is, of course, difficult to compare data of PAHs from different studies due to differences in phases analysed (dissolved, particulate or both), analytical methods and compounds considered. \sum_{16} PAHs concentrations of present study was found to be on higher side than Qiantang river of China (0.0703-1.844 ng/ml) (Chen et al., 2007) but comparable to Tiber river of Italy (0.024-0.072 ng/ml) (Patrolecco et al., 2010). However, PAHs concentration in Bharalu water was lower than that of Kori river of Iran (45.4-375.1) (Kafizadeh et al., 2011) and Yellow river of China (48.2-206) (Yu et al., 2009) (Table 3).

Spatial and Temporal Variation

Sitewise \sum_{16} PAHs is shown in Figures 2a and 2b for post-monsoon and pre-monsoon seasons respectively. On spatial basis, the highest concentration was observed at R5 during pre-monsoon. The river channel receives input from the catchment of the industrial belt of the city where the refinery and many industries are located. The industrial area around the refinery hosts few coke industries also which would have deposited large volumes of PAHs that are drained to the Bharalu river. Continuous input from various domestic and commercial discharges along with vehicular contribution could be the possible reason for such high concentration. The lowest concentration was found at site R1, during post-monsoon. Confluence of Bharalu to Brahmaputra at this site might lead to dilution of concentrated PAHs or their absorbance to surface sediment particles in mixing zone (Chen et al., 2007).

Almost all the sites showed an increase in \sum_{16} PAHs concentrations with high standard deviation during pre-monsoon compared to post-monsoon periods. Such

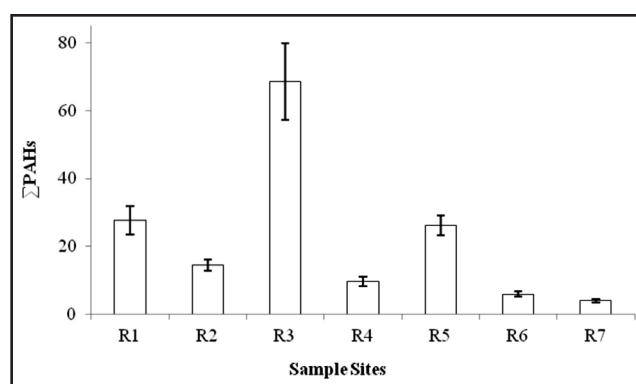


Figure 2a: \sum PAHs concentration (ng/ml) in Bharalu river water at seven sites during post-monsoon.

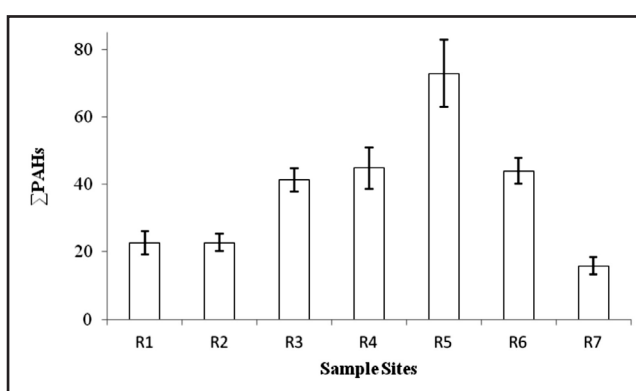


Figure 2b: \sum PAHs concentration (ng/ml) in Bharalu river water at seven sites during pre-monsoon.

results can be attributed to difference in the discharge regime of the river between the seasons. High runoff together with prevailing atmospheric conditions might have triggered PAHs dissipation and decomposition that in turn resulted into lower PAHs levels during post-monsoon (Gaga et al., 2009). On the other hand, atmospheric conditions like higher emission rates from various sources, lower inversion height, and lower intensity of sunshine with less efficient photochemical decomposition might favour more atmospheric deposition of PAHs during pre-monsoon time (Hoyau et al., 1996).

Table 3: Concentration ranges of PAHs (ng/ml) reported from different river waters

Site	Period	Total studied PAHs	\sum PAHs Conc.	Reference
Qiantang River, China	2005	15 PAHs	0.0703-1.844	Chen et al., 2007
Yellow River, China ^a	2005	16 PAHs	48.2-206	Yu et al., 2009
Tiber River, Italy	2007	6 PAHs	0.024-0.072	Patrolecco et al., 2010
Kori River, Iran	2010	16 PAHs	45.4-375.1	Kafizadeh et al., 2011
Bharalu River, India (Present study)	2012-2013	16 PAHs	3.351-72.893	Present study

^aSediment-pore water

PAHs Profile

PAHs profile was dominated mainly by 2, 3 and 4-ring PAHs in most sites (Figure 3). However, R3 sample had dominance of 5-ring PAHs. In samples of pre-monsoon, high molecular weight PAHs mainly 3-5 ring PAHs prevailed in the sites.

Percentage of carcinogenic PAHs (CPAHs = BaA + Chry + BbF + BkF + BaP + DBA + IP) to others was almost same in both the sampling time with 53% during post-monsoon time to 54% during pre-monsoon time

(Figure 4). Individually, seasonal average of the species were found to be in the order Naph>BbF>Chry>Phen>Pyr>Anth and Phen>>BbF>IP>Flan>Chry during post- and pre-monsoon seasons respectively. High abundance of Naph and Phen could be due to their high solubility in water (Appendix A). Concentration of 5-6 ring PAHs in many samples were found below detection limit (BDL).

Presence of 2-ring PAHs during post-monsoon time and its drastic decrease during pre-monsoon time

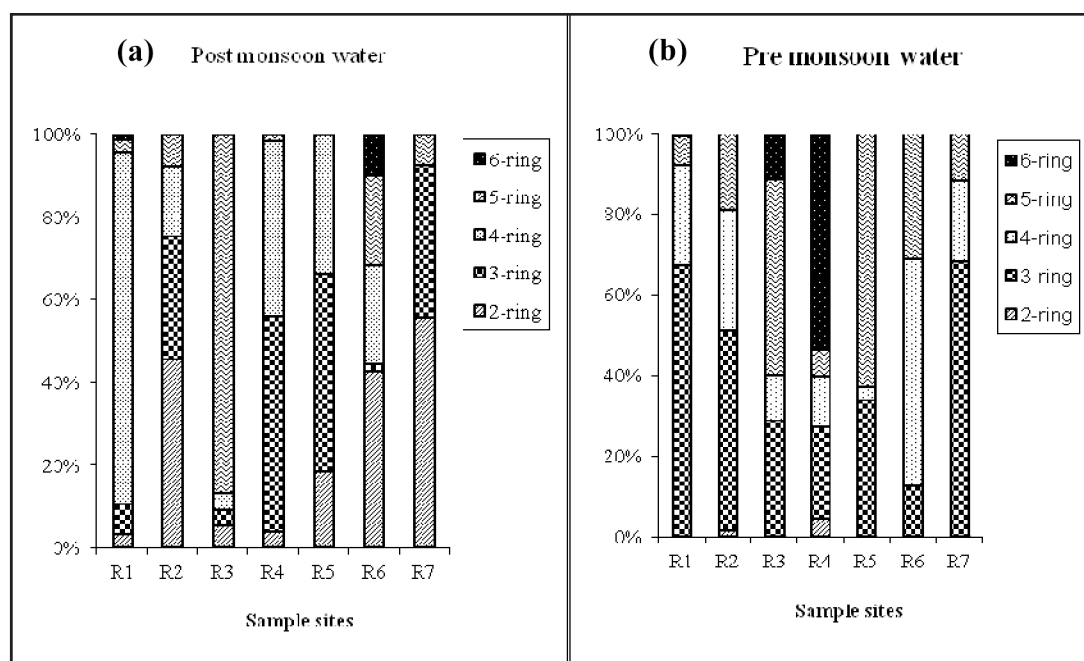


Figure 3: Percentage composition of three-, four-, five- and six-ring PAHs at seven sampling sites in Bharalu river water during (a) post-monsoon and (b) pre-monsoon seasons.

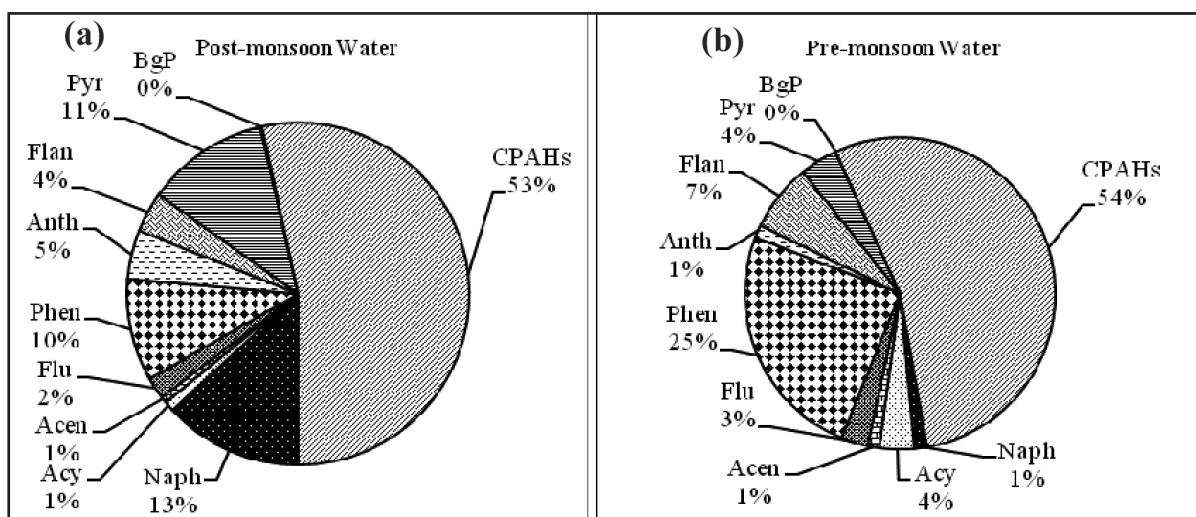


Figure 4: Abundance of carcinogenic PAHs (CPAHs) in Bharalu river during (a) post-monsoon and (b) pre-monsoon season (mean of seven sites presented).

directly indicated their photochemical degradation. The low molecular weight PAHs which used to come from various pyrogenic and petrogenic sources during heavy discharge of monsoon time prevails till post-monsoon. Gradually they undergo photochemical degradation. Similar contribution of CPAHs during both the sampling time showed a continuous input of carcinogenic PAHs from same type of sources in water. This is a matter of concern for the river system.

Toxicity Assessment

Toxic equivalency factors (TEFs) were employed to evaluate carcinogenic potential of individual PAH relative to BaP as BaP-equivalent concentration (BaPq). The calculation of BaPq is according to that of Tsai et al. (2004):

$$\text{Total BaPq} = \sum C_i \times \text{TEF}_i \quad (1)$$

where C_i is the individual PAH concentration and TEF_i is the respective toxic equivalency factor. Total BaPq concentration ranged 0.028-9.886 ngBaPq/ml with mean 2.274 ± 3.234 ngBaPq/ml (Table 2). The highest value was found at site R3 during pre-monsoon and lowest in R7 during post-monsoon season in Bharalu water. Thus the risk is comparatively high during pre-monsoon period. There is not regulation of PAHs concentrations in aquatic environment so far in India. More so in the Northeast India no systematic PAHs study has been taken up so far.

Carbon

Range of TC, OC and IC in Bharalu water were 157.5-9690 mg/l, BDL-9500mg/l and 108.3-220.2 mg/l respectively. Pearson's correlations were built between the PAHs and carbon to explore if any relationship of PAHs in Bharalu water with TC, OC and IC actually existed (Table 4). Good correlation was observed for Flan, BaA, Chry and IP with both TC and OC. However, IC showed significant negative correlation only with BaP. Thus OC could play important role in dispersion of multiple ring PAHs in water. Thus, concentration of water PAHs could also be a function of organic matter present in water, which could also mean that organic content of water favoured solubility of PAHs. The relationship of BaP with IC could not be explained. Does it indicate whether in atmospheric precipitation there is co-deposition of PAHs and carbonate/bicarbonate?

Probable Sources of PAHs of Bharalu Water

Ratios of PAHs provide accurate and reliable diagnostic tool to get clue of their sources (Perugini et al., 2007;

Table 4: Correlation matrix of PAHs with organic carbon (OC), inorganic carbon (BC) and total carbon (TC) in Bharalu river water

	TC	OC	IC
Naph	-0.137	-0.133	-0.026
Acy	-0.061	-0.06	-0.488
Acen	-0.105	-0.115	-0.601
Flu	-0.238	-0.248	-0.585
Phen	0.052	0.028	-0.515
Anth	0.099	0.082	0.256
Flan	0.602*	0.594	0.001
Pyr	0.277	0.269	0.106
BaA	0.738**	0.733**	0.144
Chry	0.462	0.438	-0.093
BbF	-0.159	-0.169	-0.462
BkF	0.303	0.295	-0.029
BaP	-0.108	-0.113	-0.569*
DBA	0.101	0.096	-0.192
BgP	-0.154	-0.112	-0.111
IP	0.673**	0.675**	0.105
ΣPAHs	0.314	0.293	-0.505

**Correlation is significant at the 0.01 level (2-tailed).

*Correlation is significant at the 0.05 level (2-tailed).

Singh et al., 2010). The average ratio C*PAHs/TPAHs close to 1 implies combustion derived PAHs in water (Parhle et al., 1984; Takada et al., 1990; Mantis et al., 2005; Ravindra et al., 2006; Gogou et al., 1996). C*PAHs/TPAHs of Bharalu water was found to be 0.465 ± 0.3 and 0.487 ± 0.22 during post-monsoon and pre-monsoon periods respectively.

The ratio IP/(IP + BgP) between 0.35 and 0.70 is considered as specific marker for diesel exhaust (Kavouras et al., 2001). Average IP/(IP + BgP) during post-monsoon and pre-monsoon period were found to be 0.664 ± 0.17 and 0.692 ± 0.12 respectively, which indicated that diesel exhaust emission could be an important source of PAHs in Bharalu water. The ratio Flu/(Flu + Pyr) > 0.5 has been inferred to indicate diesel engine emission of PAHs (Rogge et al., 1993a, 1993b; Mandalakis et al., 2002; Fang et al., 2004). In water samples the average ratios were found to be 0.664 ± 0.45 and 0.813 ± 0.364 during post-monsoon and pre-monsoon respectively. This further confirmed that there could have been input of diesel exhaust emitted matter into Bharalu river water.

Anth/(Anth + Phen) and Flan/(Flan + Pyr) ratios of >0.1 and >0.5 respectively indicate pyrolytic origin; while the ratios <0.1 and <0.5 indicated petrogenic sources of PAHs (Yunker et al., 2002). In the present study, during pre-monsoon and post-monsoon Anth/

Table 5: Average diagnostic ratio of PAHs in Bharalu river water

	<i>PoM water</i>	<i>PrM water</i>
IP/(IP + BgP)	0.664±0.17	0.692±0.12
Flu/(Flu + Pyr)	0.664±0.447	0.813±0.364
Phen/(Phen + Anth)	0.628±0.311	0.912±0.17
Naph/Phen	42.153±53.356	0.058±0.078
Anth/(Anth + Phen)	0.372±0.311	0.088±0.17
Flan/(Flan + Pyr)	0.796±0.346	0.877±0.2
C*PAHs/TPAHs	0.465±0.3	0.487±0.22

Note: C*PAHs = Flu + Pyr + BaA + Chry + BbF + BkF + BaP + IP + BgP

(Anth + Phen) and Flan/(Flan + Pyr) ratio ranged from 0.088±0.17 to 0.372 ± 0.311 and 0.796 ± 0.346 to 0.877 ± 0.24 respectively indicating for mixed petrogenic and pyrogenic origins of PAHs. Similarly, Naph/Phen ratio was found to be << 1 during pre-monsoon time, which also indicated petrogenic origin of PAHs during that period (Dahle et al., 2003).

High Phen/(Phen + Anth) of 0.76 is considered as specific marker for coal combustion (Dickhut et al., 2000). Phen/(Phen + Anth) ratios of 0.628 ± 0.311 and 0.912 ± 0.17 found during post-monsoon and pre-monsoon respectively indicated coal combustion as one of the sources of PAHs in water.

The petrogenic PAHs could be a result of direct release of effluents or those carried by stormwater from fuel stations, vehicle workshops and storage tanks besides the inputs from the refinery.

This would, therefore, mean that there is considerable input of PAHs from combustion sources with some

moderate input from petrogenic sources also. PAHs of combustion origin would have met the Bharalu river through atmospheric deposition directly to the water body or carried by storm water from the land and streets that were deposited there.

Source apportionment and quantification of source strength of PAHs in aerosol, soil and sediment is often carried out by researcher using Principal Component Analysis (PCA). However, due to the fact that each PAH species has different solubility in water PCA may not be a suitable tool to appreciate PAH sources in water.

Conclusion

ΣPAHs concentration ranged between 3.351 and 72.893 ng/ml with their BaPq values indicates high potential risk for aquatic environment of Bharalu river. Temporal variation was prominent with highest concentrations observed during the pre-monsoon. Signatures of both pyrogenic and petrogenic sources of PAHs were found for Bharalu river water. PAHs in sediment of Bharalu river and surrounding atmosphere could reveal interesting trends.

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Appendix A

<i>Name</i>	<i>Abbreviation</i>	<i>Retention time</i>	<i>LOD (µg/l)</i>	<i>Solubility in water (mg/l)</i>
Napthalene	Naph	14.35	32.9	3.93
Acenaphthylene	Acy	15.5	8.5	3.93
Acenaphthene	Acen	16.65	6.2	1.93
Fluorene	Flu	18.42	7.9	1.68-1.98
Phenanthrene	Phen	19.15	5.4	1.2
Anthracene	Anth	19.75	3.6	0.076
Fluoranthene	Flan	20.65	22.2	0.2-2.6
Pyrene	Pyr	21.43	1.4	0.077
Benzo(a)anthracene	BaA	22.71	4.2	0.01
Chrysene	Chry	23.75	29.0	0.0028
Benzo(b)fluoranthene	BbF	24.37	4.8	0.0012
Benzo(k)fluoranthene	BkF	24.59	5.1	0.00076
Benzo(a)pyrene	BaP	25.43	6.9	0.0023
Dibenzo(a,h)anthracene	DBA	26.81	7.9	0.0005
Benzo(g,h,i)perylene	BgP	27.57	2.8	0.00026
Indeno(1,2,3-cd)pyrene	IP	28.02	4.3	0.062

References

- Agarwal, T. (2009). Concentration level, pattern and toxic potential of PAHs in traffic soil of Delhi, India. *Journal of Hazardous Material*, **171(1-3)**: 894-900.
- APHA (1998). Standard methods for the examination of water and wastewater. 20th edition. American Public Health Association; American Water Works Association. Water Environment Federation for extraction of water.
- Beasley, G. and P. Kneale (2004). Assessment of heavy metal and PAH contamination of urban streambed sediments on microvertebrates. *Water Air and Soil Pollution*, **4(3)**: 563-578.
- Chen, Y., Zhu, L. and R. Zhou (2007). Characterization and distribution of polycyclic aromatic hydrocarbon in surface and sediment from Qiantang River, China. *Journal of Hazardous Materials*, **141(1)**: 148-155.
- Claxton, L.D. and Jr. G.M. Woodall (2007). A review of the mutagenicity and rodent carcinogenicity of ambient air. *Mutation Research*, **636(1-3)**: 36-94.
- Clean Water Act (1993). Suspect Chemicals Source book. In: Clansky, K.B. and M.D. Bethesda (eds). Source List 3B, Clean Water Act Section 307, Priority Pollutants, 1st ed., Roytech Publications, Inc., USA.
- Connel, D.W., Hawker, D.W., Warne, M.J. and P.P. Vowles (1997). Polycyclic aromatic hydrocarbons (PAHs). In: McCombs, K. and A.W. Starkweather (eds). Introduction into Environmental Chemistry. CRC Press LLC, Boca Raton, FL.
- Cornelissen, G., Breedveld, G.D., Kalaitzidis, S., Christanis, K., Kibsgaard, A. and A.M.P. Oen (2006). Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. *Environmental Science and Technology*, **40(4)**: 1197-1203.
- Dahle, S., Savinov, V.M., Matishov, G.G., Evenset, A. and K. Nas (2003). Polycyclic aromatic hydrocarbons (PAHs) in bottom sediments of the Kara Sea shelf, Gulf of Ob and Yenisei Bay. *Science of the Total Environment*, **306(1-3)**: 57-71.
- Dickhut, R.M., Canuel, E.A., Gustafson, K.E., Liu, K., Arzayus, K.M., Walker, S.E., Edgecombe, G., Gaylor, M.O. and E.H. Macdonald (2000). Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. *Environmental Science and Technology*, **34(21)**: 4635-4640.
- European Communities (Drinking Water) Regulations (2007). Handbook on implementation for Water Services Authorities for public water supplies. (S.I. 278 of 2007), section 2: 1-12.
- Fang, G.C., Wu, Y.S., Chen, M.H., Ho, T.T., Huang, S.H. and J.H. Rau (2004). Polycyclic aromatic hydrocarbons study in Taichung, Taiwan, during 2002-2003. *Atmospheric Environment*, **38 (21)**: 3385-3391.
- Gaga, E., Tuncel, G. and S. Tuncel (2009). Sources and wet deposition fluxes of polycyclic aromatic hydrocarbons (PAHs) in an urban site 1000 meters high in central Anatolia (Turkey). *Environmental Forensics*, **10(4)**: 286-298.
- Gogou, A., Stratigakis, N., Kanakidou, M. and E.G. Stephanou (1996). Organic aerosol in Eastern Mediterranean: Components source reconciliation by using molecular markers and atmospheric back trajectories. *Organic Geochemistry*, **25(1-2)**: 79-86.
- Guzzella, L. and A. Depaolis (1994). Polycyclic aromatic hydrocarbons in sediments of the Adriatic Sea. *Marine Pollution Bulletin*, **28(3)**: 159-165.
- Hoyau, V., Jaffrezo, J.L., Garrigues, P.H., Clain, M.P. and P. Masclet (1996). Deposition of aerosols in polar regions-contamination of the ice sheet by Polycyclic Aromatic Hydrocarbons. *Polycyclic Aromatic Compounds*, **8(1)**: 35-44.
- IARC (1983). Approaches to Classifying Chemical Carcinogens According to Mechanism of Action. IARC intern. tech. Rep. No. 83/001, 1983.
- Kafizadeh, F., Houshang Shiva, A. and R. Malekpour (2011). Determination of polycyclic aromatic hydrocarbons (PAHs) in water and sediment of the Kori river, Iran, Middle East. *Journal of Scientific Research*, **10(1)**: 01-07.
- Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Baer, D. Von and P. Oyola (2001). Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. *Environmental Science and Technology*, **35(11)**: 2288-2294.
- Li, X., Shang, Z., Zhao, R., Tanguay, L., Dong, Q. and C. Huang (2010). Polycyclic aromatic hydrocarbons in water, sediment, soil, and plants of the Aojiang River waterway in Wenzhou, China. *Journal of Hazardous Materials*, **173(1-3)**: 75-81.
- Liang, Y., Tse, M.F., Young, L. and M.H. Wong (2007). Distribution patterns of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong. *Water Research*, **41(6)**: 1303-1311.
- Maliszewaska-Kordybach, B. (1999). Sources, concentration, fate and effects of Polycyclic aromatic hydrocarbons (PAHs) in the environment. Part A: PAHs in air. *Polish Journal of Environmental Studies*, **8(3)**: 131-136.
- Mandalakis, M., Tsapakis, M., Tsoga, A. and E.G. Stephanou (2002). Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). *Atmospheric Environment*, **36(25)**: 4023-4035.
- Manoli, E., Sarma, C., Konstantinou, I. and T. Albanis (2000). Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. *Chemosphere*, **41(12)**: 1845-1855.
- Mantis, J., Chaloulakou, A. and C. Sarma (2005). PM10-bound polycyclic aromatic hydrocarbons (PAHs) in the

- greater area of Athens, Greece. *Chemosphere*, **59(5)**: 593-604.
- Marsalek, J., Rochfort, Q., Brownlee, B., Mayer, T. and M. Servos (1999). An explanatory study of urban runoff toxicity. *Water Science and Technology*, **39(12)**: 33-39.
- Matsumoto, Y., Ide, F., Kishi, R., Akutagawa, T., Sakai, S., Nakamura, M., Ishikawa, T., Fujii-Kuriyama, Y. and Y. Nakatsuru (2007). Aryl hydrocarbon receptor plays a significant role in mediating airborne particulate-induced carcinogenesis in mice. *Environmental Science and Technology*, **41(10)**: 3775-3780.
- Metre, P.C. van, Mahler, B.J. and E.T. Furlong (2000). Urban sprawl leaves its PAH signature. *Environmental Science and Technology*, **34(19)**: 4064-4070.
- Müller, S., Wilcke, W., Kanchanakool, N. and W. Zech (2000). Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in particle-size separates of urban soils in Bangkok, Thailand. *Soil Science*, **165(5)**: 412-419.
- Nikolaou, A., Kostopoulou, M., Lofrano, G. and S. Meric (2009). Determination of PAHs in marine sediments: Analytical methods and environmental concerns. *Global NEST Journal*, **11(4)**: 391-405.
- O'Reilly, K., Pietari, J. and P. Boehm (2010). PAHs review, Polycyclic aromatic hydrocarbons in stormwater and urban sediments. *Stormwater*, September 2010, <http://www.stormh20.com>.
- Okay, O.S., Donkin, P., Peters, L.D. and D.R. Livingstone (2000). The role of algae (Isochrysis) enrichment on the bioaccumulation of benzo[a]pyrene and its effects on the blue mussel *Mytilus edulis*. *Environmental Pollution*, **110(1)**: 103-113.
- Parhle, F.G. and E.R. Crecellus (1984). Carpenter, Polycyclic aromatic hydrocarbons in Washington coastal sediments: An evaluation of atmospheric and riverine routes of introduction. *Environmental Science and Technology*, **18(9)**: 687-693.
- Patrolecco, L., Ademollo, N., Capri, S., Pagnotta, R. and S. Polesello (2010). Occurrence of priority hazardous PAHs in water, suspended particulate matter, sediment and common eels (*Anguilla Anguilla*) in the urban stretch of the river Tiber (Italy). *Chemosphere*, **81(11)**: 1386-1392.
- Perugini, M., Visciano, P., Giammarino, A., Manera, Nardo, W. di. and M. Amorena (2007). Polycyclic aromatic hydrocarbons in marine organisms from the Adriatic Sea, Italy. *Chemosphere*, **66(10)**: 1904-1910.
- Ravindra, K., Bencs, L., Wauters, E., Hoog, J.de, Deutsch, F., Roekens, E., Bieus, N., Berghmans, P. and R.V. Grieken (2006). Seasonal and site specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. *Atmospheric Environment*, **40(4)**: 771-785.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A. and G.R. Cass (1993a). Source of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy duty-diesel trucks. *Environmental Science and Technology*, **27(4)**: 636-651.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and B.R.T. Simoneit (1993b). Source of fine organic aerosol. 5. Natural gas home appliances. *Environmental Science and Technology*, **27(13)**: 2736-2744.
- Singh, D.P., Gadi, R. and T.K. Mandal (2010). Emissions of polycyclic aromatic hydrocarbons in the atmosphere: an Indian perspective. *Human and Ecological Risk Assessment*, **16(5)**: 1145-1168.
- Takada, H., Onda, T. and N. Ogura (1990). Determination of polycyclic aromatic hydrocarbons in urban street dust and their source material by capillary gas chromatography. *Environmental Science and Technology*, **24(8)**: 1179-1186.
- Thyssen, J., Althoff, J., Kimmerle, G. and U. Mohr (1981). Inhalation studies with benzo[a]pyrene in Syrian golden hamsters. *Journal of the National Cancer Institute*, **66(3)**: 575-577.
- Tsai, P.-J., Shih, T.-S., Chen, H.-L., Lee, W.-J. C.-H. and H. Liou (2004). Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station workers. *Atmospheric Environment*, **38(2)**: 333-343.
- Vagi, M.C., Kostopoulou, M.N., Petsas, A.S., Lalousi, M.E., Rasouli, Ch. and T.D. Lekkas (2005). Toxicity of organophosphorus pesticides to the marine alga *Tetraselmis suecica*. *Global NEST Journal*, **7(2)**: 222-227.
- Yu, Y., Xu, J., Wang, P., Sun, H. and S. Dai (2009). Sediment-porewater partition of polycyclic aromatic hydrocarbons (PAHs) from Lanzhou Reach of Yellow River, China. *Journal of Hazardous Materials*, **165(1-3)**: 494-500.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D. and S. Sylvestre (2002). PAHs in the Fraser river basin: A critical appraisal of PAH ratios as indicators of PAH sources and composition. *Organic Geochemistry*, **33(4)**: 489-515.
- Zanieri, L., Galvan, P., Checchini, L., Cincinelli, A., Lepri, L., Donzelli, G.P. and M.D. Bubba (2007). Polycyclic aromatic hydrocarbons (PAHs) in human milk from Italian women: Influence of cigarette smoking and residential area. *Chemosphere*, **67(7)**: 1265-1274.